Advances in Isotope Geochemistry

Hans Eggenkamp

The Geochemistry of Stable Chlorine and Bromine Isotopes

Springer

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Springer

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Bussum
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ISBN 978-3-642-28505-9 ISBN 978-3-642-28506-6 (eBook)
DOI 10.1007/978-3-642-28506-6
Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014945773

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Preface

In 2014, it is 30 years ago that the Ph.D. thesis written by Ronald Kaufmann "Chlorine in Ground Water: Stable Isotope Distribution" was published. This thesis definitely is the landmark publication of all articles, book chapters, conference proceedings, and other papers written on halogen stable isotopes as it, for the very first time, showed that natural chlorine stable isotope variations were clearly, and actually easily, measurable. Earlier papers were published on chlorine (and even bromine) isotopes, but these were published at a very low frequency of less than one paper per year on average. These papers, mostly aimed at the development of analytical methods and experimentally measuring fractionation in the laboratory, showed that, unfortunately, natural variations were too small to be detected. Ronald Kaufmann was the first to develop a method by which it was shown that not only natural variations existed, but also that they showed clear systematics.

Once it was proven that small natural chlorine isotope variations could be measured, it was expected that the number of published studies would rise significantly and quickly. However, it took 10 years until the average number of chlorine isotope publications rose above five per year. Even today, after 30 years, the total number of papers on chlorine and, since the year 2000, bromine isotopes is only about 300, recently averaging at about 20 papers per year.

As a result, it is possible to contain almost the whole combined knowledge on stable chlorine and bromine isotope geochemistry into one small volume in the series "Advances in Isotope Geochemistry". In this volume, I present the development of our knowledge on chlorine and bromine stable isotope geochemistry. The book starts with an introduction on chlorine and bromine, their history, chemistry, and isotope behavior. A large part of the book is filled with the numerous methods that have been developed to analyze chlorine and bromine stable isotope ratios. Striking with this regard is that several methods have been developed within laboratories that presented very little scientific chlorine or bromine isotope work thereafter. It could be questioned what would be the reason for this striking observation.

The book then describes the various processes that fractionate chlorine and bromine isotopes. It is important to realise that chlorine and bromine are predominantly present on earth in the -I oxidation state as chloride and bromide ions, and as a result oxidation–reduction processes that impose large isotope fractionation on other light stable isotope systems are mostly absent.

The range of measured isotope ratios goes rarely beyond 10 ‰, and about 80 % of all chlorine and bromine isotope measurements are between −1 and +1 ‰ of the internationally accepted standard (ocean chloride and ocean bromide). Finally, the book describes the chlorine and bromine isotope variation that has been observed. This includes not only observations on chloride and bromide samples from earth, but also extra-terrestrial material such as meteorites and moon rocks and samples with different oxidation states such as perchlorates and organic molecules.

The number of laboratories that has been involved in chlorine and bromine isotope studies has never been very large. I believe the number has hardly been over 10 worldwide at any one time. It is hoped that the data provided in this book will increase the interest in the study of chlorine and bromine isotopes, and that more laboratories are going to realise the opportunities that investing time and resources in the study of chlorine and bromine isotopes can give a healthy reward. The equipment is present in virtually every isotope laboratory, and with only small adoptions and a small investment every isotope geochemist who wishes can become part of the halogen isotope community.

Hans Eggenkamp

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Part I
Introduction

The Halogen Elements

1

Group 17 of the periodic table of the elements (see Table 1.1) consists of the so called halogen elements fluorine, chlorine, bromine, iodine, astatine and the recently discovered element 117 (Organessian et al. 2010), although it is not yet known if this element behaves similar to the other group 17 elements due to possible relativistic effects (see e.g. Pyykkö 2011b). Group 17 elements are characterised by an outer electron shell which contains seven electrons, so that only one electron needs to be added to give it a full noble gas configuration. This property makes that the dominant oxidation state, especially for the lighter elements of this group, is the -I oxidation state and they predominantly form ionogenic compounds. In the earth's surface reservoir chlorine and bromine are most commonly found in aqueous solution in the oceans, as most of their salts are readily soluble in water, and in evaporite deposits while fluorine is most common in some fluoride rich minerals such as fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$), and cryolite (Na_3AlF_6) as the alkaline earth fluorides (e.g. CaF_2, MgF_2) have a low solubility and precipitate out of waters with significant alkaline earth concentrations. Iodine has a relatively low concentration in seawater as it is efficiently removed from it by certain brown algae which are able to heavily concentrate iodine.

In their elemental form group 17 elements form diatomic molecules with a single covalent bond between the atoms. At standard temperature and pressure fluorine and chlorine are gaseous elements, bromine is a liquid and iodine and astatine are solids. No chemical and physical properties are known yet from element 117, although they have been predicted in the past (Seaborg 1968; Fricke et al. 1971; Fricke and Waber 1971). These authors even predicted some properties for the next group 17 element (element 171) which may be so unstable that it will probably never be discovered. The electronegativity of the group 17 elements decreases from fluorine to astatine. Fluorine is the most electronegative element known. As a result fluorine is also one of the strongest oxidising agents that is known. In the same direction the elements also become weaker oxidising agents. Some characteristic chemical and physical properties for the group 17 elements can be found in Table 1.2.

1.1 Discovery of the Halogen Elements

As the group 17 elements are reactive elements they are not normally found as "native" elements in nature. As a consequence they were discovered at a relatively late date. The discovery history of the group 17 elements with stable isotopes is described in detail by Weeks (1942).

The first group 17 element that was discovered was chlorine. It was discovered by Scheele (1774) who, while studying manganese, in the reaction between hydrochloric acid and pyrolusite (MnO_2) noticed that a gas with the odour of warm aqua regia escaped. He was able to detect several of the

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_1,

Table 1.1 Characteristics of the group 17 elements

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	group 14	Group 15	Group 16	Group 17	Group 18
Period 1	1 H 1.0																	2 He 4.0
Period 2	3 Li 7.0	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
Period 3	11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	**17** **Cl** **35.5**	18 Ar 39.9
Period 4	19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	**35** **Br** **79.9**	36 Kr 83.8
Period 5	37 Rb 85.47	38 Sr 87.62	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 96.0	43 Tc (97)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
Period 6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
Period 7	87 Fr (223)	88 Ra (226)	Ac-Lr	104 Rf (267)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (282)	112 Cn (285)	113 Uut (285)	114 Fl (289)	115 Uup (289)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

Period 6	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
Period 7	89 Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Group 17 elements are shown in light grey, chlorine and bromine in darker grey. Within the cells the number at the top is the atomic number, in the middle the symbol and the number at the bottom is the rounded atomic mass after Wieser et al. 2013. For elements without a stable isotope the mass of the longest living isotope according to Wieser et al. 2013 is taken.

properties of this gas, such as its green colour, its solubility in water which produces a weakly acid taste to the water and its bleaching capabilities. However, as in those days all acids were believed to contain oxygen he considered this gas as the oxide obtained from hydrochloric acid, which was then called muriatic acid, and as such failed to recognise it as a new element. In spite of this he still is credited with the discovery of the element. Gay-Lussac and Thénard (1809) tried to remove the oxygen from this gas, but failed to do so. Although they indicated that, because of this observation oxygenated muriatic acid might be a chemical element they did not yet consider it as such as they believed that their observations on it could still be explained more appropriate as it being a compound substance. Finally Davy (1811) after failing to decompose "oxygenated muriatic acid" again realised that it could only be a "simple body" (element) and he proposed the name of (eu)chlorine for it after its bright yellow green colour.

The second halogen coming to surface was iodine. It was discovered in 1811 by Bernard Courtois who was a producer of saltpetre (KNO_3). Considering that France was a country at war in those days, and saltpetre was used as one of the main gunpowder ingredients, saltpetre was in great demand. Production of saltpetre required Na_2CO_3 which was made from ash prepared from seaweed. Seaweed was burned to isolate the Na_2CO_3, and the ash was washed with water. To destroy the remaining waste sulphuric acid was added. When Courtois added an excess of sulphuric acid accidentally a cloud of a purple vapour rose. It was observed that this vapour condensed on cold surfaces thereby forming dark crystals. He suspected that these crystals might be an at that moment unknown element but he was unable to continue his research because of lack of funding. Courtois supplied the new substance to his friends Charles Bernard Desormes and Nicolas Clément for further analyses after which they presented the discovery to the scientific world (Courtois 1813). The new substance was further investigated by Joseph Louis Gay-Lassac and Humphry Davy who independently concluded that it was a newly discovered element and was subsequently called "iode" after the purple colour of iodine vapour by Gay-Lassac. Davy also discovered the chemical similarities between this newly discovered element and chlorine which he studied a few years earlier (Gay-Lussac 1813a, b, 1814; Davy 1813, 1814a).

Bromine has been discovered independently by Antoine Jérôme Balard and Karl Löwich in 1825/1826. Because Balard was the first to publish on his observations (Balard 1826) he is credited with the discovery of this element although Löwich might have prepared it a little earlier (Löwich 1827, 1828) than Balard. Balard discovered bromine when he extracted iodine from seaweed. During this process he distilled a substance from which he discovered that it has properties that were intermediate between chlorine and iodine. He tried to prove that this substance was iodine chloride (ICl) but failed in this process. He concluded that the substance was an element that he called muride. However, this was renamed bromide as the name proposed by Balard did not get approval by the French Academy of Sciences and it was renamed bromine after its "bad odour". Löwich discovered bromine when he oxidized salty springwater with elementary chlorine. He found a red liquid that he showed to his professor (Leopold Gmelin). Gmelin asked Löwich to produce some more of the substance so that it could be studied in more detail. While he was working on this task Balard's discovery was made public, indicating the same properties as the red liquid discovered by Löwich.

Due to its extremely reactive behaviour the discovery of fluorine was delayed for a very long time. Hydrogen fluoride was already described for the first time in 1768 (Marggraf 1768) and the results of these experiments were confirmed by Scheele three years later (Scheele 1771). As in that period it was believed that all acids contain oxygen it was concluded that hydrofluoric acid should also contain oxygen. However. Davy (1814b) showed that this was not the case. It was Ampère (1816) who realised that hydrofluoric acid must be a compound between hydrogen and an, at that moment, unknown element. Searching for the pure element was a very delicate task. Considering the fact that fluorine is the most

Table 1.2 Characteristics of the group 17 elements

Colour	F	Cl	Br	I	At	E117	E171
	Light yellow	Yellow green	Red brown	Black			
Atomic number	9	17	35	53	85	117	171
Atomic weight	18.9984032 (5)	[35.446;35.457]	[79.901; 79.907]	126.90447 (3)	[210][a]	[294][b], [313][c]	[500][c]
Stable isotopes	19 (100 %)	35 (75.76 %), 37 (24.24 %)	79 (50.69 %), 81 (49.31 %)	127 (100 %)			
Melting point (°C)	−219.62	−101.5	−7.3	113.7	302	350 − 550	
Boiling point (°C)	−118.12	−34.04	59	184.3	337	610	
Electronegativity (pauling)	3.98	3.16	2.96	2.66	2.2		
Oxidation states	−I	−I, 0, + I, + III, + IV, +V, (+VI), +VII	−I, 0, + I, + III, + V, (+VII)	−I, 0, +I, +III, +V, +VII	−I, 0, +I, +III, +V, (+VII)	+I, +III	+I, +III, +V
Oxidation potential ($2X^- \leftrightarrow X_2 + 2e^-$, V)	+3.05	+1.36	+1.07	+0.54	+0.36	+0.25 − +0.5	
Ionic radius (X^-, pm)	119	167	182	206			
Year of discovery	1810, 1886	1774	1826	1811	1939	2010	Not discovered

Most data in this table are taken from data available at the WebElements internet site (http://www.webelements.com) authored by Dr Mark J Winter. Data from elements 117 en 171 are mostly taken from Seaborg (1968), Fricke and Waber (1971) and Fricke et al. (1971). The redox potential from astatine is taken from Champion et al. (2010), the atomic weights of the known elements are taken from Wieser et al. (2013) and their isotopic compositions from Berglund and Wieser (2011)

[a] Isotope with longest half life

[b] Isotope with longest known half life

[c] Undiscovered isotope with the longest expected half life

electronegative element known and it is extremely reactive, it prefers to form chemical compounds with virtually all other elements making it very difficult to produce it in its pure form. It was believed that pure fluorine could be obtained by electrolysis of hydrogen fluoride. Electrolysis of solutions of hydrogen fluoride in water did however not proceed to produce fluorine gas due to the extreme corrosiveness of both hydrogen fluoride and fluorine gas. Attempts by Edmond Frémy to use pure hydrogen fluoride to obtain fluorine by electrolysis failed due to the fact that pure hydrogen fluoride does not conduct electricity (Frémy 1850). The experiments were continued by Henri Moissan who experimented with mixtures of potassium bifluoride and hydrogen fluoride, a mixture that conducts electricity and which, finally, made it possible to produce free fluorine by electrolysis (Moissan 1887).

Fluorine was the last group 17 element containing at least one stable isotope that was isolated. Element 85, the later astatine consists solely of short living radioactive isotopes. The longest living isotope is ^{210}At with a half-life of only 8.1 h. Although present (in minute quantities) on earth it was first discovered after synthesis of the element at the University of California, Berkely by Corson et al. (1940). They found the element after bombarding ^{209}Bi with alpha particles. Three years later the element was also discovered as occurring naturally in the uranium decay chains (Karlik and Bernert 1943a, b).

The last group 17 element discovered until now is element 117. The element was discovered in 2010 by an international team of scientists from Russia and the USA (Organessian et al. 2010). The element was formed after bombarding a ^{249}Bk target with ^{48}Ca particles during which process the isotopes ^{293}117 (5 events) and ^{294}117 (1 event) where detected. The existence of element 117 was confirmed in 2014 (Khuyagbaatar et al. 2014) using the same fusion reaction at GSI in Darmstadt where also the isotope ^{294}117 was observed.

It is not expected that any more group 17 elements elements will ever be discovered. The next group 17 element is expected to be element 171. It is predicted however that elements above number 137 may not exist as such as according to the Bohr model electrons in the 1 s shell would get a speed faster than that of light. Also according to the semi-relativistic Dirac equation problems would arise above element number 137. This effect was first noticed by Feynman (1948) for which reason element 137 is sometimes called Feynmanium (Elert 1998–2012). Khazan (2007) made calculations on where the end of the periodic table would be found and concluded that the upper limit of the periodic table would be at element 157 which he called after himself Khazanium. On the other hand other calculations that have been made to define the electron configurations of elements up to 164 (Nefedov et al. 2006) and 172 (Pyykkö 2011a) indicate that at least in theory element 171 might exist. Early predictions on chemical and physical characteristics of this element were published by Fricke and Waber (1971) and Fricke et al. (1971) and these can be found in Table 1.2.

1.2 Abundance of the Halogen Elements

1.2.1 Abundance in the Solar System and on Earth

All halogen elements are, within the solar system, relatively minor elements. Being elements with an odd proton number they are all less abundant than their neighbouring elements with even numbers of protons. 20th century studies (e.g. Goldschmidt 1937; Suess and Urey 1956; Cameron 1970; Anders and Ebihara 1982), agreed very much on the order of magnitude of the solar abundance of these elements although slightly different abundances were found as a result of increasing knowledge during the 20th century. Relative to 10^6 silicon atoms there are 843 fluorine atoms, 5,240 chlorine atoms, 11.8 bromine atoms and 0.9 iodine atoms in the solar system.

On earth the distribution is different from the solar system. As the earth is mostly a rocky planet the most common elements are the rock forming elements, especially silicon, aluminium, magnesium, calcium and oxygen. Due to mass differentiation during the early age of the earth the heavy elements iron and nickel, which are also common on earth, have been concentrated in the core. The halogen elements are relatively rare when considering the whole earth. The most common of them is chlorine with a content of 10 ± 5 ppm for the whole earth, the concentrations of the other elements being: fluorine 5.12 ± 0.5 ppm, bromine 400 ± 150 ppb and iodine 40.5 ± 15 ppb (Allegre et al. 2001). The halogen elements are however among the most volatile of all elements and they are not very compatible with most rock types. Especially chlorine and bromine are what we can call excess volatiles and prefer to concentrate in fluid phases. On earth this means that they are very heavily concentrated in the oceans. Except in oceans they are only found in high concentrations in evaporites, which are formed from the evaporation of ocean or lake waters. Also iodine is concentrated in the oceans, but the iodide ion is too large to fit into common salt minerals (Boeke 1908) and stays either in the fluid phase, or forms minerals of its own. As iodine is more easily to oxidise than chlorine or bromine iodine minerals very often contain iodates, although iodides of transition minerals are also found. Iodine is further concentrated in certain brown algae such as *Laminaria* and *Fucus*, which can contain up to 0.4 % iodine by dry weight (Lyday 2005). Bromine does not form minerals of its own (except for bromargyrite; AgBr) and is always found as solid solution in chloride minerals, especially in evaporites. Fluorine has a different behaviour than the other halogens as its alkaline earth salts (such as calcium and magnesium fluoride) have very low solubilities. As a consequence the fluoride concentration in seawater and thus in evaporites is very low. Due to the size of the fluoride ion fluorine is not commonly found in silicates, but forms mineral of its own, of which fluorite, fluorapatite and cryolite are the most common and even to such an extent that they can be used and mined as natural fluorine resources. Summarising the concentrations of the halogens in the crust are: fluorine 300 ppm, chlorine 314 ppm, bromine 1.6 ppm and iodine 0.3 ppm (Mason 1952). The concentrations of the halogens in ocean salt is on average: fluorine 37 ppm, chlorine 54.3 %, bromine 0.19 % and iodine 1.8 ppm (recalculated from Turekian 1971). These data indicate that the halogens are very much concentrated in the oceans and the crust, so that, as a consequence, the concentrations of these elements in the mantle must be very low.

Astatine, although found naturally on earth is particularly rare in nature, and it is calculated that at any one moment less than 30 grams of this element is present on earth. Astatine is produced naturally in the decay chains of ^{238}U (isotope ^{218}At) and ^{235}U (isotope ^{215}At and ^{219}At) in minute quantities as it is formed solely on very low probability decay branches. An other isotope does theoretically exist in nature in even smaller amounts as decay product of the neptunium chain (^{217}At), however the parent isotope of this chain has virtually decayed completely on earth due to its short half-life.

1.2.2 Distribution and Fluxes of Chlorine and Bromine Between Major Reservoirs on Earth

The main halogen reservoirs on earth can be defined as the mantle, the oceanic and continental lithospheres and the oceans. The atmosphere is only a very limited reservoir. The continental lithosphere is probably better described as being split into three very different reservoirs, being the silicate lithosphere, the evaporites and the (saline) porewater found in sediments and rocks. The study by Schilling et al. (1978) is probably still one of the most comprehensive studies on the chlorine and bromine contents of the major reservoirs and fluxes between these reservoirs. In the following section the chlorine and bromine contents and fluxes between the major reservoirs are described as these elements are the main subject of this book. As chlorine and bromine are the only two halogen elements to have two stable isotopes they are the only halogens for which variations in the stable isotope ratios exist and

Table 1.3 Chlorine and bromine in the various reservoirs on earth

	Mass (kg)	%	Cl conc (ppm)	Br (conc (ppm)	Total Cl (kg)	Total Br (kg)	$10^3 \times$ (Br/Cl)	Cl (% of total)	Br (% of total)	References
Atmosphere	5.1×10^{18}	0.0001	0.0016	0.0000078	8.16×10^{9}	3.98×10^{7}	4.88	0.00000001	0.00000001	Stacy (1969), Rahn (1976)
Oceans	1.4×10^{21}	0.023	19353	67	2.71×10^{19}	9.38×10^{16}	3.46	17.8	19.1	Stacy (1969), Pytkowicz and Kester (1971)
Evaporites	3.12×10^{19}	0.033	606838	151	1.89×10^{19}	4.70×10^{15}	0.25	12.4	1.0	Hay et al. (2006), Braitsch and Hermann (1963)
Sediment (incl. pore water)	1.97×10^{21}	0.033	19206	97	3.78×10^{19}	1.91×10^{17}	5.06	24.8	39.0	Land (1995), Knauth (1998)
Continental crust	1.08×10^{22}	0.18	210	1	2.27×10^{18}	1.08×10^{16}	4.76	1.5	2.2	Gast (1972), Turekian (1971)
Oceanic crust	4.8×10^{21}	0.08	48	0.17	2.30×10^{17}	8.16×10^{14}	3.54	0.2	0.2	Gast (1972), Schilling et al. (1978)
Mantle	4.01×10^{24}	67.07	16	0.05	6.59×10^{19}	1.90×10^{17}	2.88	43.3	38.6	http://www.colorado.edu/physics/phys2900/homepages/Marianne.Hogan/inside.html, McDonough (2000)
Core	1.95×10^{24}	32.61	200(?)	0.7(?)	3.9×10^{20}(?)	1.37×10^{18}	3.50(?)	n.a.	n.a.	http://www.colorado.edu/physics/phys2900/homepages/Marianne.Hogan/inside.html, McDonough (2000)

n.a. means not taken into account

thus for which the fluxes may cause part of the observed isotope variations. Schilling et al. (1978) attempted to establish the origin of the chloride and bromide in the surface reservoir. They concluded that chlorine and bromine in the surface reservoirs (defined as the oceans, atmosphere and sediments, including the evaporites) reached their current concentrations due to continuous outgassing over the history of the earth. Current knowledge more and more agrees on a relatively early and fast outgassing of the earth during its primordial state, so that already during Achaean times most chlorine (and bromine) was stored in the oceans, which would indicate that the chloride concentration in the oceans even decreased since these early times (Knauth 1998; 2005; Hay et al. 2006). These modern studies assume more and more that the total chlorine in the surface reservoirs has been more or less in steady state since early Proterozoic times, indicating also a steady state between the different reservoirs. Considering however the fact that the fluxes between the reservoirs are not very well understood in detail, estimations by Schilling et al. (1978) and Ito et al. (1983) can still be used as estimations for these fluxes.

Considering the chlorine and bromine circulation the following general reservoirs can be considered. The mantle, continental crust, oceanic crust, sediments and sedimentary rocks, evaporites, oceans and atmosphere. The core can also be considered a reservoir, but not much exchange between the core and the surface reservoirs is to be expected. Schilling et al. (1978) considered the sedimentary and evaporite reservoirs as one reservoir, however they should be considered as two different reservoirs for the purpose of chlorine and bromine isotope studies as within the evaporite reservoir chlorine and bromine are mostly present as solid salts, while in the sediment reservoir they are mostly present in solution in saline porewaters. The known inventory of evaporites has increased considerably since the study of Schilling et al. (1978). The study by Hay et al. (2006), which meticulously prepares an inventory of all evaporites deposited since the Ediacaran also attempts to estimate the amount of these evaporites eroded since their deposition. They conclude that the total mass of currently present evaporites (as halite) is 3.12×10^{19} kg. This amount is equivalent to 1.89×10^{19} kg chloride, even more than the 1.84×10^{19} kg chloride as estimated by Schilling et al. (1978) for all chloride present in sedimentary rocks (including evaporites). Table 1.3 shows the amounts of chloride and bromide in the various reservoirs on earth. Data from seawater, atmosphere, oceanic and continental crust are taken from Schilling et al. (1978). The data for evaporites are recalculated from data taken from Hay et al. (2006). The amount of bromide in evaporites is estimated from average bromide contents in evaporites from Braitsch (1962). The amount of chloride in sediment (mostly present as chloride in formation brines) is estimated by Land (1995) and Knauth (1998) and estimated as perhaps two to three times as much as the chloride in evaporites (in the table it is assumed as being the double amount). Bromide in these brines is calculated as if the bromide is the amount that is not precipitated in evaporites compared to seawater. As a consequence the concentration of bromide in sediments (brines) is higher than in the oceans and evaporites. Data for the mantle are taken from McDonough (2000). The actual chlorine concentrations of the mantle are still not known in detail, however they can be as low as a few ppm. Studies on chlorine isotopes in MORBs that indicate lower δ^{37}Cl values for basalts with lower chlorine concentrations (Bonifacie et al. 2008; Layne et al. 2009) found the lowest δ^{37}Cl values in MORBs with chlorine concentrations below 50 ppm. These studies are contradicted by studies by Sharp et al. (2007, 2013) who concluded that no significant difference in chlorine isotope composition between the mantle and surface reservoirs could be observed. The estimates for the mantle are for that reason very unsure. As an example Graedel and Keene (1996) estimate that the total chlorine content of the mantle is 4.61×10^{21} kg, estimating that 99.6 % of all chlorine is present in the mantle. This value would indicate an average concentration of 1,150 ppm for the mantle, much higher than most

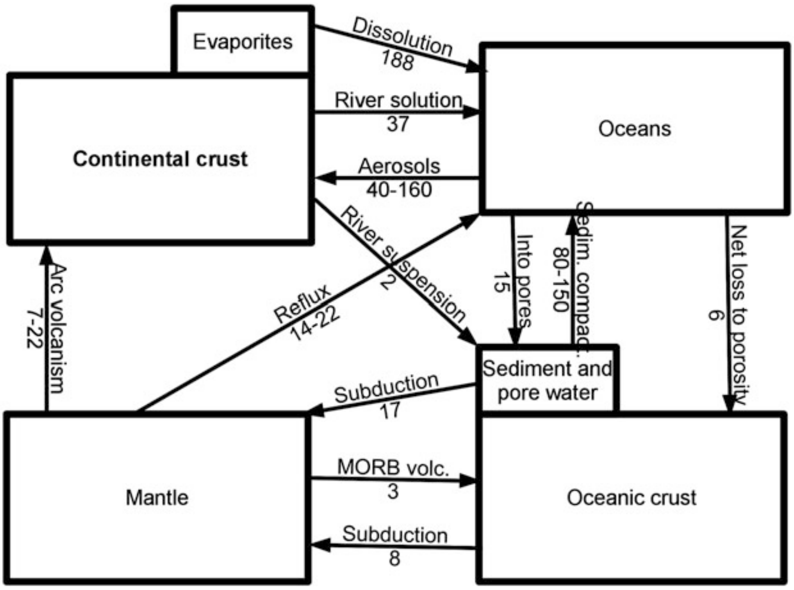

Fig. 1.1 The chlorine cycle of the earth. Fluxes (simplified) are in 10^{12} g/year. Figure after Jarrard (2003) with additional data (evaporites) from Hay et al. (2006)

other estimates. Harben and Kužvart (1996) estimate the total amount of bromine in the mantle as 1.0471 × 10^{19} kg, estimating that 98.9 % of all bromine is present in the mantle. This value would indicate that the average bromine concentration in the mantle is 2.6 ppm. In the study by McDonough (2000) the concentration of chlorine and bromine in the core is assumed to be relatively high at 200 and 0.17 ppm respectively. It is not clear from this publication where these concentration data come from, although the chlorine concentration in silicate inclusions in iron meteorites, which may be considered as an analogue to the core of rocky planets(?), is on average 285 ppm (Garrison et al. 2000), but this is obviously not the average chloride concentration in the bulk iron meteorites. Because of this uncertainty the amounts of chlorine and bromine in the core are not taken into account in the calculations of the total amounts of chlorine and bromine on earth in Table 1.3.

Some of the chlorine and bromine fluxes between the reservoirs were estimated by Schilling et al. (1978). Some more data on the chlorine fluxes were published by Ito et al. (1983) and nicely visualised by Kaufmann (1984). As the sedimentary reservoir can be considered to exist of as two different reservoirs (solid chlorides in evaporites and dissolved chlorides in sediment brines, with clearly distinguishable characteristics) the figure presented by Kaufmann (1984) could better be presented with these reservoirs separated. Figure 1.1 shows a simplification of the chlorine cycle as presented by Jarrard (2003) with the addition of the evaporite reservoir and the flux of chloride from the continents split between chloride coming from evaporites and the rest of the continents (which is the sum of chloride coming from formation waters and chloride leached from rocks). The erosion of evaporites in this figure has been estimated from Hay et al. (2006). Most fluxes are only very roughly known, and it is still not known if a steady state exists between the mantle and surface reservoirs. Bromine fluxes are hardly studied and they have not been added to this figure as they are virtually unknown at the present day. Although estimates could theoretically be deducted from the chloride data and Br/Cl ratios of the reservoirs these were not incorporated into this figure. As a result all fluxes must be considered as very rough estimates.

References

Allegre C, Manhès G, Lewin É (2001) Chemical composition of the Earth and the volatility control on planetary genetics. Earth Planet Sci Lett 185:49–69

Ampère AM (1816) D'une classification naturelle pour les corps simples. Annal Chim Phys 2:6–21

Anders E, Ebihara M (1982) Solar-system abundances of the elements. Geochim Cosmochim Acta 46:2363–2380

Balard AJ (1826) Sur une substance particulière contenue dans l'eau de la mer. Annal Chim Phys 2^{me} series 32:337–381

Berglund M, Wieser ME (2011) Isotopic compositions of the elements 2009 (IUPAC Technical Report). Pure Appl Chem 83:397–410

Boeke HE (1908) Über das Krystallisationsschema der Chloride, Bromide, Jodide von Natrium, Kalium und Magnesium, sowie über das Vorkommen des Broms und das Fehlen von Jod in den Kalisalzlagerstätten. Z Kristallogr 45:346–391

Bonifacie M, Jendrzejewski N, Agrinier P, Humler E, Coleman M, Javoy M (2008) The chlorine isotope composition of earth's mantle. Science 319:1518–1520

Braitsch O (1962) Entstehung und Stoffbestand der Salzlagerstätten. Springer, Berlin

Braitsch O, Hermann AG (1963) Zur Geochemie des Broms in salinaren Sedimenten: Teil I: Experimentelle Bestimmung der Br-Verteilung in verschiedenen natürlichen Salzsystemen. Geochim Cosmochim Acta 27:361–391

Cameron AGW (1970) Abundances of the elements in the solar system. Space Sci Rev 15:121–146

Champion J, Alliot C, Renault E, Mokili BM, Chérel M, Galland N, Montavon G (2010) Astatine standard redox potentials and speciation in acidic medium. J Phys Chem A 114:576–582

Corson DR, MacKenzie KR, Segrè E (1940) Artificially radioactive element 85. Phys Rev 58:672–678

Courtois B (1813) Découverte d'une substance nouvelle dans le Vareck. Annal Chim 88:304–310

Davy H (1811) On a combination of oxymuriatic gas and oxygene gas. Phil Trans R Soc Lond 101:155–162

Davy H (1813) Sur la nouvelle substance découverte par M. Courtois, dans le sel de Vareck. Annal Chemie 88:322–329

Davy H (1814a) Some experiments and observations on a new substance which becomes a violet coloured gas by heat. Phil Trans R Soc Lond 104:74–93

Davy H (1814b) Mémoire sur la nature de l'acide fluorique, lu á la Societé Royale de Londres, le 8 julliet 1814, et Annal Chim 88:271

Elert G (1998–2012) The physics hypertextbook, atomic models. http://physics.info/atomic-models/. Accessed 12 Aug 2014

Feynman RP (1948) Relativistic cut-off for quantum electrodynamics. Phys Rev 74:1430–1438

Frémy E (1850) Recherches sur les fluorures. Ann Chim Phys 2^{me} Serie, t. LXVII, p 5

Fricke B, Waber JT (1971) Theoretical predictions of the chemistry of superheavy elements. Actinides Rev 1:433–485

Fricke B, Greiner W, Waber JT (1971) The continuation of the periodic table up to Z = 172. The chemistry of superheavy elements. Theoret Chim Acta 21:235–260 (Berlin)

Garrison D, Hamlin S, Bogard D (2000) Chlorine abundances in meteorites. Meteor Planet Sci 35:419–429

Gast PW (1972) The chemical composition of the earth, the moon and chondritic meteorites. In: Nature of the solid earth; edt. EC Robertson. McGraw-Hill, New York pp 19-40

Gay-Lussac J (1813a) Sur un nouvel acide formé avec la substance décourverte par M. Courtois. Annal Chim 88:311–318

Gay-Lussac J (1813b) Sur la combination de l'iode avec d'oxigène. Annal Chimie 88:319–321

Gay-Lussac J (1814) Mémoire sur l'iode. Annal Chim 91:5–160

Gay-Lussac J, Thénard L (1809) De la nature et des propriétés de l'acide muriatique et de l'acide muriatique oxigéné. Mém Phys Chim Société d'Arcueil 2:339–358

Goldschmidt VM (1937) The principles of distribution of chemical elements in minerals and rocks. J Chem Soc 1937:655–673

Graedel TE, Keene WC (1996) The budget and cycle of Earthś natural chlorine. Pure Appl Chem 68:1689–1697

Harben PW, Kužvart M (1996) Industrial minerals—a global geology. Industrial Minerals Information Ltd., Metal Bulletin PLC, London 462 pp

Hay WW, Migdisov A, Balukhovsky AN, Wold CN, Flögel S, Söding E (2006) Evaporites and the salinity of the ocean during the phanerozoic: implications for climate, ocean circulation and life. Pal Pal Pal 240:3–46

Ito E, Harris DM, Anderson AT Jr (1983) Alteration of oceanic crust and geologic cycling of chlorine and water. Geochim Cosmochim Acta 47:1613–1624

Jarrard RD (2003) Subduction fluxes of water, carbon dioxide, chlorine, and potassium. Geochem Geophys Geosystems 4. doi:10.1029/2002GC000392

Karlik B, Bernert T (1943a) Eine neue natürliche α-Strahlung. Naturwissenschaften 31:298–299

Karlik B, Bernert T (1943b) Das Element 85 in den natürlichen Zerfallsreihen. Z Physik A 123:51–72

Kaufmann RS (1984) Chlorine in groundwater: Stable isotope distribution. Ph.D. thesis, University of Arizona, Tucson, Ariz

Khazan A (2007) Effect from hyperbolic law in periodic table of elements. Prog Phys 2:83–86

Khuyagbaatar J, Yakushev A, Düllmann ChE, Ackermann D, Andersson LL, Asai M, Block M, Boll RA, Brand H, Cox DM, Dasgupta M, Derkx X, Di Nitto A, Eberhardt K, Even J, Evers M, Fahlander C, Forsberg U, Gates JM, Gharibyan N, Golubev P, Gregorich KE, Hamilton JH, Hartmann W, Herzberg RD, Heßberger FP, Hinde

DJ, Hoffmann J, Hollinger R, Hübner A, Jäger E, Kindler B, Kratz JV, Krier J, Kurz N, Laatiaoui M, Lahiri S, Lang R, Lommel B, Maiti M, Miernik K, Minami S, Mistry A, Mokry C, Nitsche H, Omtvedt JP, Pang GK, Papadakis P, Renisch D, Roberto J, Rudolph D, Runke J, Rykaczewski KP, Sarmiento LG, Schädel M, Schausten B, Semchenkov A, Shaughnessy DA, Steinegger P, Steiner J, Tereshatov EE, Thörle-Pospiech P, Tinschert K, Torres De Heidenreich T, Trautmann N, Türler A, Uusitalo J, Ward DE, Wegrzecki M, Wiehl N, Van Cleve SM, Yakusheva V (2014) ^{48}Ca + ^{249}Bk fusion reaction leading to element Z = 117: Long-lived α-decaying ^{270}Db and discovery of ^{266}Lr. Phys Rev Lett 112:172501

Knauth LP (1998) Salinity history of the Earth's early ocean. Nature 395:554−555

Knauth LP (2005) Temperature and salinity history of the Precambrian ocean: implications for the course of microbial evolution. Pal Pal Pal 219:53–69

Land LS (1995) The role of saline formation water in crustal cycling. Aquat Chem 1:137–145

Layne GD, Kent AJR, Bach W (2009) δ^{37}Cl systematics of a backarc spreading system: the Lau Basin. Geology 37:427–430

Löwich C (1827) Über Brombereitung und eine auffallende Zersetzung des Aethers durch Chlor. Mag Pharmacie 21:31–36

Löwich C (1828) Über einige Bromverbindungen und über Bromdarstellung. Ann Phys Chem 14:485–499

Lyday PA (2005) Iodine and iodine compounds, in ullmann's encyclopedia of industrial chemistry, Wiley-VCH, Weinheim, vol A14, pp 382–390

Marggraf AS (1768) Observation concernant une volatilisation remarquable d'une partie de l'espèce de pierre, à laquelle on donne les noms de Flosse, Flusse, Flus-Spaht, et aussi celui d'hespéros; laquelle volatilisation a été effectuée au moyen des acides. Histoire de l'Académie Royale des Sciences et des Belles-Lettres de Berlin. 1768:1–11

Mason B (1952) Principles of geochemistry. Wiley, New York

McDonough WF (2000) The composition of the earth. In: Teisseyre R, Majewski E (eds) Earthquake thermodynamics and phase transformations in the earth's interior

Moissan H (1887) Recherges sur l'isolement du fluor. Annal Chim Phys 6^{me} serie, t. XII, Gauthiers-Villars, Paris, 66 pp

Nefedov VI, Trzhaskovskaya MB, Yarzhemskii VG (2006) Electronic configurations and the periodic table for superheavy elements. Dokl Phys Chem 408:149–151

Organessian YUTS, Abdullin FSH, Bailey PD, Benker DE, Bennett ME, Dmitriev SN, Ezold JG, Hamilton JH, Henderson RA, Itkis MG, Lobanov YUV, Mezentsev AN, Moody KJ, Nelson SL, Polyakov AN, Porter CE, Ramayya AV, Riley FD, Roberto JB, Ryabinin MA, Rykaczewski KP, Sagaidak RN, Shaughnessy DA, Shirokovsky IV, Stoyer MA, Subbotin VG, Sudowe R, Sukhov AM, Tsyganov YuS, Utyonkov VK, Voinov AA, Vostokin GK, Wilk PA (2010) Synthesis of a new element with atomic number Z = 117. Phys Rev Lett 104:142502

Pytkowicz RM, Kester DR (1971) Physical chemistry of sea water. Oceanogr Mar Biol A Rev 9:11–60

Pyykkö P (2011a) A suggested periodic table up to $Z \leq 172$, based on Dirac-Fock calculations on atoms and ions. Phys Chem Chem Phys 13:161–168

Pyykkö P (2011b) Relativistic effects in chemistry: more common than you thought. Ann Rev Phys Chem 63:45–64

Rahn KA (1976) Technical Report. University of Rhode Island

Seaborg GT (1968) Elements beyond 100, present status and future prospects. Ann Rev Nucl Sci 18:53–152

Scheele CW (1771) Undersökning om fluss-spat och dess syra. Kongl Vetenskaps Academiens Handlingar 32:120–137

Scheele CW (1774) On Brun-sten eller Magnesia, och dess Egenskaper. Kongl Vetenskaps Academiens Handlingar 35:89–116

Schilling JG, Unni CK, Bender ML (1978) Origin of chlorine and bromine in the oceans. Nature 273:631–636

Sharp ZD, Barnes JD, Brearly AJ, Chaussidon M, Fisher TP, Kamenetsky VS (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature 446:1062–1065

Sharp ZD, Mercer JA, Jones RH, Brearley AJ, Selverstone J, Bekker A, Stachel T (2013) The chlorine isotope composition of chondrites and Earth. Geochim Cosmochim Acta 107:189–204

Stacy FD (1969) Physics of the earth, 3rd edn. Wiley Interscience, New York

Suess H, Urey H (1956) Abundances of the Elements. Rev Mod Phys 28:53–74

Turekian KK (1971) Geochemical distribution of elements. McGraw-Hill Encyclopedia of Science and Technology 4:627–630

Weeks ME (1942) The discovery of the elements. XVIII. The halogen family. J Chem Ed 9:1915–1939

Wieser ME, Holden N, Coplen TC, Böhlke JK, Berglund M, Brand WA, De Biévre P, Gröning M, Loss RD, Meija J, Hirata T, Prohaska T, Schoenberg R, O'Connor G, Walczyk T, Yoneda S, Zhu XK (2013) Atomic weights of the elements 2011 (IUPAC Technical Report). Pure Appl Chem 85:1047–1078

Chlorine

2

2.1 Isotopes of Chlorine

2.1.1 Stable Isotopes

Chlorine is the second element of the halogen group (group 17 of the periodic table) and is positioned between sulphur and argon in period 3 of this table. Its nucleus consists of 17 protons. It has two stable isotopes as discovered by Aston (1919), ^{35}Cl with 18 neutrons and ^{37}Cl with 20 neutrons. According to the latest report from the IUPAC (Berglund and Wieser 2011) ^{35}Cl is the most common stable isotope with an abundance of 75.76 % of the chlorine, while ^{37}Cl consists of the remaining 24.24 %.

2.1.2 Notation of Stable Isotope Variations and Reference Standard

Variations in chlorine isotope data are reported in the familiar delta notation. The definition for chlorine is:

$$\delta^{37}\mathrm{Cl} = \frac{(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{sample} - (^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{standard}}{(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{standard}} \times 1{,}000 \qquad (2.1)$$

Although no standard has been formally defined it was already shown by Kaufmann (1984) that no significant variability was found between seawater samples from different locations and depths. For that reason he proposed to use ocean water as international standard. As name for this standard he proposed Standard Mean Ocean Chloride (SMOC) which has been in informal use since then by most laboratories working in chlorine isotope geochemistry. The big advantage of the use of ocean chloride as isotope standard is that it can be obtained easily and can be used and exchanged between laboratories without any problem (Kaufmann 1984). Godon et al. (2004) did collect ocean water samples from 15 different locations worldwide, and from three of these locations they collected also a depth profile. No significant variation was observed between all measured samples and from these observations it was concluded that ocean water has an invariant δ^{37}Cl of 0.00 ‰ versus SMOC within analytical error, and could thus be used as isotope standard. This study has been confirmed by Liu et al. (2013), who analysed, as part of their study to test a new on-line method to analyse chlorine isotopes with the use of a GasBench to purify chloromethane gas, 10 different seawaters taken from the Chinese coast. The measurements on these samples were all within 0.1 ‰ of their ocean water standard, with an average and standard deviation of 0.00 ± 0.06 ‰.

In two studies it was suggested that variations in ocean water chlorine stable isotopes exist (Shirodkar et al. 2003, 2006). These variations were partly unexplainable, and partly explained as due to evaporation of the upper layer of ocean water. Considering these variations the authors

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_2,

suggested that it would be advisable to use the ISL354 standard (as developed by Xiao et al. 2002) in stead of ocean chloride as standard for chlorine isotope research. The samples that showed isotope variations in ocean water were measured by a different technique than the samples that indicated no variation (TIMS vs. IRMS) and they were measured in only one laboratory. Considering the fact that the divergent analyses were done in only one laboratory it would be advisable that interlaboratory exchange and measurement of samples between this laboratory and laboratories that analyse by IRMS is organised so that the differences in results between the two techniques can be independently confirmed.

2.1.3 Radioactive Isotopes

Aside from the two stable isotopes 22 radioactive isotopes of chlorine are known. These have mass numbers 28–51, thus containing 11–34 neutrons. The isotopes ^{28}Cl–^{30}Cl decay by proton decay, and they have extremely low half-lives of less than 30 ns. They are found beyond the so called proton drip-line, which can be considered as the edge of the "stable" radioactive isotopes. The isotopes ^{31}Cl–^{34}Cl decay primarily by positron or β^+ decay and the isotopes ^{38}Cl–^{51}Cl decay by electron of β^- decay. All these isotopes have (very) short half-lives, the longest living of these is ^{39}Cl with a half-life of 55.6 min. ^{36}Cl which can decay with both β^- decay to ^{36}Ar and with electron capture to ^{36}S has a much longer half-life of 301,000 years. This cosmogenic isotope is formed by cosmic radiation in the upper atmosphere and is present in environmental chlorine at a ratio of about 7×10^{-13} compared to ^{37}Cl. The relatively long half-life of ^{36}Cl makes it useful for radioactive dating, especially for groundwater samples up to about one million years old.

2.2 Chemistry of Chlorine

As with all halogen elements the most common oxidation state is −I and the most common form of chlorine in nature is the chloride ion (Cl^-). Negative ions are formed by the addition of electrons to the valence shell by a process called electron affinity. Of all the elements chlorine has the highest electron affinity (349 kJ mol^{-1}), which is even higher than the electron affinity of fluorine. The reason for this is that the fluorine atom is very small and the high electron density in the valence shell compared to chlorine makes it slightly less favourable to add an electron to the shell as compared to chlorine.

Higher oxidation states for chlorine are very well known. They are all strong oxidisers and have different uses as such, mainly as bleaching agents for the lower oxidation states and in pyrotechnics, for example as solid rocket fuel in the higher oxidation states. In these higher oxidation states chlorine is present in the oxyanions hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) where chlorine is in the +I, +III, +V and +VII oxidation state respectively. Oxidation state +IV is also found in the gas chlorine dioxide, and oxidation state +VI in the compound Cl_2O_6 when in the gaseous state. As can be deducted from the Frost diagram [Frost (1951), Fig. 2.1] in acid solutions only chloride, chlorine and perchlorate are stable as the other forms tend to disproportionate, while in alkaline solutions chloride, hypochlorite, chlorite, chlorate and perchlorate can be stable while chlorine and chlorine dioxide tend to disproportionate.

The reduction potentials used in this figure were taken from www.webelements.com. Well known is the hypochlorite ion which, in the form of sodium hypochlorite is commonly used as a bleaching agent. It is the strongest oxidiser of all chlorine oxyanions and it is a very unstable ion that only exists in solutions. When water is removed from a sodium hypochlorite solution it converts to a mixture of sodium chloride and sodium chlorate. It is a very effective oxidizer used to kill germs while cleaning. It is also used, mainly in the form of calcium hypochlorite as "chlorine" in swimming pools.

Chlorite is mainly used for the generation of chlorine dioxide which is also used as a bleaching agent. Sodium chlorite itself was used in the past as a chlorinating agent for the disinfection of

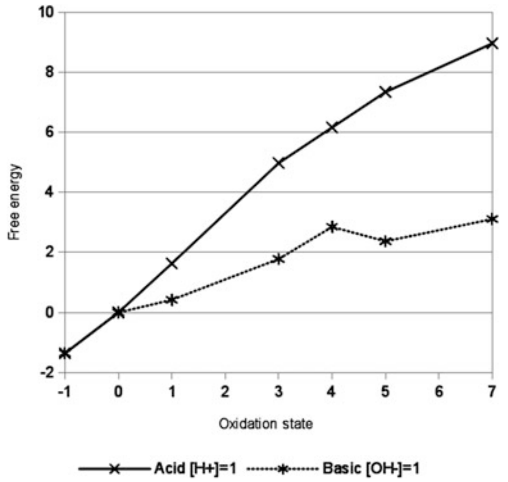

Fig. 2.1 Frost diagram of the chlorine species showing the relative stability of these species in acid and basic solutions

drinking water, as it, contrary to chlorine did not produce trihalomethanes organic contaminants. Since 2009 it is however phased out in the European Union.

Chlorates are mainly used as herbicides and oxidants in explosives and rock fuel. Little is known about its occurrence on earth but it appears to be associated with perchlorate occurrences (Rao et al. 2010) which are very well know from the Atacama desert in Chile (Ericksen 1981) and also from more recent studies in the United States (Rajagopalan et al. 2006; Parker et al. 2008) and Antarctica (Kounaves et al. 2010). As these studies indicate that chlorate is almost always associated with perchlorate it is also likely that chlorate is present at the Phoenix landing site on Mars (Hanley et al. 2012) where perchlorate was detected. Chlorate salts have very strong freezing point depression capabilities and the eutectic point of magnesium chlorate dissolved in water is only 204 K (−66 °C). As a result it is theoretically possible that liquid water on Mars is present as concentrated chlorate solutions (Hanley et al. 2012). Chlorate is also common in municipal drinking water as a result of chlorination of with chlorine dioxide. Concentration in drinking water can be as high as 3.2–7.0 mg/L (Michael et al. 1981) and the WHO (2005) has proposed a provisional guideline value of 0.7 mg/L. This guideline value is designated as provisional because use of chlorine dioxide as a disinfectant may result in the chlorate guideline value being exceeded, and difficulties in meeting the guideline value should never be a reason for compromising adequate disinfection according to the WHO (2005). One study is known in which chlorine isotope ratios of chlorate compounds have been measured. Ader et al. (2001) analysed the chlorine isotope composition of several man made chlorates and found that δ^{37}Cl values in commercially produced sodium and potassium chlorates are +0.2 to +0.3 ‰ versus SMOC.

Perchlorates do have comparable applications as chlorates. Unlike chlorates however there is considerable more knowledge on the occurrence and distribution of perchlorates on earth. It is at present generally well known that it is much more widely distributed than was assumed in the past. Perchlorate is produced naturally by atmospheric oxidation of chlorine species with ozone (e.g. Kang et al. 2008) and due to the solubility of most perchlorate salts it is mostly concentrated in the driest regions on the earth. Perchlorates are also manufactured industrially by electrolysis of sodium chloride brines. The annual production is in the order of 10^7 kg year^{-1} (Dasgupta et al. 2006). Its isotopic behaviour is by now fairly well established. Following preliminary studies by Ader et al. (2001) it is now possible to determine various sources of perchlorate by its chlorine and oxygen isotopes (e.g. Sturchio et al. 2011) and it has also been possible to determine the isotope effects of microbial perchlorate reduction (Ader et al. 2008).

Chlorine is also present in organic compounds. Although minor amounts of organochlorine compounds are known to be from natural origins larger amounts are produced annually in industrial processes. Analyses of the chlorine isotopic composition of organochlorine compounds potentially found in geologic environments started with the development of several methods using dual inlet techniques in the 1990s (Van Warmerdam et al. 1995; Holt et al. 1997; Jendrzejewski et al. 1997; Beneteau et al. 1999). During the early years of the 21st century techniques were developed using continuous flow techniques (Shouakar-Stash et al. 2003; Wassenaar and Koehler 2004) and with ICP-MS (Van Acker et al. 2006). More recently also techniques were developed where these isotopes are measured directly on whole molecules and fragments of them using isotope ratio mass spectrometry (e.g. Shouakar-Stash et al. 2006) and quadrupole mass spectrometry (Jin et al. 2011; Bernstein et al. 2011).

References

Ader M, Coleman ML, Doyle SP, Stroud M, Wakelin D (2001) Methods for the stable isotopic analysis of chlorine in chlorate and perchlorate compounds. Anal Chem 73:4946–4950

Ader M, Chaudhuri S, Coates JD, Coleman M (2008) Microbial perchlorate reduction: a precise laboratory determination of the chlorine isotope fractionation and its possible biochemical basis. Earth Planet Sci Lett 269:604–612

Aston FW (1919) The constitution of the elements. Nature 104:393

Beneteau KM, Aravena R, Frape SK (1999) Isotopic characterization of chlorinated solvents-laboratory and field results. Org Geochem 30:739–753

Berglund M, Wieser ME (2011) Isotopic compositions of the elements 2009 (IUPAC technical report). Pure Appl Chem 83:397–410

Bernstein A, Shouakar-Stash O, Ebert K, Laskov C, Hunkeler D, Jeannottat S, Sakaguchi-Söder K, Laaks J, Jochmann MA, Cretnik S, Jager J, Haderlein SB, Schmidt TC, Aravena R, Elsner M (2011) Compound-specific chlorine isotope analysis: a comparison of gas chromatography/isotope ratio mass spectrometry and gas chromatography/quadrupole mass spectrometry methods in an interlaboratory study. Anal Chem 83:7624–7634

DasGupta PK, Dyke JV, Kirk AB, Jackson WA (2006) Perchlorate in the United States. Analysis of relative source contributions to the food chain. Environ Sci Technol 40:6608–6614

Ericksen GE (1981) Geology and origin of the Chilean nitrate deposits. USGS Prof Paper 1188:37 pp

Frost AA (1951) Oxidation potential—free energy diagrams. J Amer Chem Soc 73:2680–2683

Godon A, Jendrzejewski N, Eggenkamp HGM, Banks DA, Ader M, Coleman ML, Pineau F (2004) A cross calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. Chem Geol 207:1–12

Hanley J, Chevrier JF, Berget DJ, Adams RD (2012) Chlorate salts and solutions on Mars. Geophys Res Lett 39:L08201. doi:10.1029/2012GL051239

Holt BD, Sturchio NC, Abrajano TA, Heraty LJ (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. Anal Chem 69:2727–2733

Jendrzejewski N, Eggenkamp HGM, Coleman ML (1997) Sequential determination of chlorine and carbon isotopic composition in single microliter samples of chlorinated solvent. Anal Chem 69:4259–4266

Jin B, Laskov C, Rolle M, Haderlein SB (2011) Chlorine isotope analysis of organic contaminants using GCqMS: method optimization and comparison of different evaluation schemes. Environ Sci Technol 45:5279–5286

Kang N, Jackson WA, Dasgupta PK, Anderson TA (2008) Perchlorate production by ozone oxidation of chloride in aqueous and dry systems. Sci Total Environ 405:301–309

Kaufmann RS (1984) Chlorine in groundwater: stable isotope distribution. Ph.D. thesis, University of Arizona, Tucson, Ariz

Kounaves SP, Stroble ST, Anderson RM, Moore Q, Catling DC, Douglas S, McKay CP, Ming DW, Smith PH, Tamppari LK, Zent AP (2010) Discovery of natural perchlorate in the Antarctic Dry Valleys and its global implications. Environ Sci Technol 44:2360–2364

Liu YD, Zhou AG, Gan YQ, Liu CF, Yu TT, Li XQ (2013) An online method to determine chlorine stable isotope composition by continuous flow isotope ratio mass spectrometry (CF-IRMS) coupled with a Gasbench II. J South Centr Univ 20:193–198

Michael GE, Miday RK, Bercz JP, Miller RG, Greathouse DG, Kraemer DF, Lucas JB (1981) Chlorine dioxide water disinfection: a prospective epidemiology study. Arch Environ Health 36:20–27

Parker DR, Seyfferth AL, Reese BK (2008) Perchlorate in groundwater: a synoptic survey of "pristine" sites in the conterminous Unites States. Environ Sci Technol 42:1465–1471

Rajagopalan S, Anderson TA, Fahlquist L, Rainwater KA, Ridley M, Jackson WA (2006) Widespread presence of naturally occurring perchlorate in high plains of Texas and New Mexico. Environ Sci Technol 40:3156–3162

Rao B, Hatzinger PB, Bohlke JK, Sturchio NC, Andraski BJ, Eckardt FD, Jackson WA (2010) Natural chlorate in the environment: application of a new IC-ESI/MS/MS method with a (ClO_3^-)–^{18}O internal standard. Env Sci Tech 44:8429–8434

Shirodkar PV, Xiao YK, Hai L (2003) Boron and chlorine isotopic signatures of seawater in the Central Indian ridge. Current Sci 85:313–320

Shirodkar PV, Xiao YK, Sarkar A, Dalal SG, Chivas AR (2006) Influence of air-sea fluxes on chlorine isotopic composition of ocean water: Implications for constancy in $\delta^{37}Cl$—a statistical inference. Environ Intern 32:235–239

Shouakar-Stash O, Drimmie RJ, Frape SK (2003) Stable hydrogen, carbon and chlorine isotope measurements of selected chlorinated organic solvents. J Contam Hydrol 60:211–228

Shouakar-Stash O, Drimmie RJ, Zhang M, Frape SK (2006) Compound-specific chlorine isotope ratios of TCE, PCE and DCE isomers by direct injection using CF-IRMS. Appl Geoch 21:766–781

Sturchio NC, Böhlke JK, Gu BH, Hatzinger PB, Jackson WA (2011) Isotopic tracing of perchlorate in the environment. In: Baskaran M (ed) Handbook of environmental isotope geochemistry, Advances in Isotope Geochemistry. Springer, Berlin, Heidelberg

Van Acker MRMD, Shahar A, Young ED, Coleman ML (2006) GC/multiple collector-ICPMS method for chlorine stable isotope analysis of chlorinated aliphatic hydrocarbons. Anal Chem 78:4663–4667

Van Warmerdam EM, Frape SK, Aravena R, Drimmie RJ, Flatt H, Cherry JA (1995) Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. Appl Geochem 10:547–552

Wassenaar LI, Koehler G (2004) On-line technique for the determination of the δ^{37}Cl of inorganic and total organic Cl in environmental samples. Anal Chem 76:6384–6388

WHO (World Health Organization) (2005) Chlorite and chlorate in drinking-water. Background document for development of WHO guidelines for drinking-water quality. Available from http://www.who.int/entity/water_sanitation_health/dwq/chemicals/chlorateandchlorite0505.pdf. Last accessed 12 Aug 2014

Xiao YK, Zhou YM, Wang QZ, Wei HZ, Liu WG, Eastoe CJ (2002) A secondary isotopic reference material of chlorine from selected seawater. Chem Geol 182:655–661

Bromine

3

3.1 Isotopes of Bromine

3.1.1 Stable Isotopes

Bromine is the third of the group 17 elements (halogens) and is positioned between selenium and krypton in period 4 of the periodic table. Its nucleus has 35 protons and the two stable isotopes, (^{79}Br and ^{81}Br) have 44 and 46 neutrons respectively. Both isotopes have about comparable abundances although the lighter ^{79}Br is slightly more common than the heavier ^{81}Br with 50.69 and 49.31 % respectively (Berglund and Wieser 2011).

3.1.2 Notation of Stable Isotope Variations and Reference Standard

Variations in bromine isotope data are reported in the familiar delta notation. The definition for bromine is:

$$\delta^{81}Br = \frac{(^{81}Br/^{79}Br)_{sample} - (^{81}Br/^{79}Br)_{standard}}{(^{81}Br/^{79}Br)_{standard}} * 1{,}000 \tag{3.1}$$

No standard has yet been defined officially, and unlike the situation for chlorine there has not been yet an exhaustive study to examine the natural variation of bromide in the oceans. Despite this lack of knowledge Eggenkamp and Coleman (2000) proposed to use the isotope ratio of seawater as its international stable isotope standard. They considered this ratio as constant in the oceans as the residence time of bromide in the oceans (130,000,000 years; Broeker and Peng 1982) is even longer than the residence time of chloride in the oceans (87,000,000 years, Berner and Berner 1987). These values indicate that the oceans are a very well mixed and homogeneous bromide reservoir. They proposed to call this reference Standard Mean Ocean Bromide (SMOB) as analogue to SMOC for chlorine. The first possible confirmation of the assumption that the isotope composition of ocean water is constant comes from Du et al. (2013) who analysed the bromine isotope composition of five seawater samples collected along the Chinese coast and observed that they all had bromine isotopes ratios which were within 0.1 ‰ of each other.

3.1.3 Radioactive Isotopes

Aside from the two stable isotopes 30 radioactive isotopes are known. These have mass numbers 66–97, thus containing 31–62 neutrons. The isotopes ^{66}Br to ^{69}Br decay by proton decay. They have extremely low half-lives of less than 24 ns. They are found beyond the proton drip-line, which can be considered as the edge of the "stable" radioactive isotopes. The isotopes ^{70}Br to ^{77}Br decay mostly by positron or β^+

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Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_3,

decay and the isotopes ^{82}Br to ^{94}Br decay by electron or β^- decay. ^{78}Br and ^{80}Br can decay by either β^+ or β^- decay. All these isotopes have a (very) short half-life, the longest living of these is ^{77}Br with a half-life of only 57.036 h. It is not known yet what is the decay mode for the isotopes ^{95}Br to ^{97}Br. Unlike chlorine there is no radioactive isotope with a half-life long enough to be of geological importance.

3.2 Chemistry of Bromine

As with all halogen elements the most common oxidation state is −I and the most common form of bromine in nature is the bromide ion (Br^-). Negative ions are formed by the addition of electrons to the valence shell by a process called electron affinity, the value of which is 324 kJ mol^{-1} for bromine.

As for chlorine, higher oxidation states for bromine are well known. They are comparable to those of chlorine and oxidation states +I and +V are well established. Although salts of the +III oxidation state (bromites) are stable they are less well established and no data for their oxidation potential were published at www.WebElements.com. The relative stability of the bromine oxidation states is shown in a frost diagram (Frost 1951), see Fig. 3.1.

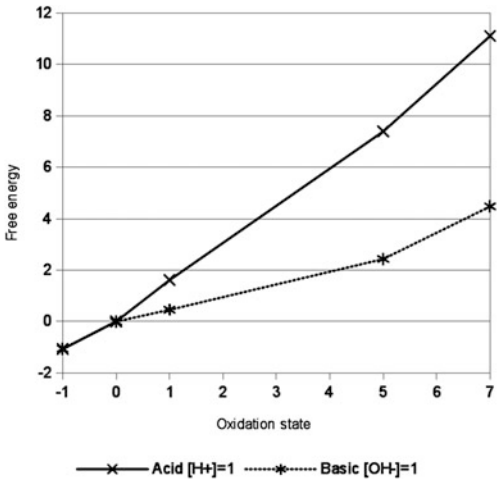

Fig. 3.1 Frost diagram of the bromine species showing the relative stability of these species in acid and basic solutions

The reduction potentials used in this figure were taken from www.webelements.com. From this figure it can be deducted that in acid solutions bromide, bromine and bromate are stable, while hypobromite will disproportionate, in alkaline solutions bromine will disproportionate to bromide and hypobromite. Bromide and bromate are also stable. Contrary to the situation with chlorine the +VII oxidation state of bromine is very difficult to obtain and perbromates and perbromic acid were unknown prior to 1968. They were for the first time synthesised in 1968, originally through radioactive decay of ^{83}Se to ^{83}Br in $^{83}SeO_4^{2-}$ forming $^{83}BrO_4^-$ plus a β^- particle (Appelman 1968). A few years later Appelman (1973) managed to produce perbromate ions from bromate ions through the oxidation with fluorine and xenondifluoride gas. Due to the difficulty to oxidise bromate to perbromate, perbromate and perbromic acid are not found in nature. Hypobromite is formed by the disproportionation of bromine in alkaline solution. It has a very specific use in the defence system of higher animals as certain white blood cells prefer to oxidise bromide dissolved in the blood to hypobromite above the oxidation of chloride to attack certain parasites (Mayeno et al. 1989) even when chloride concentrations in the blood are more than a thousand times higher than bromide concentrations.

The more stable oxyanions of bromine are sometimes found in drinking waters as bromide, which is always present in small concentrations in drinking water, can easily be oxidised by ozone or other oxidizing agents (such as chlorine or even the presence of sunlight). The formation of bromates is not desired in drinking waters as they are a suspected carcinogen (Kurokawa et al. 1990) and the EU maximum allowable concentration in drinking water is 0.01 mg L^{-1} (Diduch et al. 2011). Bromates are however often found in variable quantities in drinking waters and considerable efforts are being taken to remove it from these waters (e.g. Genuino and Espino 2012; Wisnieuwski et al. 2011).

The further existence of oxidised bromine species in nature is only recently established. Bobrowski et al. (2003) determined bromine oxide (BrO) in the plume of the volcano Monserrat. Not much is known about the occurrence of bromine oxyanions in other environments, but considering their occurrence in drinking waters and their stability they must be present in other environments. No research is done yet on the bromine isotope composition of bromine oxyanions. Considering the low concentrations of these ions in the natural environment and the infancy of the bromine isotope studies this does not come as a surprise, although hopefully in the future techniques will be developed to make it possible to study the isotope behaviour of these compounds.

Bromine is also found in organic compounds. Compared to chlorine it has a much more important organic geochemistry and it is found in a considerable number of natural and artificial compounds. This last group consists for a large part of fire retardants. From a relatively early date methods were developed to analyse stable isotope compositions of organically bound bromine (Sylva et al. 2007) and although the number of scientific papers on bromine isotopes is still very modest a significant number of them is on organic compounds (e.g. Carrizo et al. 2011; Hitzfeld et al. 2011; Holmstrand et al. 2010).

References

Appelman EH (1968) Synthesis of perbromates. J Amer Chem Soc 90:1900–1901

Appelman EH (1973) Nonexistent compounds. Two case histories. Acc Chem Res 6:113–117

Berglund M, Wieser ME (2011) Isotopic compositions of the elements 2009 (IUPAC technical report). Pure Appl Chem 83:397–410

Berner EK, Berner RA (1987) The global water cycle: geochemistry and Environment. Prentice-Hall, Inc., Englewood Cliffs

Bobrowski N, Hönninger G, Galle B, Platt U (2003) Detection of bromine monoxide in a volcanic plume. Nature 423:273–276

Broeker WS, Peng TH (1982) Tracers in the sea. Eldigio Press Lamont Doherty Geological Observatory

Carrizo D, Unger M, Holmstrand H, Andersson P, Gustafsson Ö, Sylva SP, Reddy CM (2011) Compound-specific bromine isotope compositions of one natural and six industrially synthesised organobromine substances. Environ Chem 8:127–132

Diduch M, Pokowska Ź, Namieśnik J (2011) Chemical quality of bottled waters: a review. J Food Sci 76:178–196

Du Y, Ma T, Yang J, Liu L, Shan HM, Cai HS, Liu CF, Chen LZ (2013) A precise analytical method for bromine stable isotopes in natural waters by GasBench II-IRMS. Int J Mass Spectrom 338:50–56

Eggenkamp HGM, Coleman ML (2000) Rediscovery of classical methods and their application to the measurement of stable bromine isotopes in natural samples. Chem Geol 167:393–402

Frost AA (1951) Oxidation potential—free energy diagrams. J Amer Chem Soc 73:2680–2683

Genuino HC, Espino MPB (2012) Occurrence and sources of bromate in chlorinated tap drinking water in Metropolitan Manila, Philippines. Arch Env Cont Toxic 62:369–379

Hitzfeld KL, Gehre M, Richnow HH (2011) A novel online approach to the determination of isotopic ratios for organically bound chlorine, bromine and sulphur. Rapid Commun Mass Spectrom 25:3114–3122

Holmstrand H, Unger M, Carrizo D, Andersson P, Gustafsson Ö (2010) Compound-specific bromine isotope analysis of brominated diphenyl ethers using GC-ICP-multicollector-MS. Rapid Commun Mass Spectrom 24:2135–2142

Kurokawa Y, Maekawa A, Takahashi M, Hayashi Y (1990) Toxicity and carcinogenicity of potassium bromate—a new renal carcinogen. Env Health Persp 87:309–335

Mayeno AN, Curran AJ, Roberts RL, Foote CS (1989) Eosinophils preferentially use bromide to generate halogenating agents. J Biol Chem 264:5660–5668

Sylva SP, Ball L, Nelson RK, Reddy CM (2007) Compound-specific ^{81}Br/^{79}Br analysis by capillary gas chromatography/multicollector inductively coupled plasma mass spectrometry. Rapid Commun Mass Spectrom 21:3301–3305

Wisniewski JA, Kabsch-Korbutowicz M, Lakomska S (2011) Donnan dialysis and electrodialysis as viable options for removing bromates from natural water. Desalination 281:257–262

Part II

Preparation Techniques

Preparation Techniques for the Analysis of Stable Chlorine Isotopes

4

4.1 Classical Methods

Before the development of "modern" isotope ratio mass spectrometers (Nier 1947; McKinney et al. 1950) stable isotope ratios and variations in these ratios were measured by techniques such as gravimetric determination (e.g. Richards and Wells 1905; Curie 1921) and mass spectrography (Aston 1921, 1931; Von Kallman and Lasareff 1932; Nier and Hanson 1936). Although these techniques produced results that were not as precise as the more modern mass spectrometric techniques surprisingly good results were already obtained with them and the atomic weight of chlorine could be determined with good precision using these techniques. Isotope ratio variations however were not yet observed using these techniques as they are smaller than the precisions of these techniques. A short description of these techniques however seems viable here as they facilitated the later development of more advanced isotope ratio analysis techniques.

4.1.1 Gravimetric Determination of the Atomic Weight of Chlorine

Using chemicals which were purified from commercially available reagents Richards and Wells (1905) were able to determine the atomic weights of sodium and chlorine by conversion of sodium chloride to silver chloride and silver to silver chloride and exactly weighing the reaction products. They observed that the atomic weight of chlorine is either 35.470 or 35.473 depending on the atomic weight of silver (107.920 in the former and 107.930 in the latter), as the atomic weight of silver was not yet known to the same precision as Richards and Wells (1905) were able to weigh the silver chloride precipitate. Using the same technique they were also able to determine the atomic weight of sodium as either 23.006 or 23.008. These values are only very slightly higher (0.05–0.07 %) than the values accepted today (107.8682 for silver, 22.9898 for sodium and about 35.45 for chlorine (Wieser and Coplen 2010). The error in the measurement of the chlorine atomic weight is almost perfectly explainable by the fact that the value for the atomic weight of silver that was used in their study was too high, indicating the great quality of their work.

Gravimetric determination of the atomic weight was also used in a few more studies from the early 20th century which were done to determine the atomic weight of chlorine from various natural rock samples. In these studies (Curie 1921; Gleditsch and Samdahl 1922; Dorenfeldt 1922; Harkins and Stone 1926) small variations between different rock samples were found, however in all cases these variations were smaller than the precision of their determinations.

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Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_4,

4.1.2 Mass Spectrographic Analyses

Very shortly after the development of the mass spectrograph (Aston 1919b) it was determined that chlorine was composed of only two stable isotopes with masses 35 and 37, from which it was clear that the isotope with mass 35 was the most common (Aston 1919a, 1920, 1921). In these early mass spectrographic studies the isotopes were detected on photographic plates (Aston 1925) and the determination of the actual ratio between the isotopes was complex.

In the following years improved mass spectrographs were developed and it was possible to increase the quality of the isotope measurements (Aston 1931; Von Kallman and Lasareff 1932; Nier and Hanson 1936). The ratio between the two stable ions was determined in this period with good precision (about 3.1; Aston 1931), however, in spite of these improvements the precision of the measurements did not improve beyond the point where natural variations became measurable.

4.1.3 Early Mass Spectrometric Analyses

Only after the development of mass spectrometers with double ion collectors (Nier et al. 1946; Nier 1947; McKinney et al. 1950; Nier 1955) it became possible to determine variations beyond the analytical precision and finally it was possible to analyse isotope variations produced in chemical fractionation experiments (e.g. Bartholomew et al. 1954; Klemm and Lundén 1955; Lundén and Herzog 1956; Herzog and Klemm 1958; Hill and Fry 1962; Howald 1960). That these measurements were of very good quality can be concluded from the results that were obtained already very early by Madorsky and Strauss (1947) who determined that, during the process of diffusion, the diffusion coefficient of ^{35}Cl was about 1.0012 to 1.0022 times that of ^{37}Cl. These values have been confirmed in almost all subsequent determinations of the isotope fractionation that is caused by diffusion of chloride in aqueous solutions, both in experimental and natural systems.

4.2 General Methods to Analyse Stable Chlorine Isotopes

The information presented in this chapter is for a large part described earlier in both my PhD thesis (Eggenkamp 1994) as well as the chapter I wrote for the "Handbook of Stable Isotope Analytical Techniques" (De Groot 2004). It has been repeated here to fully describe the various methods that have been developed in search for the "best" method to analyse chlorine isotopes. The information is supplemented with methods that have been developed after 2002 when I finished writing my chapter for De Groot (2004).

4.2.1 Methods Using Other Gases than Chloromethane in Dual Inlet IRMS

4.2.1.1 Application of Hydrogen Chloride as Gas in Dual-Inlet IRMS

Hydrogen chloride was used in several early chlorine isotope studies (Nier and Hanson 1936; Madorsky and Strauss 1947; Johnston and Arnold 1953; Hoering and Parker 1961) as the gas that was introduced into the mass spectrometer. Among these studies was the first comprehensive chlorine isotope study of natural, geological samples (Hoering and Parker 1961). They measured the chlorine isotope composition for 81 samples of different geological material ranging from aqueous samples to rock samples. Hoering and Parker (1961) were able to analyse the chlorine isotope ratio in hydrogen chloride gas with a precision of 0.8 ‰. The reason why hydrogen chloride gas was used as mass spectrometer gas was that it can be prepared quantitatively and because it produces a very simple mass scan with only four ion species (Table 4.1). A big disadvantage of hydrogen chloride as mass spectrometer gas is however that it sticks to the walls of the vacuum system, and as a result that it has a large memory effect.

