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Geophysical Monograph 146

The Extreme Proterozoic: Geology, Geochemistry, and Climate

Gregory S. Jenkins
Mark A. S. McMenamin
Christopher P. McKay
Linda Sohl
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American Geophysical Union
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Library of Congress Cataloging-in-Publication Data

The extreme Proterozoic : geology, geochemistry, and climate / Gregory S. Jenkins ...
[et al.], editors.
p. cm.— (Geophysical monograph ; 146)
Includes bibliographical references.
ISBN 0-87590-411-4 (alk. paper)
1. Paleoclimatolog—Proterozoic. 2. Climatic Extremes. 3. Glacial climates. I.
Jenkins, Gregory S. II. Series.

QC884.E985 2004
551.6'09'012—dc22

2004058023

ISBN 0887590-411-4
ISSN 0065-8448

Front Cover: Margerie Glacier, Glacier Bay, Alaska (courtesy of Victor A. Gostin, Geology and Geophysics, University of Adelaide).

Printed in the United States of America.

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PREFACE

Earth climate is uniquely determined at any time by the varied interactions of its components: lithosphere, biosphere, atmosphere, hydrosphere (ocean, lakes and rivers) and cryosphere. Over the past 544 million years (the Phanerozoic Eon), these components of the climate system have undergone significant changes but perhaps none more extreme than in the Proterozoic Era (2.5 Ga-544 Ma) With at least three periods with low-latitude glacial deposits (during the Palaeoproterozoic and Neoproterozoic), the cryosphere may have dominated the earth's surface, possibly the only such event in earth's history. Indeed, if the Earth had an obliquity similar to the present (23.45), then low-latitude glaciation could represent a nearly ice- and snow-covered globe. Effects would have been multiform: The influence of the hydrosphere would have been at a minimum and most living organisms would have been confined to small areas of open ocean if they existed at all, or possibly near hydrothermal vents. The atmosphere would have been very dry and nearly cloud-free.

Currently it is not clear what role the lithosphere played in the triggering or termination of such low-latitude glacial events. The contiguity of events, however, is clear, with the Huronian and Sturtian occurring when landmasses occupied low latitudes. At the end of the Neoproterozoic, the rapidly drifting and colliding cratons that extended from the equator to the Southern Hemisphere high latitudes may have also triggered extreme climatic conditions. At the same time, life in the oceans may have played a role in producing extreme climatic conditions. Despite major uncertainties here, it has been suggested that the rise of atmospheric oxygen at the beginning of the Palaeoproterozoic led to a significant reduction in methane producing bacteria, causing a reduction in temperature and triggering widespread glaciation. Similar scenarios might also exist for the Neoproterozoic period as a possible trigger for widespread glaciation.

This monograph responds to such issues, and more, by interpreting the geologic rock record and its relationship to extreme conditions in the Proterozoic Era, with primary focus on the Palaeoproterozoic and Neoproterozoic. However tentative results may be, at least in terms of a definitive understanding, the problems associated with extreme conditions in the Proterozoic continue to prompt important research. For example, if present-day orbital parameters are assumed, then glacial deposits would strongly suggests sea-ice covered areas from the poles to the Equator (Snowball Earth conditions). If this was the case, how did life survive these extreme conditions and how did the Earth exit these harsh conditions? Is there evidence for mass extinction? What does the rock record and geochemical studies tell us about the timing and duration of these events? Are there other alternatives to a completely snow- and ice-covered Earth? Is it possible to model low-latitude glaciation in climate models and what are the caveats?

In order to help clarify these areas, we have divided the monograph into four sections. Section I presents observations of extreme conditions during the Proterozoic eon, including: evidence of glacial deposit, reconstructions of the continents and geochemical analysis of observed data. Section II presents geochemical and coupled climate modeling studies, examining the processes associated with low-latitude glaciation and the escape from potential Snowball Earth conditions. Section III offers alternative hypotheses and views for explaining low-latitude glacial deposits. The role of high obliquity and tectonic forces are presented as alternatives for explaining low-latitude glacial deposits. Section 4 concludes with research relating biological processes to extreme Neoproterozoic conditions.

In total, this monograph offers an opportunity for readers to capture our current view of the state of research on the extreme earth conditions during the Proterozoic. Contrastive views as surmised from low-latitude glacial deposits, even the different interpretations of evidence from the geologic rock record, sustain our sense of a fascinating, if open, field of research. At the same time, because each position finds support in a set of observations that may or may not be complete enough to determine with conclusive accuracy, we have encouraged our contributors to assess study limitations and apply appropriate constraints to their views. It is our hope, of course, that a multidisciplinary view of the problems at hand will provide the necessary synergy for progress in this, and related areas, of research on extreme Proterozoic climatic conditions. Moreover, we believe that this multidisciplinary approach will help to generate a more holistic view of the problem that has captured the imagination and attention of scientists for several decades. This is only the beginning.

The book derives from a union session entitled "Snowball Earth," held during the Spring 2001 meeting of the American Geophysical Union. The session examined early (~2.2 Ga) and Neoproterozoic (~700-580 Ma) extreme climatic conditions as surmised from low-latitude glacial deposits. The conveners of the sessions, Gregory Jenkins, Chris McKay, Mark McMenamin and Linda Sohl, each had a particular interest in

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10.1029/146GM00

the geochemical, climatic and biological aspects of low latitude glaciation during the Proterozoic. The goal of the session was to gather scientists from various disciplines studying the different aspects of Neoproterozoic low-latitude glaciation.

We are indebted to our contributing authors and reviewers for their efforts in making this monograph possible. We also wish to thank the AGU books program, especially our acquisitions editor, Allan Graubard, for his guidance, assistance and patience, and the AGU production staff for their help in publishing this monograph in its final form.

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Introduction: The Proterozoic

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The Proterozoic (2.5 Ga–545 Ma) is perhaps the most intriguing period in Earth's history. In a typical high school physical science textbook it may be presented as a rather boring period that today's student is happy to pass over in lieu of the Mesozoic and the extinction of *Tyrannosaurus rex* by a large asteroid. In reality this was a period full of excitement as it opens (in the PalaeoProterozoic) with low-latitude glaciation in concert with a rise in atmospheric oxygen. The Proterozoic ends with a glacial period and a possible rise in atmospheric oxygen levels. Other highlights of the Proterozoic include: three or more severe glacial events, a long period (1 billion years) of apparent warmth without evidence of glacial deposits, significant fluctuations in δC^{13}, two or more periods where supercontinents were assembled, cap carbonates, banded iron formations, the rise of eukaryotes and the first complex life. The juxtaposition of extreme climate conditions and major evolutionary change among complex organisms during the Proterozoic is particularly puzzling, and begs the following question: What are the factors controlling the appearance of complex life?

The great paradox of the Proterozoic is related to large swings in climate that may have been controlled by geochemical, geophysical or even biological factors. There are at minimum three glacial events in the Proterozoic that have no rivals in Earth's history [*Evans et al.* 1997; *Evans*, 2000; *Chumakov and Elson*, 1989; *Schmidt and Williams*, 1995; *Park*, 1997; *Hoffman et al.* 1998]. These events are noted in the PalaeoProterozoic (2.4–2.1 Ga) and the NeoProterozoic (~725 Ma and 610 Ma). The Proterozoic glacial events are considered extreme because in each case the deposits are found in low paleo-latitudes with at least one event found near the PaleoEquator [*Schmidt and Williams,* 1995].

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The glacial periods of the Proterozoic differ significantly from those of the Quaternary in both spatial and temporal extent. The ice ages over the last several million years have been largely driven by the Milkanovich cycle, have affected mid and high latitudes, and have periods of approximately 100 thousand years. The glacial periods of the Proterozoic may have been global in extent and lasted from 4–30 million years [*Hoffman et al.* 1998]. The work by Evans [2000] shows that the majority of the glacial deposits are found at low latitudes with little evidence of glacial deposits >60°.

Based on our current understanding of the climate system, these low-latitude events would have been global in extent–assuming Earth's tilt was approximately 23.5°. Sea-ice would have migrated from the high to low latitudes giving the Earth a Europa-like appearance from space. During these periods, sea ice would have been rather thick (>200 meters), the atmosphere very dry, and patches of open land would have provided the only heterogeneity in locations not occupied by land-glaciers. Providing a framework that can explain the Proterozoic low-latitude glacial events remains a challenge. Thus far there are two hypothesis that best explain low-latitude glacial events—The Snowball Earth hypothesis [*Kirschvink*, 1992; *Hoffman et al.* 1998] and the high obliquity hypothesis [*Williams*, 1993].

With the aid of geologic data from Nambia and geochemical analysis, Hoffman et al. [1998] proposed that global glaciation had occurred two to four times during the Neo-Proterozoic. Hoffman et al. (1998) argue that glacial deposits in low latitudes in combination with multiple negative δC^{13} excursions, banded iron formations, and carbonate caps represents clear evidence of a global glacial cycle (termed Snowball Earth).

The initiation and termination for Snowball Earth is driven by fluctuations in greenhouse gases (primarily CO_2 and CH_4). Snowball Earth is initiated by a reduction in atmospheric CO_2 from intense weathering associated with the breakup of the super-continent of Rodinia near 750 Ma. As atmospheric CO_2 levels are reduced, the sea-ice begins to migrate towards the Equator. A positive feedback is then setup as sea-ice reflects more solar radiation until the entire Earth is covered by oceanic sea-ice and ice-sheets over land. In this process there is a near shut-down of the hydrologic cycle and global mean temperatures fall to -50°C [*Jenkins and Smith,* 1999]. Hoffman et al. [1998] suggest that sea-ice thicknesses of 1 km are possible under these conditions.

While most components of the Earth System are significantly altered (oceans, atmosphere, biosphere, cryosphere), the lithosphere, which operates on the longest time-scales, is not and volcanic activity allows for the slow accumulation of atmospheric CO_2. This accumulation over millions of years allows for warmer atmospheric conditions and the melting of Equatorial ice. Once the ice has melted a second greenhouse gas, water vapor, increases leading to the termination of Snowball Earth. With the end of the glaciation global mean temperatures increase to values greater than 50°C [*Jenkins*, 2003]. It is during this very warm period that carbonate caps are formed in the Snowball Earth hypothesis.

If, on the other hand [as suggested by *Williams* 1975; *Williams*, 1993], Earth's obliquity was considerably higher than present, then the appearance of low-latitude glacial deposits would not be considered exceptional but rather normal. This is due to the fact that under high obliquity conditions, the Sun's direct rays are focused on the high latitudes while the indirect rays are focused on low latitudes. Consequently, the warmest regions would be in high latitudes and the coldest regions in the low latitudes.

In the event of a landmass that is assembled or migrates in low-latitudes even colder conditions would result because of land's lower thermal heat capacity. Consequently, the probability of ice-sheets forming would increase especially in elevated areas. It would be possible to have seasonal sea-ice around the low-latitude continental margins. On such a landmass, there would be extreme seasonality with very cold winter hemisphere conditions and warmer summer hemisphere conditions. Contrary to the Snowball Earth hypothesis, Williams and Schmidt [2000] suggest that the hydrologic cycle continued to function and that the ocean was not frozen based on tidal rhythmites and tidal-deltaic deposits showing ripples generated by wind-wave action.

Climate model simulations have provided support for both hypotheses with a number of important caveats [*Jenkins and Smith,* 1999; *Hyde et al.* 2000; *Jenkins*, 2000; *Donnadieu et al.* 2002, *Jenkins*, 2003]. There have also been a number of climate modeling studies that do not support these hypotheses [*Poulsen et al.* 2001; *Poulsen et al.* 2002; *Poulsen,* 2003; *Donnadieu et al.* 2002]. Representing the dynamic state of the ocean in climate studies does not support the Snowball Earth hypothesis because the sinking of sea water near the edge of sea ice edge limits the migration of that ice into low-latitudes [*Poulsen et al.* 2001; *Poulsen et al.* 2002; *Poulsen*, 2003]. Moreover, the possibility of high latitude glacial deposits would not support the high obliquity hypothesis in the Neoproterozoic [*Donnadieu et al.* 2002].

Some simulations have found solutions that allow for areas of open ocean in the low paleo-latitudes [*Hyde et al.* 2000; *Chandler and Sohl,* 2000]. Such a zone may have provided a refuge for life from Snowball Earth given the assumption of an obliquity similar to present-day values. Nonetheless, given the extreme conditions over much of the Earth then, a significant reduction in life would have occurred. The negative $\delta^{13}C$ excursions suggests that there may have been reductions in biological activity, but positive $\delta^{13}C$ excursions occurring within periods of glacial activity make it difficult to draw conclusions about biological activity [*Kennedy et al.* 1998].

The Proterozoic marine biosphere was filled with four of the five main kingdoms of life: bacteria (Monera), protists, fungi, and animals. The only kingdom missing consisted of the vascular land plants, although the green algal ancestors to land plants were presumably present during the Proterozoic. Once again, the influence of extreme climate on the development of the biosphere at this time is less than clear. Some researchers [e. g. *Fedonkin*, 1983] have linked the glaciations to extinction and delayed development of the marine biota, but if anything the opposite appears to be the case. It seems possible that extreme climate conditions served as a stimulus to the evolution of complex life in the marine biota. An important question, addressed in this volume, is whether or not the Late Proterozoic biota bears any evidence of its sojourn beneath the ice.

The Proterozoic apparently sees the earliest development in the biosphere of complex eukaryotic multicellularity. A few microbial protists, via a variety of symbiosis-inducing and colony-forming processes that are not yet well understood, underwent a transformation from unicellular to multicellular [or at least metacellular; *McMenamin*, 1998] bodies. The first of these, appearing as fully-grown organiams around 600 Ma in Sonora, Mexico, and northwestern Canada, are the Ediacarans.

Ediacarans are quintessentially enigmatic fossil forms that have been subjected in recent decades to prolonged debate over their affinities and origin. Originally described as the earliest animal fossils, they were referred to an extinct kingdom in the 1970s and 1980s. Recent opinion seems to indicate a swing of the pendulum back in the opposite direction, with some forms (*Spriggina*, *Parvancorina*, *Kimberella*) being placed more-or-less confidently in the animal kingdom. Other forms remain quite puzzling, however, such as the Namibian specimens of *Pteridinium simplex* and the spindle-shaped forms of Mistaken Point, Newfoundland [*Peterson et al.* 2003, *Narbonne*, 2004]. With the exception of *Spriggina* and *Parvancorina* [possible trilobitoid arthropods; *McMenamin*, 2003b] and *Kimberella* [a possible radula-bearing mollusk; *Fedonkin and Waggoner*, 1997], phylogenetic links between the Ediacarans and animals of the Cambrian and later are difficult to come by. An exception to this rule is the confirmation of a prediction made in 1987 [*McMenamin*, 1987] of the presence of conulariids in the Proterozoic biota. This new fossil, *Vendoconularia triradiata* , however, is of not much help in determining the biological affinities of the Ediacarans, as the conulariids themselves (a Paleozoic group of ice-cream cone shaped fossils) remain enigmatic [*Ivantsov and Fedonkin*, 2002].

With evidence for Proterozoic arthropods and mollusks, it appears that the metazoan diversification was well underway before the beginning of the Cambrian. With the exception of the cloudinids, the first abundant shelly fossils, shelled animals are generally not seen in the rock record before the Cambrian. This transformation to a shelled fauna has been linked to ecological change near the Proterozoic–Cambrian boundary, and recent evidence strongly supports the notion that such an ecological transformation indeed took place [*McMenamin*, 2003a]. The changing ecology was associated with a transition from a Proterozoic seafloor dominated by microbial mats to a Phanerozoic seafloor characterized by a mixed layer at the sediment–water interface (Seilacher and Pflüger, 1994).

The study of the Proterozoic and the connection between evolution and the extreme climate events that appear to have occurred also provides lessons related to the search for life on the other worlds of our solar system. Beyond the Earth the two worlds that are most promising for the search for past or present life are Mars and Europa (a satellite of Jupiter). Both worlds could be aptly described as "snowballs". Mars has a mean annual temperature of -60°C with polar temperatures that reach down to -130° C. Ice is present at the surface near the polar regions and there is ice-rich permafrost extending toward the equator to about 60 degrees in both hemispheres.

Europa, at 5 astronomical units from the sun has a mean surface temperature of -160°C and a surface of ice. Beneath that ice there is good evidence for an ocean. The cracks and icebergs in the icy surface of Europa indicate that these features formed with liquid water under the ice. But this does not necessarily indicate that the water is present at this time. The indication of present water comes primarily from the magnetic disturbance Europa makes as it moves through Jupiter's magnetic field. These results indicate that Europa has a large conductor, most likely to be a global salty layer of water.

A key question for astrobiology is to determine if either of the snowball worlds of Mars and Europa support life. Among other applications, studies of the survival and evolution of life on Earth during the global glacial events of the Proterozoic can inform our understanding of how to search for life on snowball worlds and how to interpret what we find.

Acknowledgments. Thanks to L. Margulis, D. L. S. McMenamin and A. Seilacher for insightful discussion related to this volume.

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Paleomagnetic Constraints on Neoproterozoic 'Snowball Earth' Continental Reconstructions

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The Neoproterozoic glacial intervals represent one of the most curious expressions of Earth's climate. Despite the popularity of the hard "Snowball" hypothesis in the popular press, the scientific community remains divided over the extent of the Neoproterozoic glaciations, the age of the glaciations, the number of glacial events and the triggering mechanism for the glaciations. A major, and yet unresolved issue, is knowledge of the exact paleogeography during the so-called Sturtian and younger Vendian glaciations. The problem stems from the paucity of Neoproterozoic paleomagnetic data, in particular data for the interval from 600–720 Ma along with the varied interpretations of the extant database. Here we present 4 scenarios for the paleogeographic settings in the Neoproterozoic. The first two paleogeographies are thought to be representative of the Sturtian [700–800 Ma] glaciations and the younger reconstructions represent possible extremes for the Vendian glacial events [570–650 Ma]. The paleogeographies presented here have important ramifications for the development of climatic models and possible triggering mechanisms for the Neoproterozoic glacials.

1. INTRODUCTION

In 1959, W. B Harland and D. E. T. Bidgood completed a paleomagnetic study of the Moelv tillite and associated sedimentary rocks in the Sparagmite district of central Norway [*Harland & Bidgood,* 1959]. Those results, conducted without demagnetization, indicated a depositional paleolatitude of ~11 degrees. Harland and Bidgood [1959] argued that the Precambrian glaciations were far more severe and widespread than the Phanerozoic glaciations and they further suggested that the end of these glaciations led to the explosion of life in the Cambrian. The notion of a severe 'anti-greenhouse' effect in the Neoproterozoic was also discussed, in seldomly cited papers, by *J. D. Roberts* [1971, 1976]. *Roberts* [1971] based his arguments on the ubiquitous presence of dolomitic rocks in pre and post-glacial successions and concluded that CO_2 drawdown, via carbonate sedimentation, was likely the trigger for globally synchronous glaciations in the Neoproterozoic. In 1976, Roberts expanded on the anti-greenhouse concept and discussed a variety of other possible explanations for the presence of similar-age tillites on a global scale. A number of other possible explanations for the Neoproterozoic glaciations have been argued through the years [see *Meert and Van der Voo, 1994; Evans, 2000*; *Hoffman et al., 1998*]. Although the exact nature and severity of the Neoproterozoic glacial epochs are controversial, it is clear that paleomagnetic studies have played, and will play, a crucial role in determining the best explanation for the apparently enigmatic latitudinal distribution of tillites.

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If rapid true polar wander did occur in the manner proposed by *Evans [2003]*, it would likely hinder our ability to distinguish between the high-obliquity and snowball earth models using paleomagnetic methods.

6. CONCLUSIONS

Climatic models for the Neoproterozoic glaciations depend upon numerous factors including, but not limited to, the paleogeographic setting. Current knowledge of Neoproterozoic paleogeography is hindered by the rather limited dataset, particularly for the interval from 600–720 Ma [*Meert and Powell, 2001*]. Current paleogeographic models for the Sturtian glaciations, taken here as the interval from 700–800 Ma, are more robust than the younger Vendian glaciations. The most robust paleomagnetic data indicate that the supercontinent of Rodinia had begun to disperse. Climate models suggest that continental rifting may lead to an overall cooling trend that may have facilitated the climatic conditions necessary for an icehouse planet. The low-latitude position of this supercontinent [or fragments of the supercontinent] is also compatible with the high-obliquity model. The younger Neoproterozoic glacial epoch [Vendian-Varangian] has a less certain paleogeography [*Meert and Torsvik, 2003*]. The 'high-latitude' model is favored here, but the configuration is not without critics [*Pisarevsky et al., 2000*]. If the high-latitude model proves correct, then the high-obliquity scenario is invalidated. If the low-latitude model is correct, then both the high-obliquity model and the severe icehouse models would be untestable for this interval of time.

Acknowledgments. The authors wish to thank anonymous reviewers for valuable comments on the manuscript.

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Geochemical Climate Proxies Applied to the Neoproterozoic Glacial Succession on the Yangtze Platform, South China

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A Neoproterozoic succession of glaciomarine deposits of probably Sturtian age is preserved on the Yangtze Platform in South China. At that time, the South China block was located in intermediate to low paleolatitudes at ca. 40°. The snowball Earth hypothesis offers one possible explanation for the occurrence of low latitude tillites. The hypothesis is largely based on geological and geochemical observation made in deposits underlying or overlying such tillites on several continents. In contrast our study focuses on evidence offered by the tillites themselves. We use major, trace and rare earth geochemistry to evaluate the environmental conditions prevailing during the glaciation. Of particular interest are the intensity of chemical weathering and the relative degree of oxygenation of Neoproterozoic (Nanhuan-Sinian) marine bottom waters. CIA values were obtained from preglacial sand- and siltstones, the matrix of the glacial deposits, fine-grained clastic sediments of a unit intercalated in the glacial succession, and postglacial siltstones and black shales. The data indicate relatively low degrees of chemical weathering for the glacial deposits. In contrast, pre- and postglacial deposits display comparatively elevated levels. This is also true for the intercalated unit, which we interpret as the product of a warmer and more humid interglacial period. Data for S/TOC, U/Th, Cd, Mo, and the Ce_{anom} of the glaciomarine samples indicate the presence of oxic bottom waters during the glaciation. The snowball Earth hypothesis predicts the shutdown of chemical weathering on the continents and complete anoxia of the global ocean largely covered by sea ice for several million years. The geochemical record of the Neoproterozoic tillites on the Yangtze Platform is difficult to reconcile with the snowball Earth hypothesis.

1. INTRODUCTION

Neoproterozoic sedimentary successions on several continental blocks contain evidence of widespread glaciation in the form of glaciogenic deposits *[e.g. Martin, 1964, Harland, 1964; Deynoux et al., 1994; Crowell, 1999]*. The continents were arranged in low to intermediate latitudes between 5° and 40°, and deposition of some tillites occurred at sea

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level *[Schmidt and Williams, 1995; Evans, 2000]*. Evidence of near-equatorial positions is derived from lithostratigraphic and paleomagnetic data *[Harland and Bidgood, 1959; Harland, 1964; Meert and van der Voo, 1994; Li et al., 1995; Rui and Piper, 1997; Evans et al., 2000]*. In many locations, glacial deposits are sandwiched between or associated with sedimentary rocks typical of low latitudes and presumably warmer climate such as red beds, carbonates and phosphorites [*Roberts, 1976; Hambrey and Harland, 1981; Fairchild et al., 1994*].

In particular, the formation of glacial deposits at low latitudes suggests that icehouse climates in Neoproterozoic time progressed very differently from respective Phanerozoic cases *[Frakes, 1979; Evans, 2000]*. They coincided with very severe environmental changes recorded by global perturbations in the carbon cycle *[Kaufman et al., 1997; Kennedy et al., 2001 a, b; Schrag et al., 2002]*. The glaciation events are immediately preceded by an evolution of the $\delta^{13}C$ signal to negative values close to -5 ‰. It is interpreted as a substantial decline to complete termination of photosynthetic carbon fixation. This led *Kirschvink [1992]* and *Hoffman et al. [1998]* to synthesize the available evidence in the snowball Earth hypothesis. It states that at least twice during the Neoproterozoic, Earth was hidden under an all-encompassing ice cover for several million years. Main consequences are the termination of major geological processes including the hydrological cycle, chemical weathering, marine autotrophic activity and organic carbon burial. The near complete separation of atmosphere and oceans through ice coverage, lasting approximately 5–10 Ma *[Hoffman et al., 1998; Hoffman and Schrag, 2002]*, caused ocean waters to become anoxic very quickly, and remain so. Cap carbonates directly overlying the glacial deposits in many places mark the termination of the glacial periods and a rapid change to initially extreme greenhouse climates. These are thought to be associated with accelerated and large-scale chemical weathering on the continents following the onset of the hydrological cycle, at least a temporary return to vigorous ocean circulation and a correlative shift in $\delta^{13}C$ to values around +5‰.