Table 4.1 Mass scan for HCl as mass spectrometer gas (Hoering and Parker 1961)

Species	m/z	Relative intensity
$^{35}Cl^+$	35	17.0
$H^{35}Cl^+$	36	100
^{37}Cl	37	5.4
$H^{37}Cl^+$	38	32.5

Table 4.2 Mass scan for Cl_2 gas as mass spectrometer gas according to Eggenkamp (2004)

Species	m/z	Relative intensity
$^{35}Cl^+$	35	13
$^{37}Cl^+$	37	4
$^{35}Cl_2{}^+$	70	100
$^{35}Cl^{37}Cl^+$	72	64
$^{37}Cl^+$	74	10

The pattern is based on the abundances of the isotopes ^{35}Cl and ^{37}Cl and assumes that the total intensity of the monoatomic species is 10 % of the total intensity of the diatomic species

Chloride samples were precipitated as silver chloride (AgCl). For rock and mineral samples this was produced according to the method described by Kuroda and Sandell (1953). Samples were then dissolved in ammonium hydroxide, to which magnesium metal was added in excess. The magnesium displaces the silver, and the ammonium chloride solution that was formed was filtered. The remaining solution was evaporated to dryness in a vacuum oven. The solution from which the ammonium chloride was precipitated has a high pH, and care must be taken that it would not react with atmospheric carbon dioxide as this can not be separated from hydrogen chloride, and as such it will interfere during isotope analysis. The ammonium chloride residue was converted to hydrogen chloride by reaction with sulphuric acid under vacuum. The gaseous hydrogen chloride was trapped onto frozen phosphorus pentoxide to remove traces of water, and the dried hydrogen chloride was frozen into a sample container for introduction into the mass spectrometer.

4.2.1.2 Application of Chlorine Gas in Dual-Inlet IRMS

Chlorine gas has only been used rarely as mass spectrometer gas. It could be considered as a potentially useful mass spectrometer gas due to its simple mass scan which should be approximately as shown in Table 4.2. As shown in this table only ^{35}Cl and ^{37}Cl peaks are present near the atomic mass of chlorine so that no calculations have to be made to take interference into account. If the larger peaks around mass 70–74 are used to calculate the isotope ratio the presence of the mixed $^{35}Cl^{37}Cl^+$ ion must be taken into account, introducing a more complex calculation. A major disadvantage of this gas is however the fact that it produces very large memory effects.

Bartholomew et al. (1954) used chlorine gas as their mass spectrometer gas to study the isotope effects in reactions of *tert*-butyl chloride (2-chloro-2-methyl-propane). Hydrogen chloride was prepared from silver chloride using a method comparable to Hoering and Parker (1961). In their preparation technique however, Bartholomew et al. (1954) heated ammonium chloride with concentrated sulphuric acid, and the hydrogen chloride that was produced was trapped in a bubbler containing a small amount of cold water by means of a stream of nitrogen gas. The aqueous hydrogen chloride was oxidised to chlorine gas by persulphate oxidation (Brown et al. 1953) in a stream of helium. The chlorine gas was frozen in a cold trap, and the helium pumped away. The chlorine gas was then transferred to the mass spectrometer and analysed.

4.2.2 Application of Chloromethane in Dual-Inlet IRMS

The most commonly used gas for both dual inlet and continuous flow isotope ratio mass spectrometry of chlorine at the moment is chloromethane (methyl chloride, CH_3Cl). At least three different methods have been proposed to produce quantitative yields of this gas. Chloromethane is much less reactive than either hydrogen chloride or chlorine gas and it shows no memory effects in the inlet and vacuum systems of mass spectrometers.

Table 4.3 Mass scan for chloromethane as mass spectrometer gas according to Owen and Schaeffer (1955) and Taylor and Grimsrud (1969)

Species	m/z	Relative intensity	
		Owen and Schaeffer (1955)	Taylor and Grimsrud (1969)
$^{35}Cl^+$	35		2.8
$H^{35}Cl^+$	36		1.2
$^{37}Cl^+$	37		1.0
$H^{37}Cl^+$	38		0.4
$^{12}C^{35}Cl^+$	47	6.0	7.7
$^{12}CH^{35}Cl^+$	48	3.2	3.2
$^{12}CH_2{}^{35}Cl^+ + {}^{12}C^{37}Cl^+$	49	9.0	9.6
$^{12}CH_3{}^{35}Cl^+ + {}^{12}CH^{37}Cl^+$	50	100	100
$^{13}CH_3{}^{35}Cl^+ + {}^{12}CH_2{}^{37}Cl^+$	51	3.7	3.4
$^{12}CH_3{}^{37}Cl^+$	52	31.7	31.4
$^{13}CH_3{}^{37}Cl^+$	53		0.5

Owen and Schaeffer (1955) only published the mass scan of chloromethane in the region m/z = 47–52

Chlororomethane can be produced from several chloride compounds. In the chlorine stable isotope literature the most important of these are: chloromethane produced from ammonium chloride (Owen and Schaeffer 1955; Herzog and Dörnenburg 1958), chloromethane produced from silver chloride (Langvad 1954; Hill and Fry 1962; Taylor and Grimsrud 1969; Kaufmann 1984; Long et al. 1993; Eggenkamp 1994; Godon 2000; Godon et al. 2004a), and chloromethane produced from copper chloride (Holt et al. 1997). This last technique was developed with the purpose of analysing organochlorine compounds and will be discussed in Sect. 4.6.1.3.

Chlororomethane can be measured both as positive or negative ions. Currently most laboratories using chlororomethane as the mass spectrometer gas measure chlorine isotopes as the positive CH_3Cl^+ ion. The positive ions are measured at m/z 50 and 52 at which positions the main peaks are found. Its mass scan is much more complex than that of hydrogen chloride or chlorine gas and shows several more peaks in its isotope spectrum as not only chlorine but also carbon has a minor isotope with a relatively large abundance, as is shown in Table 4.3.

In the case of negative ions the isotope composition is determined on chloride ions formed by the decomposition of chloromethane molecules in the ion source. In the case of negative ions the mass scan that appears is very simple with only two major peaks at m/z 35 and 37 (see Table 4.4) as shown in both major studies on chlorine isotope analyses using a negative ion source (Taylor and Grimsrud 1969; Pelc and Halas 2008).

4.2.2.1 Preparation of Chloromethane from Ammonium Chloride

Chloromethane can be produced from ammonium chloride, and this technique was commonly used during chlorine isotope in studies from the 1950s (Owen and Schaeffer 1955; Herzog and Dörnenburg 1958). Silver chloride was precipitated from a liquid sample containing dissolved chloride. The silver chloride was subsequently dissolved in ammonia. Silver was removed from this solution as silver sulphide. After evaporation of the remaining solution pure ammonium chloride was left. Ammonium chloride can than be reacted into chloromethane following a procedure described by Blatt (1943). 240 ml of concentrated sulphuric acid is diluted with 40 ml of distilled water, to which is added 350 ml of methanol. During this procedure the temperature must be kept below 70 °C at all times. Approximately 2 ml of this solution is added to 50 mg of ammonium chloride under vacuum. The following reactions can potentially occur:

Table 4.4 Mass scan of chloromethane when analysed as negative ions in dual-inlet mass spectrometry

Species	m/z	Relative intensity	
		Taylor and Grimsrud (1969)	Pelc and Halas (2008)
CN^-	26		0.05
CO^-	28		0.05
$^{35}Cl^-$	35	100	100
$^{37}Cl^-$	37	32.4	32
$^{12}C^{35}Cl^-$	47	0.25	
$^{12}CH^{35}Cl^-$	48	0.20	
$^{12}CH_2{}^{35}Cl^- + {}_{12}C^{37}Cl^-$	49	0.50	
$^{12}CH^{37}Cl^-$	50	0.10	
$^{12}CH_2{}^{37}Cl^-$	51	0.14	

The results obtained by Taylor and Grimsrud (1969) and Pelc and Halas (2008) agree very well with respect to the most common ions in the mass spectrometer source

$$(CH_3)_2SO_4 + 2NH_4Cl > 2CH_3Cl + (NH_4)_2SO_4 \tag{4.1}$$

$$CH_3OH > (CH_3)_2O(\text{Catalysed by sulphuric acid}) \tag{4.2}$$

$$2NH_4Cl + H_2SO_4 > 2HCl + (NH_4)2SO_4 \tag{4.3}$$

The second reaction can be minimised by keeping the temperature of the mixture below 50 °C. A weighed sample of ammonium chloride is placed into a bulb and evacuated. Approximately 2 mL of sulphuric acid and methanol are added through a stopcock. The mixture is heated using an infrared lamp until the reaction ceases. The reaction tube is then chilled with dry ice and the chloromethane that has formed is distilled into an evacuated sample bulb. A potassium hydroxide trap removes any hydrogen chloride that is formed during this reaction. The major disadvantage of this technique is that the yield will not be higher than approximately 35 %. Several tests were done by Owen and Schaeffer (1955) to determine the potential errors caused because of this low yield and it was observed that data were reliable within an experimental error of 2 ‰. However, as it is currently known that the large majority of all measured $\delta^{37}Cl$ data are within 2 ‰ of SMOC, an experimental error with the size of ±2 ‰ is definitely not acceptable for natural chlorine isotope measurements.

4.2.2.2 Preparation of Chloromethane from Silver Chloride

The most commonly used technique at present to produce chloromethane for dual inlet and continuous flow IRMS is the production of chloromethane from silver chloride that has been precipitated from an aqueous solution. The first to apply this technique was Langvad (1954) in a study on potential isotope fractionation of chlorine isotopes by ion chromatography. Over the next 50 years this method was improved considerably by Hill and Fry (1962), Taylor and Grimsrud (1969), Kaufmann (1984), Long et al. (1993), Eggenkamp (1994) and finally Godon (2000). The production of chloromethane from chloride in aqueous solution involves in principle three steps, precipitation of silver chloride, reaction of silver chloride with iodomethane in evacuated glass capsules to form chloromethane and finally the gas chromatographic separation of chloromethane from iodomethane prior to isotope analysis.

Precipitation of Silver Chloride

Depending on the chloride concentration of the solution the silver chloride is precipitated in slightly different ways. When the chloride concentration is lower than about 500 mg/L silver chloride is precipitated after the addition of dry chemicals to the sample solution, if the chloride concentration is higher by the addition of these chemicals in dissolved form. Originally the amount of chloride estimated to be necessary for chlorine isotope measurements was 0.1 mol (Kohnen 1988). As the result from improvements in sample preparation the minimum amount necessary for dual inlet mass spectrometric measurements is presently about 0.02 mol, although 0.05 mol seems to be a relatively ideal amount. The amount of sample containing this amount of chloride is put in a glass beaker. In the case of higher chloride concentrations (<10 mL solution needed for analysis) to the solution 4 mL of a 1 M KNO_3 solution and 2 mL of a Na_2HPO_4-citric acid buffer solution is added.

The potassium nitrate solution is necessary to reach a high ionic strength. Taylor and Grimsrud (1969) discovered that if the ionic strength of the solution from which silver chloride is to be precipitated is less than 0.4 M the chloromethane yield fell below 100 %. For example at an ionic strength of 0.2 M it was only 45 %. This effect is probably caused because smaller silver chloride crystals are formed at higher ionic strengths which react completely to silver iodide while the larger crystals that precipitated at lower ionic strengths form a thicker layer of silver iodide which prevents the inner silver chloride from reacting to iodomethane so that it does not react completely. This effect leads to isotope fractionation for which Taylor and Grimsrud (1969) found an average value of +0.43 ‰. The buffer solution is used to reach a constant pH of 2.2. This is necessary to remove small amounts of sulphide which also precipitates with silver ions and forms silver sulphide (Kaufmann 1984), but also to prevent potential precipitation of other silver salts such as phosphates and carbonates (Vogel 1951). Kaufmann (1984) and Long et al. (1993) proposed to acidify the solution with HNO_3 while Eggenkamp (1994) followed Kohnen (1988) who proposed to use a pH 2.2 buffer solution after McIlvaine (1921) which is a solution containing 0.71 g (0.004 mol) $Na_2HPO_4.2H_2O$ and 20.6 g (0.098 mol) $HOC(CH_2CO_2H)_2CO_2H.H_2O$ (citric acid) per litre.

The mixture (sample plus pH buffer and ionic strength buffer) is placed on a boiling ring and heated to almost 100 °C. To this hot solution 1 mL of a 0.2 M silver nitrate solution is added. At the same moment that silver nitrate is added silver chloride starts to precipitate. This solution will not be stirred using a magnetic stirrer during silver chloride precipitation since silver chloride may clot and it will be difficult to scrape it from a magnetic stirrer which would result in loss of sample. The suspension is filtered over a Whatman® glass fibre filter, type GF/F with a retention of 0.7 μm and a standardized filter speed of 6 mL/s. During filtration the suspension is rinsed with a diluted (1 mL concentrated nitric acid in 500 mL water) nitric acid solution. This is done because when silver chloride is washed with distilled water it can become colloidal and run through the filter. For this reason the wash solution must contain an electrolyte. Nitric acid is chosen for this purpose as it is without action on the precipitate and is readily volatile (Vogel 1951). It is essential that glass fiber filters are used for filtering the silver chloride suspension as other filter types will react with iodomethane later in the procedure so that no (or little) chloromethane is formed during the last step of its preparation.

As already mentioned above, samples with low chloride concentrations are treated in a different way. As it would be necessary to add very large amounts of potassium nitrate and buffer solutions to these samples, and as such to avoid the handling of unnecessarily large sample volumes the reagents are added as dry chemicals. Per 100 mL of sample 6.00 g (0.06 mol) potassium nitrate, 2.06 g (0.0098 mol) citric acid and 0.07 g (0.0004 mol) $Na_2HPO_4.2H_2O$ is added after which the solution is heated to a temperature of almost 100 °C. Then 1 mL silver nitrate solution is added. Silver chloride will then start to precipitate and the suspension is treated as described above.

After filtration the filter containing the precipitate is dried overnight in an oven at a temperature of about 80 °C. During the drying process and after the filters were dried they need to be stored in a dark place to avoid the decomposition of silver chloride under the influence of light according to the reaction:

$$AgCl > Ag + Cl_2 \tag{4.4}$$

Treatment of Samples with Very High PH Values

Samples with a high pH will precipitate silver oxide when they are treated with silver nitrate. This may lead to reduced silver chloride yields, as well as other problems during the preparation of chloromethane and thus during measurement of the gas sample in the mass spectrometer. It is suggested that dimethyl ether can be formed during the procedure which might not be separated properly from chloromethane later in the procedure. If the pH is only moderately high, it will be decreased properly by the addition of the citric acid/phosphate buffer. However, in those cases where samples have a very high pH the buffer will not be efficient enough to decrease the pH to values close to 2. To prevent silver oxide from precipitating in this case nitric acid is added to the sample solution in stead of the buffer solution. Enough nitric acid needs to be added to decrease the pH to a value below 2 after which the silver nitrate solution can be added and silver chloride will precipitate without problems.

Treatment of Samples Containing High Sulphide Concentrations

Samples that contain high sulphide concentrations will precipitate silver sulphide in stead of silver chloride when silver nitrate is added to this solution. As a result the silver chloride yield will be lower but also dimethyl sulphide can be produced during the reaction with iodomethane and this will interfere during the isotope measurement. If the sulphide content is low enough it will evaporate as hydrogen sulphide from the sample solution after adding either the citric acid/phosphate buffer or nitric acid (Kaufmann 1984). However, this is not sufficient for samples with higher sulphide concentrations. To remove the sulphide from these samples it is oxidised through the addition of a few ml 30 % hydrogen peroxide and heated to a temperature of approximately 80 °C for approximately 1 h. After this treatment silver nitrate can be added as if it were originally a normal sample.

Removal of Sulphate from Samples with Excessive Sulphate

Samples that also need to be analysed for ^{36}Cl by accelerator mass spectrometry need to be sulphate free to avoid the presence of the isotope ^{36}S which would completely swamp the small amount of ^{36}Cl in a sample. In samples that are only to be measured for chlorine stable isotopes excessive amounts of sulphate may need to be removed as this can be precipitated as silver sulphate leading to a miscalculation of the amount of silver chloride and subsequently lowering the apparent yield of chloromethane in the sample. Long et al. (1993) proposed to remove (excessive) sulphate by leaving the filter with silver chloride on the filtration set up. After emptying and cleaning the filtrate flask the silver chloride is dissolved in an ammonia solution which is filtered and collected in a small flask. Barium nitrate is added to precipitate the remaining sulphate. If it is necessary to keep silver chloride in solution some extra ammonia solution may be added. After all sulphate is precipitated as barium sulphate it is filtrated. This filtrate should than be free of sulphate. Finally the pH is decreased to <2 by adding some nitric acid. Silver chloride should precipitate in this process because at low pH values the ammonia-ammonium equilibrium moves towards more ammonium so that less ammonia is available as ligand to the silver ion. To ensure that all silver chloride is precipitated a few extra drops of silver nitrate solution are added. The purified silver chloride can be treated further to produce chloromethane.

Preparation of Glass Reaction Capsules

The reaction from silver chloride to chloromethane takes place in glass capsules. From a length (150 cm) of Pyrex tubing (with outer diameter of 12 mm) parts of about 38 cm are cut. After melting and separating this piece of tubing in the middle two tubes with a length of about 19 cm and sealed at one end are formed (see Fig. 4.1).

Fig. 4.1 Photograph showing the writer while melting a piece of glass tubing into two reaction tubes. Photograph taken by MHC Vlaanderen and used with permission

After cooling and drying a filter containing silver chloride is put in the tube. A capillary is then drawn about 7 cm from the closed end. The tube is put onto a vacuum line which is pumped down to a pressure of less than 10^{-1} mbar. The tubes are filled with nitrogen gas to avoid the presence of oxygen that might react with iodomethane later in the procedure, are removed from the extraction line and closed with a rubber stopper to prevent leakage of air. 100 µl (1.6 mol) iodomethane is added in a fume hood. The tube is returned to the vacuum line and there the iodomethane is frozen on to the silver chloride with liquid nitrogen and then pumped vacuum to a value of less then 1×10^{-1} mbar). At the capillary the capsule is flame closed and molten from the line, keeping a glass ampoule containing solely the filter with silver chloride and the iodomethane. The capsule is placed in an oven for 48 h at a temperature of 80 °C. In the oven the reaction from silver chloride to chloromethane takes place according to:

$$\mathrm{AgCl} + \mathrm{CH_3I} > \mathrm{AgI} + \mathrm{CH_3Cl} \qquad (4.5)$$

As this reaction is an equilibrium reaction iodomethane needs to be added in excess. If the reaction temperature is too high iodomethane may decompose following:

$$\mathrm{CH_3I} > \mathrm{C_2H_6} + \mathrm{I_2} \qquad (4.6)$$

as proposed by Eastoe et al. (1989). If iodomethane decomposes the normally colourless liquid will change to yellow, red or brown. Measured δ^{37}Cl values of samples that showed colourisation of the iodomethane have less accurate values (the standard deviation of repeatedly measured values is higher than normal) and it appears that the measured isotope ratio is too high. When a mass (m/z) scan is made from a sample containing decomposed iodomethane it shows the presence of a peak with mass 29 which is not normally present. This peak may represent the ion $C_2H_5^+$. Except peak 29 also peaks with masses 45 and 46 which are not present in clean samples can be found in decomposed samples (see Fig. 4.2). This contamination will probably also affect peaks with m/z 50 and 52 and as such depreciate the quality of the analysis.

Cryogenic Separation of Chloromethane from Iodomethane

The two most common techniques to obtain pure chloromethane are cryogenic and gas chromatographic separation from iodomethane. In the oldest studies in which chloromethane was produced from the reaction of silver chloride with iodomethane chloromethane was separated from iodomethane cryogenically (Langvad 1954; Hill and Fry 1962). In these studies separation was obtained by dry ice-acetone and dry ice-isopropyl alcohol (propan-2-ol) cryogenic mixtures respectively. In later studies the preferred method to separate chloromethane from iodomethane was gas chromatography (Taylor and Grimsrud 1969; Kaufmann 1984). More recently new methods to separate chloromethane from iodomethane cryogenically were proposed by Holt et al. (1997) and Wu and Satake (2006).

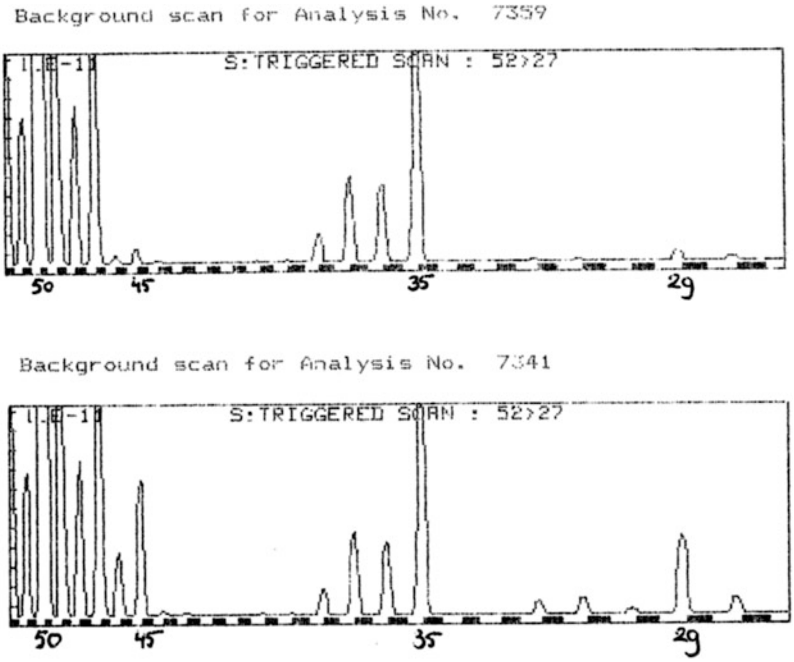

Fig. 4.2 Mass scans of chloromethane samples from the SIRA 24 mass spectrometer at Utrecht University taken using the original SIRA software running on a Hewlett Packard computer. Analysis 7359 shows a sample that was not overheated, analysis 7341 shows a sample that was overheated. Note that in this sample the intensities of the peaks at m/z 29, 45 and 46 have been increased significantly (Eggenkamp 1994)

Holt et al. (1997) used melting n-pentane (−130 °C) to separate chloromethane from iodomethane. The capsule containing chloromethane and iodomethane was frozen in dry ice-acetone slush (−79 °C), and two cold traps were frozen with melting n-pentane and liquid nitrogen respectively. After breaking the capsule that was frozen in the dry ice-acetone slush chloromethane and iodomethane slowly evaporate and move to the n-pentane cold trap. Iodomethane is trapped here while chloromethane moves to the second cold trap that is frozen with liquid nitrogen. This separation is done twice to ensure that chloromethane and iodomethane are perfectly separated. According to Holt et al. (1997) the iodomethane content in the resulting pure chloromethane must be lower than 0.2 %. This threshold was reached after two cryogenic separations and further (gas chromatographic) purification was not necessary.

Wu and Satake (2006) considered using n-pentane a serious risk due to its flammability. To overcome this problem they proposed to seal the cold traps as proposed earlier by Kusakabe (2005) for the separation of sulphur dioxide from carbon dioxide for precise $\delta^{18}O$ and $\delta^{34}S$ measurements. They also observed that apparently at the temperature of the n-pentane trap neither iodomethane nor chloromethane vaporised, and that they both vaporise at higher temperatures, although of course chloromethane vaporises earlier than iodomethane. Wu and Satake (2006) searched for another compound that could be used for cryogenic separation and found that 2,2,4-trimethylpentane (iso-octane) with a melting point of −107 °C was able to release chloromethane at its melting point, while iodomethane was only released after the complete melting of the 2,2,4-trimethylpentane. Their procedure is as follows. A scratched capsule with a mixture of chloromethane and iodomethane is put on-line in a tube cracker. The lowest part of the sample capsule is cooled to −72 °C with a dry ice-ethanol slush. On the vacuum line two sealed cold traps are installed containing 2,2,4-trimethylpentane. The line is evacuated after which the lower three quarters of the cold traps are frozen with liquid nitrogen. After breaking the sample capsule its content is slowly frozen to the first cold trap. After freezing all chloromethane and iodomethane to the first cold trap the liquid nitrogen from this trap is removed so that he temperature could increase.

At the melting point of 2,2,4-trimethylpentane chloromethane vaporises and is frozen onto the second cold trap which is still frozen with liquid nitrogen. As long as both liquid and solid 2,2,4-trimethylpentane is present in the first trap only chloromethane is transferred to the second trap. After transferring all chloromethane, which is monitored from the pressure in the vacuum line the two cold traps are separated by closing a valve. To remove all remaining iodomethane from the chloromethane in the sample the separation is repeated by freezing the chloromethane to a third trap containing liquid nitrogen while the temperature of the second trap is increased to the melting point of 2,2,4-trimethylpentane. As long as both liquid and solid 2,2,4-trimethylpentane are present in the second trap only chloromethane is transferred to the third trap. Using this two step technique Wu and Satake (2006) managed to transfer chloromethane with a yield between 96 and 101 %. The δ^{37}Cl of the transferred chloromethane was not significantly different before and after the separation. Analysis after only one separation step revealed still some iodomethane in the sample which led to δ^{37}Cl values in the samples which were higher than the original δ^{37}Cl values of the chloromethane by about 0.2–0.3 ‰, showing that a second separation step was essential to implement on their extraction line.

Gas Chromatographic Separation of Chloromethane from Iodomethane

The second method to separate chloromethane from iodomethane for dual inlet mass spectrometry is by gas chromatography. Considering the relatively large amount of chloromethane necessary for the isotope analysis the gas chromatographic separation proposed is using a packed column. Taylor and Grimsrud (1969) used Apiezon-L on Teflon T as stationary phase in a $^{5}/_{16}''$ glass capillary column for the separation of chloromethane from iodomethane. Kaufmann (1984) and Long et al. (1993) proposed the use of Porapack Q 80–100 mesh in a single column to separate chloromethane from iodomethane. Eggenkamp (1994) concluded that a two stage separation of chloromethane from iodomethane would reduce the risk of keeping any iodomethane in the chloromethane that is measured for isotope analysis. Godon (2000) improved the gas chromatographic separation by physically separating the two gas chromatography runs completely. In more detail the procedure developed, and still used at Utrecht University is as follows (Eggenkamp 2004): chloromethane and iodomethane are separated first on a 75 cm, ¼″ OD SS column, filled with Porapak-Q 80–100 mesh. Because there is a risk that this column is overloaded with the large excess of iodomethane, the gasses are separated in two runs. The carrier gas is helium, at a pressure of 3 bars and a gas flow of about 100 mL/min. The column temperature is kept at 140 °C. The procedure starts with back-flushing the gas chromatograph in order to minimize iodomethane contamination of the column and detector. The Pyrex reaction tube is scratched by a glass cutting knife, and placed in a tube cracker. The tube cracker is evacuated and liquid nitrogen is placed around the first cold trap. This cold trap is isolated from the rest of the gas chromatograph and the reaction capsule is broken. A helium flow is put on the cold trap to collect all chloromethane and iodomethane within this trap. After a short time, when all chloromethane and iodomethane are trapped the liquid nitrogen around the first cold-trap is replaced with warm water and the liquid nitrogen is now placed around the second cold-trap. The gas chromatography recorder is started and a chloromethane peak is detected after about 2 min. When the recorder is back on the base line, but before the iodomethane peak is detected (after about 4 min) valves are switched so that the first column is now back flushed. At that moment the chloromethane is trapped in the second cold trap, and only very little iodomethane should be mixed with it. Then the liquid nitrogen around the second cold-trap is replaced with warm water to release the chloromethane. Liquid nitrogen is placed around the sample cask. Chloromethane is swept over the second gas chromatographic column with the same characteristics as the first column. After the chloromethane has passed the column it is collected, frozen onto liquid nitrogen, in a sample vessel. The gas yield in the vessel is determined by measuring the chloromethane pressure in the vessel after heating the sample vessel with a hair dryer to evaporate the chloromethane. Finally the valves on the vessel are closed and the vessel can be removed from the gas chromatograph and subsequently attached to the mass spectrometer for isotopic analysis.

4.2.2.3 Measurement of Chloromethane as Positive Ions

Measurements of chlorine stable isotopes with most modern isotope ratio mass spectrometers, both dual inlet and continuous flow, are done on positive CH_3Cl^+ ions. These positive ions are produced from chloromethane when a positive acceleration voltage is applied in the ion source of the mass spectrometer (Taylor and Grimsrud 1969). For most modern mass spectrometer this is the normal mode of operation. It leads to a relatively high yield of positive ions. A potential disadvantage of the use of positive CH_3Cl^+ ions is however the relatively complex mass spectrum (see Table 4.3). This mass spectrum is so complex as both chlorine and carbon have minor isotopes (which is ^{13}C for carbon) and thus a large number of different ions can be formed from a chloromethane molecule in the ion source. Under normal conditions the isotope ratio is determined from the m/z mass ratio 52/50, where the major ions are $CH_3^{37}Cl^+$ and $CH_3^{35}Cl^+$. While $CH_3^{37}Cl$ is the only important ion at m/z = 52 at m/z = 50 also a significant fraction (about 1 %) of the mass is from the ion $CH^{37}Cl^+$. As the isotope variation of chlorine is relatively modest (most data observed in natural samples are between +2.0 and −2.0 ‰ relative to SMOC) the error introduced by this small amount of $CH^{37}Cl^+$ is not normally measurable at the precision of the "best" possible measurements of chlorine isotopes, which are in the order of ±0.05 to ±0.1 ‰. For this reason most laboratories do not apply a correction factor to correct for this effect.

4.2.2.4 Measurement of Chloromethane as Negative Ions

In a few studies it is proposed to measure chlorine isotope compositions on Cl^- which is produced if the accelerating voltage in the ion source is switched to negative values. The advantage of negative ions is that a very simple mass spectrum is formed (Table 4.4) and the ions measured are $^{37}Cl^-$ and $^{35}Cl^-$ at m/z = 37 and m/z = 35. As these ions are also the only ions formed at these mass to charge ratios there is no necessary at all to apply correction factors to the measurement of chlorine isotopes this way.

Taylor and Grimsrud (1969) were the first to propose to analyse chlorine isotopes on negative ions. They compared positive and negative ions from chloromethane formed in their ion source by switching the acceleration voltage between +3,000 and −3,000 V. Although the ion yield for negative ions was about 30 times smaller than for positive ions the analytical error (standard deviation) was about ±0.22 ‰ and this was comparable to studies for positive ions. These results made that Taylor and Grimsrud (1969) recommended negative ions for future studies on chlorine isotopes. However, probably because chlorine isotopes in later studies were always measured on mass spectrometers that were also used for other isotope systems where positive ions were used, these recommendations were largely ignored.

A new ion source for the measurement of chlorine isotopes by negative ions was developed by Pelc and Hałas (2008). Based upon the original observations by Taylor and Grimsrud (1969) they build a new ion source specifically for negative ion measurements. As a negative ion yield is relatively low compared to a positive ion yield considerable effort was made to select the most appropriate filament material. It was found that the most suitable material to be used as a filament was a $Mo_{52.5}Re_{47.5}$ alloy as both the ion current intensity and the background were fully acceptable. As shown in Table 4.4 the mass spectrum for chlorine was comparable to that of Taylor and Grimsrud (1969). It was found however that small peaks of m/z 26 and 28 were found, probably consisting of the ions CN^- and CO^-. The development of this negative ion source also led to the development of an adapted technique to analyse chlorine isotopes using negative ions (Halas and Pelc 2009). The preparation of chloromethane from chloride is comparable to the method described above (precipitation of silver chloride and subsequent reaction of silver chloride with iodomethane. The reaction is done in glass ampoules with Teflon stopcocks and chloromethane and iodomethane are separated cryogenically according to the method developed by Wu and Satake (2006). The analysis of a standard sample seems very promising with an internal precision better than 0.01 ‰. External precision was not determined yet, but seemed to be in the order of a few hundredths of a per mill.

4.2.3 Continuous Flow GC-IRMS

4.2.3.1 Gas Separation by Capillary Gas Chromatography

A large part of the currently measured chlorine stable isotope data are determined by continuous flow gas chromatography IRMS. Two techniques to establish this have been proposed in the literature. The first was proposed by Wassenaar and Koehler (2004). Their method included off line preparation of chloride bearing samples until the formation of chloromethane in stopper sealed glass vials. Silver chloride was produced from aqueous samples according to techniques described by Long et al. (1993) and Eggenkamp (1994). Conversion of silver chloride to chloromethane was done in 10 mL serum bottles crimp sealed with thick 13 × 20 mm butyl blue stoppers. Vials containing filters with silver chloride were evacuated through a hollow needle trough the stopper and subsequently iodomethane was injected through this stopper. The conversion to chloromethane is then done conventionally at 80 °C for 48 h.

To analyse the chlorine stable isotope ratio of a sample 150–700 μL of headspace is injected into a 2 meter Porapack-Q $^1/_4$ inch stainless steel packed column. The column was held at 160 °C with a helium flow of 100 mL/min and a column head pressure of about 150 kPa. At the beginning of a run a 30 s reference chloromethane puls is introduced trough the dual-inlet bellows. The chloromethane peak followed at about 4 min. The rest of the gas introduced to the gas chromatograph (mainly iodomethane) was diverted to the waste through the open split. Due to the time necessary to get rid of the total iodomethane present in the sample the total analysis takes about 14.5 min. The standard deviation of a large series of measurements of the same sample is about 0.06 ‰.

Shouakar-Stash et al. (2005) proposed to analyse stable chlorine isotopes with continuous flow using a capillary gas chromatography column. The procedure also starts with precipitating silver chloride from an aqueous solution as described by Taylor and Grimsrud (1969) and Eggenkamp (1994). The conversion from silver chloride to chloromethane takes place in 20 mL amber crimp cap vials. As a capillary column is easily overloaded with large amounts of chloromethane and iodomethane small samples (0.2 mg) are weighted and added to the vials. Iodomethane is added in a glove bag and vials are sealed to avoid evaporation of iodomethane. The conversion reaction takes place in an oven at 80 °C for 48 h. After the conversion is complete the vials are loaded onto a CombiPAL autosampler. From each sample 750 μL of the headspace is taken and injected into an Agilent 6890 gas chromatograph containing a 60 m, 0.32 mm ID DB-5 column with a 1 μm film thickness. After injection the temperature is held at 35 °C for 7 min, then the temperature is increased quickly (at 35 °C per minute) to 250 °C and held at that temperature for 2 min. The advantage of this temperature program is that the separation between chloromethane and iodomethane is complete and iodomethane is flushed rather quickly reducing overall analysis time. From the gas chromatograph the gas is diverted into the mass spectrometer. The mass spectrometer program is set as such that only the chloromethane peak is diverted to the mass spectrometer, while the iodomethane is diverted to the flame ionization detector from the gas chromatograph, avoiding contamination of the mass spectrometer but also making it possible to monitor the development of the iodomethane peak. Before and after the chloromethane peak several reference gas peaks are measured, and each sample is measured at least in triplicate. Shouakar-Stash et al. (2005) report an internal precision better than ±0.04 ‰ and an external precision better than ±0.07 ‰ (1 standard deviation) for this method.

4.2.3.2 Separation of Chloromethane and Iodomethane by a GasBench

Liu et al. (2013) proposed to use a Gasbench II as the interface to transmit chloromethane onto the mass spectrometer. Chloromethane was produced from chloride in aqueous solution after precipitation with silver nitrate and subsequent reaction of the formed silver chloride with iodomethane in a glass vial. Vials used by Liu et al. (2013) were of the screw cap type. Unlike reaction vials for previous techniques they were flushed with helium before iodomethane was added and the reaction between silver chloride and chloromethane takes place in a helium atmosphere and not in vacuum as in previously developed methods. The separation and subsequent measurement of the chlorine isotope composition is carried out after a reaction time of 48 h at 80 °C. The gas is sampled through a special dual-hole needle which is connected to the CombiPAL autosampler. A helium flow (0.5 mL/min) is delivered to the vial trough the side hole and the sample is flushed into the GasBench system through the needle tip. The helium flow gently transfers chloromethane and other gas species from the vial into the fused-silica capillary within the needle tip. The gas mixture is transferred through a Nafion® guard trap to remove water and through a Valco valve. It is then set onto the GasBench gas chromatography (GC) PoraPlot Q column. This is done through a 100 µL loop in the loop injection system. Here chloromethane is separated from all other gas species, most importantly iodomethane. The flow rate on the gas chromatograph is set at 2 mL/min and the helium pressure at 12 psi. The temperature of the gas chromatographic column is kept at 120 °C. After the chloromethane has been eluted from the column it is passed through a second Nafion® guard column and introduced into the isotope ratio mass spectrometer via the active open split. The reference pulse of chloromethane gas, which is of 99.95 % purity, is automatically introduced into the mass spctrectrometer via a reference gas injection system. Two Faraday cup detectors monitor simultaneously and continuously the CH_3Cl^+ signals for the two major ions at m/z 50 ($CH_3^{35}Cl^+$) and 52 ($CH_3^{37}Cl^+$). The active open split is closed immediately after the chloromethane signal has passed to prevent iodomethane from flowing into the mass spectrometer. The chlorine isotope composition of the chloromethane from a single vial can be analysed several times by switching the contents of the loop injection system forth and back onto the gas chromatography column. The precision of of this method, deducted from twelve measurements of the secondary isotope standard ISL 354 produced from seawater (Xiao et al. 2002), and seven measurements of the sodium chloride standard NIST SRM 975 was 0.07 ‰.

4.2.4 N-TIMS

In theory the measurement of chlorine isotopes by negative thermal ionization mass spectrometry is very simple. The method was for example used by Shields et al. (1962) in their study to establish the absolute isotopic abundance ratio and atomic weight of chlorine. They concluded that they were able to analyse stable chlorine isotopes with a precision of ±2 ‰. After the first studies of chlorine isotopes with “measurable” natural chlorine isotope variations (Kaufmann et al. 1984; Desaulniers et al. 1986) Vengosh et al. (1989) attempted to apply a new method to directly measure both boron and chlorine isotopes by negative thermal ionization mass spectrometry. They added droplets containing 1–500 µg chloride (and 50–200 ng boron) to rhenium filaments which were dried in an oven at about 50 °C. Fifteen of these filaments were loaded into a sample carousel of a Nuclide mass spectrometer and evacuated to 10^{-7} to 10^{-8} Torr. Applying a technique that was strictly repeated for each measurement they were able to analyse first the chlorine isotope ratio and subsequently the boron isotope ratio. Briefly the procedure to analyse chlorine isotopes was to slowly heat the filament to 1.7–2.2 A filament current, then the signal was optimised by focusing the ion beam and slowly increasing the filament current. When a $^{37}Cl^-$ ion intensity of 2–3 V was reached chlorine isotope data were collected for 30–45 min. During this period a total of 96–192 ratio measurements ($^{37}Cl/^{35}Cl$) were made. From 18 analyses of a seawater standard it was revealed that the analytical error was ±2.0 ‰, which is surprisingly similar to the value determined by Shields et al. (1962). More surprisingly however was the fact that (with analytical errors of 1.4–2.9 ‰) very large variations between different samples were found (from −7.2 to +24.7 ‰ relative to their seawater sample) without a clear relationship with the origin of the samples. Several of these samples were later remeasured by Xiao et al. (1995) and these measurements showed a much smaller, and perhaps more realistic, range in chlorine isotope compositions. One other study is known in which attempts were made to analyse chlorine isotopes by N-TIMS from this period (Gaudette 1990). In Antarctic ice very negative $\delta^{37}Cl$ values were found with values between −14 and −10 ‰ relative to their ocean chloride standard. These extreme variations were however never observed with other analytical techniques and apparently the negative ion beams were not stable enough for precise chlorine isotope analysis due to the effect of isotope fractionation during the evaporation and ionisation process and large filament blanks (Magenheim et al. 1994; Fujitani et al. 2010).

Despite these analytical problems potential interest continued to exist in this technique as very small amounts of sample, only several hundreds nanograms of chloride or ten times less than necessary for P-TIMS, are necessary for analysis as was shown by Fujitani and Nakamura (2006) in their study to analyse very small chloride concentrations by isotope dilution mass spectrometry. Their approach to solve the analytical problems was to apply a total evaporation method. The total evaporation method indicates that during measurement of a sample the whole sample is evaporated from the filament and analysed. Because of this total evaporation the entire ion beam is integrated so that the effect of isotopic fractionation during data acquisition is minimised. The total evaporation technique was originally developed for analysing the isotope composition of uranium, plutonium (Callis and Abernathey 1991) and neodymium (Wakaki et al. 2007). Another application to analyse stable isotopes with this technique was in a study of rhenium isotopes (Suzuki et al. 2004). In their analytical method Fujitani et al. (2010) added either 100, 200 or 500 ng chloride on the filaments and increased the ionization current to 1.8 A, corresponding to a filament temperature of about 1,300 °C, while keeping the evaporation filament at 0 A throughout the analysis. The chloride was evaporated from the filament at such a rate that the complete sample was evaporated within 100 to 200 scans. Fujitani et al. (2010) compared results from these N-TIMS analyses with P-TIMS analyses from Numata et al. (2001). The results showed that at 500 and 200 ng chloride samples could be measured with an error of ±0.9 ‰, while at smaller sample amounts the error increased to ±2.0 ‰. In comparison a sample containing 2,000 ng chloride (seawater) showed an error of ±0.31 ‰. These results showed that there may be potential for N-TIMS for chlorine isotope analysis for very small samples, however only when a relatively large variation in chlorine isotope values is expected. Realising that there is only a relatively small natural variation in chlorine isotope ratios application of this technique will continue to be rather limited.

4.2.5 P-TIMS

The application of positive ion thermal ionization mass spectrometry for chlorine isotopes has been developed as a spin-of of the development of boron isotope analysis by the same technique. It was already known for some time (see the review by Xiao et al. 1991) that $M_2BO_2^+$ (where M = Li, Na, K, Rb or Cs) ions could be used to determine boron isotope compositions using thermal ionization mass spectrometry with a better precision. Xiao et al. (1991) considered the possibility to extent this technique to chlorine isotope analyses and measured the chlorine in the form of M_2Cl^+ ions. They realised that it would be a big challenge as it is very difficult to obtain a strong stable M_2Cl^+ ion beam. Xiao et al. (1988) had already discovered that a relatively strong Cs_2Cl^+ ion peak was formed when they analysed boron isotopes on ${Cs_2BO_2}^+$ ions when the filament was first covered with graphite, while no Cs_2Cl^+ ion peak was found in the absence of graphite. Xiao et al. (1991) considered this a good opportunity to study the possibility of analysing chlorine isotopes using TIMS in the presence of graphite on the filament. During experiments with rubidium chloride as the compound to study isotope ratios it was confirmed that in the presence of graphite Rb_2Cl^+ ions were emitted, while no Rb_2Cl^+ ions were emitted in the absence of graphite. In the absence of graphite just Rb^+ ions were emitted. It was concluded that in those experiments where the filament was covered with graphite the ionization potentials of the M_2Cl^+ ions and the temperatures at which a strong ion beam could be emitted were reduced. This effect resulted in increased M_2Cl^+ intensities. Studies on the formation of M_2Cl^+ ions from rubidium chloride and caesium chloride were performed by Xiao et al. (1991). The initial results were very promising and as caesium has only one stable isotope it was decided to continue the experiments with this element. Another very important consideration was the high mass of the Cs_2Cl^+ ion. This ion is measured at $m/z = 301$ and 303 and this high mass makes it more easy to control the mass spectrometric discrimination factor. As the mass spectrometric discrimination is small and reproducible this results in precise isotope measurements. Finally, addition of caesium chloride to a filament covered with graphite was ultimately shown to give a successful procedure to analyse chlorine isotopes (Xiao and Zhang 1992).

Xiao and Zhang (1992) applied this method using tantalum filaments. These filaments were treated with 3 μL of a graphite slurry that consisted of about 100 μg graphite in a mixture of 80 % ethanol/20 % water (v/v). This slurry was allowed to dry almost completely. Then a sample solution, containing of 1–6 μg chloride was added to the filament. To prepare this sample solution the original chloride solution was transferred into a hydrochloric acid solution by cation exchange chromatography with resin in the Ba^{2+} form. This acid solution was neutralised with a caesium carbonate solution. The sample solution was dried for 2 min while passing a current of 2 A through the filament. When the filaments were dry they were loaded into the source. After evacuation of the ion source the analysis was started by increasing the filament current to 1.1 A. Cs_2Cl^+ ions that were emitted were monitored and data were collected by switching between the masses 301 and 303. Data were acquired for a period of 1.5 h. Seawater and samples from terrestrial salt lakes in China were measured in these original studies. Results obtained by this technique were reported to have errors better than 0.1 ‰ (Liu et al. 1997; Shirodkar et al. 2006).

The method developed by Xiao and Zhang (1992) was adapted in several laboratories. Magenheim et al. (1994) adopted the method to study chlorine stable isotope variations in small natural samples such as rocks and aerosols. They discovered that large quantities of sulphate, fluoride and organics in samples resulted in ionization suppression, so they developed techniques to remove them during sample preparation. They used ion exchange to remove sulphate, chemical precipitation to remove fluoride and extraction by activated carbon powder to remove organics. Magenheim et al. (1994) produced a stoichiometric (1:1) caesium chloride solution by eluting their acid solution over an ion-exchange resin in the Cs^+ form. This way they removed all acidity, which is important as acidity present as hydrochloric acid could cause isotope fractionation in the sample (Volpe and Spivack 1994). The precision of this technique was found to be better than ±0.2 ‰ in general. More recently comparable methods to analyse chlorine isotope compositions with positive thermal ionization mass spectrometry were proposed by Numata et al. (2001) and Nešković et al. (2002). Numata et al. (2001) prepared samples as silver chloride precipitate and converted to caesium chloride with metallic magnesium and ion exchange resin in its caesium form. Samples were loaded on tantalum filaments and the reported precision is about 0.1–0.2 ‰. Nešković et al. (2002) used rhenium filaments and they neutralised their hydrochloric acid solution with a caesium carbonate solution as Xiao and Zhang (1992) did. The preliminary results published in their report showed a very large difference in isotope ratio between the measurement of their seawater sample from a sodium chloride working standard (8.8 ± 1.2 ‰) and a measurement of the same material done by the method described by Long et al. (1993) in Arizona (0.39 ± 0.03 ‰). Because of this large difference it was concluded that more development of the method was necessary, however no more reports from this group have unfortunately appeared since then.

4.2.6 SIMS

A method to analyse chlorine isotopes using secondary ion mass spectrometry has been developed by Layne et al. (2004). The advantage of analysing chlorine isotopes by this technique is the fact that is is able to analyse the composition on a very small spatial resolution (10–20 μm) so that in theory very small samples can be analysed, or that spatial variations can be determined in larger samples. The technique however is only viable in samples with relatively large variations as the overall reproducibility of this technique is only 1.5 ‰. In spite of this the first published results were encouraging.

Layne et al. (2004) used a Cameca IMS 1270 ion microprobe to analyse their samples. They tested the method for very small spots from rock samples and direct determinations of the contents of small dried samples of natural fluids such as fluid inclusions.

SIMS techniques for chlorine isotopes can only be successful if isobaric interferences are suppressed. Natural samples almost always contain sulphur which forms $^{34}SH^-$ ions that interfere with $^{35}Cl^-$. Modern ion microprobes however have very high mass resolution capabilities and they make it possible to analyse the proper ions ($^{35}Cl^-$ and $^{37}Cl^-$). In the IMS 1270 chlorine concentration and chlorine isotopes are analysed simultaneously. The sample is bombarded with a microbeam of Cs^+ ions focused on a 10–20 μm diameter spot. This bombardment releases secondary ions which are accelerated into the mass spectrometer. Peaks for $^{30}Si^-$, $^{35}Cl^-$ and $^{37}Cl^-$ are obtained by cyclical magnetic peak switching. The isotope composition is determined from switching between $^{35}Cl^-$ and $^{37}Cl^-$ and the chlorine concentration from comparing $^{35}Cl^-/^{30}Si^-$ (normalised for SiO_2 content) for unknown and standard glasses (see e.g. Hauri et al. 2000). As chlorine has a very high ionization efficiency under Cs^+ bombardment high count rates are found. This implicates that high internal precisions are reached, while only a few ng of sample from the small sputtered crater is consumed. The measurements normally yield internal precisions which are better than ±0.9 ‰. Overall reproducibility generally is better than ±1.5 ‰ for samples with as little as 250 ppm chloride. Layne et al. (2004) state that their method is able to analyse samples with chloride concentrations down to 100 ppm, while IRMS and TIMS techniques become difficult at 100–200 ppm. More recent IRMS analysis however yielded reproducible results for rock samples with chloride concentrations as low as 50 ppm (Bonifacie et al. 2008), so that this no longer is a major advantage. The main advantage however will continue to be that very small samples can be analysed and that the distribution of chlorine isotopes in individual minerals in larger samples can be analysed. Considering the small natural variation in chlorine isotopes it is hoped that the precision of this technique has prospect for improvement.

4.2.7 Laser Ablation Multi Collector ICP-MS

Fietzke et al. (2008) proposed a relatively simple method to analyse chlorine isotopes from aqueous fluids and rocks using laser ablation multi collector ICP-MS. Chloride is extracted from rocks with pyrohydrolysis methods as described by Dreibus et al. (1979), Schnetger and Muramatsu (1996) and Bonifacie et al. (2007). Chloride is precipitated as silver chloride following precipitation by addition of 8 mL of a (1 part 65 %) HNO_3/(6 parts 0.1 N) $AgNO_3$ mixture to 25 mL of the sample containing enough chloride for analysis. An advantage of this procedure is the fact that the chloride in all samples is in a pure silver chloride matrix which largely reduces matrix effect problems during measurement.

A problem with analysing chlorine isotopes by ICP-MS is interference of $^{36}ArH^+$ from the plasma with $^{37}Cl^+$. This problem was by-passed through simultaneously monitoring masses 35 ($^{35}Cl^+$), 37 ($^{37}Cl^+ + {}^{36}ArH^+$) and 41 ($^{40}ArH^+$). The $^{36}Ar/^{40}Ar$ ratio is constant at 0.003 and this ratio is used to correct the peak with mass 37 for the ArH^+ peak. This correction is shown to be very efficient. Without the correction $^{37}Cl/^{35}Cl$ ratios of the SMOC standard range from 0.351 to 0.356, while with the correction (subtraction of 0.003*mass 41) this is reduced to a range from approximately 0.3558 to 0.3562, a factor of 12 smaller. Using this correction it was possible to analyse the chlorine isotope composition with a precision of ±0.06 ‰ (2 SE) with the use of less than 1 μg chloride.

4.2.8 Measurement of Chlorine Isotopes with Neutron Activation Analysis

The samples obtained during diffusion experiments with molten salts (which are to be described in Sect. 7.1.2) were analysed after irradiation with thermal neutrons of silver chloride prepared from these samples. The procedure that was followed is described by Klemm and Lundén (1955). The salt obtained from the experiments was dissolved and the chloride was precipitated as silver chloride after addition of a silver nitrate solution. The silver chloride was then irradiated with neutrons and the chlorine isotopes were partly changed into the isotopes with one extra neutron (n,γ-process). ^{36}Cl and ^{38}Cl have a considerable different half-life, and from the β-activity in the sample the percentage ^{37}Cl could be determined. This method is not very precise, and the percentage ^{37}Cl in the samples could only be determined with a precision of about 1 %. For that reason the chlorine isotope compositions in later studies were also determined using the then newly developed chloromethane method (Herzog and Dörnenburg 1958).

4.2.9 Measurement of Chlorine Isotopes Using Fast Atom Bombardment Mass Spectrometry

Westaway et al. (1998) proposed a method to analyse the chlorine isotope composition of silver chloride precipitated from a chloride solution by Fast Atom Bombardment using a modified, hybrid model MI 1201E FAB isotope ratio mass spectrometer (PO Electron, Ukraine) equipped with three collectors: two Faraday cups with fixed focus and an electron multiplier with pulse analyser and a single-ion counter. Using this method silver chloride was put on a silver filament and melted. This was then mounted into the mass spectrometer and bombarded with xenon atoms. Negative ions ($^{35}Cl^-$ and $^{37}Cl^-$) were formed of which the ratio could be determined in 30–50 different determinations. The precision of this method was about ±1 ‰ and its main advantage was to avoid the time-consuming preparation, purification, and recovery of the gaseous methyl chloride.

4.2.10 Comparisons Between Different Measurement Techniques

As chlorine isotopes are analysed by so many different techniques it is essential to know that they are mutually comparable, and that a sample analysed with one technique has the same value as it is measured with a different technique. Only a few studies are known where different techniques are compared. Two of these studies compare P-TIMS with IRMS techniques and one study compares IRMS with SIMS techniques. Rosenbaum et al. (2000) compared P-TIMS with IRMS measurements of five samples with a δ^{37}Cl range between −4.4 and +0.3 ‰ relative to SMOC. They found that within analytical precision the two techniques yielded similar results. It was concluded that P-TIMS would be the most appropriate technique for small samples with an optimal chloride amount of 0.1–0.3 µmol per analysis and an analytical uncertainty of ≤0.2 ‰, while IRMS would be more appropriate for larger samples with an optimal chloride amout of >10 µmol per analysis, but with a significantly better analytical uncertainty of ≤0.1 ‰. Godon et al. (2004a) extended this study by comparing both techniques for 6 samples with a total δ^{37}Cl range from −3 to +6 ‰. They also found a very good agreement between the two techniques.

Godon et al. (2004b) compared the results from analysis of chlorine isotopes from SIMS and IRMS techniques. They compared eight synthetic aluminosilicate glasses. They observed that the raw results of the measurements from both techniques did not agree very well but discovered that this was the result of a very systematic instrumental mass fractionation. It was found that the instrumental mass fractionation had a very good relation with the normalised major element composition of the analysed synthetic glasses. When the SIMS data are corrected for this mass fractionation the chlorine isotope data do agree very well within the errors of the measurements. This indicates that it is possible to compare results of the two techniques, but it also means that the instrumental mass fractionation needs to be determined. To obtain this information it is necessary that also IRMS measurements are produced. The combination of the two techniques however is very useful as using SIMS it is possible to analyse very small areas on a certain rock so that very detailed variations in specimens can be determined. The two techniques can thus be very complementary in their possible use to study chlorine isotope variations in rock samples.

4.3 Extraction of Chlorine from Silicate Rocks for Isotope Analysis

4.3.1 Alkali (NaOH) Fusion Method

Eggenkamp (1994) developed a method which was largely derived from the sodium hydroxide fusion method as used by Behne (1953). This procedure was described by Eggenkamp (1994; 2004) as follows: X grams of powdered rock, in which X is an amount of rock containing enough chloride to obtain one or more δ^{37}Cl analyses, is heated together with 10X g of sodium hydroxide pellets for about 30 min in a nickel crucible. The rock dissolves in the molten sodium hydroxide and Si–O bonds are partly destroyed. The temperature must not be too high since sodium hydroxide will evaporate at high temperatures. The vapour pressure of sodium hydroxide is 1 mmHg (1.33 mbar) at 739 °C and 10 mmHg (13.3 mbar) at 897 °C (Stull 1947). After cooling the sample is dissolved in 35X ml distilled water. This is achieved by putting the nickel crucible in a beaker with water on a magnetic stirrer. After 2 h of stirring the content of the crucible is dissolved or suspended in the water. This suspension is exposed to air for some time (overnight) to oxidise Fe^{2+} and other reduced ions. The solution has a very high pH so that addition of Ag^{+} ions would result in precipitation of silver oxide; therefore the solution must be acidified. This is done by adding 17.5X mL 65 % HNO_3 which produces a colloidal “solution” of silica gel according to:

$$SiO_4^{4-} + 4HNO_3 \Rightarrow H_4SiO_4 \downarrow + 4NO_3^- \quad (4.7)$$

This colloidal solution can unfortunately not be filtered and to make this possible 3X mL hydrofluoric acid 40 % is added. The silica gel reacts with the hydrofluoric acid to form a combined silica oxyfluoride. This reaction does not go to completion. The oxyfluoride precipitates slowly (overnight) to the bottom of the glass container. Then 10.9X mL of a 2.5 mol kg^{-1} magnesium nitrate ($Mg(NO_3)_2.6H_2O$) solution is added (64.1 g $Mg(NO_3)_2.6H_2O$ and 35.9 g H_2O which is a solution with a density 1.25 g ml^{-1}). Excess toxic HF will react to poorly soluble magnesium fluoride. The resulting suspension is filtered. The residue contains reacted silica gel, magnesium fluoride, insoluble hydroxides and rock components that were not dissolved in the sodium hydroxide melt. Chloride is concentrated in the filtrate. The filtrate has a low pH and a high ionic strength, so that the silver chloride can be precipitated directly from this solution without adding any buffer or potassium nitrate.

Interestingly when this method was repeated during a stay of the author at the Institut de Physique du Globe in Paris in early 2013 it appeared that the hydrofluoric acid was not removed from the solution after the addition of the magnesium nitrate solution. The result was that the final solution still contained hydrofluoric acid which made it impossible to filtrate the suspension as the remaining hydrofluoric acid dissolved the glass fibre filter during filtration of this suspension. While the procedure described above was successfully applied during the PhD study of the author (see Eggenkamp 1994, Chap. 11; Eggenkamp and Schuiling 1995) it apparently didn't work during a later test. The only differences between the procedures as described above and as applied during the stay at the IPGP was the fact that during the PhD studies all solutions were kept in glass beakers while, due to the potential to dissolve glass by hydrofluoric acid, in Paris they were all kept in plastic beakers. What perhaps actually happened was that the hydrofluoric acid dissolved part of the glass and neutralised itself in this action, something that did obviously not happen with the plastic containers in Paris. This interesting effect should be studied in the future to explain what really occurs during the procedure and perhaps to be able to develop a more convenient method to extract chloride from silicate rock samples.

The method was later slightly modified by Godon et al. (2004b) who decided to centrifuge the solution after acidification with HNO_3 to remove the silica gel that has formed. After centrifuging a clear solution could be decanted containing the chloride. This way they were able to avoid the addition of hydrofluoric acid to their sample.

4.3.2 Hydrogen Fluoride Decomposition Method

Musashi et al. (1998) pointed to the fact that a weak point of the technique described in Sect. 4.3.1 is the addition of large amounts of chemicals to the samples, although the changes proposed later by Godon et al. (2004b) addressed this matter to a large part. Addition of large amounts of chemicals has the risk that the sample is contaminated with chloride that may be present in those chemicals. However, tests done by Eggenkamp (1994) showed no measurable chloride in a blank (chloride free sea-sand) that was treated in the same way as actual samples, and it was also shown that no fractionation of chlorine was found due to the complex chemistry. However, Musashi et al. (1998) considered the drawback such that they decided to develop a different technique to extract chloride from rocks.

Musashi et al. (1998) proposed a method to extract chloride from rock by dissolving it in a concentrated hydrofluoric acid solution. They added approximately 1 g of rock, 1 ml distilled water and 4 ml of 17 M hydrofluoric acid solution into a Teflon centrifuge tube. This tube was closed and shaken overnight (or longer) to dissolve the silica rock. The next day 10 mL distilled water was added and 5 mL of a slurry containing 2–3 g calcium hydroxide. The calcium in this slurry did precipitate the fluoride in the solution as calcium fluoride immediately. Again the solution was shaken overnight to assure that as much fluoride as possible has reacted to calcium fluoride. Then the tube was centrifuged and the suspension was filtered over a glass fibre filter. This treatment was repeated twice, and the filtrated solutions we added together. To remove the remaining fluoride from the solution it was passed over a strongly acidic cation exchanger and to increase the chloride concentration in the final solution this was passed over a strongly basic anion-exchange resin. This resin has a higher affinity for chloride compared to fluoride so that it separates them effectively. The chloride is then removed by rinsing a 20–25 mL 0.5 M potassium nitrate solution over the column. As the affinity for nitrate is larger than for chloride this is exchanged and eluted from the column. Chlorine isotopes in the eluted solution can be analysed as described earlier by whatever technique is available in the laboratory of the researcher.

4.3.3 Pyrohydrolysis Methods

The principle of pyrohydolysis is the extraction of chloride and other volatile compounds from molten rock by a stream of water vapour. These volatile compounds are then trapped into distilled water. From this solution chloride ions can be analysed by mass spectrometry either directly or after subsequent clean-up.

The first pyrohydrolysis method for chlorine isotope measurements was proposed by Magenheim et al. (1994). They applied the method that was originally developed by Dreibus et al. (1979). They used an induction furnace to heat a sample to 1,300–1,400 °C in a pre-cleaned platinum boat. During extraction water vapour carrier gas was applied at a flow rate of 0.3 g water per minute for 50 min. After this period the induction furnace was turned of and the system was flushed with 2.5 g water per minute for another 20 min. Finally the interior of the combustion tube was also rinsed with distilled water. The sample was collected by condensation in a water cooled fused silica condenser and ultimately collected in a polyethylene bottle. The chlorine isotope ratio of the extracted chloride was analysed following the positive TIMS method developed by Xiao and Zhang (1992). Before using this method however fluoride and sulphate were removed from the solution by precipitation as calcium fluoride and cation exchange as barium sulphate respectively.

Pyrohydrolysis for the analyses of chlorine isotopes has also been applied at the University of New Mexico (Barnes et al. 2006; Sharp et al. 2007) and the Institut de Physique du Globe de Paris (Bonifacie et al. 2007). Barnes et al. (2006) used the method as described by Magenheim et al. (1994) while Bonifacie et al. (2007) developed their method after Whitehead and Thomas (1985). In this technique the sample is mixed with 5 to 6 times its mass of vanadium pentoxide as flux. The mixture is heated (in a platinum boat) to a temperature of 1,200 °C and extraction is done with a water vapour flow of about 1.5 mL/min for 25 min, after which it is purged with pure air to dry the system. The sample is collected by condensation in a water cooled fused silica condenser and finally collected in a Nalgene bottle. After extraction all glassware is rinsed with distilled water to ensure that the recovery of the chloride from the sample is as complete as possible. The main differences between the techniques developed by Magenheim et al. (1994) and Bonifacie et al. (2007) are the addition of vanadium pentoxide as flux to optimise the release of halogens from the sample and to lower the melting temperature of the samples, as well as keeping the whole system above 300 °C by the use of a resistance furnace and heating coil. The advantage of this system is that no condensation of water takes place before the collection flask.

After pyrohydrolysis both groups applied continuous flow or dual inlet isotope ratio mass spectrometry on chloromethane gas which was prepared from the dissolved chloride according to the techniques described in Long et al. (1993), Eggenkamp (1994) and Godon (2000).

4.4 Extraction of Chloride from Non-silicate Rocks

Eggenkamp (1994, 2004) described a few methods to extract chloride for chlorine isotope analysis from non-silicate rocks and minerals, such as evaporites and carbonatite samples.

4.4.1 Evaporites

Evaporites can simply be prepared by dissolution of a known amount of sample in distilled water (Eggenkamp et al. 1995). This solution can then be treated as any aqueous chloride solution for isotope analysis.

4.4.2 Carbonatites

Most carbonatites, with the exception of natro-carbonatites, contain little chloride. Eggenkamp and Koster van Groos (1997) extracted chloride from the carbonate fraction of carbonatites by the following method. Five gram of carbonatite was suspended in 100 mL distilled water and stirred in a glass beaker on a magnetic stirrer/heating plate at a temperature of 50 °C. The pH of this suspension was monitored. Concentrated nitric acid was added drop by drop from a burette until the suspension stopped effervescing which happened at the moment that the pH was as low as 0.5. Next, the solution was filtered. Only chloride present in carbonates and apatites is liberated with this method. The sample can further be treated as a dilute water sample. In the case of natro-carbonatites, which contain much more chloride (Keller and Krafft 1990), a much smaller amount of sample is required (Eggenkamp and Koster van Groos 1997).

4.4.3 Other Non-silicate and Non-carbonate Minerals

Other minerals such as phosphates and hydroxide chlorides can generally be dissolved in dilute (1:5) nitric acid (Hintze 1915). Some minerals of this type, especially those originating from oxidised sulphide ores have been shown to have extreme δ^{37}Cl values (Eggenkamp and Schuiling 1995).

4.5 Chlorine Isotopes in Chlorate and Perchlorate

Although Hoering and Parker (1961) already measured chlorine isotope compositions of two samples of Chilean perchlorate they did not specify how they reduced the perchlorate to chloride for isotope analysis. Renewed interest in the chlorine isotope composition of chlorates and perchlorates developed at the end of the 20th century due to potential applications of their study as environmental pollutants (Ader et al. 2001). Only later it was realised that perchlorates are also produced under natural conditions other than those existing in the ultra-dry Chilean Atacama desert and that their isotope composition can be studied to trace natural and anthropogenic origins of perchlorates in groundwaters (Sturchio et al. 2003, 2006, 2007; Böhlke et al. 2005). The isotope composition of chlorates and perchlorates is measured after reduction to chloride which is than reacted with iodomethane to form chloromethane for isotope ratio analysis. The methods applied are described in the following sections.

4.5.1 Chlorate

Chlorate is not normally naturally produced but mostly artificial and used as herbicide, or in combination with perchlorate as oxidant in explosives and solid fuel rockets. It is also present in many drinking waters that are treated with chlorine for disinfection purposes. Considering its potentially toxic properties its isotopic composition might be useful to be traced for forensic reasons. Chlorine isotope analyses on chlorate (ClO_3^-) have been conducted in only one study. Ader et al. (2001) developed a method to analyse the chlorine isotope composition and analysed a set of chemical reagents (sodium chlorate; $NaClO_3$ and potassium chlorate; $KClO_3$). To analyse the chlorine isotope composition the chlorate must be reduced to chloride which can be analysed by classic methods. Chlorate can be quantitatively reduced by heating it with excess iron(II) in the presence of a relatively high concentration of sulphuric acid, following the procedure for the quantitative analysis of chlorate by Vogel (1989). For the method proposed by Ader et al. (2001) an amount of 2.5 mL of a 0.02 M chlorate solution is reduced by the addition of 2.5 mL of a 0.2 M ammonium iron(II) sulphate solution in 2 M sulphuric acid and 1 mL of concentrated sulphuric acid. This mixture was heated to 80 °C for 10 min and cooled to ambient temperature afterwards. Chlorine isotope composition then can be determined after transformation of chloride to chloromethane as described by Eggenkamp (1994).

4.5.2 Perchlorate

Perchlorate is more common in natural samples than chlorate. It is found in quantities of up to 0.6 % in the ultra-dry Atacama Desert in Northern Chile (Ericksen 1981). It was long assumed that these were the only natural occurrences of perchlorates in the world, but recently indigenous perchlorate has been detected in the drier regions of the United States (Plummer et al. 2006; Jackson et al. 2005; Rajagopalan et al. 2006, 2009; Rao et al. 2007; Parker et al. 2008). Also in Antarctic and Martian soils perchlorates have been detected recently (Hecht et al. 2009; Ming et al. 2010; Catling et al. 2010; Kounaves et al. 2010). Perchlorates from the Atacama Desert have been transported in large quantities to the United States as the major component of the soils they originated from is nitrate and as such this was worldwide used as fertilizer. Besides these natural perchlorates very large amounts have been artificially produced to be used as rocket propeller, and for purposes such as explosives, fire works, road flares and electroplating solutions. These discoveries have triggered interest in the measurement of the stable chlorine and oxygen isotope composition of the perchlorates as the isotope composition can supply information on the origin and behaviour of this potentially harmful ion in the environment.

4.5.2.1 Chemical Reduction of Perchlorate to Chloride

The first method to analyse the chlorine isotope composition of perchlorates was proposed by Ader et al. (2001). They applied two different methods to reduce perchlorate to chloride for subsequent isotope analysis following classical techniques. The first method they proposed applied the reduction of perchlorate with titanium (III)sulphate according to Von Rothmund (1909) a method that was originally developed to determine the perchlorate concentration in solution by back-titration of the excess of titanium (III) in solution. Ader et al. (2001) found that the perchlorate conversion yields of this method were very irregular and varied somewhere between 0 and 90 % proving this method useless for isotope analysis for which a yield as closely as possible to 100 % is necessary. The second method that was applied by Ader et al. (2001) was developed by Joan and Reedy (1940). For this method the perchlorate solution is made alkaline using potassium carbonate (approximately 300 mg of potassium carbonate for each 50 μmol of perchlorate) and evaporated to dryness. In a muffle furnace the resulting slid is heated for 45 min to a temperature of 600 °C and subsequently cooled to ambient temperature. Distilled water is added until the potassium carbonate is dissolved completely and the solution is acidified with nitric acid until the pH has decreased to a value lower than 3. All perchlorate has been reduced by then to chloride and the solution can be treated according to classic methods for chlorine isotope analysis.

4.5.2.2 In Vacuo Decomposition of Perchlorate to Chloride

In their first study on microbial reduction of perchlorate Sturchio et al. (2003) developed a different method to reduce perchlorate for isotope analysis. The samples they used in their experiments contained both chloride and perchlorate. The chloride was removed by the addition of a 1 M silver nitrate solution. The chloride precipitates as silver chloride which is insoluble while silver perchlorate is very soluble so that the perchlorate stays in solution. After the chloride is removed the resulting solution containing both perchlorate ions and silver nitrate is evaporated until near dryness. This substance is put into a Pyrex combustion tube and dried completely. The tube then is frozen by liquid nitrogen, evacuated and sealed off. Then the evacuated tube is combusted for 1 h at 550 °C. During this process the perchlorate is reduced to chloride which is combined with silver ions present in the tube to form silver chloride. If the silver is present in excess the formation of silver chloride will be complete. The silver chloride that is produced is subsequently washed with dilute nitric acid to remove excess nitrates. The purified silver chloride is dried and iodomethane is added. The procedure to form chloromethane is the same as for common chlorine (chloride) isotope analysis, i.e. a short reaction time at high temperature and cryogenic separation of chloromethane and iodomethane as described by Holt et al. (1997). In a later paper Sturchio et al. (2007) changed the procedure to separate perchlorate and chloride from a mixture containing both anions through the use of a highly selective bi-functional anion exchange resin (Purolite A530E). Perchlorate is precipitated from the solution by the addition of caesium chloride, as the solubility of caesium perchlorate is relatively low. These anion exchange techniques have been developed by Gu et al. (2001) and Bao and Gu (2004) and they facilitate the collection of purified perchlorate for combined analysis of chlorine and oxygen isotopes.

4.5.3 Collection of Perchlorate from Natural Samples Containing Low Perchlorate Concentrations

In natural groundwater samples perchlorate is always a trace component at concentrations which are virtually always lower than 10 μg/L and in most cases even lower than 1 μg/L. The low concentrations make it very difficult to extract perchlorate from natural samples. Sturchio et al. (2011) summarised the methods and results of the chlorine and oxygen isotope determinations on perchlorates, most of which had been done in one single laboratory. For the purpose of the large scale water treatment necessary to extract the small amounts of perchlorate from the samples a special anion-exchange resin was developed to extract perchlorate from aqueous solutions (Gu et al. 2001, 2007, 2011). This ion-exchange resin, commercially available as A530E, is suitable for the direct pre-concentration of perchlorates from aqueous solutions. The sample from which perchlorate has to be removed is passed through a column packed with this resin. As common with ion exchange resins it is also (but less) sensitive for ions such as chloride, nitrate and sulphate. These interfering ions decrease the perchlorate efficiency, so that a larger amount of sample should normally be passed through the column than would expected from the known concentration of perchlorate in this sample. This also indicates that after the passage of the sample trough the ion-exchange column besides perchlorate several other ions are present that need to be removed. The recovery of perchlorate is done by flushing the column firstly with hydrochloric acid to remove most nitrate, sulphate, carbonate and organic anions from the column. As a result the amount of chloride on the column increases to substantial amounts. The perchlorate is then eluted from the column through elution with a 1 M iron(III) chloride solution that displaces the perchlorate ions with $FeCl_4^-$ ions on the column. The eluted perchlorate can be purified further following techniques described by Gu et al. (2011). Perchlorate concentrations above 1 μg/L can generally be recovered fairly well, while lower concentrations are considerably more challenging (Sturchio et al. 2011). The purified perchlorate is normally precipitated as caesium perchlorate and its purity is checked by ion chromatography or Raman spectrometry. The caesium perchlorate is treated for isotope analysis as described by Sturchio et al. (2007, 2011).

4.6 Chlorine Isotopes in Organic Molecules

There are several possible techniques to analyse the chlorine isotope composition of chlorinated organic compounds. Originally they were measured by extracting, through reduction, the chlorine from the compounds, often in the form of an inorganic chloride, and analyse this according to the techniques available for inorganic chloride isotope analyses. More recently on-line techniques have been developed that directly introduce organic compounds into isotope ratio or quadrupole mass spectrometers.

Chlorine isotope measurements of organic compounds were already done before it was known that stable isotope variations also exist in natural samples. These measurements were done on samples that were obtained from experiments to determine kinetic chlorine isotope effects. These experiments (e.g. Bartholomew et al. 1954; Howald 1960; Hill and Fry 1962; Turnquist et al. 1973; Williams and Taylor 1973) conducted S_N1 and S_N2 reactions in which the chloride ion was one of the reaction products. This free chloride could be analysed according to methods described above (such as the methods developed and described by Langvad (1954), Hill and Fry (1962) and Taylor and Grimsrud (1969). Based on the development of the chlorine isotope data of the free chloride the kinetic fractionation in these processes could be determined.

After the development of more precise methods to analyse inorganic chloride in natural samples studies were started to analyse chlorine isotopes in organic samples too. As it was known from experiments as cited above that during the processes to produce anthropogenic organic compounds large kinetic fractionation occurred (e.g. Hill and Fry 1962; Turnquist et al. 1973) it was expected that chlorine isotope variations in organic compounds would be larger than in inorganic compounds, and thus it was considered feasible to search for these variations.

4.6.1 Methods that Apply Reduction of Chlorine to Chloride

During the early period several laboratories developed their own methods to analyse chlorine isotope variations in organic compounds. These early techniques focussed on the development of methods to analyse pure compounds, only later methods evolved such that it was possible to concentrate and analyse the very low concentrations that are usually found in natural environments.

4.6.1.1 Reduction of Organochlorine Compounds with Metallic Lithium

The first direct measurements of stable chlorine isotopes from organochlorine compounds were made by Tanaka and Rye (1991). They analysed a set of six compounds to determine whether the variations in chlorine isotope compositions in organic compounds would be large enough to be determined in naturally occurring (stratosphere) environments.

To extract the chlorine from the organochlorine compounds Tanaka and Rye (1991) heated these compounds with lithium metal in evacuated sealed quartz tubes. The lithium reduces the chlorine in the organochlorine compounds to chloride which is recovered from the tube as lithium chloride. The chlorine isotope composition of this lithium chloride was determined after dissolution in water and following the procedure as described by Taylor and Grimsrud (1969). The reported analytical precision of this technique, based on one or two determinations per organochlorine compound was 0.15 ‰.

4.6.1.2 Parr Bomb Technique

Van Warmerdam et al. (1995) were the first to realise the strength of analysing both carbon and chlorine isotopes on the same sample. Although they did not analyse both isotopes on the same aliquot of sample it showed that for fingerprinting purposes analysing both isotopes in organic compounds is very useful. To analyse the chlorine isotopes in their samples they combusted the organochlorine compounds according to ASTM method D808-91. This method is developed for the analysis of chlorine in combustible solids and liquids and applies a Parr 1901 Oxygen Bomb. In short the method works as follows. 5 mL of a 5 % calcium carbonate solution is injected into the bomb for absorption of the combustion products. Then the sample capsule is sealed with cellophane tape to prevent loss of the sample by volatilization. The sample is injected through the tape seal with the use of a gas tight syringe. Not more than 50 μL of chlorinated compound (sample) is added to avoid overpressure of the bomb during combustion. Then the fuse wire loop is put in contact with the centre of the tape cover after which the bomb is sealed and a maximum pressure of 20 atmosphere of oxygen is added to the bomb. The bomb is then placed in an ice-water bath and the fuse is ignited. After combustion the bomb is de-pressurised and rinsed with ultrapure water to collect the combustion products. Among these is the chlorine which is now present as chloride and which is analysed for chlorine isotopes according to the technique described by Long et al. (1993). The chlorine yield of the Parr bomb technique was within a narrow range between 65 and 75 % and no isotope differences were observed in cases when lower or higher yields were obtained. The isotope measurements had an analytical reproducibility of ±0.29 ‰ (standard deviation), based on 21 analyses of a trichloroethylene sample, while for the other measured compounds the standard deviation of three to ten measurements was between 0.10 and 0.68 ‰. The carbon isotope ratios of the same compounds were determined according to the technique described by Boutton et al. (1983). Interestingly the combination of both chlorine and carbon isotope analyses of the various samples made it possible to better characterise the individual samples as it was observed that samples with comparable chlorine isotope ratios could have very different carbon isotopes, while samples with comparable carbons isotope ratios could have clearly different chloride isotone ratios.

4.6.1.3 Non-aqueous High Temperature Conversion Methods for Both Chlorine and Carbon Isotopes

A non-aqueous method to convert organochlorine compounds such that both the carbon and chlorine isotope ratios could be analysed in the same aliquot of sample was developed by Holt et al. (1997). An aliquot of sample is injected into a glass ampoule that contains about 1 g copper (II) oxide wire, frozen with liquid nitrogen and evacuated. The ampoule is sealed at a restriction and hated for 2 h at 550 °C. The copper(II) oxide wire oxidises carbon in the organic compound to CO_2 and reduces the chlorine to chloride that is retained as copper(I) chloride. During this process one part of the ampoule is frozen into a beaker containing liquid nitrogen to trap carbon dioxide and water, probably to avoid the pressure from getting too high. After the reaction has finished the ampoule is put into a tube cracker attached to a vacuum line and first the carbon dioxide is transferred and cleaned for carbon isotope analysis. In the remaining part of the reaction ampoule the original chlorine is still present as copper(I) chloride. This is reattached to the vacuum line and after evacuation 35 μL iodomethane is frozen onto the copper(I) chloride using a syringe trough a septum. The reaction ampoule is sealed again and heated for 2 h at a temperature of 300 °C. During this reaction copper(I) chloride is reacted to copper(I) iodide and iodomethane to chloromethane. Finally the chloromethane was cryogenically separated from iodomethane following the method described in section "Cryogenic Separation of Chloromethane from Iodomethane". The chlorine yield from different chlorinated compounds with this method varied between 80 and 100 %, and generally it appeared that the more complex the chlorinated hydrocarbon was the lower the yield was. The chlorine isotope data obtained by this method showed to be very precise. Most duplicate measurements of a single compound for chlorine isotopes were within 0.05 ‰ from each other and it was concluded that chlorine isotope ratios could be measured with a precision that is generally better than 0.1 ‰.

At about the same time Holt et al. (1997) developed their method a group in Reading (UK) independently developed a method which was comparable to the method developed by Holt et al. (1997). Jendrzejewski et al. (1997) also added one to three μL of a chlorinated hydrocarbon to a glass capsule containing about 1 g copper(II) oxide. The capsule then was evacuated and sealed and heated in a furnace at 400 °C for at least 1 h. After this time the capsules are further heated to the final reaction temperature, which is 620 °C for borosilicate capsules. After the reaction has finished the capsule was put into a tube cracker and attached to a vacuum-line. After cracking condensible gases are transferred, and carbon dioxide is separated out and cleaned for carbon isotope measurement. All solid residues (glass, remaining copper oxide and newly formed copper chloride were then recovered into a glass beaker, rinsed with and dissolved in distilled water to dissolve the chloride into the water. After dissolution of all chloride it was analysed for the isotope composition according to the methods described by Long et al. (1993) and Eggenkamp (1994). Both the chlorine yields and the precision of the chlorine isotope measurements were comparable to the method developed by Holt et al. (1997) showing chloride yields between 86 and 119 % and a 0.08 ‰ reproducibility for the stable chlorine isotope measurements.

4.6.1.4 On-line IRMS Technique for the Analysis of Total Organic Chlorine in Environmental Samples

The first on-line technique to analyse the chlorine isotope composition of the total organic chlorine in environmental samples was developed by Wassenaar and Koehler (2004). The first stage of their method still concerned off-line preparation of chloromethane according to techniques described by Long et al. (1993) and Eggenkamp (1994), while organic samples were converted through the Parr Bomb technique (Van Warmerdam et al. 1995). The on-line part of the technique consisted of injection of the chloromethane and iodomethane mixture onto a 2 m ¼" GC column packed with Porapack Q, where the two gases were separated and from which the chloromethane was directly introduced onto the mass spectrometer, while iodomethane was directed through a waste line. The chlorine isotope composition was determined through comparison of the sample peaks with reference gas peaks and it was found that the repeatability of the technique reached about 0.06 ‰ (1σ). The main advantage of this method was the time saving because of the direct injection of the chloromethane and iodomethane mixture onto the gas chromatograph and subsequent introduction to the MS.

4.6.2 Measurement of Organochlorine Compounds Using TIMS

Numata et al. (2001) and Holmstrand et al. (2004) developed methods to analyse the chlorine isotope composition of organic compounds by thermal ionization mass spectrometry. The advantage of this technique is that very small amounts of organochlorine compounds can be measured for their chlorine isotopes which is important as in natural environments the concentrations of organochlorine compounds are, in most cases, very small.

Numata et al. (2001) extracted chlorine as chloride from organochlorine compounds using a sodiumbiphenyl reagent following Liggett (1954) with some modifications after Numata et al. (2001). The method had the organochlorine compound (containing about 1.0 mg chlorine) reacted with some organic solvent (toluene, n-decane or di-iso-propylether) in a test tube (sealed with rubber stopper in a nitrogen atmosphere) to which 0.2 mL sodiumbiphenyl reagent is added. Sodiumbiphenyl reagent is a 1 M sodiumbiphenyl solution in dimethoxiethane. After the reaction has finished (which takes 30 min) 0.5 mL water is added to extract the chloride ions from the organic mixture. The chloride that is extracted is converted to caesium chloride according to the method described by Numata et al. (2001) for measurement on a Finnigan MAT262 thermal ionization mass spectrometer.

Holmstrand et al. (2004) used a different method to extract chloride from the chlorinated solvents. They extracted chloride from the solvent by combustion using copper(II) oxide comparable to methods established by Holt et al. (1997) and Jendrzejewski et al. (1997). The chloride extracted this way was purified and converted to caesium chloride according to the technique described by Numata et al. (2001) and analysed on a Finnigan MAT261 thermal ionization mass spectrometer.

4.6.3 Techniques to Introduce Organic Molecules into a Mass Spectrometer Directly

The first study in which it was attempted to analyse chlorine isotopes by directly introducing organic molecules and fragments into the mass spectrometer was done by Shouakar-Stash et al. (2006). This followed the application of using mass fragments to explore stable isotope analyses as was done for the first time by Rees (1978) who directly introduced SF_5^+ fragments into the mass spectrometer that were obtained from SF_6 for sulphur isotope studies. The aim of this study for chlorine isotopes was to attempt to analyse them using less preparative steps and improve sensitivity and precision.

Shouakar-Stash et al. (2006) used an Agilent 6890 gas chromatograph coupled to an Isoprime isotope ratio mass spectrometer with collectors for masses m/z 94 and 96. The procedure was based on the fact that fragments with masses 94 and 96, 95 and 97 and 96 and 98 were produced from PCE (tetrachloroethene), TCE (trichloroethene) and DCE (dichloroethene) respectively. Chlorinated solvents were introduced directly onto the gas chromatograph using a gas-tight syringe. The samples injected were either pure chemicals or the headspace sampled from above aqueous solutions. Separation of the gaseous phases was performed on a DB-5 column and the purified compounds were introduced onto the mass spectrometer where outside the window of interest the flow was directed to the FID to avoid introduction of unwanted compounds in the mass spectrometer. The isotope ratios were analysed from the masses masses 94 and 96. Shouakar-Stash et al. (2006) discovered that the reported δ^{37}Cl values of the organochlorine compounds were highly non-linear. For example in the case of tetrachloroethene where depending on the peak area values between −4.0 and +3.0 ‰ were found while the actual values should have been 0.0 ‰. As the non-linearity was very systematic this could be corrected for. Thanks to this systematic correction it is possible to obtain precisions as low as ±0.06 to 0.12 ‰ depending on the compound studied. One of the biggest improvements of this techniques was the possibility to analyse very small sample amounts. It was found that concentrations as low as 5 to 20 µg/L, equivalent to amounts of 6 to 9 nmole of chlorine and approximately 80 times lower than off-line methods developed earlier, could be analysed using this technique.

4.6.4 Analysis of Chlorine Isotopes in Organic Molecules by ICP-MS

At about the same time experiments were done to analyse chlorine isotope compositions on organochlorine molecules using multi collector ICP-MS. Van Acker et al. (2006) were the first to describe a successful method to do so. Using their method the individual organochlorine compounds are separated using gas chromatography as in earlier mentioned methods, and the organochlorine compounds are introduced separately into a multi collector ICP-MS. Potential difficulties with this method are the low ionization yield for chlorine due to its high first ionization potential and the fact that helium carrier gas is mixed with argon. Argon produces $^{1}H^{36}Ar^{+}$ ions in the plasma which has a large interference with $^{37}Cl^{+}$. This problem was solved by using a very high mass resolving power of about 10,000. This is enough to find a small shoulder on the mass 37 peak which is from $^{37}Cl^{+}$, due to a small mass difference between $^{1}H^{36}Ar^{+}$ (m/z = 36.97537) and $^{37}Cl^{+}$ (m/z = 36.96590). The width of this shoulder is only about 0.0004 amu, but enough to be able to analyse the δ^{37}Cl with a precision of about 0.12 ‰. The δ^{37}Cl was determined in a way that was comparable to continuous flow GC-IRMS, thus by comparing the unknown sample with a known standard. With this technique it was possible to analyse very small amounts of sample. The precision of 0.12 ‰ was reached with sample sizes between 200 nmole to 1.3 µmole, while worse precisions were found with smaller sample sizes. This analytical method applied a more direct method to measure the chlorine isotope composition by ICP-MS as compared to the previously described method by Fietzke et al. (2008) where the $^{37}Cl^{+}$ signal was corrected for the presence of $^{1}H^{36}Ar^{+}$ in the sample.

4.6.5 Analysis of Chlorine Isotopes by Quadrupole Mass Spectrometry

The most recently developed analytical technique for the measurement of chlorine stable isotopes in organic compounds is the analyses with conventional quadrupole gas chromatography mass spectrometry (GC-qMS). With this method a mixture of chlorinated solvents is separated into individual compounds using a gas chromatograph and subsequently introduced into a quadrupole mass spectrometer. The isotope composition of the individual compounds is then calculated from the peak areas of several selected molecular ions and fragment ions of the analysed substances (Sakaguchi-Söder et al. 2007; Sakaguchi-Söder 2010). Although the method is straightforward, calculation of the isotope composition is done using a relatively complex set of mathematical equations. In their original study Sakaguchi-Söder et al. (2007) used an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 N quadrupole mass selective detector. They separated the compounds using a DB-624 capillary column, which is sensitive to chlorinated ethenes and vinylchloride. To determine the isotope composition of an individual compound a selection of the most common mass fragments of this compound were measured. Unlike previously described methods where the isotope composition is determined on mass fragments containing only one chlorine atom, the isotope composition with quadrupole mass spectrometry is determined on all major fragments which may contain more chlorine atoms and an individual mass may contain either both isotopes or only one isotope as described in detail by Sakaguchi-Söder et al. (2007). The set of mathematical formulas can be solved and in their preliminary study they managed to get an internal precision of 0.4–1.1 ‰ on samples with a size of between 10 to 1,000 pmol. The theoretical basis for the calculation of chlorine isotope ratios was improved by Elsner and Hunkeler (2008). The method was further developed by Aeppli et al. (2010) and Jin et al. (2011). Their methods showed that even smaller samples, down to 1.6 pmol could be analysed with comparable precisions as found by Sakaguchi-Söder et al. (2007).

The method is currently in use in several, mostly German laboratories. In a large intercomparison study Bernstein et al. (2011) studied the results from several of these laboratories and compared them to results obtained by GC-IRMS in other laboratories. After sometimes complex correction methods it was found that the results of the various direct injection methods were in good agreement with each other even when it was considered that the precision for the IRMS methods was much better (±0.1 ‰) compared to the qMS methods (0.2–0.5 ‰ or 0.2–0.9 ‰, depending on the type of quadrupole mass spectrometer used).

4.6.6 Measurement of Chlorine Isotopes in Organic Molecules After High Temperature Conversion

Hitzfeld et al. (2011) proposed a new method to analyse chlorine isotopes in organic molecules after simple high temperature conversion to hydrogen chloride and subsequent measurement in a Balzers GAM 445 Analyzer. A mixture of organic molecules are separated by capillary gas chromatography and then led into a high temperature conversion oven. Using hydrogen as make-up gas chlorine in the organic molecules is converted to hydrogen chloride at temperatures between 1,300 and 1,400 °C. The isotope composition of the hydrogen chloride is determined directly at the isotope analyser at $m/z = 36$ and 38. The precision of the method is not very good at just under 1 ‰, but the authors saw possibilities for the improvement of the method in the future.

4.6.7 A Method for the Measurement of Stable Chlorine Isotopes in Polyvinylchloride

Plastics such as polyvinylchloride can not be introduced into gas chromatographic systems as they are polymerised solids. Musashi et al. (2010) developed a method to be able to analyse the chlorine isotope composition of this type of compounds with the use of supercritical water. Supercritical water, at pressures above 30 MPa and temperatures above 600 °C, was able to extract about 80 % of the chlorine from polyvinylchloride. Chlorine isotopes were analysed from the extracted chloride following the method described by Eggenkamp (1994) and preliminary results indicated that no obvious isotope fractionation appeared. Unfortunately this promising method was not yet developed further.

4.7 Extraction of Chlorinated Solvents from (Ground)Water Samples

After the establishment of the first techniques to analyse chlorine isotope compositions of organochlorine compounds it was realised that it would be essential to be able to extract these compounds from the natural environment. As the concentrations of these compounds in natural environments, especially ground waters always is relatively low these methods were important to be developed as otherwise it would never be possible to study their behaviour in natural environments.

Holt et al. (2001) were the first to develop a method to extract organochlorine compounds from water samples. To extract organochlorine compounds from groundwater they have helium bubbled through a sample and trapped the organochlorine compounds into a cold trap cooled by a dry ice—acetone slush after the sample was led trough a cold water condenser. Through this procedure the amount of water in the cold trap is minimised. The procedure is repeated to a second cold trap which was also cooled with a dry ice—acetone slush and the organochlorine compounds are finally trapped in a cold trap containing liquid nitrogen. The water free organochlorine compounds are collected in a combustion tube and subsequently analysed as described by Holt et al. (1997). This method has later been adapted by Gan et al. (2013) who used a comparable technique to extract carbon and chlorine from organochlorine compounds using copper(II) oxide combustion, but used a Gas-Bench II analogue to Liu et al. (2013) to introduce the produced chloromethane into the mass spectrometer.

4.8 Extraction of Chloromethane from the Atmosphere for Isotope Analysis

Thornton et al. (2013) developed a cryosampler and sample purification system that allowed them to extract large enough quantities of chloromethane from the atmosphere for isotope analyses. As their method was primarily developed to be able to extract and analyse bromomethane from the atmosphere it is described in more detail in the following Chap. 5.

4.9 Recapitulation of Analytical Methods

As shown in this chapter the development of the analytical methods to analyse chlorine isotopes has a considerable history. Most laboratories that are able to analyse chlorine isotopes use their own method, that they also published when this was developed to such a level that the isotopes could be measured with good (or acceptable) precision. Striking in this respect is that several laboratories published a method, but did publish little or no case studies later, so that it can be concluded that they have abandoned the field of chlorine isotope geochemistry research shortly after their method was developed and published.

It is clear from the method descriptions in this chapter that chlorine isotopes have been analysed by virtually all techniques and instruments that have been developed to measure stable isotopes in the past. Considering the small number of laboratories that still analyse chlorine stable isotopes routinely it is expected that in the near future in inorganic chlorine isotope research preferably IRMS measurements with chloromethane as mass spectrometer gas [both dual-inlet and continuous flow; according to the techniques as developed by Long et al. (1993), Eggenkamp (1994) and Shouakar-Stash et al. (2005)] and P-TIMS measurements [as developed by Xiao and Zhang (1992)] will be used in chlorine isotope studies. Other techniques, such as ICP-MS will remain rarely used considering the difficulty to separate $^{36}ArH^+$ from $^{37}Cl^+$. Also techniques that have relatively large errors of measurement, such as SIMS and N-TIMS will only be applied rarely because the natural variation of chlorine isotope ratios is smaller than their routine measurement error. These techniques will only be applied for specific applications such as extremely small samples or samples with large isotope ratio variations and not as routine chlorine isotope techniques.

The development of techniques to analyse organochlorine compounds is still very much in progress. Considering the complexity of several compounds it is expected that the quality of the techniques that analyse whole fragments of chlorinated organic compounds will continue to be improved. Results by quadrupole mass spectrometer are promising, although the precision of the measurements is still not optimal. Again considering the small numbers of laboratories analysing chlorine isotopes the technique as developed by Shouakar-Stash et al. (2006) by continuous flow IRMS and that by Holmstrand et al. (2004) by sealed tube combustion and subsequent analysis by P-TIMS will definitely continue to be used in the foreseeable future to analyse the chlorine isotope composition of organochlorine compounds.

References

Ader M, Coleman ML, Doyle SP, Stroud M, Wakelin D (2001) Methods for the stable isotopic analysis of chlorine in chlorate and perchlorate compounds. Anal Chem 73:4946–4950

Aeppli C, Holmstrand H, Andersson P, Gustafsson Ö (2010) Direct compound-specific stable chlorine isotope analysis of organic compounds with quadrupole GC/MS using standard isotope bracketing. Anal Chem 82:420–426

Aston FW (1919a) The constitution of the elements. Nature 104:393

Aston FW (1919b) A positive ray spectrograph. Philos Mag 38:707–714

Aston FW (1920) The mass spectra of the chemical elements. Phil Mag 39:611–625

Aston FW (1921) The mass spectra of the chemical elements—Part 3. Phil Mag 42:140–144

Aston FW (1925) Photographic plates for the detection of mass rays. Math Proc Cambridge Phil Soc 22:548–554

Aston FW (1931) The isotopic constitution and atomic weights of selenium, bromine, boron, tungsten, antimony, osmium, ruthenium, tellurium, germanium, rhenium and chlorine. Proc R Soc Lond A 132:487–498

Bao H, Gu B (2004) Natural perchlorate has its unique oxygen isotope signature. Environ Sci Technol 38:5073–5077

Barnes JD, Selverstone J, Sharp ZD (2006) Chlorine isotope chemistry of serpentinites from Elba, Italy, as an indicator of fluid source and subsequent tectonic history. Geochem Geophys Geosys 7 Article number Q08015

Bartholomew RM, Brown F, Lounsbury M (1954) Chlorine isotope effect in reactions of *tert*-butyl chloride. Canadian J Chem 32:979–983

Behne W (1953) Untersuchungen zur Geochemie des Chlor und Brom. Geochim Cosmochim Acta 3:186–214

Bernstein A, Shouakar-Stash O, Ebert K, Laskov C, Hunkeler D, Jeannottat S, Sakaguchi-Söder K, Laaks J, Jochmann MA, Cretnik S, Jager J, Haderlein SB, Schmidt TC, Aravena R, Elsner M (2011) Compound-specific chlorine isotope analysis: a comparison of gas chromatography/isotope ratio mass spectrometry and gas chromatography/quadrupole mass spectrometry methods in an interlaboratory study. Anal Chem 83:7624–7634

Blatt AH (1943) Organic synthesis, Col vol II. Wiley, New York, p 251

Böhlke JK, Sturchio NC, Gu B, Horita J, Brown GM, Jackson WA, Batista JR, Hatzinger PB (2005) Perchlorate isotope forensics. Anal Chem 77:7838–7842

Bonifacie M, Jendrzejewski N, Agrinier P, Coleman M, Pineau F, Javoy M (2007). Pyrohydrolysis-IRMS determination of silicate chlorine stable isotope compositions. Application to oceanic crust and meteorite samples. Chem Geol 242:187–201

Bonifacie M, Jendrzejewski N, Agrinier P, Humler E, Coleman M, Javoy M (2008) The chlorine isotope composition of earth's mantle. Science 319:1518–1520

Boutton TW, Wong WW, Hachey DL, Lee LS, Cabrera MP, Klein PD (1983) Comparison of quartz and pyrex tubes for combustion of organic samples for stable carbon isotope analysis. Anal Chem 55:1832–1833

Brown F, Gillies A, Stevens WH (1953) A note on the preparation of chlorine gas containing ^{36}Cl. Can J Chem 31–768

Callis E L, Abernathey RM (1991) High-precision analyses of uranium and plutonium by total sample volatilization and signal integration. Int J Mass Spectrom Ion Proc 103:93–105

Catling DC, Clair MW, Zahnle KJ, Quinn RC, Clarc BC, Hecht MH, Kounaves SP (2010) Atmospheric origins of perchlorate on Mars and in the Atacama. J Geophys Res 115:E00E11. doi:10.1029/2009JE003425

Curie I (1921) Sur le poids atomique du chlore dans quelques mineraux. Compte Rend Sean 172:1025–1028

De Groot PA (2004) Handbook of stable isotope analytical techniques, vol I. Elsevier, Amsterdam

Desaulniers DE, Kaufmann RS, Cherry JA, Bentley HW (1986) ^{37}Cl-^{35}Cl variations in a diffusion controlled groundwater system. Geochim Cosmochim Acta 50:1757–1764

Dorenfeldt M (1922) Relative determination of the atomic weight of chlorine in Bamle apatite. J Amer Chem Soc 45:1577–1579

Dreibus C, Spettel B, Wänke H (1979) Halogens in meteorites and their primordial abundances. In: Ahrens LH (ed) Origin and distribution of the elements, vol 34. Pergamon Press, Oxford, pp 33–38

Eastoe CJ, Guilbert JM, Kaufmann RS (1989) Preliminary evidence for fractionation of stable chlorine isotopes in ore forming hydrothermal systems. Geology 17:285–288

Eggenkamp HGM (1994) δ^{37}Cl; the geochemistry of chlorine isotopes. Geol Ultrai 116:1–150 (Thesis Utrecht University)

Eggenkamp HGM (2004) Summary of methods for determining the stable isotope composition of chlorine and bromine in natural materials. In: de Groot PA (ed) Handbook of stable isotope analytical techniques, Chapter 28. Elsevier, Amsterdam, pp 604–622

Eggenkamp HGM, Schuiling RD (1995) δ^{37}Cl variations in selected minerals: a possible tool for exploration. J Geochem Expl 55:249–255

Eggenkamp HGM, Koster van Groos AF (1997) Chlorine stable isotopes in carbonatites: evidence for isotopic heterogeneity in the mantle. Chem Geol 140:137–143

Eggenkamp HGM, Kreulen R, Koster van Groos AF (1995) Chlorine stable isotope fractionation in evaporites. Geochim Cosmochim Acta 59:5169–5175

Elsner M, Hunkeler D (2008) Evaluating chlorine isotope effects from isotope ratios and mass spectra of polychlorinated molecules. Anal Chem 80:4731–4740

Ericksen GE (1981) Geology and origin of the Chilean nitrate deposits. USGS professional paper 1188, p 37

Fietzke J, Frische M, Hansteen TH, Eisenhauer A (2008) A simplified procedure for the determination of stable chlorine isotope ratios (δ^{37}Cl) using LA-MC-ICP-MS. J Anal Atom Spectrom 23:769–772

Fujitani T, Nakamura N (2006) Determination of chlorine in nine rock reference materials by isotope dilution mass spectrometry. Geostd Geoanl Res 30:113–120

Fujitani T, Yamashita K, Numata M, Kanazawa N, Nakamura N (2010) Measurement of chlorine stable isotopic composition by negative thermal ionization mass spectrometry using total evaporation technique. Geochem J 44:241–246

Gan YQ, Yu TT, Zhou AG, Liu YD, Liu CF (2013) A Technique for Carbon and Chlorine isotope analyses of chlorinated aliphatic hydrocarbons in groundwater. J Earth Sci 24:274–281

Gaudette HE (1990) Chlorine and boron isotopic analyses of Antarctic ice and snow: indicators of marine and volcanic atmospheric inputs. Geol Soc Amer Ann Meeting 1990:173

Gleditsch E, Samdahl B (1922) Radioactivité sur le poids atomique de chlore dans un mineral ancien, l'apatede Balme. Compte Rend Sean 174:746–748

Godon A (2000) La subduction des Petites Antilles: apports de la géochimie isotopique du chlore. PhD thesis, Paris VII University, p 300 (Abstract in English)

Godon A, Jendrzejewski N, Eggenkamp HGM, Banks DA, Ader M, Coleman ML, Pineau F (2004a) A cross calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. Chem Geol 207:1–12

Godon A (2000) La subduction des Petites Antilles: apports de la géochimie isotopique du chlore. PhD thesis, Paris VII Univ. 300 pp (In French with abstract in English)

Godon A, Webster JD, Layne GD, Pineau F (2004b) Secondary ion mass spectrometry for the determination of δ^{37}Cl. Part II. Intercalibration of SIMS and IRMS for aluminosilicate glasses. Chem Geol 207:291–303

Gu B, Brown GM, Maya L, Lance MJ, Moyer BA (2001) Regeneration of perchlorate (ClO_4^-)-loaded anion exchange resins by novel tetrachloroferrate ($FeCl_4^-$) displacement technique. Environ Sci Technol 35:3363–3368

Gu B, Brown GM, Chiang CC (2007) Treatment of perchlorate contaminated groundwater using highly selective, regenerable ion-exchange technologies. Environ Sci Technol 41:6277–6282

Gu B, Böhlke JK, Sturchio NC, Hatzinger PB, Jackson WA, Beloso AD Jr, Heraty LJ, Bian Y, Brown GM (2011) Removal, recovery and fingerprinting of perchlorate by ion exchange processes. In: SenGupta AK (ed) Ion exchange and solvent extraction: a series of advances, vol 20. CRC Press, Boca Raton

Halas S, Pelc A (2009) New isotope ratio mass spectrometric method of precise δ^{37}Cl determinations. Rapid Commun Mass Spectrom 23:1061–1064

Harkins WD, Stone SB (1926) The isotopic composition and atomic weight of chlorine from meteorites and from minerals of non-marine origin. J Amer Chem Soc 48:938–949

Hauri E, Wang J, Dixon JE, King PE, Mandeville C, Newman S (2000) SIMS analysis of volatiles in silicate glasses: 1. Calibration, matrix effects and comparisons with FTIR. Chem Geol 183:99–114

Hecht MH, Kounaves SP, Quinn RC, West SJ, Young SMM, Ming DW, Catling DC, Clark BC, Boynton WV, Hoffman J, DeFlores LP, Gospodinova K, Kapit J, Smith PH (2009) Detection of perchlorate and the soluble chemistry of Martian soil at the Phoenix Lander site. Science 325:64–67

Herzog W, Dörnenburg E (1958) Die Verwendung van Methylchlorid zur massenspektrometrichen Isotopenanalyse von Chlor. Z Naturforschg 13a:51–52

Herzog W, Klemm A (1958) Die Temperaturabhängigkeit des Isotopie-Effekts bei der elektrolytischen Wanderungen der Chlorionen in herschmolzenem Thallium (I)-chlorid. Z Naturforschg 13a:7–16

Hill JW, Fry A. (1962) Chlorine isotope effects in the reactions of benzyl and substituted benzyl chlorides with various nucleophiles. J Amer Chem Soc 84:2763–2769

Hintze C (1915) Handbuch der Mineralogie. Verlag von Veit & Comp. Leipzig

Hitzfeld KL, Gehre M, Richnow HH (2011) A novel online approach to the determination of isotopic ratios for organically bound chlorine, bromine and sulphur. Rapid Commun Mass Spectrom 25:3114–3122

Hoering TC, Parker PL (1961) The geochemistry of the stable isotopes of chlorine. Geochim Cosmochim Acta 23:186–199

Holmstrand H, Andersson P, Gustafsson Ö (2004) Chlorine isotope analysis of submicromole organochlorine samples by sealed tube combustion and thermal ionization mass spectrometry. Anal. Chem. 76:2336–2342

Holt BD, Sturchio NC, Abrajano TA, Heraty LJ (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. Anal Chem 69:2727–2733

Holt BD, Heraty LJ, Sturchio NC (2001) Extraction of chlorinated aliphatic hydrocarbons from groundwater at micromolar concentrations for isotopic analysis of chlorine. Environ Poll 113:263–269

Howald RA (1960) Ion pairs. I. Isotope effects shown by chloride solutions in glacial acetic acid. J Amer Chem Soc 82:20–24

Jackson WA, Anandam SK, Anderson T, Lehman T, Rainwater K, Rajagopalan S, Ridley M, Tock R (2005) Perchlorate occurrence in the Texas southern high plains aquifer system. Ground Water Monit Rem 25:137–149

Jendrzejewski N, Eggenkamp HGM, Coleman ML (1997) Sequential determination of chlorine and carbon isotopic composition in single microliter samples of chlorinated solvent. Anal Chem 69:4259–4266

Jin B, Laskov C, Rolle M, Haderlein SB (2011) Chlorine isotope analysis of organic contaminants using GCqMS: method optimization and comparison of different evaluation schemes. Environ Sci Technol 45:5279–5286

Joan M, Reedy JH (1940) The detection of oxy-halogen anions. Trans Illinois State Acad Sci 33:123–125

Johnston WH, Arnold JR (1953) The existence of multiply charged molecular ions of HBr, HCl, and DCl. J Chem Phys 21:1499–1502

Kaufmann RS (1984) Chlorine in groundwater: Stable isotope distribution. Ph.D. thesis, University of Arizona, Tucson, Ariz

Kaufmann RS, Long A, Bentley H, Davis S (1984) Natural chlorine isotope variations. Nature 309:338–340

Keller J, Krafft M (1990) Effusive natrocarbonatite activity of Oldoinyo Lengai, June 1988. Bull Volcanol 52:629–645

Klemm A, Lundén A (1955) Isotopenanreicherung beim Chlor durch electrolytische Überfürung in geschmolzenem Bleichlorid. Z. Naturforschg. 10A:282–284

Kohnen MEL (1988) Stabiele chloorisotopen onderzoek. Internal report, University of Utrecht, p 17

Kounaves SP, Stroble ST, Anderson RM, Moore Q, Catling DC, Douglas S, McKay CP, Ming DW, Smith PH, Tamppari LK, Zent AP (2010) Discovery of natural perchlorate in the Antarctic Dry Valleys and its global implications. Environ Sci Technol 44:2360–2364

Kuroda PK, Sandell EB (1953) Chlorine in igneous rocks. Bull Geol Soc Amer 64:879–896

Kusakabe M (2005) A closed pentane trap for separation of SO_2 from CO_2 for precise $\delta^{18}O$ and $\delta^{34}S$ measurements. Geochem J 39:285–287

Langvad T (1954) Separation of chlorine isotopes by ion-exchange chromatography. Acta Chem Scand 8:526–527

Layne GD, Godon A, Webster JD, Bach W (2004) Secondary ion mass spectrometry for the determination of $\delta^{37}Cl$. Part I. Ion microprobe analysis of gasses and fluids. Chem Geol 207:277–289

Liggett LM (1954) Determination of organic halogen with sodium biphenyl reagent. Anal Chem 26:748–750

Liu WG, Xiao YK, Wang QZ, Qi HP, Wang YH, Zhou YM, Shirodkar PV (1997) Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. Chem Geol 136:271–279

Liu YD, Zhou AG, Gan YQ, Liu CF, Yu TT, Li XQ (2013) An online method to determine chlorine stable isotope composition by continuous flow isotope ratio mass spectrometry (CF-IRMS) coupled with a Gasbench II. J South Centr Univ 20:193–198

Long A, Eastoe CJ, Kaufmann RS, Martin JG, Wirt L, Finley JB (1993) High-precision measurement of chlorine stable isotope ratios. Geochim Cosmochim Acta 57:2907–2912

Lundén A, Herzog W. (1956) Isotopenanreicherung bei Chlor durch electrolytische Überführung in geschmolzenem Zinkchlorid. Z Naturforschg 11a:520

Madorsky SL, Strauss S (1947) Concentration of isotopes of chlorine by the counter-current electromigration method. J Res Nat Bur Stand 38:185–189

Magenheim AJ, Spivack AJ, Volpe C, Ransom B (1994) Precise determination of stable chlorine isotopic ratios in low-concentration natural samples. Geochim Cosmochim Acta 58:3117–3121

McIlvaine TC (1921) A buffer solution for colorimetric comparison. J Biol Chem 49:183–186

McKinney CR, McCrea JM, Epstein S, Allen HA, Urey HC (1950) Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios. Rev Sci Inst 21:724–730

Ming DW, Smith PH, Tamppari LK, Zent AP (2010) Discovery of natural perchlorate in the Antarctic Dry Valleys and its global implications. Environ Sci Technol 44:2360–2364

Musashi M, Markl G, Kreulen R (1998) Stable chlorine-isotope analysis of rock samples: new aspects of chlorine extraction. Anal Chem Acta 362:261–269

Musashi M, Eggenkamp HGM, Van Cappellen PH (2010) Experiment on chlorine extraction from chlorinated pollutants by supercritical water and their Cl isotope analysis. Bull Sc Technol Shibaura Inst Technol 54:57–61 (In Japanese with English abstract)

Nešković OM, Veljković MV, Veličković SR, Derić AJ, Miljević NR, Golobočanin DD (2002) Precise measurement of chlorine isotopes by thermal ionization mass spectrometry. Nukleonika. 1(Supp 47):s85–s87

Nier AO (1947) A mass spectrometer for isotope and gas analysis. Rev Sci Inst 18:398–411

Nier AO (1955) Determination of isotopic masses and abundances by mass spectrometry. Science 121:737–744

Nier AO, Hanson EE (1936) A mass-spectrographic analysis of the ions produced in HCl under electron impact. Phys Rev 50:722–726

Nier AO, Ney EP, Inghram MG (1946) A null method for the comparison of two ion currents in a mass spectrometer. Phys Rev 70:116–117

Numata M, Nakamura N, Gamo T (2001) Precise measurement of chlorine stable isotopic ratios by thermal ionization mass spectrometry. Geochem J 35:89–100

Owen HR, Schaeffer OA (1955) The isotope abundances of chlorine from various sources. J Amer Chem Soc 77:898–899

Parker DR, Seyfferth AL, Reese BK (2008) Perchlorate in groundwater: a synoptic survey of "pristine" sites in the conterminous Unites States. Environ Sci Technol 42:1465–1471

Pelc A, Halas S (2008) Negative ion source for chlorine isotope ratio measurements. Rapid Commun Mass Spectrom 22:3977–3982

Plummer LN, Böhlke JK, Doughten MW (2006) Perchlorate in Pleistocene and Holocene groundwater in north-central New Mexico. Environ Sci Technol 40:1757–1763

Rajagopalan S, Anderson TA, Fahlquist L, Rainwater KA, Ridley M, Jackson WA (2006) Widespread presence of naturally occurring perchlorate in high plains of Texas and New Mexico. Environ Sci Technol 40:3156–3162

Rajagopalan S, Anderson TA, Cox S, Harvey G, Cheng Q, Jackson WA (2009) Perchlorate in wet deposition across North America. Environ Sci Technol 43:616–622

Rao B, Anderson TA, Orris GJ, Rainwater KA, Rajagopalan S, Sandvig RM, Scanlon BR, Stonestrom DA, Walvoord MA, Jackson WA (2007) Widespread natural perchlorate in unsaturated zones of the Southwest United States. Environ Sci Technol 41:4522–4528

Rees CE (1978) Sulphur isotope measurements using SO_2 and SF_6. Geochim Cosmochim Acta 42:383–389

Richards TW, Wells RC (1905) A revision of the atomic weights of sodium and chlorine. J Amer Chem Soc. 27:459–529

Rosenbaum JM, Cliff RA, Coleman M.L. (2000) Chlorine stable isotopes: a comparison of dual inlet and thermal ionization mass spectrometric measurements. Anal Chem 72:2261–2264

Sakaguchi-Söder KA (2010) New method for compound-specific stable chlorine isotope analysis: basics and application. PhD thesis, Technische Universität, Darmstadt, Germany

Sakaguchi-Söder K, Jager J, Grund H, Matthäus F, Schüth C (2007) Monitoring and evaluation of dechlorination processes using compound-specific chlorine isotope analysis. Rapid Commun Mass Spectrom 21:3077–3084

Schnetger B, Muramatsu Y (1996) Determination of halogens, with special reference to, iodine, in geological and biological samples using pyrohydrolysis for preparation and inductively coupled plasma mass spectrometry and ion chromatography for measurement. Analyst 121:1627–1631

Sharp ZD, Barnes JD, Brearly AJ, Chaussidon M, Fisher TP, Kamenetsky VS (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature 446:1062–1065

Shields WR, Murphy TJ, Garner EL, Dibeler VH (1962) Absolute isotopic abundance ratios and the isotopic weight of chlorine. J Amer Chem Soc 84:1519–1522

Shirodkar PV, Xiao YK, Sarkar A, Dalal SG, Chivas AR (2006) Influence of air-sea fluxes on chlorine isotopic composition of ocean water: Implications for constancy in δ^{37}Cl—a statistical inference. Environ Intern 32:235–239

Shouakar-Stash O, Drimmie RJ, Frape SK (2005) Determination of inorganic chlorine stable isotopes by continuous flow isotope ratio mass spectrometry. Rapid Commun Mass Spectrom 19:121–127

Shouakar-Stash O, Drimmie RJ, Zhang M, Frape SK (2006) Compound-specific chlorine isotope ratios of TCE, PCE and DCE isomers by direct injection using CF-IRMS. Appl Geoch 21:766–781

Stull DR (1947) Vapour pressure of pure substances. Inorganic compounds. Ind Eng Chem 39:540–550

Sturchio NC, Hatzinger PB, Arkins MD, Suh C, Heraty LJ (2003) Chlorine isotope fractionation during microbial reduction of perchlorate. Environ Sci Technol 37:3859–3863

Sturchio NC, Böhlke JK, Gu B, Horita J, Brown GM, Beloso AD Jr, Hatzinger PB, Jackson WA, Batista JR

(2006) Stable isotopic compositions of chlorine and oxygen in synthetic and natural perchlorates. In: Gu B, Coates JD (eds) Perchlorate environmental occurrences, interactions, and treatment. Springer, New York, pp 93–109

Sturchio NC, Böhlke JK, Beloso AD Jr, Streger SH, Heraty LJ, Hatzinger PB (2007) Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: laboratory results and implications for forensics and natural attenuation studies. Environ Sci Technol 41:2796–2802

Sturchio NC, Böhlke JK, Gu BH, Hatzinger PB, Jackson WA (2011) Isotopic tracing of perchlorate in the environment. In: M Baskaran (ed) Handbook of environmental isotope geochemistry, advances in isotope geochemistry. Springer, Berlin Heidelberg

Suzuki K, Miyata Y, Kanazawa N (2004) Precise Re isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS) using total evaporation technique. Int J Mass Spectrom 235:97–101

Tanaka N, Rye DM (1991) Chlorine in the stratosphere. Nature 353:707

Taylor JW, Grimsrud EP (1969) Chlorine isotopic ratios by negative ion mass spectrometry. Anal Chem 41:805–810

Thornton B, Horst A, Carrizo D, Holmstrand H, Andersson P, Crill PM, Gustafsson Ö (2013) A high-volume cryosampler and sample purification system for bromine isotope studies of methyl bromide. J Atmos Ocean Techn 30:2095–2107

Turnquist CR, Taylor JW, Grimsrud EP, Williams RC (1973) Temperature dependence of chlorine kinetic isotope effects for aliphatic chlorides. J Amer Chem Soc 95:4133–4138

Van Acker MRMD, Shahar A, Young ED, Coleman ML (2006) GC/multiple collector-ICPMS method for chlorine stable isotope analysis of chlorinated aliphatic hydrocarbons. Anal Chem 78:4663–4667

Van Warmerdam EM, Frape SK, Aravena R, Drimmie RJ, Flatt H, Cherry JA (1995) Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. Appl Geochem 10:547–552

Vengosh A, Chivas AR, McCulloch MT (1989) Direct determination of boron and chlorine isotopic compositions in geological materials by negative thermal-ionization mass spectrometry. Chem Geol (Isot Geosci Sect) 79:333–343

Vogel AI (1951) A textbook of quantitative inorganic analysis, theory and practice. Longmans, Green and Co., London, p 918

Vogel AI (1989) A textbook of quantitative inorganic analysis, theory and practice, 5th ed.; revised by Jeffrey GH et al. Longmans, Green and Co., London

Volpe C, Spivack AJ (1994) Stable chlorine isotopic composition of marine aerosol-particles in the Western Atlantic Ocean. Geophys Res Letters 21:1161–1164

Von Kallman H, Lasareff W (1932) Über die Isotopenuntersuchungen (Sauerstoff, Neon und Chlor). Z Phys 80:237–241

Von Rothmund V (1909) Concerning the reduction and determination of perchlorate. Z Anorg Chem 62:108–113

Wakaki S, Shibata S, Tanaka T (2007) Isotope ratio measurements of trace Nd by the total evaporation normalization (TEN) method in thermal ionization mass spectrometry. Int J Mass Specrrom 264:157–163

Wassenaar LI, Koehler G. (2004) On-line technique for the determination of the δ^{37}Cl of inorganic and total organic Cl in Environmental Samples. Anal Chem 76:6384–6388

Westaway KC, Koerner T, Fang YR, Rudziñski J, Paneth P (1998) A new method of determining chlorine kinetic isotope effects. Anal Chem 70:3548–3552

Whitehead D, Thomas JE (1985) Use a nebulizer in pyrohydrolytic decomposition of silicate materials for determination of fluorine and chlorine. Anal Chem 57:2421–2423

Wieser ME, Coplen TB (2010) Atomic weights of the elements 2009 (IUPAC technical report). Pure Appl Chem 83:359–396

Williams RC, Taylor JW (1973) Chlorine kinetic isotope-effect models. 1. Isotopic dependence in nominal C-Cl stretching vibrations of aliphatic chlorides and vibrational analysis of *tert*-butyl chloride ground-state. J Amer Chem Soc 95:1710–1714

Wu JH, Satake H (2006) Purification of CH_3Cl from CH_3I using cold trap with sealed 2,2,4-trimethylpentane for δ^{37}Cl measurement. Anal Chim Acta 555:41–46

Xiao YK, Zhang CG (1992) High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the Cs_2Cl^+ ion. Intl J Mass Spectrom Ion Proc 116:183–192

Xiao YK, Beary ES, Fassett JD (1988) An improved method for the high-precision isotopic measurement of boron by thermal ionization mass-spectrometry. Intl J Mass Spectrom Ion Proc 85:203–213

Xiao YK, Jin L, Qi HP (1991) Investigation of thermal ion emission characteristics of graphite. Intl J Mass Spectrom Ion Proc 107:205–213

Xiao YK, Zhou YM, Liu WG (1995) Precise measurement of chlorine isotopes based on Cs_2Cl^+ by thermal ionization mass-spectrometry. Anal Lett 28:1295–1304

Xiao YK, Zhou YM, Wang QZ. Wei HZ, Liu WG, Eastoe CJ (2002) A secondary isotopic reference material of chlorine from selected seawater. Chem Geol 182:655–661

5 Preparation Techniques for the Analysis of Stable Bromine Isotopes

5.1 Early Attempts to Analyse Bromine Isotopes

Shortly after the development of the mass spectrograph it was discovered that bromine consists of two stable isotopes (Aston 1920a, c). Later it was confirmed that the two isotopes have abundances which are bout equal (Aston 1931). More precise measurements on the ratio between the two stable bromine isotopes were done by Blewett (1936) who was able to analyse variations with a precision of about 25 ‰. After the development of a new type of mass spectrometers by Nier (1940), Williams and Yuster (1946) were able to measure the bromine isotope composition with a precision of about 4 ‰. The first negative ion thermal ionization mass spectrometry study (Cameron and Lippert 1955) in which attempts were made to find natural bromine variations with a precision of (also) approximately 4 ‰ did not find natural bromine isotope variations. Techniques improved to about a precision of 1.8 ‰ in the early 1960s (Catanzaro et al. 1964), while the first study showing that very precise measurements would be possible was published in 1993 (Xiao et al. 1993), using positive ion thermal ionization mass spectrometry on the Cs_2Br^+ ion. Since Willey and Taylor (1978), who were the first to test bromomethane as mass spectrometer gas it is expected that this will be the most promising gas for gas source isotope ratio mass spectrometry (both for dual inlet and continuous flow techniques) and it was using this gas that the first natural variations were finally determined by Eggenkamp and Coleman (2000). The techniques that were used by Eggenkamp and Coleman (2000) in their first study to determine natural bromine isotope variations are also described in De Groot (2004). They are repeated here due to the importance of these methods for the development of bromine isotope analysis techniques. Especially the method to separate bromide from a large excess of bromide (Dechan 1886; Friedheim and Meyer 1892; Boeke 1908) is still almost universally used in laboratories that study bromine isotope variations in groundwaters.

5.2 Techniques to Separate Bromine from Chlorine in Natural Samples

As chlorine and bromine are chemically very similar they are difficult to separate in samples where they are both present. However, considering the importance to analyse the composition of samples containing multiple halogens (chlorine, bromine and iodine) several attempts had been made during the 19th century to physically separate the halogens from mixtures to analyse them individually by gravimetric means. It took until the end of that century before fast and quantitative methods were developed (Dechan 1886). Friedheim and Meyer (1892) summarised the previous

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_5,

attempts and described the method that was later adopted by Eggenkamp and Coleman (2000) to extract bromide from saline samples in their first study reporting natural bromine isotope variations. Friedheim and Meyer (1892) mixed known amounts of chloride, bromide and iodide salts and separated them very efficiently, all with less than 0.5 % contamination of the other halogens. Boeke (1908) finally adopted the method for geological (evaporite) samples, which are normally characterised by a large excess of chlorine over bromine. Typical Cl/Br ratios (w/w) are 50–5,000, for example in seawater it is 292 (Rankama and Sahama 1950). Most methods currently in use for the isotopic ratio analyses of bromine still use this technique, although small variations in the method exist between the different labs.

The technique to separate bromine from an excess of chlorine used by Eggenkamp and Coleman (2000) very closely followed the procedure developed by Friedheim and Meyer (1892). The method used is based upon the well known (see e.g. already Löwich 1829) difference in oxidation–reduction behaviour of the halogen elements. With increasing atomic number the halide ions are increasingly more easy to oxidise to the native elements. So, excluding iodine, which has only one stable isotope so that there is no need to separate it for isotope measurements, the difference in redox-potential between chloride and bromide is used. It is possible to oxidise bromide to bromine by a boiling solution containing potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4), while chloride is not. The separation of bromine from chlorine takes place in a simple distillation apparatus (Fig. 5.1).

The left flask (a) is filled with the sample (either in solution or as a water-soluble salt), containing approximately 2–10 mg bromide. Then 10 g potassium dichromate ($K_2Cr_2O_7$) and subsequently distilled water is added until the flask contains approximately 100 mL solution in total. To facilitate gentle boiling an amount of anti-bumping granules are added to this flask. Through the separating funnel (b) 20 mL of a 1:1 H_2SO_4:H_2O mixture is added, after which the fluid in flask (a) is diluted to approximately 200 mL with distilled water. The right flask (c) is filled with 100 mL of a solution containing 1 g potassium hydroxide. This flask is put into a tray containing cooling water. This water is stagnant, so that it slowly increases in temperature during the distillation process. The left flask (a) is then heated. When the contents of this flask starts to boil a yellow-brown, very pale, cloud is distilled over to flask (b) through connection (d). This is bromine gas. A small part (<1 %) of the chloride present in flask (a) is transferred to flask (b) in the form of hydrogen chloride, and another small amount is reacted with the potassium dichromate to form chromyl chloride (CrO_2Cl_2), which is not carried over in the distillation (Dechan 1886). The bromine will react with the hydroxide in flask (b) to form hypobromite (BrO^-) and bromide (Br^-) ions. While the solution slowly increases in temperature due to the distillation of boiling water into flask (b) the hypobromite ions slowly decompose to bromide ions and dissolved oxygen (O_2, Bremner 1965). Although the bulk of bromine is transferred over in the first few minutes, the distillation is proceeded for 20 min to facilitate a 100 % yield of bromine. After 20 min the boiling is stopped and the distillation set-up is disassembled and the contents of flask (b) is transferred into a 500 mL Erlenmeyer flask to which approximately 2 g of zinc dust is added, and the mixture is boiled for 10 min. Any residual hypobromite left in solution will then be reduced to bromide which can be processed further. As a few tenths of a percent of the originally present chloride is also transferred the procedure should be repeated for samples with high (>1,000) initial Cl/Br ratios. The resulting solutions can be stored until they are analysed, for example in polyethylene bottles.

5.3 Analysis of Stable Bromine Isotopes from Inorganic Bromides

5.3.1 N-TIMS

Cameron and Lippert (1955) used negative thermal ionization mass spectrometry in their first attempt to find natural bromine isotope variations.

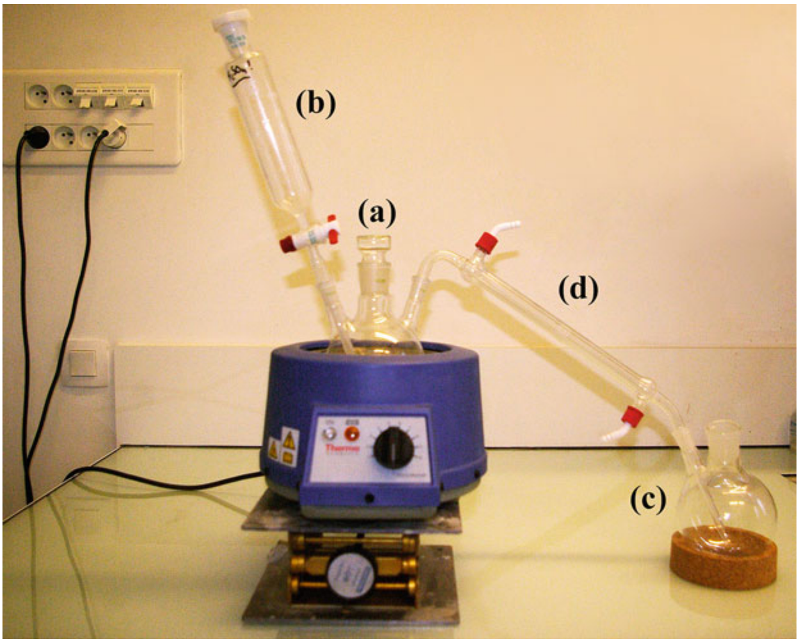

Fig. 5.1 Distillation equipment used for the separation of bromine from chlorine. **(a)** and **(c)** are 500 mL round-bottom flasks, **(b)** is a separating funnel and **(d)** is the connection between the round-bottom flasks **(a)** and **(c)**. For operation of this equipment see text. Photograph taken by Thomas Giunta and used by permission

Cameron and Lippert (1955) obtained bromine samples which were acquired from several suppliers who prepared their bromine from bromide obtained from different salt deposits as well as Pacific ocean water. The bromine was treated with ammonium hydroxide, evaporated till dryness and treated with sodium hydroxide to produce sodium bromide. This sodium bromide was added to a nickel filament as aqueous solution, dried and installed in the ion source of the mass spectrometer. The bromide was evaporated in the source and the ratio of $^{79}Br/^{81}Br$ was measured with a precision of approximately 4 ‰. The five samples analysed had $^{79}Br/^{81}Br$ ratios between 1.0206 and 1.0231, well within the precision of the measurements.

5.3.2 P-TIMS

Xiao et al. (1993) developed a method to analyse bromine isotope compositions using positive ion thermal ionization mass spectrometry applying a method that is equivalent to the method they developed earlier for chlorine isotopes. As an analogue to that method it involved transferring bromide to caesium bromide which is attached to the filament and which is analysed as Cs_2Br^+ ions. Xiao et al. (1993) tested the method with pure potassium bromide and copper(II) bromide reagents from various sources. These salts were converted to a hydrogen bromide solution (hydrobromic acid) using a cation exchange resin. This acid solution was neutralised to a pH of 3–4 using solid caesium carbonate. Filaments in the mass spectrometer were at first treated with about 3 μL of a graphite slurry containing about 100 μg graphite. Then the sample solution was added to the filament and dried for 2 min with a current of 1.1 A. When the filaments were dry the samples were loaded into the instrument and were analysed after evacuation. The Cs_2Br^+ ions were monitored and its intensity was adjusted to $3\text{–}4 \times 10^{-12}$ A by adjusting the filament current. Data were collected by switching between the masses 345 ($Cs_2^{79}Br^+$) and 347 ($Cs_2^{81}Br^+$). Several sample sizes were tested (2–32 μg) and it appeared that at sample sizes below 4 μg both the intensity and the stability degraded, so that preferentially the size of a sample should be above this limit. The method appeared to be very precise with a relative standard deviation (at the 95 % confidence limit) of 0.11 ‰. Relatively small amounts of chloride in the samples seemed not to have large effects on the measured bromine isotope measurements. Amounts of up to 51.5 μg Cl per 24 μg Br did not change the isotope measurements significantly. Unfortunately no natural samples were analysed in this study, and it appears that the method has never been applied to natural bromide samples since its development.

5.3.3 Dual Inlet IRMS

The first natural bromine isotope variations were observed using dual inlet mass spectrometry. This was done on samples from which chloride and bromide were separated from each other using the classical technique where bromide was oxidised to bromine that could be evaporated from the sample solution while chloride was not (Friedheim and Meyer 1892; Boeke 1908; Eggenkamp and Coleman 2000; see Sect. 5.2).

After the separation of bromide from chloride according to the technique described above, an amount of the solution containing 2–8 mg bromide is poured into a glass beaker. As the pH of this solution, being effectively a potassium hydroxide solution, is high nitric acid is added until the pH is decreased to a value less than 2. This procedure is followed as otherwise not silver bromide, but silver oxide will precipitate when silver nitrate is added to the solution later in the procedure. Unlike the method described by Eggenkamp (1994) for the analysis of chlorine isotopes no pH buffer is added, as after the addition of nitric acid the pH will remain low enough to prevent precipitating of silver oxide. An ionic strength buffer (6 g potassium nitrate per 100 mL sample solution) is added to facilitate small silver bromide crystals which will react with more ease later on in the sample preparation procedure (after Taylor and Grimsrud 1969). The remainder of the procedure, such as precipitation of silver bromide, and the reaction to form bromomethane after addition of iodomethane in a glass ampoule is entirely comparable to the method for samples containing small concentrations of chloride as described in Sect. 4.2.2.2. The separation of bromomethane from iodomethane needs to be done more carefully than the separation of chloromethane from iodomethane as the two peaks are much closer to each other when they are separated by gas chromatography (actually the bromomethane peak is found between chloromethane and iodomethane on a Porapack Q column), and as a small amount of chloride is always transferred in the procedure to separate bromide from chloride always a small amount of chloromethane is present in the gas mixture and this is preferably also removed during the gas-chromatographic separation. This means that the timing of the gas-chromatographic separation is much more important than in the chloromethane separation for chlorine isotopes. The separation through two gas chromatograph runs is in the case of bromine isotope analyses even more important than in the case of chlorine isotopes. Data obtained by Eggenkamp and Coleman (2000) indicate that if the intensity of the chloromethane peak in the mass spectrometer is more than 10 % of the intensity of the bromomethane peak the measured δ^{81}Br is in error, with a value that is more positive than would otherwise be measured in a clean sample.

5.3.4 Continuous Flow GC-IRMS

Considering the fact that the bromide concentration in most samples is relativity low, it has been considered very important that methods would be developed that use much less sample than the 2–8 mg necessary for dual inlet mass spectrometry. Shouakar-Stash et al. (2005b) proposed to use continuous flow mass spectrometry to obtain this goal. The initial step in their procedure is the separation of bromine from chlorine according to the technique described in Sect. 5.2. Then silver bromide is precipitated from the solution and this is reacted with iodomethane in a procedure comparable to the method described earlier by Shouakar-Stash et al. (2005a) for chlorine isotopes. The reaction from silver bromide to bromomethane is done in crimp cap vials that can be used in a gas chromatograph auto sampler.

For the final step, the isotope analysis of the bromomethane, the CH_3Br/CH_3I gas mixture is injected into an Agilent 8690 GC through a CombiPal autosampler. During this procedure the injection needle is thoroughly cleaned with air and helium, to avoid any cross contamination between samples. The gas mixture is separated on a DB-5 capillary column. The temperature program used is the same as for the measurement of chlorine isotopes (Shouakar-Stash et al. 2005a). To avoid the entrance of iodomethane into the mass this is diverted to an FID detector. As the measurement of a sample takes a relatively long time (about 15 min) both before and after the bromomethane peak four reference peaks are measured. The precision of this method is found to be about 0.06 ‰. In spite of the fact that in a continuous flow process much smaller samples can be analysed than in a dual-inlet set up the minimum sample size that can be analysed is still about 1 mg bromide. The reason for this is that the initial step, the separation of the bromide from the large excess of chloride, still has the same dimensions as in the original development of the method by Eggenkamp and Coleman (2000).

5.3.5 Continuous Flow Analysis After GasBench II Chromatography

Du et al. (2013) developed a method to analyse bromine isotopes after separation of bromomethane and iodomethane on a GasBench II system as an analogue to the chlorine isotope determination from Liu et al. (2013). Bromide is separated from chloride following a combination of the methods described by Eggenkamp and Coleman (2000) and Shouakar-Stash et al. (2005b), but maintaining the temperature in the oxidation (left) flask well below the boiling temperature at about 60 °C. At this temperature the oxidation of bromide already takes place and bromine gas is transferred to the second flask as a gas but because the solution doesn't boil the amount of chloride that is transferred is reduced considerably. Silver bromide is produced as described in earlier sections and the reaction between silver bromide and iodomethane is done in 8 mL screw-cap vials which are filled with helium before adding iodomethane. The reaction to bromomethane takes place for 56 h at 80 °C. The vials are sampled through a CombiPAL autosampler. The gas is dried over a perfluorinated sulfonic acid resin trap, and then introduced on a CP-PoraPlot-Q chromatographic column (27.5 m × 0.32 mm) to separate bromomethane from iodomethane and introduced into the mass spectrometer. During each run three reference peaks, three sample peaks and tree reference peaks are measured from which the isotope composition is determined.

5.3.6 ICP-MS

Gelman and Halicz (2011) developed a method to analyse the stable bromine isotope composition in very small inorganic samples by miniaturizing the oxidation/distillation set up in which bromide is separated from chloride in combination with MC-ICPMS analyses of the molecular bromine formed in the oxidative separation. Gelman and Halicz (2011) decreased the size of the oxidation vessel such that only 1 mL of sample (containing only about 0.02 mg bromide), 2 mL of a 1 M potassium dichromate solution and 3 mL of a 2:1 H_2SO_4:H_2O mixture are used for the separation procedure. The reaction vessel is continuously purged with helium which transfers the produced bromine to a wash bottle containing anhydrous sulphuric acid to remove any moisture. Then the helium/bromine mixture is combined with an argon stream and transferred quantitatively into the MC-ICPMS. The instrumental mass bias is corrected using a strontium external spike (Gelman and Halicz 2010). Isotope analyses are done by simultaneously analysing $^{79}Br^+$ and $^{81}Br^+$ ions. Thanks to the mass bias correction with Sr they managed to increase the precision of the method from about 0.6 ‰ to about 0.1 ‰ (1σ), about equal to other bromine isotope techniques, but with the added benefit of being able to analyse samples containing about 50 times less bromide than could be measured with these other techniques.

5.3.7 Measurement of Bromine Isotopes with Neutron Activation Analyses

The samples obtained during the diffusion experiments with molten bromide salts (see Sect. 7.1.2) were analysed after irradiation with thermal neutrons of the silver bromide prepared from these samples. The procedure that was followed is described by Cameron et al. (1956). The salts obtained from the experiments were dissolved in water and bromide was precipitated as silver bromide after addition of a silver nitrate solution. Then the silver bromide is irradiated with neutrons and the bromine isotopes are partly changed into isotopes with one extra neutron (n, γ-process). Radioactive isotopes ^{80}Br and ^{82}Br are formed in this process and from their decay energies the percentage ^{79}Br in the original sample can be determined. This method is not very precise, and the percentage ^{79}Br in the samples could only be determined with a precision of about 1 %. For that reason the bromine isotope composition was also determined using the N-TIMS method described by Cameron and Lippert (1955).

5.4 Measurements of Bromine Isotopes in Organic Molecules

5.4.1 Measurements by ICP-MS

Isotope techniques to analyse the stable bromine isotope composition in organic molecules have been developed since about 2007. Most techniques apply direct introduction of individual organic compounds of bromine into an MC-ICPMS after separation the compounds by gas chromatography. Sylva et al. (2007) were the first to analyse organobromine compounds by this technique. They separated a mixture of three brominated benzenes on a DB-1 capillary column in a Hewlett-Packard 5890 gas chromatograph. The individual compounds were then introduced into a Thermo Neptune ICP-MS. In the plasma ^{79}Br$^+$ and ^{81}Br$^+$ ions are formed from which the isotope ratio could be determined with a precision of about 0.3 ‰. Holmstrand et al. (2010) extended the range of compounds to be analysed for bromine isotopes. They used the same type of gas chromatograph but applied with a Factor Four VF-5 ms (equivalent to a DB-5 ms column) to separate their phases. Their GC was coupled to a VG Isoprobe ICPMS. They constructed three different torch assemblies to test different set-ups for bromine analyses. They observed that the precision of the measurements for brominated diphenyl ethers was only 1.4–1.8 ‰, as compared to a precision of 0.4 ‰ for monobromobenzene (that was also used by Sylva et al. 2007). It appeared that the precision of the bromine isotope measurements is dependent on the compounds that are analysed, apparently due to a different behaviour in the torch where they are ionised and where the bromine ions are formed.

Horst et al. (2011) extended this system to the measurement of the extremely small amounts of bromomethane that can be extracted from air samples. Their system shows a precision better than 0.1 ‰ for samples as small as 40 ng and still better than 0.7 ‰ for samples in the range between 5 and 20 ng. Linearity of the measured isotope ratios was shown over the entire range of tested concentrations. The long-term reproducibility was determined by measuring three batches of commercially available bromomethane gases against each other over a time period of 3 months and their long-term precision was 0.4 ‰ or better.

Gelman and Halicz (2010) managed to improve the precision of ICP-MS measurements considerably in a comparable set up through the simultaneous introduction of strontium and bromine into the ICP-MS. Strontium is used as a spike to correct for mass bias and matrix effects. Strontium can be used for this purpose as its m/z is close to that of bromine, in spite of their large differences in first ionization energy. It was proposed to use strontium as it is well known as a spike to correct for mass bias and matrix effects in ^{87}Sr/^{86}Sr analyses (Ehrlich et al. 2001a, b). Using this correction they were able to improve the precision of bromine isotope measurements to about 0.2 ‰ for samples containing about 1 nmole (80 ng) of bromine injected to 0.5 ‰ for samples from which only 0.02 nmole (1.6 ng) was injected into the mass spectrometer. As was also observed by Holmstrand et al. (2010) they also found that different compounds showed different precisions. The precisions for tribromophenol measurements were in all different sample amounts that were measured much better than for bromotoluene for example.

5.4.2 High Temperature Conversion of Organic Molecules

Hitzfeld et al. (2011) described a method to directly analyse chlorine, bromine and sulphur isotopes after gas chromatographic separation and subsequent high temperature conversion with hydrogen as make-up gas (see Sect. 4.6.6 for the procedure for the measurement of chlorine isotopes using this technique). For the determination of bromine isotopes the conversions is to hydrogen bromide gas, which is measured at m/z values of 80 and 82. Just as was observed for chlorine the precision of this method is about 1 ‰.

5.4.3 Measurement of Bromine Isotope Compositions by Quadrupole Mass Spectrometry

The method to analyse the chlorine isotope composition of organic molecules by direct introduction into a quadrupole mass spectrometer as developed by Aeppli et al. (2010) can also be used as a method to analyse bromine isotopes in organic compounds as was indicated by Thornton et al. (2013) when they described their method to extract bromomethane from the atmosphere.

5.5 Extraction of Bromomethane from the Atmosphere for Isotope Analysis

A system for the collection of the methyl halides bromomethane and chloromethane from the ambient atmosphere in quantities sufficient for bromine and chlorine isotope analysis was developed and described in detail by Thornton et al. (2013) and shorter by Horst (2013). Their system consists of a sampler that features a stainless steel cryotrap with a volume of approximately 1 L which is immersed in liquid nitrogen and filled with glass beads to increase the condensation surface. A vacuum pump is used to pull air through the trap at flow rates between 10 and 20 L/min making it possible to sample the nearly 40 ng required for subsequent δ^{81}Br-CH_3Br analyses from 4 to 5 m^3 of air in 4 h. Water is removed with a condenser and a Drierite® trap at the inlet. Carbon dioxide is separated from the sample with a Carbosorb® trap during transfer to a storage canister. In the laboratory, the air sample is extracted from the canister again and the collected amounts of bromomethane are quantified and purified from co-trapped interfering compounds (such as nitrous oxide) using a packed column mounted into a GC-MS. Thornton et al. (2013) were able to show that neither the cryogenic trapping in parts of the system nor the complete sampling and purification method caused any isotope fractionation, which definitely was the most crucial requirement for their trapping system intended to collect samples for isotope analysis. The study by Thornton et al. (2013) demonstrated the capability of the cryosampler by quantifying the chloromethane and bromomethane collected from atmospheric samples and the non-fractionating bromine isotope fingerprint of bromomethane from synthetic air samples of controlled compositions. The sample purification system was designed around a packed column gas chromatography-quadropole-mass spectrometry (GCqMS) system with three additional cryotraps and backflushing capacity. The system's suitability was tested by observing both the mass recovery and the lack of Δ^{81}Br isotope fractionation induced during sample purification under varying flowrates and loading scenarios. To demonstrate that the entire system samples and subsequently delivers bromomethane to the isotope analysis system without inducing isotope fractionation, diluted synthetic air mixtures were prepared from standard gases with known isotope compositions and were processed through the entire system, showing a Δ^{81}Br-CH_3Br of +0.03 ± 0.10 ‰ relative to the original starting isotope composition. The combined cryosampler-purification and analysis system was applied to measure δ^{81}Br-CH_3Br in ambient atmosphere with two samples, yielding δ^{81}Br values of −0.08 ± 0.43‰ and +1.75 ± 0.13 ‰ respectively versus standard mean ocean bromide for samples that were collected at a suburban Stockholm, Sweden, site.

5.6 Recapitulation and Expectation of the Use of Bromine Isotope Measurements in the Near Future

The techniques that are applied to analyse stable bromine isotopes are still very much in development. The number of laboratories where currently bromine isotopes are analysed is however very limited. For example the far majority of all published data on inorganic bromide are measured in only one laboratory. Also for the isotope analyses of organobromine compounds the majority of the published data are from only one or two laboratories, although a few more techniques have been published so that there is hope that studies from more laboratories may be published in the near future.

It is expected that stable bromine isotope isotope ratios in the future will less and less be analysed in ways that are analogue to chlorine isotope analyses. For the originally developed duel inlet technique the amount of sample that is necessary is so large that in most cases only deep saline formation waters can successfully be analysed. Even the on-line method developed by Shouakar-Stash et al. (2005b) needs more than 1 mg of bromine and in many cases the available amount of sample is (much) less. Possible methods that could successfully be applied would then be P-TIMS, for which a method has been developed (Xiao et al. 1993), but unfortunately without any natural case study until the present day, or ICP-MS as developed by Gelman and Halicz (2011) which developed the method including a miniaturised version of the oxidative separation of bromine from chlorine. ICP-MS techniques for bromine are more comfortable than for chlorine as there are no problems with interference from argon. The advantage of these methods is the smaller sample consumption and for that reason it is expected it will see a larger number of studies where natural samples are measured in the future.

In the case of organobromine compounds it appears that ICP-MS techniques are the techniques that are developing as the most common method to analyse these compounds for bromine isotopes. Several laboratories have developed techniques using ICP-MS (Sylva et al. 2007; Holmstrand et al. 2010, Gelman and Halicz 2010), and the impression is that, until the present day, most organobromine isotope studies use these techniques. It is however not to be excluded that other techniques like direct injection techniques with IRMS and quadrupole mass spectrometry techniques will be developed and tested in the near future.