The snowball Earth hypothesis can be tested in several ways. Climate modeling studies applying energy balance and global circulation models have produced conflicting results. They allow a frozen ocean at the equator only when extreme conditions were assumed *[Crowley and Baum, 1993; Jenkins and Smith, 1999; Hyde at al., 2000; Poulsen, 2001, Poulsen, 2003]*. In many cases, oceans within 20° of the equator remained ice-free *[e.g. Hyde et al., 2000]*. The recurrence of glacial rainout intervals in several Neoproterozoic glaciomarine successions on different continents demonstrates that the oceans were not completely frozen and that the hydrological cycle was operating *[Condon and Prave, 2000; Condon et al., 2002]*. Furthermore, carbon isotope data do not unequivocally support the inferences made by *Hoffman et al. [1998]* and *Schrag et al. [2002]* regarding the alleged long-term changes to the carbon flux *[Kennedy et al., 2001a]*. Also, the Neoproterozoic glacial successions do not record any distinct changes in $^{87}Sr/^{86}Sr$ composition, which should be expected in view of the 5–10 Ma time frame and the large-scale weathering events affecting the continents at the end of the glaciations *[Jacobsen and Kaufman, 1999; Kennedy et al., 2001a]*.

Most of the geochemical data bearing on this discussion were obtained from sedimentary rocks directly underlying and overlying the glacial intervals. Here we present initial results from a geochemical study of glaciomarine successions, which are exposed in the Anhui, Hunan, Hubei and Guizhou provinces on the Yangtze Platform in South China. One of the postulates of the snowball Earth hypothesis is that during glaciation chemical weathering on the continents was shut down and that oceanic bottom waters were anoxic. We apply major, trace and rare earth element geochemistry to the glaciomarine deposits in order to trace (i) the degree of chemical weathering recorded in the glaciomarine deposits, and (ii) the redox conditions of marine bottom waters at the time of sediment deposition.

2. GEOLOGICAL SETTING AND AGE

The Yangtze Platform extends from the east coast of South China more than 1000 km to the west, with a north-south extent between 250 and 600 km (Figure 1). South China consists of two terranes, the Yangtze craton, which represents the Mesoproterozoic basement of the Yangtze Platform, and the Cathaysia block. The Cathaysia block and the Yangtze craton collided at ca. 1 Ga to form the South China block *[Guo et al., 1980; Li et al., 1995]*.

The Neoproterozoic recorded the progressive fragmentation of the Rodinia supercontinent *[Hoffman, 1991]*. South China had been sandwiched between Australia and western Laurentia and had have a paleogeographic affinity to India, as shown by the similarities between the Neoproterozoic successions of South China, the Adelaide Fold Belt in southeastern Australia *[Li and Powell, 2001]* and the Lesser Himalaya in India *[Jiang et al., 2003]*. Separation of South China from both continents occurred stepwise between 700 Ma and 550 Ma *[Li et al., 1995; Rui and Piper, 1997, Hoffman, 1999; Powell and Pisarevsky, 2002]*. Rifting and related magmatism proceeded in two pulses from 830–745 Ma incorporating the southern part of the Yangtze block [present coordinates] as a rifted margin basin *[Li et al., 2003]* which eventually accommodated the glaciomarine deposits of Neoproterozoic age.

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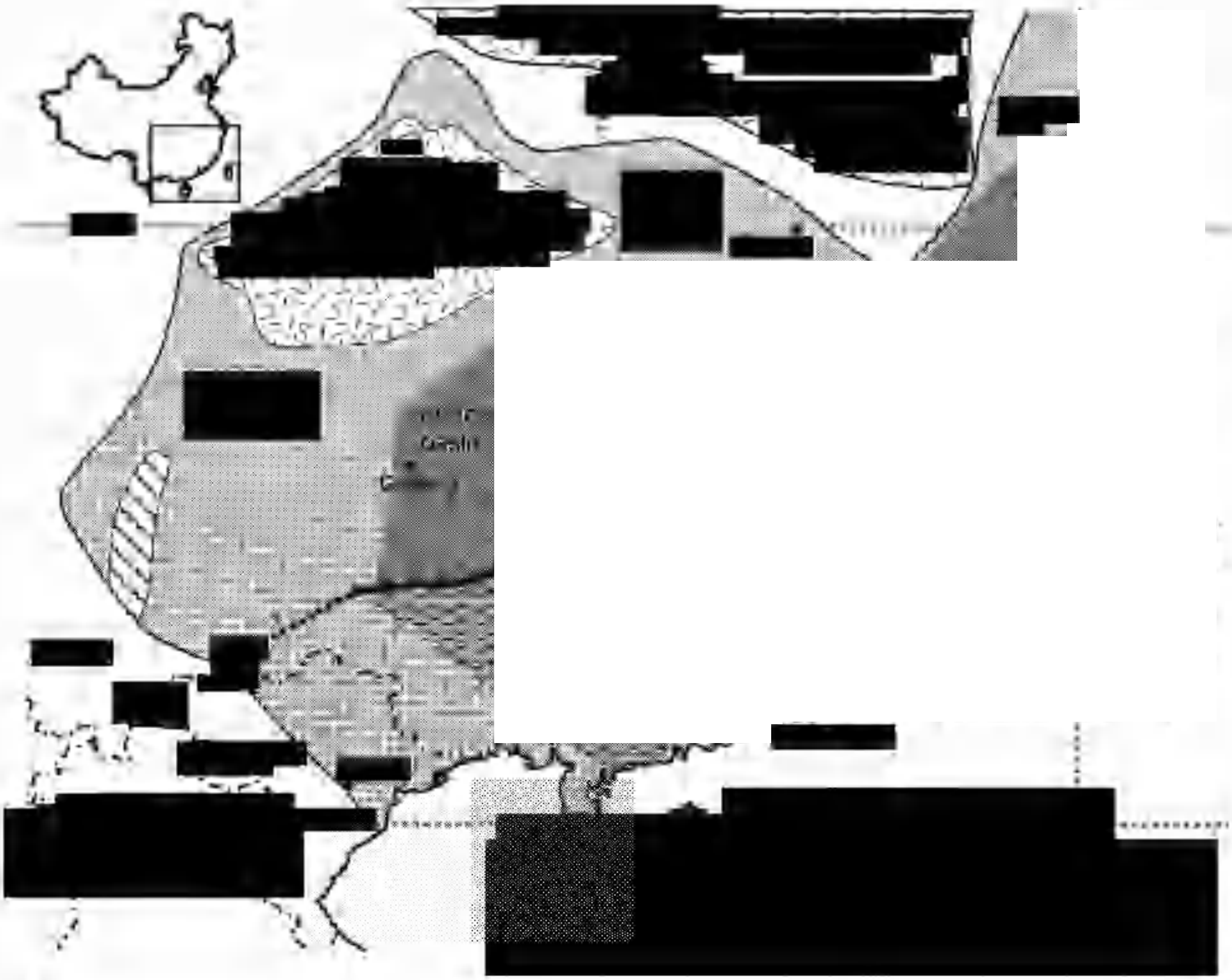

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Table 1. Geochemical data of the Nanhuan-Sinian glacial succession (minimum, maximum and average values)

UNITS	Preglacial unit			Lower diamictite unit						Intercalated unit					
LITHOLOGY	sand- and siltstones			carbonate-rich diamictites matrix			siliciclastic diamictites matrix			carbonate-rich mudstones			mudstones		
	min.	max.	Ø$_{N=14}$	min.	max.	Ø$_{N=4}$	min.	max.	Ø$_{N=29}$	min.	max.	Ø$_{N=5}$	min.	max.	Ø$_{N=16}$
SiO_2	62.67	79.55	69.83	14.10	53.52	34.84	58.73	77.15	68.20	27.26	71.74	58.62	45.04	98.61	67.70
Al_2O_3	10.26	19.19	14.94	1.28	9.81	6.31	8.22	19.12	13.58	5.76	13.42	8.84	0.54	17.02	12.81
Fe_2O_3	0.98	5.67	3.90	1.23	3.90	2.60	1.72	6.52	4.10	1.01	7.22	3.43	0.12	40.52	6.87
MgO	0.35	2.12	1.65	0.46	3.26	1.89	0.87	4.52	2.02	0.99	4.00	2.26	0.01	4.88	2.12
MnO	0.02	0.15	0.07	0.52	2.50	1.36	0.02	1.91	0.20	0.10	1.55	0.57	0.01	0.28	0.11
CaO	0.05	0.56	0.25	14.43	46.25	27.28	0.05	5.32	1.74	5.27	32.70	11.56	0.02	1.05	0.40
Na_2O	0.02	4.08	1.16	0.06	2.11	1.12	0.03	6.21	1.37	0.01	3.66	0.98	0.01	3.33	0.60
K_2O	1.53	6.75	4.19	0.27	2.02	1.11	1.67	6.21	3.68	0.84	3.37	1.74	0.29	7.63	3.63
TiO_2	0.33	0.71	0.55	0.06	0.39	0.26	0.34	1.06	0.59	0.22	0.58	0.34	0.02	0.87	0.60
P_2O_5	0.01	0.18	0.06	0.04	0.45	0.23	0.03	0.25	0.10	0.03	0.16	0.09	0.01	0.73	0.15
LOI	1.40	3.90	3.14	12.60	35.60	22.93	3.10	8.70	4.56	5.00	27.40	11.34	0.10	8.60	4.54
SUM	99.61	99.99	99.87	99.78	100.11	99.95	99.73	100.31	99.92	99.47	100.02	99.82	99.55	100.20	99.89
CIA*	57	78	69	-	-	-	50	73	62	-	-	-	57	83	71
S	0.01	0.44	0.14	0.22	0.65	0.43	0.01	3.64	0.36	0.01	0.17	0.06	0.01	1.80	0.37
C	0.00	7.64	0.62	3.23	10.06	6.15	0.04	1.63	0.42	1.05	7.36	3.01	0.01	3.55	0.73
TIC	0.00	7.51	0.55	3.15	10.08	6.12	0.00	1.29	0.39	1.02	7.41	2.99	0.00	1.42	0.13
TOC§	0.00	0.52	0.07	0.00	0.11	0.05	0.00	0.33	0.06	0.00	0.12	0.04	0.01	3.54	0.60
S/TOC	0.21	12.75	3.45	3.96	7.98	5.97	0.05	72.77	13.71	0.51	0.64	0.58	0.01	15.72	3.18

*CIA=$(Al_2O_3/Al_2O_3+CaO_{silicate}+Na_2O+K_2O)*100$ calculated from molecular ratios.
§TOC=C-TIC.

3. OVERVIEW OF THE LITHOSTRATIGRAPHY

The Nanhuan-Sinian glaciomarine succession is exposed in a number of sections on the Yangtze Platform (Figure 1). The degree of deformation and the metamorphic grade of the rocks in the study area are very low. Eleven sections were measured, most of them are located in Hunan province. The glaciomarine succession overlies marine siliclastic rocks. The glacial facies varies from shallow marine in the North to deeper marine in the South (Figure 1). The glacial rocks are generally tripartite comprising a lower glacial unit of diamictites conformably overlain by an intercalated unit of bright or dark fine-grained clastic sediments *[Lu et al., 1985]*. The upper glacial unit disconformably overlies the intercalated unit above an erosional base. The end of the glacial period is marked by deposition of postglacial carbonates and black shales. The thickness of the formations generally thins to the north. Their spatial arrangement produces an onlap geometry on the Yangtze block.

Preglacial Unit (Xieshuihe Formation, Wuqiangxi Formation, Zitang Formation)

The preglacial unit consists of sand- and siltstones, which sometimes show a fine lamination and current cross bedding. The lower part of the unit was probably deposited in a fluvial environment. Graded bedding becomes more frequent toward the top, and marine deposition is inferred *[Lu and Qu, 1987]*. More detailed information is given by *Zhang [1994]*.

Lower Diamictite (Dongshanfeng Formation, Jiangkou Formation, Tie-si-ao Formation)

The lower diamictite features marked variations in thickness and sedimentology. In central Hunan, the unit reaches 100 m in thickness, and consists of sand- and siltstones with conglomeratic layers. Cross bedding is frequent and in some parts coarse laminae show graded bedding. Some layers are rich

Table 1. (continued).

UNITS	Upper diamictite unit						Postglacial unit					
LITHOLOGY	carbonate-rich diamictites matrix			diamictites matrix			lime- and dolostones			mudstones		
	min.	max.	$Ø_{N=7}$	min.	max.	$Ø_{N=67}$	min.	max.	$Ø_{N=21}$	min.	max.	$Ø_{N=11}$
SiO_2	52.49	76.88	61.81	60.87	81.65	66.63	3.69	40.36	13.47	61.22	81.25	68.92
Al_2O_3	7.06	14.07	11.85	8.83	18.62	13.71	0.68	8.32	1.99	7.20	16.93	13.24
Fe_2O_3	0.95	8.65	3.78	1.84	8.16	5.42	0.42	8.09	2.03	0.66	7.61	3.62
MgO	0.76	6.16	3.29	0.56	7.36	2.38	8.86	20.47	16.34	0.83	2.64	1.48
MnO	0.12	0.38	0.19	0.01	0.29	0.13	0.02	1.46	0.40	0.01	0.10	0.05
CaO	4.52	7.25	5.35	0.01	7.11	1.52	12.04	31.20	25.99	0.04	0.46	0.18
Na_2O	0.04	3.86	0.97	0.01	4.95	0.99	0.01	0.58	0.11	0.02	0.87	0.15
K_2O	0.27	6.23	3.81	0.55	6.02	3.96	0.10	2.82	0.69	2.07	8.21	4.96
TiO_2	0.32	0.88	0.58	0.38	1.85	0.65	0.04	1.01	0.13	0.58	1.84	0.87
P_2O_5	0.05	0.41	0.17	0.04	0.21	0.12	0.02	0.28	0.12	0.02	0.13	0.06
LOI	4.00	14.00	7.91	1.30	8.70	4.71	17.80	45.20	38.60	2.70	21.50	6.22
SUM	99.59	100.28	99.91	99.67	100.23	99.92	99.74	100.06	99.94	99.67	100.05	99.92
CIA*	49	54	51	51	85	65	-	-	-	60	81	70
S	0.02	0.54	0.19	0.01	3.64	0.28	0.01	0.56	0.14	0.01	3.28	1.03
C	0.81	2.93	1.55	0.01	1.55	0.55	4.23	12.11	10.42	0.03	2.90	1.22
TIC	0.08	3.01	1.33	0.00	1.39	0.34	4.02	12.17	9.91	0.00	0.03	0.01
TOC§	0.00	0.73	0.24	0.01	0.38	0.22	0.00	1.35	0.52	0.03	2.90	1.21
S/TOC	0.19	11.74	3.52	0.05	82.69	4.48	0.01	1.11	0.35	0.13	37.59	7.21

*CIA=(Al_2O_3/Al_2O_3+$CaO_{silicate}$+Na_2O+K_2O)*100 calculated from molecular ratios.
§TOC=C-TIC.

in carbonate. The unit thins northward until it tapers out north of Hunan province. In northern Hunan, where the thickness is only 3.0 m, the lower diamictite consists of clasts up to 5 mm in diameter in a dark silty to muddy matrix particularly rich in carbonate. The clast content is relatively low, e.g., clasts form 15 to 25 volume percent of the rocks. East of Hunan in Anhui province, equivalents of the lower diamictite are well stratified and occasionally graded. Distinct layers contain cm-sized dropstones.

Intercalated Fine-grained Sediments (Datanpo Formation, Xianmeng Formation, Lantian Formation)

This unit, sandwiched between the two diamictite units, generally consists of interbedded laminated mudstones, dark shales and siltstones. The latter may contain small current ripples. Carbonaceous layers occur within this unit in some sections. The appearance of stratified siltstones, shales and carbonate beds together with lenses of thin beds of argillaceous manganiferous dolostones led *Lu et al., [1985]* to the interpretation, that this unit reflects an interglacial period.

Upper Diamictite (Nantuo Formation, Hongjiang Formation, Leigongwu Formation)

The upper glacial unit is dominated by massive matrix-supported diamictites. Rarely, a fine lamination can be observed. The upper diamictite unit is generally clast-rich with a silty to sandy, sometimes muddy dark gray matrix. Locally, boulders up to 1 m across are included at the top of the unit. Clasts are sedimentary and metasedimentary in origin, while magmatic pebbles are very rare. Several clasts exhibit striated surfaces, a feature typical of glacial abrasion. Dropstones also provide evidence of glacial and additionally marine origin of the deposits. The upper diamictite unit has an average thickness of 90 m in northern Hunan province and reaches a thickness of approximately 1200 m in central Hunan province.

Postglacial Deposits (Doushantuo Formation, Jinjiadong Formation)

The upper diamictite unit is overlain by limestones in some sections, followed by black shales and dolomites. In some

Table 1. (continued).

UNITS LITHOLOGY	Carbonate-poor clastics of the Sinian glacial succession			Total Sinian glacial succession		
	min.	max.	$Ø_{N=137}$	min.	max.	$Ø_{N=174}$
SiO_2	45.04	98.61	67.69	3.69	98.61	59.89
Al_2O_3	0.54	19.19	14.00	0.54	19.19	12.14
Fe_2O_3	0.12	40.52	4.73	0.12	40.52	4.28
MgO	0.01	7.36	2.09	0.01	20.47	3.86
MnO	0.01	1.91	0.12	0.01	2.50	0.20
CaO	0.01	7.11	1.08	0.01	46.25	5.23
Na_2O	0.01	6.21	1.00	0.01	6.21	0.91
K_2O	0.29	8.21	4.02	0.10	8.21	3.48
TiO_2	0.02	1.85	0.66	0.02	1.85	0.57
P_2O_5	0.01	0.73	0.10	0.01	0.73	0.11
LOI	0.10	21.50	4.39	0.10	45.20	9.29
SUM	99.55	100.31	99.92	99.47	100.31	99.92
CIA*	51	85	66	49	85	66
S	0.01	3.64	0.35	0.01	3.64	0.31
C	0.01	7.64	0.47	0.00	12.11	1.97
TIC	0.00	7.51	0.27	0.00	12.17	1.73
TOC§	0.00	3.54	0.21	0.00	3.54	0.24
S/TOC	0.01	82.69	6.58	0.01	82.69	5.50

*CIA=(Al_2O_3/Al_2O_3+$CaO_{silicate}$+Na_2O+K_2O)*100 calculated from molecular ratios.
§TOC=C-TIC.

outcrops the carbonates are strongly silicified. The carbonates overlie the upper diamictites as cap carbonates with conformable transitions. In some sections postglacial deposition starts conformably with dark shales and siltstones, and cap carbonates are absent. Full descriptions of different parts of the succession on the Yangtze Platform are given by *Lu et al. [1985]*, and *Lu and Qu [1987]*, *Lui [1990]*, *Zhang [1994]* and *Zhang [1995]*.

Cap carbonates abruptly overly Neoproterozoic glacial units on several continents and are considered regional to global stratigraphic marker horizons *[Kennedy et al., 1998; Hoffman et al., 1998; Prave, 1999]*. They are usually dolomitic and may include stromatolites, microbial laminites, different types of current ripples, aragonite crystal fans of variable sizes, and tube like structures potentially associated with methane release *[Kennedy et al., 2001a,b; Hoffman and Schrag, 2002]*. None of these features were observed in the respective rocks on the Yangtze Platform. However, in view of the conformable contact between the upper diamictite and the basal carbonates of the Doushantuo Formation, these layers, where present, occupy the same lithostratigraphic position as those on other continents. Consequently, we consider them to represent cap carbonates.

4. ANALYTICAL METHODS

4.1. Sampling

The 174 analyzed rocks include samples of diamictite matrix, siliciclastic and carbonate rocks. All samples were collected from different sections in Anhui, Hubei, Hunan and Guizhou provinces, South China. Fresh rock samples (ca. 500 g), free of weathering rinds and visible clasts (>0.25mm) were chipped and pulverized in an agate-grinding vessel.

4.2. Analytical Procedure

Samples were analyzed for major and trace elements. Major elements were determined by ICP-ES after a $LiBO_2$ fusion, and trace elements determined by ICP-MS at ACME Analytical labs, Vancouver, Canada.

Total carbon (TC) and total inorganic carbon (TIC) contents were measured with a 5500 CS-Mat in Muenster, Germany. On this basis, the amount of CaO in silicicate minerals (CaO*) was calculated.

5. GEOCHEMISTRY

The composition of clastic sediments is affected by source area lithologies, weathering, transport and sorting, redox environment and diagenesis *[Johnsson, 1993]*. The analyzed suite contains glacial deposits ideally considered to have undergone minimal chemical weathering, and no sorting. The focus of this study is the identification of weathering and paleoredox conditions as a function of Neoproterozoic climate change. Therefore we use major, trace and rare earth elements (Tab. 1) to evaluate temporal and spatial changes in weathering conditions and the chemical environment of deposition of the Neoproterozoic glaciomarine rocks from the Yangtze Platform.

5.1. Geochemical Rock Composition

The basement of the Yangtze Craton representing the source lithologies for the glaciogenic rocks is composed mainly of granitic gneisses, amphibolites and metasediments (schists and marbles), and minor ophiolite exposures *[Lu et al., 1985; Chen and Jahn 1998, Gu et al., 2002]* and thus has on average a felsic composition.

Th/Sc vs. Zr/Sc The Th/Sc ratio is a reliable provenance indicator, as both elements are immobile under surface conditions and therefore preserve the characteristics of their source *[Taylor and McLennan, 1985]*. Compatible Sc traces mafic source components, whereas incompatible Th is enriched in felsic rocks. Average upper continental crust has a Th/Sc ratio of 0.79 *[McLennan, 2001]*. The carbonate-poor clastic sediments of Nanhuan-Sinian glacial succession have average Th/Sc values of 0.94 (min: 0.41, max: 3.03; Figure 2, Tab. 1), very similar to the composition of the upper conti-

Table 1. (continued).