References

Aeppli C, Holmstrand H, Andersson P, Gustafsson Ö (2010) Direct compound-specific stable chlorine isotope analysis of organic compounds with quadrupole GC/MS using standard isotope bracketing. Anal Chem 82:420–426

Aston FW (1920a) The constitution of the elements. Nature 105:547

Aston FW (1920b) The mass spectra of the chemical elements. Phil Mag 39:611–625

Aston FW (1920c) The mass spectra of the chemical elements - part 2. Phil Mag 40:628–634

Aston FW (1931) The isotopic constitution and atomic weights of selenium, bromine, boron, tungsten, antimony, osmium, ruthenium, tellurium, germanium, rhenium and chlorine. Proc R Soc Lond A 132:487–498

Blewett JP (1936) Mass spectrograph analysis of bromine. Phys Rev 49:900–903

Boeke HE (1908) Über das Krystallisationsschema der Chloride, Bromide, Jodide von Natrium, Kalium und Magnesium, sowie über das Vorkommen des Broms und das Fehlen von Jod in den Kalisalzlagerstätten. Z. Kristallogr 45:346–391

Bremner JM (1965) In: Methods of Soil Analysis, Part 2. Agronomy 9. American Society of Agronomy, Madison, pp 1179–1237

Cameron AE, Lippert EL (1955) Isotope composition of bromine in nature. Science 121:136–137

Cameron AE, Herr W, Herzog W, Lundén A (1956) Isotopen-Anreicherung beim Brom durch electrolytische Überführung in geschmolzenem Bleibromid. Z Naturforschng 11a:203–205

Catanzaro EJ, Murphy TJ, Garner EL, Shields WR (1964) Absolute isotopic abundance ratio and the atomic weight of bromine. J Res Nat Bur Stand (US) 68A:593–599

De Groot PA (2004) Handbook of stable isotope analytical techniques, vol I. Elsevier, London

Dechan M (1886) Detection and estimation of iodine, bromine, and chlorine. J Chem Soc 49:682–685

Du Y, Ma T, Yang J, Liu L, Shan HM, Cai HS, Liu CF, CHen LZ (2013) A precise analytical method for bromine stable isotopes in natural waters by GasBench II-IRMS. Int J Mass Spectrometry 338:50–56

Eggenkamp HGM (1994) δ^{37}Cl; the geochemistry of chlorine isotopes. Geol Ultrai 116:1–150 (Thesis Utrecht University)

Eggenkamp HGM, Coleman ML (2000) Rediscovery of classical methods and their application to the measurement of stable bromine isotopes in natural samples. Chem Geol 167:393–402

Ehrlich S, Karpas Z, Ben-Dor L, Halicz L (2001a) High precision lead isotope ratio measurements by multi-collector-ICP-MS in variable matrices. J Anal Atom Spectrom 16:975–977

Ehrlich S, Gavrieli I, Ben-Dor L, Halicz L (2001b) Direct high-precision measurements of the ^{87}Sr/^{86}Sr isotope ratio in natural water, carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). J Anal Atom Spectrom 16:1389–1392

Friedheim C, Meyer RJ (1892) Über die quantitative Trennung und Bestimmung von Chlor. Brom und Jod Z Anorg Chemie 1:407–422

Gelman F, Halicz L (2010) High precision determination of bromine isotope ratio by GC-MC-ICPMS. Int J Mass Spectrom 289:167–169

Gelman F, Halicz L (2011) High-precision isotope ratio analysis of inorganic bromide by continuous flow MC-ICPMS. Int J Mass Spectrom 307:211–213

Hitzfeld KL, Gehre M, Richnow HH (2011) A novel online approach to the determination of isotopic ratios for organically bound chlorine, bromine and sulphur. Rapid Commun Mass Spectrom 25:3114–3122

Holmstrand H, Unger M, Carrizo D, Andersson P, Gustafsson Ö (2010) Compound-specific bromine isotope analysis of brominated diphenyl ethers using GC-ICP-multicollector-MS. Rapid Commun Mass Spectrom 24:2135–2142

Horst A (2013) Stable bromine isotopic composition of methyl bromide. Method development and applications. PhD thesis, Stockholm University

Horst A, Holmstrand H, Andersson P, Andersson A, Carrizo D, Thornton BJ, Gustafsson Ö (2011) Compound-specific bromine isotope analysis of methyl bromide using gas chromatography hyphenated with inductively coupled plasma multiple-collector mass spectrometry. Rapid Comm Mass Spectrom 25:2425–2432

Liu YD, Zhou AG, Gan YQ, Liu CF, Yu TT, Li XQ (2013) An online method to determine chlorine stable isotope composition by continuous flow isotope ratio mass spectrometry (CF-IRMS) coupled with a Gasbench II. J South Centr Univ 20:193–198

Löwich C (1829) Das Brom und seine chemischen Verhaltnisse. Heidelberg. 175 pp

Nier AO (1940) A mass spectrometer for routine isotope abundance measurements. Rev Sci Inst 11:212–216

Rankama K, Sahama TG (1950) Geochemistry. The University of Chicago Press, Chicago

Shouakar-Stash O, Drimmie RJ, Frape SK (2005a) Determination of inorganic chlorine stable isotopes by continuous flow isotope ratio mass spectrometry. Rapid Commun Mass Spectrom 19:121–127

Shouakar-Stash O, Frape SK, Drimmie RJ (2005b) Determination of bromine stable isotopes using continuous-flow isotope ratio mass spectrometry. Anal Chem 77:4027–4033

Sylva SP, Ball L, Nelson RK, Reddy CM (2007) Compound-specific ^{81}Br/^{79}Br analysis by capillary gas chromatography/multicollector inductively coupled plasma mass spectrometry. Rapid Commun Mass Spectrom 21:3301–3305

Taylor JW, Grimsrud EP (1969) Chlorine isotopic ratios by negative ion mass spectrometry. Anal Chem 41:805–810

Thornton B, Horst A, Carrizo D, Holmstrand H, Andersson P, Crill PM, Gustafsson Ö (2013) A high-volume cryosampler and sample purification system for bromine isotope studies of methyl bromide. J Atmos Ocean Techn 30:2095–2107

Williams D, Yuster Ph (1946) Isotopic constitution of tellurium, silicon, tungsten, molybdenum, and bromine. Phys Rev 69:556–567

Willey JF, Taylor JW (1978) Capacitive integration to produce high precision isotope ratio measurements on methyl chloride and bromide. Anal Chem 50:1930–1933

Xiao YK, Liu WG, Qi HP, Zhang CG (1993) A new method for the high precision isotopic measurement of bromine by thermal ionization mass spectrometry. Intl J Mass Spectrom Ion Proc 123:117–123

Part III

Theoretical and Experimental Estimates of Chlorine and Bromine Isotope Fractionation

6

Fractionation

Variations in light stable isotope ratios (such as hydrogen, carbon, nitrogen, oxygen, sulphur, chlorine and bromine) are caused by processes that are called isotope fractionation. Fractionation is caused by differences in physical or chemical processes that are mostly caused by the difference in weight of the isotopes. Variations in the isotope composition of an element can also have its origin from radioactive decay of mother isotopes which may be present in different quantities in the original environment. In this case we call these daughter isotopes radiogenic. The isotope geochemistry of strontium is a good example of an element where isotope variations are mainly caused by radioactive decay of a mother isotope, in this case that of β-decay of ^{87}Rb to stable ^{87}Sr. Chlorine and bromine do not have any radiogenic isotopes and all isotope variations found for chlorine and bromine are caused by fractionation processes on these isotopes.

In isotope geochemistry two major types of fractionation are distinguished. These are equilibrium fractionation and kinetic fractionation. Equilibrium fractionation is the isotope effect that is observed if two phases are found in equilibrium. Due to the mass difference of the isotopes of an element the zero-point energies of the isotopes are different. The heavier isotope has a lower zero-point energy and as a result the energy necessary to break a bond with the heavier isotope is higher. As a consequence the heavier isotope is concentrated in the phase in which it is most strongly bound. As the difference between the zero-point energies of the lighter and heavier isotopes decreases when the temperature increases equilibrium fractionation has the tendency to decrease with increasing temperature. In theory at infinitely high temperatures it reduces to zero. A very important effect that has been observed is that oxidation and reduction processes are associated with very large equilibrium fractionation.

Kinetic fractionation on the contrary is a non-equilibrium process. It is found in systems where variations arise as a result of a velocity difference between a heavier and a lighter isotopes, such as diffusion, or if one phase is removed preferentially from a system that is formed in equilibrium, so that the reaction moves to one side. A very well known example of this effect is the removal of water from a cloud in the form of rain or snow which ultimately leads to very low oxygen and hydrogen isotope values in precipitation. This process can be treated as a fractional distillation under equilibrium conditions as is expressed by the Rayleigh (1896) equation. A short but clear introduction in the different fractionation processes is given by Hoefs (2009). Detailed introductions to the theoretical backgrounds can be found in classic works such as Urey and Greiff (1935), Bigeleisen and Mayer (1947), Urey (1947), Melander (1960), Bigeleisen (1965) and Richet et al. (1977). Schauble et al. (2003) have estimated the theoretical equilibrium fractionation for different systems concerning chlorine isotopes. Theoretical estimates for both chlorine and bromine equilibrium fractionation in

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Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_6,

gas-solution systems have been calculated by Czarnacki and Hałas (2012).

On earth chlorine and bromine are primarily found as chloride and bromide ions. This means that redox reactions are not normally playing a large role in the chemistry of these elements. The result is that isotope variations are in most cases rather modest. Equilibrium fractionation between phases where chlorine and bromine are present in the chloride and bromide form in both phases is generally not very large and kinetic effects are in many cases responsible for most of the observed isotope variations. In the following chapters the various process that cause variations in chlorine and bromine isotopes will be described. Results obtained in theoretical, experimental and field studies are reported and compared. Even before it was possible to measure natural variations of chlorine and bromine isotopes attempts were made to estimate, both theoretically and experimentally, the fractionation that might be expected if it would ever become possible to measure the actual variations. When natural variations became measurable in the 1980s the results confirmed for a large part the results of these early experimental studies. Given the still fragmentary knowledge of the chlorine and bromine isotope geochemistry some of these early data have still not been either confirmed or re-analysed in modern studies. Especially with respect to the isotope fractionation of bromine isotopes much future work is needed to obtain a complete knowledge of its isotope behaviour.

In the following chapters the different isotope fractionation processes are described. These processes are not always described as being either equilibrium or kinetic fractionation as such as in many cases the variations that are observed are the result of a combination of both types of fractionation. As in many cases the size of equilibrium fractionation is relatively modest a large part of the fractionation is caused by kinetic effects taking place for example by the removal of one of the phases in a system. Relatively large equilibrium fractionation is only expected during reduction/oxidation reactions between phases of different oxidation states, which are, as already cited above, relatively rare processes in the earth's surface reservoirs.

References

Bigeleisen J (1965) Chemistry of isotopes. Science 147:463–471

Bigeleisen J, Mayer MG (1947) Calculation of equilibrium constants for isotopic exchange reactions. J Chem Phys 15:261–267

Czarnacki M, Hałas S (2012) Isotope fractionation in aqua-gas systems: Cl_2-HCl-Cl^-, Br_2-HBr-Br^- and H_2S-S^{2-}. Isot Environ Health Stud 48:55–64

Hoefs J (2009) Stable isotope geochemistry, 6th edn. Springer, Berlin

Melander L (1960) Isotope effects on reaction rates. Ronald, New York

Rayleigh L (1896) Theoretical considerations respecting the separation of gases by diffusion and similar processes. Philos Mag Ser 5(42):493–498

Richet P, Bottinga Y, Javoy M (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. Ann Rev Earth Planet Sci 5:65–110

Schauble EA, Rossman GR, Taylor HP (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochim Cosmochim Acta 67:3267–3281

Urey HC (1947) The thermodynamic properties of isotopic substances. J Chem Soc 1947:562–581

Urey HC, Greiff LJ (1935) Isotope exchange equilibria. J Chem Soc Amer 57:321–327

7 Theoretical and Experimental Fractionation Studies of Chloride and Bromide Isotopes

7.1 Diffusion

Diffusion probably is the most well known and most well understood process that is responsible for variations in chlorine and bromine isotope compositions. Molecular diffusion is the process in which matter is transported from one part of a system to another as a result of arbitrary molecular movements (Crank 1956). It was first described by Fick (1855). This work is now referred to as Fick's First and Second Laws, and was published even before quantitative experimental measurements had ever been done. Lindemann (1921) already realised that, due to the mass difference of isotopes from a single element isotopes could theoretically be separated electrolytically. The first study where fractionation due to diffusion of chlorine isotopes was studied was already done in the 1940s (Madorsky and Strauss 1947) and several more studies have been applied since then going from theoretical, experimental and field studies.

7.1.1 Diffusion of Chloride and Bromide in Aqueous Solutions

7.1.1.1 Theoretical Fractionation During Aqueous Diffusion

The chlorine isotope fractionation factor due to diffusion can be estimated in several ways. Firstly, by analogy to ideal gases the isotopic fractionation factor in aqueous solution can be estimated from the ratio of the square root of their masses (Graham's Law):

$$\alpha = \sqrt{\frac{m_L}{m_H}} \tag{7.1}$$

where m_L is the molecular mass of the lighter diffusing isotope and m_H that of the heavier isotope. There are, however, two problems when applying this approach: (A) Collisions between gas molecules are elastic, whereas those between hydrated molecules and water molecules are inelastic. (B) The masses of actual diffusing molecules in the solution must be known. This requires knowledge of the degree of chloride hydration, and the residence time of a water molecule next to a chloride ion relative to the residence time of a water molecule next to another water molecule. There is much confusion about the degree of hydration of the chloride ion. The hydration number is generally assumed to be ≤6 (Powell et al. 1988). Impey et al. (1983) defined a dynamic hydration number which is 2.6 at 287 K. Marchese and Beveridge (1984) suggested a nine fold hydration. Samoilow (1957) even assumed a negative hydration number on the basis of his calculations which showed that a water molecule stays for a shorter period next to a chloride ion than next to another water molecule. On the basis of a commonly assumed hydration number of 6, the diffusion coefficient ratio (D_{35Cl}/D_{37Cl}) would be 1.0080, much higher than found in both experimental and field studies.

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Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_7,

Considering the fact that dissolved species in a solution do not behave like an ideal gas a different approach is needed. Within solutions it was already realised by Lindemann (1921) that different isotopes of an element had different velocities which would mean that isotopes can be separated electrolytically. This effect can be described using the reduced masses of the colliding species in solution. The reduced mass is defined as:

$$\mu_i = \frac{m_i M}{m_i + M} \tag{7.2}$$

where m_i and M are the masses of the colliding species (in an aqueous solution of chloride, m_i is a hydrated chloride ion and M is a water molecule). This kinetic theory was described for gases (Tabor 1991; Bird et al. 2002) but it was shown that it is also valid for species in aqueous solution (e.g. Jähne et al. 1987). The definition of the fractionation as a result of diffusion ($^{35/37}\alpha$) for chlorine is:

$$^{35/37}\alpha = \frac{D_{35}}{D_{37}} = \sqrt{\frac{\mu_{37}}{\mu_{35}}} = \sqrt{\frac{m_{37}(m_{35} + M)}{m_{35}(m_{37} + M)}} \tag{7.3}$$

where D_{35} and D_{37} are the diffusion coefficients of the light and heavy isotopes of chlorine (Richter et al. 2006). Calculation of $^{35/37}\alpha$ requires knowledge of the hydration number n of the diffusing chloride ion $[Cl(H_2O)_n^-]$, as would also be the case if Graham's Law was applicable. Based on the Debye-Hückel å parameter (Appelo and Postma 2005) the hydration number n of Cl^- would be 3: $[Cl(H_2O)_3^-]$.

A problem with the use of either Graham's Law or the reduced masses theory to determine fractionation of the diffusing species became apparent when the diffusion fractionation of divalent species such as Mg^{2+} and Ca^{2+} was studied (Richter et al. 2006). They observed that the experimentally determined fractionation was much lower than expected based upon the reduced masses of the species in solution. For this reason Richter et al. (2006) proposed that fractionation due to diffusion is better described by the empirical inverse power relation:

$$^{35/37}\alpha = \frac{D_{35}}{D_{37}} \propto \left(\frac{m_{37}}{m_{35}}\right)^{-\beta} \tag{7.4}$$

where m is the mass of the light or heavy isotope without considering any water of hydration. Molecular dynamics simulations (Alder et al. 1974; Impey et al. 1983; Nuevo et al. 1995; Willeke 2003) as applied by Bourg and Sposito (2007) produced results on the potential isotope fractionation due to diffusion for different ions in water which were similar to those experimentally determined by Richter et al. (2006). Further investigations by Bourg and Sposito (2008) and Bourg et al. (2010) revealed β-values between 0 and 0.2 for different noble gas atoms and mono- and divalent ions in solution. The numerical value of β was found to be dependent on the strength of the solute-solvent interaction which is defined as the average residence time of water molecules in the first solvation shell of ions. The value of β varies from ~0.00 to ~0.01 for divalent ions; from ~0.01 to ~0.06 for monovalent ions and from ~0.05 to ~0.19 for noble gases (Bourg et al. 2010). For chloride in solution it was simulated to be 0.034 ± 0.018 by Bourg and Sposito (2007), indicating a fractionation factor $^{35/37}\alpha$ for chloride of 1.0019 ± 0.0010. For bromide (Bourg et al. 2010) did not do molecular dynamics simulations, but calculated the β-value 0.0320 ± 0.0097 from the experimentally obtained data published by Eggenkamp and Coleman (2009). This β-value agrees to a $^{79/81}\alpha$ of 1.0008 ± 0.0002 (see Sect. 7.1.1.2).

These data on the fractionation due to diffusion can be used to predict possible chloride concentration and chlorine isotope profiles (and of course of other species) in systems where simple diffusion takes place. With the aim to study diffusion of radioisotopes in sediments Duursma en Hoede (1967) presented mathematical solutions for various diffusion models. Three of these were applied to chlorine isotope diffusion/fractionation systems by Eggenkamp (1994). Eggenkamp (1994) showed examples of what kind of chloride concentration and chlorine isotope profiles could be expected depending on the source of the chloride: diffusion from a source with a constant concentration, diffusion

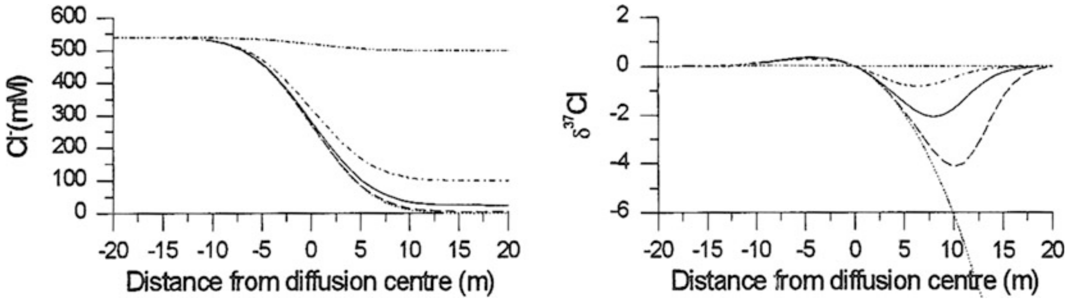

Fig. 7.1 Chloride concentration (*left*) and chlorine isotope variation (*right*) profiles for a system with diffusion from a constant source for different chloride concentrations in the low concentration part of the system. Profiles are developed from Eq. 7.5, and drawn with a diffusion time of 250 years, a diffusion coefficient of 15×10^{-10} m^2 s^{-1}, a diffusion coefficient ratio ($^{35/37}\alpha$) of 1.00245, a chloride concentration in high concentration part of the system of 540 mM, and in the low concentration part of 0, 5, 25, 100 and 500 mM (from Eggenkamp 1994)

after a momentary release of chloride and diffusion from a source with a constant inflow.

Diffusion from a Source with a Constant Concentration

Diffusion from a source with a constant concentration can be described as the situation where an infinite amount of matter with high chloride content diffuses into an infinite amount of matter with low chloride content. The chloride concentration at the boundary between these two parts will be constant during diffusion. The solution for the concentration as a function of x (distance from the boundary) and t (time) is (see e.g. Carslaw and Jaeger 1959):

$$c_{(x,t)} = c_0 erfc \frac{x}{2\sqrt{Dt}} \tag{7.5}$$

where *erfc* is the complementary error function. Characteristic of this diffusion model is that in parts of the system with a low original chloride concentration δ^{37}Cl can be very low and also that it depends very much on the chloride concentration ratio between maximum and minimum original chloride concentrations in the system. Calculations from Eggenkamp (1994) showed that in extreme cases very large δ^{37}Cl variations could be obtained which, as shown later by experiments reported in Eggenkamp and Coleman (2009), can only be observed when the concentration in the low concentration part is so low that the analysis becomes non-trivial. In the part of the system with the higher original chloride concentration the δ^{37}Cl does increase due to the faster diffusion of the isotope ^{35}Cl. As the chloride concentration in this part of the system is relatively high the isotope effect is much less than in the low concentration part of the system (Fig. 7.1).

Diffusion After a Momentary Release of Chloride or Bromide

In this model, at time t = 0 a fixed amount of chloride ions is released into the system. From the injection point (at location x = 0) the chloride/bromide will start to diffuse. In the following it is assumed that the original concentration in the region around the injection point is lower than the concentration after injection of the fixed amount of chloride/bromide at the injection point, the moment it is injected. As the release of chloride or bromide is momentarily the concentration at x = 0 will decrease from the start as t increases. The equation for linear diffusion after a momentary release of chloride or bromide is:

$$c_{(x,t)} = \frac{s}{\sqrt{4\pi Dt}} \exp - \frac{x^2}{4\mathrm{Dt}} \tag{7.6}$$

where s is the amount of the original momentary release of chloride/bromide. In this system the concentration of chloride/bromide in the diffusion centre decreases rapidly, while the isotope ratio in the centre increases due to the higher diffusion

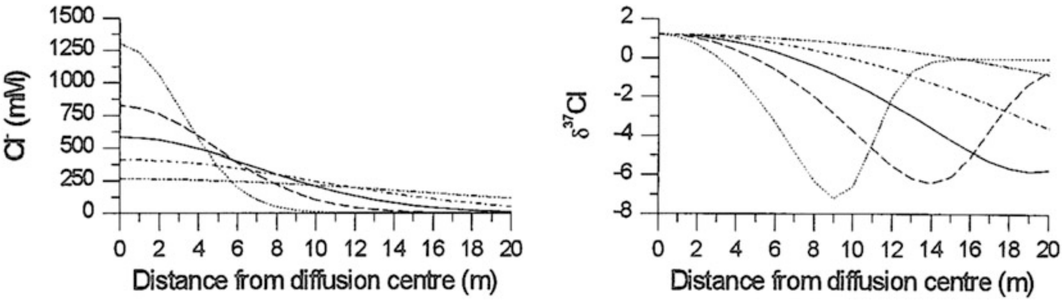

Fig. 7.2 Chloride concentration (*left*) and chlorine isotope variation (*right*) profiles for a system with diffusion after a momentary release of chlorine. The figure shows the effects for subsequent linear diffusion after Eq. 7.6, and is drawn for an initial release of chloride of 10 mol, a diffusion coefficient of 15×10^{-10} m^2 s^{-1}, a diffusion coefficient ratio ($^{35/37}\alpha$) of 1.00245, and diffusion times of 100, 250, 500, 1000 and 2500 years. The initial chloride concentration in the area around the initial release was 5 mM (from Eggenkamp 1994)

coefficient of the isotope ^{35}Cl or ^{79}Br relative to ^{37}Cl or ^{81}Br. The isotope ratio in the transported chloride/bromide can also reach very low values in this scenario, while, just as in the former model, the lowest values depend on the original chloride or bromide concentration in the environment where the momentary release diffuses to. The diffusion profile seems rather similar to the profile in the first model, however, as the chloride concentration in the diffusion centre decreases the isotope effect also decreases as the chloride or bromide concentration near the diffusion centre approaches the original chloride or bromide concentration in the environment. Figure 7.2 shows the effect on the chloride concentration and the chlorine isotope composition for a system where after the initial release the chloride diffuses in one dimension (linear) away from the location of the initial momentary release.

Diffusion from a Source with a Constant Inflow

In this model, a constant inflow of chloride or bromide with an infinitely small volume is introduced from a source at a constant rate. It can be considered as an extension of the former model. The diffusion solution of this model can be found by integrating Eq. 7.6 over time, replacing *s* by *q*d*t*, (see Carslaw and Jaeger 1959). In the mathematical solutions that describe the diffusion from a constant inflow *q* defines the amount of chloride added per unit of time.

For linear diffusion the solution is given by Carslaw and Jaeger (1959):

$$c(x,t) = \frac{qx}{2\mathrm{D}\sqrt{\pi}}\Big[\frac{2\sqrt{Dt}}{x}\exp\Big(\frac{-x}{4\mathrm{Dt}}\Big) - \sqrt{\pi}erfc\frac{x}{2\sqrt{Dt}}\Big)\Big] \tag{7.7}$$

In this system a continuously increasing chloride concentration at the location of the inflow is observed that decreases at larger distances from the inflow. The chlorine or bromine isotope ratios of the transported chloride or bromide reach a minimum which moves slowly away from the source as time progresses. As the chloride or bromide concentration at the source increases the isotope ratio of the minimum decreases due to the larger ratio between the chloride or bromide concentration between the source and the background. Figure 7.3 shows how the chloride or bromide concentration and chlorine or bromine isotope compositions evolve over time in the case of one dimensional diffusion where chloride or bromide is continuously added at the source.

7.1.1.2 Experimental Studies to Determine Fractionation Due to Diffusion of Chlorine and Bromine

Although it was already suggested that, in theory, the isotopes of elements should fractionate during the process of diffusion (Lindemann 1921) it

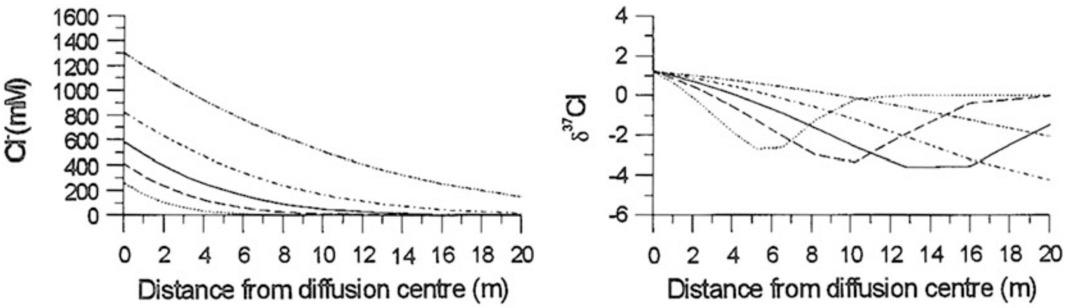

Fig. 7.3 Chloride concentration (*left*) and chlorine isotope variation (*right*) profiles for a system with diffusion from a constant inflow of chloride. The figure shows the effects for subsequent linear diffusion after Eq. 7.7, and is drawn for an influx of chloride equal to 10 mol/year, a diffusion coefficient of 15×10^{-10} m^2 s^{-1}, a diffusion coefficient ratio ($^{35/37}\alpha$) of 1.00245, and diffusion times of 100, 250, 500, 1000 and 2500 years. The initial chloride concentration in the area around the initial release was 5 mM (from Eggenkamp 1994)

took some time before it could actually be observed. Fink et al. (1934) probably were the first to observe actual fractionation of isotopes as the result of diffusion. In their experiment, in which they let hydrogen diffuse through a thin palladium foil, they observed that protium, the isotope ^{1}H, was diffusing more readily than the heavy isotope deuterium (^{2}H). With the improvement of analytical methods to determine the isotope composition of chemical species more of these diffusion studies were done. Klemm (1943) studied for example how the isotope composition of copper changes when it diffuses into silver sulphide. Only a few years later the first experimental study in which the difference in velocity, and thus the fractionation of chlorine isotopes as a result of diffusion was determined, was done by Madorsky and Strauss (1947). They determined how the two isotopes of chloride in solution can be separated by the then recently developed counter current electromigration method (Brewer et al. 1947). As the result of this technique ^{35}Cl is concentrated in an anode compartment, while the isotope ratio is kept constant at a cathode compartment. In a 1:30 sodium chloride solution which was used as the electrolyte the concentration of ^{35}Cl could be increased to almost 81 % (from the initial 75 %) after a migration time of close to 500 h (20–21 days). The initial enrichment factor of ^{35}Cl compared to ^{37}Cl in the five experiments that Madorsky and Strauss (1947) conducted was between 1.00115 and 1.00207. During all experiments the enrichment factors dropped during the course of the experiments due to the formation of silica gel as the result of interaction with the sodium hydroxide anode restituent.

The second study in which the relative mobilities of ^{35}Cl and ^{37}Cl in solution were determined was conducted by Konstantinov and Bakulin (1965). They determined the isotope separation of lithium chloride, sodium chloride and hydrochloric acid in a system where solutions of the chloride salts could exchange with potassium dichromate through a quartz filled capillary at a temperature of 50 °C. The ions could move under an electric current and after some time (6–12 h) the isotopic composition had changed enough to be analysed. It was observed that the chlorine isotope separation for lithium chloride and sodium chloride was about twice as large as for hydrochloric acid, and it was also shown that the isotope separation was larger if higher concentrations were applied. For lithium chloride it increased from 1.0012 in a 1N solution to 1.0018 in a 7.5N solution, for sodium chloride it increased from 1.0010 in a 1N solution to 1.0014 in a 5.4N solution. Contrary to these observed large fractionation in salt solutions, in a hydrochloric acid solution the isotope separation increased from 1.00022 in a 2N solution to 1.00068 in a 10N solution.

With the improvement of analytical techniques it also became possible to conduct diffusion experiments without applying electrical currents to increase isotope separation. Eggenkamp and Coleman (2009) determined isotope fractionation as a result of diffusion for both chloride and bromide ions in a system that would approach natural diffusion rather closely. Their diffusion experiments were similar in concept to those developed to analyse the diffusion of actinides in clay (Schreiner et al. 1982). They filled a piece of glass tubing halfway with a polyacrylamide gel to which little or no sodium chloride or bromide solution was added, while the other half was filled with a gel with a high sodium chloride or bromide concentration. This system was left to diffuse for some time. Several experiments were prepared with different chloride or bromide concentrations, and with different diffusion temperatures. In these experiments is was observed that the fractionation due to diffusion for chloride seemed to increase at higher temperatures, while no variations depending on the concentration were observed. In the case of bromide however no significant variations in fractionation due to diffusion were observed for either the temperature or the concentration. The results of these experiments indicate that for chlorine the ratio D_{35Cl}/D_{37Cl} seems to increase from 1.00128 ± 0.00017 (1σ) at 2 °C to 1.00192 ± 0.00015 at 80 °C (see also Fig. 7.4). For bromine the ratio D_{79Br}/D_{81Br} does not suggest a temperature dependency with the observations varying from 1.00098 ± 0.00009 at 2 °C to 1.0064 ± 0.00013 at 21 °C and 1.00078 ± 0.00018 (1σ) at 80 °C.

7.1.1.3 Observations on Natural Systems to Determine the Isotope Fractionation

The first study in which chlorine isotope diffusion was detected in a natural system was conducted by Desaulniers et al. (1986) in groundwater sampled from Quaternary glacial deposits in Ontario, Canada. This natural system has a low permeability so that even after long diffusion times chloride concentrations and chlorine isotope signals have not been levelled out. Based on observations that chloride in these deposits must have its origin from underlying saline formations (Desaulniers et al. 1981) it was possible to estimate the diffusion of chloride from these underlying sediments. Assuming simple diffusion it was possible, after chlorine isotopes were measured from these groundwater samples, to determine the fractionation between the light and heavy isotope of chlorine in an environmental setting for the first time. As diffusion of chloride in this system was upward from saline deposits into younger deposits containing freshwater it was observed that δ^{37}Cl values increased with depth. Desaulniers et al. (1981) were able to model the chloride concentrations at their sites assuming diffusion times between 10000 and 16000 years. They calculated possible isotope fractionation factors depending on the groundwater flow during this period, which was modelled to be between 0 and 0.4 cm per year. Applying their model with current chloride concentrations in the system Desaulniers et al. (1986) could conclude that diffusion times from 12000 to 16000 years and a groundwater flow close to 0 cm per year would fit the chloride concentration data best. These data were used to calculate a best fit for the fractionation of chlorine isotopes due to diffusion and the results showed that in this system the diffusion coefficient of ^{35}Cl was about 1.0012 times larger than the diffusion coefficient of ^{37}Cl, actually just within the range determined by both Madorsky and Strauss (1947) and Konstantinov and Bakulin (1965) in earlier experiments.

Eggenkamp et al. (1994) determined the chlorine isotope fractionation in a diffusion system where saline ocean water diffused downwards into sediments containing relatively freshwater. Currently Kau Bay on the Indonesian Island of Halmahera is connected to the ocean trough a shallow sill that, during the last glacial period, was above sea-level so that fresh and brackish sediments were deposited in what was a lake then. After the glacial period sea-level rose and when it increased to a level above the sill the lake changed into a bay and the water turned saline. Since then downward diffusion of chloride took place in the sediments of Kau Bay (Middelburg and de Lange 1989). This diffusion was also clear from the chlorine isotope ratios

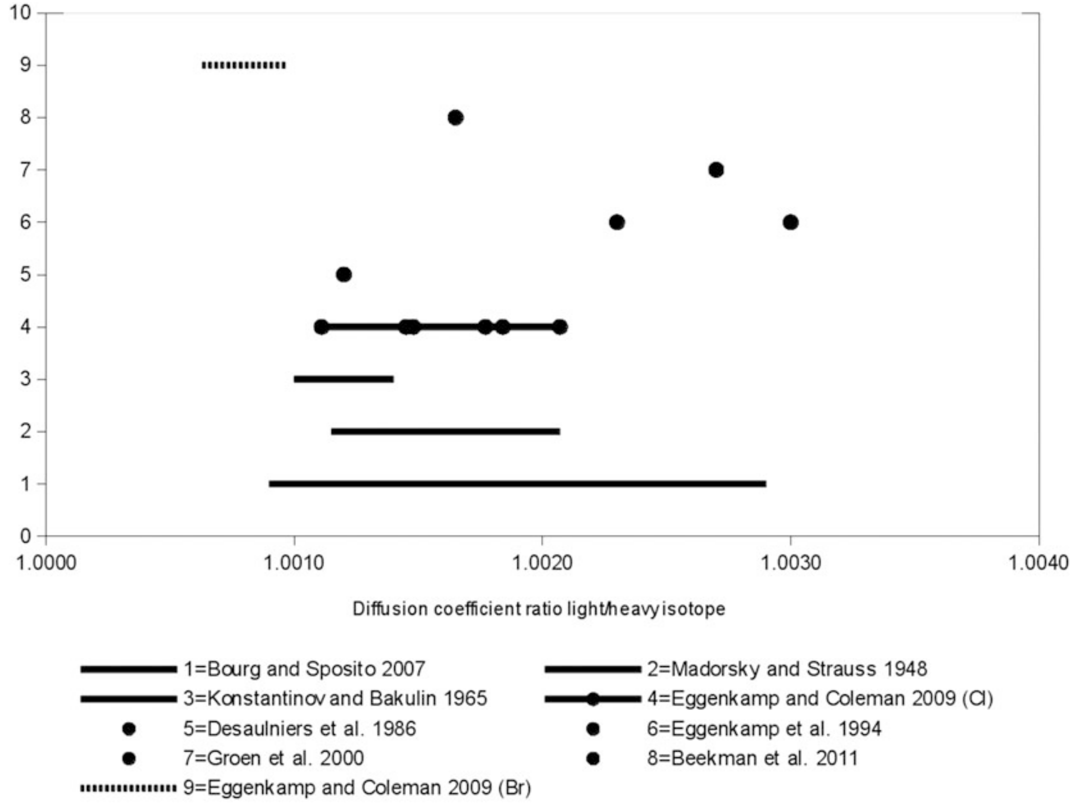

Fig. 7.4 Overview of modelled, experimentally determined and natural observations of $^{35/37}\alpha$ values (ratio of diffusion coefficients from ^{35}Cl and ^{37}Cl) and $^{79/81}\alpha$ values (ratio of diffusion coefficients from ^{79}Br and ^{81}Br). Studies in which an average with error, or a range of data are reported are displayed with a *line*, studies where just a value is reported are represented by *dots*. The results from Eggenkamp and Coleman (2009) are represented by three *lines* between *dots*, the *left* part represents the results at 2 °C, the *middle* part the results at 21 and 54 °C and the *right* part the results at 80 °C, suggesting an increase of $^{35/37}\alpha$ with temperature. Although a fairly large range has been observed in the different studies for $^{35/37}\alpha$ the results indicate that the most probable value falls between 1.0015 and 1.0020, without indications of increase by temperature as these studies are all done at approximately environmental temperatures. For bromine the most probable $^{79/81}\alpha$ is between 1.0006 and 1.0010

that were analysed in the sediment pore waters which showed a decrease in δ^{37}Cl with depth. After correction for advective porewater flow the fractionation could be determined in two different sediment cores. They were reported as 1.0023 and 1.0030. Unfortunately no errors were determined, but probably these were rather large given the small total variation in δ^{37}Cl measurements. The D_{35Cl}/D_{37Cl} values obtained are at the upper limit when compared to the experimental data from Madorsky and Strauss (1947), and a bit outside the limits obtained by both Konstantinov and Bakulin (1965) and later by Eggenkamp and Coleman (2009).

More recently two more studies have determined chlorine isotope fractionation factors from natural settings. Groen et al. (2000) determined it from sediment porewater profiles sampled along the Surinam coast where salt water diffuses into sediments containing fresh porewater from both overlying younger saline sediments and underlying older saline sediments. Although they only analysed the chlorine isotope composition of a rather limited number of samples they were able to estimate the ratio in diffusion coefficient between ^{35}Cl and ^{37}Cl as being 1.0027.

The most recent study in which the difference in diffusion coefficient between ^{35}Cl and ^{37}Cl is determined described one of the more complex systems in which this fractionation is determined (Beekman et al. 2011). The Dutch IJsselmeer area has a fairly complex history. The area was a relative freshwater lake until medieval times after which its salinity slowly increased. During this period the area was also prone to storm surges and during the very short period a storm surge lasted salt water from the North Sea was introduced into the sediment. After 1932 the area was closed from the sea by a dam, and it turned into a fresh water lake. The only possibility to model both chloride concentration as well as chlorine isotope composition in this system was to take the whole (known) history into account and to apply numerical modelling. A very satisfactory model was developed and a best fit D_{35Cl}/D_{37Cl} value of 1.00165 was found, which agrees very well with the experimental data obtained by Eggenkamp and Coleman (2009).

In all three studies in which the D_{35Cl}/D_{37Cl} value in aqueous solutions is determined experimentally, four in which it is determined from observations in natural systems, plus one in which it is determined through molecular dynamics simulations are known for chlorine, while only one such study is known for bromine. Figure 7.4 shows an overview of these data. Within reasonable limits the results of all studies agree fairly well with each other. In the different studies D_{35Cl}/D_{37Cl} has been determined as between 1.0010 and 1.0030 for chlorine, while most data are between 1.0015 and 1.0020. Although experimental results may indicate that the D_{35Cl}/D_{37Cl} ratio is dependent on the temperature of the experiments the results from the environmental studies show a larger range in the D_{35Cl}/D_{37Cl} ratios than the experiments from Eggenkamp and Coleman (2009) show so that further research is obviously needed to get a better understanding of the potential temperature dependency of the D_{35Cl}/D_{37Cl} ratio.

Currently only one study is known in which the fractionation due to diffusion for bromide is determined. The results of this study (Eggenkamp and Coleman 2009) are also included in Fig. 7.4. It is hoped that, when more of these studies are done, they are conducted on bromine isotopes too. The results obtained for bromine up to now agree very well with the data as they were expected with respect to chlorine considering the smaller relative mass difference between both stable bromine isotopes as compared to both chlorine isotopes (Eggenkamp and Coleman 1997).

7.1.2 Diffusion in Molten Salts

During the 1950s several experimental studies have been published in which the isotope fractionation due to diffusion of chloride and bromide in molten salts was determined by researchers from the Max Planck Institute in Mainz and the Higher Technical Institute in Göteborg. Chloride diffusion was determined in lead chloride ($PbCl_2$, Klemm and Lundén 1955), zinc chloride ($ZnCl_2$, Lundén and Herzog 1956) and thallium chloride (TlCl, Herzog and Klemm 1958). From the last system also the temperature dependence has been determined. Bromide diffusion was determined on lead bromide ($PbBr_2$, Cameron et al. 1956) and on zinc bromide ($ZnBr_2$, Lundén and Lodding 1960). In these experiments the isotopes ^{35}Cl or ^{79}Br were enriched by the application of an electric current on the molten salts. The difference in diffusion coefficient for the two isotopes was determined in each case. Figure 7.5 shows the results of these determinations.

The data obtained in these experiments are either comparable to the maximum values or slightly larger than the data obtained from the chloride and bromide diffusion experiments and observations in aqueous solutions. Konstantinov and Bakulin (1965) observed that their fractionation data increased with the electrolyte concentration and concluded that the highest values they observed approached in absolute magnitude the values obtained in these earlier experiments with molten salts.

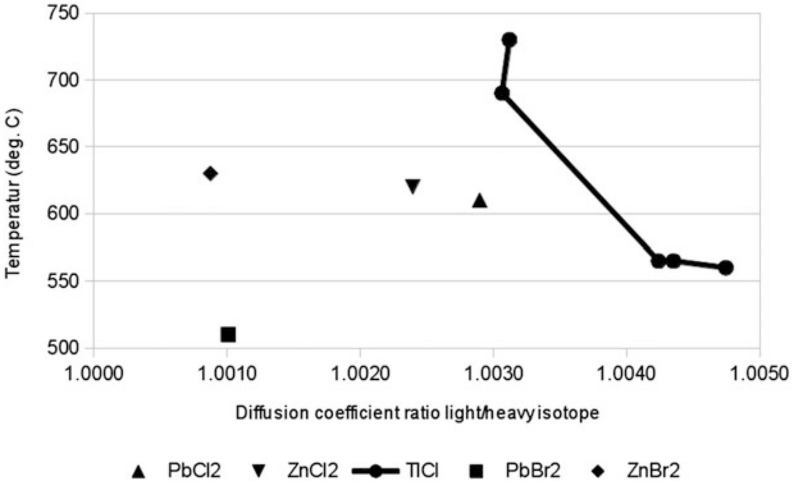

Fig. 7.5 Overview of experimentally determined $^{35/37}\alpha$ values (ratio of diffusion coefficients from ^{35}Cl and ^{37}Cl) and $^{79/81}\alpha$ values (ratio of diffusion coefficients from ^{79}Br and ^{81}Br) in molten salts. The values obtained are mostly larger than for the determinations in aqueous solutions. Unlike the experimental results for $^{35/37}\alpha$ in aqueous solutions, the results obtained for TlCl indicate a decrease in $^{35/37}\alpha$ with temperature

7.2 Ion Filtration/Ion Exclusion

When a solution is forced through a semi-permeable membrane the effect can be that the solvent passes though the membrane with much more ease than the solute. The reason for this effect can be for example the difference in size between the ions and molecules of the solvent and the solute or the difference in charge. As a result of this effect, which is called ion-filtration, isotope fractionation can occur. During the development of chlorine isotope techniques at the University of Arizona a few studies were done in which the isotope fractionation of chlorine as a result of ion filtration effects were studied.

7.2.1 Theory

Phillips and Bentley (1987) described the theory of ion-filtration with respect to chlorine isotopes in some detail. During the ion-filtration process the solvent is able to, while the dissolved ions are unable to move through the membrane. Ion-filtration is a process which is similar to reverse osmosis. Following the description by Kaufmann (1984) osmosis is the effect that appears when two reservoirs, one with water and one with an aqueous salt solution are in connection to reach other through a semi-permeable membrane. During this process water will be able to pass the membrane while the dissolved salt will not. As a result of this process the contents of the reservoirs will interact through the membrane and will try to balance the chemical potential between the two reservoirs. That means that water flows through the semi-permeable membrane in the direction of the reservoir with the higher chemical potential (concentration of salts) in an attempt to equalise the potentials, effectively diluting the contents of the reservoir with the higher concentration. In the case of reverse osmosis the process is comparable (two reservoirs with aqueous solutions of different chemical potential), but now a pressure is applied on the reservoir with the higher concentration. Because of this pressure water is forced through the membrane in the direction of the freshwater side. As a result the salinity increases on the saline side of the membrane. This effect may have a consequence on the isotope composition of the chlorine in the water. In many cases semi-permeable membranes are consisting of clay-minerals. These minerals have negative charges at their surfaces, which means that negative ions are repelled from the membrane. The effect is comparable to diffusion as the lighter ion will be repelled more efficiently than the heavier ion, so that isotope fractionation will take place.

Phillips and Bentley (1987) describe a different model to explain chlorine isotope fractionation occurring from ion-filtration. In their model actually ions move through the membrane, but because the lighter isotope moves away from the membrane more efficiently than the heavier isotope the result was that more of the heavier isotopes are actually transferred through the membrane, increasing the δ^{37}Cl in the sedimentary layer behind the membrane. In their simplified model development of the chloride concentration and chlorine isotopes is described as the result of compaction of three sedimentary layers. At the start the chloride concentration is highest in the lower and lowest in the shallowest sedimentary layer, and the chlorine isotope composition is chosen to be zero in the upper two layers and +0.25 ‰ in the lowest. When pressure is applied it is assumed that the compaction starts in the lower and progresses to the shallower layers. In step 1 the lowest layer is compacted. As a result of this both water as well as chloride with an increased δ^{37}Cl moves to the second layer, and in this layer both the chloride and the chlorine isotope composition increase. When the lowest layer is fully compacted the second layer starts to compact. During this process again water and isotropically heavy chloride move to the third layer. As a result the chloride concentration increases and the isotope ratio decreases in this second layer, while in the upper layer both the concentration and the isotope composition increase. When the second layer is fully compacted the third starts to compact resulting in higher concentrations and a lower isotope composition in this layer. The effect of this process is that considerable positive δ^{37}Cl values can be theoretically be found in transported chloride as opposed to diffusion which tents to lead to more negative δ^{37}Cl values in transported chloride.

7.2.2 Experimental

The effects of ion-filtration on chlorine isotope fractionation have been experimentally established by Campbell (1985). In one of her experiments she forced a chloride solution with a δ^{37}Cl value of 0.04 ‰ through a thick (2.5 cm) plug of bentonite clay and measured the δ^{37}Cl of the effluent solution. It was found that the δ^{37}Cl of the effluent solution had a significantly increased δ^{37}Cl value. Also the results from several other experiments in which chloride was transported through different types of man-made semi-permeable membranes showed in most cases elevated δ^{37}Cl values in the effluent solutions.

Unfortunately these experiments were conducted in the period that the technique to analyse chlorine isotope variations was still under development at the University of Arizona. For that reason the results were in general not very conclusive. It is unfortunate that the experiments conducted in these studies have never been repeated after the analytical techniques to analyse chlorine isotopes had been improved, so that it is still not very well understood what the effects of chlorine isotope fractionation as a result of ion-filtration are in natural samples.

7.3 Fractionation During Ion-Exchange Chromatography of Chloride

As it was shown that halogenides in a mixture could be separated using ion-exchange methods (Atteberry and Boyd 1950; Riemann and Lindenbaum 1952) using a column filled with an ion-exchange resin of a strong base type Langvad (1954) attempted to apply this method with a pure chloride solution with the aim to test if he was able to separate the two stable isotopes of this element also using this technique. For his test he filled two columns with an inner diameter of 2.7 cm and a length of 150 cm with Amberlite IRA-400 in the nitrate form. The isotope separation was effectively applied by moving a potassium chloride solution continuously from column A into column B until it had virtually moved for 43 m. At that moment the solution was sampled into ten fractions of which five were analysed for chlorine isotopes. To analyse the chlorine isotopes Langvad (1954) developed the analytical method using chloromethane gas which is still, after several later improvements, the most precise method to measure chlorine isotopes to date. The results he obtained (see Fig. 7.6), recalculated to δ^{37}Cl values, showed that the first fractions were enriched in ^{37}Cl and the later fractions in ^{35}Cl. In spite of the very large errors (mostly 2–4 ‰, in one case almost 10 ‰!) it is obvious that the total variation of about 44 ‰ between different fractions that was found by Langvad (1954) was a very significant isotope fractionation. As the isotope data obtained were unfortunately not very precise it was however not yet possible to calculate an enrichment factor from these data.

Heumann and Hoffmann (1976) conducted a similar test using an 80 cm long column with an internal diameter of 1.5 cm filled with the strongly basic anion exchanger AG1-X 10 (nitrate form, 200–400 mesh). They analysed small chloride samples (200 mg) which they eluted with nitrate at three different concentrations, 0.01, 0.1 and 1M. Their samples were analysed using thermal ionization mass spectrometry. They found the same characteristic isotope profile as Langvad (1954), thus it was observed that the first fractions were enriched in ^{37}Cl, and they were able to obtain enrichment factors (α) which were shown to be different for the different nitrate concentrations. They found that for a 0.01M nitrate eluent α had a value of 1.00054, for a 0.1M nitrate eluent a value of 1.00030 and for a 1.0M nitrate eluent a value of 1.00019.

Musashi et al. (2004, 2007) were the latest to determine chlorine isotope fractionation during the passage of chloride over anion exchange columns. In both studies a strongly basic anion exchanger, Muromac 1 × 8 analytical grade was used (mesh size, 200–400 mesh; ionic form, Cl^-; total exchange capacity, 1.2 eq/l; cross linkage, 8 % divinylbenzene (DVB); moisture, 45–55 %). The resin was packed in the column and was conditioned to the hydroxide form with a 2 mol/L sodium hydroxide solution fed into the column by a high pressure pomp (Nihon Seimitsu). Then, chloride-free distilled water was fed into the column in order to remove sodium ions from the column. During these experiments at first the column was fed with a 0.1M hydrochloric acid solution and subsequently with a 0.1M nitric acid solution. During this process the column was first saturated with chloride which in the second phase was replaced with nitrate and removed from the column. The isotope compositions could be measured from the fractions containing chloride. It was observed that in the two experiments the isotope fractionation of chlorine between the stationary phase and the solution was 1.00030 and 1.00034 respectively, values which are not only in good agreement with each other but also in very good agreement with the values obtained by Heumann and Hoffmann (1976) when their experiment with a nitrate concentration of 0.1M is compared. It was concluded that on this ion-exchange resin ^{35}Cl is concentrated on the resin, while ^{37}Cl prefers to concentrate in solution, as was actually already also observed by Langvad (1954) and Heumann and Hoffmann (1976). As normally the heavier isotope concentrates in the most strongly bound phase it was concluded by Musashi et al. (2007) that this effect represents a hydration effect and the results were discussed in comparison with isotope fractionation between sodium chloride brine and halite precipitate where the heavier isotope is concentrated in the precipitate and not the solution.

7.4 Salt Precipitation

Attempts to determine isotope fractionation of chloride ions between a saturated solution and its coprecipitating solid have been made in theoretical, experimental as well as field studies. Most of these studies were done with sodium chloride (halite) solutions, which is not surprising as sodium is the most common cation in most saline solutions and chloride the most common anion. As potassium and magnesium are also common cations in salt deposits salts from these elements are studied as well especially in relationship to potash deposits in China. More recently also some experiments have been published in which fractionation between bromide solutions and precipitates are determined.

7.4.1 Experimental Determination of the Chlorine Isotope Fractionation During Precipitation of Salt Minerals

Hoering and Parker (1961) were the first to study the chlorine isotope fractionation between sodium chloride (halite) and a saturated sodium chloride solution. The fractionation factor obtained in their experiment was 1.0002 ± 0.0003, indicating that the chlorine isotope composition of the precipitated sodium chloride was probably higher then that of the saturated solution. Unfortunately, as their analytical precision was still not good enough to determine small variations they could not conclude that this result indicated any significant fractionation.

As part of their study on Zechstein evaporites Eggenkamp et al. (1995) determined equilibrium fractionation factors between sodium chloride, potassium chloride and magnesium chloride saturated solutions and their precipitating salts. They observed that the chlorine isotope fractionation is dependent on the cation that precipitates together with the chloride. Near-saturated solutions of reagent grade sodium chloride, potassium chloride, and magnesium chloride were allowed to evaporate at ambient temperature. After precipitates of the respective salts were formed, the solutions and the precipitates were separated by decanting the brine and filtering the precipitate. To remove any adhering solution the precipitate was rinsed with acetone. Both the brine and the salt were analysed for chlorine isotopes composition and the fractionation was defined as the difference between the δ^{37}Cl of the precipitate and of the remaining brine. For sodium chloride they observed that the precipitate was 0.26 ± 0.07 ‰ heavier than the brine, while for potassium chloride and magnesium chloride it was respectively 0.09 ± 0.07 and 0.06 ± 0.10 ‰ lighter. These fractionation factors were interpreted to explain the lack of variations in the studied Zechstein evaporites. As the sign of the isotope fractionation reverses from sodium chloride to potassium chloride this would mean that at a certain moment a minimum δ^{37}Cl would be reached, after which the δ^{37}Cl would increase again due to the domination of potassium and magnesium salt precipitate in the last stages of salt precipitation. The results obtained by Eggenkamp et al. (1995) were, at least qualitatively, confirmed in an experiment reported by Eastoe et al. (1999) who evaporated a batch of seawater and analysed the δ^{37}Cl of the remaining water and the precipitated halite at certain stages. The δ^{37}Cl of the brine decreased during the early stages, but increased again during the later. The observation that in all stages the halite that was analysed was considerably enriched in δ^{37}Cl compared to the brine was also in good agreement with earlier measurements.

Studies done in the Chinese Tarim and Western Qaidam Basins (Tan et al. 2005, 2006, 2009) indicated that during the latest stages of salt precipitation in these basins δ^{37}Cl continued to decrease, and this effect was used locally as a proxy for the exploration of potassium deposits. It was shown however in an earlier study by Xiao et al. (2000) that equilibrium isotope fractionation in potassium and magnesium chlorides was not as large as chlorine isotope fractionation during halite precipitation. A recent study by Luo et al. (2012) confirmed these results. The effect that the chlorine isotope composition continues to decrease during precipitation of magnesium chlorides might however be the result of the specific character of these deposits, which are terrestrial rather than marine, or perhaps of kinetic effects.

Just before this this book went to print Luo et al. (2014) presented newly determined fractionation factors for the precipitation of sodium, potassium and magnesium chloride from their respective saturated brines. The values they obtained appeared all to be higher than the data obtained by Eggenkamp et al. (1995), and more importantly in all three salts the precipitate

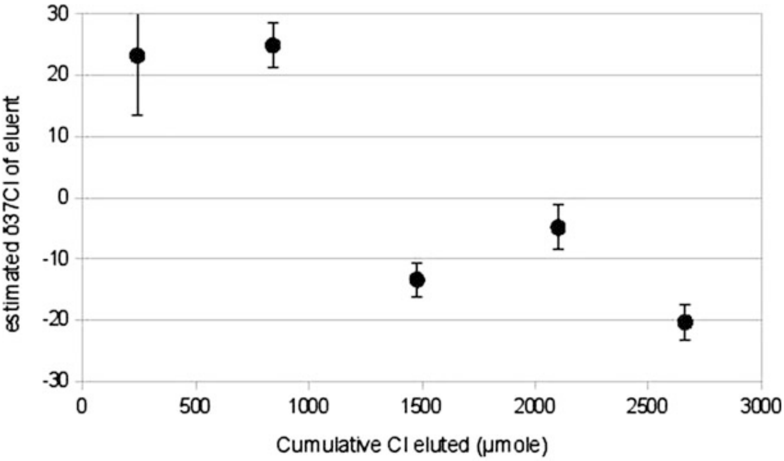

Fig. 7.6 Fractionation factors obtained by Langvad (1954) during his ion-exchange experiments

appeared to have more positive δ^{37}Cl values than the brine. The error of the measurements seemed however to be rather large. The data obtained (with one standard deviation of the published measurements done per salt) were: NaCl 1.00055 ±0.00046, KCl 1.00025±0.00010 and $MgCl_2.6H_2O$ 1.00012±0.00050. Except for KCl it is thus not obvious that these data are significantly different from the data presented by Eggenkamp et al. (1995).

Recently Eggenkamp et al. (2011) presented determinations of chlorine isotope fractionation between several more chloride (and bromide) salts and their saturated solutions. These results have been presented at a conference only and the fractionation factors were only presented in a figure. It was clear however that different salts show very different isotope fractionation factors when they precipitate from a saturated brine, ranging from about +0.4 ‰ for barium chloride to about −0.2 ‰ for caesium chloride. For bromide salts the fractions factors appeared to be rather modest compared to the chloride salts.

7.4.2 Theoretical Isotope Fractionation Between Chlorides in Different Phases

Schauble et al. (2003) presented a study updating the theoretical knowledge on chlorine isotope fractionation. They also studied chlorine isotope fractionation of inorganic chloride that is distributed between different phases. One of the main discoveries they made was that chloride would concentrate in phases where it is bonded to +II cations relative to phases where it is bonded to +I cations. They attempted to calculate isotope fractionation for salts that precipitate from solution, however this appeared very difficult to calculate. Schauble et al. (2003) were able to estimate the differences between sodium chloride and potassium chloride in case these salts would coexist. Their calculation indicated that chloride in sodium chloride would be about 0.8 ‰ heavier than chloride in potassium chloride. Considering all uncertainties they concluded that these results are at least qualitatively in agreement with the experimental results reported by Eggenkamp et al. (1995).

7.5 Volcanic Systems

It was found that, under certain circumstances, extreme δ^{37}Cl values could exist in samples taken from volcanic systems. Eggenkamp (1994) for example recorded a δ^{37}Cl value as high as +9.5 ‰ in Giggenbach bottles containing fumaroles collected from Lewotolo Volcano on Lomblen Island, Indonesia. At the main fumarole of Poás Volcano, Costa Rica, Sharp et al. (2010) also observed very high δ^{37}Cl values which even could be as high as +12 ‰. On the other hand, most chlorine isotope observations related to volcanic systems seem to have rather modest δ^{37}Cl values that are within 1 ‰ from SMOC (e.g. Eggenkamp 1994; Barnes et al. 2008, 2009).

7.5.1 Chlorine Isotope Fractionation Between $HCl_{(g)}$ and $Cl^-_{(aq)}$

Under normal conditions equilibrium fractionation between $HCl_{(g)}$ and $Cl^-_{(aq)}$ is expected to be the main fractionation process in volcanic systems. The fractionation factor for this system has been calculated as +1.7 ‰ at about 60 °C and is expected to be decreasing both at lower and higher temperatures by Schauble et al. (2003) while Czarnacki and Hałas (2012), taking into account the hydration of the chloride ion, even predict that the fractionation is at most 1.55 ‰ at about 60 °C and further showing the same characteristics. Sharp et al. (2010) conducted experiments in which they equilibrated $HCl_{(g)}$ with a 1M HCl solution. They analysed the δ^{37}Cl of the gaseous hydrochloric acid as well as the solution and found that the difference in δ^{37}Cl between the two phases at 50 °C was 1.6 ‰, which is very close to the theoretically obtained value for this system. These fractionation data can explain the generally small variations in δ^{37}Cl values, but not directly the extreme data that were observed by Eggenkamp (1994) and Sharp et al. (2010) in some volcanic samples.

7.5.2 Chloride Isotope Fractionation During Ammonium Chloride Formation

Hoering and Parker (1961) conducted various experiments to determine and understand potential chlorine isotope fractionation in a period that no natural variations had ever been detected. One of these experiments consisted of the determination of the fractionation between chlorine isotopes in the process of the formation of ammonium chloride in equilibrium with hydrogen chloride in volcanic systems. They measured chlorine isotope data from the reaction:

$$NH_4{}^{37}Cl_{(s)} + H^{35}Cl_{(g)} \Leftrightarrow NH_4{}^{35}Cl_{(s)} + H^{37}Cl_{(g)} \qquad (7.8)$$

at 200 °C and found a fractionation factor of 1.0009 ± 0.0003 which indicates that solid ammonium chloride is about 0.9 ‰ heavier than gaseous hydrogen chloride when it is precipitated in equilibrium with gaseous hydrogen chloride. Eggenkamp (1994) reported a δ^{37}Cl value of ammonium chloride sampled from the Vesuvius volcano in Italy of −4.9 ‰. Assuming an initial δ^{37}Cl of the hydrogen chloride of 0 ‰ such a low value could only be reached after 99.85 % of all hydrogen chloride has precipitated as ammonium chloride when we assume that the salt is formed according to a simple Rayleigh type of fractionation. Considering this very negative value a different method of formation can not be excluded.

7.5.3 Kinetic Fractionation Due to Hydrogen Chloride Escaping from an Acid Solution

Sharp et al. (2010) conducted experiments to obtain information on the origin of the extreme δ^{37}Cl values they observed in samples from the Poás volcano fumarole in Costa Rica. They bubbled dry air through an Erlenmeyer flask filled with hydrochloric acid in concentrations between 0.6 and 2.9M at temperatures of at most 95 °C for 10–20 min, and collected the hydrogen chloride that escaped from this solution in a second Erlenmeyer flask. They observed that the δ^{37}Cl of the hydrogen chloride in this second flask had highly increased values (+7.9 to +9.6 ‰ vs. SMOC, compared to +0.8 ‰ vs. SMOC for the original hydrochloric acid solution). When this experiment was conducted with fuming hydrogen chloride (11.6M) hardly any measurable fractionation was observed. Equilibrium in this system was not explained as equilibrium between liquid and gas phases with the same chemical bonds. The gas phase consists of diatomic hydrogen chloride molecules, whereas the chlorine in solution consists of the solvated chloride ion. Because the hydrogen-chloride bond in the diatomic molecule is much stronger than the loosely bound solvated chloride ion in aqueous solution, the heavy isotope ^{37}Cl tends to be preferentially partitioned into the hydrogen chloride gas (i.e., the stronger bond). Sharp et al. (2010) were able to explain the large isotope variations in this system through the occurrence of a Rayleigh type fractionation, where the very first fraction of hydrogen chloride that is transferred to the second flask has the most extreme δ^{37}Cl which was found in their fumarole experiment. Very important in this system is the fact that the evaporating hydrochloric acid solution is continuously condensing on the walls of the system, so that most hydrogen chloride returns to the original solution and only a small part is transferred to the fumarole outlet. They explained the observation that no fractionation occurred when the experiment was conducted with fuming hydrogen chloride solution with the fact that in this solution hydrogen chloride in solution consists overwhelmingly of non-dissociated HCl molecules in solution so that the same type of chemical bond is present in both the solution and the vapour. To understand the fractionation during simple evaporation they conducted a different experiment where 1 L of a 1M hydrochloric acid solution was left to evaporate until only 0.1 L of solution was left. The δ^{37}Cl of the hydrochloric acid solution increased during this evaporation process to +10.3 ‰ versus SMOC, indicating that in this case *light* isotope ^{35}Cl was escaping preferentially with a fractionation factor ($10^3\ln\alpha$) of about −4 ‰.

7.6 High Temperature Equilibrium Fractionation in Rocks

Sharp et al. (2007) determined the equilibrium isotope fractionation for the system:

$$nepheline + \mathrm{NaCl} \Rightarrow sodalite \tag{7.9}$$

They reacted nepheline with a large excess of sodium chloride at a temperature of 825 °C. All nepheline reacted to sodalite in this reaction and the chlorine isotope composition of both the sodalite and the excess sodium chloride was determined. The $10^3\ln\alpha$ for this reaction (sodalite-NaCl) was observed to be -0.3 ± 0.1.

7.7 Fractionation Due to Acid Displacement in Aerosols

7.7.1 Observations of Chlorine Isotope Variation on Aerosols

When aerosols consisting of primarily sodium chloride from sea spray react with atmospheric acid particles chlorine may escape from the aerosols as hydrogen chloride molecules. This process was already recognised a considerable time ago (Eriksson 1959). During this process the chloride ions in the aerosols are displaced with sulphate and nitrate ions (acid displacement). When they studied bulk aerosols Volpe and Spivack (1994) discovered that the δ^{37}Cl values of the aerosols show a positive correlation with the so called non-sea-salt sulphate concentrations and the chloride deficiency. Chloride deficiency is defined as the Na/Cl ratio in the aerosol as compared to the Na/Cl ratio in seawater. This effect could be explained trough a kinetic isotope fractionation which was associated with the volatilisation of hydrogen chloride. From experiments that Volpe and Spivack (1994) conducted and which they compared with the data measured in natural aerosols it was possible to calculate an experimental fractionation factor for this effect of 0.9969. In a second paper on chlorine isotope variations from marine aerosols Volpe et al. (1998) sampled aerosols with different particle sizes and found differences between aerosol groups of different sizes. They observed that in smaller particles δ^{37}Cl increases with increasing chloride deficiency, while in larger particles it decreases with increasing chloride deficiency. The effect that is seen in the smaller particles is the same effect as Volpe and

Spivack (1994) observed in their study on bulk aerosols from Bermuda. In the larger particles Volpe et al. (1998) were able to calculate a relationship between the δ^{37}Cl and the chloride deficiency. They concluded that if during acid replacement reactions chloride in the particles is replaced with sulphate and nitrate the chloride is released in the form of isotopically heavy hydrogen chloride from the particles. The related isotope fractionation with this second process was either 1.00303 ± 0.0005 if a first order mechanism was assumed or 1.00280 ± 0.0005 when a zeroth order mechanism was assumed. Considering the scatter in the data it was not possible to decide which mechanism actually occurred.

7.7.2 Experimental Determination on Hydrogen Chloride Escape in the Reaction of Sodium Chloride with Sulphuric Acid

To test the hypothesis that the δ^{37}Cl of sodium chloride decreases as a result of escape of hydrogen chloride from a solution containing sodium chloride and sulphuric acid, Eggenkamp (1994) conducted the following experiment: A solution containing 0.2M sodium chloride and 0.1M sulphuric acid was prepared. This solution was evaporated to dryness at 50 °C and the residue was examined for its chloride isotope composition. Unlike the original sodium chloride, the dry residue was birefringent, and the chloride content had decreased from about 60 to 15 %. Evidently, part of the chloride in the solution was evaporated due to the reaction:

$$2\mathrm{NaCl} + \mathrm{H_2SO_4} \Rightarrow \mathrm{Na_2SO_4} + 2\mathrm{HCl}\uparrow \quad (7.10)$$

The δ^{37}Cl of the remaining salt was 0.52 ± 0.05 ‰ higher than that of the original sodium chloride. This also shows that δ^{37}Cl increases when part of the chloride escapes as hydrogen chloride gas. The result was used to make a rough estimate of the fractionation factor. A Rayleigh fractionation curve was drawn through the point were three quarters of chloride is removed with a total fractionation of +0.52 ‰. The fractionation factor ($\alpha_{\mathrm{gas/solution}}$) based on this single measurement was about 0.99963. Although considerably smaller than the value obtained by Volpe et al. (1998) it was clear that the same effect had taken place, and the different value obtained may be caused by the fact that in this case only a single, fairly rough experiment was conducted.

7.8 Equilibrium Fractionation in Systems with Lesser Geologic Relevance

7.8.1 Equilibrium Fractionation Between Chloride and Hexchloroplatinate

Although not of geologic relevance Hoering and Parker (1961) also conducted an experiment determining the chlorine isotope fractionation in the exchange reaction between chloride and hexachloroplatinate:

$$\left(\mathrm{Pt}^{35}\mathrm{Cl}_6\right)^{2-} + 6^{37}\mathrm{Cl}^- \leftrightarrow \left(\mathrm{Pt}^{37}\mathrm{Cl}_6\right)^{2-} + 6^{35}\mathrm{Cl}^- \quad (7.11)$$

This reaction was studied to check their experimental procedures and to show that relatively small variations in the ratio of chlorine isotopes could indeed be detected with their analytical method. This experiment obtained an equilibrium fractionation of 1.0009 ± 0.0003, indicating that the lighter isotope is concentrated in the hexachloroplatinate ion.

7.8.2 Equilibrium Between Hydrogen Chloride Gas and Chlorides Dissolved in Glacial Acetic Acid

Howald (1960) studied chlorine isotope fractionation between hydrogen chloride gas in equilibrium with chloride solutions in glacial acetic acid. The purpose of this study was to understand the behaviour of ion-pairs in solutions with a low dielectric constant. The dielectric constant of glacial acetic acid is about 6.15 as compared to 80.37 for water at 20 °C (Maryott and Smith 1951). The experiments were done between hydrogen chloride in the gas phase and HCl, H_3OCl, $HgCl_2$, LiCl and $SrCl_2$ dissolved in glacial acetic acid. From the experiments it appeared that at higher salt concentrations in the acetic acid the isotope effect is negative, i.e. the $^{37}Cl/^{35}Cl$ ratio in the solution is lower than in the hydrogen chloride gas above, while at low concentrations the hydrogen chloride gas is heavier than the salt in solution. From the experimental data that were obtained Howald (1960) calculated the following isotope fractionation factors, LiCl; 1.0040 ± 0.0003, $SrCl_2$; 1.0042 ± 0.0003, H_3OCl; 1.0039 ± 0.0003, $HgCl_2$; 1.0061 ± 0.0009 and HCl; 1.0059 ± 0.0002. These results suggest that ionic species, which exist as free chloride ions in the glacial acetic acid (LiCl, $SrCl_2$, H_3OCl) have lower fractionation factors than more covalent species which are present as molecules in glacial acetic acid ($HgCl_2$, HCl).