UNITS	Preglacial unit			Lower diamictite unit						Intercalated unit					
LITHOLOGY	sand- and siltstones			carbonate-rich diamictites matrix			siliciclastic diamictites matrix			carbonate-rich mudstones			mudstones		
	min.	max.	$Ø_{N=14}$	min.	max.	$Ø_{N=4}$	min.	max.	$Ø_{N=29}$	min.	max.	$Ø_{N=5}$	min.	max.	$Ø_{N=16}$
Ba	432	3592	1286	62	469	272	397	3770	1062	302	1380	603	131	5449	1195
Cd	0.1	0.5	0.2	0.0	0.0	< .1	0.1	1.7	0.4	0.1	1.3	0.5	0.2	0.6	0.4
Co	1.4	14.3	5.7	1.2	8.0	4.8	1.0	30.9	9.9	2.8	14.3	6.4	1.7	34.2	13.5
Cr	6.8	95.8	25.4	13.7	47.9	31.9	0.0	150.5	35.5	6.8	27.4	18.2	13.7	253.2	69.3
Cs	1.4	10.7	4.9	0.3	2.9	1.5	1.8	11.0	5.1	1.1	4.9	2.5	0.8	9.5	5.3
Cu	0.6	29.2	10.0	0.9	8.9	5.5	1.7	37.4	14.5	3.0	23.3	9.9	2.0	57.7	23.7
Hf	4.5	10.0	6.8	0.8	4.5	2.9	3.0	8.6	6.2	2.0	5.9	3.2	1.3	7.7	5.4
Mo	0.3	2.0	0.9	0.2	1.9	1.0	0.1	9.0	1.3	0.2	1.4	0.7	0.1	14.3	2.2
Nb	7.8	17.1	11.6	1.1	9.2	5.6	4.7	27.6	12.5	3.3	9.1	5.9	4.6	22.4	14.0
Ni	2	27	8	1	11	5	3	85	19	3	23	9	1	85	27
Pb	0.9	37.0	9.1	1.6	33.4	17.7	1.8	112.8	17.7	1.9	57.3	14.2	3.0	104.0	30.8
Rb	47	202	117	9	59	34	51	155	104	27	113	55	14	181	112
Sc	4.0	16.0	11.2	1.0	8.0	4.8	4.0	18.0	10.2	3.0	10.0	6.0	5.0	18.0	12.8
Sn	1.0	3.0	2.0	1.0	2.0	1.5	1.0	5.0	2.6	1.0	2.0	1.3	1.0	4.0	2.7
Sr	8	150	47	218	1033	587	13	138	58	47	609	291	10	117	36
Ta	0.50	1.50	0.91	0.10	0.50	0.33	0.40	2.20	0.94	0.30	0.70	0.44	0.30	1.70	1.11
Th	5.2	13.7	9.6	0.5	5.7	3.6	4.2	12.5	8.9	2.3	8.8	4.8	4.1	20.0	12.0
U	1.2	2.2	1.7	0.8	1.8	1.4	0.7	3.5	1.7	0.5	1.3	0.9	1.0	4.1	2.3
V	8	65	41	19	34	29	24	120	60	21	60	36	27	206	81
Y	18.2	45.4	32.5	8.4	30.2	21.2	18.3	53.5	32.3	15.5	28.6	21.9	10.0	171.0	41.9
Zn	5	72	34	4	26	17	5	294	42	19	272	80	15	98	44
Zr	154	332	233	25	146	97	114	287	214	68	212	111	10	276	180

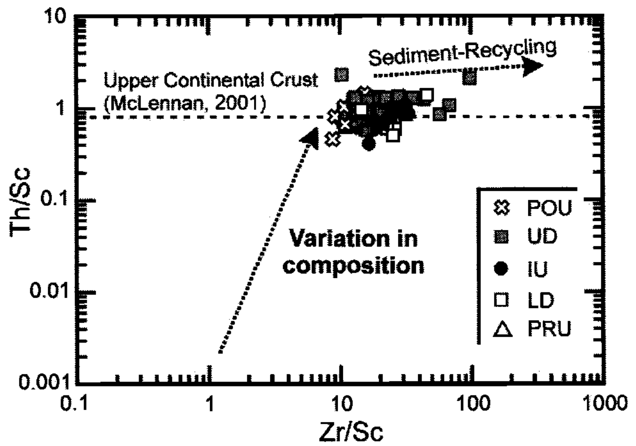

Figure 2. Plot of Zr/Sc vs. Th/Sc ratios of the analyzed values of the Nanhuan-Sinian glacial succession on the Yangtze Platform *[slightly modified from McLennan et al., [1993]*. Preglacial unit (PRU); lower diamictite unit (LD); intercalated unit (IU), upper diamictite unit (UD); postglacial unit (POU); Upper Continental Crust composition (UCC) of *McLennan [2001]*.

nental crust. The Zr/Sc ratio, in turn, commonly indicates the degree of sediment recycling, leading to the enrichment of the stable heavy mineral zircon, and thus Zr, in the deposits *[McLennan et al., 1993]*. Applied to the Nanhuan-Sinian glacial suite, average values of 19.96 (min: 6.68, max: 98.10; Figure 2, Tab. 1) demonstrate the minor effect of sediment recycling in the bigger part of the succession *[cf. McLennan et al., 1990]*.

The chondrite-normalized REE patterns for the siliciclastic rock samples within the Nanhuan-Sinian glacial succession (not shown) are similar to those of the upper continental crust *[UCC, McLennan, 2001]*.

5.2. Weathering and Diagenesis

CIA and ACNK. In this study, major and trace element concentrations are applied to unravel changing climatic conditions connected to the Neoproterozoic glaciation event. Of particular interest are elements, which serve as proxy signals for changing weathering conditions. Considering Al_2O_3, CaO* (CaO in silicates), Na_2O, and K_2O, the Chemical Index of

Table 1. (continued).

UNITS	Upper diamictite unit						Postglacial unit					
LITHOLOGY	carbonate-rich diamictites matrix			diamictites matrix			lime- and dolostones			mudstones		
	min.	max.	$Ø_{N=7}$	min.	max.	$Ø_{N=67}$	min.	max.	$Ø_{N=21}$	min.	max.	$Ø_{N=11}$
Ba	172	4714	1644	166	3404	1157	46	6528	663	625	6768	2169
Cd	0.1	0.2	0.2	0.1	0.5	0.2	0.1	0.8	0.3	0.1	0.6	0.4
Co	2.2	17.8	10.0	2.1	37.2	11.6	0.7	20.5	3.8	0.6	29.1	13.4
Cr	6.8	390.0	86.0	0.0	109.5	56.9	6.8	54.7	15.0	20.5	150.5	64.7
Cs	0.5	9.9	4.9	1.1	10.8	5.8	0.3	2.2	0.9	3.4	8.1	5.7
Cu	4.5	28.4	16.4	3.2	125.0	20.2	1.7	30.9	7.4	3.9	50.0	29.5
Hf	4.0	6.9	5.4	4.0	20.1	6.0	0.5	3.2	1.3	2.7	7.6	4.6
Mo	0.1	0.4	0.2	0.1	3.4	0.8	0.1	11.3	0.8	0.2	17.0	7.6
Nb	4.7	14.1	10.7	6.7	23.4	12.8	0.5	10.8	2.0	8.3	25.4	14.6
Ni	4	171	42	5	108	28	1	38	6	0	132	39
Pb	2.9	18.9	8.5	0.6	49.3	16.7	0.7	121.0	10.9	3.2	48.0	23.4
Rb	11	138	94	25	170	114	3	58	16	52	158	113
Sc	3.0	18.0	11.3	3.0	17.0	12.0	1.0	12.0	2.6	8.0	30.0	15.2
Sn	1.0	5.0	2.5	1.0	9.0	2.7	1.0	5.0	2.2	1.0	7.0	3.9
Sr	106	267	167	13	195	72	69	1164	363	10	47	24
Ta	0.40	1.30	0.87	0.60	1.80	1.02	0.10	0.70	0.28	0.70	1.80	1.20
Th	3.2	41.5	13.1	6.1	18.2	11.3	0.4	5.9	1.5	5.3	15.0	11.3
U	0.7	7.0	2.1	0.8	11.5	2.1	0.1	2.7	0.8	1.2	12.0	4.4
V	23	115	66	21	122	72	5	80	24	94	335	208
Y	17.7	44.2	28.0	18.3	47.9	35.0	2.4	24.2	9.5	15.8	104.5	32.1
Zn	5	155	47	3	183	52	2	38	11	1	79	26
Zr	153	219	184	149	752	201	8	114	22	88	270	157

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Table 1. (continued).

UNITS / LITHOLOGY	Carbonate-poor clastics of the Sinian glacial succession			Total Sinian glacial succession		
	min.	max.	$\varnothing_{N=137}$	min.	max.	$\varnothing_{N=174}$
Ba	131	6768	1160	46	6768	1083
Cd	0.1	1.7	0.3	0.1	1.7	0.3
Co	0.6	37.2	10.8	0.6	37.2	9.7
Cr	0.0	253.2	45.0	0.0	390.0	43.1
Cs	0.8	11.0	5.6	0.3	11.0	4.9
Cu	2.0	125.0	18.8	0.6	125.0	16.8
Hf	1.3	20.1	6.1	0.5	20.1	5.7
Mo	0.1	17.0	1.5	0.1	17.0	1.3
Nb	4.6	27.6	12.9	0.5	27.6	11.4
Ni	0	132	23	0	171	21
Pb	0.6	112.8	16.6	0.6	121.0	15.5
Rb	14	202	114	3	202	98
Sc	3.0	30.0	11.9	1.0	30.0	10.5
Sn	1.0	9.0	2.8	1.0	9.0	2.7
Sr	10	195	56	8	1164	116
Ta	0.30	2.20	1.02	0.10	2.20	0.95
Th	4.1	20.0	10.4	0.4	41.5	9.1
U	0.7	12.0	2.1	0.1	12.0	1.9
V	21	335	77	5	335	69
Y	10.0	171.0	33.6	2.4	171.0	29.8
Zn	1	294	46	1	294	42
Zr	10	752	206	8	752	178

sized material in the former was connected to mechanical degradation, whereas in the latter this was due to chemical weathering.

CIA values of the analyzed samples vary between 49 and 85 (Figure 3). Samples of the preglacial, postglacial and the intercalated fine-grained unit have mainly high CIA values between 65–85, whereas values of the two diamictite units span the whole spectrum, containing low values of 49 as well as high values of 85. The glaciogenic rocks are derived from older sedimentary materials, thus the CIA is influenced by the degree of weathering of the source rocks. Incorporation of older sedimentary material is also indicated by the Zr/Sc ratios, pointing to moderate sediment recycling for a few diamictite matrix samples (Figure 2).

The triangular A-CN-K diagram (Figure 3) allows the differentiation of compositional changes associated with chemical weathering and/or source rock composition *[Fedo et al., 1997]*. The arrow in figure 3 marks the predicted average weathering trend of a rock sample with UCC composition. Kaolinite is formed predominantly during weathering of plagioclase–rich source rocks because plagioclase is destroyed more rapidly than K-feldspar. Weathering trends are parallel to the A-CN boundary, which makes it possible to use the trends displayed by sedimentary rock samples to project backward to the original composition of the source rocks. Significant compositional changes as a result of transport and sorting are not expected for the ice-transported diamictites.

The spread of data in our suite of samples particularly in the pre- and postglacial units and in the intercalated clastics is probably due to potassium enrichment as the result of a minor diagenetic or metasomatic overprint. However, variations in source area composition and resulting weathering resistance can also influence the CIA. Therefore we compare the CIA as a climate proxy with the Th/Sc ratio as a proxy for source composition. As an example, we examine the temporal evolution recorded in the Yangjiaping section (Figure 4).

Stratigraphic Variation of the CIA and Th/Sc in the Yangjiaping Section

CIA values (Figure 4) in the preglacial unit in the Yangjiaping section are moderate (62–69). The lower diamictite unit has low CIA values (57–68). In the fine-grained intercalated unit the chemical weathering increases (CIA between 70 and 74). At the base of the upper diamictite the CIA is still high with values of 67–73, but decreases rapidly to values of around 55. A single CIA value of 63 of the postglacial unit in this section marks the slight increase of the CIA within this unit. It is representative of an increase of the CIA also in samples of the postglacial shales and siltstones in other sections (Tab. 1).

The CIA values indicate a greater degree of chemical weathering for the pre- and postglacial unit and a lesser degree of chemical weathering for both diamictites. CIA values of the intercalated unit also reveal stronger chemical weathering, which supports the interpretation as an interglacial period with warmer and humid conditions *[Lu and Qu, 1987]*. The high CIA values at the base of the upper diamictite could be indicative of the incorporation of reworked material of the underlying unit *[e.g. Young and Nesbitt, 1999]*, because the Th/Sc ratios show that no change in source occurred. Recycling of older sedimentary material would be in agreement with the unconformable contact between the intercalated unit and the upper diamictite unit. Comparable decrease of CIA values upsection is visible in other localities including Tianping, Liuchapo and Jiangkou section.

K/Cs McLennan et al. [1990] used the ratio of Cs and K as an indicator for climate conditions, because both elements are characteristically adsorbed on clay minerals during weathering, Cs as the larger ion is preferently adsorbed over K. Thus, the K/Cs ratio should decrease with increasing chemical weathering.

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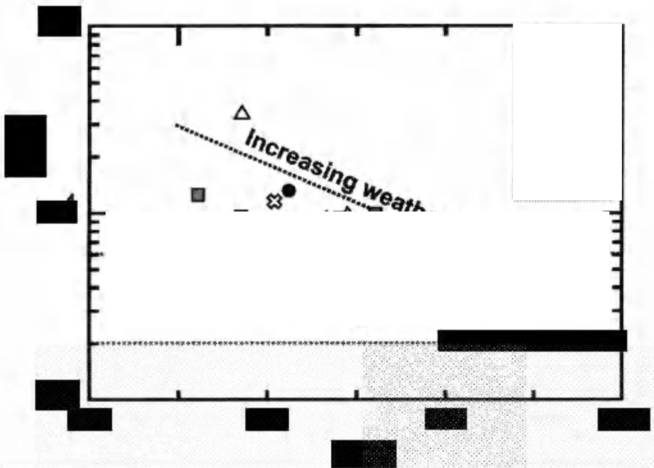

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Table 1. (continued).

UNITS / LITHOLOGY	Carbonate-poor clastics of the Nanhuan-Sinian glacial succession			Total Nanhuan-Sinian glacial succession		
	min.	max.	$Ø_{N=137}$	min.	max.	$Ø_{N=174}$
La	12.1	112.7	39.8	2.8	142.1	35.1
Ce	8.6	249.7	72.7	5.6	249.7	64.0
Pr	2.5	26.4	8.5	0.5	26.4	7.5
Nd	9.5	112.1	33.5	2.2	112.1	29.5
Sm	2.4	24.7	6.5	0.4	24.7	5.8
Eu	0.38	4.27	1.25	0.09	4.27	1.15
Gd	1.80	26.75	5.64	0.32	26.75	5.06
Tb	0.28	4.86	0.92	0.07	4.86	0.82
Dy	2.16	29.01	5.42	0.33	29.01	4.81
Ho	0.54	5.59	1.12	0.10	5.59	0.99
Er	1.74	14.07	3.36	0.21	14.07	2.95
Tm	0.24	1.83	0.50	0.05	1.83	0.45
Yb	1.63	9.69	3.36	0.10	9.69	2.93
Lu	0.28	1.28	0.51	0.03	1.28	0.45
Ce_{anom}	-0.71	0.05	-0.09	-0.71	0.26	-0.09
K/Cs	2756	33858	6331	553	33858	6534
Th/Sc	0.41	3.03	0.94	0.30	3.03	0.91
U/Th	0.07	1.88	0.21	0.07	3.00	0.28
Zr/Sc	6.68	98.10	19.96	4.12	98.10	18.98

concentration and a low carbon concentration might indicate postdiagenetic sulfidization resulting in a secondary sulfur enrichment *[Leventhal, 1995]*. Low S/TOC < 0.36 ratios might be due to freshwater influence with low sulphate concentrations *[Wignall, 1994]*, which limits the activity of sulphate reducing bacteria.

The S content of our samples range between 0 and 3.64%, with most of them below 0.6% sulfur. TOC varies between 0 and 3.54%. The diamictite units show a maximum of 0.52%. S/TOC varies between 0.01 and 82.69, partly showing strong sulfur enrichment.

The majority of our diamictite samples have low organic carbon and low pyrite sulfur contents. Thus an unequivocal distinction between anoxic and oxic conditions is difficult. However, we interpret the low contents as being more suggestive of oxic bottom water conditions. The signatures of preglacial, interglacial and in particular postglacial sediments are generally consistent with normal marine (oxygenated bottom water) conditions.

A number of samples from the glacial and the non-glacial units show high sulfur contents at very low organic carbon contents, resulting in unusually high S/TOC ratios. In consideration of the complete suite of samples this is most likely interpreted as a sign of secondary sulfide deposition during later diagenesis.

U/Th ratio. We also used the U/Th ratio to evaluate the environmental conditions during deposition according to *Jones and Manning [1994]* and *Wignall and Twitchett [2002]*. The stratigraphic development of these parameters together with the redox-sensitive elements Mo and Cd is displayed for the Yangjiaping section as an example (Figure 7; Tab.1).

We already used U and Th as climate proxies, because of their similarity in behavior, their occurrence in common rocks and rock-forming minerals as immobile trace elements and because U is easily mobilized during weathering. Furthermore, we reiterate that U is enriched under anoxic conditions *[Taylor and McLennan, 1985]*. Thus, the U/Th ratio bears evidence of the oxygenation of bottom waters during deposition. U/Th > 0.75 has been utilized as threshold for the transition into anoxic conditions *[Jones and Manning, 1994]*. In this case effects of oxygenated conditions and weathering processes cannot be separated from each other. Thus, if considered in isolation, U/Th ratios for our samples are no firm evidence for redox conditions. However, in connection with other redox-sensitive parameters they could support an indication given by other proxies.

The Nanhuan-Sinian glacial succession shows U/Th values between 0.07 and 3.0. All tillite samples except one show U/Th values < 0.75 indicating oxic seawater conditions during the glaciation. Higher values have only been measured for one tillite sample at the top of the upper diamictite, and in the black shales of the postglacial Doushantuo Formation.

Cd and Mo Cadmium is a redox-sensitive trace elements and relatively immobile in sulfidic environments. Cd favors an association with sulfur and is controlled by greenockite (CdS) precipitation. The absence of metal enrichments including Cd and Mo is firm evidence that sedimentation occurred under oxygenated bottom water conditions *[Calvert and Pedersen, 1993]*. Cadmium enrichment is independent of the accumulation rates of terrigenous detrital input *[Calvert and Pedersen, 1993]*. Cd concentrations of the analyzed rocks are often below the detection limit of 0.1 ppm and reach maximum values of 1.7 ppm. Such values do not reflect enrichment.

Mo is co-precipitated with sulfur and therefore is also enriched during anoxic conditions *[Calvert and Pedersen, 1993]*. Mo concentrations of the analyzed rocks are also generally low and mostly below the detection limit of 0.1 ppm, but reach maximum values of 17 ppm. Overall, Cd and Mo concentrations are very low and indicate oxic conditions of the Nanhuan-Sinian marine bottom waters (Fig 7; Tab.1).

Cerium Anomaly [Ce_{anom}] The Cerium anomaly (Ce_{anom}) has been used as redox indicator in several studies *[Wilde et al., 1996; Yang, et al., 1999, Feng et al., 2000, Girard and Lécuyer, 2002]* althought the application is controversial

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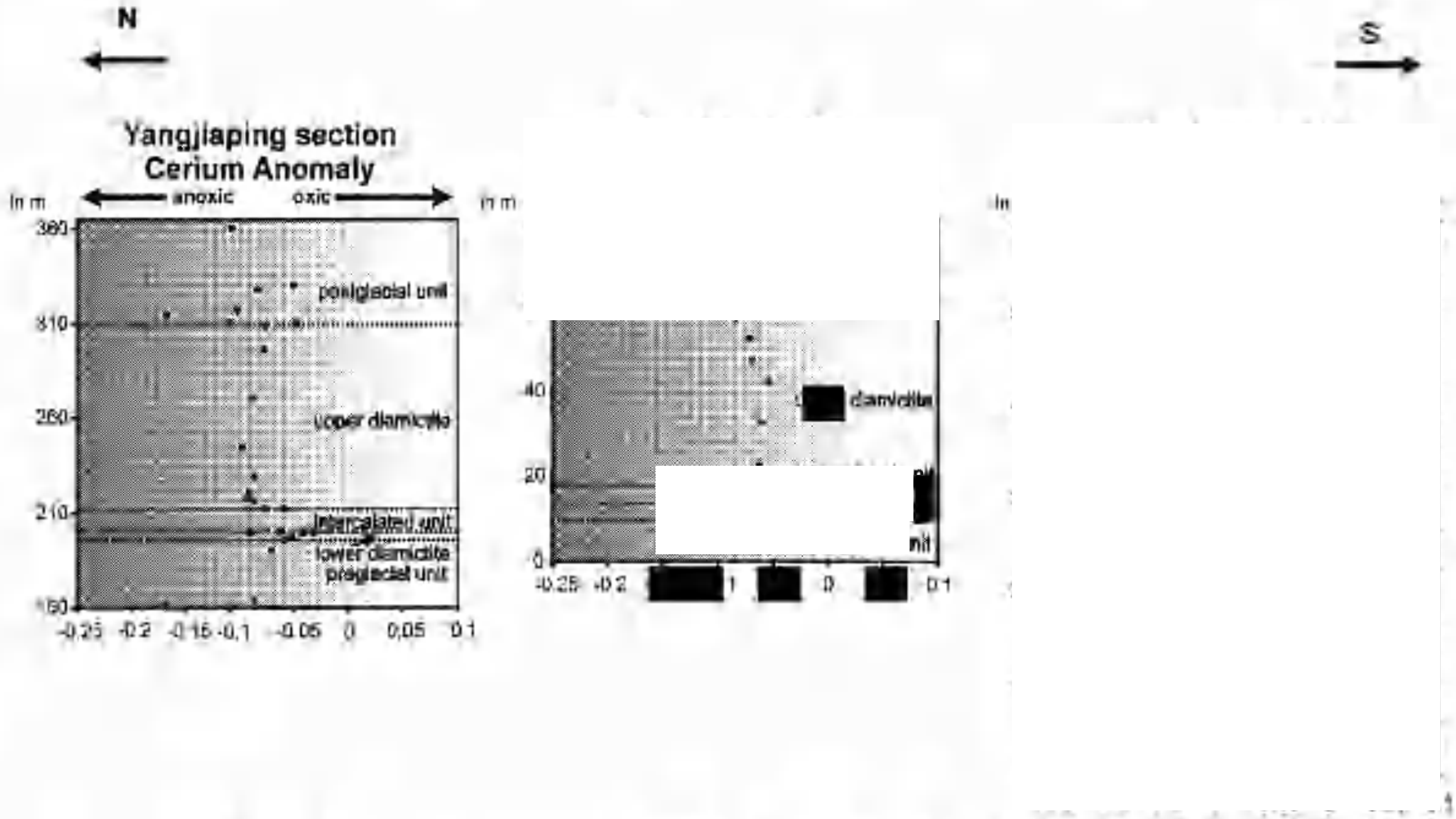

Figure 8b. Illustration of the environmental [redacted]s of the [redacted]lapin[redacted]anp[redacted], and Liuchi[redacted] sections.

of anoxic seawaters is additionally based on the presence of dropstones in banded iron formations *[Kirschvink, 1992]*.

The values of paleoredox indices S/TOC, U/Th, Cd, Mo and Ce_{anom} presented by us are in conflict with the postulated global anoxia. Most of the samples indicate deposition in shallow glaciomarine environments under oxic bottom waters (at least in shallow marine basins) during most of the Nanhuan glaciation. This suggests that the ocean-atmosphere interaction was vigorous not only at 40° latitude, the respective paleogeographic position of the Yangtze platform in Sturtian time. *Young [2001]* explains that the formation of banded iron formations in the Neoproterozoic can also occur in rift-related, hydrothermally influenced basins.

Finally, there are two possible implications of our results irrespective of whether the studied units are of Sturtian or Marinoan age: (i) The snowball Earth scenario did not occur exactly as postulated and needs to consider climate variability and long-term ocean-atmoshere interaction, or (ii) the Nanhuan glaciation evolved independently from the global glaciations considered by the snowball Earth hypothesis. The latter in particular emphasizes the need for further chronostratigraphic dating.

Acknowledgment. Our study was supported by the Deutsche Forschungsgemeinschaft (grant Ba 1011/23-1+2), and by travel funds of the National Science Foundation of China. This paper is a contribution to IGCP project 440: "Amalgamation of the Rodinian Supercontinent". The suggestions of two anonymous reviewers improved this paper and are gratefully acknowledged.

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Formerly-Aragonite Seafloor Fans from Neoproterozoic Strata, Death Valley and Southeastern Idaho, United States: Implications for "Cap Carbonate" Formation and Snowball Earth

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Seafloor-precipitated calcium carbonate fans, exceedingly rare in post-Paleoproterozoic time, make a dramatic reappearance in the post-glacial cap carbonates associated with Neoproterozoic low latitude glaciation (snowball Earth). Their presence is commonly interpreted to indicate elevated seawater alkalinity; the source of the anomalous alkalinity has been a critical, much-debated component in competing "snowball Earth" hypotheses. Two new Neoproterozoic seafloor fan occurrences have been reported recently in the Western United States (Death Valley and southeastern Idaho). Each were deposited during transgression and record negative $\delta^{13}C$ values as do all known cap carbonates, but they lack a known underlying glacial deposit and do not necessarily rest on the transgressive surface. It is possible, but not likely, that the units represent post-glacial cap carbonates without a preserved/discovered underlying glaciogenic unit. More likely, processes independent of glaciation may cause negative $\delta^{13}C$ excursions and cap carbonate-like facies and caution must be exercised when interpreting the meaning of seafloor precipitates in association with snowball Earth events.

1. INTRODUCTION

Neoproterozoic glacial intervals have received much attention, a testament to our inherent attraction to end-member phenomena ("the most extreme glaciation of all time", i.e. snowball Earth). The distribution of Neoproterozoic glacial deposits indicates glaciation so extreme that ice was present in equatorial latitudes [e.g., *Sohl et al.*, 1999; *Evans*, 2000]. Associated deposits are replete with unusual features, including iron-formation (absent from the geologic record for over a billion years)[*Kirschvink*, 1992], extreme $\delta^{13}C$ and $\delta^{34}S$ isotopic perturbations [e.g., *Kaufman et al.*, 1997; *Hoffman et al.*, 1998b; *Kennedy et al.*, 1998; *Kennedy et al.*, 2001a; *Kennedy et al.*, 2001b; *Hurtgen et al.*, 2002], and in the case of the post-glacial carbonates that cap the glacial units, unusual carbonate textures [e.g., *Kennedy*, 1996; *Kennedy et al.*, 1998; *James et al.*, 2001; *Hoffman and Schrag*, 2002; *Sumner*, 2002; *Corsetti and Kaufman*, 2003]. The effect on the course of evolution has been predicted as extreme, although the data are less supportive [*Corsetti et al.*, 2003; *Grey et al.*, 2003]. Regardless, it has not escaped attention that the explosive diversification of metazoa did not occur until after the last snowball glaciation [e.g., *Narbonne and Gehling*, 2003].

The glacial aftermath has been the focus of most recent snowball Earth studies; the cap carbonates that form on the transgressive surface during post-glacial sealevel rise are the primary archive of textural, mineralogical, and isotopic data with which to interpret snowball Earth processes. As stated in Hoffman and Schrag (2002), carbonate petrologists have had a veritable field day describing and interpreting the unusual carbonate textures found in the cap carbonates. Interesting

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around the world. Notable occurrences include the Maieberg Formation, Otavi Group, Northern Namibia [*Hoffman et al.*, 1998a; *Hoffman and Schrag*, 2002] (fig.1a, b), the Bambui Group, Brazil [*Sumner*, 2002] (fig. 1c), and the Hayhook Formation, Northwestern Canada [*James et al.*, 2001; *Hoffman and Schrag*, 2002]. In many cases, they occur near the shelf-slope break [*Hoffman and Schrag*, 2002].

1.1.1. Pseudomorph fans as an anachronistic facies. The Neoproterozoic occurrence of the pseudomorph fans is considered anachronistic [in the sense of *Sepkoski et al.*, 1991]. They are ubiquitous on Neoarchean carbonate platforms, become more localized on Paleoproterozoic platforms, and are exceedingly rare throughout the rest of geologic time [*Sumner and Grotzinger*, 1996; *Sumner and Grotzinger*, 2000; *Sumner*, 2002]. Their apparent environmental restriction is coincident with the oxygenation of the atmosphere, the emergence of widespread continental shelves associated with the Archean-Proterozoic transition, and a shift from micrite-poor to micrite-rich facies [*Sumner and Grotzinger*, 1996; *Sumner and Grotzinger*, 2000; *Sumner*, 2002]. Sumner (2002) suggests that carbonate inhibitors such as Fe^{2+} and Mn^{2+}, which were more widespread prior to the oxygenation of the atmosphere, would suppress micrite formation in the water column and foster the growth of seafloor precipitates. Thus, elevated alkalinity is only one component of seafloor fan formation: the presence of micrite inhibitors and/or low sediment fallout may also be necessary [*Sumner*, 2002]. Seafloor precipitated fans make a widespread reappearance in the cap carbonates during Neoproterozoic time and a more limited resurgence in Late Permian [*Grotzinger and Knoll*, 1995] and Early Triassic time associated with the end-Permian extinction event and the protracted biotic recovery from the extinction event [*Woods et al.*, 1999]. Interestingly, oceanic anoxia is suggested for both resurgent intervals [*Wignall and Hallam*, 1992; *Grotzinger and Knoll*, 1995; *Hallam and Wignall*, 1997; *Isozaki*, 1997]. The anachronistic nature of seafloor fans would suggest anomalous oceanic chemistry existed during their reappearance in the geologic record.

1.2. Seafloor Fans, Alkalinity, and Competing Hypotheses

The presence of the anachronistic seafloor fans indicates unusually elevated alkalinity in the post-glacial oceans and perhaps the presence of carbonate inhibitors such as Fe^{2+} and Mn^{2+}. The source of elevated alkalinity is central to the competing hypothesis regarding the aftermath of low latitude glaciation. Currently, there are three "contenders" and each contains a different set of predictable consequences. Model A would suggest increased silicate weathering in the presence of a high CO_2 atmosphere in post-glacial time delivered the alkalinity rapidly to the oceans to precipitate the cap carbonates [*Hoffman et al.*, 1998b]. This would require a long-lived glaciation (>5–10 m.y.) such that significant amounts of CO_2 could build up in the atmosphere via volcanic outgassing. Model B would suggest that the oceans were significantly stratified and anoxic such that sulfate reduction in the water column would promote increased alkalinity [*Grotzinger and Knoll*, 1995]. Note that this model does not actually require glaciation, it simply requires significant ocean anoxia. Model C would suggest that the disassociation of methane clathrates in postglacial time and concomitant alkalinity rise due to microbial degradation of methane was responsible for cap carbonate formation [*Kennedy et al.*, 2001b].

Each of these models has strengths and weaknesses. For example, they all account for the fact that the $\delta^{13}C$ is negative (see each paper for a detailed discussion). However, Model A would predict an influx of clay and dissolved silica (via silicate weathering) but these features are not noted in cap carbonates. Furthermore, the Gaskiers glaciogenic deposit in Newfoundland, representing a discrete "snowball" glaciation, has been constrained to a duration of no more than 1 m.y. [*Bowring et al.*, 2003] [as predicted by *Jacobsen and Kaufman*, 1999 via Sr isotopic modeling], far shorter than the 5–10 m.y. required by Model A for CO_2 buildup. Model B requires the overturn of the ocean via upwelling to precipitate the cap and thus might predict more variability in $\delta^{13}C$ between caps or carbonate concentration in upwelling areas. It is not clear that enough alkalinity could be stored via this mechanism to precipitate the volume of carbonate necessary. H_2S is also a byproduct of sulfate reduction and must be removed from the system (perhaps by pyrite precipitation) for alkalinity to rise. Model C would predict methane seep facies throughout the glacial deposits, but none are currently known. Also, the carbonate precipitated in direct association with the methane should be highly depleted with respect to $\delta^{13}C$, but few published examples of known cap carbonates are lighter than ~-6‰. All three models would predict elevated alkalinity that could foster the precipitation of seafloor fans; models A and C require a preceding glaciation, whereas B does not. The new Neoproterozoic fan occurrences presented below may provide new clues with which to interpret the source of alkalinity and by association the most parsimonious snowball Earth model.

2. TWO NEW NEOPROTEROZOIC SEAFLOOR FAN OCCURRENCES

Neoproterozoic strata are well-exposed throughout eastern California, Nevada, Utah, and Idaho [e.g., *Stewart and Poole*, 1974; *Stewart and Suczek*, 1977; *Link et al.*, 1993]. Many of these successions contain direct evidence (e.g., drop-

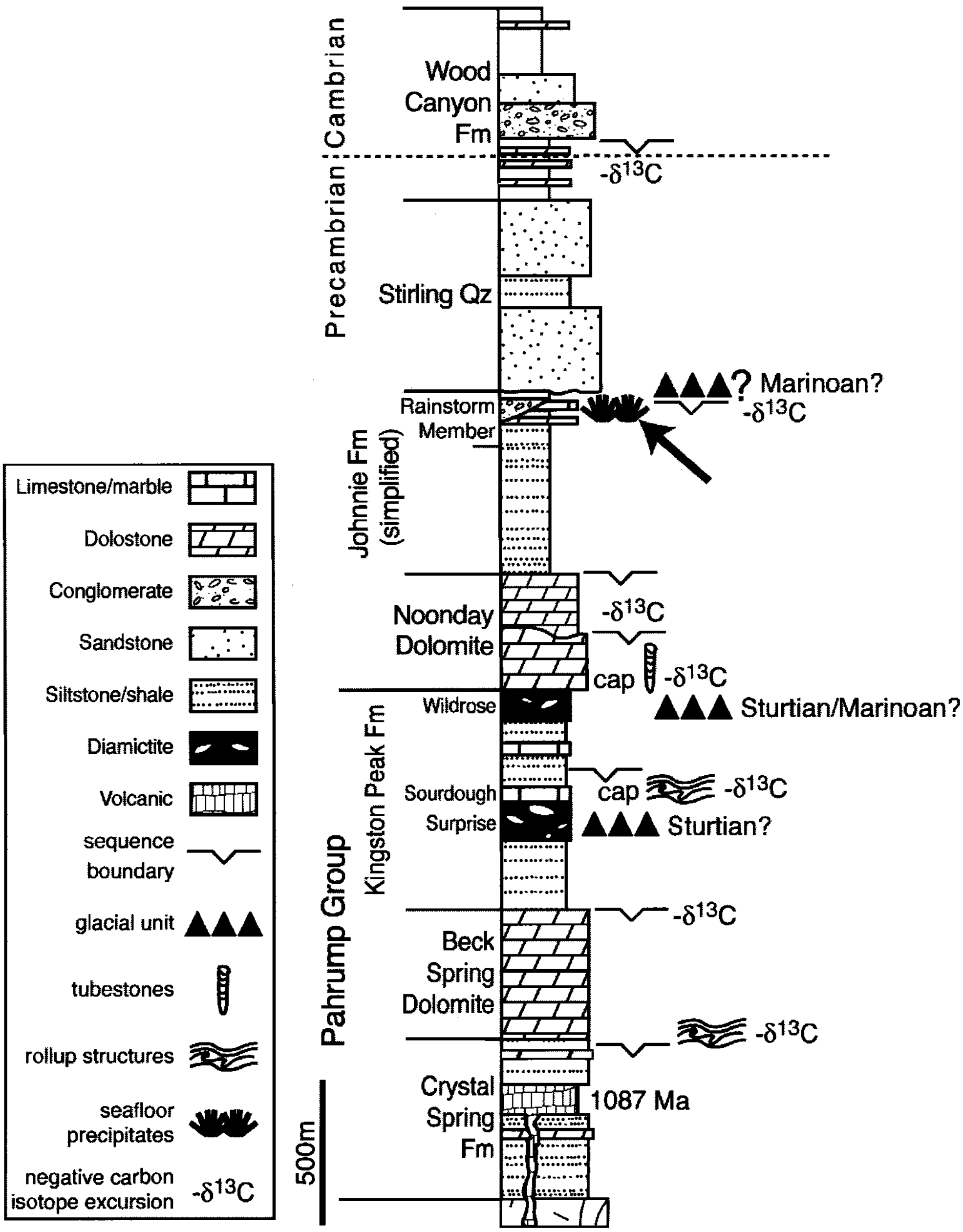

Figure 2. Generalized stratigraphic column for the Death Valley succession [modified from *Corsetti and Kaufman*, 2003]. Cap-like facies with negative $\delta^{13}C$ values are noted at four stratigraphic levels, although only two follow recognized glacial deposits. The age of the glacial deposits is debated [e.g., *Corsetti*, 1998; *Prave*, 1999; *Corsetti and Kaufman*, 2003]. A major incision in the Rainstorm Member of the Johnnie Formation has been correlated by Abolins et al. [2000] to "Marinoan" sealevel drawdown [but see *Summa*, 1993].

stones, striated clasts within diamictite, etc.) and indirect evidence (e.g., presumed glacioeustatic drawdown events/incised valleys and diamictite without striated clasts) for glaciation. The Death Valley and southeastern Idaho successions contain one or more glacial-cap carbonate couplets [*Link*, 1983; *Prave*, 1999; *Corsetti and Kaufman*, 2003] as well as the new seafloor fan localities [*Lorentz et al.*, 2004; *Pruss and Corsetti*, 2002] and will be the focus of this investigation. The stratigraphic setting will be reviewed for the Death Valley and southeastern Idaho successions and the new seafloor fan sites will be described and placed into stratigraphic context.

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outcrop extent of the Rainstorm Member [*Pruss and Corsetti*, 2002] (fig. 4). The fans represent a significant, regional precipitation event [*Stewart*, 1970, estimated the regional extent of the Rainstorm Member to exceed 16,000 km^2]. They were first noted, but not described in detail, by Summa [1993]. They occur in the stratigraphic succession well above the Noonday Dolomite cap carbonate and just below the incised valley system correlated by some to glacio-eustacy in association with Marinoan glaciation. Thus, they do not appear to be associated with a known glaciation. The crystal units are isolated to centimeter-sized gray limestone beds within the predominantly pink limestones. The crystals grew as discrete fans and as beds of upward-oriented crystal units (fig. 4), and are typically 1 to 3 centimeters in height. The fact that the limestones associated with the crystal beds contain some hummocky cross-stratification might suggest that the crystal beds were precipitated during quiescent periods in between storms, or that the initial deepening represented by the crystal beds was below storm wave base.

Most crystal fans averaged ~100 μm in diameter at their base and expanded to ~300 μm at their termination (fig. 4a–d), most were ~1 cm tall, but examples exceeded 3.0 cm. Each fan is composed of a mosaic of smaller equant calcite crystals. The crystals display square terminations and are commonly draped by overlying grainstone or more rarely micrite. In horizontal cross-section, the crystals display a hexagonal shape (fig. 4d). The preserved crystallographic features would suggest an aragonite precursor. Abundant opaque grains (~50 μm in diameter), rare ooids (200–300 μm), and intraclasts are found in the interspaces between the crystals, and the precipitate beds are frequently overlain by intraclastic limestone. Reflected light microscopy and EDS analysis indicate that the opaque grains are now hematite [*Pruss and Corsetti*, 2002]. Commonly, the precipitates nucleated on concentrations of opaque grains atop minor erosive surfaces and/or hardgrounds.

2.2. Neoproterozoic Glaciation in Southeastern Idaho

The Neoproterozoic succession in southeastern Idaho consists of the Pocatello Formation, the Blackrock Canyon Limestone, and the Brigham Group (fig. 5) [*Link et al.*, 1993]. The Pocatello Formation contains two glaciogenic diamictite units interpreted as stades within the "Sturtian" glaciation [*Crittenden et al.*, 1983], the uppermost of which is capped by a ~1-meter thick, ^{13}C-depleted, pink dolostone [*Smith et al.*, 1994]. An incised valley system in the Caddy Canyon Quartzite of the Brigham Group ~2000 meters above the Pocatello Formation has been interpreted to represent sea level drawdown associated with "Marinoan" glaciation [*Levy et al.*, 1994] (commonly considered ca. 600 Ma) though no glaciogenic deposits are associated with this incised valley system. The incision is constrained to be older than 580 Ma, the age of volcanics in the overlying Browns Hole Formation [*Christie-Blick and Levy*, 1989].

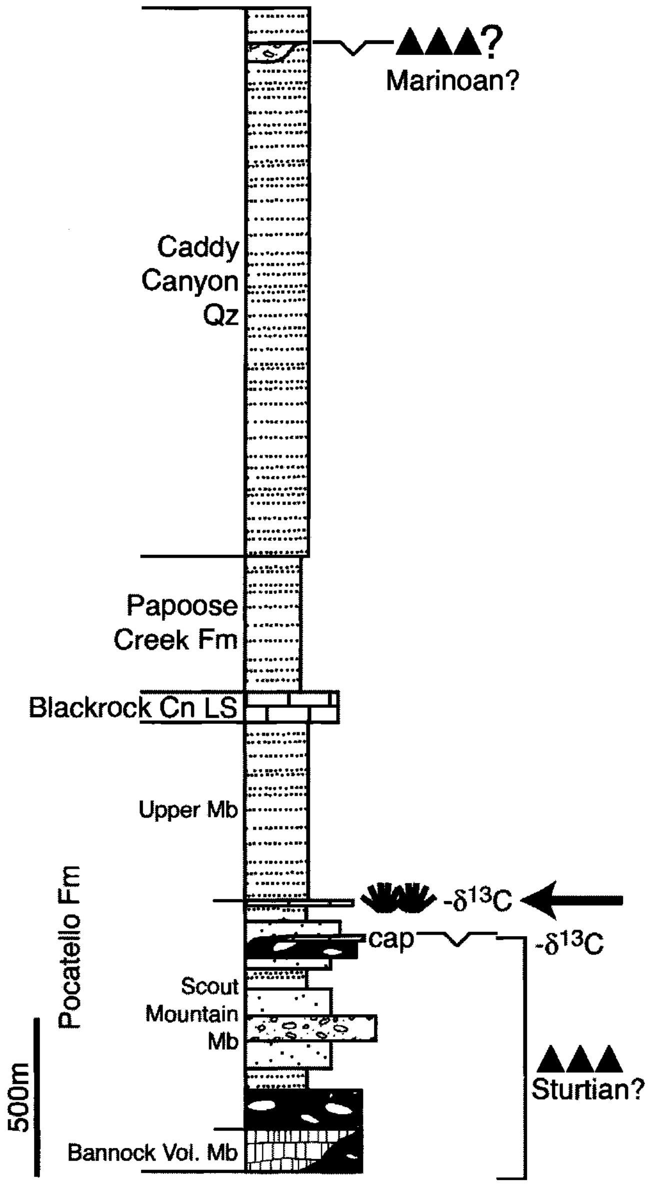

Figure 5. Generalized stratigraphic column for the Pocatello area [after *Christie-Blick and Levy*, 1989; *Link et al.*, 1993; *Levy et al.*, 1994; *Smith et al.*, 1994; *Lorentz et al.*, 2004]. Symbols as in fig. 2. The seafloor precipitates occur between units correlated to the Sturtian and Marinoan intervals, just above an ash dated at 667±5 Ma [*Fanning and Link*, 2003].

The Pocatello Formation is divided into three members: the Bannock Volcanic Member, the Scout Mountain Member, and the (informal) upper member [*Link*, 1983]. The medial

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water anoxic water mass and the surface oxygenated water mass; as the deep water transgressed across the shelf, the fans were formed; the hematite formed as the deep water eventually contacted and mixed with oxygenated surface waters. In fact, the two new fan occurrences occur in transgressive systems tracts near maximum flooding, as would be necessary for the hypothesized process. This has a further prediction: the water mass must have been low in sulfate since sulfur will scavenge iron. Hurtgen et al. [2002] demonstrated that Neoproterozoic carbonates are quite low in trace sulfate concentration.

The Pocatello examples, on the other hand, are draped with micrite, as are most of the "real" cap carbonate examples. How do fans *and* micrite form at the same time if inhibitors are an important factor? We suggest that the interaction of a deep, anoxic, inhibitor-rich water mass with the surface, oxidized water mass is the key; the fans form predominantly in the deeper water mass and the micrite drapes form as the deep water mass mixes with oxic surface waters to produce micrite. This has predictable consequences for the competing snowball Earth models: fan formation with concomitant micrite formation would *require* a deep source for the alkalinity but does not preclude a shallow source in addition to the deep source. Model A (alkalinity delivered predominantly from the continental runoff) would not be favored as the sole mechanism since it would predict a shallow source for alkalinity. Micrite would be expected to form in oxygenated surface waters; excess alkalinity would most likely be consumed in the surface waters before it reached deeper levels where the fans formed. Therefore, we favor Model B, the upwelling of anoxic, alkaline deep waters, since it satisfies all of the criteria necessary to form fans and micrite and does not necessarily require a preceding glaciation. Caution must be exercised when interpreting the meaning of seafloor precipitates in association with the snowball Earth aftermath because they may form without glacial influence.

4. CONCLUSION

Anachronistic carbonate seafloor fans, nearly absent since Paleoproterozoic time, make a reappearance in the rock record in the Neoproterozoic and figure prominently in "snowball Earth" hypotheses. Most commonly, they are associated with post-glacial cap carbonates and are therefore considered to represent post-glacial phenomena. However, two new occurrences in the western United States occur in the absence of glacial deposits and between known glacial intervals. Processes independent of glaciation may cause negative excursions and cap carbonate-like facies and caution must be exercised when interpreting the meaning of seafloor precipitates in association with snowball Earth events.

Acknowledgments. We thank Paul K. Link for introducing us to the Pocatello succession, generously spending time with us in the field and in discussion, and sharing geochronologic data. Paul Hoffman introduced FAC to the Otavi Group in Namibia and Alan J. Kaufman aided with the isotopic analysis and interpretation. The Geological Society of America, and the Evolving Earth Foundation provided funding to NJL. The USC Earth Sciences Department provided funding to NJL and SBP.

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Analysis of Carbon Cycle System During the Neoproterozoic: Implication for Snowball Earth Events

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Carbon cycle and climate change during the Neoproterozoic have not been understood well. In that period, global glaciations may have occurred several times. Carbon isotopic composition of seawater was generally heavy and fluctuated with very large amplitudes, suggesting unusual behaviors of the carbon cycle system. In this study, the carbon cycle and the climate change during the Neoproterozoic are analyzed quantitatively using an improved carbon isotope mass balance model with a one-dimensional energy balance climate model. According to the results, the organic carbon burial rate is generally high and the carbonate precipitation rate is generally low through the Neoproterozoic. However, before the glaciations, the organic carbon burial increases and the carbonate precipitation decreases. On the other hand, the organic carbon burial decreases and the carbonate precipitation increases after the glaciations. Because the carbonate precipitation rate should balance with the cation supply rate due to chemical weathering, the climate factors (i.e., T and pCO_2) also decrease before the glaciations and increase after the glaciations. The climate is, however, too warm to initiate glaciations when present values of the CO_2 degassing rate and the organic carbon weathering rate are assumed in the model. If the global glaciations were caused at the positive excursions of $\delta^{13}C$, the CO_2 degassing rate should have decreased to < 1/4–1/2 times the present rate at the same time. In order to reconstruct the carbon cycle and the climate change in further detail, we need to know variations of the tectonic forcing (e.g., volcanic activities) during the Neoproterozoic.

1. INTRODUCTION

Climate change during the Proterozoic seems to be enigmatic. There are ice ages in the Early Proterozoic (the Huronian glaciations) and in the Late Proterozoic (the Sturtian and the Varanger-Marinoan glaciations) [e.g., *Hambrey and Harland*, 1981; *Crowell*, 1999]. Each episodes may have multiple glacial events (at least, more than a single event) suggested from existence of multiple diamictite layers and carbon isotopic excursions, although the exact number of glacial events has been controversial [e.g., *Kaufman et al.*, 1997; *Kennedy et al*, 1998; *Hoffman and Schrag*, 2002]. On the other hand, although possible glacial deposits have been found in north-central Siberia and north Scotland [e.g., *Crowell*, 1999], there is no certain evidence of glaciations during the Middle Proterozoic. Therefore, two big ice ages are separated by a 1.5-billion-year warm period during the Proterozoic.

Paleomagnetic studies have revealed that there is evidence for low-latitude ice sheets both in the Late and the Early Proterozoic glaciations [e.g., *Evans*, 2000]. There are also several features associated with the Proterozoic glaciations. Glacial diamictites in the Neoproterozoic are overlain by thick carbonate sediments (called "cap carbonate") which may have deposited under tropical environment, showing unusual tex-

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dissolved inorganic carbon and carbonate minerals, and isotopic shift associated with secondary biological processes [e.g., *Hayes et al.*, 1999]. When there is time series data set of $\delta^{13}C_a$ with assumed values of $\delta^{13}C_r$ and Δ, the factor f_o which represents the fraction of carbon that is buried in organic form can be obtained.

$$f_o = F_B{}^O/(F_B{}^C + F_B{}^O) = (\delta^{13}C_a - \delta^{13}C_r)/\Delta. \quad (3)$$

This is essential information obtained from the carbon isotope mass balance model. Here, if we assume the riverine flux of carbon F_r in addition to $\delta^{13}C_r$ and Δ, two unknown fluxes ($F_B{}^C$ and $F_B{}^O$) can be estimated separately from the equations (1) and (2) as follows:

$$F_B{}^C = (\Delta - \delta^{13}C_a + \delta^{13}C_r)\, F_r / \Delta \quad (4)$$

$$F_B{}^O = (\delta^{13}C_a - \delta^{13}C_r)\, F_r / \Delta. \quad (5)$$

To summarize, using the two equations of (1) and (2), we can estimate two unknown parameters ($F_B{}^O$ and $F_B{}^C$) when other parameters (F_r, $\delta^{13}C_r$, and Δ) are assumed to be constant, and time series data set of $\delta^{13}C_a$ is given as input data.