References

Alder BJ, Alley WE, Dymond JH (1974) Studies in molecular dynamics. XIV. Mass and size` dependence of the binary diffusion coefficient. J Chem Phys 61:1415–1420

Appelo CAJ, Postma D (2005) Geochemistry, groundwater and pollution, 2nd edn. Balkema, Leiden

Atteberry RW, Boyd GE (1950) Separation of seventh group anions by ion-exchange chromatography. J Amer Chem Soc 72:4805–4806

Barnes JD, Sharp ZD, Fischer TP (2008) Chlorine isotope variations across the Izu-Bonin-Mariana arc. Geology 36:883–886

Barnes JD, Sharp ZD, Fisher TP, Hilton DR, Carr MJ (2009) Chlorine isotope variations along the Central American volcanic front and back arc. Geochem Geophys Geosys 10:Q11S17

Beekman HE, Eggenkamp HGM, Appelo CAJ (2011) An integrated modelling approach to reconstruct complex solute transport mechanisms—Cl and $\delta^{37}Cl$ in pore water of sediments from a former brackish lagoon in The Netherlands. Appl Geochem 26:257–268

Bird RB, Steward WE, Lightfoot EN (2002) Transport Phenomena, 2nd ed. Wiley, New York

Bourg IC, Sposito G (2007) Molecular dynamics simulations of kinetic isotope fractionation during the diffusion of ionic species in liquid water. Geochim Cosmochim Acta 71:5583–5589

Bourg IC, Sposito G (2008) Isotopic fractionation of noble gases by diffusion in liquid water: molecular dynamics simulations and hydrologic applications. Geochim Cosmochim Acta 72:2237–2247

Bourg IC, Richter FM, Christensen JM, Sposito G (2010) Isotopic mass dependence of metal cation diffusion coefficients in liquid water. Geochim Cosmochim Acta 74:2249–2256

Brewer AK, Madorsky SL, Taylor JK, Dibeler VH, Bradt P, Parham OL, Britten RJ, Reid JG (1947) Concentration of isotopes of potassium by the counter-current electromigration method. J Res Natl Bur Stand 38:137–168

Cameron AE, Herr W, Herzog W, Lundén A (1956) Isotopen-Anreicherung beim Brom durch electrolytische Überführung in geschmolzenem Bleibromid. Z Naturforschng 11a:203–205

Campbell DJ (1985) Fractionation of stable chlorine isotopes during transport through semipermeable membranes. MS thesis, University of Arizona

Carslaw HS, Jaeger JC (1959) Conduction of heat in solids, 2nd edn. Oxford University Press, London

Crank J (1956) The mathematics of diffusion. Oxford University Press, London, p 347

Czarnacki M, Hałas S (2012) Isotope fractionation in aqua-gas systems: Cl_2-HCl-Cl^-, Br_2-HBr-Br^- and H_2S-S^{2-}. Isot Environ Health Stud 48:55–64

Desaulniers DE, Cherry JA, Fritz P (1981) Origin, age and movement of pore water in argillaceous Quaternary deposits at four sites in southwestern Ontario. J Hydrol 50:217–231

Desaulniers DE, Kaufmann RS, Cherry JA, Bentley HW (1986) ^{37}Cl-^{35}Cl variations in a diffusion controlled groundwater system. Geochim Cosmochim Acta 50:1757–1764

Duursma EK, Hoede C (1967) Theoretical, experimental and field studies concerning molecular diffusion of radioisotopes in sediments and suspended solid particles of the sea. Part A: theories and mathematical calculations. Neth J Sea Res 3:423–457

Eastoe CJ, Long A, Knauth LP (1999) Stable chlorine isotopes in the Palo Duro Basin, Texas: evidence for preservation of Permian evaporite brines. Geochim Cosmochim Acta 63:1375–1382

Eggenkamp HGM (1994) $\delta^{37}Cl$; the geochemistry of chlorine isotopes. Geol Ultrai 116:1–150. Thesis Utrecht University

Eggenkamp HGM, Coleman ML (1997) Comparison of chlorine and bromine isotope fractionation in diffusion: geochemical consequences. In: In proceeding of the 7th Annual Goldschmidt conference, Tucson, p 213

Eggenkamp HGM, Coleman ML (2009) The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes. Geochim Cosmochim Acta 73:3539–3548

Eggenkamp HGM, Middelburg JJ, Kreulen R (1994) Preferential diffusion of ^{35}Cl relative to ^{37}Cl in sediments of Kau Bay, Halmahera, Indonesia. Chem Geol (Isot Geosc Sect) 116:317–325

Eggenkamp HGM, Kreulen R, Koster van Groos AF (1995) Chlorine stable isotope fractionation in evaporites. Geochim Cosmochim Acta 59:5169–5175

Eggenkamp HGM, Bonifacie M, Ader M, Agrinier P (2011) Fractionation of Cl and Br isotopes during precipitation of salts from their saturated solutions. 21th Annual V.M. Goldschmidt Conference. Prague, Czech Republic. Mineral Mag 75:798

Eriksson E (1959) The yearly circulation of chlorines and sulfur in nature: Meteorological, geochemical and pedological implications. Tellus l:375–403

Fick A (1855) Über Diffusion. Ann Phys 170:59–86

Fink CG, Urey HC, Lake DB (1934) The diffusion of hydrogen through metals: fractionation of hydrogen isotopes. J Chem Phys 2:105–106

Groen J, Velstra J, Meesters AGCA (2000) Salinization processes in paleowaters in coastal sediments from Suriname: evidence from δ^{37}Cl analysis and diffusion modelling. J Hydrol 234:1–20

Herzog W, Klemm A (1958) Die Temperaturabhängigkeit des Isotopie-Effekts bei der elektrolytischen Wanderungen der Chlorionen in herschmolzenem Thallium (I)-chlorid. Z Naturforschg 13a:7–16

Heumann KG, Hoffmann R (1976) Chlorine isotope effects in ion exchange chromatography. Angew Chem Int Ed Eng 15:55

Hoering TC, Parker PL (1961) The geochemistry of the stable isotopes of chlorine. Geochim Cosmochim Acta 23:186–199

Howald RA (1960) Ion pairs. I. Isotope effects shown by chloride solutions in glacial acetic acid. J Amer Chem Soc 82:20–24

Impey RW, Madden PA, McDonald IR (1983) Hydration and mobility of ions in solution. J Phys Chem 87:5071–5083

Jähne B, Heinz G, Dietrich W (1987) Measurement of the diffusion coefficients of sparingly soluble gases in water. J Geophys Res 92:10767–10776

Kaufmann RS (1984) Chlorine in groundwater: stable isotope distribution. PhD thesis, University of Arizona, Tucson

Klemm A (1943) Isotopenanreicherung bei Diffusion von Kupfer in Silbersulfid. Z physikal Chemie 193:29–39

Klemm A, Lundén A (1955) Isotopenanreicherung beim Chlor durch electrolytische Überfürung in geschmolzenem Bleichlorid. Z. Naturforschg. 10A:282–284

Konstantinov BP, Bakulin EA (1965) Separation of chloride isotopes in aqueous solutions of lithium chloride, sodium chloride and hydrochloric acid. Rus J Phys Chem 39:315–318

Langvad T (1954) Separation of chlorine isotopes by ion-exchange chromatography. Acta Chem Scand 8:526–527

Lindemann FA (1921) Discussion on isotopes. Proc Royal Soc London. Series A 99:102–104

Lundén A, Herzog W (1956) Isotopenanreicherung bei Chlor durch electrolytische Überführung in geschmolzenem Zinkchlorid. Z Naturforschg 11a:520

Lundén A, Lodding A (1960) Isotopenanreicherung bei Brom durch electrolytische Überführung in geschmolzenem Zinkbromid. Z. Naturforschg. 15A:320–322

Luo CG, Xiao YK, Wen HJ, Ma HH, Ma YQ, Zhang YL, Zhang YX, He MY (2014) Stable isotope fractionation of chloride during the precipitation of single chloride minerals. Appl Geochem 47:141–149

Luo CG, Xiao YK, Ma HZ, Ma YQ, Zhang YL, He MY (2012) Stable isotope fractionation of chlorine during evaporation of brine from a saline lake. Chin Sci Bull 57:1833–1843

Madorsky SL, Strauss S (1947) Concentration of isotopes of chlorine by the counter-current electromigration method. J Res Nat Bur Stand 38:185–189

Marchese FT, Beveridge DL (1984) Pattern recognition approach to the analysis of geometrical features of solvation: application to the aqueous hydration of Li+, Na+, K+, F-, and Cl-. J Amer Chem Soc 106:3713–3720

Maryott AA, Smith ER (1951) Table of dielectric constants of pure liquids. Nation Bur Stand Circ 514:44

Middelburg JJ, De Lange GJ (1989) The isolation of Kau Bay during the last glaciation: direct evidence from interstitial water chlorinity. Neth J Sea Res 24:615–622

Musashi M, Oi T, Eggenkamp HGM (2004) Experimental determination of chlorine isotope separation factor by anion-exchange chromatography. Anal Chim Acta 508:37–40

Musashi M, Oi T, Eggenkamp HGM, Yato Y, Matsuo M (2007) Anion-exchange chromatographic study of the chlorine isotope effect accompanying hydration. J Chrom A 1140:121–125

Nuevo MJ, Morales JJ, Heyes DM (1995) Mass dependence of isotope selfdiffusion by molecular dynamics. Phys Rev E 51:2026–2032

Phillips FM, Bentley HW (1987) Isotopic fractionation during ion filtration: I. Theory. Geochim Cosmochim Acta 51:683–695

Powell DH, Barnes AC, Enderby JE, Neilson GW, Salmon PS (1988) The hydration structure around chloride ions in aqueous solution. Faraday Discuss Chem Soc 85:137–146

Richter FM, Mendybaev RA, Christensen JN, Hutcheon ID, Williams RW, Sturchio NC, Beloso AD Jr (2006) Kinetic isotopic fractionation during diffusion of ionic species in water. Geochim Cosmochim Acta 70:277–289

Riemann W, Lindenbaum S (1952) Analysis of mixtures of chloride and bromide by ion-exchange chromatography. Anal Chem 24:1199–1200

Samoilov OY (1957) A new approach to the study of hydration of ions in aqueous solutions. Disc Faraday Soc 24:141–146

Schauble EA, Rossman GR, Taylor HP (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochim Cosmochim Acta 67:3267–3281

Schreiner F, Fried S, Friedman AM (1982) Measurement of radionuclide diffusion in oceanfloor sediment and clay. Nucl Technol 59:429–438

Sharp ZD, Barnes JD, Brearly AJ, Chaussidon M, Fisher TP, Kamenetsky VS (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature 446:1062–1065

Sharp ZD, Barnes JD, Fischer TP, Halick M (2010) An experimental determination of chlorine isotope fractionation in acid systems and applications to volcanic fumaroles. Geochim Cosmochim Acta 74-264–273

Tabor D (1991) Gases, Liquids and Solids, 3rd edn. Cambridge University Press, Cambridge

Tan HB, Ma HZ, Xiao YK, Wei HZ, Zhang XY, Ma WD (2005) Characteristics of chlorine isotope distribution and analysis on sylvinite deposit formation based on ancient salt rock in western Tarim basin. Sc China (ser. D) 48:1913–1920

Tan HB, Ma HZ, Wei HZ, Xu JX, Li TW (2006) Chlorine, sulfur and oxygen isotopic constraints on ancient evaporite deposit in the Western Tarim Basin, China. Geochem J 40:569–577

Tan HB, Ma HZ, Zhang XY, Xu JX, Xiao YK (2009) Fractionation of chlorine isotope in salt mineral sequences and application: research on sedimentary stage of ancient salt rock deposit in Tarim Basin and western Qaidam Basin. Acta Petrol Sinica 25:955–962 (in Chinese with English abstract)

Volpe C, Spivack AJ (1994) Stable chlorine isotopic composition of marine aerosol-particles in the Western Atlantic Ocean. Geophys Res Letters 21:1161–1164

Volpe C, Wahlen M, Pszenny AAP, Spivack AJ (1998) Chlorine isotopic composition of marine aerosols: implications for the release of reactive chlorine and HCl cycling rates. Geophys Res Letters 25:3831–3834

Willeke M (2003) Limits of the validity of the mass ratio independence of the Stokes-Einstein relation: molecular dynamics calculations and comparisons with the Enskog theory. Mol Phys 11:1123–1130

Xiao YK, Liu WG, Zhou YM, Wang YH, Shirodkar PV (2000) Variations in isotopic compositions of chlorine in evaporation controlled salt lake brines of Qaidam Basin, China. Chin J Ocean Limn 18:169–177

Theoretical and Experimental Fractionation Between Species with Different Oxidation States

8

8.1 Theoretical Fractionation Between Chlorine and Bromine Species with Different Oxidation States

After it had become clear that equilibrium fractionation between chemical phases containing different hydrogen isotopes could be both theoretically and experimentally determined with perfect agreement (Urey and Rittenberg 1933; Rittenberg and Urey 1934; Rittenberg et al. 1934) interest in the equilibria between isotopes of the other light elements also grew.

Urey and Greiff (1935) published the first comprehensive theoretical study on isotope equilibrium fractionation between molecules of different oxidation state from most light elements, including chlorine and bromine. They calculated that for chlorine the equilibrium fractionation factor (enrichment factor) at 25 °C between hydrogen chloride and chlorine gas was 1.003, while between hydrogen bromide and bromine gas this factor was only 1.0004, with the heavier isotope concentrated in chlorine and bromine. The fractionation factors were also calculated at 0 °C (1.004 for chlorine and 1.0005 for bromine) and at 326.9 °C (1.00055 for chlorine and 0.99997 for bromine). Interestingly at the higher temperature the heavier bromine isotope is (only just) concentrated in hydrogen bromide. Several more equilibrium fractionation factors for chlorine and bromine were published by Urey (1947) in his by now classic paper on equilibrium isotope fractionation. Fractionation factors between HCl, Cl_2, ClO_2, ClO_3^- and ClO_4^- and all their combinations were computed for five different temperatures (273.1, 298.1, 400, 500 and 600 K). Following these calculations isotope fractionation between species with different oxidation states can be considerably large. For example the equilibrium fractionation factor between HCl and ClO_4^- is 1.080 at 298.1 K (25 °C). A much more limited set of equilibrium fractionation factors was computed for bromine. The fractionation factors between HBr, Br_2 and BrO_3^- were determined for the same temperatures as for chlorine. The equilibrium fractionation factors for bromine are considerably lower than those for chlorine. For example the largest value for a fractionation between bromine species in the table is the equilibrium between HBr and BrO_3^-, 1.008, while the equivalent equilibrium fractionation for chlorine (HCl and ClO_3^-) is 1.050 (both at 273.1 K). Newer data for the fractionation factors for the equilibrium between HCl and Cl_2 were determined by Richet et al. (1977), Schauble et al. (2003) and Czarnacki and Halas (2012). In these studies equilibrium fractionation for different temperature ranges with values between −120 and 1,300 °C (153.15 and 1,573.15 K) were calculated. Figure 8.1 shows the calculated equilibrium fractionation for the equilibrium between HCl and Cl_2 in a

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Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_8,

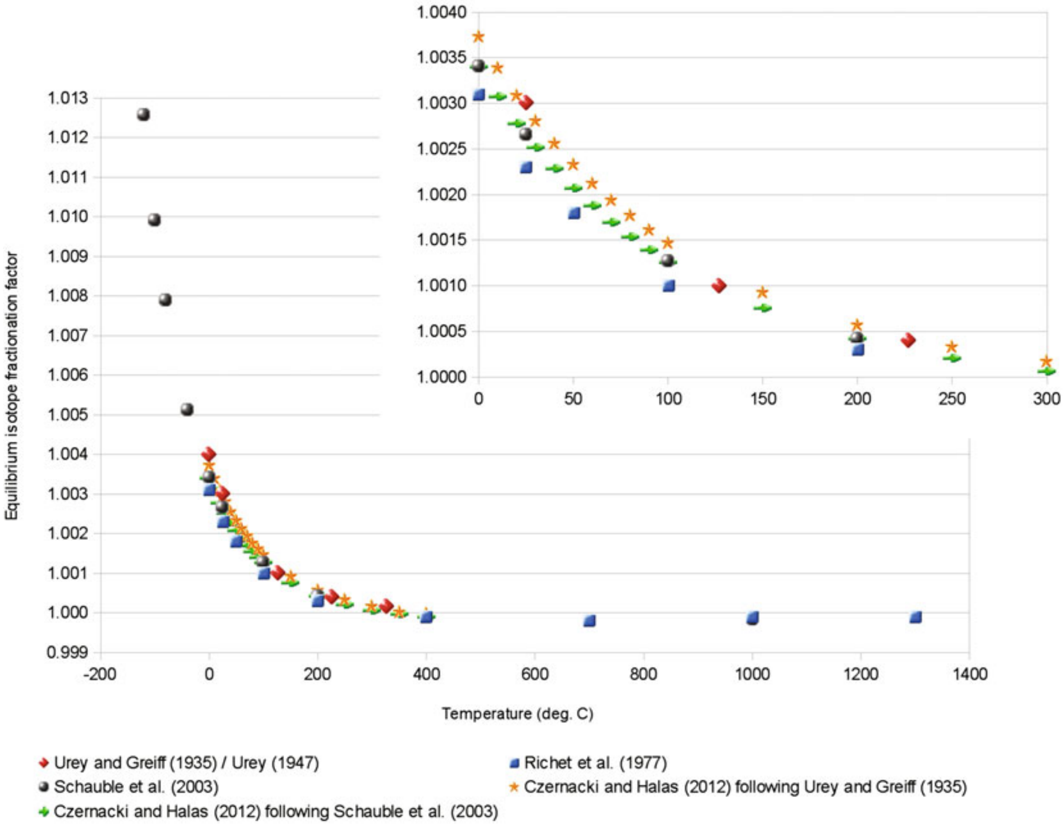

Fig. 8.1 Equilibrium isotope fractionation for the Cl_2–HCl equilibrium as published in the various papers in which this equilibrium was studied

temperature versus fractionation factor diagram for these studies. In this figure it is clearly visible that the different calculations led to slightly different isotope fractionation factors. At low temperatures (0 °C, 273.15 K) these differences add up to almost 1 ‰, which is decreasing to about 0.3 ‰ at temperatures above 120 °C. As is also observed for the equivalent equilibrium reaction for bromine the fractionation factor deceases below 1 for temperatures above approximately 340 °C. The calculations done by Richet et al. (1977) show that a minimum equilibrium fractionation factor of 0.9998 is reached at a temperature of about 1,000 K (726.85 °C) and that it increases again (to ultimately 1.0000) above that temperature.

8.2 Experimental Determination of Isotope Fractionation Between Species with Different Oxidation States

8.2.1 Experimental Determination of Isotope Fractionation Between HX and X_2 (X = Cl, Br)

The only known published experimental determination of any chemical equilibrium between chlorine species of different oxidation state is the determination by Hoering and Parker (1961) of the exchange reaction between chlorine and hydrogen chloride. The chemical and mass spectrometric procedures were tested by measuring the small equilibrium isotope effect in the exchange between gaseous hydrogen chloride and chlorine:

$$H^{37}Cl + \frac{1}{2}{}^{35}Cl_2 \Leftrightarrow H^{35}Cl + \frac{1}{2}{}^{37}Cl_2 \qquad (8.1)$$

The rate to reach isotopic equilibrium in this system has been studied by Dodgen and Libby (1949) and Johnston and Libby (1951) using radioisotopes of chlorine. They found that the reaction was heterogeneously catalysed by the walls of Pyrex vessels with an exchange half time of 3 min. Hoering and Parker (1961) repeated the experiment as done by Dodgen and Libby (1949) and Johnston and Libby (1951). The reactants were allowed to exchange for 24 h or longer. After separation, the two reactants were converted to silver chloride and subsequently to hydrogen chloride for isotope analysis. The magnitude of the isotope fractionation in this exchange reaction had been calculated by Urey (1947). Since both molecules are gases with a simple structure and for which good values of the vibrational frequencies were known, there was good reason to assume that the calculated value of the equilibrium fractionation factor is close to the true value. Hoering and Parker (1961) conducted five such exchange experiments and obtained an average equilibrium fractionation factor of 1.0038 ± 0.0004. The calculated values for this reaction are between 1.0031 and 1.0040 at 0 °C and 1.00266 and 1.0030 at 25 °C. The good agreement between the observed and the theoretical values gives confidence in the experimental procedures. Giunta et al. (2013) reported the results of experiments to determine chlorine isotope fractionation in the reaction between hydrochloric acid and hydrogen peroxide where chloride is oxidised to chlorine gas. Preliminary results indicated that $10^3 \ln\alpha\left(Cl_{2gas} - Cl^-_{aq}\right) = 3.72 \pm 0.25$ ‰ at ~20 °C, a value that is very close to the number obtained by Hoering and Parker (1961).

The (fast) exchange reaction between bromine and hydrogen bromide containing a radioactive bromine isotope:

$$H^{@}Br + \frac{1}{2}Br_2 \Leftrightarrow HBr + \frac{1}{2}{}^{@}Br_2 \qquad (8.2)$$

where $^{@}Br$ indicates a radioactive bromine isotope, has been experimentally determined already at an early date (Brejneva et al. 1936; Liberatore and Wiig 1940; Libby 1940), but has unfortunately never been repeated to establish the stable isotope exchange experimentally between the two gases.

8.2.2 Experimental Determination of Equilibrium Chlorine Isotope Fractionation Between Hypochlorous Acid ($ClOH_{aq}$) and Chloride (Cl^-_{aq})

When chlorine gas is trapped in an alkaline solution it disproportionates into chloride (Cl^-) and hypochlorous acid (ClOH). In the same experiment in which Giunta et al. (2013) determined the equilibrium fractionation between chloride and chlorine they were also able to determine the equilibrium fractionation between Cl^- and ClOH, although the method they applied was not described in their abstract. $10^3 \ln\alpha(ClOH_{aq}–Cl^-_{aq})$ was determined as 3.04 ± 0.20 ‰ at ~20 °C, which is about 1 ‰ less than was predicted by Schauble et al. (2003).

8.3 Microbial Reduction of Perchlorates

At the end of the 20th century it became clear that perchlorates actually pose a health threat when they are present in drinking water (Urbansky 1998). Perchlorates were previously not known to exist in the environment except for their occurrence in the Atacama desert in Chile (Ericksen 1981), but it was realised that, especially in the South-Western United States its presence in drinking water supplies could be high enough to posses health risks to the general population. Due to their stability in the environment it was also realised that remediation of perchlorates would be a difficult task. In the same period it was discovered that several specialised microbes had evolved that can couple growth to anaerobic reduction of perchlorate and completely reduce it to chloride (Romanenko et al. 1976; Stepanyuk et al. 1992; Malmqvist et al. 1994 ; Rikken et al. 1996; Bruce et al. 1999; Coates et al. 1999; Michaelidou et al. 2000). It was considered that the microbial reduction could be a good way to remediate perchlorates from the environment. In the same period it became possible to analyse the chlorine isotope composition of perchlorates (Ader et al. 2001; Sturchio et al. 2003). Considering the fact that the calculated equilibrium fractionation between the +VII (perchlorate) and −I (chloride) oxidation states of chlorine is very large (80 ‰ at 25 °C; Urey 1947), it was realised that during microbial reduction a relatively large chlorine isotope fractionation could be expected, and it was also expected that it could be a perfect tracer for actual perchlorate reduction (Coleman et al. 2003). Coleman et al. (2003) tested the possible chlorine isotope fractionation with the help of *Azospira suillum*, a microbe that reduces perchlorate in an anoxic environment using acetate as proton donor. They found that in a medium with only acetate as electron donor and perchlorate as electron acceptor the chloride concentration increased considerably, while the perchlorate concentration decreased. During this process also a considerable chlorine isotope fractionation was observed. During the process a Rayleigh type fractionation was observed with a fractionation between the original perchlorate and the produced chloride of −14.8 ± 0.7 ‰. Experiments done by Sturchio et al. (2003) of the same process yielded comparable isotope fractionation data for this process between −16.6 and −12.9 ‰. Further experiments were done later by Sturchio et al. (2007) using both *Dechlorospirillum* sp. and *A. suillum* at 22 and 10 °C. They observed isotope fractionation values between perchlorate and chloride which were between −14.5 and −11.5 ‰. Ader et al. (2008) published the full experimental data and methodology used to calculate the results reported by Coleman et al. (2003) along with a re-evaluation of this result using an improved statistical treatment. Using this treatment a much more constraint experimental isotope fractionation of −14.94 ± 0.15 ‰ was concluded upon. On the basis of these results a hypothetical model was proposed for the biochemical control of the chlorine isotope fractionation induced by microbial perchlorate reduction. As the calculated equilibrium fractionation between perchlorate and chloride is much larger than the observed fractionation during microbial reduction it is concluded that the microbial reaction is not occurring at isotope equilibrium between chloride and perchlorate. Ader et al. (2008) however concluded that the observed fractionation is about equal to the expected fractionation between perchlorate and a hypothetical chlorine molecule or radical with oxidation state +VI. They hypothesise that this step is in thermodynamic equilibrium and is the rate determining step in the reduction reaction, while the following steps (until the formation of chloride) are not in thermodynamic equilibrium with the result that they do not show isotope fractionation.

References

Ader M, Coleman ML, Doyle SP, Stroud M, Wakelin D (2001) Methods for the stable isotopic analysis of chlorine in chlorate and perchlorate compounds. Anal Chem 73:4946–4950

Ader M, Chaudhuri S, Coates JD, Coleman M (2008) Microbial perchlorate reduction: a precise laboratory determination of the chlorine isotope fractionation and its possible biochemical basis. Earth Planet Sci Lett 269:604–612

Brejneva N, Roginsky S, Schilinsky A (1936) Methodology of the introduction of radioactive halogens to organic molecules. Acta Physicochemical URSS 7:549–574

Bruce RA, Achenbach LA, Coates JD (1999) Reduction of (per)chlorate by a novel organism isolated from a paper mill waste. Environ Microbiol 1:319–331

Coates JD, Michaelidou U, Bruce RA, O'Connor SM, Crespi JN, Achenbach LA (1999) The ubiquity and diversity of dissimilatory (per)chlorate-reducing bacteria. Appl Environ Microbiol 65:5234–5241

Coleman ML, Ader M, Chaudhuri S, Coates JD (2003) Microbial isotopic fractionation of perchlorate chlorine. Appl Environ Microbiol 69:4997–5000

Czarnacki M, Hałas S (2012) Isotope fractionation in aqua-gas systems: Cl_2–HCl–Cl–, Br 2-HBr–Br- and H_2S–S_2–. Isot Environ Health Stud 48:55–64

Dodgen HW, Libby WF (1949) The exchange reaction between the hydrogen halides and the halogens in the gaseous state. J Chem Phys 17:951–957

Ericksen GE (1981) Geology and origin of the Chilean nitrate deposits. USGS Prof Paper 1188:37 pp

Giunta T, Labadi J, Eggenkamp HGM (2013) Experimental determination of chlorine isotope fractionation in Cl_2–$Cl^{-}{}_{aq}$ and $ClOH_{aq}$–$Cl^{-}{}_{aq}$. In: 23th annual V.M. Goldschmidt conference. Firenze, Italy

Hoering TC, Parker PL (1961) The geochemistry of the stable isotopes of chlorine. Geochim Cosmochim Acta 23:186–199

Johnston WH, Libby WF (1951) The exchange reaction between hydrogen chloride and chlorine in the gaseous state. J Amer Chem Soc 73:854–855

Libby WF (1940) Mechanism of the exchange reaction between gaseous bromine and hydrogen bromide. J Chem Phys 8:348

Liberatore LC, Wiig EO (1940) Exchange reaction of gaseous bromine and hydrogen bromide. J Chem Phys 8:165–170

Malmqvist A, Welander T, Moore E, Ternstrom A, Molin G, Stenstrom IM (1994) *Ideonella dechloratans* gen. nov., sp. nov., a new bacterium capable of growing anaerobically with chlorate as an electron acceptor. Syst Appl Microbiol 17:58–64

Michaelidou U, Achenbach LA, Coates JD (2000) Isolation and characterization of two novel (per) chlorate-reducing bacteria from swine waste lagoons. In: Urbansky ED (ed) Perchlorate in the environment. Kluwer Academic/Plenum, New York, pp 271–283

Richet P, Bottinga Y, Javoy M (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. Ann Rev Earth Planet Sci 5:65–110

Rikken G, Kroon A, Van Ginkel C (1996) Transformation of (per)chlorate into chloride by a newly isolated bacterium: reduction and dismutation. Appl Microbiol Biotechnol 45:420–426

Rittenberg D, Urey HC (1934) The thermal decomposition of deuterium iodide. J Amer Chem Soc 56:1885–1889

Rittenberg D, Bleakney W, Urey HC (1934) The equilibrium between the three hydrogens. J Chem Phys 2:48–49

Romanenko VI, Korenkov VN, Kuznetsov SI (1976) Bacterial decomposition of ammonium perchlorate. Mikrobiologiia 45:204–209

Schauble EA, Rossman GR, Taylor HP (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochim Cosmochim Acta 67:3267–3281

Stepanyuk V, Smirnova G, Klyushnikova T, Kanyuk N, Panchenko L, Nogina T, Prima V (1992) New species of the *Acinetobacter* genus *Acinetobacter thermotoleranticus* sp. nov. Microbiology 61:347–356

Sturchio NC, Hatzinger PB, Arkins MD, Suh C, Heraty LJ (2003) Chlorine isotope fractionation during microbial reduction of perchlorate. Environ Sci Technol 37:3859–3863

Sturchio NC, Böhlke JK, Beloso AD Jr, Streger SH, Heraty LJ, Hatzinger PB (2007) Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: laboratory results and implications for forensics and natural attenuation studies. Environ Sci Technol 41:2796–2802

Urbansky ET (1998) Perchlorate chemistry: implications for analysis and remediation. Bioremediat J 2:81–95

Urey HC (1947) The thermodynamic properties of isotopic substances. J Chem Soc 1947:562–581

Urey HC, Greiff LJ (1935) Isotope exchange equilibria. J Chem Soc Amer 57:321–327

Urey HC, Rittenberg D (1933) Some thermodynamic properties of the H^1H^2, H^2H^2 molecules and compounds containing the H^2 atom. J Chem Phys 1:137–143

Isotope Fractionation Related to Organochlorine and Organobromine Compounds

9

9.1 Early Experimental Determination of Chlorine Isotope Fractionation

The first studies in which chlorine isotope variations concerning organic compounds were experimentally determined were done during the 1950s. Probably the earliest of these studies was done by Bartholomew et al. (1954a, b) who studied the chlorine isotope effect in reactions of 2-chloro-2-methyl-propane (*tert*-butyl chloride). In these studies essentially the isotope effect of the reaction

$$C_4H_9Cl \leftrightarrow C_4H_9^{\cdot} + Cl^{\cdot} \quad (9.1)$$

was studied. Two of these reactions were studied. The first of these experiments was done in an ethanol-silver nitrate solution. When this solution is used the back reaction can not take place due to the precipitation of chloride in the form of silver chloride. As a result in the following step the $C_4H_9^{\cdot}$ radical reacts with the solvent to form 2-ethoxy-2-methyl-propane (ethyl-*tert*-butyl-ether)

$$C_4H_9^{\cdot} + C_2H_5OH \rightarrow C_4H_9OC_2H_5 + H^{\cdot} \quad (9.2)$$

The other reaction they studied was the experiment in which 2-chloro-2-methyl-propane was allowed to react with an aqueous alcoholic sodium hydroxide solution. In this solution two possible reactions take place, either the $C_4H_9^{\cdot}$ radical reacts with the solvent to form 2-ethoxy-2-methyl-propane (ethyl-*tert*-butyl-ether) or it reacts with the hydroxide ions so that 2-methyl-2-propanol (*tert*-butanol) is formed. In this experiment the back reaction is prevented by the alkaline nature of the solution as both 2-ethoxy-2-methyl-propane and 2-methyl-2-propanol do not react with chloride in alkaline solutions. Reactions were performed in such a manner that different fractions of the reaction products could be sampled. Chloride was precipitated as silver chloride and converted to chlorine gas for isotope analyses. The observations made on these experiments indicated that the reaction rate k for ^{35}Cl was slightly larger than for ^{37}Cl. The isotope effect for the reaction was determined as $k^{35}/k^{37} = 1.008 \pm 0.002$. This result is in the expected direction as the heavier isotope is bound more firmly to the carbon atom than the lighter isotope and consequently undergoes bond breaking reactions less rapidly.

A second study, unfortunately only described in the PhD dissertation of Nair (1956), was done by Nair and Fry and studied the isotope effect of the reaction between chloride and cyanide ions in aqueous ethanol. They observed a comparable chlorine isotope effect of 1.0074 ± 0.0005. The next, published, experimental study was presented by Hill and Fry (1962) who studied isotope effects in the reactions of benzyl- and substituted benzyl-chlorides with various necleophiles. In these experiments they studied the isotope effects of the substitution of the chlorine atom in aromatic compounds. They determined the chlorine isotope effects for unsubstituted,

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_9,

p-methoxy-, *p*-methyl-, *p*-chloro- and *p*-nitrobenzyl chlorides with each of three nucleophiles: water (plain hydrolysis), cyanide ion and thiosulfate ion. The reactions were done in an aqueous dioxane solution containing 80 % dioxane by weight. The effect of these reactions was that the chloride in the benzenes was substituted with the nucleophiles. The isotope effect of these reactions was determined after precipitating the liberated chloride as silver chloride and subsequent reaction to chloromethane for isotope analysis. During these reactions plots were made that showed the progress of the reaction. Two types of plots were produced. First so called first order plots, showing the decrease of the original chloride bearing aromatic compound. Second order plots were made for the reactions with the cyanide and thiosulphate ions and these plots show the increase of the substituted aromatic compounds. A clear difference exists between reactions where the first order plots show a straight line, and these where they show a clear curvature. On the other hand plots are recognised which have curved first order plots and straight second order plots. The differences between the two types of plots are explained as follows: The first type describes first order kinetics, and the second type describes second order kinetics. Very interesting results were obtained for the isotope effects, which seemed to be related to the type of kinetics that was found. In the experiments where the first order plots were linear the isotope effect k^{35}/k^{37} is close to 1.0078, while in those experiments where the second order plot were linear it is close to 1.0058. Because of these differences it was concluded that there is a relationship between the kinetic behaviour of the reaction and the chlorine isotope effect. From these results it was also concluded that measuring the kinetic isotope effect in these reactions can be a valuable tool in mechanism studies and the understanding of these reactions.

During the 1970s James W. Taylor, who was also responsible for considerable improvements in the analytical methods for both chlorine and bromine isotopes (Taylor and Grimsrud 1969; Willey and Taylor 1978), presented several more studies in which chlorine (and even bromine) isotope effects were studied (Grimsrud and Taylor 1970; Turnquist et al. 1973; Williams and Taylor 1973, 1974; Graczyk and Taylor 1974; Julian and Taylor 1976; Graczyk et al. 1978; Willey and Taylor 1980). These chlorine isotope studies confirmed the rate of the chlorine isotope effects that were observed in the earlier studies. Depending on the reaction the chlorine kinetic isotope effects are in general somewhere between 1.005 and 1.010. Turnquist et al. (1973) also determined the temperature dependence of the chlorine isotope effects and discovered that they were close to linearly dependent with the reciprocal temperature, and decreased towards higher temperatures. Willey and Taylor (1980) presented the only study in which also bromine isotope effects are examined. They presented the bromine isotope effects for the solvolysis reaction of 2-bromo-2methyl-propane (*tert*-butyl bromide) in methanol and the reaction between bromo-butane (*n*-butyl bromide) and thiophenoxide anion in 0.25 M lithium methoxide at various temperatures. These reactions were chosen so that they were able to compare the results obtained from experiments to determine the bromine isotope effects to the results obtained by Turnquist et al. (1973) who did the chlorine equivalent experiments of these reactions. The results showed that there were considerably smaller bromine isotope effects than chlorine isotope effects. While Turnquist et al. (1973) found chlorine isotopes effects in the solvolysis reaction of 2-chloro-2methyl-propane of 1.0109 at 10 °C to 1.0095 at 60 °C, the solvolysis reaction of 2-bromo-2methyl-propane varied from 1.00325 at 0 °C to 1.00303 at 40 °C (Willey and Taylor 1980). The reaction of chloro-butane with the thiophenoxide anion yield chlorine isotope effects between 1.0096 at 0 °C and 1.0079 at 60 °C, while the equivalent bromine reactions isotope effects were only 1.00191 at −10 °C to 1.00158 at 40 °C (see Fig. 9.1).

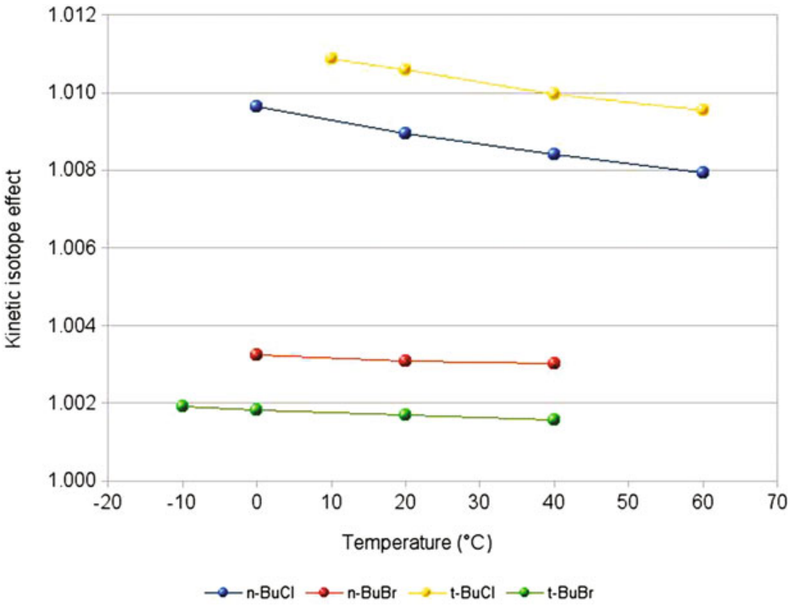

Fig. 9.1 Isotope effects of n-butyl- and tert-butyl-chlorides and -bromides

9.2 Theoretical Estimates on Chlorine Isotope Fractionation Between Organochlorine Molecules and Chloride

Schauble et al. (2003) calculated the reduced partition function ratios for a significant number of organochlorine compounds that can be used to calculate the theoretical isotope fractionation between two molecules in equilibrium. These data were all for species which are in principle in the gaseous state but it gives a good impression what size of fractionation can be expected. Czarnacki and Hałas (2012) also calculated the reduced partition function ratios for the aqueous chloride ion at various temperatures. These data can be combined to estimate equilibrium fractionation between organochlorine compounds and chloride in solution. The data calculated by Schauble et al. (2003) are of considerable interest as they indicate very clearly that isotope fractionation between organochlorine compounds and chloride (either as aqueous, dissolved chloride or as hydrogen chloride gas) can be relatively large (several ‰), but not as large as the equilibrium fractionation between chloride and perchlorates. When data calculated by Schauble et al. (2003) for organic molecules and Czarnacki and Hałas (2012) for aqueous chloride are combined an equilibrium fractionation of about 8 ‰ at 0 °C, 7 ‰ at 25 °C and 4.5 ‰ at 100 °C between these two phases (organochlorine and aqueous chloride) is expected. The calculations from Schauble et al. (2003) indicate that larger fractionation factors will be observed for molecules that contain more chloride atoms in them such as perchloroethylene as compared to trichloroethylene and tetrachloromethane as compared to chloromethane.

9.3 Modern Experimental Determination of Chlorine Isotope Fractionation in Organic Compounds

After the first attempts to analyse the stable chlorine isotope composition of organochlorine compounds of environmental and geological interest (Van Warmerdam et al. 1995; Holt et al. 1997; Jendrzejewski et al. 1997) research was initiated to extract organochlorine compounds from environmental samples (Sturchio et al. 1998; Holt et al. 2001). In the same period more studies on chemical fractionation were published while also the first studies on microbiological reduction of chlorine from organochlorine compounds were published.

9.3.1 Chemical Fractionation Studies

In their study on a more convenient (albeit much less precise) method to analyse the chlorine leaving group kinetic isotope effect for the S_N2 reduction of benzyl chloride to toluene by sodium borohydride in dimethyl suphoxide (DMSO) at 30 °C, equivalent to the studies by Hill and Fry (1962) and the group around J.W. Taylor, Westaway et al. (1998) determined the fractionation both by analysing the chlorine isotope composition with the chloromethane method and by fast atom bombardment mass spectrometry. They observed that the results of the isotope effect measurements from this reaction was within error equal at about 1.008 for both methods (this value is equivalent to the value obtained by Hill and Fry (1962), but with large differences in precision between the two methods (see also Sect. 4.2.9).

More recently Audí-Miró et al. (2013) studied the effectiveness of the degradation of chlorinated ethenes by zero-valent iron. Zero-valent iron degradation of chlorinated ethenes is an efficient way to remove these compounds from contaminated sites through reductive dechlorination. The advantage to microbial degradation is twofold. It is more efficient so that toxic intermediates such as vinyl chloride do not accumulate in the environment while it also operates a second reductive pathway (vicinal β-dichloroelimination) during which two chlorine atoms are split off the chlorinated ethenes rapidly leading to harmless products such as ethene and ethane (Arnold and Roberts 2000; Liu et al. 2006; Elsner et al. 2008). Audí-Miró et al. (2013) determined both the chlorine and the carbon isotope fractionation during this process. During this process the apparent kinetic isotope effect for the chlorine isotopes was 1.008 ± 0.001 for trichloroethene and 1.013 ± 0.002 for *cis*-dichloroethene. Measuring both chlorine and carbon isotopes showed interesting results especially when the data were compared with the data obtained by Abe et al. (2009) for the reduction of *cis*-dichloroethene. While the slope in the δ^{37}Cl versus δ^{13}C plot for the abiotic reduction with zero-valent iron obtained by Audí-Miró et al. (2013) was 3.1 ± 0.2 Abe et al. (2009) found a slope of 11.4 ± 0.6 when they reduced *cis*-dichloroethene through microbial reduction with the mixed culture KB-1, a slope that is almost four times as large. This observation was a clear indication that fundamentally different chemical processes are in effect between the two types of dechlorination.

9.3.2 Thermal Decomposition of 1,2-Dichloroethane in Air

One of the first studies in which attempts were made to use chlorine isotope variations to solve environmental problems concerned the thermal decomposition of 1,2-dichloroethane in air. 1,2-dichloroethane was used as an additive to leaded car fuel and at temperatures from about 300 °C it starts to lose its chlorine atoms. Baumann and Heumann (1988) set up experiments to estimate the chlorine isotope fractionation during this decomposition. In their experiments they heated 1,2-dichloroethane in air to a temperature of about 300 °C en collected the first chloride that escaped from it. They analysed the chlorine isotope composition of the liberated chloride and found that its isotope composition was 2–3 ‰ lighter than that of the original 1,2-dichloroethane. At this temperature the decomposition only just started and only between 0.5 and 5 % of the 1,2-dichloroethane was decomposed. Baumann and Heumann (1988) explained their results by the fact that the heavier isotopes is bound more strongly than the lighter molecule so that the lighter isotope escapes more easily from these molecules during thermal decomposition.

9.3.3 Chlorine Isotope Fractionation Induced by Microbially Activity

Several microbes are able to either produce or decompose organohalogen compounds. Especially the formation of halomethanes from fungi (Harper 1985, 1994; Harper et al. 1988) has been studied well and currently something like 3700 halogen containing chemicals are known to be produced in nature (Gribble 2010). The organic cycle of chlorine is very well reviewed by Öberg (2002) who described the many paradoxes when organochlorine compounds in nature are considered.

9.3.3.1 Chlorine Isotope Effects During Microbially Induced Organochlorine Compound Production

Several organochlorine compounds are known to be produced in nature. To examine the isotope fractionation during these processes Reddy et al. (2002) determined the chlorine isotope effects during the enzyme catalysed chlorination of 1,3,5-trimethoxybenzene and 3,5-dimethylphenol. They actually extracted the catalyst Fe(III)-heme-chloroperoxidase from the fungus *Caldariomyces fumago* and treated this with either 1,3,5-trimothoxybenzene or 3,5-dimethylphenol, potassium chloride and hydrogen peroxide in a citrate/phosphate buffer (McIlvaine 1921) at pH 3. The potassium chloride used in these reactions had a known δ^{37}Cl of −0.76 ± 0.07 ‰. It was found that the 1,3,5-trimethoxybenzene was almost fully dichlorinated and its δ^{37}Cl was observed to be −12.06 ± 0.18 ‰. The 3,5-dimethylphenol was either trichlorinated (about 75 % of it) or dichlorinated (about 25 % of it) and the bulk δ^{37}Cl of this mixture was −11.08 ± 0.08 ‰. These results indicated that ^{35}Cl was preferentially incorporated in the substrate, and that the isotope fractionation of this process is rather large. As Reddy et al. (2002) indicated that anthropogenic chlorinated organic compounds have δ^{37}Cl values which are mostly between −5.1 and +1.2 ‰ (Reddy et al. 2000, 2001; Drenzek et al. 2002) natural and anthropogenic chlorinated organic compounds should be easily distinguishable in nature due to the much lower δ^{37}Cl values of natural chlorinated organic compounds that were expected to have values between −4 and −10 ‰ as compared to anthropogenic compounds which would have values close to 0 ‰.

The results of this study were partly confirmed by Aeppli et al. (2013b) who studied the chlorine isotope fractionation during two important pathways for enzymatic natural halogenation: chlorination by chloroperoxidase and flavin-dependent halogenases. Of these chloroperoxidase chlorination showed a very large fractionation of −12.6 ± 0.9 ‰ which is comparable to the results obtained by Reddy et al. (2002). On the other hand flavin-dependent halogenases showed no significant fractionation with a value of −0.3 ± 0.6 ‰. This large variation is attributed to the largely different reaction mechanisms employed by these enzymes. Aeppli et al. (2013b) also showed that the δ^{37}Cl in bulk organochlorine compound mixtures extracted from boreal forest soils were only slightly depleted in ^{37}Cl relative to inorganic chlorine. This showed to be in contrast to previous suggestions (Reddy et al. 2002) that chloroperoxidase chlorination plays a key role in production of soil chlorinated organic compounds. Aeppli et al. (2013b) conclude that this observation points to the additional involvement of either other chlorination pathways, or that dechlorination of naturally produced chlorinated organic compounds can neutralize δ^{37}Cl shifts caused by chloroperoxidase chlorination.

9.3.3.2 Fractionation of Chlorine During Microbial Decomposition of Organochlorine Compounds

During bacterial dehalogenation of organochlorine compounds bacteria obtain energy through reduction of organically bound chlorine to chloride ions which are then released into the environment. Potentially this process can cause isotope fractionation and this may be used to understand the processes that have taken place since a contamination has appeared. Due to the importance of these processes in remediation of organochlorine contamination in the environment much more attention has been paid to these processes than to the natural chlorination of organic compounds.

One of the first studies in which both chlorine and carbon isotope fractionation as a result of microbial degradation was determined was the experimental study by Heraty et al. (1998) on dichloromethane. They determined both the chlorine and carbon isotope composition in the remaining dichloromethane, and compared it to the original isotope compositions, after it was aerobically degraded by MC8b, a gram-negative methylotrophic bacteria related to *Methylobacterium* or *Ochrobactrum*. The isotope fractionation factor that was determined from this reaction was 0.9962 ± 0.0003 for chlorine and 0.9576 ± 0.0015 for carbon, indicating that both δ^{37}Cl and δ^{13}C of the remaining dichloromethane decreased. These fractionation factors correspond to kinetic isotope effects of 1.0038 and 1.0424 respectively for chlorine and carbon.

Chlorine isotope fractionation during bacterial dehalogenation of dichloromethane was also shown by Zyakun et al. (2007). They determined the isotope fractionation of dichloromethane during microbial dehalogenation by *Methylobacterium dichloromethanicum* and *Albibacter methylovorans*. Contrary to the study by Heraty et al. (1998) they determined the isotope composition of the reacted dichloromethane directly on the dichloromethane molecule that was introduced into the mass spectrometer. To determine isotope fractionation masses 84 ($^{35}Cl_2CH_2$), 86 ($^{35}Cl^{37}ClCH_2$) and 88 ($^{37}Cl_2CH_2$) were compared. The dichloromethane that remained after the reaction had more positive isotope ratios than the original dichloromethane, which is quite the opposite when compared to the experimental observations from Heraty et al. (1998). The increased isotope ratio was explained by the process of diffusion of isotopically lighter dichloromethane through the cell walls of the bacteria so that the residual dichloromethane ends up being more positive. Considering the strong effect is it not clear if any microbial isotope effect did actually take place during their experiments.

Drenzek et al. (2004) studied the change in chlorine isotope composition during microbial decomposition of 2,3,4,5-tetrachlorobifenyl. During the reaction to 2,3,5-trichlorobifenyl the isotope composition of the 2,3,4,5-tetrachlorobifenyl did not change, even after 90 % of the original amount had reacted. Assuming that other processes would fractionate the chlorine isotope composition it was concluded that biological activity could be discriminated against other isotope transformation processes.

Abe et al. (2009) determined chlorine and carbon isotope fractionation during both aerobic and reductive dechlorination of vinyl chloride and *cis*-dichloroethene. Their results showed that in the case of aerobic oxidation there were very different isotope enrichment factors for carbon and chlorine isotopes. In the case of carbon isotopes they found enrichment factors of −7.2 ‰ for vinyl chloride and −8.5 ‰ for *cis*-dichloroethene, while both compounds showed only an isotope enrichment factor of −0.3 ‰ for chlorine isotopes. In the case of reductive dechlorination the carbon isotope enrichment factors were much larger with values of −25.2 ‰ for vinyl chloride and −18.5 ‰ for *cis*-dichloroethene. The chlorine isotope enrichment factors were also larger than in the case of aerobic oxidation with values of −1.8 ‰ for vinyl chloride and −1.5 ‰ for *cis*-dichloroethene. Abe et al. (2009) concluded that these values were less than expected for a primary chlorine isotope effect and these data suggested that no cleavage of C–Cl bonds takes place during the initial rate-limiting step. Interestingly these data show a very different slope in the δ^{37}Cl versus δ^{13}C plot for *cis*-dichloroethene compared to the slope measured by Audí-Miró et al. (2013) in their abiotic reduction experiments with zero valent iron, which made the latter conclude that during biotic and abiotic dechlorination very different dehalogenation pathways take place.

In a study on the potential microbial (fungal) degradation of 2,4,6-trichlorophenol Aeppli et al. (2013a) determined the chlorine and carbon isotope fractionation that is the result of this reaction. During this reaction 2,4,6-trichlorophenol is oxidised, using the enzyme chloroperoxidase, extracted from the fungus *Caldariomyces fumago*, to 2,6-dichloro-*para*-benzoquinone and a chloride ion. It was observed that during the reaction the remaining, unreacted 2,4,6-trichlorophenol increased in δ^{37}Cl and that it followed a very good Rayleigh fractionation curve. From that curve it could be calculated that the δ^{37}Cl values of the liberated chloride, which were unfortunately not determined in this experiment, would be 2.1 ± 0.4‰ lower than that of the 2,4,6-trichlorophenol. This value would agree to the value of the apparent kinetic isotope effect of 1.0021 ± 0.0004. Interestingly it was concluded that the δ^{37}Cl of the reaction product 2,6-dichloro-*para*-benzoquinone would be constant and equal to the original δ^{37}Cl at the beginning of the reaction. The reason for this is that the two chlorine atoms at the unreactive 2,4,6-trichlorophenol position preserve the original δ^{37}Cl, similar to the trichloroethene-to-cis-dichloroethene hydrogenolysis as determined by Hunkeler et al. (2009). Unfortunately Aeppli et al. (2013a) were unable to determine the δ^{37}Cl of the 2,6-dichloro-*para*-benzoquinone due to the instability of this compound, so that this behaviour, the constancy of its δ^{37}Cl, could not be verified.

The maximum values that could be expected for the chlorine kinetic isotope effects during dechlorination of organic compounds were evaluated by Świderek and Paneth (2012). According to experiments done by Streitwieser et al. (1958) on hydrogen isotopes in cyclopentyl tosylates it could be calculated that the maximum chlorine kinetic isotope effects would be 1.013. These values appeared too low when it was shown experimentally that during reduction of perchlorate (although this is no organic ion) the chlorine kinetic isotope effect is in the range of 1.015–1.017 (Coleman et al. 2003; Sturchio et al. 2003). Earlier Paneth (1992) calculated that that the maximum kinetic isotope effect could theoretically be as large as 1.019 on the basis of BEBOVIB calculations (Sims and Lewis 1985). Using this BEBOVIB methodology Burton et al. (1977) calculated that the chlorine kinetic isotope effect in the ionisation reaction of *tert*-butyl chloride could be as large as 1.0256, which was in serious disagreement with the experimentally determined value of 1.011 (Turnquist et al. 1973). Świderek and Paneth (2012) made new calculations which indicated that chlorine kinetic isotope effects in dehalogenation reactions from heavy compounds containing at least three chlorine atoms could show that these isotope effects would be as large as 1.025. They conclude that these large kinetic isotope effects can be associated with reactions in which chlorine is passed between two heavy atoms and is shielded from interactions with solvent molecules.

The experimental results that are obtained in these studies suggest that chlorine isotope fractionation during microbial degradation of organochlorine compounds is very much dependant of the reaction path. The data obtained so far show that a reaction can either induce isotope fractionation, or show no fractionation at al. The processes that take place during degradation of chlorinated organic compounds are slowly better understood and it is important to realise that the chlorine isotope effects are dependent on the type and the pathway of the reactions that take place.

9.3.4 Kinetic Fractionation of Organochlorine Compounds in the Environment

Chlorinated organic compounds behave rather complex when they are present in the environment. Apart from fractionation that is caused by chemical or microbiological decomposition they can also fractionate kinetically in circumstances such as evaporation from or diffusion through a system. Although normally considered minor causes for fractionation compared to the decomposition of chlorinated organic compounds in certain circumstances the variations it cause can so be remarkable that the effects are described here.

9.3.4.1 Evaporation of Organochlorine Compounds

Already very early isotope studies on the distillation process of chloroform ($CHCl_3$) and carbon terachloride (CCl_4) in which both carbon and chlorine isotope compositions were studied indicated that while ^{13}C is enriched in the distillate, ^{37}Cl is enriched in the residue (Baertschi et al. 1953; Baertschi and Kuhn 1957). Interestingly it was concluded that there already were indications as early as 1945 that ^{35}Cl was enriched in the distillate using density measurements, spectroscopic methods and nuclear reactions (Wieland 1943; Alder [unpublished], in Baertschi et al. 1953). Even earlier attempts to measure this fractionation (Grimm 1929; Rank and Kargarise 1951) were unable to indicate isotope fractionation due to the (density) methods used. Baertschi et al. (1953) discovered that the same characteristics were also found for oxygen isotopes and suggested that the origin of this effect is that perhaps a molecule with a heavier central atom exhibits a somewhat higher vapour pressure than the molecule with the lighter isotope as the central atom. These results appear to show the same effect as comparable experiments with boron trichloride that were applied by Green and Martin (1952). In this last study only the isotope fractionation of the central, boron, atom was determined and not that of the chlorine atoms.

The results obtained with chloroform and carbon tetrachloride by Baertschi et al. (1953) were confirmed by the experiments Huang et al. (1999) applied on chlorinated ethanes. They determined the chlorine isotope fractionation during evaporation of chlorinated aliphatic hydrocarbons. They evaporated two different solvents (trichloroethene [TCE] and dichloromethane [DCM]) at room temperature (24 ± 1 °C) and measured both the carbon and chlorine isotope composition of the fraction remaining. Both solvents showed the same characteristics during evaporation. Carbon and chlorine isotopes changed during evaporation according to a Rayleigh fractionation. Interestingly the $\delta^{37}Cl$ of the residue was more positive than the original solvent while the $\delta^{13}C$ in the residue decreased during evaporation. Fractionation factors for chlorine isotopes are 0.99818 ± 0.00022 for TCE and 0.99952 ± 0.00006 for DCE and for carbon isotopes 1.00031 ± 0.00004 for TCE and 1.00065 ± 0.00002 for DCE. The mechanism for this inverse isotope fractionation was not well understood. The results of the chlorine and carbon isotope fractionation found in this study could be compared to the results obtained by Heraty et al. (1998) in experiments of microbial degradation of dichloromethane. In this study both $\delta^{37}Cl$ and $\delta^{13}C$ of the remaining solvent (dichloromethane) decreased and Huang et al. (1999) concluded that the relationship between $\delta^{37}Cl$ and $\delta^{13}C$ in chlorinated aliphatic hydrocarbons can be used to distinguish evaporation from biodegradation in contaminated systems.

9.3.4.2 Fractionation Due to Diffusion of Chlorinated Organic Compounds in the Environment

Although it would be expected that organochlorine compounds could fractionate due to diffusion in the environment this effect, according to Schmidt et al. (2004), did not significantly influence the isotopic composition. This effect may be limited as the mass difference between isotopologues of many organo-chlorine compounds is relatively small. In these cases isotope effects due to fractionation of the compounds may easily be masked by chlorine isotope effects of dehalogenation of the compounds (e.g. Lewandowicz et al. 2001).

Jeannottat and Hunkeler (2012) studied the chlorine and carbon isotope fractionation during volatilisation and diffusive transport of trichloroethene in the unsaturated zone. They found that the different processes produced very distinct isotope effects for carbon and chlorine isotopes which potentially made it possible to distinguish between younger and older organo-chlorine contaminated zones and between the processes that were responsible for the fractionation that occurred during these processes. Unlike the studies cited above Jeannottat and Hunkeler (2012) observed a considerable chlorine isotope fractionation during diffusion controlled evaporation of trichloroethene from a sand column of −1.39 ± 0.06 ‰. This is considerable larger than the carbon isotope fractionation in the same process which was only +0.10 ± 0.05 ‰, effectively insignificant. This difference was explained by the different effects that apply to chlorine and carbon isotopes during the processes of vaporising the non-aqueous phase liquid and normal diffusion. In the case of carbon the isotope effect for the two processes are opposite, thus showing a heavier vapour than the liquid, cancelling out the negative isotope effect caused by diffusion, while in the case of chlorine the vapour is lighter in the case of non-aqueous phase liquid-vapour equilibrium so that the effect of normal diffusion is even cumulated.

9.4 Isotope Fractionation of Bromine in Organic Compounds

Of all organobromine compounds bromomethane (CH_3Br) is by far the most important. This compound has the highest concentration of all long living organobromine compounds in the atmosphere (Schauffler et al. 1993) and is known to originate from both natural and anthropogenic sources. As bromomethane is about 50 times as efficient as chloromethane to break down atmospheric ozone even the small concentrations that are present in the stratosphere could be responsible for as much as 5 % of the global loss of stratospheric ozone (WMO 1994; UNEP 1992). For that reason production of bromomethane was largely prohibited under the Montreal Protocol (Cincinelli et al. 2012). Considering however the fact that it is also produced naturally it is very important to understand the origin of bromomethane in the stratosphere and several isotope studies have been conducted to help understand its origin. These studies however concerned only the carbon and not the bromine isotope variations of bromomethane (Bill et al. 2002a, b, 2004). Considering the fact that currently only a few methods have been developed to analyse bromine isotopes in organic compounds (Sylva et al. 2007; Gelman and Halicz 2010; Holmstrand et al. 2010; Hitzfeld et al. 2011) it is perhaps not surprising that only a very small number of studies have been conducted to determine bromine isotope fractionation during production or decomposition of these organic compounds since the early research by Willey and Taylor (1980).

The bromine isotope composition of atmospheric bromomethane has been determined for the first time by Horst et al. (2013). Their data indicated more negative δ^{81}Br values in subarctic samples from the north of Sweden as compared to more positive values in the Stockholm area. The bromomethane concentration in the subarctic samples were two to three times lower than the Stockholm samples, and it was concluded that the Stockholm samples were contaminated with industrial bromomethane. More details of this study will be given in Sect 10.5.2.

The first attempt to estimate the isotope difference between natural and anthropogenic organobromine compounds was done by Carrizo et al. (2011). Although this study did not measure the actual fractionation during formation of a compound from its source material it compared industrially and naturally produced 2,4-bromophenol. They found that the δ^{81}Br value for an industrially produced 2,4-dibromophenol sample was −1.1 ± 0.9 ‰ (1 SD) while a naturally produced 2,4-dibromophenol sample had a δ^{81}Br of +0.2 ± 1.6 ‰ (1 SD). This difference indicated a statistically significant difference between the two samples of about 1.4 ‰. They concluded that different pathways of formation of these compounds lead to different isotope compositions, implicating that significant isotope fractionation during their formation exist.

Horst (2013) and Horst et al. (2014) attempted to determine isotope fractionation of bromomethane during its release from plant matter. They investigated bromomethane formed from pectin (fortified with KBr) and from *Salicornia fruticosa*, a halophytic plant with a high salt content. They found that the bromomethane released from both pectin and *Salicornia fruticosa* showed δ^{81}Br values that were about 2 ‰ lower than the original KBr suggesting a fractionation of this order during the formation of bromomethane.

During photolysis of brominated phenols both bromine and carbon isotopes fractionate. Zakon et al. (2013) observed that bromine isotope fractionation, with values up to +5.1 ‰ was opposite in sign to carbon isotope fractionation with values between −12.6 and −23.4 ‰. These results may be attributed to the coexistence of both mass-dependent and mass-independent isotope fractionation of the carbon-bromine bond cleavage. These effects were found for different bromophenols that were dissolved in ethanol, but not in water. In water this effect was only found for 4-bromophenol, while in the case of 2-bromophenol no fractionation was observed and in the case of 3-bromophenol only fractionation of bromine was observed. It was suggested that these different results might be explained in the case of 2-bromophenol with the fact that carbon-bromine bond cleavage is not a rate-limiting step in the reaction, and in the case for 3-bromophenol that a mass independent fractionation effect takes place.

References

Abe Y, Aravena R, Zopfi J, Shouakar-Stash O, Cox E, Roberts JD, Hunkeler D (2009) Carbon and chlorine isotope fractioantion during aerobic oxidation and reductive dechlorination of vinyl chlorde and cis-1,2-dichloroethane. Environ Sci Technol 43:101–107

Aeppli C, Tysklind M, Holmstrand H, Gustafsson Ö (2013a) Use of Cl and C isotopic fractionation to identify degradation and sources of polychlorinated phenols: mechanistic study and field application. Environ Sci Technol 47:6864–6871

Aeppli C, Bastviken D, Andersson P, Gustafsson Ö (2013b) Chlorine isotope effects and composition of naturally produced organochlorines from chloroperoxidases, flavin-dependent halogenases, and in forest soil. Environ Sci Technol 47:790–797

Arnold WA, Roberts AL (2000) Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. Environ Sci Technol 34:1794–1805

Audí-Miró C, Cretnik S, Otero N, Palau J, Shouakar-Stash O, Soler A, Elsner M (2013) Cl and C isotope analysis to assess the effectveness of chlorinated ethene degradation by zero-valent iron: Evidence from dual element and product isotope values. Appl Geochem 32:173–175

Baertschi P, Kuhn W (1957) Dampfdruckunterschiede isotoper Verbindungen (Infrarot-Anteil der Dispersionswechselwirkung als Ursache für grössere Flüchtigkeit der schweren Molekelspezies). Helv Chim Acta 40:1084–1103

Baertschi P, Kuhn W, Kuhn H (1953) Fractionation of isotopes by distillation of some organic substances. Nature 171:1018–1020

Bartholomew RM, Brown F, Lounsbury M (1954a) Chlorine isotope effect. Nature 174:133

Bartholomew RM, Brown F, Lounsbury M (1954b) Chlorine isotope effect in reactions of *tert*-butyl chloride. Canadian J Chem 32:979–983

Baumann H, Heumann KG (1988) Chlorisotopenseparation als möglicher Indikator für Emissionsquellen chlorhaltiger Verbindungen. Fresenius Z Anal Chem 330:637–638

Bill M, Rhew RC, Weiss RF, Goldstein AH (2002a) Carbon isotope ratios of methyl bromide and methyl chloride emitted from a coastal salt marsh. Geophys Res Lett 29: doi: 10.1029/2001GL012946

Bill M, Miller LG, Goldstein AH (2002b) Carbon isotope fractionation of methyl bromide during argricultural soil fumigations. Biogeochemistry 60:181–190

Bill M, Conrad ME, Goldstein AH (2004) Stable carbon isotope composition of atmospheric methylbromide. Geophys Res Lett 31:L04109

Burton GW, Sims LB, Wilson JC, Fry A (1977) Calculation of ^{14}C, ^{37}Cl, and deuterium kinetic isotope effects in solvolysis of tert-butyl chloride. J Amer Chem Soc 99:3371–3379

Carrizo D, Unger M, Holmstrand H, Andersson P, Gustafsson Ö, Sylva SP, Reddy CM (2011) Compound-specific bromine isotope compositions of one natural and six industrially synthesised organobromine substances. Environ Chem 8:127–132

Cincinelli A, Pieri F, Zhang Y, Seed M, Jone KC (2012) Compound specific isotope analysis (CSIA) for chlorine and bromine: a review of techniques and applications to elucidate environmental sources and processes. Environ Poll 169:112–127

Coleman ML, Ader M, Chaudhuri S, Coates JD (2003) Microbial isotopic fractionation of perchlorate chlorine. Appl Environ Microbiol 69:4997–5000

Czarnacki M, Hałas S (2012) Isotope fractionation in aqua-gas systems: Cl_2-HCl-Cl-, Br_2-HBr-Br- and H_2S-S^{2-}. Isot Environ Health Stud 48:55–64

Drenzek NJ, Tarr C, Eglinton TI, Heraty L, Sturchio NC (2002) Stable chlorine and carbon isotopic compositions of selected semi-volatile organochlorine compounds. Org Chem 33:437–444

Drenzek NJ, Eglinton TI, Wirsen CO, Sturchio NC, Heraty LJ, Sowers KR, Wu QZ, May HD, Reddy CM (2004) Invariant chlorine isotopic signatures during microbial PCB reductive dechlorination. Environ Poll 128:445–448

Elsner M, Chartrand M, Vanstone M, Lacrampe-Couloume G, Lollar BS (2008) Identifying abiotic chlorinated ethene degradation: characteristic isotope patterns in reaction products with nanoscale zero-valent iron. Environ Sci Technol 42:5963–5970

Gelman F, Halicz L (2010) High precision determination of bromine isotope ratio by GC-MC-ICPMS. Int J Mass Spectrom 289:167–169

Graczyk DG, Taylor JW (1974) Chlorine kinetic isotope-effects in nucleophilic-substitution reactions—support for ion-pairs mechanism in reactions of p-methoxy-benzyl chloride in 70 % aqueous acetone. J Amer Chem Soc 96:3255–3261

Graczyk DG, Taylor JW, Turnquist CR (1978) Use of chlorine kinetic isotope effects for evaluating ion-pairing in nucleophilic displacements at saturated carbon. J Amer Chem Soc 100:7333–7339

Green M, Martin GR (1952) The vapour pressure of isotopic substances. 1. Boron trichloride. Trans Farad Soc 48:416–421

Gribble GW (2010) Naturally occurring organohalogen compounds—a comprehensive update. Progress in the chemistry of organic natural products 91. Springer, Berlin

Grimm HG (1929) Tests on the determination of vapour differences of isotopes through fractional distillation. I. Distallation testing on CCl_4. Z Phys Chem 2:181–199

Grimsrud EP, Taylor JW (1970) Chlorine kinetic isotope effects in nucleophilic displacements at a saturated carbon. J Amer Chem Soc 92:739–741

Harper DB (1985) Halomethane from halide ion—a highly efficient fungal conversion of environmental significance. Nature 315:55–57

Harper DB (1994) Biosynthesis of halogenated methanes. Biochem Soc Trans 22:1007–1011

Harper DB, Kennedy J, Hamilton JTG (1988) Chlromethane biosynthesis in poroid fungi. Phytochem 27:3147–3153

Heraty LJ, Fuller ME, Huang L, Abrajano T Jr, Sturchio NC (1998) Isotope fractionation of carbon and chlorine by microbial degradation of dichloromethane. Org Geochem 30:793–799

Hill JW, Fry A (1962) Chlorine isotope effects in the reactions of benzyl and substituted benzyl chlorides with various nucleophiles. J Amer Chem Soc 84:2763–2769

Hitzfeld KL, Gehre M, Richnow HH (2011) A novel online approach to the determination of isotopic ratios for organically bound chlorine, bromine and sulphur. Rapid Commun Mass Spectr 25:3114–3122

Holmstrand H, Unger M, Carrizo D, Andersson P, Gustafsson Ö (2010) Compound-specific bromine isotope analysis of brominated diphenyl ethers using GC-ICP-multicollector-MS. Rapid Commun Mass Spectr 24:2135–2142

Holt BD, Sturchio NC, Abrajano TA, Heraty LJ (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. Anal Chem 69:2727–2733

Holt BD, Heraty LJ, Sturchio NC (2001) Extraction of chlorinated aliphatic hydrocarbons from groundwater at micromolar concentrations for isotopic analysis of chlorine. Environ Poll 113:263–269

Horst A (2013) Stable bromine isotopic composition of methyl bromide. Method development and applications. Ph.D. thesis Stockholm University

Horst A, Thornton BJ, Holmstrand H, Andersson P, Crill PM, Gustafsson Ö (2013) Stable bromine isotopic composition of atmospheric CH_3Br. Tellus Ser B—Chem Phys Meteor 65, no 21040

Horst A, Andersson P, Thornton BJ, Holmstrand H, Wishkerman A, Keppler F, Gustafsson Ö (2014) Stable bromine isotopic composition of methyl bromide released from plant matter. Geochim Cosmochim Acta 125:186–195

Huang L, Sturchio NC, Abrajano T, Heraty LJ, Holt BD (1999) Carbon and chlorine isotope fractionation of chlorinated aliphatic hydrocarbons by evaporation. Org Geochem 30:777–785

Hunkeler D, Van Breukelen BM, Elsner M (2009) Modelling chlorine isotope trends during sequential transformation of chlorinated ethenes. Environ Sci Technol 43:6750–6756

Jeannottat S, Hunkeler D (2012) Chlorine and carbon isotopes fractionation during volatilization and diffusive transport of trichloroethane in the unsaturated zone. Env Sci Technol 46:3169–3176

Jendrzejewski N, Eggenkamp HGM, Coleman ML (1997) Sequential determination of chlorine and carbon isotopic composition in single microliter samples of chlorinated solvent. Anal Chem 69:4259–4266

Julian RL, Taylor JW (1976) Evaluation of possible S_N2 transition-state models for reaction of n-butyl chloride using chlorine kinetic isotope effects. J Amer Chem Soc 98:5238–5248

Lewandowicz A, Rudzinski J, Tronstad L, Widersten M, Ryberg P, Matsson O, Paneth P (2001) Chlorine kinetic isotope effects on the haloalkane dehalogenase reaction. J Am Chem Soc 123:4550–4555

Liu CC, Tseng DH, Wang CY (2006) Effects of ferrous iron on the reductive dechlorination of trichloroethylene by zero-valent iron. J Hazard Mater B136:706–713

McIlvaine TC (1921) A buffer solution for colorimetric comparison. J Biol Chem 49:183–186

Nair PM (1956) PhD dissertation, University of Arkansas

Öberg G (2002) The natural chlorine cycle—fitting the scattered pieces. Appl Microbiol Biotech 58:565–581

Paneth P (1992) In isotopes in organic chemistry. In: Buncel E, Saunders WH (eds). Elsevier

Rank DH, Kargarise RE (1951) Vapour pressure of isotopic carbon tetrachlorides. Nature 168:740–741

Reddy CM, Heraty LJ, Holt BD, Sturchio NC, Eglinton T, Drenzek NJ, Xu L, Lake JL, Maruya KA (2000) Stable chlorine isotopic compositions of arochlors and arochlor-contaminated sediments. Environ Sci Technol 34:2866–2870

Reddy CM, Drenzek NJ, Eglinton TI, Heraty LJ, Sturchio NC, Shiner VJ (2001) Environ Sci Pollut Res 9:183

Reddy CM, Xu L, Drenzek NJ, Sturchio NC, Heraty LJ, Kimblin C, Butler A (2002) A chlorine isotope effect for enzyme-catalyzed chlorination. J Amer Chem Soc 124:14526–14527

Schauble EA, Rossman GR, Taylor HP (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochim Cosmochim Acta 67:3267–3281

Schauffler SM, Heidt LE, Pollock WH, Gilpin TM, Vedder JF, Solomon S, Lueb RA, Atlas EL (1993) Measurements of halogenated organic compounds near the tropical tropopause. Geophys Res Lett 20:2567–2570

Schmidt TC, Zwank L, Elsner M, Berg M, Meckenstock RU, Haderlein SB (2004) Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. Anal Bioanal Chem 378:283–300

Sims LB, Lewis ED (1985) In Isotopes in organic chemistry. In: Buncel E, Saunders WH (eds). Elsevier

Streitwieser A, Jagow RH, Fahey RC, Suzuki S (1958) Kinetic isotope effects in the acetolyses of deuterated cyclopentyl tosylates. J Amer Chem Soc 80:2326–2332

Sturchio NC, Clausen JL, Heraty LJ, Huang L, Holt BD, Abrajano TA (1998) Chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer. Env Sci Technol 32:3037–3042

Sturchio NC, Hatzinger PB, Arkins MD, Suh C, Heraty LJ (2003) Chlorine isotope fractionation during microbial reduction of perchlorate. Environ Sci Technol 37:3859–3863

Świderek K, Paneth P (2012) Extending limits of chlorine kinetic isotope effects. J Org Chem 77:5120–5124

Sylva SP, Ball L, Nelson RK, Reddy CM (2007) Compound-specific ^{81}Br/^{79}Br analysis by capillary gas chromatography/multicollector inductively coupled plasma mass spectrometry. Rapid Commun Mass Spectrom 21:3301–3305

Taylor JW, Grimsrud EP (1969) Chlorine isotopic ratios by negative ion mass spectrometry. Anal Chem 41:805–810

Turnquist CR, Taylor JW, Grimsrud EP, Williams RC (1973) Temperature dependence of chlorine kinetic isotope effects for aliphatic chlorides. J Amer Chem Soc 95:4133–4138

UNEP [United Nations Environment Programme] (1992) Methyl bromide: its atmospheric science, technology, and economics (montreal protocol assessment supplement)

Van Warmerdam EM, Frape SK, Aravena R, Drimmie RJ, Flatt H, Cherry JA (1995) Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. Appl Geochem 10:547–552

Westaway KC, Koerner T, Fang YR, Rudziñski J, Paneth P (1998) A new method of determining chlorine kinetic isotope effects. Anal Chem 70:3548–3552

Wieland K (1943) Spektroskopische Bestimmung der Anreicherung eines Chlorisotopen mit minimalen Mengen von Quecksilber(II)-chlorid (Sublimat). Helv Chim Acta 26:1939–1944

Willey JF, Taylor JW (1978) Capacitive integration to produce high precision isotope ratio measurements on methyl chloride and bromide. Anal Chem 50:1930–1933

Willey JF, Taylor JW (1980) Temperature-dependence of bromine kinetic isotope effects for reactions of normal-butyl and *tert*-butyl bromides. J Amer Chem Soc 102:2387–2391

Williams RC, Taylor JW (1973) Chlorine kinetic isotope-effect models. 1. Isotopic dependence in nominal C-Cl stretching vibrations of aliphatic chlorides and vibrational analysis of *tert*-butyl chloride ground-state. J Amer Chem Soc 95:1710–1714

Williams RC, Taylor JW (1974) Chlorine kinetic isotope-effect models. 2. Vibrational analysis and kie calculations of tert-butyl chloride transition-state models. J Amer Chem Soc 96:3721–3726

WMO [World Meteorological Organization] (1994) Scientific assessment of ozone depletion: global ozone research and monitoring project report no 37, Geneva, 1995

Zakon Y, Halicz L, Gelman F (2013) Bromine and carbon isotope effects during photolysis of brominated phenols. Environ Sci Technol 47:14147–14153

Zyakun AM, Firsova YuE, Torgonskaya ML, Doronina NV, Trotsenko YuA (2007) Changes of chlorine isotope composition characterize bacterial dehalogenation of dichloromethane. Appl Biochem Microbiol 43:593–597

Part IV

Natural Chlorine and Bromine Isotope Variations

Natural Variations of Stable Chlorine and Bromine Isotopes on Earth

10

Chlorine and bromine on earth are distributed quite systematically in the large geological reservoirs. Due to their chemical character, both elements are primarily concentrated in the fluid phase of any system and as a consequence, they are highly concentrated in the oceans on earth. The concentrations in rocks and sediments are relatively low, except for evaporites where a considerable part of the chloride and to a lesser extend the bromide that was once stored in the oceans is concentrated (Schilling et al. 1978; Knauth 1998). The main geological reservoirs that can be recognised concerning the distribution of chlorine and bromine are, as already discussed in Sect. 1.1.2, the oceans, the mantle, evaporites, sediment (pore water), the continental crust and the oceanic crust. Although the atmosphere is only a small reservoir the relatively few chlorine isotope measurements of atmospheric chlorine and bromine will be described in this chapter, as atmospheric chlorine and bromine have a considerable influence on environmental processes. In the following sections an overview will be given about our knowledge on chlorine and bromine isotope compositions of the major reservoirs, as well as their variations within these reservoirs. Chlorine isotopes have been studied, at least globally, in most of the reservoirs. The knowledge on bromine isotopes is still very rudimentary, but enough information is available to present some basic information on its distribution on earth.