Next, we improve this simple model to include weathering fluxes and degassing flux in order to discuss climate changes and roles of each carbon flux in the carbon cycle system. The carbon flux into the atmosphere-ocean system is divided into three fluxes, that is, degassing of CO_2 via metamorphism and volcanism (F_D), weathering of carbonate ($F_W{}^C$), and oxidative weathering of organic carbon ($F_W{}^O$). Each carbon source has each specific carbon isotope value (represented here as $\delta^{13}C_M$, $\delta^{13}C_C$, and $\delta^{13}C_O$, respectively). In this case, the carbon mass balance and the carbon isotope mass balance equations are represented by

$$F_D + F_W{}^C + F_W{}^O = F_B{}^C + F_B{}^O \quad (6)$$

$$\delta^{13}C_M F_D + \delta^{13}C_C F_W{}^C + \delta^{13}C_O F_W{}^O = \delta^{13}C_a F_B{}^C + (\delta^{13}C_a - \Delta) F_B{}^O. \quad (7)$$

In order to solve these equations, we need additional constraints and assumptions. One is the alkalinity budget in the ocean, that is,

$$F_B{}^C = F_W{}^C + F_W{}^S \quad (8)$$

where $F_W{}^S$ represents silicate weathering rate. This equation represents a net carbonate precipitation (difference between the rates of the precipitation and the weathering of carbonates) which should be equal to the cation supply derived from the chemical weathering of silicate minerals [*Berner*, 1991, 1994].

Because Δ varies with concentration of dissolved CO_2 (hence partial pressure of atmospheric CO_2, that is, pCO_2) as well as other factors such as growth rate and the ratio of cellular volume to surface area of phytoplankton [e.g., *Bidigare et al.*, 1997; *Kump and Arthur*, 1999], and also because pCO_2 must have changed greatly through the ice ages, variations of Δ should be important during the Neoproterozoic.

Hayes et al. [1999] compiled not only $\delta^{13}C_a$ data but also $\delta^{13}C_g$ data to estimate variations of Δ during the later Neoproterozoic (between 800 Ma and 540 Ma). The method they adopted is: (1) samples were sorted in order of assigned age, thus producing a sequence in which samples from different tectonic provinces were interspersed, and (2) values of $\delta^{13}C_a$ and $\delta^{13}C_g$ were compared among samples with closely similar ages, without regard for location [*Hayes et al.*, 1999]. Therefore, validity of the approach depends on the accuracy of the age assignments that guide the comparisons [*Hayes et al.*, 1999]. Although this method may be the best way to compile existing data sets to compare among samples from different localities, uncertainties due to age assignments cannot be eliminated. Therefore, although we use the data sets of $\delta^{13}C_a$ and $\delta^{13}C_g$ compiled by *Hayes et al.* [1999], we also use higher resolution data set of $\delta^{13}C_a$ compiled also by *Hayes et al.* [1999] (Figure 1) and the theoretical formulation of Δ proposed by *Kump and Arthur* [1999]. The formulation of Δ as a function of pCO_2 is expressed as

$$\Delta = A/(B \times pCO_2) - 33 \quad (9)$$

where A=2301.91 and B=0.034 [*Kump and Arthur*, 1999]. This formulation is based on data set for haptophyte algae [*Bidigare et al.*, 1997] with Henry's Law at 25°C and $[PO_4]$ = 0.25 μmol/kg. Although this may not be appropriate for the Neoproterozoic ocean and biosphere, we will use this formulation as one of possible expressions of Δ as a function of pCO_2.

The chemical weathering reaction is known to have dependencies on temperature (T) and pCO_2 [e.g., *Walker et al.*, 1981; *Schwartzman and Volk*, 1989, 1991; *Berner*, 1991, 1994]. A function f_B which represents the dependencies of weathering rate on T and pCO_2 is assumed here as follows [e.g., *Walker et al.*, 1981; *Schwartzman and Volk*, 1989, 1991; *Tajika and Matsui*, 1990, 1992; *Tajika*, 2003]:

$$f_B = (pCO_2/pCO_2{}^*)^n \exp(-E/RT) \quad (10)$$

where n is an exponent of pCO_2 dependency, E is activation energy of reaction, R is gas constant, and * represents the present value. For Ca-, Mg-silicates exposed on the continents of an abiotic Earth, n is probably between 0.3 and 0.4 [*Schwartzman and Volk*, 1989]. For simplicity, we assume 0.3

[*Walker et al.*, 1981; *Schwartzman and Volk*, 1989, 1991; *Tajika and Matsui*, 1990, 1992] in this study. Activation energy of chemical dissolution of various silicates is estimated ranging from 10 to 20 kcal/mol [*Schwartzman and Volk*, 1989; *Lasaga et al.*, 1994]. We use 15 kcal/mol [*Berner*, 1994] in this study. For simplicity, a dependency of the weathering rate on temperature through runoff is not considered (hence negative feedback should be minimum strength). Similarly, other factors (such as river runoff due to changes in paleogeography, land area, uplift and physical erosion, and lithology) are not considered here for simplicity. The silicate and carbonate weathering rates are assumed here as follows:

$$F_W{}^S = f_B(T, pCO_2) f_E \, F_W{}^{S*} \qquad (11)$$

$$F_W{}^C = f_B(T, pCO_2) f_E \, F_W{}^{C*} \qquad (12)$$

where f_E is a soil biological activity factor which represents efficiency of weathering due to plants and microbes on land [*Schwartzman and Volk*, 1989, 1991; *Berner*, 1991, 1994].

Plants accelerate the uptake of CO_2 during weathering by secretion of organic acids by roots and associate symbiotic microflora, recirculation of water by transpiration and accelerated rainfall, and retention by roots of soil from removal by erosion [*Schwartzman and Volk*, 1989, 1991; *Berner*, 1991, 1994]. Because there were not higher terrestrial plants before the Silurian, efficiency of silicate weathering rate due to the soil biological activity should have been very low during the Neoproterozoic ($f_E << 1$) compared to that at present ($f_E = 1$). However, microbial and possibly lichen colonization on the continents in the Precambrian probably resulted in a considerable increase in chemical weathering relative to abiotic conditions [*Schwartzman and Volk*, 1989]. The factor before the Silurian may be estimated from the weathering rate in unvegetated region on the present Earth. On the basis of such an estimate [*Drever and Zobrist*, 1992], a value for f_E of 0.15 [*Berner*, 1994] is assumed in this study.

We combine the carbon isotope model described above with a simple climate model. We use a one-dimensional energy balance climate model (1D-EBM) with CO_2-dependent outgoing radiation [*Caldeira and Kasting*, 1993; *Ikeda and Tajika*, 1999]. The model is based on the Budyko-Sellers-type EBM, which employs diffusive-type of heat transport and discontinuous albedo at the ice cap edge, and takes into account dependency of CO_2 on the outgoing infrared radiation (see *Caldeira and Kasting* [1993] and *Ikeda and Tajika* [1999]). From this model, we can estimate latitudinal temperature distribution as functions of the effective solar constant (S_{eff}) and pCO_2.

Figure 2a shows an example of variations of latitudinal temperature distribution (S_{eff} is assumed to be 0.94 for the Neoproterozoic). As pCO_2 decreases, temperature lowers at every

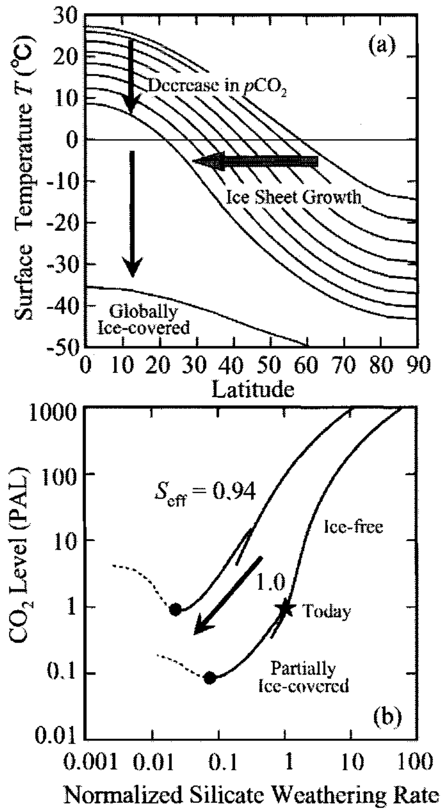

Figure 2. (a) Variation of latitudinal distribution of surface temperature due to decrease in pCO_2. The results obtained from the 1-D EBM with standard parameters' values (ice albedo = 0.62 and land/ocean albedo = 0.3, and diffusion coefficient for latitudinal heat transport of 0.455 $Wm^{-2} K^{-1}$). (b) Variation of silicate weathering rate (normalized to the present rate of 6.65 x 10^{12} mol/year [*Berner*, 1994]) due to decrease in pCO_2 (PAL= present atmospheric level). Solid lines represent stable solutions (ice-free and partially ice-covered), and dotted lines represent unstable solutions. The effective solar constant S_{eff} is 1 at present and 0.94 for the Neoproterozoic.

latitude, although the tropics remains warmer. However, when pCO_2 achieves the critical level at which the stable solution for partially ice-covered branch disappears, the Earth becomes globally ice-covered (under freezing condition globally). The critical level of pCO_2 depends on model parameters (albedo and diffusion coefficient) and also on climate models (EBMs, Atmospheric GCMs, or Atmosphere-Ocean-Coupled-GCMs), but the basic behaviors of the climate system, that is, global cooling due to pCO_2 decrease and globally freezing condition at very low CO_2 level, might be the same [e.g., *Jenkins and Smith*, 1999] (note, however, that there may be a quasi-stable state of ice-covered Earth with an equatorial open ocean [e.g., *Hyde et al.*, 2000]). In the following arguments, we assume this relationship as the most likely behaviors of the climate system for the case of pCO_2 decrease.

We estimate global chemical weathering rate from these temperature distributions and pCO_2 conditions. Figure 2b shows a relationship between pCO_2 and the global silicate weathering rate, which is obtained from the integration of the silicate weathering rate from the pole to the equator as a function of temperature at each latitude. For simplicity, we assume uniform distribution of continents and oceans from the pole to the equator as an ideal case. If continents concentrate in low latitudes and contribution of chemical weathering in low latitude is large, then the curve would shift rightward in this diagram (Figure 2b). The chemical weathering is assumed to occur as long as the surface temperature is above 0°C. When we obtain the silicate weathering rate from the carbon isotope model described above, we can estimate pCO_2 and the temperature distribution (or the globally-averaged surface temperature, T_S) from this relationship.

To summarize, using the six equations of (6)–(9), (11), and (12), we can estimate six unknown parameters ($F_B{}^O$, $F_B{}^C$, $F_W{}^C$, $F_W{}^S$, f_B, and Δ) when other parameters (F_D, $F_W{}^O$, $\delta^{13}C_C$, $\delta^{13}C_O$, and $\delta^{13}C_M$) are assumed to be constant and time series data set of $\delta^{13}C_a$ is given as input data. When we combine the carbon isotope model with the climate model, we can further estimate pCO_2 and T_S.

3. RESULTS AND DISCUSSION

As a standard case, we assume the present values of F_D (= 7.9 x 10^{12} mol/year) and $F_W{}^O$ (= 3.75 x 10^{12} mol/year) [Berner, 1991], and average isotopic values of $\delta^{13}C_C$ (=0‰), $\delta^{13}C_O$ (= -25 ‰), and $\delta^{13}C_M$ (= -5 ‰) [e.g., *Schidlowski*, 1988]. We will discuss results of parameter studies in the later section. We use two kinds of data set of $\delta^{13}C_a$ for the later Neoproterozoic compiled by Hayes et al. [1999] as input data to the model: one is high resolution (Figure 1) and the other is low resolution but with the data set of $\delta^{13}C_g$ (i.e., with the data set of Δ).

3.1. Organic Carbon Burial

Figure 3a shows variations of the burial rate of organic carbon ($F_B{}^O$) obtained from the models. There are results for three cases: (I) high resolution $\delta^{13}C_a$ data set by *Hayes et al.* [1999] with the formulation of Δ by *Kump and Arthur* [1999] are used (solid curve), (II) low resolution $\delta^{13}C_a$ and $\delta^{13}C_g$ (i.e., Δ) data sets by *Hayes et al.* [1999] are used (dashed curve), and (III) the simple carbon isotope mass balance model (the equations (1) and (2)) with low resolution $\delta^{13}C_a$ and $\delta^{13}C_g$ (i.e., Δ) data sets by *Hayes et al.* [1999] are used (dotted curve).

As shown in this figure, the results of the Cases II and III are similar to each other. This is because the carbon isotope model depends strongly on input data of $\delta^{13}C_a$. The difference between the Cases II and III is owing to difference between the models: the model developed here (Cases I and II) may partially include the effects of climate change through variations of chemical weathering, which may affect the estimate of $F_B{}^O$. The value of $F_B{}^O$ is generally high between the glaciations (especially before the glaciations), but decreases rapidly after the glaciations for all three cases. In particular, for the Case I, $F_B{}^O$ becomes almost zero after the Sturtian and the Marinoan glaciations. This might be consistent with the arguments by *Hoffman et al.* [1998b]. On the other hand, before the glaciations, $F_B{}^O$ becomes very high (up to 8.0–9.5 x 10^{12} mol/year) compared with the present value of 5 x 10^{12} mol/year or the values estimated for the Phanerozoic (except for the time of the Late Paleozoic glaciations) [*Berner*, 1991]. This is consistent with the view obtained from the equation (3), that is, the fraction of organic carbon burial f_o is generally higher in the Neoproterozoic than the Phanerozoic [e.g., *Hayes et al.*, 1999].

It is, however, noted that absolute values of $F_B{}^O$ should depend on assumed values of model parameters (especially on F_D and $F_W{}^O$, that is, the input fluxes of carbon into the atmosphere-ocean system). If these fluxes are smaller than the present values assumed here, the absolute values of $F_B{}^O$ during the Neoproterozoic can be similar to or even lower than those during the Phanerozoic (see the section 3.4).

3.2. Carbonate Precipitation

Figure 3b shows variations of the carbonate precipitation rate ($F_B{}^C$) for the three cases. The carbonate precipitation rate is generally low between the glaciations (especially before the glaciations), and increases rapidly after the glaciations (part of these increases might represent precipitation of cap carbonates deposited above the glacial diamictites).

For the carbonate precipitation, the results of the Cases I and II are more similar than the result of the Case III: the amplitudes of variations are larger in the Cases I and II than in the Case III. This is because $F_B{}^C$ should balance with the rate of cation supply to the ocean due to silicate and carbonate weathering, both of which depend on the climate (i.e., T and pCO_2). Because of this, the amplitudes of variations of $F_B{}^C$ are larger in the model developed here (which may include the effects of climate change through the chemical weathering) than the simple carbon isotope model (which assumes constant riverine input rate).

It is, however, noted that climate change through variations of pCO_2 should be contributed not only by variations of biological forcing such as organic carbon budget and the soil biological activity, but also contributed by variations of tectonic forcing such as volcanic activity (seafloor spreading and superplume) and orogenic activity, which are not con-

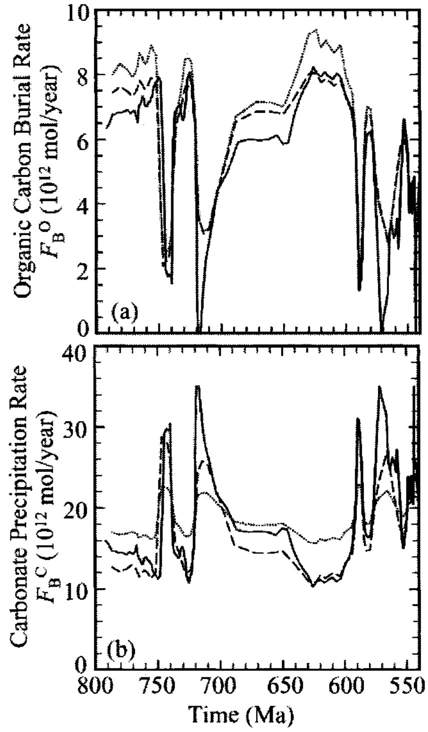

Figure 3. Variations of (a) organic carbon burial rate and (b) carbonate precipitation rate during the Neoproterozoic. Solid curves represent the Case I (high resolution $\delta^{13}C_a$ data set by *Hayes et al.* [1999] with the formulation of Δ by *Kump and Arthur* [1999]). Dashed curves represent the Case II (low resolution $\delta^{13}C_a$ and $\delta^{13}C_g$ data sets by *Hayes et al.* [1999]). Dotted curves represent the Case III (the simple carbon isotope mass balance model with low resolution $\delta^{13}C_a$ and $\delta^{13}C_g$ data sets by *Hayes et al.* [1999]).

sidered in the carbon isotope mass balance models. As a result, estimates of $F_B{}^C$ from the carbon isotope mass balance models can only represent the contribution of variations of biological forcing.

Tajika [1999] compared the results of $F_B{}^O$ and $F_B{}^C$ between a simple carbon isotope mass balance model and a "full" model of the carbon cycle (similar to GEOCARB model developed by *Berner* [1994]). According to the result, the estimates of $F_B{}^O$ from the two models seem to be very similar to each other except for their absolute values. On the other hand, the estimates of $F_B{}^C$ from the two models are quite different. The result of the simple model clearly reflects the input data of $\delta^{13}C$. Because riverine inputs of carbon and calcium to the ocean due to chemical weathering must depend largely on T and pCO_2 (which should be affected both by the biological forcing and the tectonic forcing), both the pattern and the absolute values of $F_B{}^C$ are different between the results of the two different methods.

Therefore, it appears that the simple carbon isotope mass balance models would be useful for estimating the pattern of $F_B{}^O$, but may not be appropriate for its absolute value, and cannot estimate $F_B{}^C$ [*Tajika*, 1999]. Because the model developed in this study may include effects of climate change through the chemical weathering, the amplitudes of variations of carbon fluxes (including $F_B{}^O$ and $F_B{}^C$) would be estimated more properly than those estimated from the simple carbon isotope mass balance model, although the contribution of tectonic forcing to the carbon cycle system is not included in both models.

In this respect, the result of the variations of $F_B{}^C$ obtained here is not equivalent to the result of either the simple carbon isotope model or the full carbon cycle model, but is similar to the result of a system analysis of the full carbon cycle model which only considers variations of the biological forcing [*Tajika*, 1998, 1999].

3.3. Chemical Weathering and Climate Change

Figure 4 shows variations of chemical weathering rate normalized to the present rate ($=f_B \times f_E$) for the Cases I and II. Note that the Case III (the simple carbon isotope model) assumes it to be constant (= 1). The weathering rate is generally low (especially before the glaciations), but increases rapidly after the glaciations, as well as the variations of the carbonate precipitation rate. Because the weathering rate responds to climate change, this indicates that the climate is cool between the glaciations (especially before the glaciations) but becomes warm temporarily after the glaciations. It is noted that, although the variations of the weathering rate can be interpreted as the effect of climate change, the variations obtained here should only represent the effects of the biolog-

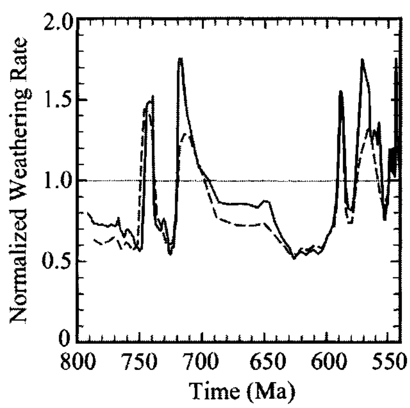

Figure 4. Variations of chemical weathering rate normalized to the present rate ($=f_B \times f_E$) during the Neoproterozoic for the Cases I (solid curves), II (dashed curves), and III (dotted curves).

ical forcing, and do not include effects of the tectonic forcing, as mentioned in the previous section.

Figure 5 shows variations of pCO_2 and T_S. These results are obtained from numerical iteration which estimates the factor f_B so that the value estimated from the carbon isotope model may be consistent with the value estimated from the climate model (integration of the factor $f_B(T, pCO_2)$ from the pole to the equator). Then, the globally-averaged surface temperature is obtained from averaging the surface temperatures from the pole to the equator.

As expected from the results of weathering rate, pCO_2 and T_S are low before the glaciations, but become high after the glaciations, consistent with the view from the carbon isotope data [e.g., *Kaufman et al.*, 1997; *Hoffman et al.*, 1998a, 1998b]. The pCO_2 and T_S are, however, too high to initiate glaciations (Figure 5): T_S varies between 20°C and 30°C throughout the Neoproterozoic in these cases. This is essentially because we assumed present values of F_D and $F_W{}^O$ for the standard case, and also because we assumed small value of f_E (= 0.15) during the Neoproterozoic. Because the estimate of $F_B{}^C$ should be affected by F_D and $F_W{}^O$ through the carbon isotope mass balance model, $F_B{}^C$ cannot be small as far as the present values of F_D and $F_W{}^O$ are assumed (i.e., $F_W{}^C \sim F_W{}^{C*} = 20 \times 10^{12}$

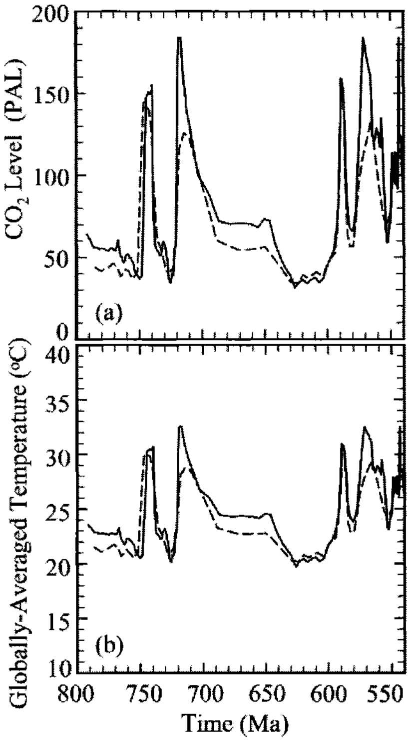

Figure 5. Variations of (a) CO_2 level (in PAL) and (b) globally-averaged surface temperature during the Neoproterozoic for the Cases I (solid curves) and II (dashed curves).

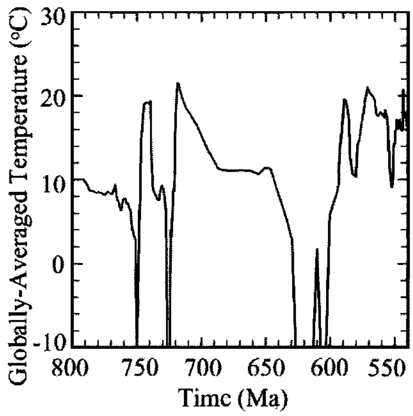

Figure 6. Variations of the globally-averaged surface temperature during the Neoproterozoic for the case of low CO_2 degassing rate (= 1.7 x 10^{12} mol/year, < 1/4 of the present rate) with high resolution $\delta^{13}C_a$ data set by *Hayes et al.* [1999] and the formulation of Δ by *Kump and Arthur* [1999].

mol/year; Figure 3b). According to the equation (8), $F_B{}^C$ should balance with $F_W{}^S$ and $F_W{}^C$, so the weathering rate cannot be small whereas the soil biological activity is small (i.e., $f_B \times f_E \sim 1$ with $f_E = 0.15$). Therefore, f_B, hence pCO_2 and T_S should be high in this case.

These results would, however, change when we assume different values of carbon fluxes in the model. We therefore need parameter studies in order to investigate relationship between the carbon cycle and the climate change.

3.4. Effects of Carbon Fluxes

Figure 6 shows the result of the case for assuming the lower degassing rate ($F_D = 1.7 \times 10^{12}$ mol/year). In this case, T_S and pCO_2 become low enough to initiate global glaciations when $F_B{}^O$ increases. It is noted that the condition for initiation of global glaciation used here is obtained from the 1D-EBM (see the section 2 and Figure 2), so the condition may be different when one assumes different values of the model parameters or different climate models.

It is, however, important to note here that the increase in the organic carbon burial rate as inferred from the positive excursion of $\delta^{13}C_a$ [e.g., *Kaufman et al.*, 1997; *Hoffman et al.*, 1998b] may not be enough to cause global glaciations, and carbon fluxes other than the organic carbon burial rate may also be important for considering the climate change during the Neoproterozoic. In this case (Figure 6), global glaciations occur four times during the Neoproterozoic because of low F_D in addition to the increases of $F_B{}^O$. It is, however, noted that, because the input flux of CO_2 into the atmosphere-ocean system is low, $F_B{}^O$ increases to the level similar to the present but never becomes larger in this case.

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from now [e.g., *Opdyke and Wilkinson*, 1988; *Volk*, 1989], indicating that the CO_2 degassing rate might have been generally lower and varied owing to changes in the sedimentary environment for carbonates in addition to variation of seafloor spreading rate.

There is, however, an enigma: the $\delta^{13}C$ value of seawater might have decreased before the younger Neoproterozoic glaciation [e.g., *Hoffman et al.*, 1998b; *Hoffman and Schrag*, 2002; *Schrag et al.*, 2002]. If it is not an artifact of some unusual alteration process [*Kennedy et al.*, 1998], but is primary and real, then the cause for the global glaciation cannot be explained easily. *Hoffman et al.* [1998b] considered that this is due to cessation of marine biological productivity because of colder conditions. There is another interpretation which attributes the negative excursion of $\delta^{13}C$ to release of methane owing to dissociation of seafloor methane hydrate [*Schrag et al.*, 2002]. Because accumulation of ^{13}C-depleted carbon from volcanic gas, organic carbon, or methane hydrate may result in an increase of pCO_2, it seems to be difficult to explain the global glaciation. However, *Schrag et al.* [2002] considered that pCO_2 should have decreased considerably owing to accumulation of methane (which is a strong greenhouse gas and could maintain the warm climate) because pCO_2 is controlled through the carbonate-silicate geochemical cycle over millions of years [*Walker et al.*, 1981]. When the release of methane ceased, all the methane is converted to CO_2, but pCO_2 would have been too low to maintain the warm climate, resulting in the global glaciation. Hence methane release might explain not only the negative excursion of $\delta^{13}C$ just before the glaciation but also the cause for the global glaciation [*Schrag et al.*, 2002]. Although this hypothesis may be fascinating, it requires continuous release of methane from hydrates over $>10^5$ years (i.e., it should not be a single event nor several discrete events) and very long residence time of methane in the atmosphere (more than 1000 years compared with less than 10 years today).

The negative excursion might be explained by suppression of marine biological productivity in a stagnant equatorial surface ocean during the climate instability, or by an increase in the organic carbon weathering (see the previous section) or dissociation of methane hydrate at the last stage of cooling with an increase in marine biological productivity (this is required in order to remove an extra light carbon isotope from the surface water). In these cases, the negative excursion may reflect the drop in $\delta^{13}C$ of the surface water, and the timescale should be rather short ($< 10^4$ years). Unfortunately, because the detailed timescale for the negative excursion before the glaciation has not been certain so far, it may still be a matter of debate.

4. CONCLUSION

The carbon cycle and the climate change during the Neoproterozoic are estimated from the improved carbon isotope mass balance model combined with the 1-D EBM and from the $\delta^{13}C$ data. In general, the organic carbon burial rate ($F_B{}^O$) is high and the carbonate precipitation rate ($F_B{}^C$) is low during the Neoproterozoic. However, $F_B{}^O$ increases and $F_B{}^C$ decreases before the glaciations, and $F_B{}^O$ decreases and $F_B{}^C$ increases after the glaciations. Because $F_B{}^C$ should be equal to the cation supply rate due to chemical weathering, the weathering rates, hence T and pCO_2 are also generally low, but decrease before the glaciations and increase after the glaciations. However, when present values of the CO_2 degassing rate (F_D) and the weathering rate of organic carbon are assumed in the model, the climate is too warm to initiate glaciations. In order to cause global glaciations, F_D should be low (< 1/4–1/2 times the present rate) at the time of the positive excursions of $\delta^{13}C$.

Acknowledgments. I would like to thank two anonymous reviewers for their helpful comments. This research was partially supported by Grant-in-Aid for Scientific Research (No.12640419 and No.14403004) of the Japan Society of Promotion of Science.

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Secular Changes in the Importance of Neritic Carbonate Deposition as a Control on the Magnitude and Stability of Neoproterozoic Ice Ages

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We hypothesize that secular evolution in the control of calcium carbonate deposition dictated the severity of Neoproterozoic ice ages. In the modern ocean, reduction in carbonate deposition on the continental shelves can be compensated for by the increased preservation in deep sea sediments of biogenic carbonate originating from planktic calcifiers living in the open ocean. The result is that ocean carbonate chemistry is strongly buffered and the carbon-climate system relatively stable. However, before the advent of metazoan biomineralization in the Cambrian and proliferation of calcareous plankton during the Mesozoic, carbonate deposition would have been largely restricted to shallow water photic environments in the Neoproterozoic. A fall in sea level acting to restrict the photosynthetic area within Precambrian seas would necessarily initially decrease the global rate of carbonate deposition without being compensated by the typical Phanerozoic deep sea sedimentary 'buffer'. Ultimately, carbonate precipitation would reestablish itself at a greater local rate throughout the more areally restricted seas. The resulting higher degree of ocean saturation translates to substantially lower atmospheric CO_2 and colder terrestrial conditions. Ice ages of near-global extent and multi million-year duration can thus be understood as a direct consequence of the weak 'buffering' of the Precambrian carbon cycle, amplified by feedbacks involving CO_2 and climate. Both the widespread occurrence and observed thickness of 'cap' (dolostone) carbonate deposited during postglacial flooding of the shelves are explicit predictions of this hypothesis, and record the rapid removal from a highly oversaturated ocean of excess alkalinity accumulated during the glacial.

1. INTRODUCTION

The close timing of the first appearance of multicellular organisms [*Runnegar*, 2000] with the last of what were likely the most severe ice ages of Earth history [*Crowell et al.*, 1999] raises the obvious question of causality. Phenomena associated with these ice ages imply an extremity of climate unmatched by the Phanerozoic record and include; (i) grounded ice sheets at equatorial paleolatitudes [*Evans*, 2000; *Sohl et al.*, 1999], (ii) high magnitude variations in the carbon isotope (carbonate $\delta^{13}C$) record (+10 to -6‰ PDB) [*Hoffman et al.*, 1998; *Jacobsen and Kaufman*, 1999; *Kennedy et al.*, 1998], and (iii) ubiquitous precipitation of a thin layer of carbonate (known as "cap carbonate") directly overlying glacial deposits [*Williams*, 1979; *Hoffman and Schrag*, 2002; *James et al.*, 2001; *Kennedy*, 1996; *Kennedy et al.*, 1998, 2001a,b; *Myrow and Kaufman*, 1999]. In the controversial 'snowball Earth'

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10.1029/146GM06

hypothesis [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2002], the severe perturbation to the global carbon cycle implied by these physical features is taken as evidence for a prolonged period of surface ocean freezing (ca. 10 Ma), which extinguishes marine ecosystems and provides an 'evolutionary bottleneck', ultimately driving the proliferation of Metazoa. While changes in the biosphere are likely to have important evolutionary influences on life, it is also apparent that life can strongly affect the biosphere. Here we adopt a different strategy for understanding these anomalous Neoproterozoic glacial phenomena by identifying the first order difference between Phanerozoic and Precambrian carbon cycling that arises with the addition of carbonate depositional controls imparted by carbonate secretion bio-innovation. Through this approach, we find that the phenomena present in the Neoproterozoic record are predictable consequences of a less highly 'evolved' global carbon cycle.

2. HARD 'SNOWBALL' OR SOFT 'SLUSHBALL EARTH'?

2.1. The 'Snowball'

In an attempt to make sense of the variety of both physical and geochemical data available from the Precambrian geological record, *Kirschivink* [1992] proposed the occurrence of a 'snowball Earth'. He envisaged the Earth entering a completely frozen state several times during the late Neoproterozoic (although the exact number of distinct glacial episodes is still controversial [*Kennedy et al.*, 1998]); a state terminated once out-gassed mantle CO_2 accumulating in the atmosphere became sufficient to warm the Earth and melt the ice cover. These ideas were subsequently extended to consider certain aspects of the carbonate $\delta^{13}C$ record and the enigmatic presence of the 'cap' carbonates, the latter being explained as a consequence of greatly enhanced silicate rock weathering rates in an intense 'greenhouse' climate immediately following ice melt-back [*Hoffman et al.*, 1998].

Underpinning this thesis is an 'ice-albedo' feedback instability in the Earth system [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2002], the theoretical existence of which was originally predicted by early energy balance climate models [*Budyko*, 1969; *Cahalan and North*, 1979]. The climatic instability is triggered by the extension of sea ice to some critical latitude; perhaps lying ±30° from the Equator [*Caldeira and Kasting*, 1992]. Any further cooling of climate then initiates a runaway chain of events involving sea ice expansion and further cooling (the 'ice-albedo' feedback [*Budyko*, 1969]), until sea ice reaches the Equator [*Caldeira and Kasting*, 1992] and the ocean is everywhere covered in (sea) ice. The existence of a reflective ice cover results in highly inefficient capture of solar energy and an extreme cooling of the Earth's surface [*Caldeira and Kasting*, 1992]. For the system to exit this state, a very substantial radiative forcing of climate is required in order to warm the Equator sufficiently to start melting back the sea ice. One possible means of achieving this forcing could arise should no weathering of silicate rock take place on the frozen planet. Without any means of removal by weathering reactions, CO_2 originating from volcanic and metamorphic sources would gradually accumulate in the atmosphere. When the partial pressure of CO_2 reaches ca. 0.12 bar, the trapping of outgoing infra-red radiation would result in a surface warming (via the 'Greenhouse effect') sufficient to make the equatorial ice line unstable [*Caldeira and Kasting*, 1992]. The albedo feedback then operates in reverse, the ice melts rapidly and the glacial ends. The time scale for this slow warming process to be completed could be as long as 30 Ma [*Caldeira and Kasting*, 1992]. *The 'snowball Earth' hypothesis thus accounts for the inferred multi-million year duration of the glacial event in terms of the length of time required to buildup the required excess CO_2 in the atmosphere and exit from the ice-albedo feedback instability* [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2002].

The sea ice instability required by the snowball Earth hypothesis has been demonstrated in a number of GCM and coupled climate-ice sheet models [*Baum and Crowley*, 2001; *Crowley et al.*, 2001; *Donnadieu et al.*, 2003; *Hyde et al.*, 2000; *Jenkins and Smith*, 1999]. However, the use of a fixed depth mixed layer ('slab') representation of the ocean in all these models cautions against drawing firm conclusions regarding whether an ice-albedo instability exists in the real Earth system [*Jenkins and Smith*, 1999; *Poulsen*, 2003]. In contrast, atmospheric GCM models coupled either to a deeper seasonal mixed layer ocean [*Chandler and Sohl*, 2000] or a full ocean GCM [*Poulsen et al.*, 2001, 2002; *Poulsen*, 2003] have conspicuously failed to find any evidence for an ice-albedo instability, regardless of how 'favorably' the initial conditions are set [*Poulsen*, 2003]. Re-analysis with coupled models in which both oceanic and atmospheric meridional energy transports are separately resolved indicates that the strength of the (sea) ice-albedo feedback is much weaker than earlier idealized models suggested [*Bendtsen*, 2002]. This questions the underpinning assumption of *Kirschivink* [1992] and *Hoffman et al.* [1998]. Because the viability of a 'snowball Earth' state rests fundamentally on the existence and latitudinal limits of sea-ice instability, further work with particular focus on fully-resolved coupled ocean-atmosphere models is essential for the further support or falsification of this hypothesis.

2.2. The 'Slushball'

A climate state characterized by the equilibrium co-existence of Equatorial ice sheets with an open tropical ocean is consistent with geological evidence for low latitude glaciation and represents an alternative interpretation to an entirely ice-covered 'hard snowball' world. This 'open water' climatic solution (dubbed 'slushball Earth') is also predicted by coupled climate-ice sheet models [*Baum and Crowley*, 2001; *Crowley et al.*, 2001; *Hyde et al.*, 2000]. However, this interpretation does offer certain advantages over the 'snowball Earth'. For instance, the widespread occurrence of cyclic Ice Rafted Debris (IRD) rich and IRD-absent diamictite layers are suggestive of periodic and widespread surges of an ice sheet into the open ocean [*Condon et al.*, 2002] and may be analogous to the generation of Heinrich layers in the North Atlantic during the late Quaternary [*Heinrich*, 1988]. Similarly, Neoproterozoic age glaciogenic sedimentary rocks of the Ghadir Manqil Formation, Oman, have been interpreted as recording cycles of relative sea-level change and of strongly pulsed glacial advance and retreat [*Leather et al.*, 2002]. These geological observations appear to be at odds with a completely frozen surface ocean. In general, evidence of an active cryosphere and hydrological cycle during the glaciation [*Arnaud and Elyes*, 2002; *Condon et al.*, 2002; *Leather et al.*, 2002; *McMechan*, 2000] is more easily reconcilable with the presence of a substantial area of open water to act as a moisture source.

Furthermore, the open water solution requires only moderate changes in atmospheric CO_2 to terminate glacial conditions [*Crowley et al.*, 2001]. It is also easier to understand the persistence of viable life through the glacial if the ocean surface is not entirely ice-covered. In the 'slushball', an equatorial belt of open water provides a refugium for multicellular life [*Hyde et al.*, 2000, 2001; *Runnegar*, 2000].

Despite these advantages, the open water solution has been dismissed by the proponents of the 'snowball Earth' hypothesis. Two primary grounds for rejection have been advanced; (i) glacial longevity—it is argued that only a 'snowball Earth', locked in a frozen state is inherently long-lived. An ice-free equatorial ocean, with "ice fronts [that] miraculously approach but never cross the ice-albedo instability threshold" [*Hoffman and Schrag*, 2002] could not be stable [*Hoffman*, 2000; *Hoffman and Schrag*, 2002; *Schrag and Hoffman*, 2001], and (ii) 'cap' carbonate occurrence—the snowball Earth hypothesis posits extremely rapid weathering following deglaciation to provide the necessary alkalinity. This was originally envisaged as being the weathering of silicate rocks [*Hoffman et al.*, 1998], but more recently assumes a two-stage process with a transition from a dominance of carbonate to silicate rock weathering [*Higgins and Schrag*, 2003]. In contrast, the 'slushball' has no inherent mechanism to explain the occurrence of the 'cap' carbonate layers [*Hoffman and Schrag*, 2002; *Schrag and Hoffman*, 2001].

Here we identify a first order difference between Precambrian and modern carbon cycles which explains the extremity of Neoproterozoic glaciation: the absence of a well-developed deep-sea carbonate sink prior to the proliferation of calcareous plankton in the Phanerozoic. This leads us to a geochemical model [*Ridgwell et al.*, 2003b] that supports a 'slushball' interpretation of glacial climate. The model predicts both extensive and long-lived glaciation, as well as the timing of the alkalinity flux recorded by the 'cap' carbonate.

3. CARBONATE DEPOSITIONAL CONTROL OF NEOPROTEROZOIC ICE AGES— A NEW HYPOTHESIS

3.1. Modern Carbon Cycling

A key component of the global carbon cycle throughout Earth history has been the cycling of calcium carbonate ($CaCO_3$). Today, biogenic precipitation of $CaCO_3$ in the open ocean dominates the marine carbonate budget [*Milliman*, 1993; *Milliman and Droxler*, 1996]. This, in turn, is dominated by the calcification activity of planktic foraminifers and coccolithophores [*Schiebel*, 2002]. Although more than 80% of carbonate precipitated in the open ocean dissolves either in the water column or within the uppermost sediment layers, accumulation of $CaCO_3$ in deep sea sediments still represents around half of the present-day global burial rate of $CaCO_3$, with the remainder accumulating in shallow water environments [*Milliman and Droxler*, 1996].

The importance of the deep sea sedimentary $CaCO_3$ sink lies in the fundamental role it plays in stabilization of the concentration of CO_2 in the atmosphere. This works as follows. Any change in the dissolved inorganic carbon (DIC = $CO_{2(aq)} + HCO_3^- + CO_3^{2-}$) inventory or *p*H of the ocean will affect the amount of DIC in the form of carbonate ions (CO_3^{2}) [*Zeebe and Wolf-Gladrow*, 2001]. The stability of the calcium carbonate crystal structure, represented by the saturation state (also known as the solubility ratio) Ω, is directly related to the ambient concentration of CO_3^{2-}; $\Omega = [Ca^{2+}]\times[CO_3^{2-}]/K_{sp}$, where K_{sp} a solubility constant [*Zeebe and Wolf-Gladrow*, 2001]. As a result, the dissolution of $CaCO_3$ in deep sea sediments will respond to changes in ocean carbonate saturation. Furthermore, because the removal rate of CO_3^{2-} is positively correlated with $[CO_3^{2-}]$, the response is of the form of a negative (stabilizing) feedback. For instance, higher $[CO_3^{2-}]$ will equate to increased $CaCO_3$ stability and $CaCO_3$ burial rate, which in turn equates to a higher removal rate of CO_3^{2-} from the ocean. This provides a restoring forc-

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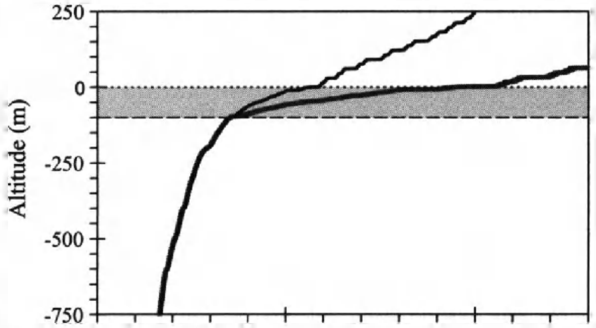

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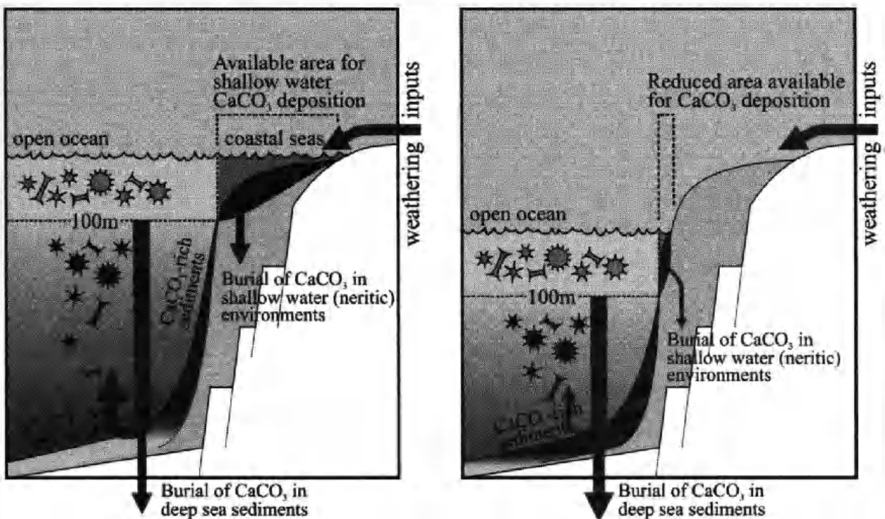

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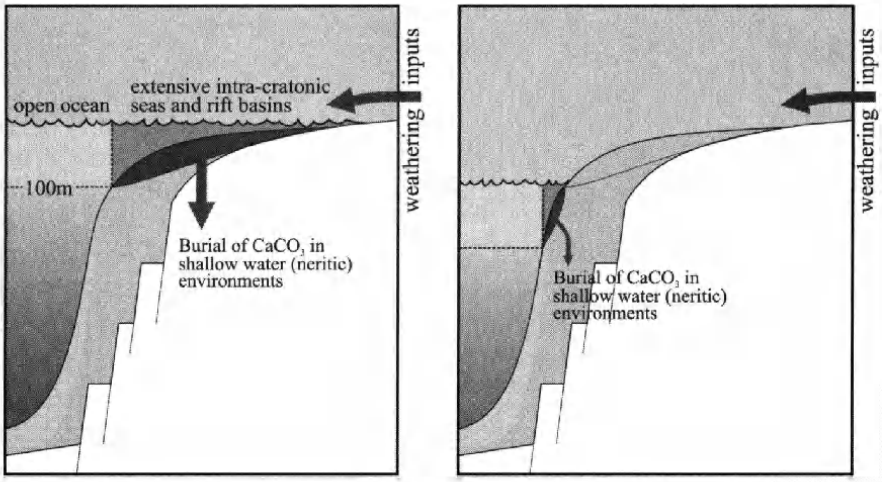

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ical model for this analysis [*Ridgwell et al.*, 2003b]. This calculates the change in ocean carbonate saturation and atmospheric CO_2 that would arise from a reduction in the area available for (neritic) carbonate deposition.

4. A MODEL FOR NEOPROTEROZOIC CO_2

4.1. Model Description

Analysis of the global carbon cycle on timescales relevant to Neoproterozoic glaciation requires model integration for >1 Myr. In contrast, air-sea gas exchange processes which link ocean and atmospheric carbon reservoirs require a time step of order months for numerical stability of the model. Use of a relatively spatially unresolved model is therefore essential. Our chosen strategy is based on the 'PANDORA' atmosphere-ocean carbon cycle 'box' model of *Broecker and Peng* [1986]. The ocean is coupled to a representation of the preservation and burial of $CaCO_3$ in deep sea sediments, following *Ridgwell* [2001] and *Ridgwell et al.* [2002]. The overall atmosphere-ocean-sediment scheme is similar to established modeling tools such as devised by *Caldeira and Rampino* [1993], *Munhoven and François* [1996], and *Walker and Opdyke* [1995].

Loss of dissolved inorganic carbon (DIC) and alkalinity (ALK) from the ocean due to sedimentary burial of $CaCO_3$ is balanced by prescribing DIC and ALK fluxes following *Walker and Opdyke* [1995], but omitting terms representing the erosion (and formation) of sedimentary kerogen. Long-term (order $>10^5$ yr) stabilizing feedback on the system is provided by modifying the DIC (15 Tmol yr^{-1}) and ALK (40 Tmol eq yr^{-1}) fluxes arising from terrigeneous silicate and carbonate rock weathering according to the pre-vascular plant formulation of the GEOCARB model [*Berner*, 1990]. The rate of volcanic CO_2 out-gassing (5 Tmol yr^{-1} [*Walker and Opdyke*, 1995]) is left constant. We impose no additional reduction in global weathering rates explicitly associated with an increase in terrestrial ice cover, consistent with analyses of the late Quaternary glacial geochemical system which indicate little difference in solute fluxes between glacial and interglacial times [*Gibbs and Kump*, 1994; *Jones et al.*, 2002; *Munhoven*, 2002].