As the average δ^{37}Cl values of the major reservoirs appear to be relatively close to zero most variations within the reservoirs are either the result of fractionation within the reservoirs or fractionation during transfer between the reservoirs. The main processes that cause fractionation of chlorine and bromine isotopes have been described in Chap. 7. In this chapter I present a number of studies in which variations in natural systems are observed. I will evaluate how these natural variations are interpreted, either in the sense of fractionation in a certain environment or to use the chlorine and bromine isotope compositions as a tracer for the origin of chlorine or bromine in a system.

In the following sections mostly the chlorine isotope distribution and variations will be discussed in fairly large detail. Only if there is published knowledge on the bromine isotope distribution this will also be described.

10.1 The Hydrosphere

Due to the high solubility of most chloride and bromide salts chloride and bromide are heavily concentrated in the hydrosphere. This includes not only the oceans but also sediment formation waters where according to Land (1995) and Knauth (1998) even more chloride and bromide is present than in the oceans (see Chap. 1). As indicated in Table 1.3 42.6 % of all chloride and 58.1 % of all bromide on earth is present in aqueous solution, either in the oceans or in formation waters in sediments.

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_10,

10.1.1 Oceans

10.1.1.1 Chloride

Considering the long residence time of chloride in the oceans (87,000,000 years, Berner and Berner 1987) it was already proposed in early studies (Hoering and Parker 1961) that ocean water might be used as reference standard for chlorine isotope studies. As no studies were done on natural samples which resulted in significant variation before Kaufmann (1984) this standard was not defined, and formally it still is not defined. Although an isotope reference material was available, NIST SRM 975, which was used to define the absolute atomic weight of chlorine (Shields et al. 1962), this was never really used as chlorine reference standard for stable isotope measurements and has been exhausted for some time. It has been replaced with SRM 975a (NIST 2001) which is depleted in δ^{37}Cl relative to SRM 975 by 0.23 ‰. Kaufmann (1984) measured the isotope composition of eight seawater samples from different locations and depths. The standard deviation of 12 measurements of these 8 samples was only 0.06 ‰. As it was also considered that ocean water is probably the ultimate source of most ground water chloride ocean water chloride was selected as the standard for stable chlorine isotope measurements. At this point we have to realise that in this early research from The University of Arizona the main target was to study the chloride cycle in groundwater. Kaufmann (1984) suggested to call this standard SMOC (Standard Mean Ocean Chloride). This name was called a misnomer by Xiao et al. (2002) because actually no formally accepted chlorine isotope ocean water standard exists. Godon et al. (2004a) collected 24 ocean water samples from all major oceans. Most of these waters were collected from the surface of the oceans and relatively close to the coast. Also samples from three depth profiles were analysed. These samples were analysed and all were within 0.1 ‰ of the laboratory reference ocean water standard. From this study it was concluded that there is no need to define a specific international standard for chlorine stable isotope measurements. This conclusion was confirmed again by Liu et al. (2013) who analysed 10 seawater samples taken from different locations along the Chinese coast and found that all samples were within 0.01 ‰ (with a standard deviation of 0.006 ‰) of their seawater standard. As a result of these observations the name SMOC is used by most students of chlorine stable isotopes and refers in their research to their own internal laboratory chloride standard.

A few studies exist however where variations in chlorine isotope compositions in ocean water samples were observed. Shirodkar et al. (2003) measured chlorine isotope isotope profiles at three locations on the Indian Ocean Mid-Oceanic Ridge. At all three locations significant variations in the δ^{37}Cl were found. Surprisingly at all three locations the δ^{37}Cl of surface water was highly positive relative to ISL354, a standard sodium chloride produced from ocean water collected from the Pacific Ocean. Samples from greater depth are more negative, at one station even as negative as −0.53 ‰. This decrease with depth correlates also with the salinity of the water (Fig. 10.1) and it is explained that chlorine isotope variations are caused by evaporation of ocean water as described by Xiao et al. (2000). They observed that δ^{37}Cl values of seawater are regulated by the evaporation to precipitation ratio. They suggest that during evaporation the chloride of the seawater is volatilized as hydrogen chloride, causing enrichment of ^{37}Cl in surface seawater, explaining higher δ^{37}Cl values at the surface.

This effect appears to be confirmed by the study of ocean surface waters that were collected from the upper meter of four major world oceans (Shirodkar et al. 2006). In this study with samples from 51 stations it was observed that ocean water samples show δ^{37}Cl values between −0.76 and +0.74 ‰ relative to ISL354. These variations were related to different air–sea fluxes. A statistical approach using Q mode factor analysis determined four distinct groups of samples in this set. Although slightly different average δ^{37}Cl values were found in each of these four groups they were not significantly different from each

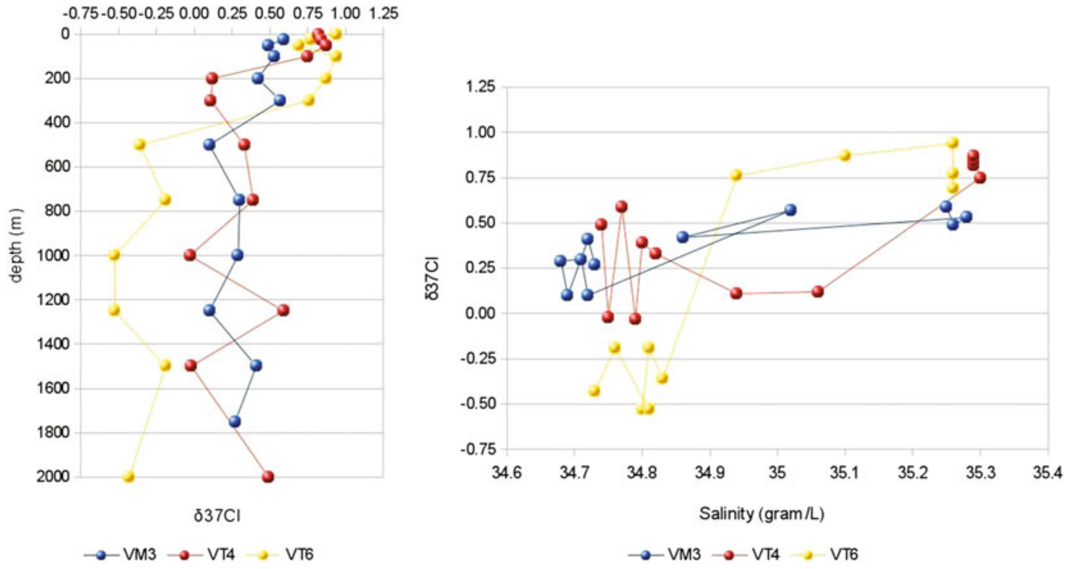

Fig. 10.1 δ^{37}Cl-depth and δ^{37}Cl-salinity diagrams of de data obtained by Shirodkar et al. (2003). In these figures it is visible that apparently the δ^{37}Cl decreases with depth in the Indian Ocean. The relationship between δ^{37}Cl and salinity is related to the fact that salinity in these profiles decreases with depth, just like δ^{37}Cl in these profiles

other. The conclusion of this study was that δ^{37}Cl values of individual ocean water samples are constant, but a defined seawater sample has to be used when it is taken as a reference standard for isotopic analyses. The results from these studies indicate that, although δ^{37}Cl values of ocean water are between +1 and −1 ‰, it is not constant enough to use a general ocean water as standard. This conclusion is opposite to the conclusions reached by Kaufmann (1984), Godon et al. (2004a) and Liu et al. (2013). These results at least indicate that there might be some uncertainty about the constancy of the δ^{37}Cl of the oceans and it might be recommended to compare the ocean water in use as standard in the various laboratories with ISL954 which can be considered homogeneous and can act as fixed zero on the chlorine isotope scale. In spite of this recommendation most laboratories working on chlorine isotopes still work with their own laboratory ocean water standard, and no problems with this policy have been encountered yet. Following this most laboratories are still convinced that the δ^{37}Cl of the oceans are invariable. Unfortunately the samples reported by Shirodkar et al. (2003, 2006) were all measured using the P-TIMS method at the Xining Laboratory, while most other laboratories still work with IRMS techniques. Considering the conflicting conclusions between the results obtained by P-TIMS from just one single laboratory and IRMS analyses from a variety of laboratories it would be very valuable if more interlaboratory comparison would be organised, and it would be especially useful if samples presented in the studies from Shirodkar et al. (2003, 2006) would have been reanalysed in one or more of the laboratories using IRMS techniques.

10.1.1.2 Bromine

As the residence time in the oceans for bromide is even longer than for chloride (130,000,000 years; Broeker and Peng 1982) it is expected, just as for chloride that the bromine isotope composition of the oceans is constant. Unfortunately no larger or interlaboratory comparison study on the bromine isotope composition of the oceans has been done yet, but Du et al. (2013) analysed 5 different seawater samples which were taken from different locations along the coast of China. They observed that the variation between these samples was less than 0.1 ‰,

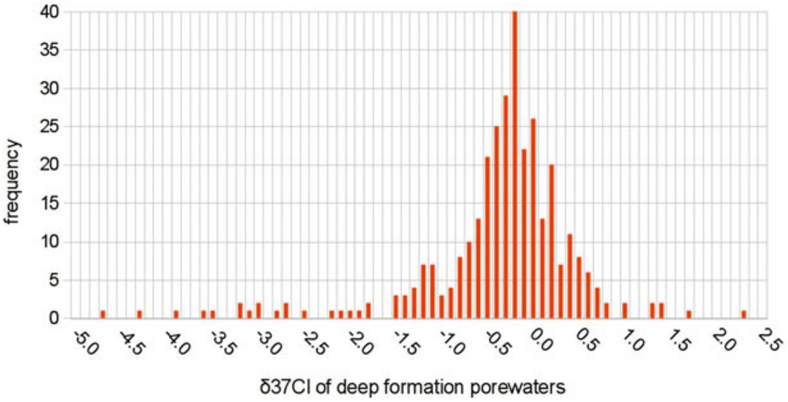

Fig. 10.2 Histogram of 324 δ^{37}Cl values of deep saline formation waters

and their preliminary conclusion was that the bromine isotope composition of the oceans would be, as it is for chlorine, constant so that it could indeed be used as international standard. This standard is still, as an analogue to chlorine, normally called SMOB or Standard Mean Ocean Bromide (Eggenkamp and Coleman 2000).

10.1.2 Sediment Pore Water

Pore water is present in virtually all sedimentary basins. This pore water is, especially at greater depths, mostly saline, indicating that a large amount of chloride and bromide is present in this water. Recent estimates are that the amount of chloride in these pore waters may be even larger than the total amount of chloride in the oceans and more than double the amount of chloride in evaporites at about 330 × 10^{20} g (Land 1995). The origin of all pore water ultimately is from the oceans as it was suggested by Knauth (1998) that before the development of the continental crust, all salt and brine currently found on the continents would have been entirely in the oceans. The composition of the pore waters is changed by chemical processes such as water-rock interaction, salt dissolution, albitization as well as physical processes such as diffusion, ion exchange and ion-filtration and mixing of water bodies with different compositions. During these processes not only the chemical but also the chlorine and bromine isotopic composition of the water can alter considerably.

Table 10.1 Basic statistical characteristics of 324 chlorine and 128 bromine isotope ratio measurements of deep formation waters

	δ^{37}Cl value	δ^{81}Br value
Average	−0.37	+0.57
Standard deviation	0.85	0.63
1 % percentile	−3.60	−0.34
10 % percentile	−1.21	−0.06
1st quartile	−0.55	+0.16
Median	−0.23	+0.37
3rd quartile	+0.04	+0.68
90 % percentile	+0.40	+1.48
99 % percentile	+1.38	+2.24

10.1.2.1 Chlorine Isotope Variations in Sediment Pore Waters

Porewaters have been studied from environments such as shield brines [Canada (Desaulniers et al. 1986; Kaufmann et al. 1987; Stotler et al. 2010), Sweden (Wirt 1988; Sie and Frape 2002), Finland (Stotler et al. 2010) and Siberia (Shouakar-Stash et al. 2007)], oil-field formation waters (Kaufmann et al. 1988, 1993; Eggenkamp 1994; Ziegler et al. 2001; Bagheri 2013; Bagheri et al. 2014a, b) and sedimentary aquifer waters (Martin 1993; Li et al. 2012).

Figure 10.2 shows a histogram with the δ^{37}Cl values from 324 sediment pore water samples taken from the above publications. This histogram shows very clearly that most measurements have negative δ^{37}Cl values, with as largest sample class −0.2 ‰. Some basic statistics from these data can be found in Table 10.1. The data in this figure confirm the fact that negative δ^{37}Cl

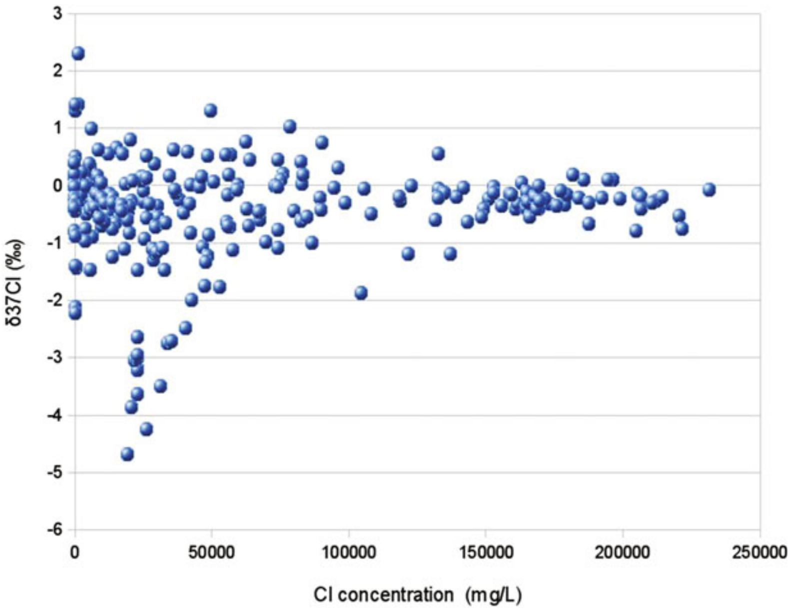

Fig. 10.3 Relationship between the chloride concentrations and chlorine isotope composition of 274 formation water analyses from which both data are reported. From this figure it is visible that at higher chloride concentrations the variation in δ^{37}Cl values is smaller, but that the average δ^{37}Cl value still is less than 0 ‰

data are more common than positive data with a median value of −0.23 ‰. What is well known regarding chlorine isotopes is the narrow range of the data. 50 % of the measurements are between −0.55 and +0.04 ‰ versus SMOC. Virtually all samples have values that are not more than 2 ‰ from SMOC, the only real deviating samples are a few samples of formation waters sampled from the Oseberg and Forties Fields in the North Sea (Eggenkamp 1994; Ziegler et al. 2001). These observations are also nicely illustrated in Fig. 10.3, showing the chloride concentrations and the δ^{37}Cl data from the 274 samples taken from the above publications from which also chloride concentrations were reported. In this figure it is clearly visible that the total δ^{37}Cl variation is larger at lower chloride concentrations than at higher chloride concentrations. The reason for this is that physical processes such as diffusion and ion-filtration cause larger variations at lower concentrations than at higher concentrations.

10.1.2.2 Bromine Isotope Variations in Sediment Pore Waters

As the bromide concentrations in sedimentary pore waters are in many cases relatively high the bromine isotope composition has been studied already in several locations by now, and for that reason a good impression of the bromine isotope composition of sediment pore waters can be given at this moment. One of the first observations that can be made is the striking dissimilarity between chlorine and bromine isotope compositions of pore waters. It was expected, before bromine isotope studies had been done, that, as chlorine and bromine have an apparently comparable chemistry, their isotope geochemistries would be reasonably similar. Already in the first study reporting natural bromine isotope measurements (Eggenkamp and Coleman 2000) it was shown that this was definitely not the case. Figure 10.4 shows a histogram of the 128 bromine isotope measurements published in Eggenkamp and Coleman (2000), Shouakar-Stash et al. (2007), Stotler et al. (2010) and Boschetti et al. (2011). In this histogram it is clearly shown that bromine isotopes tend to have mostly positive values in pore waters. The median value for example is +0.37 ‰ relative to SMOB, compared to −0.23 ‰ relative to SMOC for chlorine. Other statistical characteristics can be found in Table 10.1 where they can be compared to chlorine isotope characteristics.

This effect is also seen in Fig. 10.5 where the relationship between the bromide concentrations

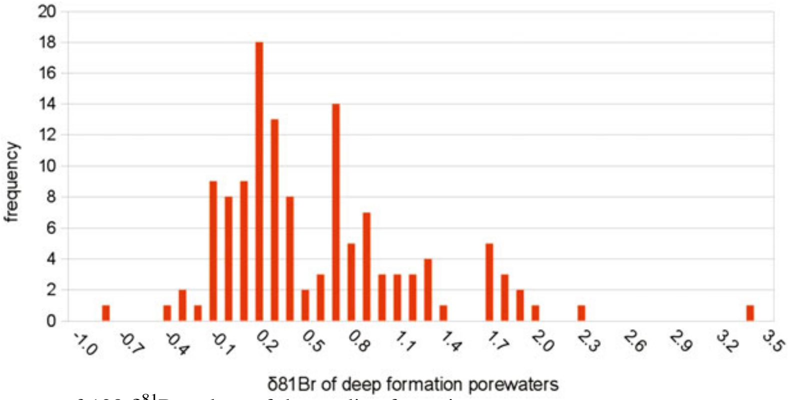

Fig. 10.4 Histogram of 128 δ^{81}Br values of deep saline formation waters

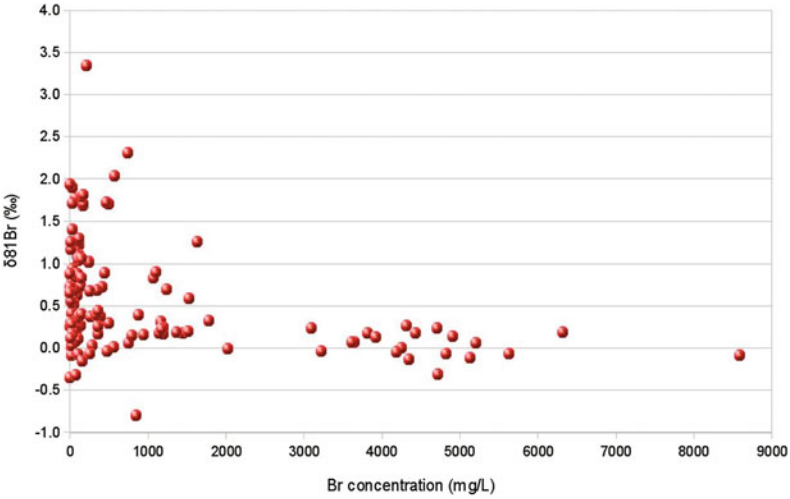

Fig. 10.5 Relationship between the bromide concentrations and bromine isotope composition of 128 formation water analyses from which both data are reported. From this figure it is visible that at higher bromide concentrations the variation in δ^{81}Br values is smaller, and that the average δ^{81}Br value is fairly close to 0 ‰

and the bromine isotope composition in these samples is shown. In this figure it is easily visibly that in samples with lower bromide concentrations the bromine isotope variations are much larger than in samples with higher concentrations, and also that in samples with high bromide concentrations (>2,000 ppm) the isotope compositions tend to be relatively close to SMOB (see Fig. 10.5). Considering the fact that it can be expected that, just as for chloride, all bromide in sediment pore waters is ultimately of ocean water origin (with a δ^{81}Br of 0 ‰) these data confirm again that the fractionation processes that define the bromine isotope ratios in sedimentary basins are quite different than the processes that define the chlorine isotope ratios.

10.1.2.3 The Relationships Between Bromine and Chlorine Isotope Ratios in Porewaters

Bromine isotopes in inorganic systems have, until now, only been studied thoroughly in formation water settings. Sediment formation waters, which contain generally very high chloride and bromide concentrations are the only type of samples where it is possible, with the current analytical techniques, to study bromine isotopes in detail, as in most other settings bromide concentrations are too low to study the isotope geochemistry in detail. The first small set of data in which bromine isotope variations in natural samples was shown was published by Eggenkamp and Coleman (2000). Although it was already shown by Willey and Taylor (1978) and Xiao et al. (1993) that it would be possible to measure bromine isotopes using methods comparable to the measurement of chlorine isotopes, by analysing CH_3Br molecules in IRMS or Cs_2Br^+ ions in P-TIMS, no studies on the natural variation of bromine isotopes were made in these early days, perhaps due to the expected difficulty to separate bromine from a very large excess of chlorine. An other reason that no attempts to measure bromine isotope compositions were made may be the fact that it was assumed, due to the comparability of the chemistry of chlorine and bromine, that the bromine isotope composition of a sample would mirror its chlorine isotope composition. This effect was shown for example in the simple diffusion experiments presented by Eggenkamp and Coleman (1997). In these experiments it was shown that the fractionation factor of bromine due to diffusion was just about half the fractionation factor of chlorine due to diffusion, and further that both diffusion systems (chlorine and bromine) showed the same characteristics. To the surprise of the researchers it was found already in the first study on natural bromine isotope variations that the bromine isotope variation in a set of formation waters from the Norwegian Oseberg field was completely opposite to the chlorine isotope variation in the same samples. The relation between chlorine and bromine isotopes in this dataset was negative and the correlation coefficient was significantly below 1 which indicated that different fractionation processes for chlorine and bromine isotopes must have taken place. No interpretation was presented by Eggenkamp and Coleman (2000) for their results as the chlorine isotope data from this set were only published at a later date by Ziegler et al. (2001). After Shouakar-Stash et al. (2005) published their method to analyse bromine isotopes using an on-line technique they analysed the bromine isotope composition in several studies on formation waters from Precambrian shields in Siberia (Shouakar-Stash et al. 2007) and Canada and Fennoscandia (Stotler et al. 2010). The combination of chlorine and bromine isotopes was also determined in a set of Italian formation waters from the Northern Apennine Foredeep Basin in northern Italy (Boschetti et al. 2011), the Williston Basin in North Dakota (Shouakar-Stash et al. 2006), the Kangan gas field in Iran (Bagheri 2013; Bagheri et al. 2014b) and from groundwater from the Great Artesian Basin in Australia (Gwynne et al. 2013). Figure 10.6 shows the chloride and bromide concentrations of the samples from which these data are provided by the respective studies and Fig. 10.7 the isotope data from the same studies.

Chloride and bromide concentrations in formation waters and salt deposits have been studied extensively as proxies for their origin (e.g. Valyashko 1956; Rittenhouse 1967; Kühn 1968; Matray et al. 1989; Davies et al. 1998). Looking at the chloride and bromide concentrations Rittenhouse (1967) was able to determine five groups of formation waters. These five groups were defined by him as follows: I. Formation waters in which the bromine and total mineralisation approximate that what would be expected from simple evaporation of seawater (“Seawater evaporation” on Fig. 10.6) or dilution of seawater with water of low mineralisation and bromide content (“Dilution with fresh water” on the figure). II. formation waters which are similar to formation waters of group I except for having about twice as much bromine for a specified total mineralisation. The additional bromine may have been added during early diagenesis. III. Formation waters in which the total-dissolved-solids content is greater than that of seawater but the bromine content is less than would be expected from simple concentration of seawater. These waters appear to have dissolved some halite. IV. Formation waters in which the total dissolved solids content is less than that of seawater but the bromine content is less than would be expected from simple dilution of seawater with water of low total mineralisation and bromine content. These waters may have been diluted with water having fairly high dissolved solids concentrations but low bromine

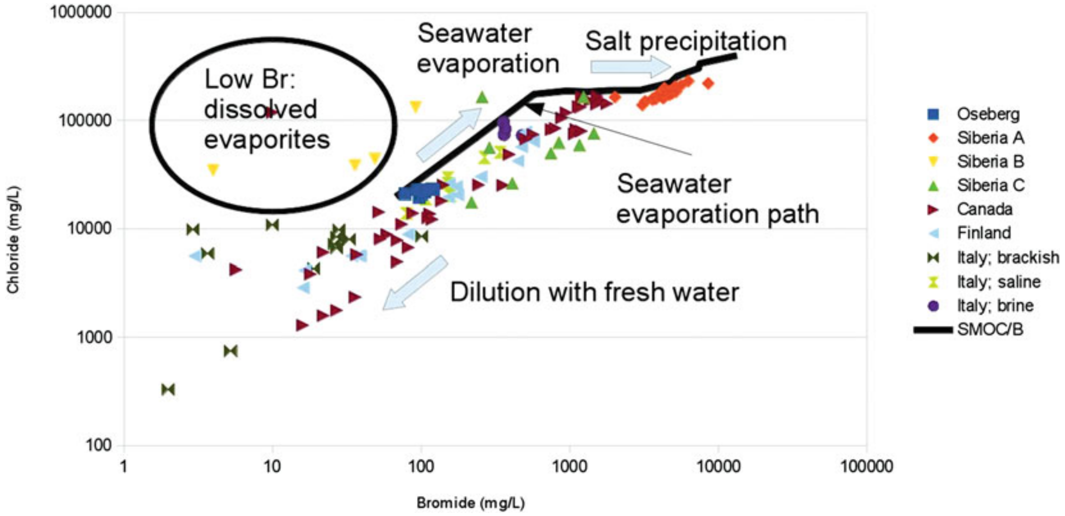

Fig. 10.6 Chloride and bromide concentrations from formation waters in those studies that reported both concentration and isotope data. Chloride and bromide contents and the Cl/Br ratio can give valuable information on the origin and evolution of formation water, as indicated by the different field in this figure. The data are taken from the following studies: Oseberg: Eggenkamp and Coleman (2000) and Ziegler et al. (2001), Siberia: Shouakar-Stash et al. (2007), Canada and Finland: Stotler et al. (2010), Italy: Boschetti et al. (2011)

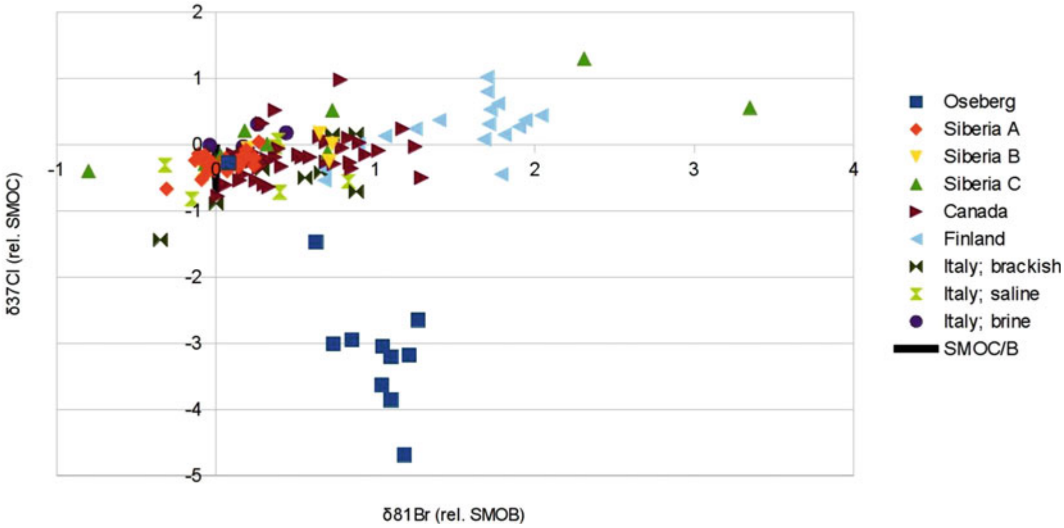

Fig. 10.7 Chloride and bromide isotope data from formation waters in those studies that reported both concentration and isotope data. Isotope date seem not to be as straightforward as the concentration data. In this figure it is clearly visible that most δ^{81}Br data are positive. The origin of the data are the same as in Fig. 10.6

content, or may have been group III waters diluted with water of low total mineralisation and bromine content. V. These formation waters have a high salinity and higher bromide contents than waters from group II. Some of these waters are associated with thick salt deposits and appear to be the residual brine which is left after salt deposition (“Salt precipitation” on Fig. 10.6).

Figure 10.6 shows the chloride and bromide concentrations of the samples that are reported in Eggenkamp and Coleman (2000), Ziegler et al. (2001), Shouakar-Stash et al. (2007), Stotler

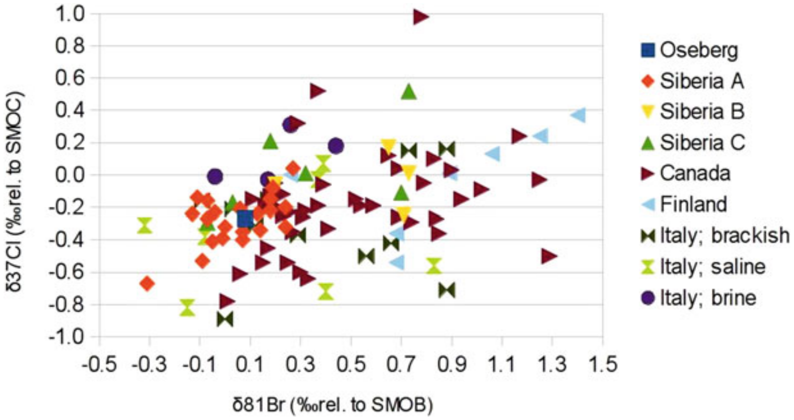

Fig. 10.8 Chlorine and bromine isotope data of formation waters. In this figure only samples with δ^{37}Cl values between −1.0 and +1.0 ‰ and δ^{81}Br values between −0.5 and +1.5 ‰ are shown. Origin of the data are the same as in Figs. 10.6 and 10.7

et al. (2010) and Boschetti et al. (2011). Samples from Siberia are subdivided into the three groups as defined by Shouakar-Stash et al. (2007) and the samples from Italy are subdivided according to the subdivisions from Boschetti et al. (2011). The other samples are plotted according to the country they come from. In this figure the seawater evaporation path is also shown. The groups as they were defined by Rittenhouse (1967) are indicated in this figure and fairly easy to recognise, although it is also clear that there are no easily recognisable borders visible between the different groups, so that not all samples can be placed easily into a certain group. When the distribution of the chlorine and bromine isotopes of the same samples are plotted on a δ^{37}Cl versus δ^{81}Br diagram the groups as observed by Rittenhouse (1967) are much less clear. Figure 10.7 shows the chlorine and bromine isotope data of all samples plotted together. As most samples fall into the fairly restricted area with values for chlorine between −1 and +1 ‰ and for bromine between −0.5 and +1.5 ‰ this area is blown up in Fig. 10.8. Looking at this figure it is clear that the origin of the samples is probably not as simple as could be deducted from the chloride and bromide concentrations only.

The most extreme samples with regard to chlorine isotopes, the samples from the Norwegian Oseberg field with δ^{37}Cl values as low as −4.7 ‰ have chloride and bromide concentrations which are very close to seawater. The low δ^{37}Cl values indicate however very clearly that these waters are not simply seawater. Ziegler et al. (2001) explained the low δ^{37}Cl values as the result of a combination of strong diffusion and membrane-filtration effects. Unfortunately the bromine isotope composition in this study have not been interpreted together with the chlorine isotope compositions as they were not published together.

Samples from later studies were interpreted in tandem. Shouakar-Stash et al. (2007) analysed a large set of formation brines from Siberia. They were able to divide their dataset into four groups, one of which contained of fresh waters with bromide concentrations too low to be analysed for bromine isotopes. The other groups however could be distinguished based on chlorine and bromine concentrations and isotopes. The first group, Siberia A in Figs. 10.6, 10.7, and 10.8, consists of calcium-chloride brines that are believed to be the residual of an evaporated paleoseawater, which is indicated by Br/Cl ratios in these samples which are much higher than the Br/Cl ratio in seawater, and isotopic compositions which are fairly close to 0 for both isotopic systems. The second group, Siberia B consists of sodium chloride brines that are derived mainly from halite dissolution, as is shown by very low Br/Cl ratios. These samples are characterised by relatively positive δ^{81}Br data, and from this set it was concluded for the first time that evaporites might be characterised by generally positive δ^{81}Br data. The third grouping consisted of mostly very saline waters (although not as saline as group Siberia A) from which the origin could not be clearly determined, although the chemical and isotopic characteristics of this group suggested that they were the product of various complex scenarios such as metamorphism, water-rock interaction, permafrost freezing and mixing. This group showed very large variations in both chlorine and bromine isotope compositions, among which the most positive bromine isotope data from which also chlorine isotope data were measured. Because of the large variation in chlorine and bromine isotope compositions it was impossible to obtain a clear explanation of the origin of these samples and for that reason a complex origin was suggested.

Stotler et al. (2010) analysed the chlorine and bromine isotope compositions of a large group of 42 samples from the Canadian shield and 18 samples from the Fennoscandian shield. Based on the chloride and bromide concentrations these samples would mostly fall into group 2 of Rittenhouse's (1967) classification. The Br/Cl ratio of the Canadian samples averages around 0.009 and of the Fennoscandian samples around 0.007, which is between twice and three times the ratio in seawater. The δ^{37}Cl values of the Canadian samples vary between −0.78 and +0.98 ‰ and the δ^{81}Br between +0.01 and +1.29 ‰. For the Fennoscandian samples the chlorine isotopes vary between −0.54 and +1.52 ‰ and the bromine between +0.26 and +2.04 ‰. A weak positive correlation between chlorine and bromine isotopes (with an r^2 of 0.36) was observed in this set. At one site with serpentinite rocks present it was observed that the δ^{37}Cl isotope values showed a large range while these samples showed only very small variations in δ^{81}Br values and this was attributed to ion filtration through serpentinite, which apparently affected the chloride but not the bromide ions. Comparisons with other isotopic systems, such as ^{87}Sr/^{86}Sr, indicated that water-rock interactions at some sites were likely to influence both halogen isotope systems. The large variation of δ^{37}Cl and δ^{81}Br values observed in the samples measured by Stotler et al. (2010) did not support a marine origin for these brines. This indicated that, if a seawater origin were to be considered for the fluids, a process or combination of processes significantly altered both the chlorine and the bromine isotope signatures. These unidentified processes probably explain the shift of the Br/Cl ratios from 0.035 to higher values showing that the samples in group II from Rittenhouse (1967) in reality do have a non seawater origin.

A large set of 23 formation waters from the Emilia-Romagna region of the Northern Apennine Foredeep in Northern Italy have been analysed for (amongst others) chloride and bromide as well as chlorine and bromine isotopes (Boschetti et al. 2011). Based on the total mineralisation of the samples the set is divided into three groups; brackish, saline and brine samples. The Br/Cl ratios indicate that the brackish samples are mostly diluted seawater (average Br/Cl is 0.0041), although a few of them have very low Br/Cl ratios indicating evaporite dissolution followed with subsequent dilution with fresher water. These samples appear to have the most positive δ^{81}Br values, showing a further independent indication for positive δ^{81}Br values in evaporite deposits. The saline samples seem to be altered samples (group II, Br/Cl is on average 0.0061) while the brine samples show Br/Cl ratios with are in between the brackish and saline samples (average Br/Cl is 0.0049). On the δ^{81}Br versus δ^{37}Cl plot the other samples show a considerable scatter. This is explained in part as a possible contribution of marine organogenic bromine. Most samples however seem to describe a rough positive trend with a ~0.5 slope. This is explained by probable halogen (both chloride and bromide) diffusion from brines toward aquifers with lower salinities. This slope seems to agree with the fact that the isotope fraction factor for chlorine diffusion is about double the isotope fractionation for bromide diffusion as shown by Eggenkamp and Coleman (2009).

Three of the four samples analysed by Bagheri et al. (2014b) show Br/Cl ratios that are between this ratio in seawater and double this amount and their isotopes indicate some moderate secondary processes. One of the samples has a low Br/Cl ratio indicating an evaporite origin, which again is confirmed by a rather positive δ^{81}Br value.

10.1.2.4 Diffusion of Chloride in Pore Waters

Diffusion is perhaps the most thoroughly evaluated fractionation process in natural aqueous systems. The reason is that due to the high diffusion coefficient of chloride in water, as well as the relatively large fractionation between the two chlorine isotopes (when compared to other possible fractionation effects) natural variations can be significant. Several studies have been published in which the isotope fractionation due to diffusion has been determined from the chlorine isotope variations in ground and pore water profiles. Among these is one of the earliest chlorine isotope studies on natural samples (Desaulniers et al. 1986). In this study diffusion of chloride from a saline bedrock was examined. In more shallow samples the chloride concentration was lower and the isotope ratio of these samples was indeed lower than in the deeper samples confirming that ^{35}Cl diffuses faster than ^{37}Cl. In this study it was was also observed that the δ^{37}Cl of the deepest samples, taken from the bedrock, was very positive with values between 1.5 and 2.0 ‰. When these values were measured they were the most positive δ^{37}Cl ever observed. They could not be explained at the moment of publication, and these very positive values are still difficult to explain even considering the progress of our knowledge (e.g. Shouakar-Stash 2008). It is however possible that this type of relatively positive values are caused by ion-filtration processes that took place in the bedrock after Phillips and Bentley (1987) showed that ion-filtration could be responsible for very positive δ^{37}Cl values. The results obtained in the study by Desaulniers et al. (1987) facilitated the calculation of the isotope fractionation due to diffusion. The fractionation factor they obtained during this study was however lower than fractionation factors found in both earlier and later experimental studies. The reason for this discrepancy may be due to the fact that natural systems are always more difficult to interpret than experimental systems.

Eggenkamp et al. (1994) determined the diffusion coefficient in a relatively simple natural system. During the last glacial period Kau Bay on the Indonesian island of Halmahera was separated from the ocean and became a freshwater lake due to the low sea level. When the sea-level increased again after the glacial period ended the bay water became saline again and salt water started to diffuse into the freshwater sediment of the former lake. As this was a simple system with a more or less constant sedimentation rate and salinity of the overlying water it was possible to determine the diffusion and its fractionation using a simple analytical model. In more complex systems it was only possible to approach the actual diffusion and fractionation using relatively simple analytical solutions such as the case of seawater intrusion along the Surinam coast (Groen et al. 2000). In this system there may have been alternation of more and less fresh water periods and as a result of this the diffusion and fractionation could only be determined approximately. To interpret the diffusion model properly for this kind of complex diffusion systems a different approach is needed. Beekman et al. (2011) managed to model both the chloride concentration as well as the chlorine isotope composition in a rather complex system by using a numerical technique. In their model the system was separated into thin layers each representing 50 cm of sediment and diffusion over time within and between these layers was determined. This way they managed to model both the chloride concentration and the chlorine isotope composition very satisfactorily. Numerical modelling has also been used to estimate the diffusion of chloride together with its isotope fractionation in the Paris Basin (Le Gal La Salle et al. 2013; Rebeix et al. 2014), while earlier studies used a more analytical approach to determine the fractionation in this complex basin that contains very thick layers of sediment (Lavastre et al. 2005). The chlorine isotope composition in porewaters taken from a 1,900 meter deep drill core in the Japanese Mobara Gas field (Mahara et al. 2013) also proved useful to determine the pore water mobility. Chloride concentration and chlorine isotope composition could be used together to estimate the porewater advection rate as 3 mm/year during the past 220,000 years using a fractionation factor of 1.002, approximately halfway fractionation factors published by Desaulniers et al. (1986; 1.0012) and Eggenkamp et al. (1994; 1.003) and close to the experimentally determined value of 1.0017 as determined by Eggenkamp and Coleman (2009). The analyses of chlorine isotope ratios in porewater samples from cores taken in Lake Kinneret (Stiller et al. 2009) which show clearly a diffusive isotope profile also proved that chlorine isotopes could be used to distinguish between different sources. While all 5 m cores taken from the bottom of this lake showed an increase in chloride concentration with depth in some of the cores the chlorine isotope variations of the porewater increased with depth while others they decreased with depth. While these profiles indicated diffusion of chloride between a chloride source at depth and the lake water, it was suggested that the isotopic differences observed were indicative of spatial variability in the porewater brine sources. In the case of Lake Kinneret it could be that long term diffusion may have altered the original, negative δ^{37}Cl of the Dead Sea Rift Valley brine (Stiller et al. 1998) from beneath the floor of the central part. If the hypothesis described by Stiller et al. (2009) is correct, then the apparent contradiction between the positive δ^{37}Cl values that are attributed to a pelagic brine source and the negative δ^{37}Cl values of three groups of Dear Sea Rift Valley type saline springs could be reconciled because each of the latter represents a deep, isolated brine reservoir (Kolodny et al. 1999), in which the original δ^{37}Cl signature of residual brines could have been preserved.

10.1.2.5 Possible Indications for the Occurrence of Isotope Fractionation Due to Ion Filtration

Although the potential of ion filtration as a process to fractionate chlorine isotopes has been studied both experimentally and theoretically already since the early 1980s (Campbell 1985; Phillips and Bentley 1987), studies in which it is recognised as one of the major processes to explain chlorine isotope variations in natural environments are rare. In several studies it is suggested as a potential process for the observed isotope variation (e.g. Lavastre et al. 2005; Li et al. 2012) but it was in many cases doubtful if ion-filtration could be an important process and it was also indicated in these studies that the results were either inconclusive or that ion-filtration as a major process could even be rejected as the process that was responsible for the observed chlorine isotope variations. Godon et al. (2004c) concluded however that the very negative δ^{37}Cl values that they encountered at the Manon site, at the outer edge of the Barbados accretionary complex were the result of ion filtration. In the system that they studied it was found that the porewaters were on mixing lines between seawater with a δ^{37}Cl value of 0 ‰ and endmember water samples that were characterised with very negative δ^{37}Cl values of −4.51, −5.19 and −5.24 ‰ at three different locations. As the chloride concentrations of these low δ^{37}Cl endmembers are relatively high diffusion was excluded as a potential source for these samples. Godon et al. (2004c) discussed that following the theoretical studies by Phillips and Bentley (1987) a ^{37}Cl depletion of 5 ‰ agrees with a 20-fold increase of chloride behind the membrane. Godon et al. (2004c) proposed a model for the generation of these low δ^{37}Cl fluids as a residual negative δ^{37}Cl fluid reservoir that is created at the bottom of a prism or a sediment pile. Further compaction and/or fracturing and/or dewatering of the slab may flush out these fluids and focus them towards the décollement zone. Mixing between the fluids and ultimately with seawater and water that has been released during gas hydrate destabilizations may explain the data set within the individual cores and between the different structures. Godon et al. (2004c) suggested that low δ^{37}Cl values that were found in a few other early chlorine isotope studies and that were not explained in these original studies (Eggenkamp et al. 1997; Hesse et al. 2000; Hesse 2003) could also be caused by ion-filtration. In a later study Hesse et al. (2006) could however not confirm this suggestion, and they were unable to identify the source of their low δ^{37}Cl fluid. The results of these studies indicate that it is still unsure as to how chlorine isotope variations observed in several natural environments can be related to the process of ion-filtration. Although ion-filtration potentially is a process that is able to fractionate chloride in solutions very efficiently it appears to be very difficult to detect its signature in natural environments.

10.1.3 Evaporites

Although evaporites are sediments, and as such they should normally perhaps not be described under the heading of "hydrosphere". However, all evaporites are the result of the evaporation of different water types (either seawater or terrestrial lake water) and their origin is in all cases the hydrosphere. The resulting evaporite sediments as such are able to give geochemical information on the original brine from which it has precipitated and for that reason it was decided to describe the isotope geochemistry of the evaporites under the heading of the hydrosphere.

10.1.3.1 The Chlorine Isotope Composition in Evaporite Deposits

Due to the high chloride contents of evaporites these deposits have been studied in considerable detail and as a result the chlorine isotope compositions of evaporites are fairly well known. Most evaporites origin from ocean water and reflect processes that take place during the precipitation of salt from ocean water in enclosed basins and from processes taking place with the evaporites under influence of changing pressure and temperature. Evaporites can also be terrestrial in origin. In this case the evaporite deposits are precipitated from originally fresh water that flows into a closed basin and that is evaporated to dryness. The isotope composition of these deposits is potentially different from marine deposits due to the different mode of formation. Terrestrial deposits form from river water which has a different chemical composition than ocean water. As the chemical composition of river water is also much more variable than the composition of ocean water the composition of the salt deposits and its chlorine isotope composition is also expected to be different. Although rivers often contain relatively high calcium and bicarbonate concentrations calcium carbonate normally precipitates at an early stage during the evaporation process and the remaining river brine is, just like ocean water, dominated by sodium and chloride, but with different contents of sulphate, potassium and magnesium.

Marine evaporites are formed from the evaporation of seas and oceans. The chemical composition of this type of deposits is studied both theoretically and experimentally for more than a century, starting with a very large numbers of papers written by Van't Hoff, who presented over 50 papers on experimental studies to determine the different salts that precipitate from seawater and the order in which they form as well as the changes due to environmental processes (pressure, temperature) after deposition, of which Van't Hoff and Mayerhoffer (1897) was the first study which were later published in book form (Van't Hoff 1905, 1909, 1912). Still probably the best monograph describing the origin and composition of salt deposits is written by Braitsch (Braitsch 1962, 1971). The most common salt that precipitates from ocean water is halite (NaCl) and this mineral dominates most marine salt deposits, and thus determines the chlorine isotope composition of most deposits.

The chlorine isotope composition of Phanerozoic salt deposits have been studied in considerable detail (Eggenkamp et al. 1995; Eastoe and Peryt 1999; Eastoe et al. 1999, 2001, 2007). During precipitation of halite from brine a small chlorine isotope fractionation of about 0.3 ‰ takes place, while during precipitation of potassium and magnesium salts the chlorine isotope fractionation is negligible. Eggenkamp et al. (1995) calculated the consequence of this small fractionation for the isotope composition of salt deposits and concluded that starting from ocean water the first salt to be deposited must have more positive δ^{37}Cl values, while later salt must have more negative δ^{37}Cl values than ocean water. Overall the variation was expected to be relatively small, with values between −0.5 and +0.3 ‰. This was confirmed in all studies on marine salt deposits. The summary compiled by Eastoe et al. (2007), containing over 230 chlorine isotope analyses from Phanerozoic marine salt deposits showed that more than 90 % of the samples had δ^{37}Cl values between +0.5 and −0.5 ‰, and no samples were outside the range of −1 to +1 ‰ relative to SMOC, the current ocean composition. These results confirmed the relatively small fractionation of chlorine from seawater during precipitation, and are also a very strong indication that the chlorine isotope composition of the oceans did not vary significantly, taking into account the errors of the measurements and secondary fractionation effects in the salts after deposition, during the whole of the Phanerozoic.

There is one region however from which Eastoe et al. (2007) did not take the analysed chlorine isotope results into account. This region is the very large inland Tarim Basin in the Xingjang Uygur Autonomous Region in China which has an area of approximately 560,000 km^2 and that has been studied very extensively for the chlorine isotope geochemistry as it was discovered that the chlorine isotope composition of the salt deposits in this basin could be used as a proxy for the exploitation of potassium deposits.

As described by Tan et al. (2005) this basin has been formed from two huge subbasins, the Kuba subbasin and the Shaqa subbasin during the Triassic period. During late Cretaceous and early Paleogene periods Paleo-Mediterranean seawater invaded regularly. Due to tectonic activities the basins were systematicaaly depressed or upheaved and broken up in a series of subdepressions. As a result of this seawater intrusions were separated from the ocean in bays, lagoons and salt lakes from which salt was later deposited.

In these studies (Xiao et al. 1997, 2000; Liu et al. 1997; Tan et al. 2005, 2006, 2009; Luo et al. 2012) it was found that the chlorine isotope variations in the basins are large. In these studies a good correlation was found between the chloride contents and the δ^{37}Cl of lake brines, where in the most concentrated brines very low δ^{37}Cl values of less than −2 ‰ were found. The δ^{37}Cl of the rock salt deposits have a sequence of values from >0 ‰ for early halite, <0 ‰ for late halite, <−0.5 ‰ for sylvite and <−1 ‰ for carnallite (Tan et al. 2009). The very negative δ^{37}Cl values in the carnallite deposits are not in agreement with data for carnallite deposited from seawater as predicted by Eggenkamp et al. (1995), according to which the value would not be lower than about −0.7 ‰ and it may be that the low observed values in the Tarim Basin are due to the fact that these deposits show an important terrestrial component and thus a possibly different chlorine isotope evolution.

10.1.3.2 Indirect Indications for the Bromine Isotope Composition of Evaporites

Although no direct bromine isotope measurements are known from evaporite deposits indirect indications from sediment porewaters, as also described in Sect. 10.1.2.5, suggest that in evaporites δ^{81}Br values between 0.5 and 1.0 ‰ can be expected. When evaporites are formed the bromide in the solution is concentrated in the brine resulting in very low bromide contents in the precipitated halite. This effect explains why evaporites contain 12.4 % of all chlorine present on earth, but only 1.0 % of all bromine. When these evaporites dissolve they result in porewaters with Br/Cl ratios which are considerably lower than in seawater. As described above, this type of porewater has been observed in several locations and it shows surprisingly similar bromine isotope values. Shouakar-Stash et al. (2007) studied the chlorine and bromine isotope composition of Siberian shield brines and reported four samples in this category with δ^{81}Br values of +0.73, +0.65, +0.71 and +0.20 ‰ respectively. Boschetti et al. (2011) determined the δ^{81}Br of three porewaters from northern Italy with very low Br/Cl ratios and observed values of +0.66, +0.88 and +0.12 ‰ respectively. Very recently also in a study from the Iranian Kangan gasfield aquifer (Bagheri 2013; Bagheri et al. 2014b) a δ^{81}Br of +0.87 ‰ was found in a sample with a low Br/Cl ratio which was

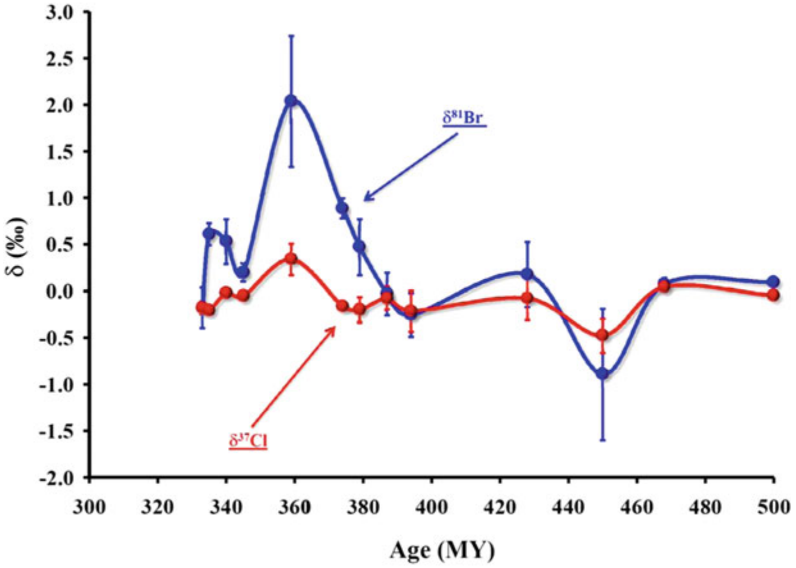

Fig. 10.9 $\delta^{81}Br_{SMOB}$ (‰) and $\delta^{37}Cl_{SMOC}$ (‰) versus Age (MY) of the Williston Basin formation waters (Mississippian—Cambrian) after eliminating samples with TDS vales less than 200,000 mg/L, samples that suffered dilution or halite dissolution and samples that were collected outside the area from 102.50° W to 104.00° W longitudes and 46.50° N to 49.00° N latitudes. The bars represent the isotopic ranges in each specific formation, and the dotes represent the average isotopic values of these stratigraphic units. Figure courtesy of Orfan Shouakar-Stash (Shouakar-Stash 2008) and used with permission

identified as dissolved halite from the Kuh-e-Namak Salt Diapir. Although the database is only of a limited size the data that are available indicate that the average δ^{81}Br in halite deposits is about 0.60 ± 0.29 ‰ (1 SD). This value is much more positive than would be expected from the fractionation factor between sodium bromide and its saturated solution ($10^3 \ln\alpha = -0.16$; Eggenkamp 1995; Eggenkamp et al. 2011). If we were to assume that bromine is precipitating from ocean brine with a δ^{81}Br of 0 ‰ we would expect that bromide in halite deposits has a δ^{81}Br of −0.16 ‰. No explanation for this discrepancy has been suggested yet.

10.1.4 Indications for the Existence of Larger Bromine Than Chlorine Isotope Variations During the Phanerozoic

Eastoe et al. (2007) concluded, based on the chlorine isotope compositions of Phanerozoic evaporites that the chlorine isotope composition of the oceans did not vary significantly during Phanerozoic times (see Sect. 10.1.3.1). Very interesting in relation herewith are the data presented by Shouakar-Stash et al. (2006) at the 16th Goldschmidt Conference in Melbourne. In their presentation they showed that in pre-Mississippian formation waters from the Williston Basin (North Dakota, these samples are 355–500 Ma old) the bromine isotope data showed a variation that was much larger than the variation in the chlorine isotope data. While the chlorine isotope data varied between approximately −0.74 and +0.47 ‰, the bromine isotope data varied from approximately −1.50 to +2.83 ‰. There also appeared to be a relation between the chlorine and bromine isotope data in this set as the Upper Ordovician, Yeoman, formation waters showed the most depleted values for both δ^{81}Br and δ^{37}Cl, while the Upper Devonian, Bakken, formation waters showed the most enriched values for both isotopes. When the results of the bromine and the chlorine isotope measurements were plotted versus time (Fig. 10.9) this variation and the similar trend for chlorine and bromine isotopes became clearly visible. Shouakar-Stash et al. (2006) suggested that these data indicate that there is a systematic temporal variation of seawater δ^{81}Br with time. This observation may be related to the fact that the bromide concentration in seawater in fact varied considerably over Phanerozoic times. Siemann (2003) showed that the bromide content in basal halite (which was defined as the first halite that precipitates from seawater when this evaporates) varied from about 28 µg/g basal halite to more than 100 µg/g basal halite. As the bromide content in halite is related to the bromide content in the brine this indicates that the variation in the bromide concentration during Phanerozoic times was much larger than the variation in the chloride concentration and this may be related to the suggestion of a relatively large bromine isotope variation in ocean water during Phanerozoic times.

10.2 The Mantle and Rocks Derived from It and Their Isotope Variation

The largest chlorine and second largest bromine reservoir on earth is the mantle. Although chlorine and bromine concentrations in the mantle are very low the sheer volume of the mantle is such that it still contains about 40 % of all chlorine and bromine on earth and the isotope composition of this chlorine and bromine is expected to be representative for the original chlorine and bromine isotope composition of the earth. For that reason a considerable effort has been made by various laboratories to obtain proper values for the chlorine isotope composition of the mantle. In spite of these efforts there still is considerable discussion on the chlorine isotope composition of the mantle due to the fact that various laboratories concluded on different values of the chlorine isotope composition of the mantle. No studies on the bromine isotope composition of the mantle have been made yet, and for that reason it is not possible to give any information yet on the bromine isotope composition of the mantle.

Mantle material exchanges with the lithosphere at various locations on earth. At mid-ocean ridges it surfaces to form the oceanic lithosphere and in subduction zones it is returned to the mantle. Basalt from the mid-ocean ridges has been used to determine the isotope composition of the mantle, while the isotope composition of pore waters in oceanic margins has been studied to discover the processes that take place during subduction of the oceanic crust. These studies have been used to examine the global cycle of chlorine and the processes that take place in this cycle.

10.2.1 The Chlorine Isotope Composition of the Mantle

The chlorine isotope composition of the mantle has been a research target ever since the development of precise techniques for the measurement of very small amounts of chloride in rocks (Magenheim et al. 1994). The chlorine isotope composition of the mantle is determined from the values obtained from the freshest, least altered mid-ocean ridge basalts. In spite of the relatively large number of studies on the chlorine isotope composition of the mantle even today there is still no general agreement on the chlorine isotope composition of the mantle due to conflicting results of the measurements that were obtained by the different laboratories that studied the chlorine isotope composition of the mantle. Magenheim et al. (1995) were the first to publish a comprehensive set of chlorine isotope data from MORB glasses. Their data, analysed by P-TIMS (Magenheim et al. 1994) after extraction of chloride from rock samples by pyrohydrolysis, were all clearly enriched in ^{37}Cl. The results showed trends towards more positive δ^{37}Cl values for samples containing lower chloride concentrations and higher F/Cl ratios. From these results it was concluded that the δ^{37}Cl value of the mantle, which was assumed to be equal to the values for MORB glasses that were not affected by high-level assimilation of wallrock into magma chambers, is somewhere between +3.0 and +7.2 ‰ versus SMOC with an average value of +4.7 ‰. Interestingly the chlorine isotope composition of mantle carbonatites was later estimated to have values close to 0 ‰ (Eggenkamp and Koster van Groos 1997) which led to the conclusion that the mantle was not a homogeneous reservoir with respect to the chlorine isotope composition.

During the early years of the 21st century methods were developed to analyse chlorine isotopes in rocks after pyrohydrolysis using IRMS techniques (Barnes et al. 2006; Bonifacie et al. 2007). Using these techniques the chlorine isotope composition of MORB specimens were also analysed. In the course of these studies the very positive δ^{37}Cl values that were observed by Magenheim et al. (1995) were not confirmed. It was concluded by both Sharp et al. (2007) and Bonifacie et al. (2008a, b) that the very positive δ^{37}Cl values that were measured by Magenheim et al. (1994, 1995) were analytical artefacts due to the introduction of sulphates or, even more devastating, fluorides in the TIMS system, as was already discussed by Stewart (2000) in his PhD dissertation. Stewart (2000) observed that especially the introduction of fluoride ions into the TIMS ionization chamber caused suppression of Cs_2Cl^+ ionization, leading to inconsistencies of the isotope measurements. Interesting with this regard is the discussion on Wei et al. (2008a). In their comment Sharp and Barnes (2008) point to the problems of having fluorides in samples which are analysed by TIMS. In their reply Wei et al. (2008b) state that there cannot be a problem with fluoride in their samples as they prepare them the same way as Sharp and Barnes (2008) do, as silver chloride precipitate from a solution containing chloride ions. Considering the high solubility of silver fluoride the final silver chloride precipitate can only have very low fluoride contents. They state that due to this effect the results they obtained cannot be analytical artefacts resulting in high δ^{37}Cl values. Although the method used by Wei et al. (2008a) was different from the method developed by Magenheim et al. (1994), it was also clear from the description of their method that Magenheim et al. (1994) already did remove both sulphates and fluorides from their samples using ion-exchange and precipitation techniques. It is not exactly known however what the remaining fluoride concentration in their samples was before they were introduced into the mass spectrometer. The exact reason for the large difference in measured δ^{37}Cl values between the different analytical methods may not be perfectly understood yet.

Although the results obtained by Sharp et al. (2007) and Bonifacie et al. (2008a, b) are closer to each other than to the values obtained by Magenheim et al. (1995) they are in clear disagreement. Sharp et al. (2007) observed that the MORB glasses that they measured were mostly between +0.5 and −0.5 ‰, with only two samples showing data at about −1 ‰. The average value of their samples was −0.2 ‰ with a standard deviation of 0.5 ‰. They observed no significant correlation between δ^{37}Cl and chloride concentration although the two most negative samples have relatively high chloride concentrations. Bonifacie et al. (2008a, b) observed different systematics. They observed a significant correlation between chloride concentration and δ^{37}Cl. Samples with lower chloride concentrations showed lower δ^{37}Cl data and it was concluded that the value of the mantle would be ≤−1.6 ‰ based on the δ^{37}Cl values of the samples with the lowest chloride concentrations. These very negative data were apparently confirmed by measurements from Layne et al. (2009) who, based on SIMS measurements of two very low chloride glassy MORB samples, that contained as little as 12 ppm chloride, concluded that the mantle δ^{37}Cl range could even be extended to ≤−3 ‰. At the Goldschmidt Conference in Prague in 2011 both the New Mexico group (Sharp et al. 2011) as well as the Paris group (Agrinier et al. 2011) presented posters showing arguments in favour of their own respective views. Sharp et al. (2013) presented new data which confirmed their views that no significant difference between surface and mantle reservoirs exist while on the other hand Nakamura et al. (2011) presented data showing a good agreement between their TIMS method for the analysis of chlorine isotopes in rocks and that of Bonifacie et al. (2007). All arguments that are presented still show that no general agreement has been

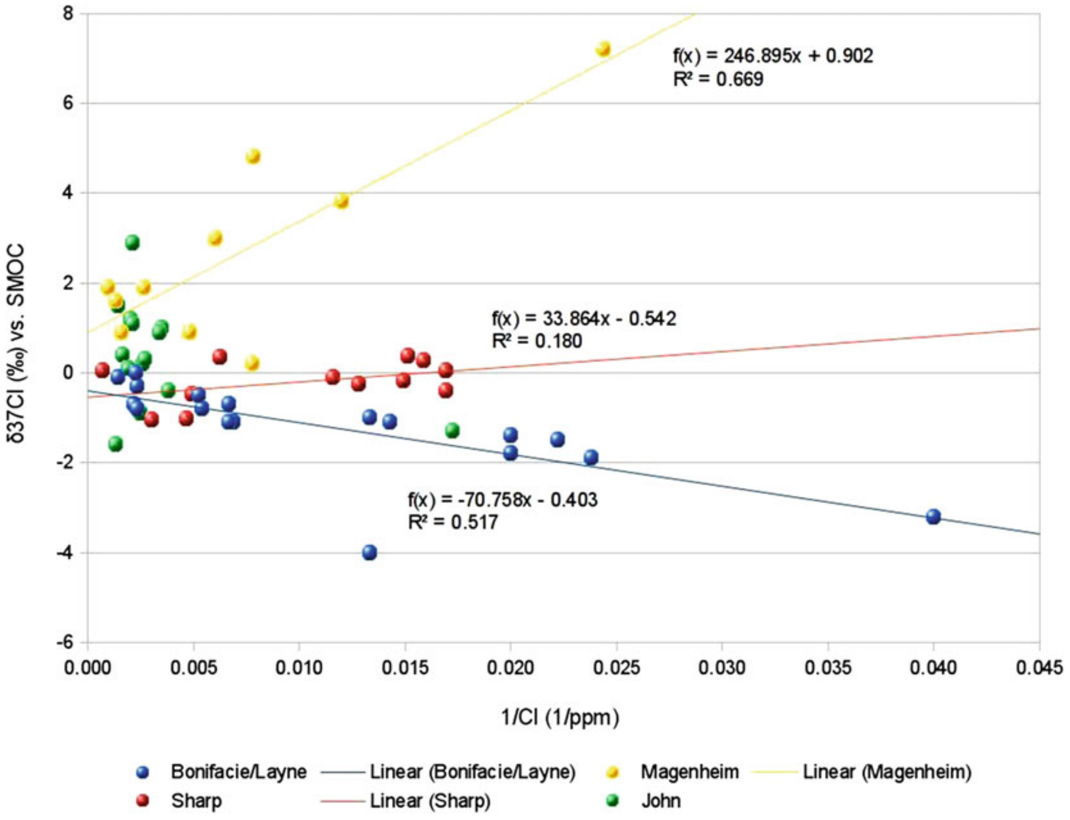

Fig. 10.10 δ^{37}Cl values and reciprocal chloride concentrations of MORB samples reported by Magenheim et al. (1994), Sharp et al. (2007), Bonifacie et al. (2008a, b), Layne et al. (2009) and John et al. (2010). The data show how the respective studies came to their conclusions regarding their estimate for the δ^{37}Cl value of the mantle

reached on what would be the real chlorine isotope composition of the mantle. As a result of this it is also problematic to assess discussions that use mantle chlorine isotope data from one of the laboratories that analysed conflicting mantle chlorine isotope compositions to discuss results to understand the data that are to be interpreted in such a study, and which conclusions could be highly dependent on the point of view they accepted for the study.

Figure 10.10 shows the δ^{37}Cl values presented by Magenheim et al. (1995), Sharp et al. (2007) and Bonifacie et al. (2008a, b), as well as those analysed by John et al. (2010) to show how each of this studies obtained their respective conclusion on the average mantle value. Considering the large discrepancies between the three studies it is striking how reasonably well the correlations between chloride concentration and δ^{37}Cl are for Magenheim et al. (1995) and Bonifacie et al. (2008a, b).

It may be however that the mantle is actually not a very homogeneous reservoir as was already argued by Eggenkamp and Koster van Groos (1997), although this discussion was based on the MORB data from Magenheim et al. (1995) and much more recently by John et al. (2010). John et al. (2010) observed δ^{37}Cl values between −1.6 and +2.9 ‰, measured by SIMS, for Ocean Island Basalts which are also regarded as representing a typical mantle reservoir. These values, many of which are positive (they are incorporated in Fig. 10.10 for comparison), can not be explained by dilution of the chlorine isotope composition by seawater. Again however, four samples of Hawaiian ocean island basalts analysed by Sharp et al. (2013) all showed values of −0.2 ± 0.2 ‰. The combination of all these results indicate that still considerable research is needed, including intensive collaboration between the laboratories that work in this field to understand both the differences obtained between the laboratories and the real value of the chlorine isotope composition of mantle material.

10.2.2 Mantle Metasomatism

Selverstone and Sharp (2011) studied the chlorine isotope composition in a large set of peridotite samples from the Finero peridotite to study the matasomatism that has appeared and to study the processes that are responsible for the fractionation of chlorine isotopes in this region. They combined chlorine, hydrogen and oxygen stable isotope geochemistry with petrologic and major and trace element data to further constrain sources and setting of the metasomatic agents and to assess fluid infiltration mechanisms. They used relatively unmetasomatised samples from the Balmuccia peridotite as their control population (a total of 13 samples with a δ^{37}Cl range between −0.7 to +0.4 ‰). Four different rock types were analysed and the δ^{37}Cl in the samples ranged from −2.0 to +2.1 ‰. This variation could not be reconciled with metasomatism by a single homogeneous fluid. They found that effectively the variability in the dataset could be described with three end-members, one with a δ^{37}Cl value close to zero and with very negative δD values, one with negative and one with positive δ^{37}Cl values, these last two with less negative δD values. Although a large variation in chlorine isotope compositions of more than 4 ‰ was found in this dataset it was not yet possible to indicate the effects that actually fractionate the chlorine isotopes. Selverstone and Sharp (2011) stated that at this moment relatively little is known about the different chlorine isotope reservoirs within both the oceanic and continental crust and chlorine might fractionate during subduction-related dehydration. In spite of this they indicated that their study shows that chlorine isotope geochemistry adds clearly new information about the processes that are associated with fluid-rock interaction., even if it is not yet possible to name the exact processes that take place in these environments.

10.2.3 Chlorine Isotopes in Volcanic Systems

Due to their often extreme chemical compositions chlorine isotopes in volcanic systems have been studied from early on. Eggenkamp (1994) measured the chlorine isotope compositions in a large set of volcanic gases, springs and lakes from Indonesia. From these data it appeared that samples close to the meteoric waterline (based on hydrogen and oxygen isotope compositions) had mostly negative δ^{37}Cl values, while samples with relatively high δ^{18}O values (samples that indicated geothermal alteration) mostly had positive δ^{37}Cl values. This difference was explained with different origins of the chloride in these samples, with meteoric waters containing chloride from seaspray and weathered rocks in the samples close to the meteoric waterline, while samples showing geothermal alteration were supposed to receive their chloride from hydrogen chloride degassing. It was suggested that this explanation is in agreement with experimental work done by Hoering and Parker (1961) who determined the isotope equilibrium between ammonium chloride and hydrogen chloride and found that the hydrogen chloride in this equilibrium concentrated the more positive chloride. Later experimental studies by Sharp et al. (2010a) seemed to confirm these conclusions.

Most chlorine isotope studies from volcanic material were done as a proxy to understand the composition of mantle material (e.g. Eggenkamp and Koster van Groos 1997; Barnes et al. 2008, 2009; Bonifacie et al. 2008a; Layne et al. 2009; John et al. 2010; Sharp et al. 2013). The reason for this is that due to the high temperature of volcanic rocks and fluids, as well as the incompatibility of chloride for rocks (and thus the concentration of chloride in the fluid phase) the isotope fractionation between these phases is negligible (Schauble et al. 2003; Liebscher et al. 2006). As such most variations in volcanic material reflect variations in mantle material. As an example Barnes et al. (2009) studied the variation on the chlorine isotope composition in different volcanoes in Central America (from Guatamala at about 14°N to Costa Rica at about 10°N). The samples analysed in their study, containing of ash, tephra and lava samples, showed $\delta^{37}Cl$ values between −2.6 and +3.0 ‰. The purpose of this study was to use chlorine isotopes as a tracer for the fluids that sourced from the subducting Cocos slab. It was found that the $\delta^{37}Cl$ values could be related to the origin of the material analysed. The volcanoes from the south and the north (Costa Rica and El Salvador/Guatamala) suggest a mantle source as they show $\delta^{37}Cl$ values close to 0 ‰ or slightly negative, assuming that mantle values are close to 0 ‰ as determined by Sharp et al. (2007). The volcanoes which are located more in the centre of the region (Nicaragua) show either more positive and more negative $\delta^{37}Cl$ values which are explained as either sediment or hydrothermally altered rock (altered oceanic crust or possible serpentinites). This is for example confirmed by high Ba/La ratios in samples from these volcanoes which indicate a sediment component and high $^{87}Sr/^{86}Sr$ ratios which indicate altered oceanic crust. Finally negative $\delta^{37}Cl$ values that are found in Honduran volcanoes in the back-arc are possibly indicative for serpentinite derived fluids. In all these cases it was possible to explain the variations of the chlorine isotope compositions in the volcanic rocks from these volcanoes from the source, indicating that no isotope fractionation of chlorine in the volcanic system occurred.

Interestingly anomalously high $\delta^{37}Cl$ values are found in fumaroles in several volcanoes in this region (Sharp et al. 2010a). These values could be explained as the result of fractionation in the fumarole system (Sharp et al. 2010a). This same kind of very high anomalous $\delta^{37}Cl$ values were observed in early studies by Eggenkamp (1994) in Indonesian fumaroles and Wahrenberger et al. (1997) in fumaroles from the Russian Federation and Italy but could not be explained in these early studies. The very high $\delta^{37}Cl$ values in Poás Volcano (Costa Rica) are confirmed by Rodríguez et al. (2013) who also confirmed that the $\delta^{37}Cl$ values are variable over time. From an extended time series it was also found that the $\delta^{37}Cl$ values in lake Poás itself vary over time. Relatively positive values mark the samples taken during an interval of peak activity of the lake (1980–1986), when chloride concentrations (<73,100 ppm) and temperatures (<65 °C) were high, pH values were <0, and its volume was strongly reduced. This elevated $\delta^{37}Cl$ is attributable to a preferential depletion of ^{35}Cl due to evaporation of $HCl_{(g)}$, or to a distinctive input flux into the lake. Variations in $\delta^{37}Cl$ values in a time series of volcanic springwater was observed earlier by Musashi et al. (2008) who observed that the $\delta^{37}Cl$ values in the Kusatsu-Bandaiko hot spring increased due to increased volcanic activity in the Kusatsu-Shirane volcanic region in Japan.