An idealized representation of shallow water carbonate buildup is formulated based on the arguments outlined earlier, and coupled to the surface ocean. Because primary precipitation of $CaCO_3$ during the Neoproterozoic is dominantly associated with phototrophic (mainly cyanobacterial) communities [*Riding*, 2000], we assume deposition to be restricted to the photic zone, which is taken to be the uppermost sunlit 100 m. The strength of the $CaCO_3$ sink is then proportional to the total neritic area, A (found by integrating the Earth's surface area flooded to a depth of 100 m or less), to give; $A \times k \times (\Omega\text{-}1)^n$. This treatment is comparable to previous schemes that have been devised for Phanerozoic shallow water carbonate deposition [*Caldeira and Rampino*, 1993; *Munhoven and François,* 1996]. The value of the precipitation rate scaling constant, k is constrained by the requirement that the system should initially be at steady state, with weathering and riverine input balancing the global (neritic) deposition rate of $CaCO_3$. The appropriate value of n for the Precambrian environment is less easy to constrain. At one extreme, abiotic precipitation of calcite exhibits a highly non-linear response to ambient saturation with n in the range $1.9 \leq n \leq 2.8$ at 25°C [*Zhong and Mucci*, 1993]. A small change in $[CO_3^{2-}]$ then has a disproportionately large influence on precipitation rate. In contrast, modern biological systems such as individual corals and whole reef communities appear to be considerably less sensitive, with an approximately first order dependence on Ω [*Leclercq et al.*, 2000; *Marshall and Clode*, 2002]. Additional complications arise because the value of n also varies with other variables such as temperature [*Burton and Walter*, 1987] (which gives neritic deposition an apparent latitudinal dependence [*Opdyke and Wilkinson*, 1993]), ionic strength [*Zuddas and Mucci*, 1998], CO_2 partial pressure [*Zuddas and Mucci*, 1994], and the presence of dissolved inorganic matter [*Lebrón and Suárez*, 1996, 1998]. We therefore initially follow previous (Phanerozoic) carbon cycling studies and assume a uniform value of $n = 1.7$ [*Caldeira and Rampino*, 1993; *Munhoven and François*, 1996]. However, we will later explore the implications of alternative dependencies.

4.2. Initial Conditions

The carbon cycle is configured for the Precambrian as follows. The absence of planktic calcifiers is achieved by setting the export flux ratio of $CaCO_3$ to particulate organic carbon (POC) in the PANDORA ocean carbon cycle model to zero. Ocean chemistry is determined consistent with two criteria; (i) surface ocean in equilibrium with a mixing ratio of CO_2 in the atmosphere of 3400 ppmv. This is a value that has been demonstrated to be sufficient to prevent the formation of ice sheets in climate models of the Neoproterozoic including the effects of a weaker Sun [*Crowley et al.*, 2001; *Hyde et al.*, 2000; *Jenkins and Smith*, 1999], and (ii) mean ocean mixed layer saturation state (calculated with respect to aragonite) of $\Omega_0 = 6.5$, which is consistent with a Neoproterozoic ocean more highly saturated than at present [*Grotzinger and James*, 2000; *Grotzinger and Knoll*, 1995; *James et al.*, 2001]. Ocean DIC and ALK are then uniquely determined if assumptions are made about $[Ca^{2+}]$, for which a present-day value of 10 mmol kg^{-1} is adopted. Mean ocean DIC and ALK are then; 9.494 mmol kg^{-1} and 9.526 mmol eq kg^{-1}, respectively. We note that analysis of the ambient and micro- geochemical conditions

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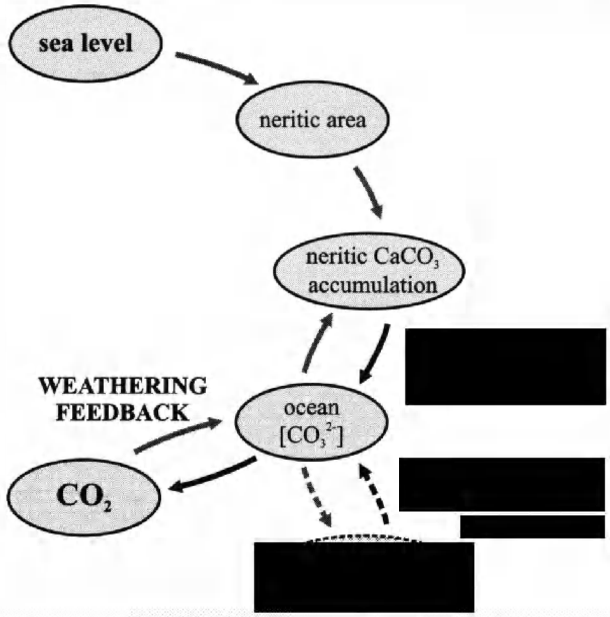

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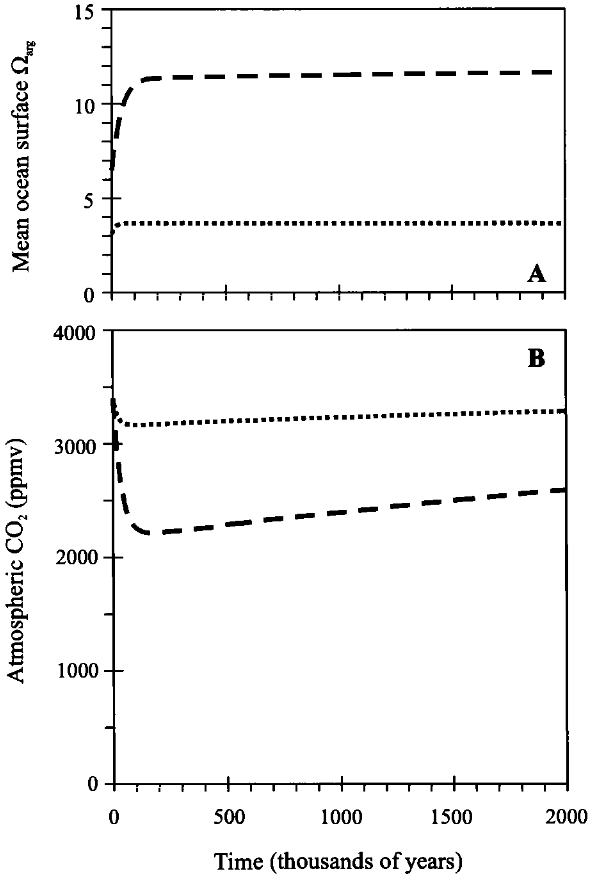

Figure 5. Sensitivity of the carbon cycle to prescribed (-100 m) sea level forcing assuming modern hypsometry and a factor 3.2 reduction in neritic area.
(A) Predicted evolution of mean surface ocean saturation state (Ω_{arg}); with (dotted line) and without (dashed line) a responsive deep sea sedimentary carbonate sink, representing late Phanerozoic and Precambrian systems, respectively.
(B) Predicted evolution of atmospheric CO_2.

ering [*Berner*, 1990], driving an excess of mantle and metamorphic CO_2 input to the system over its removal. This imbalance acts to curtail the magnitude of the CO_2 minimum that can be achieved and subsequently drives the system back towards its initial state (CO_2 = 3400 ppmv).

Thus far, we have assumed modern topography. However, the existence of extensive rifted, subsiding margin, and intracratonic shallow water environments in the late Neoproterozoic (e.g., *Arnaud and Elyes* [2002], *James et al.* [2001], *Leather et al.* [2002], *Prave* [2002]) would result in a proportionally greater reduction in neritic area occurring with a fall in sea level (Figure 3). To assess the sensitivity of CO_2 in a system with a greater shelf-to-slope contrast we modify the modern hypsographic profile by increasing the area lying above the shelf break by a factor of three (Figure 1). This gives a total initial area of shallow water (neritic) environments of 6.1×10^{13} m^2, equivalent to just over one third of present-day cratonic area, but still less than is believed to have occurred during the Paleozoic when high sea level stands resulted in typical flooding extents of between 17 and 88% of total continental area [*Algeo and Selavinsky*, 1995]. The model is re-run and forced with the same 100 m magnitude perturbation of sea level as before. Now, the enhancement of the initial neritic area results in a 10-fold reduction in area with sea level fall. The concentration of CO_2 in the atmosphere is predicted as before.

In assessing the CO_2 response, we considered a range of possible assumptions regarding how strongly $CaCO_3$ precipitation rate responds to a change in ambient [CO_3^{2-}]; n = 1.0 (modern coral-like response [*Leclercq et al.*, 2000; *Marshall and Clode*, 2002]), n = 1.7 (the baseline case, following *Caldeira and Rampino* [1993] and *Munhoven and François*

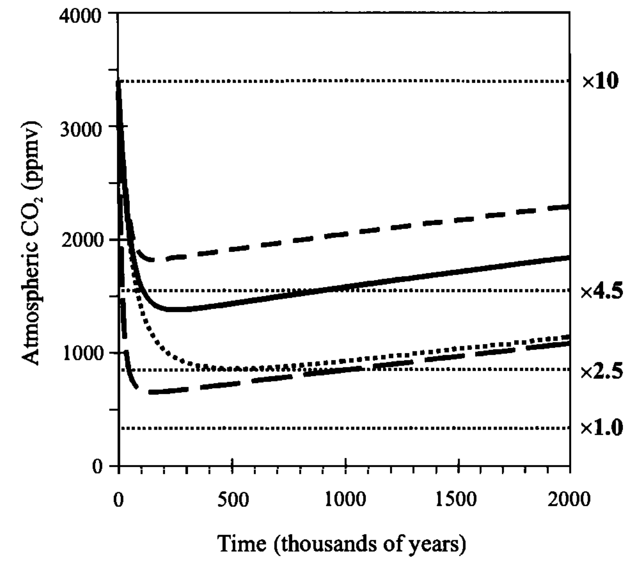

Figure 6. Sensitivity of the carbon cycle to sea level change assuming modified hypsometry. Prescribed (-100 m) sea level forcing as before, but now giving rise to a 10-fold reduction in neritic area upon sea level fall. Predicted evolution of atmospheric CO_2 is shown for different model assumptions regarding how strongly $CaCO_3$ precipitation rate responds to a change in ambient [CO_3^{2-}]; dotted, continuous, and (short) dashed lines corresponding to values of n = 1.0, n = 1.7 (baseline scenario), and n = 2.5, respectively. Also shown is the effect of erosion of previously-deposited carbonates with n = 1.7 (long dashed line). Atmospheric CO_2 concentrations relative to present atmospheric level (PAL) (and assuming 1.0 PAL = 340 ppmv) are highlighted, to indicate; initial conditions (×10 PAL), the "CO_2 attractor" of radiative forcing giving rise to ice-free equatorial waters coexisting with low latitude ice sheets (×2.5 PAL to ×4.5 PAL) [*Baum and Crowley*, 2001], and the approximate limit below which sea-ice instability and run-away ice-albedo feedback into a 'snowball Earth' has been predicted to occur (×1.0 PAL) [*Crowley et al.*, 2001; *Goddéris et al.*, 2003; *Hyde et al.*, 2000].

[1996]), and $n = 2.5$ (a more 'abiotic' mode of precipitation [*Zhong and Mucci*, 1993]). Depending on the value of the model parameter n, atmospheric CO_2 now attains a minimum as low as 859 ppmv (with $n = 1.0$), before the silicate weathering feedback starts to drive the system back towards initial conditions as before (Figure 6). However, the system is less susceptible to perturbation in the abiotic case ($n = 2.5$), and produces a less pronounced CO_2 minimum of 1820 ppmv. The corresponding reduction in radiative forcing of climate due to reduced CO_2 falls between 3.3 and 7.3 W m^{-2}.

It should be noted that the details of the atmosphere-ocean-sediment carbon cycle model used are not critical to our conclusions, and a comparable response to 10-fold reduction in neritic area is exhibited by the model of *Caldeira and Rampino* [1993] [*Caldeira*, pers com]. The assumption that prescribed sea level change takes place near instantaneously (within 1 kyr) appears to be similarly unimportant. We have tested the effect of sea level changing linearly over a period of 10 kyr, and found virtually no difference in CO_2 response. In contrast, the predicted atmospheric CO_2 minimum is highly dependent on the assumed initial value which we take to be 3400 ppmv in the baseline scenario. The results of sensitivity analysis of this dependence are shown in Figure 7. Because the magnitude of the CO_2 draw-down attained is approximately in proportion to the initial CO_2 value, the associated degree of radiative cooling is not strongly dependent on the assumed value of initial atmospheric CO_2. The *climatic* (surface cooling) importance of our mechanism is therefore independent of the assumed initial (atmospheric CO_2) conditions.

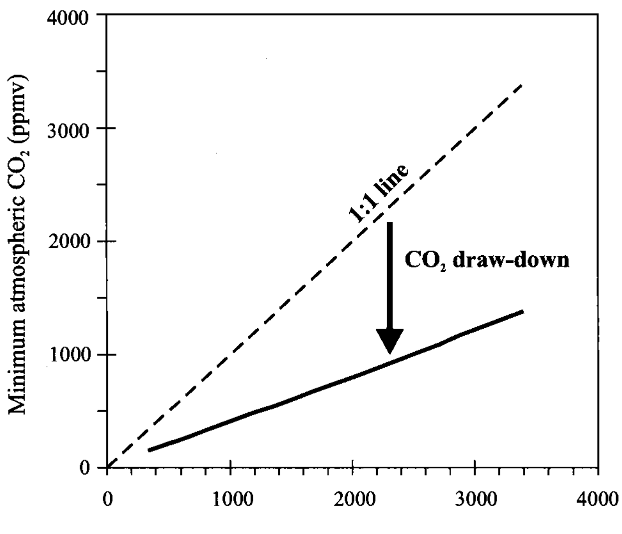

Figure 7. Sensitivity of the predicted atmospheric CO_2 minimum to the assumed initial CO_2 value. The 1:1 line is shown for comparison. Relative CO_2 draw-down (i.e., as a proportion of initial CO_2) is approximately independent of initial CO_2.

5.2. CO_2 Response Limitation by Pelagic Precipitation

An important caveat to our results concerns the possibility that significant pelagic carbonate precipitation takes place as the ocean becomes increasingly supersaturated, perhaps analogous to the occurrence of present-day 'whiting' events [*Robbins et al.*, 1997]. Precipitation of carbonate in the open ocean has the potential to limit the maximum drawdown in atmospheric CO_2 possible due to a fall in sea level. This is because it creates an additional sedimentary sink of $CaCO_3$. The difficulty in quantifying this process is in determining what the likely saturation threshold might be for pelagic carbonate precipitation to come to dominate the global mass budget. The marine geochemical conditions under which whitings occur in the modern ocean is controversial. One explanation for whitings in the Bahama Banks is biologically-induced or inorganic-physiochemical spontaneous precipitation of aragonite crystals in the water column [*Robbins and Blackwelder*, 1992; *Robbins et al.*, 1997]. If correct, the relatively low degree of super-saturation of these waters with Ω_{arg} typically lying between 1.95 and 3.5 would tend to suggest that whitings could be pervasive in the more highly supersaturated Neoproterozoic ocean. However, the balance of evidence strongly suggests that the Bahaman whitings are primarily a re-suspension of underlying sedimentary material [*Broecker et al.*, 2000; *Boss and Neumann*, 1993; *Morse et al.*, 2003]. Observations made in lake and other hydro-chemically restricted environments suggest only minor biologically-induced benthic precipitation (with no evidence of pelagic precipitation) when $7 \leq \Omega_{arg} \leq 11$ [*Arp et al.*, 1999, 2003]. Experimentally, spontaneous (homogeneous) nucleation in sea water solutions is not observed until values of $\Omega_{cal} > \sim 20–25$ [*Morse and He*, 1993]. It is only in extreme chemical environments, such the mixing zones surrounding particular thermal springs (at a theoretical 100-fold supersaturation) do apparently inorganic-physiochemical 'whitings' occur [*Arp et al.*, 1999].

Clearly, the uncertainties associated with pelagic precipitation are substantial. However, based on these arguments it would seem that biologically-induced precipitation of $CaCO_3$ in the Neoproterozoic open ocean is highly unlikely for $\Omega_{arg} < 10$. Inorganic-physiochemical precipitation could ultimately dominate the global budget, but probably only for supersaturation $\Omega_{arg} > 20$.

We illustrate the potential role of pelagic carbonate precipitation in modifying system behavior by means of a sensitivity analysis (Figure 8). In this test, we create an additional sink of $CaCO_3$ that removes all 'excess' CO_3^{2-} from each surface ocean 'box' in the model whenever the saturation state exceeds a prescribed saturation limit; in effect, we constrain the ocean everywhere to be: $\Omega_{arg} \leq \Omega_{thresh}$. The results suggest

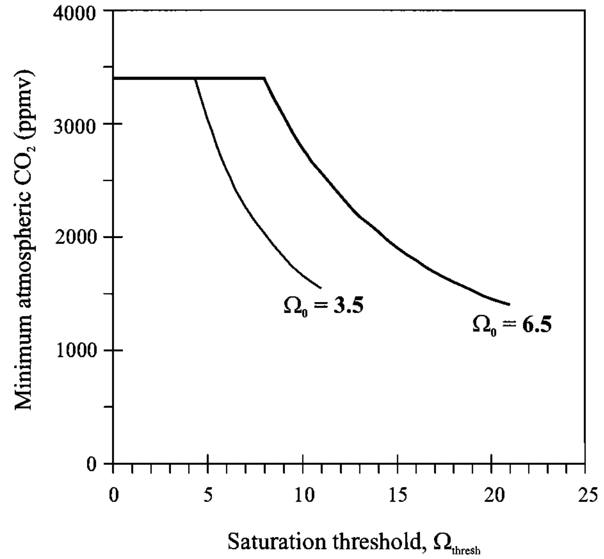

Figure 8. Effect of assumptions regarding the saturation threshold for pelagic carbonate precipitation on the predicted atmospheric CO_2 minimum. Shown is the system response with initial $\Omega_0 = 6.5$ (baseline scenario) and $\Omega_0 = 3.5$ (a saturation state much closer to that of the modern ocean).

that assuming an initial ocean saturation state of $\Omega_0 = 6.5$ (our baseline Neoproterozoic scenario), biologically-induced pelagic carbonate production may become significant for atmospheric CO_2 below ca. 2000 ppmv. It is possible that at the end of the Precambrian, the ocean saturation state was more similar to that of the modern ocean than we have previously argued. In this event, we find that with $\Omega_0 = 3.5$, pelagic carbonate production is unlikely to be important at any point, a consequence of the greater saturation gap between initial and threshold states. Our ability to determine whether CO_2 values could fall below ca. 500–2000 ppmv from an initial value of 3400 ppmv during Neoproterozoic glaciation lies within the uncertainties in knowing Precambrian ocean chemistry and the dynamics of biologically-induced $CaCO_3$ precipitation that pelagic carbonate precipitation.

5.3. The Importance of Feedbacks in the System

Thus far, our analysis has excluded the role of positive feedbacks in the Earth system, which will act to enhance the importance of the carbonate depositional mechanism. For instance, we have assumed that all carbonate, once deposited in the neritic environment is, in effect, isolated from the system. However, when sub-aerially exposed following a fall in sea level, previously deposited carbonates will be subject to erosion [*Munhoven and François*, 1996; *Walker and Opdyke*, 1995]. That this may have occurred associated with the development of glaciation in the Neoproterozoic is consistent with carbon isotopic evidence for platform carbonate truncation in the uppermost Ombaatjie Formation (Namibia) [*Halverson et al.*, 2002]. We test the potential importance of this effect by assuming that previously deposited carbonate units lying above sea level weather at a basic rate of 1.1 mol $CaCO_3$ m^{-2} a^{-1} [*Munhoven and François*, 1996]. This rate is then modified according to the GEOCARB (pre-vascular plant) weathering rate formulation [*Berner*, 1990] as per the riverine DIC and ALK fluxes to the ocean. The results of this are shown in Figure 6. Erosion of previously-deposited carbonates now drives a CO_2 drawdown to a minimum of 651 ppmv (compared to 1377 ppmv in the baseline case) as the excess CO_3^{2-} supply forces the ocean aqueous carbonate equilibrium, $CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$ further to the right to compensate. Initial atmospheric CO_2 drawdown also takes place noticeably more rapidly.

It could be argued that the importance of this carbonate erosion term is already implicit in our earlier assumption that an increase in terrestrial ice cover has no significant impact on the global weathering rate. The basic reasoning behind this is that at the Last Glacial Maximum, the land area lost to increased ice sheet cover is approximately compensated for by the area of exposed continental shelves [*Gibbs and Kump*, 1994]. If area were the only important factor, adding an explicit erosion feedback term runs the risk of counting the weathering of former neritic carbonates twice. However, the shelves contain a disproportionate fraction of carbonate rock compared to global mean lithology. This tends to be relatively recently deposited material and so is also more susceptible to weathering compared to the global average. The potential importance of these factors is reflected in the 20–30% higher bicarbonate flux to the ocean predicted during glacial compared to interglacial periods in the Quaternary glacial geochemical system [*Gibbs and Kump*, 1994; *Jones et al.*, 2002; *Munhoven*, 2002]. We therefore regard the results of the 'with-erosion' (Figure 6) scenario as a maximum end-member effect. The impact of carbonate erosion is likely to be more important during the earlier stages of ice sheet growth, when the area lost due to ice sheet growth will tend to be much less than the epicratonic area exposed by the resulting fall in sea level.

A more fundamental enhancement of the impact of incipient glaciation on atmospheric CO_2 arises through positive feedback between the carbon cycle and climate system. Two feedback loops are identified; (i) reduced neritic deposition $\rightarrow$ increased $[CO_3^{2-}]$ $\rightarrow$ lower atmospheric CO_2 $\rightarrow$ cooling $\rightarrow$ ice sheet growth and further sea level fall $\rightarrow$ reduced neritic deposition, and (ii) lower atmospheric CO_2 $\rightarrow$ cooling $\rightarrow$ higher ocean surface CO_2 solubility $\rightarrow$ lower atmospheric CO_2. These are shown schematically in Figure 9.