10.2.4 Oceanic Crust

As mentioned in Sect. 10.2.1 analyses of the most pristine oceanic crust samples available are used to determine the chlorine isotope composition of the mantle. These studies attempt to determine the chlorine isotope composition of the mantle though the analysis if samples that show clear mantle characteristics. The oceanic crust is however for the biggest part contaminated by chloride that descends from assimilation with seawater, and it is generally agreed that the oceanic crust has an average $\delta^{37}Cl$ value which is close to 0 ‰. This follows not only from the data reported by Sharp et al. (2007, 2013), who measured chlorine isotope data close to 0 ‰ in most of their samples, but this is also inferred from the data reported by Bonifacie et al. (2008a, b) and also from the data reported by Magenheim et al. (1995) who both concluded that in the samples with higher chlorine concentrations the $\delta^{37}Cl$ values appear to converge to 0 ‰.

Overall however, when the individual measurements of oceanic crust samples are considered the figure is not as simple as it seems. If we were to consider results as obtained by Magenheim et al. (1995) or Bonifacie et al. (2008a) it would be fine to conclude that MORB glasses fall on a line between basalt contaminated by seawater, with a δ^{37}Cl close to 0 ‰ and a (very) positive or negative mantle end-member. Data obtained by Sharp et al. (2007, 2013) deserve a different approach. Although the average value for the oceanic crust is slightly, but hardly significantly less than 0 ‰, thus more or less equal to SMOC, the variation is significant. With a standard deviation of the measurements of about 0.5 ‰ this indicates that the variation is much larger than the precision of the measurements, even considering that the precision of measurements for rock samples is not as good as for aqueous samples. This large variation clearly indicates that there must be processes that fractionate chlorine isotopes in the oceanic crust, during extraction of rock from the mantle in volcanic systems, or that the mantle itself is a heterogeneous reservoir.

10.2.5 Chlorine Isotope Variations in Deep Sea Pore Waters and Their Relation to Serpentinites

Ransom et al. (1995) discovered that porewaters taken from subduction zones showed very negative δ^{37}Cl values that could be as low as −8 ‰. Ransom et al. (1995) analysed the chlorine isotope compositions of porewaters from two active and one passive oceanic margin and found that porewaters from the passive margin, of the coast of West Africa, have δ^{37}Cl values very close to 0 ‰, while active margins showed (very) negative values. In the Barbados subduction zone samples were taken less than 1 meter below the seafloor and even at these shallow depths δ^{37}Cl values as low as −4.7 ‰ were observed, indicating very active advective fluid flow. At the Nankai subduction zone samples show these negative values at about 1,000 meter below the seafloor. In this region fluids move via a very complex network of microfaults as described by Kastner et al. (1993). Ransom et al. (1995) explained these negative values as the result of diagenetic and metamorphic dehydration and transformation reactions. They assumed that the low values were the result of dehydration of hydrous silica minerals which were found to have very positive δ^{37}Cl when measured by P-TIMS (Magenheim et al. 1994, 1995). Godon et al. (2004c) also studied the porewater at the Barbados accretionary complex and concluded that the very low δ^{37}Cl end-members in their systems were the result of ion-filtration. It is clear however that not in all deep ocean porewaters very low δ^{37}Cl values are found. In their study on the chlorine isotope composition of porewaters from the Brazos-Trinity Basin IV in the Gulf of Mexico Li and Jiang (2013) found δ^{37}Cl values in the range between −0.81 and +0.71 ‰, averaging “close to seawater” at −0.18 ‰ without being able to explain the observed variation properly.

In their study of porewaters from the Blake ridge gas-hydrate field in the west Atlantic Hesse et al. (2006) also encountered very negative δ^{37}Cl values at great depth. In their samples they also found a decrease of the chloride concentration with depth, which, according to Egeberg and Dickens (1999), was caused by the melting process of gas-hydrates. It was concluded however by Hesse et al. (2006) that over 50 % of the chlorinity reduction actually was occured before these hydrates melted. They concluded that the lower chlorinity was caused by advection of a strongly ^{37}Cl depleted low chlorinity fluid. The origin of this low chlorinity fluid remained however unknown.

The δ^{37}Cl values in these deep marine porewaters may be related to the chlorine isotope compositions of massive seafloor serpentinites. Sharp and Barnes (2004) indicated that the water-soluble fraction from these serpentinites may have rather negative δ^{37}Cl values of −1.5 ‰ in older and values close to zero in more recent serpentinites. The insoluble fraction has δ^{37}Cl values which are about 0.33 ‰ more positive than the soluble fraction. In a much larger study Barnes and Sharp (2006) showed that there is a considerable variation in the chlorine isotope characteristics between different cores where the chlorine isotope composition is measured on serpentinites. They also observed that the chemical composition of cores with different chlorine isotope characteristics is different. Barnes and Sharp (2006) concluded that non-zero bulk δ^{37}Cl values indicate that chloride in serpentinites was incorporated during the original hydration and is not an artefact of seawater infiltration during drilling. Cores with positive δ^{37}Cl values are most likely explained by open system fractionation during hydrothermal alteration, with preferential incorporation of ^{37}Cl from seawater into the serpentinite and loss of residual isotopically light chloride back to the ocean. Fluid/rock ratios were probably low as evidenced by the presence of water-soluble salts. The cores with isotopically negative chloride were characterized by a thick overlying sedimentary package that was in place prior to serpentinisation. Barnes and Sharp (2006) believed that the low δ^{37}Cl values of these cores were the result of hydration of ultramafic rock by infiltrating aqueous pore fluids from the overlying sediments. The resulting serpentinites inherit the characteristic negative δ^{37}Cl values of the pore waters. Chlorine stable isotopes can be used to identify the source of the serpentinising fluid and ultimately discern chemical and tectonic processes involved in serpentinisation. These studies thus indicated that the low δ^{37}Cl values found in some of the serpentinite cores may be the result and not the origin of the low δ^{37}Cl values in subduction porewaters.

Bonifacie et al. (2008b) found a range of negative δ^{37}Cl values in oceanic serpentinites. They concluded that these negative values were likely the result from water-rock interaction with fluids with negative δ^{37}Cl values. The homogeneity of δ^{37}Cl values from a high-pressure olivine-bearing vein and metaperidotite samples that they observed implied that progressive loss of chlorine inherited from oceanic alteration throughout subduction did not significantly fractionate chlorine isotopes. Bonifacie et al. (2008b) concluded that chlorine that recycled in subduction zones via metaperidotites should thus show a range of δ^{37}Cl values similar to the range found in oceanic serpentinised peridotites.

The chlorine isotope composition, as well as the halogen chemistry of serpentinites, during the progressive dehydration of serpentinites during subduction was studied by John et al. (2011). They hoped to understand how relevant serpentinites would be for the recycling of halogens during subduction and deep mantle recharge. They observed that the halogen compositions of the analysed samples indicate input from seawater and sedimentary sources during initial serpentinisation of either subducting lithospheric mantle during slab bending or forearc mantle by uprising slab fluids. During dehydratation of the serpentinites the fluids that were released were enriched in bromide and iodide relative to chloride, so that the relative chloride contents of the serpentinite increased. On the other hand they observed that the δ^{37}Cl range of the deserpentinisation samples showed only a narrow range with overlap of δ^{37}Cl values from seafloor serpentinites. Based on these observations they concluded that while no significant chlorine isotope fractionation occurred during the subduction ralated dehydration of serpentinites, subduction of serpentinites and their dehydration strongly affects the halogen budget of the mantle.

The different studies on serpentinites indicate that stable isotopes, among which chlorine stable isotopes, are effective tracers of serpentinising fluids. Barnes et al. (2013) state that the final isotopic composition of serpentinites will be determined by the isotopic composition of the serpentinising fluid, the temperature of interaction, and the water/rock ratio. For example, high δ^{18}O values may be the result of low-temperature serpentinisation by seawater (large $\Delta^{18}O_{\text{serp-water}}$) or interaction with an ^{18}O-enriched slab derived fluid. In their study on serpentinites from the Franciscan Complex, western California, USA Barnes et al. (2013) observed in their samples δ^{37}Cl values that ranged from −0.1 to +1.7 ‰ versus SMOC with 12 of the 15 samples falling between +0.2 and + 0.9 ‰ (with an average value for all samples of +0.6 ± 0.5 ‰). These data support serpentinisation via seawater on the seafloor. Extreme negative or positive δ^{37}Cl values reflecting the influence of a non-seawater fluid are not present in this data set, except for one sample with a value of +1.7 ‰.

In their discussion Barnes et al. (2013) summarise that chlorine isotope measurements of obducted serpentinites and metaperidotites show no chlorine isotope fractionation during prograde subduction metamorphism and that the chlorine isotope composition of obducted serpentinites is thought to preserve a record of seafloor tectonic processes (Barnes et al. 2006; Bonifacie et al. 2008b; John et al. 2011). Serpentinites formed via interaction with seawater have δ^{37}Cl values of about +0.2 to +0.5 ‰ (Barnes and Sharp 2006). Serpentinites formed from interaction with sedimentary pore fluids and/or sediment-derived fluid have δ^{37}Cl values of about −2.0 to −0.5 ‰ (Barnes and Sharp 2006; Barnes et al. 2006). Rare serpentinites with δ^{37}Cl values above +1.0 ‰ (n = 9) are restricted to serpentine seamounts (n = 2) and obducted serpentinites from Elba Island, Italy (n = 1) and HP/UHP localities in the western Alps (n = 6) (Barnes et al. 2006, 2008; John et al. 2011; Selverstone and Sharp 2011). Serpentinites with high δ^{37}Cl values are postulated to reflect a fluid component from the subducted slab, either high pressurised metasediments or altered oceanic crust (John et al. 2010; Selverstone and Sharp 2011). Post-serpentinization interaction with meteoric water does not alter the chlorine isotopic composition of serpentinites (Barnes et al. 2006).

10.3 Continental Magmatic Rocks

The chlorine isotope composition of continental magmatic rocks has not been studied as extensively as that of oceanic rocks. Eggenkamp (1994) analysed six rocks from the Proterozoic (1,168 ± 21 Ma; Blaxland et al. 1976) Ilímaussaq intrusion in Greenland and found δ^{37}Cl values mostly close to 0 ‰ (−0.02 to +0.11 ‰) with one exception of a sample with a value of +0.32 ‰. Markl et al. (1997) studied the chlorine isotope geochemistry of some lower crust samples from Lofoten (Norway) which indicated only minor involvement of mantle derived chlorine. δ^{37}Cl values of these rocks showed a large range with values between −1.12 and +0.79 ‰. The only information that can be obtained from these few data is that the δ^{37}Cl of the continental crust is not very homogeneous but will generally have values between approximately +1 and −1 ‰ with an average value close to SMOC.

10.4 Chlorine Isotopes in Fluid Inclusions

To asses whether chlorine stable isotopes could be useful to estimate the origin of chlorine in ore forming fluids a few studies are known in which the chlorine isotope composition was determined in fluid inclusions. To be able to estimate the chlorine isotope composition in fluid inclusions it was necessary to crush and leach a larger piece of rock to obtain enough chloride for isotope analysis. This was necessary as all studies known until present used IRMS or P-TIMS techniques to determine the chlorine isotope composition.

Eastoe et al. (1989) determined the chlorine isotope composition in several Mississippi valley type deposits from Tennessee and porphyry copper deposits from Arizona, Utah, Chile and Papua New Guinea. In their samples, which contained the leached chloride from 250 to 500 g of rock, δ^{37}Cl values between −1.0 and +0.8 ‰ were found. Although these were only preliminary results it was concluded that the high δ^{37}Cl values in the Mississippi valley type samples were related to formation waters, and that the low δ^{37}Cl waters had a different, then unknown origin. The samples from the porphyry copper deposits could not yet be explained but there seemed to be an isotopic difference between early and late chloride in some systems. It was stated however that the differences found in these samples contained indications that various processes took place, so that more research could prove useful.

Banks et al. (2000a, b) presented δ^{37}Cl measurements on fluid inclusions from the Capitan pluton in New Mexico and the southwest England batholite. In their studies the chlorine isotope composition was determined by P-TIMS at the University of Leeds and as this method introduced the possibility to analyse rather small samples only 0.5–1 g of rock was necessary to leach fluid from for isotope analysis. It was found that the fluid inclusions from the two different locations had clearly distinct characteristics. Those from New Mexico had δ^{37}Cl values clustering around 0 ‰ and Br/Cl ratios of about 0.0005, while the English samples had δ^{37}Cl values around +1.9 ‰ and Br/Cl values between 0.0010 and 0.0025. It was concluded that the chloride in the samples from New Mexico was derived from local evaporite sequences, while the samples from SW-England seemed to be more of a deep magmatic source. It has to be realised however that a deep origin for these samples was concluded because in those days the consensus was that the mantle had a strongly positive δ^{37}Cl following the conclusions by Magenheim et al. (1995), and more recent studies have shown that these values should be either close to zero or negative (Sharp et al. 2007; Bonifacie et al. 2008a, b). This actually indicates that if this study would have been done more recently a different explanation would be needed, and that the original conclusions can not be valid anymore.

Gleeson and Smith (2009) and Richard et al. (2011) presented studies in which the δ^{37}Cl is measured on fluids extracted from Swedish and Canadian ore systems. In both studies the chlorine isotope composition was determined on fluid inclusion leachates and were analysed at the Stable Isotope Hydrology and Ecology Laboratory of Environment Canada in Saskatoon (Saskatchewan, Canada) according to the technique described by Wassenaar and Koehler (2004). Gleeson and Smith (2009) determined chlorine isotope compositions in leachates from three spatially associated iron oxide with copper and gold mineralising systems from Norbotten, Sweden. They found δ^{37}Cl values that were mostly negative. It was possible to determine three different populations of samples based on the Br/Cl ratios and the δ^{37}Cl values. Based on these results Gleeson and Smith (2009) concluded that the chloride in the two systems with mostly negative δ^{37}Cl values (Greenstone- and Porphyry hosted Cu-Au doposits with δ^{37}Cl values between −5.6 and −1.3 ‰ and late stage veins in Fe-oxide-apatite deposits with δ^{37}Cl values between −3.1 and −1.0 ‰) the chloride was of mantle origin, except for the most negative samples. This was based on the observation that in more recent mantle studies negative δ^{37}Cl values appeared the most common (Bonifacie et al. 2007, 2008a; Layne at el. 2009) in mantle derived rocks although Sharp et al. (2007) indicated values much closer to zero. The values in the third system, the Nautanen Deformation Zone are mostly fairly close to zero so that these are concluded to be of a crustal, (meta-)evaporitic origin. Richard et al. (2011) studied the chlorine isotope composition and the Cl/Br ratios in fluid inclusions of uranium deposits from the Paleoproterozoic Athabasca Basin in Canada. In this study the δ^{37}Cl values were between −0.85 and +0.36 ‰ and were interpreted as evaporated seawater origin. Variations of these values were interpreted as secondary minor modifications of its seawater origin such as mixing with small amounts of evaporites, dilution with connate and/or formation waters, leaching of chloride from biotites or waterloss by hydration reactions in alteration haloes linked to the uranium deposition.

10.5 Atmosphere

The atmosphere is the only significant reservoir on earth where a large part of chlorine and bromine are present in the form of oxidised and organic molecules. The existence of these compounds, in which chlorine and bromine are present in higher oxidation states than −I is partly due to natural circumstances such as oxidation of chlorides and bromides by ozone present in the atmosphere. For a large part however it is also present from man made compounds such as chlorofluorocarbons, carbon tetrachloride, chloroform and dichloromethane, the concentrations of which have decreased considerably since the signing of the Montreal Protocol in 1987. Although most chlorine and bromine isotope studies on organic chlorine compounds will be described in Chap. 14 a short summary is given here to show the isotope composition of this small but important reservoir and to easily compare it to the other reservoirs.

In their letter to Nature Tanaka and Rye (1991) suggest a method that should be able to analyse organochlorine compounds that were expected to exist in the stratosphere. They stated however that, due to the very low concentrations of these compounds in the stratosphere, they expected that it would be very difficult to actually measure them. It was only around 2010, almost twenty years later, that the first methods were developed with which it was possible to extract amounts of chlorine and bromine compounds from atmospheric samples that were sufficient for isotope analyses.

10.5.1 Chlorine

The first real chlorine isotope data from stratospheric gas were presented by Laube et al. (2010) who analysed the chlorine isotope composition of atmospheric CF_2Cl_2. They found that with increasing altitude the $\delta^{37}Cl$ of the CF_2Cl_2 increased from 0 ‰ at 14 km to +27 ‰ at 34 km. They explained this increase due to the faster decomposition of $CF_2^{35}Cl_2$ relative to $CF_2^{37}Cl^{35}Cl$ and $CF_2^{37}Cl_2$ by photolysis and the reaction with O^1D. These data indicate that, within the fairly large errors in the measurements of up to ± 4 ‰, the lower atmosphere has a chlorine isotope composition close to SMOC, which increases to very positive values in the stratosphere due to prevalent decomposition of the molecules with ^{35}Cl bonds as compared to molecules with ^{37}Cl bonds.

10.5.2 Bromine

The first bromine isotope measurements of atmospheric CH_3Br samples were reported by Horst et al. (2013) and Horst (2013). They used the method developed by Thornton et al. (2013) to extract enough CH_3Br from atmospheric samples from sites near Stockholm (an urban site) and Abisko (a rural site) in Sweden. Further at the Abisko site also soil-air samples were collected to determine isotopic fingerprinting and the importance of this source. The results obtained by Horst et al. (2013) and Horst (2013) indicated that, overall, the air samples showed similar $\delta^{81}Br$ values for both field studies ranging from −0.47 to +1.75 ‰ versus SMOB for Stockholm samples and −0.14 to +0.48 ‰ versus SMOB for Abisko samples. However, in Stockholm the $\delta^{81}Br$ range was larger and the mixing ratios of CH_3Br were higher (14.4 ± 2.1 pptv) whereas for the Abisko samples the mixing ratios (9.8 ± 3.1 pptv) were statistically indistinguishable from global background (8 pptv). The Stockholm samples showed a clear trend of depleted bromine isotope signatures (i.e. negative $\delta^{81}Br$ values) with higher concentrations towards enriched $\delta^{81}Br$ values with lower concentrations. This trend is suggestively due to decomposition of CH_3Br in the atmosphere and/or mixing between potential sources and the background methyl bromide. The few soil-air samples that were taken at Abisko showed lower CH_3Br concentrations than the air at the site and the $\delta^{81}Br$ values seemed to be higher than in the air samples. Due to the small number and premature character of these measurements Horst et al. (2013) and Horst (2013) were not able yet to give an explanation for these results.

References

Agrinier P, Coleman M, Bonifacie M (2011) A review of the analytical accuracy of Cl isotope measurments in rocks by various techniques: a way to explain inconsistency between results. In: 21th annual V.M. Goldschmidt conference. Prague, Czech Republic (Mineral Mag 75:413)

Bagheri R (2013) Hydrochemistry and sources of connate water in the Zagros aquifers. PhD Thesis Shiraz University, Iran

Bagheri R, Nadri A, Raeisi E, Eggenkamp HGM, Kazemi GA, Montaseri A (2014a) Hydrochemistry and isotope ($\delta^{18}O$, δ^2H, $^{87}Sr/^{86}Sr$, $\delta^{37}Cl$ and $\delta^{81}Br$) applications: clues to the origin of saline produced water in a gas reservoir. Chem Geol 384:62–75

Bagheri R, Nadri A, Raeisi E, Kazemi GA, Eggenkamp HGM, Montaseri A (2014b) Origin of brine in the

Kangan Gasfield: Isotopic and hydrogeochemical approaches. Environ Earth Sci 72:1055–1072

Banks DA, Green R, Cliff RA, Yardley BWD (2000a) Chlorine isotopes in fluid inclusions: determination of the origins of salinity in magmatic fluids. Geochim Cosmochim Acta 64:1785–1789

Banks DA, Gleeson SA, Green R (2000b) Determination of the origin of salinity in granite-related fluids: evidence from chlorine isotopes in fluid incusions. J Geochem Expl 69–70:309–312

Barnes JD, Sharp ZD (2006) A chlorine isotope study of DSDP/ODP serpentinized ultramafic rocks: insights into the serpentinization process. Chem Geol 228:246–265

Barnes JD, Selverstone J, Sharp ZD (2006) Chlorine isotope chemistry of serpentinites from Elba, Italy, as an indicator of fluid source and subsequent tectonic history. Geochem Geophys Geosys 7 (Article number Q08015)

Barnes JD, Sharp ZD, Fischer TP (2008) Chlorine isotope variations across the Izu-Bonin-Mariana arc. Geology 36:883–886

Barnes JD, Sharp ZD, Fisher TP, Hilton DR, Carr MJ (2009) Chlorine isotope variations along the Central American volcanic front and back arc. Geochem Geophys Geosys 10 (Article number Q11S17)

Barnes JD, Eldam R, Lee CTA, Errico JC, Loewy S, Cisneros M (2013) Petrogenesis of serpentinites from the Franciscan Complex, western California, USA. Lithos 178:143–157

Beekman HE, Eggenkamp HGM, Appelo CAJ (2011) An integrated modelling approach to reconstruct complex solute transport mechanisms—Cl and δ^{37}Cl in pore water of sediments from a former brackish lagoon in The Netherlands. Appl Geochem 26:257–268

Berner EK, Berner RA (1987) The global water cycle: geochemistry and environment. Prentice-Hall Inc, Englewood Cliffs

Blaxland AB, Van Breemen O, Steenfelt A (1976) Age and origin of agpaitic magmatism at Ilímaussaq, South Greenland: Rb-Sr study. Lithos 9:31–38

Bonifacie M, Jendrzejewski N, Agrinier P, Coleman M, Pineau F, Javoy M (2007) Pyrohydrolysis-IRMS determination of silicate chlorine stable isotope compositions. Application to oceanic crust and meteorite samples. Chem Geol 242:187–201

Bonifacie M, Jendrzejewski N, Agrinier P, Humler E, Coleman M, Javoy M (2008a) The chlorine isotope composition of earth's mantle. Science 319:1518–1520

Bonifacie M, Busigny V, Mével C, Philippot P, Agrinier P, Jendrzejewski N, Scambelluri M, Javoy M (2008b) Chlorine isotopic composition in seafloor serpentinites and high-pressure metaperidotites. Insights into oceanic serpentinization and subduction processes. Geochim Cosmochim Acta 72:126–139

Boschetti T, Toscani L, Shouakar-Stash O, Iacumin P, Venturelli G, Mucchino C, Frape SK (2011) Salt waters of the northern apennine foredeep basin (Italy): origin and evolution. Aquat Geochem 17:71–108

Braitsch O (1962) Entstehung und Stoffbestand der Salzlagerstätten. Springer, Berlin

Braitsch O (1971) Salt deposits, their origin and composition. Springer, Berlin, 288 p

Broeker WS, Peng TH (1982) Tracers in the sea. Eldigio Press Lamont Doherty Geological Observatory

Campbell DJ (1985) Fractionation of stable chlorine isotopes during transport through semipermeable membranes. MS. thesis, University of Arizona

Davies SN, Whittemore DO, Fabryka-Martin J (1998) Use of chloride/bromide ratios in studies of potable water. Ground Water 36:338–350

Desaulniers DE, Kaufmann RS, Cherry JA, Bentley HW (1986) ^{37}Cl–^{35}Cl variations in a diffusion controlled groundwater system. Geochim Cosmochim Acta 50:1757–1764

Du Y, Ma T, Yang J, Liu L, Shan HM, Cai HS, Liu CF, Chen LZ (2013) A precise analytical method for bromine stable isotopes in natural waters by GasBench II-IRMS. Int J Mass Spectrom 338:50–56

Eastoe CJ, Peryt T (1999) Multiple sources of chloride in Badenian evaporites, Carpathian mountains: stable chlorine isotope evidence. Terra Nova 11:118–123

Eastoe CJ, Guilbert JM, Kaufmann RS (1989) Preliminary evidence for fractionation of stable chlorine isotopes in ore forming hydrothermal systems. Geology 17:285–288

Eastoe CJ, Long A, Knauth LP (1999) Stable chlorine isotopes in the Palo Duro Basin, Texas: evidence for preservation of Permian evaporite brines. Geochim Cosmochim Acta 63:1375–1382

Eastoe CJ, Long A, Land LS, Kyle JR (2001) Stable chlorine isotopes in halite and brine from the Guld Coast Basin: brine genesis. Chem Geol 176:343–360

Eastoe CJ, Peryt TM, Petrychenko OY, Geisler-Cussey D (2007) Stable chlorine isotopes in Phanerozoic evaporites. Appl Geochem 22:575–588

Egeberg PK, Dickens G (1999) Thermodynamic and pore-water halogen constraints on gas hydrate distribution at ODP site 997 (Blake Ridge). Chem Geol 153:53–79

Eggenkamp HGM (1994) δ^{37}Cl; the geochemistry of chlorine isotopes. Geol Ultrai 116:1–150 (Thesis Utrecht University)

Eggenkamp HGM (1995) Bromine stable isotope fractionation: experimental determination on evaporites. European Union of Geosciences, 8th Congress. Terra Nova 7 Abst. Supp. 1, 331

Eggenkamp HGM, Coleman ML (1997) Comparison of chlorine and bromine isotope fractionation in diffusion: Geochemical consequences. 7th annual Goldschmidt Conference, Tucson, Az. p 213

Eggenkamp HGM, Coleman ML (2000) Rediscovery of classical methods and their application to the measurement of stable bromine isotopes in natural samples. Chem Geol 167:393–402

Eggenkamp HGM, Coleman ML (2009) The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes. Geochim Cosmochim Acta 73:3539–3548

Eggenkamp HGM, Koster van Groos AF (1997) Chlorine stable isotopes in carbonatites: evidence for isotopic heterogeneity in the mantle. Chem Geol 140:137–143

Eggenkamp HGM, Middelburg JJ, Kreulen R (1994) Preferential diffusion of ^{35}Cl relative to ^{37}Cl in sediments of Kau Bay, Halmahera, Indonesia. Chem Geol (Isot Geosc Sect) 116:317–325

Eggenkamp HGM, Kreulen R, Koster van Groos AF (1995) Chlorine stable isotope fractionation in evaporites. Geochim Cosmochim Acta 59:5169–5175

Eggenkamp HGM, Pouya A, Coleman ML (1997) Can diffusion and shale compaction be causes of chlorine isotope fractionation in basinal brines? In: Second international conference on fluid evolution, migration and interaction in sedimentary basins and orogenic belts. Belfast, Northern Ireland, 10–14 March. Geofluids II '97 Extended abstract pp 322–325

Eggenkamp HGM, Bonifacie M, Ader M, Agrinier P. (2011) Fractionation of Cl and Br isotopes during precipitation of salts from their saturated solutions. 21th annual V.M. Goldschmidt conference. Prague, Czech Republic (Mineral Mag 75:798)

Gleeson SA, Smith MP (2009) The sources and evolution of mineralising fluids in iron oxide-copper-gold systems, Norrbotten, Sweden: constraints from Br/Cl ratios and stable Cl isotopes of fluid inclusion leachates. Geochim Cosmochim Acta 73:5658–5672

Godon A, Jendrzejewski N, Eggenkamp HGM, Banks DA, Ader M, Coleman ML, Pineau F (2004a) A cross calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. Chem Geol 207:1–12

Godon A, Webster JD, Layne GD, Pineau F (2004b) Secondary ion mass spectrometry for the determination of δ^{37}Cl. Part II. Intercalibration of SIMS and IRMS for aluminosilicate glasses. Chem Geol 207:291–303

Godon A, Jendrzejewski N, Castrec-Rouelle M, Dia A, Pineau F, Boulège J, Javoy M (2004c) Origin and evolution of fluids from mud volcanos in the Barbadas accretionary complex. Geochim Cosmochim Acta 68:2153–2165

Groen J, Velstra J, Meesters AGCA (2000) Salinization processes in paleowaters in coastal sediments from Suriname: evidence from δ^{37}Cl analysis and diffusion modelling. J Hydrol 234:1–20

Gwynne R, Frape S, Shouakar-Stash O, Love A (2013) ^{81}Br, ^{37}Cl and ^{87}Sr studies to assess groundwater flow and solute sources in the southwestern great Artesian Basin, Australia. Proc Earth Planet Sci 7:330–333

Hesse R (2003) Pore water anomalies of submarine gas-hydrate zones as tool to assess hydrate abundance and distribution in the subsurface: what have we learned in the past decade? Earth Sci Rev 61:149–179

Hesse R, Frape SK, Egeberg PK, Matsumoto R (2000) Stable isotope studies (Cl, O and H) of interstitial waters from site 997, Blake Ridge gas hydrate field, West Atlantic. In: Paull CK, Matsumoto R, Wallace PJ, Dillon WD (eds) Proceedings of the ocean drilling program, scientific results, 164: College Station, TX (Ocean Drilling Program) pp 129–137

Hesse R, Egeberg PK, Frape SK (2006) Chlorine stable isotope ratios as a tracer for pore-water advection rates in a submarine gas-hydrate field: implication for hydrate concentration. Geofluids 6:1–7

Hoering TC, Parker PL (1961) The geochemistry of the stable isotopes of chlorine. Geochim Cosmochim Acta 23:186–199

Horst A (2013) Stable bromine isotopic composition of methyl bromide. Method development and applications. PhD thesis Stockholm University

Horst A, Thornton BJ, Holmstrand H, Andersson P, Crill PM, Gustafsson Ö (2013) Stable bromine isotopic composition of atmospheric CH_3Br. Tellus Ser B Chem Phys Meteor 65 (Article no. 21040)

John T, Layne GD, Haase KM, Barnes JD (2010) Chlorine isotope evidence for crustal recycling into Earth's mantle. Earth Planet Sci Lett 298:175–182

John T, Scambelluri M, Frische M, Barnes JD, Bach W (2011) Dehydration of subducting serpentinite: implications for halogen mobility in subduction zones and the deep halogen cycle. Earth Planet Sci 308:65–76

Kastner M, Elderfield H, Jenkins WJ, Gieskes JM, Gamo T (1993) Geochemical and isotopic evidence for fluid flow in the western Nankai subduction zone, Japan. In: Hill IA, Taira A (eds) Proceedings of the ocean drilling program, Scientific Results, Leg 131: College Station, Texas, ODP, pp 397–416

Kaufmann RS (1984) Chlorine in groundwater: stable isotope distribution. PhD thesis, University of Arizona, Tucson, Ariz

Kaufmann RS, Frape S, Fritz P, Bentley H (1987) Chlorine stable isotope composition of Canadian shield brines. In: Fritz P, Frape SK (eds) Saline water and gases in crystalline rocks. Geol Assoc Canada (Special Paper 33:89–93)

Kaufmann RS, Long A, Campbell DJ (1988) Chlorine isotope distribution in formation waters, Texas and Louisiana. AAPG Bull 72:839–844

Kaufmann RS, Frape SK, McNutt R, Eastoe CJ (1993) Chlorine stable isotope distribution of Michigan basin formation waters. Appl Geoch 8:403–407

Knauth LP (1998) Salinity history of the Earth's early ocean. Nature 395:554–555

Kolodny Y, Katz A, Starinsky A, Moise T, Simon E (1999) Chemical tracing of salinity sources in Lake Kinneret (Sea of Galilee), Israel. Limnol Oceanogr 44:1035–1044

Kühn R (1968) Geochemistry of the German potash deposits. Geol Soc Am Spec Pap 88:427–504

Land LS (1995) The role of saline formation water in crustal cycling. Aquat Chem 1:137–145

Laube JC, Kaiser J, Sturges WT, Bönisch H, Engel A (2010) Chlorine isotope fractionation in the stratosphere. Science 329:1167

Lavastre V, Jendrzejewski N, Agrinier P, Javoy M, Evrard M (2005) Chlorine transfer out of a very low permeability clay sequence (Paris Basin, France): ^{35}Cl and ^{37}Cl evidence. Geochim Cosmochim Acta 69:4949–4961

Layne GD, Kent AJR, Bach W (2009) δ^{37}Cl systematics of a backarc spreading system: the Lau Basin. Geology 37:427–430

Le Gal La Salle C, Matray JM, Bensenouci F, Michelot JL, Dauzères A, Wittebroodt C, Frape S, Shouakar Stash O, Rebaix R, Lancelot J (2013) Modelling Cl-concentration and δ^{37}Cl profiles in porewater across a 250 m-thick indurated clayrock at the tournemire URL (France). Proc Earth Planet Sc 7:471–474

Li XQ, Zhou AG, Liu YD, Ma T, Liu CF, Liu L, Yang J (2012) Stable isotope geochemistry of dissolved chloride in relation to hydrogeology of the strongly exploited quaternary aquifers, North China Plain. Appl Geochem 27:2031–2041

Li YP, Jiang SY (2013) Major cation/chlorine ratio and stable chlorine isotopic compositions of sediment interstitial water in the Brazos-Trinity Basin IV from the Gulf of Mexico (IODP 308). J Asian Earth Sci 65:42–50

Liebscher A, Barnes J, Sharp Z (2006) Chlorine isotope vapor-liquid fractionation during experimental fluid-phase separation at 400 C/23 MPa to 450 C/42 MPa. Chem Geol 234:340–345

Liu WG, Xiao YK, Wang QZ, Qi HP, Wang YH, Zhou YM, Shirodkar PV (1997) Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. Chem Geol 136:271–279

Liu YD, Zhou AG, Gan YQ, Liu CF, Yu TT, Li XQ (2013) An online method to determine chlorine stable isotope composition by continuous flow isotope ratio mass spectrometry (CF-IRMS) coupled with a Gasbench II. J South Centr Univ 20:193–198

Luo CG, Xiao YK, Ma HZ, Ma YQ, Zhang YL, He MY (2012) Stable isotope fractionation of chlorine during evaporation of brine from a saline lake. Chin Sci Bull 57:1833–1843

Magenheim AJ, Spivack AJ, Volpe C, Ransom B (1994) Precise determination of stable chlorine isotopic ratios in low-concentration natural samples. Geochim Cosmochim Acta 58:3117–3121

Magenheim AJ, Spivack AJ, Michael PJ, Gieskes JM (1995) Chlorine stable isotope composition of the oceanic crust: implications for Earth's distribution of chlorine. Earth Planet Sci Lett 131:427–432

Mahara Y, Ohta T, Tokunaga T, Matsuzaki H, Nagao K, Nakata E, Miyamoto Y, Kubota T (2013) Pore-water mobility: Distribution of δ^{37}Cl, ^{36}Cl/Cl, ^{129}I/^{127}I and dissolved ^{4}He concentration in the core drilled in the Mobara gas field, Japan. Nucl Instr Meth Phys Res B 294:597–601

Markl G, Musashi M, Bucher K (1997) Chlorine stable isotope composition of granulites from Lofoten, Norway: Implications for the Cl isotope composition and for the source of Cl enrichment in the lower crust. Earth Planet Sci Lett 150:95–102

Martin JG (1993) Stable chlorine isotopes in the milk river aquifer, Alberta, Canada: implications for the geochemical evolution of the aquifer system. MSc thesis, Univ Arizona

Matray JM, Meunier A, Thomas M, Fontes JC (1989) Les eaux de formation du Trias et du Dogger du Bassin Parisien: Histoire et effets diagénétiques sur les réservoirs. Bull Soc Nat Elf-Aquitaine (Prod.) 13:484–504

Musashi M, Oi T, Eggenkamp HGM, Matsuo M (2008) Chlorine isotope fractionation associated with volcanic activity at the Kusatsu-Bandaiko hot spring in Japan. Isot Env Health St 44:305–313

Nakamura N, Nyquist LE, Shih CY, Fujitani T, Okano O (2011) Stable chlorine isotopes and elemental chlorine by thermal ionization mass spectrometry and ion chromatography: martian meteorites, carbonaceous chondrites and standard rocks. In: 42nd lunar and planetary science conference (abstract 2513)

Phillips FM, Bentley HW (1987) Isotopic fractionation during ion filtration: I. Theory. Geochim Cosmochim Acta 51:683–695

Ransom B, Spivack AJ, Kastner M (1995) Stable Cl isotopes in subduction-zone porewaters: implications for fluid rock reactions and the cycling of chlorine. Geology 23:715–718

Rebeix R, Le Gal La Salle C, Jean-Baptiste P, Lavastre V, Fourré E, Bensenouci F, Matray JM, Landrein P, Shouakar-Stash O, Frape SK, Michelot JL, Lancelot J (2014) Chlorine transport processes through a 2000 m aquifer/aquitard system. Mar Petr Geol 53:102–116

Richard A, Banks DA, Mercadier J, Boiron MC, Cuney M, Cathelineau M (2011) An evaporated seawater origin for the ore-forming brines in unconformity-related uranium deposits (Athabasce Basin, Canada): Cl/Br and δ^{37}Cl analysis of fluid inclusions. Geochim Cosmochim Acta 75:2792–2810

Rittenhouse G (1967) Bromine in oil field waters and its use in determining possibilities of origin of these waters. AAPG Bull 17:1213–1228

Rodríguez A, Martínez M, Eggenkamp HGM, van Bergen MJ (2013) Chlorine isotope variations in the hyper-acid lake system of Poás volcano, Costa Rica. IAVCEI 2013 Scientific Assembly, p 58

Schauble EA, Rossman GR, Taylor HP (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochim Cosmochim Acta 67:3267–3281

Schilling JG, Unni CK, Bender ML (1978) Origin of chlorine and bromine in the oceans. Nature 273:631–636

Selverstone J, Sharp ZD (2011) Chlorine isotope evidence for multicomponent mantle metasomatism in the Ivrea Zone. Earth Planet Sci Lett 310:429–440

Sharp ZD, Barnes JD (2004) Water-soluble chlorides in massive seafloor serpentinites: a source of chloride in subduction zones. Earth Planet Sci Lett 226:243–254

Sharp ZD, Barnes JD (2008) Comment to "Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean" by Wei et al. A review of the Cl isotope composition of serpentinites and the global chlorine cycle. Earth Planet Sci Lett 274:531–534

Sharp ZD, Barnes JD, Brearly AJ, Chaussidon M, Fisher TP, Kamenetsky VS (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature 446:1062–1065

Sharp ZD, Barnes JD, Fischer TP, Halick M (2010a) An experimental determination of chlorine isotope fractionation in acid systems and applications to volcanic fumaroles. Geochim Cosmochim Acta 74:264–273

Sharp ZD, Shearer CK, McKeagan KD, Barnes JD, Wang YQ (2010b) The chlorine isotope composition of the moon and implications for an anhydrous mantle. Science 329:1050–1053

Sharp ZD, Selverstone J, Mercer JA (2011) The Cl isotope composition of the mantle revisited. In: 21th annual V.M. Goldschmidt conference. Prague, Czech Republic (Mineral Mag 75:1848)

Sharp ZD, Mercer JA, Jones RH, Brearley AJ, Selverstone J, Bekker A, Stachel T (2013) The chlorine isotope composition of chondrites and earth. Geochim Cosmochim Acta 107:189–204

Shields WR, Murphy TJ, Garner EL, Dibeler VH (1962) Absolute isotopic abundance ratios and the isotopic weight of chlorine. J Amer Chem Soc 84:1519–1522

Shirodkar PV, Xiao YK, Hai L (2003) Boron and chlorine isotopic signatures of seawater in the Central Indian ridge. Current Sci 85:313–320

Shirodkar PV, Xiao YK, Sarkar A, Dalal SG, Chivas AR (2006) Influence of air-sea fluxes on chlorine isotopic composition of ocean water: implications for constancy in δ^{37}Cl—A statistical inference. Environ Intern 32:235–239

Shouakar-Stash O (2008) Evaluation of stable chlorine and bromine isotopes in sedimentary formation fluids. PhD thesis University of Waterloo

Shouakar-Stash O, Frape SK, Drimmie RJ (2005) Determination of bromine stable isotopes using continuous-flow isotope ratio mass spectrometry. Anal Chem 77:4027–4033

Shouakar-Stash O, Frape SK, Rostron BJ, Drimmie RJ (2006) Variations of the δ^{81}Br and δ^{37}Cl stable isotope signature for pre-Mississippian formation waters of the Williston Basin. In: Abstract presented at the Goldschmidt conference (Geochim Cosmochim Acta 70(suppl):A589)

Shouakar-Stash O, Alexeev SV, Frape SK, Alexeeva LP, Drimmie RJ (2007) Geochemistry and stable isotope signatures, including chlorine and bromine isotopes, of the deep groundwaters of the Siberian Platform, Russia. Appl Geochem 22:589–605

Sie PMJ, Frape SK (2002) Evaluation of the groundwaters from the Stripa mine using stable chlorine isotopes. Chemical Geology 182:565–582

Siemann MG (2003) Extensive and rapid changes in seawater chemistry during the Phanerozoic: evidence from Br contents in basal halite. Terra Nova 15:243–248

Stewart MA (2000) Geochemistry of dikes and lavas from Hess Deep: implication for crustal construction processes beneath mid-oceanic ridges and the stable chlorine isotope geochemistry of mid-ocean ridge basalts. PhD dissertation thesis, Duke University, Durham, North Carolina

Stiller M, Nissenbaum A, Kaufmann RS, Long A (1998) Cl-37 in the Dead Sea system—preliminary results. Appl Geochem 13:953–960

Stiller M, Rosenbaum JM, Nishri A (2009) The origin of brines underlying Lake Kinneret. Chem Geol 262:293–309

Stotler RL, Frape SK, Shouakar-Stash O (2010) An isotopic survey of δ^{81}Br and δ^{37}Cl of dissolved halides in the Canadian and Fennoscandian shields. Chem Geol 274:38–55

Tan HB, Ma HZ, Xiao YK, Wei HZ, Zhang XY, Ma WD (2005) Characteristics of chlorine isotope distribution and analysis on sylvinite deposit formation based on ancient salt rock in western Tarim basin. Sc China (ser D) 48:1913–1920

Tan HB, Ma HZ, Wei HZ, Xu JX, Li TW (2006) Chlorine, sulfur and oxygen isotopic constraints on ancient evaporite deposit in the Western Tarim Basin, China. Geochem J 40:569–577

Tan HB, Ma HZ, Zhang XY, Xu JX, Xiao YK (2009) Fractionation of chlorine isotope in salt mineral sequences and application: research on sedimentary stage of ancient salt rock deposit in Tarim Basin and western Qaidam Basin. Acta Petrol Sinica 25:955–962 (in Chinese with English abstract)

Tanaka N, Rye DM (1991) Chlorine in the stratosphere. Nature 353:707

Thornton B, Horst A, Carrizo D, Holmstrand H, Andersson P, Crill PM, Gustafsson Ö (2013) A high-volume cryosampler and sample purification system for bromine isotope studies of methyl bromide. J Atmos Ocean Techn 30:2095–2107

Valyashko MG (1956) Geochemsitry of bromide in the process of salt depositition and the use of the bromide content as a genetic and prospecting tool. Geochem Int 6:570–587

Van't Hoff JH (1905) Zur Bildung der ozeanischen Salzablagerungen. Teil 1. 85 p. Fr. Vieweg

Van't Hoff JH (1909) Zur Bildung der ozeanischen Salzablagerungen. Teil 2. 90 p. Fr. Vieweg

Van't Hoff JH (1912) Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen. 374 p. Leipzig; Akad Verl Ges (Reprint of the original papers taken from S-B Kgl Preuß Akad, 1897–1908

Van't Hoff JH, Mayerhoffer W (1897) Untersuchungen über die Bildungsverhältnisse der oceanischen Salzablagerungen, insbesondere des Stassfurter Salzlagers. Sitzungsb. Kön Preuß. Akad. Wissenschaften 1897:69–75

Wahrenberger C, Eastoe CJ, Seward TM, Dietrich V (1997) Stable chlorine isotope composition of volcanic gas condensates. In: 7th annual Goldschmidt conference, Tucson, Az. p 213

Wassenaar LI, Koehler G (2004) On-line technique for the determination of the δ^{37}Cl of inorganic and total organic Cl in environmental samples. Anal Chem 76:6384–6388

Wei W, Kastner M, Spivack A (2008a) Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean. Earth Planet Sci Lett 266:90–104

Wei W, Kastner M, Spivack A (2008b) Reply to comment on: "Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean". Earth Planet Sci Lett 274:535

Willey JF, Taylor JW (1978) Capacitive integration to produce high precision isotope ratio measurements on methyl chloride and bromide. Anal Chem 50:1930–1933

Wirt L (1988) The origin of chloride in groundwater in the Stripa granite, Sweden. MSc thesis, Univ Arizona

Xiao YK, Liu WG, Qi HP, Zhang CG (1993) A new method for the high precision isotopic measurement of bromine by thermal ionization mass spectrometry. Intl J Mass Spectrom Ion Proc 123:117–123

Xiao YK, Liu WG, Zhou YM, Sun DP (1997) Isotope compositions of chlorine in brine and saline minerals. Chin Sci Bull 42:406–409

Xiao YK, Liu WG, Zhou YM, Wang YH, Shirodkar PV (2000) Variations in isotopic compositions of chlorine in evaporation controlled salt lake brines of Qaidam Basin, China. Chin J Ocean Limn 18:169–177

Xiao YK, Zhou YM, Wang QZ. Wei HZ, Liu WG, Eastoe CJ (2002) A secondary isotopic reference material of chlorine from selected seawater. Chem Geol 182:655–661

Ziegler K, Coleman ML, Howarth RJ (2001) Palaeohydrodynamics of fuids in the Brent Group (Oseberg Field, Norwegian North Sea) from chemical and isotopic compositions of formation waters. Appl Geochem 16:609–632

11 Chlorine Isotope Characteristics of Extraterrestrial Material

11.1 Meteorites (Chondrites)

The earliest chlorine isotope compositions of meteorites were determined by Magenheim et al. (1994, 1995). These data, with values in the range from +2.7 and +4 ‰ were at that time considered as being intermediate between mantle and crust values and were used to determine differentiation of chlorine isotopes between the mantle and the crust of the earth, as it was considered that the chlorine isotope composition in these meteorites represented primordial chloride. These measurements, which were determined by the method developed by Magenheim et al. (1994), are currently considered as not valid anymore due to possible artefacts of the method, as discussed earlier in this book. Other early measurements were done on the water soluble chlorides and halite from the ZAG-II chondrite (Bridges et al. 2004). These samples, also analysed by P-TIMS (Cs_2Cl^+) but at the University of Leeds, showed negative values between −2.8 and −1.4 ‰. These values were explained as either a second reservoir from the early solar system, or large secondary fractionation due to low-temperature fluid activity. Nakamura et al. (2007) presented an overview of 24 bulk chondrites and observed that O-chondrites and E-chondrites have a negative correlation between the chloride concentration and chlorine isotope compositions, while C-chondrites had a positive correlation. They found a very large range in chlorine isotope compositions, from −4.6 to +5.0 ‰, analysed with (P-)TIMS. This technique was later considered as possibly delivering false results and it is not known if these data would still stand.

Sharp et al. (2007) analysed the chlorine isotope composition of chondrites by gas-IRMS (CH_3Cl) analysis. Larger samples were analysed by dual inlet, smaller by continuous flow. They analysed five chondrites, and found that their $\delta^{37}Cl$ values were relatively close to 0 ‰, although with a fairly large spread (−0.71 to +1.21 ‰), from which they concluded that the average $\delta^{37}Cl$ value of meteorites was indistinguishable from the earth's average chlorine isotope composition. Sharp et al. (2007) also analysed 10 sodalite samples from the meteorite Allende. These samples were analysed by Secondary Ion Mass Spectrometry (SIMS) using a Cameca 1270 ion microprobe at CNRS, CRPG, Vandoeuvre-les-Nancy, France. These samples were all significantly negative relative to SMOC with an average value of −1.3 ‰ (the range of values was between −2.09 and −0.39 ‰). Two possible explanations were given for these low values. Either a second nebular chlorine reservoir, or, because of equilibrium isotope fractionation during the formation of sodalite from nepheline and sodium chloride, secondary isotope fractionation. The experimentally determined fractionation between sodalite and sodium

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_11,

chloride indeed indicated negative δ^{37}Cl values for sodalite relative to sodium chloride. As this fractionation (10^3lnα) was experimentally determined as −0.3 at 825 °C, which would logically increase at lower temperatures values around −1 ‰ for the sodalite seemed reasonable due to this process.

A further set of 19 chondrites were analysed by Sharp et al. (2013). They analysed carbonaceous, ordinary and enstatite chondrites, both in altered and unaltered form. They also analysed the structurally bound and water soluble chloride separately. It was found that the bulk chlorine isotope composition of the least altered chondrites showed average values of −0.3 ± 0.5 ‰. The structurally bound values of the chloride in these chondrites is −0.3 ± 0.3 ‰. These values are indistinguishable from the bulk chlorine isotope composition of the earth as determined by Sharp et al. (2007, 2013) and are comparable to the lowest δ^{37}Cl values that are determined on the moon (Sharp et al. 2010b). For this reason Sharp et al. (2013) concluded that the inner regions of the early solar nebula had a homogeneous chlorine isotope reservoir. Sharp et al. (2013) did find larger variations in meteorites that had undergone secondary processing. Samples that were metamorphosed showed bulk δ^{37}Cl values between −1.2 and +0.8 ‰. Samples that were aqueously altered showed values between −0.3 and +0.3 ‰. The averages of both groupings are very close to 0‰ versus SMOC. These larger variations are explained by fractionation processes which are similar to processes that occur on Earth. Sharp et al. (2013) also didn't observe any relationship between the chloride concentrations and the chlorine isotope compositions. Their general conclusion is that no chlorine isotope variations existed in the primary solar nebula (thus that is was homogeneous) and that all chlorine isotope variations in meteorites, but also on earth are the result of secondary fractionation.

To assess the chlorine isotope variation in secondary processed chondrites, Schauble and Sharp (2011) modelled the chlorine isotope fractionation between gas phase HCl and crystalline phases HCl.3H_2O, NaCl, KCl and $Na_4Al_3(SiO_4)_3Cl$. They applied this exercise using a combination of experimental vibrational frequencies and electronic structure models. It was calculated that sodalite ($Na_4Al_3(SiO_4)_3Cl$) would have a δ^{37}Cl that would be about ±0.7 ‰ lower than HCl at 950 K, which is in line, although somewhat smaller, with the chlorine isotope composition of sodalite inclusions in the meteorite Allende (Sharp et al. 2007). The fractionation between the solid HCl.3H_2O and gaseous HCl is predicted to be between +3 and +6 ‰ at temperatures that are relevant to low-pressure gas/crystal partitioning, which is about 140–160 K or −133 to −113 °C. This fractionation, with heavier HCl in the crystalline form is opposite to the expected fractionation that this crystalline form would be lighter. These results led to the conclusion that it may be possible to distinguish between icy and silicate sources of chloride in planets and planetary precursors (Zolotov and Mironenko 2007), at least as long as the chloride condensation was not quantitatively complete. Very positive δ^{37}Cl values which are derived from acid hydrates could, if they were to be found, indicate a post-condensation origin of chlorine bearing minerals and would be consistent with a correlation of high chloride concentration and hydration of chloride in CI chondrites.

11.2 Moon

Sharp et al. (2010b) studied the isotope composition of twelve lunar samples, which consisted of basalts and glasses. They observed that the range of δ^{37}Cl values in these samples was much larger than on earth and ranged from about −1 to +24 ‰ versus SMOC. The variations ware observed to be related to fractionation due to devolatilization of anhydrous lunar basalts. The lowest δ^{37}Cl values measured in the study were all close to SMOC and overlap the range of terrestrial samples, indicating a homogeneous source for the Earth and Moon systems. The samples with more positive δ^{37}Cl values could then be explained by fractionation due to degassing where the light isotope got lost. On earth chlorine isotopes do not fractionate considerable during degassing of magmas and as a result the $\delta^{37}Cl$ variation in basalts on Earth is not very large. In the lunar samples this is explained as the result of the very low hydrogen content of lunar magmas. On earth the chlorine isotope fractionation is controlled by two factors. Firstly by the preferential loss of the lighter ^{35}Cl to the vapour phase due to its higher translational velocity and vapour pressure, and secondly by the preferential incorporation of the heavier ^{37}Cl into hydrogen chloride gas due to the covalent character of the bond (Schauble et al. 2003; Sharp et al. 2010a). These two effects appear to cancel each other out on circumstances that exist on Earth, but apparently not on the moon, where it appears that the second hydrogen chloride fractionating effect is much smaller than on earth. If no hydrogen (in the form of water) is present in a melt the chloride can be volatilised in the form of metal chlorides such as NaCl, $ZnCl_2$ and $FeCl_2$ (Fegley 1991; Colson 1992). The bonds in the melt and in the vapour phase are similar, so that the kinetic fractionation that occurs during loss of volatiles is cancelled out by a different fractionating effect, resulting in evaporation of the lighter isotope, and thus the increase of $\delta^{37}Cl$ in the remaining magma phase. Metal chlorides have been observed as surface coatings on lunar volcanic materials (Chou et al. 1975; McKay and Wentworth 1993), consistent with deposition of metal chloride vapour phases. Thermodynamic calculations also support that metal halide vapours deliver the dominant chlorine species when the Cl/H ratio is substantially greater than 1 (Fegley and Swindle 1993). Sharp et al. (2010b) have calculated the amount of chloride loss by volatilization of metal chlorides by assuming a Rayleigh type fractionation and found that a fractionation of 20 ‰ could be reached when 63–98 ‰ of chloride is lost assuming fractionation factors between 0.983 and 0.992. The observed fractionation of chloride in lunar rocks would only be possible if the hydrogen content in lunar magma was low compared to the chloride content in these magmas. Calculations by Sharp et al. (2010b) indicate that the original lunar mantle would have chloride concentrations of about 400 ppb, and considering that the hydrogen content must be lower than the chloride content to observe the large kinetic chloride fractionation the hydrogen content must be in the order of 10(s of) ppb, much lower (4 orders of magnitude) than the bulk earth value of 260 ppm.

11.3 Mars

As no Mars rocks have been returned to earth yet knowledge on the chlorine isotope composition of Martian rock must be concluded from meteorites that originated from Mars. Sharp et al. (2011) presented the chlorine isotope compositions of eight Martian meteorites. The $\delta^{37}Cl$ values of these samples were between −3 and +2 ‰. It was observed that shergottites had negative $\delta^{37}Cl$ values while cumulates had positive values. These preliminary results were explained as the result of near-surface contamination or volatile loss.

References

Bridges JC, Banks DA, Smith M, Grady MM (2004) Halite and stable chlorine isotopes in the Zag H3-6 breccia. Meteorit Planet Sci 39:657–666

Chou CL, Boynton WV, Sundberg LL, Wasson JT (1975) Volatiles on the surface of Apollo 15 green glass and trace-element distributions among Apollo 15 soils. Proc Lunar Planet Sci Conf 2:1701–1727

Colson RO (1992) Mineralization on the moon? Theoretical considerations of Apollo 16 ‘rusty rocks’, sulfide replacement in 67016, and surface-correlated volatiles on lunar volcanic glass. Proc Lunar Planet Sci 22:427–436

Fegley BJ (1991) Thermodinamic models of the chemistry of Lunar volcanic gases. Geophys Res Lett 18:2073–2076

Fegley BJ, Swindle TD (1993) Lunar volatiles, implications for lunar resource utilization. In: Lewis MSM, Guerrieri ML (eds) Resource of near-earth space. University of Arizona Press, Tucson, pp 367–426

Magenheim AJ, Spivack AJ, Volpe C, Ransom B (1994) Precise determination of stable chlorine isotopic ratios in low-concentration natural samples. Geochim Cosmochim Acta 58:3117–3121

Magenheim AJ, Spivack AJ, Michael PJ, Gieskes JM (1995) Chlorine stable isotope composition of the oceanic crust: implications for Earth’s distribution of chlorine. Earth Planet Sci Lett 131:427–432

McKay DS, Wentworth SJ (1993) Grain surface features of Apollo 17 orange and black glass. Lunar Planet Sci Conf 24:961–962

Nakamura N, Fujitani T, Kimura M (2007) A new isotope tracer for the early solar system processes: stable chlorine isotopes and the distribution of Cl-bearing phases in chondrites. In: 38th lunar and planetary science conference. Abstract 1707

Schauble EA, Sharp ZD (2011) Modeling isotopic signatures of nebular chlorine condensation. 21st annual V.M. Goldschmidt conference, Prague, Czech Republic. Mineral Mag 75:1810

Schauble EA, Rossman GR, Taylor HP (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochim Cosmochim Acta 67:3267–3281

Sharp ZD, Barnes JD, Brearly AJ, Chaussidon M, Fisher TP, Kamenetsky VS (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature 446:1062–1065

Sharp ZD, Barnes JD, Fischer TP, Halick M (2010a) An experimental determination of chlorine isotope fractionation in acid systems and applications to volcanic fumaroles. Geochim Cosmochim Acta 74:264–273

Sharp ZD, Shearer CK, McKeagan KD, Barnes JD, Wang YQ (2010b) The chlorine isotope composition of the Moon and implications for an anhydrous mantle. Science 329:1050–1053

Sharp ZD, Shearer CK, McCubbin FM, Agee CB (2011) The Cl isotope composition of the Moon and Mars. 21st annual V.M. Goldschmidt conference, Prague, Czech Republic. Mineral Mag 75:1848

Sharp ZD, Mercer JA, Jones RH, Brearley AJ, Selverstone J, Bekker A, Stachel T (2013) The chlorine isotope composition of chondrites and earth. Geochim Cosmochim Acta 107:189–204

Zolotov MYu, Mironenko MV (2007) Hydrogen chloride as a source of acid fluids in parent bodies of chondrites. 38th lunar and planetary science conference #2340

12 Isotope Variations of Perchlorates in the Environment

12.1 Introduction

It is only realised since about 2000 that perchlorate is a naturally occurring anion outside the Atacama desert in Chile (see e.g. Dasgupta et al. 2005; Parker et al. 2008). Interestingly this knowledge developed in the same period when the first methods were developed to analyse the stable chlorine isotope compositions of perchlorates (Ader et al. 2001; Sturchio et al. 2003). The analytical methods to analyse the chlorine isotope compositions were quickly followed by methods to analyse the oxygen isotope composition of perchlorates as well (Bao and Gu 2004; Böhlke et al. 2005).

Perchlorate is a potentially hazardous ion, and the discovery of its widespread occurrence in drinking water and food resources (Gullick et al. 2001; Kirk et al. 2003; Jackson et al. 2005) sparked more interest in knowledge of its natural behaviour as well as studies on how to remove it from the human food chain.

Basically perchlorate found in the environment can be either naturally or artificially produced. Its largest natural source is the Atacama Desert in Chile (Ericksen 1981) where it is present in concentrations of up to 0.6 % in nitrate ores. At the time of writing this report the Atacama Desert was the only known natural source of perchlorates. This perchlorate has however transported to many places in the world as the nitrate deposits in Chile were in the past the main source for fertilizer nitrate globally. More recently it has also been discovered that perchlorate is concentrated in other dry areas in the world such as in the Western United States (Rao et al. 2007). The processes by which it is produced in nature are not known for sure yet, but it appears that the most important mode of production is atmospheric oxidation of chlorine by ozone (e.g. Simonaitis and Heicklen 1975; Jaegle et al. 1996; Rao et al. 2010b). Artificial perchlorate is produced in large quantities (about 10^7 kg.year^{-1}; Dasgupta et al. 2006) by the electrolysis of sodium chloride brines (Schumacher 1960) for various military, aerospace and other industrial applications such as solid rocket fuel, explosives and fireworks, road flares and electroplating solutions.

Virtually all studies on the development of methods to concentrate perchlorates to measurable quantities from natural sources and to analyse the chlorine and oxygen isotope compositions of these samples, as well as the tracer studies in the same samples have been done by one research group led by Neil C. Sturchio. The results of these studies have been discussed comprehensively in in two chapters in books on perchlorate geochemistry and environmental isotope geochemistry (Sturchio et al. 2006, 2011) and this chapter is by necessity not more than a very short summary of these publications.

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Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_12,

12.2 Chlorine and Oxygen Stable Isotope Composition of Perchlorates

12.2.1 Natural Perchlorate

The perchlorate isotope composition of samples from two broad areas have been determined in various studies. It was observed that samples originating from different regions had clearly distinguishable isotope characterisations. The chlorine isotope compositions of perchlorates from the Atacama Desert were analysed by Böhlke et al. (2005), Sturchio et al. (2006) and Jackson et al. (2010). They observed that the chlorine isotope composition of the Atacama perchlorates were in the range from −14.5 to −11.8 ‰. These data complemented earlier measured $\delta^{18}O$ and $\Delta^{17}O$ data reported by Bao and Gu (2004) who showed that $\delta^{18}O$ values of natural (Atacama) perchlorate are between −9.3 and −4.2 ‰ and $\Delta^{17}O$ values between +8.93 and +9.57 ‰. These very positive $\Delta^{17}O$ values indicate an atmospheric origin of the Atacama perchlorates, presumably due to ozone oxidation.

The isotope composition has also been determined for a batch of samples from desert soils in the Southwestern United States (Jackson et al. 2010). Within these samples two different groups could be determined that were differentiated based on their different isotope compositions. Perchlorates from an area near Death Valley are recognisable by very positive $\Delta^{17}O$ data (up to +18.4 ‰). These studies indicated that all natural perchlorates measured today show positive $\Delta^{17}O$ values indicating mass independent formation (Thiemens 2006) of these perchlorates. Interestingly these samples have $\delta^{37}Cl$ and $\delta^{18}O$ values which are distinct from the values for Atacama desert perchlorate. Both the $\delta^{37}Cl$ and the $\delta^{18}O$ of these samples are much more positive with values between −4 and 0 ‰ and 0 and 26 ‰ respectively.

On the other hand samples extracted from groundwaters and the unsaturated zone soil leachates from the Southern High Plains and Middle Rio Grande Basin (Texas and New Mexico) showed more positive $\delta^{37}Cl$ values (+3 to +6 ‰) than the Death Valley samples, and $\delta^{18}O$ values which are equal to the lighter Death Valley samples. Interestingly $\Delta^{17}O$ values are close to 0 ‰ or only slightly positive, up to +2.6 ‰. These lower $\Delta^{17}O$ values as compared to Atacama or Death Valley perchlorate are explained from either a different oxidation process (by UV radiation rather then by ozone), or by slow exchange with water oxygen in slightly wetter climatic conditions (Jackson et al. 2010).

12.2.2 Synthetic Perchlorate

The isotopic characteristics of synthetic perchlorate appears to be very different from the known natural isotope variations (Sturchio et al. 2006). A considerable set of synthetic perchlorates was shown to have $\delta^{37}Cl$ values relatively close to zero (−3.1 to +1.6 ‰) and rather negative $\delta^{18}O$ values (−24.8 to −12.5 ‰). The $\delta^{37}Cl$ values indicate the formation of synthetic perchlorate by oxidation from brines which is a relatively efficient process. The large range in oxygen isotope composition is caused by the meteoric water used in oxidation and mass dependent fractionation of the oxygen, as this process is rather inefficient (Sturchio et al. 2006). All $\Delta^{17}O$ values of the synthetic perchlorates are 0.0 ± 0.1 ‰ indicating that the fractionation during their formation is mass dependent.

12.3 Isotopic Compositions of Perchlorates as Natural Tracers for Its Origin

As it was possible to determine that there are at least three (or four) isotopically distinct groupings of perchlorates (Bao and Gu 2004; Böhlke et al. 2005; Sturchio et al. 2006, Jackson et al. 2010) it was expected that the isotope composition of perchlorates in ground water could be used as a tracer for the origin of the perchlorate. It was argued that the isotope composition of perchlorates is retained in ground water due to the slow exchange with oxygen from water

(Bohlke et al. 2009) and because biodegradation produces both systematic stable isotope enrichments, but that does not significantly affect $\Delta^{17}O$ or $^{36}Cl/Cl$ ratios (not discussed in this book). This effect makes it possible to detect biodegradation together with the initial sources of the perchlorate (Sturchio et al. 2007; Hatzinger et al. 2009). Sturchio et al. (2008) determined the isotope composition of perchlorates extracted from groundwaters from the Chino Basin in California. Isotope data showed that the origin of these waters was predominantly Atacama perchlorate, with minor mixture with Southern High Plains perchlorates. The results showed that extensive fertilisation has taken place in the past with nitrates mined from the Atacama Desert. Bohlke et al. (2009) analysed the isotope compositions of perchlorates from groundwater from Long Island, New York. Samples taken here showed either an Atacama or synthetic origin of the analysed perchlorates, with no indication of mixing. A third study by Slaten et al. (2010) on groundwater samples from Pasadena, California indicated that the origin of the perchlorate in this region was from at least three sources, two of which were synthetic. Also perchlorate contamination in groundwater from Pomona, California could be determined using this technique. In this region the results showed that the contamination was dominantly from Atacama perchlorate that was derived from the use of imported Chilean nitrate fertilizer for citrus cultivation in the past (Sturchio et al. 2014).

Sturchio et al. (2012) applied the above mentioned techniques to map perchlorate plumes on a regional scale in the Southeastern San Bernardino Basin, California. In this basin there are two very different sources of perchlorate. One source is a contaminated former rocket testing site. The perchlorate originating from this site is predominantly synthetic. The other perchlorate type is mostly agricultural and consists of Atacama type perchlorate. It is possible to follow both perchlorate types in the groundwater. Downstream the two perchlorate plumes do intersect. At several locations in the groundwater plumes the ground water was sampled and both types could be followed along the groundwater path. From the isotopic compositions of the samples it was suggested that a third, more diffuse source of perchlorate is also present. This source is proposed as Southern High Plains perchlorate and it may be present in minor quantities of up to 20 % of the perchlorate in the samples. Interestingly the plumes intersect downstream of the originating sites and in several samples it is clear that the perchlorate is a mixture of the sources. The existence of isotopically distinct perchlorate plumes in the studied area is consistent with other data obtained from the samples and the area such as groundwater levels and flow paths as well as the historical land use and areal distribution of potential perchlorate sources.

The results of these studies show the strength of the isotope studies on the transport of perchlorates. Considering the potential hazards of perchlorates in drinking waters it is obvious that it is important to know the origin of the perchlorate sources. With this knowledge it will be possible to develop better plans to remediate known sites and it also gives indispensable information on the most important sites that need to be cleaned. The discovery that the isotope composition of perchlorates can be used to trace its fate in the environment is probably one of the most powerful applications of the use of chlorine isotopes (in combination with the use of other isotopes) discovered to this date.

References

Ader M, Coleman ML, Doyle SP, Stroud M, Wakelin D (2001) Methods for the stable isotopic analysis of chlorine in chlorate and perchlorate compounds. Anal Chem 73:4946–4950

Bao H, Gu B (2004) Natural perchlorate has its unique oxygen isotope signature. Environ Sci Technol 38:5073–5077

Bohlke JK, Hatzinger PB, Sturchio NC, Gu B, Abbene I, Mroczkowski SJ (2009) Atacama perchlorate as an agricultural contaminant in groundwater: isotopic and chronologic evidence from Long Island, New York. Environ Sci Technol 43:5619–5625

Böhlke JK, Sturchio NC, Gu B, Horita J, Brown GM, Jackson WA, Batista JR, Hatzinger PB (2005) Perchlorate isotope forensics. Anal Chem 77:7838–7842

Dasgupta PK, Martinelango PK, Jackson WA, Anderson TA, Tian K, Tock RW, Rajagopalan S (2005) The origin of naturally occurring perchlorate: the role of atmospheric processes. Environ Sci Technol 39:1569–1575

Dasgupta PK, Dyke JV, Kirk AB, Jackson WA (2006) Perchlorate in the United States. Analysis of relative source contributions to the food chain. Environ Sci Technol 40:6608–6614

Ericksen GE (1981) Geology and origin of the Chilean nitrate deposits. USGS Prof Pap 1188:37

Gullick RW, Barhorst TS, LeChevallier MW (2001) Occurrence of perchlorate in drinking water sources. J Am Water Works Assoc 93:66–77

Hatzinger P, Bohlke JK, Sturchio NC, Gu B, Heraty LJ, Borden RC (2009) Fractionation of stable isotopes in perchlorate and nitrate during in situ biodegradation in a sandy aquifer. Environ Chem 6:44–52

Jackson WA, Preethi J, Laxman P, Tian K, Smith PN, Yu L, Anderson TA (2005) Perchlorate accumulation in forage and edible vegetation. J Agric Food Chem 53:369–373

Jackson WA, Bohlke JK, Gu B, Hatzinger PB, Sturchio NC (2010) Isotopic composition and origin of indigenous perchlorate and co-occurring nitrate in the southwestern United States. Environ Sci Technol 44:4869–4876

Jaegle L, Yung YL, Toon GC, Sen B, Blavier J (1996) Balloon observations of organic and inorganic chlorine in the stratosphere: the role of $HClO_4$ production on sulfate aerosols. Geophys Res Lett 23:1749–1752

Kirk AB, Smith EE, Tian K, Anderson TA, Dasgupta PK (2003) Perchlorate in milk. Environ Sci Technol 37:4979–4981

Parker DR, Seyfferth AL, Reese BK (2008) Perchlorate in groundwater: a synoptic survey of “pristine” sites in the conterminous Unites States. Environ Sci Technol 42:1465–1471

Rao B, Anderson TA, Orris GJ, Rainwater KA, Rajagopalan S, Sandvig RM, Scanlon BR, Stonestrom DA, Walvoord MA, Jackson WA (2007) Widespread natural perchlorate in unsaturated zones of the Southwest United States. Environ Sci Technol 41:4522–4528

Rao B, Anderson TA, Redder A, Jackson WA (2010) Perchlorate formation by ozone oxidation of aqueous chlorine/oxychlorine species: role of Cl_xO_y radicals. Environ Sci Technol 44:2961–2967

Schumacher J (1960) Perchlorates: their properties, manufacture, and uses, American Chemical Society, vol 146. Reinhold, New York

Simonaitis R, Heicklen J (1975) Perchloric acid: possible sink for stratospheric chlorine. Planet Space Sci 23:1567–1569

Slaten S, Fields KA, Santos S, Barton A, Rectanus HV, Bhargava M (2010) Integrated environmental forensics approach for evaluating the extent of dissolved perchlorate originating from multiple sources. Environ Forensics 11:72–93

Sturchio NC, Hatzinger PB, Arkins MD, Suh C, Heraty LJ (2003) Chlorine isotope fractionation during microbial reduction of perchlorate. Environ Sci Technol 37:3859–3863

Sturchio NC, Böhlke JK, Gu B, Horita J, Brown GM, Beloso AD Jr, Hatzinger PB, Jackson WA, Batista JR (2006) Stable isotopic compositions of chlorine and oxygen in synthetic and natural perchlorates. In: Gu B, Coates JD (eds) Perchlorate environmental occurrences, interactions, and treatment. Springer, New York, pp 93–109

Sturchio NC, Böhlke JK, Beloso AD Jr, Streger SH, Heraty LJ, Hatzinger PB (2007) Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: laboratory results and implications for forensics and natural attenuation studies. Environ Sci Technol 41:2796–2802

Sturchio NC, Beloso AD Jr, Heraty LJ, LeClaire J, Rolfe T, Manning KR (2008) Isotopic evidence for agricultural perchlorate in groundwater of the Western Chino Basin, California. In: Sixth international conference on remediation of chlorinated and recalcitrant compounds, Monterey, CA, 18–22 May 2008

Sturchio NC, Böhlke JK, Gu BH, Hatzinger PB, Jackson WA (2011) Isotopic tracing of perchlorate in the environment. In: Baskaran M (ed) Handbook of environmental isotope geochemistry. Advances in isotope geochemistry. Springer, Berlin

Sturchio NC, Hoaglund JR III, Marroquin RJ, Beloso AD Jr, Heraty LJ, Bortz SE, Patterson TL (2012) Isotopic mapping of groundwater perchlorate plumes. Ground Water 50:94–102

Sturchio NC, Beloso A Jr, Heraty LJ, Wheatcraft S, Schumer R (2014) Isotopic tracing of perchlorate sources in groundwater from Pomona, California. Appl Geochem 43:80–87

Thiemens MH (2006) History and applications of mass-independent isotope effects. Annu Rev Earth Planet Sci 34:217–262

13 Isotope Variations of Organochlorine and Organobromine Compounds in Natural Environments

13.1 Introduction

The first analytical techniques that were developed to analyse the isotope compositions of organochlorine compounds were dual-inlet techniques that required large amounts of sample for analysis. As the concentrations of these compounds, even at contaminated sites, are relatively low, using these techniques would require the processing of large amounts of contaminated water or soil to obtain a sufficient amount of these chlorinated compounds.

It was however already realised that using Compound Specific Isotope Analysis (CSIA) it would be possible to analyse the isotope composition of different compounds in a mixture. Using CSIA the isotope composition is analysed by continuous flow methods, and as a consequence much smaller sample amounts are necessary for the analysis of a single sample. Perhaps the first (Lojkasek-Lima et al. 2012) study in which the potential of CSIA for tracing chlorinated organic compounds such as tetrachloroethene and trichloroethene from contaminated sites was examined was done by Hunkeler et al. (2004) in sandy aquifers in Canada that were contaminated with these compounds. In this study the research was done solely using carbon isotopes, as methods to measure chlorine isotopes by CSIA were not developed yet.

After the development of CSIA methods for chlorine isotopes (Shouakar-Stash et al. 2006; Sakaguchi-Söder et al. 2007) it became possible to study not only the carbon, but also the chlorine isotope compositions of chlorinated organic compounds during transport from contaminated sites. It was already realised from the onset of the analyses of chlorine isotopes in chlorinated organic compounds (Holt et al. 1997; Jendrzejewski et al. 1997, 2001) that the combination of the two isotope systems (δ^{13}C and δ^{37}Cl) showed a much more detailed characterisation on the origin and evolution of these compounds. Chlorine isotope compositions of organic compounds from environmental samples could be measured from the moment that methods were developed to extract them in sufficient amounts from natural samples (Holt et al. 2001). In modern studies the chlorinated organic compounds are extracted from water and vapour using a Multi Layer Sampler, a technique that can take weeks to obtain sufficient sample (Ronen et al. 1986, 2010), which need not necessarily be a problem for monitoring purposes.

13.2 Chlorine

13.2.1 Studies on the Dispersion of Chlorinated Solvents in Ground Waters

Chlorinated ethenes, especially perchlorethene and trichloroethene are commonly used chemicals in the dry-cleaning industry. Also other industries, such as metal-working, paint industries, organic synthesis and the military are in

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_13,

various cases a source of contamination by chlorinated organic compounds (Jendrzejewski et al. 2001). As a result of their common use, they can be a very significant source of pollution of the atmosphere, soils and aquifers (e.g. Stiber et al. 1998; Sturchio et al. 1998). Characterising these pollutants and the different processes affecting them is thus an important issue. In this respect, isotopic geochemistry of carbon and chlorine can give additional information to investigate these compounds and their by-products. In recent years several studies have been published in which these organochlorine compounds have been extracted from contaminated sites to establish their origin. A few of these studies will be discussed in more detail as examples of the possibilities that the combined analysis of carbon and chlorine isotopes can deliver to understand how these compounds behave in contaminated aquifers.

Hunkeler et al. (2011) described the behaviour of chlorinated ethenes near a former industrial facility in the vicinity of Tel Aviv, Israel. On this site, that once was occupied with mostly metal-working and plating facilities, the aquifer was contaminated with several chlorinated ethenes. This contamination occurred as the former factories disposed their used chlorinated ethenes at the factory grounds. At this location, consisting of sandstones, the water table is located some 18 meters below the ground surface. Samples were taken at various depths, both in the unsaturated zone and below the water table. Samples were taken using a Multi Layer Sampler as described by Ronen et al. (1986, 2010). From these samples the organic compounds were determined by gas chromatography and the carbon isotope compositions were determined according to the techniques described by Hunkeler and Aravena (2000) and the chlorine isotope compositions using the methods described by Shouakar-Stash et al. (2006). They observed that the concentrations of the chlorinated organic compounds were highest at the boundary between the saturated and the unsaturated zone and decreased in both zones away from the water table. Both carbon and chlorine isotopes, for the samples in which both isotopes were measured, showed no variation in the unsaturated zone, except, perhaps, as the results were non-conclusive, in those samples that were taken closest to the land surface. In the saturated zone it appeared that the carbon isotopes behaved inconclusive, at some locations they increased, at others they decreased or were invariant. At the only site were chlorine isotope compositions were analysed they decreased in value. These variations however appeared also to be very limited. The transport of the chlorinated ethenes was modelled numerically and the results of this modelling confirmed the observed relationship between the distances from the water table, the decreasing concentration and invariable carbon isotope composition for situations that are close to steady state. Before steady state was reached the carbon isotope composition was expected to be lower away from the water interface due to processes such as diffusion. In the saturated zone numerical modelling showed a steep decrease of the concentration with increasing distance from the water table combined with a steep decrease in the isotope composition for both $\delta^{13}C$ and $\delta^{37}Cl$. The different results for the unsaturated and the saturated zones appeared to be the result from the difference in speed in which equilibrium is reached in the two zones. While in the unsaturated zone equilibrium can be reached within a year in the saturated zone this can take 1,000s of years. The results obtained in this study (Hunkeler et al. 2011) indicate that carbon and chlorine isotopes can be used to link vapour phase contamination to their source even if extensive migration of the vapours occurs. The results from numerical modelling revealed that constant isotope ratios as observed in this study are only expected for systems that are close to steady state.

In a second case study Lojkasek-Lima et al. (2012) described the transport behaviour of trichlorothene trough a bedrock aquifer consisting of dolostone. In this study the transport was described fully within the saturated zone. The reason for this study was to understand the source of trichoroethylene contamination that caused the closure of a municipal water-well. In the vicinity of this well there were several industries from which it was known that they had caused trichoroethylene contamination, of which one had created a monitoring network. Samples from the municipal well, as well as from the monitoring wells were analysed for the concentration of chemical species as well as the chlorine and carbon isotope compositions of trichoroethylene and *cis*-1,2-dichloroethene. Large variations in both chlorine and carbon isotope compositions were found between the different wells. For example for trichloroethylene the carbon isotope values varied between −35.6 and −21.8 ‰ and the chlorine isotope values between +1.6 and +3.2 ‰. In the case of *cis*-1,2-dichloroethene the carbon isotope variation was between −36.3 and −18.9 ‰ and the chlorine isotope variation between 2.4 and 4.7 ‰. These data were plotted on a map and this showed that the combined chlorine and carbon isotope composition of the municipal well samples were clearly different from the samples taken from the monitoring wells. From these results it was concluded that the contamination of the municipal well could not be caused by the industrial property with the monitoring network. The study by Lojkasek-Lima et al. (2012) demonstrated that compound specific isotope analysis of both chlorine and carbon would have been useful if it ware applied much earlier to examine the sources of trichloroethylene that was found in the municipal well and if bedrock monitoring wells had been located at several depths beneath each of the potential trichloroethylene contributing properties. The results obtained using compound-specific isotope analysis also show that microbial reductive dechlorination of trichloroethylene occurs in some parts of the bedrock aquifer. At this site, the use of compound specific isotope analysis for chlorine and carbon in combination with analyses of volatile chlorinated organic compounds and redox parameters proved to be important due to the complexity introduced by biodegradation in the complex fractured rock aquifer. In this case it was highly recommended that this study was redone as soon as the municipal well is back into full operation, and make sure it is properly monitored.

In a study on the isotope ratio variations during degradation of chlorinated ethenes Wiegert et al. (2013) investigated a method to efficiently monitor this in situ degradation. They reported a field application of combined stable chlorine and carbon isotope analysis of tetrachloroethene and trichloroethene to investigate their biodegradation in a heavily contaminated aquifer. To analyse the chlorine isotope composition of the contaminants they applied the gas chromatography-quadrupole mass spectrometry (GCqMS) method developed by Aeppli et al. (2010). Both chlorine and carbon isotopes showed evidence of ongoing tetrachloroethene transformation. Applying published carbon isotope enrichment factors they were able to evaluate the extent of in situ tetrachloroethene degradation which was between 11 and 78 %. Modelling both chlorine and carbon isotopes through a reactive transport model indicated that the combined perchloroethylene and trichloroethylene mass load was dechlorinated by less than 10 %, and that cis-dichloroethene was not further dechlorinated. The combined use of chlorine and carbon isotopes in this study made it possible to estimate chlorine isotope enrichment factors, which were between −7.8 and −0.8 ‰. Interestingly they found characteristic values for the ratio of chlorine and carbon isotope enrichment factors for the reduction of tetrachloroethene at their field site. This study also demonstrated the benefit of compound specific isotope analyses of both chlorine and carbon and the beneficient use of chlorine isotope variations to evaluate tetrachloroethylene and trichloroethylene dechlorination.

Finally in a study in the industrial complex in Wonju, South Korea (Kaown et al. 2013) it was possible to asses the contamination of groundwater with chlorinated solvents such as trichloroethene and carbon tetrachloride. At the study site it was observed that trichloroethylene concentrations ranged between zero and 10,066 μg/L while carbon tetrachloride concentrations ranged between zero and 985 μg/L. Close to the contaminated site a location was found were asphalt was tested using chlorinated solvents which were disposed of without any appropriate treatment. Residual solvents were found both downstream along the flowline of groundwater as well as upstream due to ground water pumping to facilitate water for a laundry facility. In the upgradient area towards the laundry facility both trichloroethylene and carbon tetrachloride metabolites were detected while only trichloroethylene metabolites were detected in the region at lower altitudes along the groundwater flowline. These differences were apparently caused by the fact that downgradient anaerobic dechlorination took place while upgradient aerobic dechlorination took place. As the study region was an industrial area it was discovered that several small pockets of chlorinated solvents originated from several small contaminant sources. This complicated the study towards the origin of the solvent plumes. Although it was rather complex to differentiate among the contaminant sources in this complicated industrial area with several small and one large source it was possible to identify the main sources using δ^{37}Cl and δ^{13}C analyses in combination with hydrogeochemical data. Freshly recharged water with depleted δ^{37}Cl and δ^{13}C values of trichloroethylene from the upgradient recharge zone of the main sources affected the plumes and changed the δ^{37}Cl and δ^{13}C values of trichloroethylene in the local source zones. Despite the complicated states of contamination, dual isotope analysis data could usefully be applied to evaluate the fate and transport of the contaminants as well as to differentiate among five different contaminant sources. Kaown et al. (2013) concluded that the results they obtained supported the usefulness of compound specific isotope analysis as a method for differentiating multiple plume sources. The results obtained from this study could be used to assign remediation responsibilities to the responsible parties.

The case studies described in this section show that especially the use of the combination of both chlorine and carbon isotopes in the study of dispersion of chlorinated organic compounds in groundwaters is a very successful technique to understand the fate of these compounds in the environment. Due to the use of the dual isotope technique, in combination with the measurements of the concentration of the contaminants, it is possible to understand how they disperse on a site, how they degrade to compounds containing less chloride atoms per molecule and how solvents from different sources with different isotope compositions behave and mix with each other. Considering these successful case studies this is a very successful way to understand the fate of these contaminants in the environment. If it would become more common to analyse (also) the chlorine isotopes of these compounds, which are currently only measured in a limited number of laboratories, this could become probably a very useful application for chlorine isotopes in the future.

13.2.2 The Use of Chlorine Isotopes to Test the (Anthropogenic) Origin of a Chlorinated Compound

Holmstrand et al. (2010b) determined the chlorine isotope composition of the persistent and bioaccumulating compound tris-(4-chlorophenyl) methane to elucidate whether its main source is natural or anthropogenic. In this study they extracted blubber from a Baltic grey seal (*Halichoerus grypus*) by continuous acetonitrile partitioning (Jensen et al. 1992), and the tris-(4-chlorophenyl)methane was isolated from the extract by preparative-capillary gas chromatography (Holmstrand et al. 2007). Chlorine isotope analysis was subsequently performed by sealed-tube combustion in conjunction with thermal-ionization mass spectrometry. The δ^{37}Cl of tris-(4-chlorophenyl)methane was -3.5 ± 0.5‰, similar to the previously reported δ^{37}Cl of technical grade p,p′-DDT (Holmstrand et al. 2006). The data obtained from the blubber is not consistent with a putative marine natural source of tris-(4-chlorophenyl)methane, as enzymatic (biotic) production is reported to give values of $\delta^{37}\text{Cl} < -10$ ‰ (Reddy et al. 2000, 2002). The δ^{37}Cl-tris-(4-chlorophenyl)methane data obtained by Holmstrand et al. (2010b) thus support the hypothesis that tris-(4-chlorophenyl) methane is produced as a byproduct during DDT synthesis and is released to the environment through the same pathways as DDT.

13.3 Bromine Isotopes in Naturally Occurring Organic Compounds

Although a few methods have been developed to analyse the bromine isotope compositions of organic compounds (Sylva et al. 2007; Holmstrand et al. 2010a; Gelman and Halicz 2010; Hitzfeld et al. 2011) not many studies have been published showing bromine isotope data in natural samples.

The first such study was conducted by Carrizo et al. (2011). In this study the bromine isotope compositions of six brominated compounds, produced in the chemical industry, were analysed and compared to the bromine isotope composition of a 2,4-dibromophenol sample that was extracted from whale blubber. Results obtained showed that the anthropogenic brominated organic compounds had a bromine isotope variation from −4.3 to −0.4 ‰. The 2,4-dibromophenol extracted from the whale blubber (Teuten et al. 2006) had a value of 0.2 ± 1.6 ‰ (1 SD), which was significantly different from the average value of −1.1 ± 0.9 ‰ (1 SD) of the anthropogenic 2,4-dibromophenol. This difference, about 1.4 ‰ showed a P of less than 0.05. The results showed that the δ^{81}Br of four out of six industrial compounds was found to be significantly different from that of the natural sample. The study by Carrizo et al. (2011) indicated a baseline for future work employing δ^{81}Br variations between organobromine compounds to study the sources and degradation of organobromine compounds in the environment. They concluded that it is conceivable that ambient microbial and photochemical degradation of brominated flame retardants, for example, induces bromine isotope effects so that bromine isotope analysis can be used to assess the extent of environmental degradation of such chemicals, in analogy to the known isotope fractionation for chlorine in organochlorine compounds.

References

Aeppli C, Holmstrand H, Andersson P, Gustafsson Ö (2010) Direct compound-specific stable chlorine isotope analysis of organic compounds with quadrupole GC/MS using standard isotope bracketing. Anal Chem 82:420–426

Carrizo D, Unger M, Holmstrand H, Andersson P, Gustafsson Ö, Sylva SP, Reddy CM (2011) Compound-specific bromine isotope compositions of one natural and six industrially synthesised organobromine substances. Environ Chem 8:127–132

Gelman F, Halicz L (2010) High precision determination of bromine isotope ratio by GC-MC-ICPMS. Int J Mass Spectrom 289:167–169

Hitzfeld KL, Gehre M, Richnow HH (2011) A novel online approach to the determination of isotopic ratios for organically bound chlorine, bromine and sulphur. Rapid Commun Mass Spectrom 25:3114–3122

Holmstrand H, Mandalakis M, Zencak Z, Gustafsson Ö, Andersson P (2006) Chlorine isotope fractionation of a semi-volatile organochlorine compound during preparative megabore-column capillary gas chromatography. J Chromatogr A 1103:133–138

Holmstrand H, Mandalakis M, Zencak Z, Andersson P, Gustafsson O (2007) First compound-specific chlorine-isotope analysis of environmentally-bioaccumulated organochlorines indicates a degradation-relatable kinetic isotope effect for DDT. Chemosphere 69:1533–1539

Holmstrand H, Unger M, Carrizo D, Andersson P, Gustafsson Ö (2010a) Compound-specific bromine isotope analysis of brominated diphenyl ethers using GC-ICP-multicollector-MS. Rapid Commun Mass Spectrom 24:2135–2142

Holmstrand H, Zencak Z, Mandalakis M, Andersson P, Gustafsson Ö (2010b) Chlorine isotope evidence for the anthropogenic origin of tris-(4-chlorophenyl)methane. Appl Geochem 25:1301–1306

Holt BD, Sturchio NC, Abrajano TA, Heraty LJ (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. Anal Chem 69:2727–2733

Holt BD, Heraty LJ, Sturchio NC (2001) Extraction of chlorinated aliphatic hydrocarbons from groundwater at micromolar concentrations for isotopic analysis of chlorine. Environ Pollut 113:263–269

Hunkeler D, Aravena R (2000) Determination of stable carbon isotope ratios of chlorinated methanes, ethanes and ethenes in aqueous samples. Environ Sci Technol 34:2839–2844

Hunkeler D, Chollet N, Pittet X, Aravena R, Cherry JA, Parker BL (2004) Effect of source variability and transport processes on carbon isotope ratios of TCE en PCE in two sandy aquifers. J Contam Hydrol 74:265–282

Hunkeler D, Aravena R, Shouakar-Stash O, Weisbrod N, Nasser A, Netzer L, Ronen D (2011) Carbon and chlorine isotope ratios of chlorinated ethenes migrating through a thick unsaturated zone of a sandy aquifer. Environ Sci Technol 45:8247–8253

Jendrzejewski N, Eggenkamp HGM, Coleman ML (1997) Sequential determination of chlorine and carbon isotopic composition in single microliter samples of chlorinated solvent. Anal Chem 69:4259–4266

Jendrzejewski N, Eggenkamp HGM, Coleman ML (2001) Characterisation of chlorinated hydrocarbons from chlorine and carbon isotopic compositions: scope and application to environmental problems. Appl Geochem 16:1021–1031

Jensen S, Athanasiadou M, Bergman Å (1992) A technique for separation of xenobiotics from large amounts of lipids. Organohalogen Compd 8:79–80

Kaown D, Shouakar-Stash O, Yang J, Hyun YJ, Lee KK (2013) Identification of multiple sources of groundwater contamination by dual isotopes. Ground Water. doi:10.1111/gwat.12130

Lojkasek-Lima P, Aravena R, Parker BL, Chrry JA (2012) Fingerprinting TCE in a bedrock aquifer using Compound-Specific Isotope Analysis. Ground Water 50:754–764

Reddy CM, Heraty LJ, Holt BD, Sturchio NC, Eglinton T, Drenzek NJ, Xu L, Lake JL, Maruya KA (2000) Stable chlorine isotopic compositions of arochlors and arochlor-contaminated sediments. Environ Sci Technol 34:2866–2870

Reddy CM, Xu L, Drenzek NJ, Sturchio NC, Heraty LJ, Kimblin C, Butler A (2002) A chlorine isotope effect for enzyme-catalyzed chlorination. J Am Chem Soc 124:14526–14527

Ronen D, Magaritz M, Levy I (1986) A multilayer sampler for the study of detailed hydrochemical profiles in groundwater. Water Res 20:311–315

Ronen D, Lev-Wiener H, Graber E, Dahan O, Weisbrod N (2010) Simultaneous counter-flow of chlorinated volatile organic compounds across the saturated-unsaturated interface region of an aquifer. Water Res 29:261–280

Sakaguchi-Söder K, Jager J, Grund H, Matthäus F, Schüth C (2007) Monitoring and evaluation of dechlorination processes using compound-specific chlorine isotope analysis. Rapid Commun Mass Spectrom 21:3077–3084

Shouakar-Stash O, Drimmie RJ, Zhang M, Frape SK (2006) Compound-specific chlorine isotope ratios of TCE, PCE and DCE isomers by direct injection using CF-IRMS. Appl Geochem 21:766–781

Stiber NA, Small MJ, Fischbeck PS (1998) The relationship between historic industrial site use and environmental contamination. J Air Waste Manage Assoc 48:809–818

Sturchio NC, Clausen JL, Heraty LJ, Huang L, Holt BD, Abrajano TA (1998) Chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer. Env Sci Technol 32:3037–3042

Sylva SP, Ball L, Nelson RK, Reddy CM (2007) Compound-specific ^{81}Br/^{79}Br analysis by capillary gas chromatography/multicollector inductively coupled plasma mass spectrometry. Rapid Commun Mass Spectrom 21:3301–3305

Teuten EL, King GM, Reddy CM (2006) Natural ^{14}C in *Saccoglossus bromophenolosus* compared to ^{14}C in surrounding sediments. Mar Ecol Prog Ser 324:167

Wiegert C, Aeppli C, Knowles T, Holmstrand H, Evershed R, Pancost RD, Macháčková J, Gustafsson O (2013) Dual Carbon-chlorine stable isotope investigation of sources and fate of chlorinated ethenes in contaminated groundwater. Environ Sci Technol 46:10918–10925

Part V

Historical Overview and Future Development of Halogen Isotope Geochemistry

14

Halogen Isotope Studies in Historical Perspective and Future Outlook

In 2014 it was 30 years ago that the first major work on chlorine isotopes was published (Kaufmann 1984). In his thesis Ronald Kaufmann described the first method by which it was possible to measure the small natural variations of chlorine stable isotopes that appear in groundwaters and applied this technique to start to understand the chloride hydrological cycle. Considering the fact that no chlorine isotope variations in natural samples were observed before Ronald Kaufmann started his PhD the research focussed on ground water for the following three reasons: (1) The only samples that (perhaps) showed natural variations in the study by Hoering and Parker (1961) were ground waters; (2) Groundwater environments are diverse and many locations might have fractionated chlorine due to processes that could be understood at that time; (3) Chlorine could be removed quantitatively from water samples through a relatively simple technique by precipitating chloride with silver ions as silver chloride. Kaufmann (1984) studied chlorine isotope variations in different types of water samples, such as hydrothermal waters, formation waters and aquifer samples. He also analysed a few halite samples. These initial measurements showed already that the chlorine isotope ratio varied by at least 2.1 ‰, with values between −1.3 and +0.8 ‰ relative to SMOC, a much larger variation than was observed earlier and probably also a much larger variation than expected (Kaufmann et al. 1984). Interestingly in oil field brines samples the δ^{37}Cl values showed an increasing trend with depth and it was suggested that this enrichment with depth might reflect an isotope fractionation mechanism related to the electrostatic properties of subsurface clays. These early studies also showed positive evidence that chlorine isotope variations could be applied in studies of groundwater diffusion (Desaulniers et al. 1986) and ion-filtration (Campbell 1985).

The outlook for the future of chlorine isotope geochemistry in 1984 was very optimistic. As it was finally shown that natural chlorine isotope variations could be measured in natural samples without problems it was expected that other laboratories would step in to start analysing chlorine isotopes quickly. It was expected that most research would be done towards three known fractionation processes at the time. These processes were diffusion, equilibrium and kinetic fractionation during precipitation. Both laboratory and field experiments were anticipated. It was expected that counter-current diffusion experiments would be more simple to simulate than simple diffusion due to larger sample size and longer time constraints. Fractionation of chlorine isotopes during halite precipitation was also anticipated as a valid experimental proposal. It was expected that isotope fractionation in silicate melts would be the most difficult to test experimentally, which indeed is one of the processes that has not yet been determined experimentally.

It was anticipated that an inventory of chlorine isotope data in different kinds of geological materials, waters, rocks and gases would be made

H. Eggenkamp, *The Geochemistry of Stable Chlorine and Bromine Isotopes*,
Advances in Isotope Geochemistry, DOI: 10.1007/978-3-642-28506-6_14,

as a first step to answer the main geochemical questions considering the geochemical cycle of chlorine such as the origin of the distribution of chlorine between the major reservoirs and the possible mechanisms of mass exchange between these reservoirs about which one could only speculate at the time of writing of Kaufmann's thesis. Some of the questions that were expected to be solved in the near future (counted from 1984) were questions regarding the variability of the chlorine isotope compositions through time by analysing their variations in salt deposits and the distribution of chlorine isotopes between mantle and surface reservoirs by analysis of chlorine isotope compositions in mantle derived rocks. It is very interesting to realise that scientific discussions are still being held about these processes as they, in spite of numerous studies of their chlorine isotope compositions, are not completely understood yet. These examples indicate that in many cases it was not trivial to analyse the chlorine isotope compositions (such as in rocks) and secondary fractionation that could appear could hinder the understanding of the variations that were found in these samples.

Before the research by Kaufmann (1984) most studies on chlorine isotopes were just "one off" studies. With this I mean that they were apparently conducted to test the hypothesis that natural chlorine isotope variations could be determined which was abandoned after these variations were not found. Some important studies of this category were Curie (1921), Harkins and Stone (1926), Owen and Schaeffer (1955) and Hoering and Parker (1961). Only two research groups focussed on chlorine isotope variations in longer term projects. A collaborative research project between the Max-Planck Institute for Chemistry in Mainz and the Physical Institute of the Chalmers University of Technology in Göteborg initiated by Prof Alfred Klemm resulted in several publications between 1955 and 1960 on the experimentally determined isotope enrichment of chlorine and bromine during diffusion in molten salts (e.g. Klemm and Lundén 1955; Lundén and Herzog 1956; Cameron et al. 1956; Herzog and Klemm 1958; Lundén and Lodding 1960). A research group led by James W Taylor published several studies on the kinetic isotope effects of chlorine and bromine in S_N1 and S_N2 systems in the period between 1969 until 1980 (e.g. Taylor and Grimsrud 1969; Grimsrud and Taylor 1970; Turnquist et al. 1973; Graczyk and Taylor 1974; Willey and Taylor 1980).

The research group from Tucson, Arizona continued with chlorine isotope research during the 1980s in which period several MSc students finished their course with chlorine isotope research (e.g. Campbell 1985; Wirt 1988; Martin 1993) until they published their improved method for chlorine isotope analysis (Long et al. 1993). Apparently interest in chlorine isotope research faded after the retirement of Austin Long, although Chris Eastoe published several important papers on evaporites and formation brines (e.g. Eastoe et al. 1999, 2001, 2007) until the break-down of the mass spectrometer rendered further research impossible. Sadly Ron Kaufmann had already passed away in 2005.

The first research group to take interest in chlorine isotope research after Arizona was from the Department of Earth Sciences from the University of Waterloo in Canada. Shaun Frape and Peter Fritz were already collaborating with their colleagues from Tucson in their study on Canadian Shield brines (Kaufmann et al. 1987) and later on other formation waters (Kaufmann et al. 1993). This group was also the first to explore the possibilities to analyse chlorine isotopes in organic compounds for potential environmental study purposes (Van Warmerdam et al. 1995; Beneteau et al. 1999). During the early 21st century the stable isotope laboratory of Waterloo University became the most productive chlorine and bromine isotope laboratory in the world after Orfan Shouakar-Stash published his methods to analyse chlorine isotope variations in organic compounds (Shouakar-Stash et al. 2003) and after they published methods to analyse chlorine and bromine isotopes online using GC-IRMS (Shouakar-Stash et al. 2005a, b, 2007). Later they also developed methods to analyse the chlorine isotope composition of organic compounds by direct injection of these compounds into the mass spectrometer (Shouakar-Stash et al. 2009). They continue to be very productive to the present day, among which several studies in which they provided stable chlorine and bromine isotope measurements to third party research (e.g. Stotler et al. 2010; Boschetti et al. 2011; Audí-Miró et al. 2013; Gwynne et al. 2013; Le Gal La Salle et al. 2013; Rebeix et al. 2014; Kaown et al. 2013).

August Koster van Groos (University of Illinois at Chicago) had learned of the appearance of Ron Kaufmann's thesis early and later had the opportunity to test the application of the technique during a sabbatical in Utrecht. Tests were promising and together with Rob Kreulen a PhD project was set up at Utrecht University, first with Math Kohnen and later Hans Eggenkamp as students. This resulted in the publication of a PhD thesis and several papers (Eggenkamp 1994; Eggenkamp et al. 1994, 1995, 1997). After Hans Eggenkamp left Utrecht the equipment continued to be used at a lower frequency for chlorine isotope analyses for third parties (such as Groen et al. 2000; Reitz et al. 2011) and the post-doctoral work from Masaaki Musashi (e.g. Musashi et al. 1998, 2004, 2008; Markl et al. 1997). Although the amount of chlorine isotope work done in Utrecht was relatively limited after this in the period from 2012 to 2016 a PhD study in which chlorine isotope measurements play an important role is again conducted (e.g. Rodriguez et al. 2013).

After Hans Eggenkamp left Utrecht he built a chlorine isotope laboratory at the University of Reading under the supervision of Prof Max Coleman. After this was done successfully several post-doctoral studies were accomplished in Reading (e.g. Jendrzejewski et al. 1997, 2001; Loomis et al. 1997; Rosenbaum et al. 2000; Coleman et al. 2001, 2003; Ader et al. 2001, 2008, Van Acker et al. 2006; Eggenkamp and Coleman 2009) among which the first study presenting a method that showed natural bromine isotope variations (Eggenkamp and Coleman 2000). After Max Coleman left Reading for the Jet Propulsion Laboratory unfortunately the possibility to analyse chlorine isotopes in Reading ceased towards the end of the first decade of the 21st century.

After Nathalie Jendrzejewski, one of Max Coleman's post-doctoral fellows, left Reading she set up a facility to analyse chlorine isotopes at the Institut de Physique du Globe de Paris. Once build it led to a series of interesting chlorine isotope papers (e.g. Godon et al. 2004; Lavastre et al. 2005; Woulé Ebongué et al. 2005). Especially interesting were the papers written by Magali Bonifacie in which important progress was shown to our understanding of the global chlorine cycle (Bonifacie et al. 2005, 2008a, b). After a few quite years research has taken up again with the PhD project of Thomas Giunta that mostly focussed on different applications of chlorine isotopes in CO_2 sequestration studies. In this period the experimental determination of isotope fractionation factors during chloride oxidation (Giunta et al. 2013) and a study on the isotope fractionation for different salts (Eggenkamp et al. 2011) were also conducted.

The first major studies showing chlorine isotope variations using thermal ionization mass spectrometry were already done during the early 1990s. It was discovered by Ying-Kai Xiao that treatment of the filament in a thermal ionization mass spectrometer with graphite improved the precision of boron isotope measurements considerably (Xiao et al. 1988). After setting up a laboratory at the Qinghai Institute of Salt Lakes in Xining he discovered that this treatment also improved the measurement of chlorine isotope ratios considerably (Xiao et al. 1991; Xiao and Zhang 1992). Only slightly later it was also shown that this method works very well for bromine isotopes too (Xiao et al. 1993). These discoveries led to many studies in which especially the isotope behaviour of chlorine during processes that exist in continental salt lakes were studied and these studies continue until the present day (e.g. Xiao et al. 1997, 2000; Liu et al. 1997; Tan et al. 2005, 2006, 2009; Luo et al. 2012). Besides these studies Prof. Xiao was also involved in studies on possible variations in seawater chloride (Shirodkar et al. 2003, 2006) and the development of an international secondary reference standard for chlorine isotopes (Xiao et al. 2002).

The second laboratory where the method to analyse chlorine isotopes with thermal ionization mass spectrometry was successfully applied was at Scripps Institution of Oceanography in San Diego. At this group the focus was on the chlorine isotope variations during subduction of pore fluids (Ransom et al. 1995) and marine aerosols (Volpe and Spivack 1994; Volpe et al. 1998). Later they managed to develop methods to analyse chlorine isotope compositions in rocks and made the first estimates on the chlorine isotope composition of the mantle (Magenheim et al. 1994, 1995). Due to possible analytical problems of their technique later studies by other laboratories using different techniques were not able to come to the same conclusions on the mantle chlorine isotope composition (Sharp et al. 2007; Bonifacie et al. 2008a). Further research on chlorine isotopes seemed to vanish, probably due to the move of Art Spivack to North Carolina and later to Rhode Island. Only during 2008 one more paper appeared in which the pyrohydrolysis method apparently was improved enough so that is was possible to present new rock data using pyrohydrolysis extraction of chloride followed by thermal ionization mass spectrometry (Wei et al. 2008a, b).

Another laboratory where chlorine isotopes were already studied at an early date was at Argonne National Laboratory. Under the directions of Neill Sturchio they developed a method to analyse both the chlorine and carbon isotope compositions of chlorinated organic compounds independently from the group at Reading and published it a few months earlier (Holt et al. 1997). They continued their research afterwards and were the first to develop methods to extract large enough quantities of chlorinated organic compounds from environmental samples to be able to analyse them for chlorine and carbon isotopes (Holt et al. 2001). After Neill Sturchio moved to the University of Illinois at Chicago the focus of the chlorine isotope research changed to isotope studies of perchlorates. They developed methods to analyse the isotope composition of perchlorates in very small sample amounts and to extract minute amounts of perchlorates from environmental samples (e.g. Böhlke et al. 2005, 2009; Sturchio et al. 2007). Their methods were improved considerably over this period and were ultimately good enough to be able to map the perchlorate isotope compositions in groundwaters for forensic purposes (Sturchio et al. 2012).

A considerable amount of research on chlorine isotopes in mantle derived rocks, lunar and other extraterrestrial material has been performed by the group around Zach Sharp. They have made great progress in our understanding of the chlorine cycling on earth (e.g. Sharp and Barnes 2004; Barnes and Sharp 2006; Barnes et al. 2006, 2008, 2009; Selverstone and Sharp 2011), the processes that are responsible for its isotope variations (e.g. Sharp et al. 2010a) and the composition of the mantle, the moon and further extraterrestrial material (e.g. Sharp et al. 2007, 2010b, 2011, 2013). In 2009 Jaimie Barnes left the laboratory in New Mexico to set up a new chlorine isotope facility in Austin, Texas. This move has already resulted in a several new chlorine isotope studies (e.g. Amundson et al. 2012; Barnes and Cisneros 2012; Rizzo et al. 2013; Barnes et al. 2013). In the meantime also Zach Sharp continued his research on chlorine isotopes resulting in two laboratories that continue to be actively involved in chlorine isotope research.

In the same period several laboratories solely involved in the study of organic compounds started to analyse chlorine and bromine isotope ratios. The first of these was the laboratory of the University of Stockholm under the direction of Henry Holmstrand were at first methods were developed to analyse chlorine and later bromine isotopes in environmental samples (Holmstrand et al. 2004, 2010; Mandalakis et al. 2008) and to apply these methods to natural samples (e.g. Holmstrand et al. 2006b, 2007, 2010; Carrizo et al. 2011). Most recently they were even able to improve their methods to the level that they were able to extract bromomethane from atmospheric samples and analyse them for bromine isotopes (Horst 2013).

An other laboratory that is progressively more involved in chlorine isotope studies on organic compounds is led by Daniel Hunkeler in Neuchâtel who have already published several studies on chlorine isotopes (e.g. Hunkeler et al. 2009, 2011). In the years before the publication of this book several more laboratories have started to study chlorine isotopes in organic compounds, which for now already resulted in a large interlaboratory comparison study (Bernstein et al. 2011). Based on this comparison study it is expected that the field of chlorine isotopes in organic compounds will grow considerably in the next few years.

Most recently the isotope laboratory of the Chinese University of Geosciences in Wuhan led by Prof. Teng Ma developed methods to analyse chlorine and bromine isotopes using a GasBench to separate chloromethane or bromomethane from the other gases present after their preparation from both inorganic chloride or bromide (Liu et al. 2013; Du et al. 2013) and chlorine in organic compounds (Gan et al. 2013). Except from the methodology they already produced a few studies on chlorine and bromine isotope variations in groundwater systems in the north east of China (Li et al. 2012; Chen et al. 2014).

Aside from these research groups there are several other research groups and laboratories where chlorine isotopes were studied in a less continuous manner. An important example of this type of research groups is found in the laboratory of David Banks (Leeds) were several important chlorine isotope studies were produced (e.g. Richard et al. 2011; Chiaradia et al. 2006; Bridges et al. 2004; Rosenbaum et al. 2000; Banks et al. 2000a, b) in which theses isotopes were measured by thermal ionization mass spectrometry. Another important example was the laboratory of the National Water Research Institute in Saskatoon, Canada where methodology for on-line techniques were developed (Wassenaar and Kohler 2004) and who did very important research on the chlorine isotope composition of rainwater (Kohler and Wassenaar 2009). In this laboratory the chlorine isotope compositions for some third party studies were analysed (e.g. Gleeson and Smith 2009; Bernal et al. 2014). Other labs published the methodology they developed for chlorine and/or bromine isotope measurements, such as Gelman and Halicz (2010, 2011) and Halas and Pelc (2009) but did publish only very limited case studies on chlorine and/or bromine isotopes, such as Zakon et al. (2013) and Baran et al. (2012) It is hoped that the number of papers by other institutions as mentioned in this section will be increased considerably in the near future.

This list of laboratories and research groups that studied chlorine and bromine isotopes is certainly not complete, and chlorine and bromine isotopes have been studied, and are actually studied at this moment at more laboratories, but it is believed that those laboratories that have contributed the most important contributions to the study of the 'stable halogen isotopes' have been mentioned above.

However, considering the fact that the development of halogen isotope applications in geology has now a reached the mature age of 30 years, it is some kind of surprising, perhaps even disappointing that the whole development can be summarised in a small volume like this. The almost complete bibliography of chlorine and bromine isotope geochemistry, published on the author's website (http://www.eggenkamp.info/halogen) counts a total of 293 chlorine and bromine isotope papers over the period 1919 (when the existence of multiple stable isotopes of chlorine and bromine was confirmed) until early 2014.

Figure 14.1 shows the development of the number of chlorine and bromine isotope papers over time, from 1919 until 2014. From this last year only the papers that were published prior to May were taken into account when I finished writing this text. The number of papers per year remained very low from the discovery of the isotopes in 1919 until 1994, when never more than 5 papers per year were published. So even after it was shown that chlorine isotope variations could be measured in natural samples (Kaufmann et al. 1984) it took about ten years before the number of publications published per annum started to increase considerably. Even after this the number increased only slowly until in 2013 for the first time more than 20 papers were published.

The development of the research on stable halogen (chlorine and bromine) isotopes is, as can be viewed from Fig. 14.1, quite the opposite when it is compared to the development of other light isotope systems such as hydrogen, oxygen,

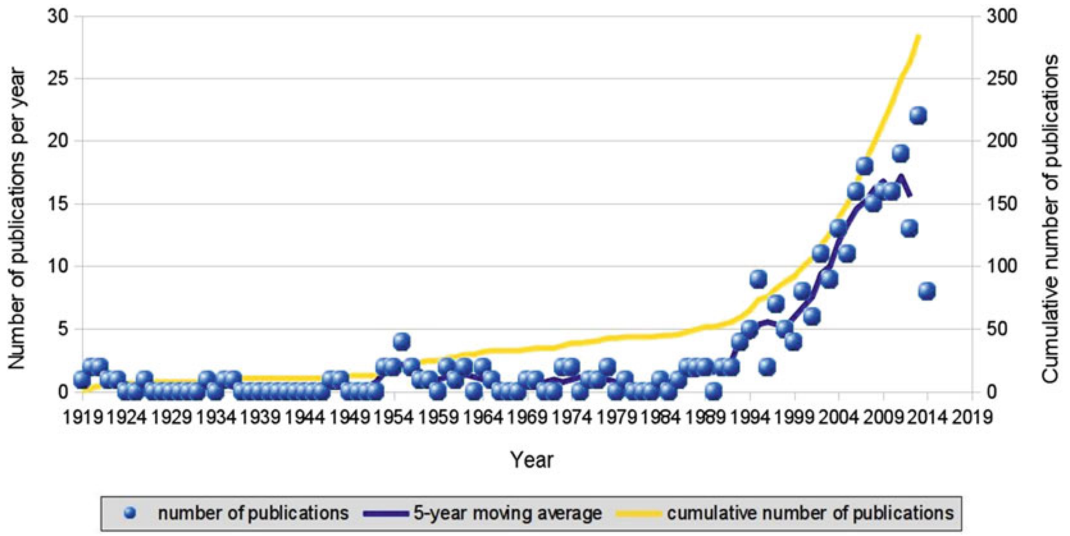

Fig. 14.1 Annual number of publications on chlorine and bromine stable isotopes

carbon or sulphur, which were, 30 years after the start of their development around 1950 (thus in about 1980), well known and commonly studied systems in a much larger number of laboratories than the number of laboratories that are currently studying halogen isotopes. The reasons for this slow development are probably related to the (chemical and physical) processes that chlorine and bromine are involved in and the relatively limited isotope variation that is observed in halogen isotope systems. In the case of bromine isotopes the lack of interest may in addition be related to the difficulties to extract bromine from samples with a large excess of chlorine (as in all natural inorganic samples) and the related problem of the small amounts of bromine that are in general present in those samples which makes it more difficult to produce high quality analyses. Combined with the relatively small variations that are observed for chlorine isotopes it is also observed that the variations that are found are often difficult to interpret. As has been stated earlier in this volume the variations that are observed within the big reservoirs are often larger that the variations that are found between these reservoirs. As a result of this overlap it is never very easy to determine what processes have taken place, and in virtually all cases additional observations and measurements of other chemical and isotopic parameters need to be taken into account for a proper interpretation of the results. This indicates that analysing chlorine isotopes as the only parameter in a system will never result in a conclusive result, unlike other isotope systems where single measurements can sometimes point to clear conclusions. On the other hand, it has been shown that in several environments the additional information that is obtained from chlorine isotope measurements actually give just the last bit of information that is necessary to solve a problem, such as has been shown for example in the complex diffusion system that appeared in the Dutch IJsselmeer (Beekman et al. 2011) where alternating freshwater and saline water phases were found in the past, and that showed that only after analysing the chlorine isotope characteristics in combination with the earlier measured parameters it was possible to fully understand the geochemical history of the system, as compared to earlier studies in the same system when chlorine isotope measurements were not available yet (Volker and Van der Molen 1991).

As shown above the number of laboratories that were involved in chlorine and bromine isotope studies during the last 30 years was small enough to mention most of them in this chapter. It can be concluded from this observation that the expectation that a new isotope system that could easily be picked up by most isotope laboratories that are also active in the other light stable isotopes (as chlorine isotopes can be analysed, just like the other light stable isotopes δD, δ^{13}C, δ^{15}N, δ^{18}O and δ^{34}S, as a gaseous compound in dual inlet mass spectrometry) did not really came through. As can be concluded from the introduction on the most active groups mentioned above every now and then halogen isotope studies are developed in new laboratories, but at the same time the research ceases to be done in other laboratories. In many cases it appears that, when the researcher that set up the halogen isotope facilities in a laboratory leaves, interest in the study vanishes. As a result of the limited number of laboratories where halogen isotopes are studied the total number of papers per years is stabilising at about 20 per year since about 2006.

It is not expected that the amount of research in chlorine and bromine isotopes will increase considerably in the near future. Individual laboratories will continue to work, generally in their own niche, and this will continue to improve our knowledge considerably. Although interest in halogen isotope research will remain, it will probably never grow to a major research field. It is expected however, due to the enthusiasm of the present leaders in the field, that new applications and further research will continue to be developed and applied to geological environments.

References

Ader M, Coleman ML, Doyle SP, Stroud M, Wakelin D (2001) Methods for the stable isotopic analysis of chlorine in chlorate and perchlorate compounds. Anal Chem 73:4946–4950

Ader M, Chaudhuri S, Coates JD, Coleman M (2008) Microbial perchlorate reduction: a precise laboratory determination of the chlorine isotope fractionation and its possible biochemical basis. Earth Planet Sci Lett 269:604–612

Amundson R, Barnes JD, Ewing S, Heimsath A, Chong G (2012) The stable isotope composition of halite and sulfate of hyperarid soils and its relation to aqueous transport. Geochim Cosmochim Acta doi:http://dx.doi.org/10.1016/j.gca.2012.04.044

Audí-Miró C, Cretnik S, Otero N, Palau J, Shouakar-Stash O, Soler A, Elsner M (2013) Cl and C isotope analysis to assess the effectiveness of chlorinated ethene degradation by zero-valent iron: Evidence from dual element and product isotope values. Appl Geochem 32:173–175

Banks DA, Green R, Cliff RA, Yardley BWD (2000a) Chlorine isotopes in fluid inclusions: Determination of the origins of salinity in magmatic fluids. Geochim Cosmochim Acta 64:1785–1789

Banks DA, Gleeson SA, Green R (2000b) Determination of the origin of salinity in granite-related fluids: evidence from chlorine isotopes in fluid incusions. J Geochem Expl 69–70:309–312

Baran A, Pelc A, Chmiel S, Halas S (2012) Pochodzenie mineralnych wód chlorkowo-sodowych w rejonie Rzeszowa w świetle badań izotopowych (δ18O i δD, δ13C, δ37Cl) i chemicznych (in Polish: Origin of saline waters in the vicinity of Rzeszów in light of isotope (δ18O i δD, δ13C, δ37Cl) and hydrochemical studies). Prz Geol 60:657–664

Barnes JD, Cisneros M (2012) Mineralogical control on the chlorine isotope composition of altered oceanic crust. Chem Geol 326–327:51–60

Barnes JD, Sharp ZD (2006) A chlorine isotope study of DSDP/ODP serpentinized ultramafic rocks: insights into the serpentinization process. Chem Geol 228:246–265

Barnes JD, Selverstone J, Sharp ZD (2006) Chlorine isotope chemistry of serpentinites from Elba, Italy, as an indicator of fluid source and subsequent tectonic history. Geochem Geophys Geosys 7 Article number Q08015

Barnes JD, Sharp ZD, Fischer TP (2008) Chlorine isotope variations across the Izu-Bonin-Mariana arc. Geology 36:883–886

Barnes JD, Sharp ZD, Fisher TP, Hilton DR, Carr MJ (2009) Chlorine isotope variations along the Central American volcanic front and back arc. Geochem Geophys Geosys 10 Article number Q11S17

Barnes JD, Eldam R, Lee CTA, Errico JC, Loewy S, Cisneros M (2013) Petrogenesis of serpentinites from the Franciscan Complex, western California, USA. Lithos 178:143–157

Beekman HE, Eggenkamp HGM, Appelo CAJ (2011) An integrated modelling approach to reconstruct complex solute transport mechanisms—Cl and δ^{37}Cl in pore water of sediments from a former brackish lagoon in The Netherlands. Appl Geochem 26:257–268

Beneteau KM, Aravena R, Frape SK (1999) Isotopic characterization of chlorinated solvents-laboratory and field results. Org Geochem 30:739–753

Bernal NF, Gleeson SA, Dean AS, Liu XM, Hoskin P (2014) The source of halogens in geothermal fluids from the Taupo Volcanic Zone, North Island, New Zealand. Geochim Cosmochim Acta 126:265–283

Bernstein A, Shouakar-Stash O, Ebert K, Laskov C, Hunkeler D, Jeannottat S, Sakaguchi-Söder K, Laaks J, Jochmann MA, Cretnik S, Jager J, Haderlein SB, Schmidt TC, Aravena R, Elsner M (2011) Compound-

Specific Chlorine Isotope Analysis: A Comparison of Gas Chromatography/Isotope Ratio Mass Spectrometry and Gas Chromatography/Quadrupole Mass Spectrometry Methods in an Interlaboratory Study. Anal Chem 83:7624–7634

Böhlke JK, Sturchio NC, Gu B, Horita J, Brown GM, Jackson WA, Batista JR, Hatzinger PB (2005) Perchlorate isotope forensics. Anal Chem 77:7838–7842

Bohlke JK, Hatzinger PB, Sturchio NC, Gu B, Abbene I, Mroczkowski SJ (2009) Atacama perchlorate as an agricultural contaminant in groundwater: isotopic and chronologic evidence from Long Island, New York. Environ Sci Technol 43:5619–5625

Bonifacie M, Charlou JL, Jendrzejewski N, Agrinier P, Donval JP (2005) Chlorine isotopic compositions of high temperature hydrothermal vent over ridge axes. Chem Geol 221:279–288

Bonifacie M, Jendrzejewski N, Agrinier P, Humler E, Coleman M, Javoy M (2008a) The chlorine isotope composition of earth's mantle. Science 319:1518–1520

Bonifacie M, Busigny V, Mével C, Philippot P, Agrinier P, Jendrzejewski N, Scambelluri M, Javoy M (2008b) Chlorine isotopic composition in seafloor serpentinites and high-pressure metaperidotites. Insights into oceanic serpentinization and subduction processes. Geochim Cosmochim Acta 72:126–139

Boschetti T, Toscani L, Shouakar-Stash O, Iacumin P, Venturelli G, Mucchino C, Frape SK (2011) Salt Waters of the Northern Apennine Foredeep Basin (Italy): Origin and Evolution Aquat Geochem 17:71–108

Bridges JC, Banks DA, Smith M, Grady MM (2004) Halite and stable chlorine isotopes in the Zag H3-6 breccia. Meteorit Planet Sci 39:657–666

Cameron AE, Herr W, Herzog W, Lundén A (1956) Isotopen-Anreicherung beim Brom durch electrolytische Überführung in geschmolzenem Bleibromid. Z Naturforschng 11a:203-205

Campbell DJ (1985) Fractionation of stable chlorine isotopes during transport through semipermeable membranes. MS. thesis, University of Arizona

Carrizo D, Unger M, Holmstrand H, Andersson P, Gustafsson Ö, Sylva SP, Reddy CM (2011) Compound-specific bromine isotope compositions of one natural and six industrially synthesised organobromine substances. Environ Chem 8:127–132

Chen LZ, Ma T, Du Y, Yang J, Liu L, Shan HM, Liu CF, Cai HH (2014) Origin and evolution of formation water in North China Plain based on hydrochemistry and stable isotopes (^{2}H, ^{18}O, ^{37}Cl and ^{81}Br). J Geochem Expl 145:250–259

Chiaradia M, Banks D, Cliff R, Marschik R, de Haller A (2006) Origin of fluids in iron oxide-copper-gold deposits: constraints from δ^{37}Cl, ^{87}Sr/^{86}Sr$_{i}$ and Cl/Br. Mineral Dep 41:565–573

Coleman ML, Eggenkamp HGM, Aranyossy JF (2001) Chlorine stable isotope characterisation of solute transport in mudrocks. in Etude pour la faisabilité des stockages de déchets radioactifs. Actes J Scientif ANDRA, Nancy, 7, 8 et 9 décembre 1999. pp 155–175

Coleman ML, Ader M, Chaudhuri S, Coates JD (2003) Microbial isotopic fractionation of perchlorate chlorine. Appl Environ Microbiol 69:4997–5000

Curie I (1921) Sur le poids atomique du chlore dans quelques mineraux. Compte Rend Sean 172:1025–1028

Desaulniers DE, Kaufmann RS, Cherry JA, Bentley HW (1986) ^{37}Cl-^{35}Cl variations in a diffusion controlled groundwater system. Geochim Cosmochim Acta 50:1757–1764

Du Y, Ma T, Yang J, Liu L, Shan HM, Cai HS, Liu CF, Chen LZ (2013) A precise analytical method for bromine stable isotopes in natural waters by GasBench II-IRMS. Int J Mass Spectrometry 338:50–56

Eastoe CJ, Long A, Knauth LP (1999) Stable chlorine isotopes in the Palo Duro Basin, Texas: evidence for preservation of Permian evaporite brines. Geochim Cosmochim Acta 63:1375–1382

Eastoe CJ, Long A, Land LS, Kyle JR (2001) Stable chlorine isotopes in halite and brine from the Guld Coast Basin: brine genesis. Chem Geol 176:343–360

Eastoe CJ, Peryt TM, Petrychenko OY, Cussey, G (2007) Stable chlorine isotopes in Phanerozoic evaporites. Appl. Geochem. 22:575–588

Eggenkamp HGM (1994) δ^{37}Cl; the geochemistry of chlorine isotopes. Geol Ultrai 116:1–150. Thesis Utrecht University

Eggenkamp HGM, Coleman ML (2000) Rediscovery of classical methods and their application to the measurement of stable bromine isotopes in natural samples. Chem Geol 167:393–402

Eggenkamp HGM, Kreulen R, Koster van Groos AF (1995) Chlorine stable isotope fractionation in evaporites. Geochim Cosmochim Acta 59:5169–5175

Eggenkamp HGM, Bonifacie M, Ader M, Agrinier P (2011) Fractionation of Cl and Br isotopes during precipitation of salts from their saturated solutions. 21th Annual V.M. Goldschmidt Conference. Prague, Czech Republic. Mineral Mag 75:798

Eggenkamp HGM, Coleman ML (2009) The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes. Geochim Cosmochim Acta 73:3539–3548

Eggenkamp HGM, Koster van Groos AF (1997) Chlorine stable isotopes in carbonatites: evidence for isotopic heterogeneity in the mantle. Chem Geol 140:137–143

Eggenkamp HGM, Middelburg JJ, Kreulen R (1994) Preferential diffusion of ^{35}Cl relative to ^{37}Cl in sediments of Kau Bay, Halmahera, Indonesia. Chem Geol (Isot Geosc Sect) 116:317–325

Gan YQ, Yu TT, Zhou AG, Liu YD, Liu CF (2013) A technique for carbon and chlorine isotope analyses of chlorinated aliphatic hydrocarbons in groundwater. J Earth Sci 24:274–281

Giunta T, Labadi J, Eggenkamp HGM (2013) Experimental determination of chlorine isotope fractionation in Cl_2–Cl^{-}_{aq} and $ClOH_{aq}$-Cl^{-}_{aq}. 23th Annual V.M.

Goldschmidt Conference. Firenze, Italy. Min Mag 77:1179

Gleeson SA, Smith MP (2009) The sources and evolution of mineralising fluids in iron oxide-copper-gold systems, Norrbotten, Sweden: Constraints from Br/Cl ratios and stable Cl isotopes of fluid inclusion leachates. Geochim Cosmochim Acta 73:5658–5672

Godon A, Jendrzejewski N, Eggenkamp HGM, Banks DA, Ader M, Coleman ML, Pineau F (2004) A cross calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. Chem Geol 207:1–12

Graczyk DG, Taylor JW (1974) Chlorine kinetic isotope-effects in nucleophilic-substitution reactions—support for ion-pairs mechanism in reactions of p-methoxy-benzyl chloride in 70 percent aqueous acetone. J Am Chem Soc 96:3255–3261

Grimsrud EP, Taylor JW (1970) Chlorine kinetic isotope effects in nucleophilic displacements at a saturated carbon. J Am Chem Soc 92:739–741

Groen J, Velstra J, Meesters AGCA (2000) Salinization processes in paleowaters in coastal sediments from Suriname: Evidence from δ^{37}Cl analysis and diffusion modelling. J Hydrol 234:1–20

Gwynne R, Frape S, Shouakar-Stash O, Love A (2013) ^{81}Br, ^{37}Cl and ^{87}Sr studies to assess groundwater flow and solute sources in the southwestern Great Artesian Basin, Australia. Proc Earth Planet Sci 7:330–333

Halas P, Pelc A (2009) New isotope ratio mass spectrometric method of precise δ^{37}Cl determinations. Rapid Commun Mass Spectrom 23:1061–1064

Harkins WD, Stone SB (1926) The isotopic composition and atomic weight of chlorine from meteorites and from minerals of non-marine origin. J Am Chem Soc 48:938–949

Herzog W, Klemm A (1958) Die Temperaturabhängigkeit des Isotopie-Effekts bei der elektrolytischen Wanderungen der Chlorionen in herschmolzenem Thallium (I)-chlorid. Z Naturforschg 13a:7–16

Hoering TC, Parker PL (1961) The geochemistry of the stable isotopes of chlorine. Geochim Cosmochim Acta 23:186–199

Holmstrand H, Andersson P, Gustafsson Ö (2004) Chlorine isotope analysis of submicromole organochlorine samples by sealed tube combustion and thermal ionization mass spectrometry. Anal Chem 76:2336–2342

Holmstrand H, Gadomski D, Mandalakis M, Tysklind M, Irvine R, Andersson P, Gustafsson Ö (2006) Origin of PCDDs in ball clay assesed with compound-specific chlorine isotope analysis and radiocarbon dating. Environ Sci Technol 40:3730–3735

Holmstrand H, Mandalakis M, Zencak Z, Andersson P, Gustafsson O (2007) First compound-specific chlorine-isotope analysis of environmentally-bioaccumulated organochlorines indicates a degradation-relatable kinetic isotope effect for DDT. Chemosphere 69:1533–1539

Holmstrand H, Zencak Z, Mandalakis M, Andersson P, Gustafsson Ö (2010) Chlorine isotope evidence for the anthropogenic origin of tris-(4-chlorophenyl)methane. Appl Geochem 25:1301–1306

Holt BD, Sturchio NC, Abrajano TA, Heraty LJ (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. Anal Chem 69:2727–2733

Holt BD, Heraty LJ, Sturchio NC (2001) Extraction of chlorinated aliphatic hydrocarbons from groundwater at micromolar concentrations for isotopic analysis of chlorine. Environ Poll 113:263–269

Horst A (2013) Stable bromine isotopic composition of methyl bromide. Method development and applications. PhD thesis, Stockholm University

Hunkeler D, Van Breukelen BM, Elsner M (2009) Modelling chlorine isotope trends during sequential transformation of chlorinated ethenes. Environ Sci Technol 43:6750–6756

Hunkeler D, Aravena R, Shouakar-Stash O, Weisbrod N, Nasser A, Netzer L, Ronen D (2011) Carbon and chlorine isotope ratios of chlorinated ethenes migrating through a thick unsaturated zone of a sandy aquifer. Env Sci Technol 45:8247–8253

Jendrzejewski N, Eggenkamp HGM, Coleman ML (1997) Sequential determination of chlorine and carbon isotopic composition in single microliter samples of chlorinated solvent. Anal Chem 69:4259–4266

Jendrzejewski N, Eggenkamp HGM, Coleman ML (2001) Characterisation of chlorinated hydrocarbons from chlorine and carbon isotopic compositions: scope and application to environmental problems. Appl Geochem 16:1021–1031

Kaown D, Shouakar-Stash O, Yang J, Hyun YJ, Lee KK (2013) Identification of multiple sources of grondwater contamination by dual isotopes. Ground Water. doi:10.1111/gwat.12130

Kaufmann RS (1984) Chlorine in groundwater: Stable isotope distribution. Ph.D. thesis, University of Arizona, Tucson, Ariz

Kaufmann RS, Long A, Bentley H, Davis S (1984) Natural chlorine isotope variations. Nature 309:338–340

Kaufmann RS, Frape S, Fritz P, Bentley H (1987) Chlorine stable isotope composition of Canadian shield brines. In: Saline water and gases in crystalline rocks. (Ed) Fritz P, Frape SK, Geol Assoc Canada, Special Paper 33:89–93

Kaufmann RS, Frape SK, McNutt R, Eastoe CJ (1993) Chlorine stable isotope distribution of Michigan basin formation waters. Appl Geochem 8:403–407

Klemm A, Lundén A (1955) Isotopenanreicherung beim Chlor durch electrolytische Überfürung in geschmolzenem Bleichlorid. Z Naturforschg. 10A:282–284

Kohler G, Wassenaar LI (2009) The stable isotopic composition (^{37}Cl/^{35}Cl) of dissolved chloride in rainwater. Appl Geochem 25:91–96

Lavastre V, Jendrzejewski N, Agrinier P, Javoy M, Evrard M (2005) Chlorine transfer out of a very low permeability clay sequence (Paris Basin, France): ^{35}Cl and ^{37}Cl evidence. Geochim Cosmochim Acta 69:4949–4961

Le Gal La Salle C, Matray JM, Bensenouci F, Michelot JL, Dauzères A, Wittebroodt C, Frape S, Shouakar Stash O, Rebaix R, Lancelot J (2013) Modelling Cl-concentration and δ37Cl profiles in porewater across a 250 m-thick indurated clayrock at the tournemire URL (France). Proc Earth Planet Sc 7:471–474

Li XQ, Zhou AG, Liu YD, Ma T, Liu CF, Liu L, Yang J (2012) Stable isotope geochemistry of dissolved chloride in relation to hydrogeology of the strongly exploited Quaternary aquifers, North China Plain. Appl Geochem 27:2031–2041

Liu WG, Xiao YK, Wang QZ, Qi HP, Wang YH, Zhou YM, Shirodkar PV (1997) Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. Chem Geol 136:271–279

Liu YD, Zhou AG, Gan YQ, Liu CF, Yu TT, Li XQ (2013) An online method to determine chlorine stable isotope composition by continuous flow isotope ratio mass spectrometry (CF-IRMS) coupled with a Gasbench II. J South Cent Univ 20:193–198

Long A, Eastoe CJ, Kaufmann RS, Martin JG, Wirt L, Finley JB (1993) High-precision measurement of chlorine stable isotope ratios. Geochim Cosmochim Acta 57:2907–2912

Loomis JL, Coleman ML, Eggenkamp HGM (1997) Effect of ion exchange on solute transport in shallow groundwaters: An experimental study using chlorine isotopes. EUG IX. Terra Nova 9 Abst. (Supp 1):659

Lundén A, Herzog W (1956) Isotopenanreicherung bei Chlor durch electrolytische Überführung in geschmolzenem Zinkchlorid. Z Naturforschg 11a:520

Lundén A, Lodding A (1960) Isotopenanreicherung bei Brom durch electrolytische Überführung in geschmolzenem Zinkbromid. Z Naturforschg. 15A:320–322

Luo CG, Xiao YK, Ma HZ, Ma YQ, Zhang YL, He MY (2012) Stable isotope fractionation of chlorine during evaporation of brine from a saline lake. Chin Sci Bull 57:1833–1843

Magenheim AJ, Spivack AJ, Volpe C, Ransom B (1994) Precise determination of stable chlorine isotopic ratios in low-concentration natural samples. Geochim Cosmochim Acta 58:3117–3121

Magenheim AJ, Spivack AJ, Michael PJ, Gieskes JM (1995) Chlorine stable isotope composition of the oceanic crust: Implications for Earth's distribution of chlorine. Earth Planet Sci Lett 131:427–432

Mandalakis M, Holmstrand H, Andersson P, Gustafsson Ö (2008) Compound-specific chlorine isotope analysis of polychlorinated biphenyls isolated from Aroclor and Clophen technical mixtures. Chemosphere 71:299–305

Markl G, Musashi M, Bucher K (1997) Chlorine stable isotope composition of granulites from Lofoten, Norway: implications for the Cl isotope composition and for the source of Cl enrichment in the lower crust. Earth Planet Sci Lett 150:95–102

Martin JG (1993) Stable chlorine isotopes in the Milk River aquifer, Alberta, Canada: Implications for the geochemical evolution of the aquifer system. MSc thesis, Univ Arizona

Musashi M, Markl G, Kreulen R (1998) Stable chlorine-isotope analysis of rock samples: New aspects of chlorine extraction. Anal Chem Acta 362:261–269

Musashi M, Oi T, Eggenkamp HGM (2004) Experimental determination of chlorine isotope separation factor by anion-exchange chromatography. Anal Chim Acta 508:37–40

Musashi M, Oi T, Eggenkamp HGM, Matsuo M (2008) Chlorine isotope fractionation associated with volcanic activity at the Kusatsu-Bandaiko hot spring in Japan. Isot Environ Health Stud 44:305–313

Owen HR, Schaeffer OA (1955) The isotope abundances of chlorine from various sources. J Am Chem Soc 77:898–899

Ransom B, Spivack AJ, Kastner M (1995) Stable Cl isotopes in subduction-zone porewaters: Implications for fluid rock reactions and the cycling of chlorine. Geology 23:715–718

Rebeix R, Le Gal La Salle C, Jean-Baptiste P, Lavastre V, Fourré E, Bensenouci F, Matray JM, Landrein P, Shouakar-Stash O, Frape SK, Michelot JL, Lancelot J (2014) Chlorine transport processes through a 2000 m aquifer/aquitard system. Mar Petr Geol 53:102–116

Reitz A, Pape T, Haeckel M, Schmidt M, Berner U, Scholz F, Liebetrau V, Aloisi G, Weise SM, Wallmann K (2011) Sources of fluids and gases expelled at cold seeps offshore Georgia, eastern Black Sea. Geochim Cosmochim Acta 75:3250–3268

Richard A, Banks DA, Mercadier J, Boiron MC, Cuney M, Cathelineau M (2011) An evaporated seawater origin for the ore-forming brines in unconformity-related uranium deposits (Athabasce Basin, Canada): Cl/Br and δ^{37}Cl analysis of fluid inclusions. Geochim Cosmochim Acta 75:2792–2810

Rizzo AL, Caracausi A, Liotta M, Paonita A, Barnes JD, Corsaro RA, Martelli M (2013) Chlorine isotopic composition of volcanic gases and rocks at Mount Etna (Italy) and inferences on the local mantle source. Earth Planet Sci Lett 371:134–142

Rodríguez A, Martínez M, Eggenkamp HGM, van Bergen MJ (2013) Chlorine isotope variations in the hyperacid lake system of Poás volcano, Costa Rica. IAVCEI 2013 Scientific Assembly, p 58

Rosenbaum JM, Cliff RA, Coleman ML (2000) Chlorine stable isotopes: a comparison of dual inlet and thermal ionization mass spectrometric measurements. Anal Chem 72:2261–2264

Selverstone J, Sharp ZD (2011) Chlorine isotope evidence for multicomponent mantle metasomatism in the Ivrea Zone. Earth Planet Sci Lett 310:429–440

Sharp ZD, Barnes JD (2004) Water-soluble chlorides in massive seafloor serpentinites: a source of chloride in subduction zones. Earth Planet Sci Lett 226:243–254

Sharp ZD, Barnes JD, Brearly AJ, Chaussidon M, Fisher TP, Kamenetsky VS (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature 446:1062–1065

Sharp ZD, Barnes JD, Fischer TP, Halick M (2010a) An experimental determination of chlorine isotope fractionation in acid systems and applications to volcanic fumaroles. Geochim Cosmochim Acta 74-264-273

Sharp ZD, Shearer CK, McKeagan KD, Barnes JD, Wang YQ (2010b) The chlorine isotope composition of the moon and implications for an anhydrous mantle. Science 329:1050–1053

Sharp ZD, Shearer CK, McCubbin FM, Agee CB (2011) The Cl isotope composition of the Moon and Mars. 21th Annual V.M. Goldschmidt Conference. Prague, Czech Republic. Mineral Mag 75:1848

Sharp ZD, Mercer JA, Jones RH, Brearley AJ, Selverstone J, Bekker A, Stachel T (2013) The chlorine isotope composition of chondrites and Earth. Geochim Cosmochim Acta 107:189–204

Shirodkar PV, Xiao YK, Hai L (2003) Boron and chlorine isotopic signatures of seawater in the Central Indian ridge. Curr Sci 85:313–320

Shirodkar PV, Xiao YK, Sarkar A, Dalal SG, Chivas AR (2006) Influence of air-sea fluxes on chlorine isotopic composition of ocean water: implications for constancy in δ^{37}Cl—a statistical inference. Environ Int 32:235–239

Shouakar-Stash O (2008) Evaluation of stable chlorine and bromine isotopes in sedimentary formation fluids. PhD Thesis, University of Waterloo

Shouakar-Stash O, Drimmie RJ, Frape SK (2003) Stable hydrogen, carbon and chlorine isotope measurements of selected chlorinated organic solvents. J Contam Hydrol 60:211–228

Shouakar-Stash O, Drimmie RJ, Frape SK (2005a) Determination of inorganic chlorine stable isotopes by continuous flow isotope ratio mass spectrometry. Rapid Commun Mass Spectrom 19:121–127

Shouakar-Stash O, Frape SK, Drimmie RJ (2005b) Determination of bromine stable isotopes using continuous-flow isotope ratio mass spectrometry. Anal Chem 77:4027–4033

Shouakar-Stash O, Alexeev SV, Frape SK, Alexeeva LP, Drimmie RJ (2007) Geochemistry and stable isotope signatures, including chlorine and bromine isotopes, of the deep groundwaters of the Siberian Platform, Russia. Appl Geochem 22:589–605

Shouakar-Stash O, Frape SK, Aravena R, Gargini B, Pasini M, Drimmie RJ (2009) Analysis of compound-specific chlorine stable isotopes of vinyl chloride by continuous flow-isotope ratio mass spectrometry (CF-IRMS). Environ Forensics 10:299–306

Stotler RL, Frape SK, Shouakar-Stash O (2010) An isotopic survey of δ81Br and δ37Cl of dissolved halides in the Canadian and Fennoscandian shields. Chem Geol 274:38–55

Sturchio NC, Böhlke JK, Beloso AD Jr, Streger SH, Heraty LJ, Hatzinger PB (2007) Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: laboratory results and implications for forensics and natural attenuation studies. Environ Sci Technol 41:2796–2802

Sturchio NC, Hoaglund JR III, Marroquin RJ, Beloso AD Jr, Heraty LJ, Bortz SE, Patterson TL (2012) Isotopic mapping of groundwater perchlorate plumes. Ground Water 50:94–102

Tan HB, Ma HZ, Wei HZ, Xu JX, Li TW (2006) Chlorine, sulfur and oxygen isotopic constraints on ancient evaporite deposit in the Western Tarim Basin, China. Geochem J 40:569–577

Tan HB, Ma HZ, Zhang XY, Xu JX, Xiao YK (2009) Fractionation of chlorine isotope in salt mineral sequences and application: research on sedimentary stage of ancient salt rock deposit in Tarim Basin and western Qaidam Basin. Acta Petrol Sinica 25:955–962 (in Chinese with English abstract)

Taylor JW, Grimsrud EP (1969) Chlorine isotopic ratios by negative ion mass spectrometry. Anal Chem 41:805–810

Turnquist CR, Taylor JW, Grimsrud EP, Williams RC (1973) Temperature dependence of chlorine kinetic isotope effects for aliphatic chlorides. J Am Chem Soc 95:4133–4138

Van Acker MRMD, Shahar A, Young ED, Coleman ML (2006) GC/Multiple Collector-ICPMS method for chlorine stable isotope analysis of chlorinated aliphatic hydrocarbons. Anal Chem 78:4663–4667

Van Warmerdam EM, Frape SK, Aravena R, Drimmie RJ, Flatt H, Cherry JA (1995) Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. Appl Geochem 10:547–552

Volker A, Van der Molen WH (1991) The influence of groundwater currents on diffusion processes in a lake bottom: an old report reviewed. J Hydrol 126:159–169

Volpe C, Spivack AJ (1994) Stable chlorine isotopic composition of marine aerosol-particles in the Western Atlantic Ocean. Geophys Res Lett 21:1161–1164

Volpe C, Wahlen M, Pszenny AAP, Spivack AJ (1998) Chlorine isotopic composition of marine aerosols: Implications for the release of reactive chlorine and HCl cycling rates. Geophys Res Lett 25:3831–3834

Wassenaar LI, Koehler G (2004) On-line technique for the determination of the δ^{37}Cl of inorganic and total organic Cl in Environmental Samples. Anal Chem 76:6384–6388

Wei W, Kastner M, Spivack A (2008a) Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean. Earth Planet Sci Lett 266:90–104

Wei W, Kastner M, Spivack A (2008b) Reply to comment on: "Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean". Earth Planet Sci Lett 274:535

Willey JF, Taylor JW (1980) Temperature-dependence of bromine kinetic isotope effects for reactions of normal-butyl and *tert*-butyl bromides. J Am Chem Soc 102:2387–2391

Wirt L (1988) The origin of chloride in groundwater in the Stripa granite, Sweden. MSc thesis, Univ Arizona

Woulé Ebongué V, Jendrzejewski N, Walgenwitz F, Pineau F, Javoy M (2005) Chlorine isotope residual salt analysis: a new tool to investigate formation waters from core analyses. AAPG Bull 89:1005–1018

Xiao YK, Zhang CG (1992) High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the Cs_2Cl^+ ion. Intl J Mass Spectrom Ion Proc 116:183–192

Xiao YK, Beary ES, Fassett JD (1988) An improved method for the high-precision isotopic measurement of boron by thermal ionization mass-spectrometry. Intl J Mass Spectrom Ion Proc 85:203–213

Xiao YK, Jin L, Qi HP (1991) Investigation of thermal ion emission characteristics of graphite. Intl J Mass Spectrom Ion Proc 107:205–213

Xiao YK, Liu WG, Qi HP, Zhang CG (1993) A new method for the high precision isotopic measurement of bromine by thermal ionization mass spectrometry. Intl J Mass Spectrom Ion Proc 123:117–123

Xiao YK, Liu WG, Zhou YM, Sun DP (1997) Isotope compositions of chlorine in brine and saline minerals. Chin Sci Bull 42:406–409

Xiao YK, Liu WG, Zhou YM, Wang YH, Shirodkar PV (2000) Variations in isotopic compositions of chlorine in evaporation controlled salt lake brines of Qaidam Basin, China. Chin J Ocean Limn 18:169–177

Xiao YK, Zhou YM, Wang QZ, Wei HZ, Liu WG, Eastoe CJ (2002) A secondary isotopic reference material of chlorine from selected seawater. Chem Geol 182:655–661

Zakon Y, Halicz L, Gelman F (2013) Bromine and carbon isotope effects during photolysis of brominated phenols. Environ Sci Technol 47:14147–14153