Because the atmosphere-ocean-sediment carbon cycle model already implicitly calculates the response of atmospheric CO_2

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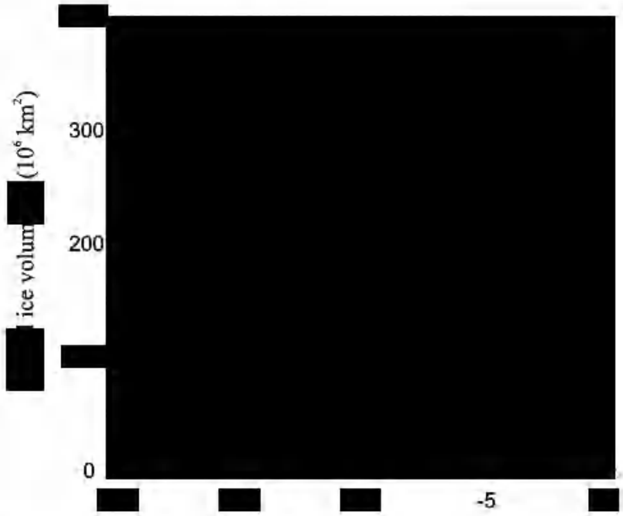

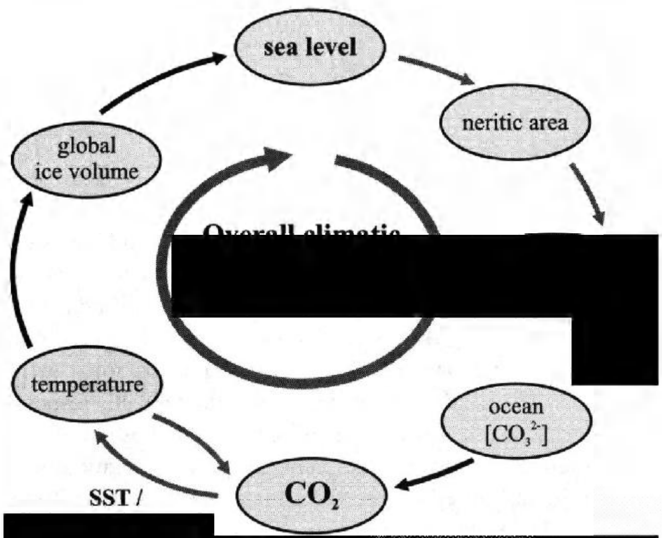

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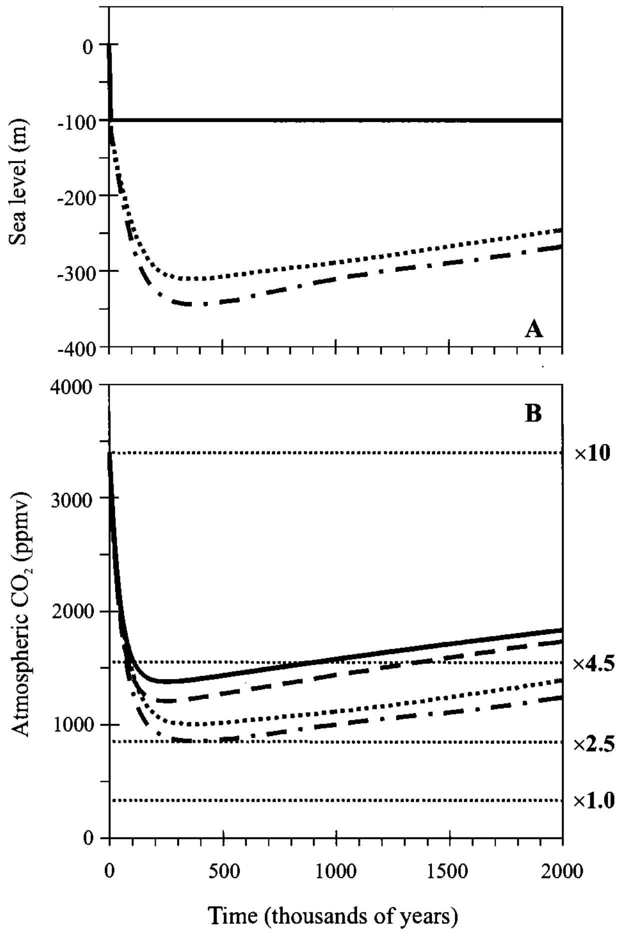

Figure 11. Effect of feedbacks in modifying the sensitivity of CO_2 to sea level change. The baseline model configuration is utilized in each case, i.e. initial 100 m sea level fall, modified bathymetry (10-fold reduction in neritic area), $n = 1.7$, no planktic calcifiers, and no explicit erosion.
(A) Prescribed basic -100 m sea level forcing (black line). Also shown is the resulting evolution of sea level under the influence of either sea level→neritic area→neritic $CaCO_3$ accumulation→$[CO_3^{2-}]$ →atmospheric CO_2→temperature→ice volume→sea level feedback (dotted line), atmospheric CO_2→temperature→atmospheric CO_2 feedback (dashed line, but identical to the solid line of the baseline model and thus hidden), or both feedbacks combined (dot-dash line).
(B) Predicted evolution of atmospheric CO_2 under the influence of the same three feedback combinations, plus the baseline response (black line) for comparison. Atmospheric CO_2 concentrations are highlighted, to indicate; initial conditions (×10 PAL), the "CO_2 attractor" of radiative forcing giving rise to ice-free equatorial waters coexisting with low latitude ice sheets (×2.5 PAL to ×4.5 PAL) [*Baum and Crowley*, 2001], and the approximate limit below which sea-ice instability and run-away ice-albedo feedback into a 'snowball Earth' has been predicted to occur (×1.0 PAL) [*Crowley et al.*, 2001; *Goddéris et al.*, 2003; *Hyde et al.*, 2000].

previously estimated for the late Phanerozoic [*Archer et al.*, 1997, 1998; *Caldeira and Rampino*, 1993]). This can be understood partly in terms of the more extreme ocean chemistry required consistent with both high atmospheric CO_2 [*Crowley et al.*, 2001; *Hyde et al.*, 2000; *Jenkins and Smith*, 1999] and a supersaturated Precambrian ocean [*Arp et al.*, 2001; *Grotzinger and Knoll*, 1995; *Riding*, 2000] (see Section **4**; "A model for Neoproterozoic CO_2"). The extended residence time of mantle and metamorphically-generated carbon in a system with an initial carbon inventory more than four times present then produces a damped feedback response. The two negative (weathering and neritic precipitation) feedbacks also interact antagonistically. For instance, an incremental increase in atmospheric CO_2 driven by 'excess' CO_2 out-gassing will make the ocean more acidic and suppress the degree of supersaturation, Ω_{arg}. The resulting reduction in $CaCO_3$ removal in neritic environments will act to restore Ω_{arg} and thus reverse much of the original atmospheric CO_2 increase. As a result of these factors, a low CO_2 state persists for millions of years. That Precambrian ocean chemistry should deviate sufficiently from the modern system to weaken the silicate weathering feedback on climate and allow long-lived and stable glaciation has not previously been recognized.

6. MAGNITUDE AND STABILITY OF NEOPROTEROZOIC ICE AGES, AND OCCURRENCE OF 'CAP' CARBONATES

6.1. The Occurrence of Extreme Ice Ages

In the absence of planktic calcifiers, the high degree of sensitivity to sea level change of atmospheric CO_2 and radiative forcing has far-reaching implications for understanding Neoproterozoic glaciation. We hypothesize that cooling and incipient ice cap growth during the Neoproterozoic triggered our carbonate depositional mechanism. Loss of depositional environments (and associated feedbacks) was then directly responsible for the unusual severity and longevity of these ice ages.

The required trigger is incipient glaciation and initial sea level fall; as limited as one third the maximum magnitude attained during the late Quaternary. A period of enhanced organic carbon burial is one possible mechanism for driving climatic cooling and incipient glaciation. This is consistent with observations of highly enriched carbonate $\delta^{13}C$ immediately prior to glaciation [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2002; *Kennedy et al.*, 1998]. Suggestions for the driver for this organic carbon burial event include an enhanced weathering flux of phosphorous to the ocean associated with hypothesized early plant colonization of land [*Lenton and Watson*, submitted]. Catastrophic cooling due to the sudden loss of a 'methane greenhouse' [*Schrag et al.*, 2002], CO_2 drawdown from the weathering of extensive fresh basaltic provinces [*Goddéris et al.*, 2003], and reduced insolation in the aftermath of a comet/asteroid impact [*Bendtsen and Bjerrum*, 2002] are other alternatives that have been suggested.

We favor a fundamental role for supercontinent formation and fragmentation phases which, in driving substantial changes in continental emergence/submergence [*Crowell*, 1999] provide the necessary topographic boundary conditions. Relocation of substantial continental area to the pole, or to the tropics (where enhanced weathering could drive CO_2 draw-down and achieve the necessary cooling threshold [*Goddéris et al.*, 2003]) would be consistent with this view. Indeed, it has been noted that episodes of Neoproterozoic glaciation are separated on a tectonic timescale [*Hoffman and Schrag*, 2002; *Kennedy et al.*, 1998; *Prave*, 1999], compatible with an overall tectonic control on the timing of glaciation. The apparent ca. 1000 Ma absence of severe glaciation prior to the Neoproterozoic [*Brasier and Lindsey*, 1998; *Crowell*, 1999] may then be due to an absence of sufficient topographic contrast in the earlier Proterozoic. An absence of extensive rifting episodes, for instance, could explain this. Unsuitable hypsometry might also help explain why glaciation at the end Ordovician was comparatively 'mild' and short lived [*Brenchley et al.*, 1994; *Crowell*, 1999], although a change in carbonate deposition with the advent of carbonate secreting organisms (metazoans) at the Precambrian-Cambrian boundary is likely to be critical [*Ridgwell et al.*, 2003].

Glaciation has been a frequent feature throughout the Phanerozoic, and has a wide variety of suspected causes [*Crowell*, 1999]. That glaciation should also occur during the Neoproterozoic is not entirely surprising. What is unusual, however, is the severity and inferred duration of the recorded ice ages. It is this aspect of the geological record that is explicitly explained by our model, rather than the initial occurrence of glaciation and sea level fall per se.

Thus, given a suitable incipient glacial trigger, we predict a dramatic reduction in the concentration of CO_2 in the atmosphere to a persistently low value in the range 800–1400 ppmv (Figures 6,11). This is a robust result with respect to a range of different model assumptions, including; (a) the dependence of $CaCO_3$ precipitation rate on ambient $[CO_3^{2-}]$ (the parameter 'n'), (b) erosion of previously deposited carbonates when sub-aerially exposed, and (c) the action of sea surface temperature and ice volume/sea level feedbacks. We find that model-predicted glacial CO_2 corresponds well with the "CO_2 attractor" of radiative forcing parameter space of *Baum and Crowley* [2001]; equivalent to ~×2.5 to ×4.5 'present-day' level (PAL) of CO_2 ,or 850 to 1530 ppmv assuming 1.0 PAL = 340 ppmv. This degree of radiative forcing gives rise to an open equatorial ocean coexisting with low latitude ice sheets in GCM and coupled climate-ice sheet models [*Baum and Crowley*, 2001]. With an open equatorial ocean there would be an active hydrological cycle, which is fully consistent with observed characteristics of glacial diamictite deposition [*Arnaud and Elyes*, 2002; *Condon et al.*, 2002; *Leather et al.*, 2002; *McMechan*, 2000]. Furthermore, multicellular life would have survived in the refugium provided by an equatorial belt of open water [*Hyde et al.*, 2000, 2001; *Runnegar*, 2000].

Our sensitivity analyses suggest that CO_2 concentrations low enough to cross the threshold required for sea-ice instability and run-away ice-albedo feedback into a 'snowball Earth' are difficult to achieve. In many climate models that exhibit a sea-ice instability, this threshold is found somewhere below ca. 340 ppmv (×1.0 PA) [*Crowley et al.*, 2001; *Goddéris et al.*, 2003; *Hyde et al.*, 2000]. Clearly, our analysis of the Precambrian carbon cycle is not exhaustive—there may be further mechanisms and feedbacks that would act to enhance the CO_2 draw-down resulting from an initial fall in sea level. However, analysis of the potential role of pelagic precipitation carried out earlier (Figure 8) suggests that there is a fundamental limitation on the degree of over-saturation (and thus CO_2 draw-down) that can be achieved in the ocean. Although the uncertainties are substantial, the associated minimum limit placed on atmospheric CO_2 may be ca. ≥500 ppmv (from an initial state of 3400 ppmv). On time scales of ca. < 1 Myr, the Neoproterozoic global carbon cycle may therefore be inherently unable to provide the radiative cooling necessary for rapid development of 'snowball' glaciation through atmospheric CO_2 draw-down. The occurrence of 'snowball Earth' conditions therefore requires that more exotic and speculative means of global cooling, such as the sudden loss of a methane 'greenhouse' [*Schrag et al.*, 2002] be invoked.

In our model, the glacial period would have persisted until reduced silicate weathering brought the system to a radiative (CO_2) threshold for deglaciation, analogous to the mechanism proposed for the termination of Late Ordovician glaciation [*Kump et al.*, 1999]. We predict that the period of time required for this would have been of the order of millions of years, consistent with the inferred duration of the glaciation [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2002]. However, in the absence of explicit representation of the interactive response of the climate-cryosphere-lithosphere system, the timing of deglaciation cannot be predicted a priori by our current model. We therefore artificially impose a reversal of the initial sea level change after 2 Myr to simulate deglaciation (Figure 12A). This leads us to a further important piece of the Neoproterozoic jigsaw.

6.2. The Origin of the 'Cap' Carbonates

An explicit prediction of our hypothesis is that a relationship should exist between the thickness of post-glacial 'cap' (dolo-

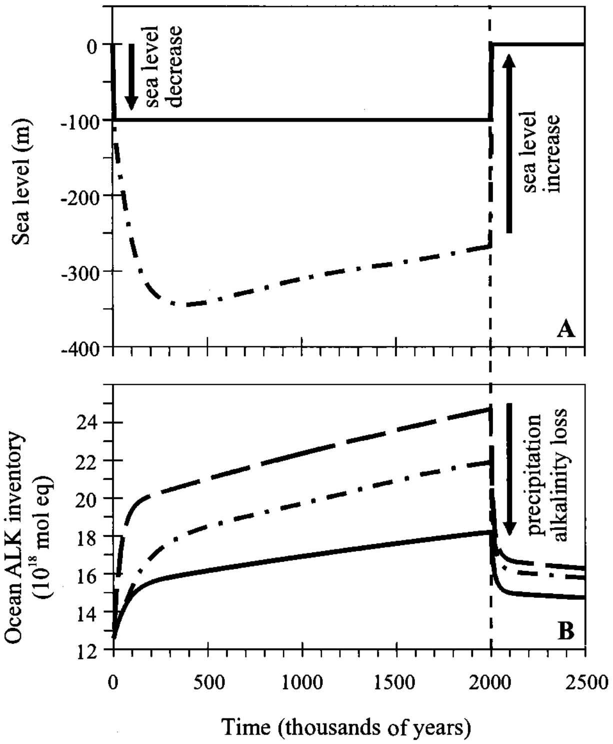

Figure 12. Response of alkalinity inventory to deglaciation. (A) Sea level change, with a 100 m sea level rise applied after 2 Myr. Curves of the evolution of sea level are shown for the following model integrations (all assuming modified hypsometry); (i) baseline (n = 1.7), no erosion or feedbacks (solid line), (ii) n = 1.7, erosion but no feedbacks (long dashed line, but identical to the solid line of the baseline model and thus hidden), and (iii) n = 1.7, no erosion but both sea level→neritic area→neritic $CaCO_3$ accumulation→$[CO_3^{2-}]$→atmospheric CO_2→temperature→ice volume→sea level and atmospheric CO_2→temperature→atmospheric CO_2 feedbacks (dot-dashed line).
(B) Oceanic alkalinity (ALK) inventory. Rapid deglacial removal of alkalinity through carbonate precipitation is highlighted by an arrow.

stone) carbonate facies and the 'excess' alkalinity accumulated in the ocean during the glacial as a result of loss of shallow water depositional environments. We find that within 5×10^4 years of deglaciation, 2.8-7.1$\times10^{18}$ mol eq of accumulated alkalinity (1.4–3.5$\times10^{18}$ mol $CaCO_3$) is lost through excess deposition in neritic environments, with over half occurring in less than 10^4 years (Figure 12B). Assuming a post-glacial neritic area of 6.1×10^7 km^2 (three times the area of the present-day shelf), this is sufficient to form a carbonate layer averaging between 0.8 and 2.1 m thick, assuming a density for aragonite of 2.9 g cm^{-3}, and zero initial porosity. The range and maximum thickness of carbonate would be considerably extended with heterogeneous distribution of the deposition, both with latitude (precipitation in warm tropics favored over that in colder polar regions) and depth (warmer shallow sunlit platforms favored over cooler deeper basins). Any porosity associated with initial precipitation and only subsequently infilled by secondary cements would also increase the effective thickness of the facies predicted by our model.

Although we chose to apply the sea level rise over an interval of 1 kyr in this analysis, by analogy with the late Quaternary, ice sheet collapse would be rapid and could be largely complete within just ~5 kyr [*Fairbanks*, 1989]. Assuming this slightly longer period of sea level rise has little effect on the total mass of $CaCO_3$ deposited. However, a slower rate of sea level rise would help account for the observed variability in 'cap' thickness, as lower-lying areas would be flooded earlier and thus experience the higher initial degree of saturation (and more rapid precipitation).

Regardless of possible modifying factors, our quantitative predictions coincide with typical 'cap' (dolostone) carbonate facies thicknesses observed in shelfal settings of order meters [*Grotzinger and Knoll*, 1995; *James et al.*, 2001; *Kennedy*, 1996; *Kennedy et al.*, 1998; *Kennedy et al.*, 2001b; *Myrow and Kaufman*, 1999]. Thus, the timing, thickness, and inferred rapid precipitation of 'cap' carbonate is consistent with a 'coral reef' like mechanism [*Kennedy*, 1996], with rapid deposition on newly flooded continental shelves taking place from a highly oversaturated ocean.

Because the glacial ocean is characterized by a high degree of super-saturation, any hiatus in the deposition of glaciogenic sedimentary material could allow the formation of sufficient in situ carbonate precipitation to form identifiable features in the geological record. The restrictive area afforded by the continental slope for deposition at low glacial sea level stand will produce a strong sampling bias against finding such evidence. In spite of this, distinctive in situ synglacial carbonates have been observed [*Kennedy et al.*, 2001a]. Such evidence is incompatible with the undersaturated to (no greater than) marginally saturated glacial ocean that is possible during a 'snowball Earth' like event [*Higgins and Schrag*, 2003; *Hoffman and Schrag*, 2002].

7. A 'SLUSHBALL EARTH' WITH CAP CARBONATES?

Where does this analysis leave the viability of an open ocean 'slushball' interpretation of Neoproterozoic glaciation as an alternative to the extreme deep freeze of a 'snowball Earth'? Both the magnitude and longevity of the glacial, as well as the post-glacial deposition of the enigmatic 'cap' carbonates can be understood in terms of weak 'buffering' of the Precambrian carbon cycle [*Ridgwell et al.*, 2003b]. Because the radiative forcing necessary for low latitude ice sheets to co-exist with an open tropical ocean is consistent with the CO_2

draw-down predicted by our model, the requirements both for viable life to persist and active hydrological cycling to continue throughout the glacial period are also easily accommodated. All these key geological observations arise naturally from the dynamics of a Precambrian carbon cycle in the absence of pelagic calcifiers, and do not require invocation of a specific sequence of poorly supported geochemical and climatic conditions. Our model of carbonate depositional control therefore helps provide a more parsimonious explanation of Neoproterozoic glaciation than does a 'snowball Earth'.

Acknowledgments. Both authors would like to thank NSF EAR for financial support, Ken Caldeira for advice on modeling strategies, and helpful feedback provided by various colleagues, with particular thanks to; Nick Christie-Blick, Sören Jensen, Bob Gaines, and Seth Finnegan. As the University of East Anglia 'John Peyton Research Fellow', AJR would like to acknowledge the Trusthouse Charitable Foundation for providing additional financial assistance.

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A Review of Neoproterozoic Climate Modeling Studies

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Over the past decade, a number of climate modeling studies have examined the possibility of simulating low-latitude glaciation using Neoproterozoic boundary conditions. Many of the studies undertaken have used the thermodynamic slab ocean, which includes the top 100 meters of the ocean. These models have successfully simulated Hard Snowball Earth conditions, while recent simulations using fully coupled atmosphere-ocean models have not been able simulated Hard Snowball Earth conditions. Moreover, ice-sheet models have been run offline using GCM fields to simulated ice-sheets on land under "Hard" and "Soft" Snowball Earth Conditions. However, until of the climate models include additional components of the climate system including geochemical, dynamic ocean, sea ice and ice-sheet components uncertainty will exist in our understanding of Neoproterozoic low-latitude glaciation.

1. INTRODUCTION

The climate of Proterozoic Eon (2.4 Ga–544 Ma) is comprised of extremes in climate conditions with evidence of glacial deposits in the Palaeoproterozoic (~ 2.4–2.1 Ga) [*Evans et al.* 1997] and the Neoproterozoic (800–580 Ma) [*Chumakov and Elston,* 1989; *Schmidt and Williams,* 1995, *Hoffman et al.* 1998, *Evans,* 2000] separated by a relatively long warm period (2.0–.8 Ga) lacking glacial deposits. The Proterozoic glacial periods differ from those of the Phanerozoic in the location of glacial deposits with Palaeoproterozoic and Neoproterozoic glacial deposits found in low-latitudes. In order to explain low-latitude deposits it would have been necessary for an ice-covered or nearly ice-covered planet unless the axial tilt were different from the present. Evans [2000] has shown that glacial deposits are found on nearly every continent at latitudes less than 60°.

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10.1029/146GM07

Two competing hypotheses can explain the observations of low-latitude glacial deposits. In the first hypothesis, called the Sno*wball Earth hypothesis [Kirschvink, 1992;* Hoffman et al. 1998], ice migrated towards the Equator via the ice-albedo feedback as first proposed by Budkyo [1969] and Sellers [1969]. The growth of sea-ice and snow was triggered by the reduction of a greenhouse gas, primarily CO_2 via silicate weathering of the tropical super-continent [*Hoffman,* 1998]. In order to support the geologic evidence of glacial deposits near the Equator, "Hard" Snowball Earth conditions (sea-ice extending from the poles to the Equator) would have been required. A number of climate modeling studies have shown that "Hard" Snowball Earth conditions are possible. "Soft" Snowball Earth conditions, with an ice-free ocean zone is also a solution for explaining low-latitude glacial deposits and would provide a refuge for life [*Hyde et al.* 2000].

In the second hypothesis, the High Obliquity hypothesis, the Earth acquired high obliquity through the collision between the Earth and a Mars sized planetesimal early in its history and remained high until the end of the Proterozoic [*Williams,* 1993]. Under high obliquity low-latitude glaciation would occur through the assemblage or migration of a landmass into low-latitudes. Simulations of high obliquity have been undertaken and provide a solution to low-latitude glacial conditions *[Jenkins,* 2000; *Jenkins,* 2003].

Testing the various hypotheses associated with extreme Proterozoic climatic conditions requires the use of climate models. Given the boundary conditions that existed for the time period in question, these models should offer some insights with respect to the validity of the Snowball Earth or High Obliquity hypothesis. The modeling efforts should also try to account for various feedbacks in the climate system, especially those associated with the hydrologic cycle. This includes: water vapor mixing ratios, clouds and precipitation and evaporation changes (Figure 1). In the case of low-latitude glaciation, it is also necessary to model the thermodynamic and dynamic features of sea-ice, snow, ocean processes and land-ice sheets. Unfortunately, state-of–the-art climate models cannot represent all the factors in a complete manner at present. Thus while it may be possible to evaluate the various hypotheses, some degree of uncertainty exists about the conclusions drawn from climate model results.

Hoffman et al. [1998] applied results from a 1-dimensional energy balance model (EBM) [*Sellers,* 1969] to support the causes for Neoproterozoic low-latitude glaciation. The EBM, however, neglects many processes and feedbacks that could either trigger or inhibit low-latitude glaciation. Two important Neoproterozoic boundary conditions were reduced solar forcing (~ 6% lower than present) and the low-latitude super-continent, Rodinia. In addition to lacking many of the physical processes (dynamics, hydrologic cycle, atmospheric thermodynamics), 1-D EBMs cannot resolve longitudinal features including the super-continent, which could have been a triggering mechanism for low-latitude glaciation.

Global climate models (GCMs) are computer programs that use the laws of physics to predict climate states. GCMs account for atmospheric motions, the hydrologic cycle, solar and infrared radiative processes, sea-ice, snow and the ocean. However the dynamic components of sea-ice and the ocean have been neglected in many of the Neoproterozoic studies. In many of the studies discussed below, only the thermodynamic state of the top 100 meters of the ocean (mixed layer or slab-ocean) is considered. Given that the mixer layer responds primarily to solar radiation and turbulent mixing on seasonal timescales the formulation gives reasonable simulation of the present-day climate. However for extreme changes in the climate systems, such as Neoproterozoic glaciation, slab ocean formulation has limitations. For example, the distribution of Neoproterozoic landmasses could produce a quite different horizontal and vertical ocean circulation. This, in turn, could alter the degree to which sea-ice migrates into lower latitudes. Moreover, the salinity/temperature/density relationship to the deep ocean circulation may be quite different from that of the present-day in the context of Snowball Earth. A fully coupled Atmosphere-Ocean GCM (AOGCM) may be the best option for examining the ocean's response to extreme climatic conditions. A similar argument can be made for sea-ice parameterizations. In many climate models sea-ice forms at a fixed temperature (such as 271.2° K) but the motion of sea-ice caused by internal and external forces are neglected. If estimates of 1 km thick sea-ice did exists during "Hard" Snowball Earth conditions in the Neoproterozoic then the thermodynamic formulation of sea ice is a poor choice because the dynamic component of sea-ice (motion, internal forces) would be quite important. Moreover, the coupling between sea-ice and the ocean through brine expulsion can produce density changes thereby influencing the ocean's vertical circulation. The goal of this paper is to review climate model simulations of Neoproterozoic low-latitude glacial events with an emphasis on GCM studies.

2. CLIMATE MODEL STUDIES OF NEOPROTEROZOIC GLACIAL CONDITIONS

2.1. EBM Studies

The 2-dimensional EBM study of Crowley and Baum [1993] was one of the first to consider simulating Neoproterozoic low-latitude glaciation. This EBM included a sea-ice and snow albedo parameterization, but did not directly account for the hydrologic cycle. Using a low-latitude idealized super-continent, a reconstruction based on Bond [1984] and a 6 percent reduction in solar forcing they were able to simulate low-latitude glaciation when CO_2 levels were approximately 120 ppmv or less. Moreover, only a super-continent that extended into middle/high latitudes could produce Snowball Earth conditions at 100 ppmv of CO_2. This study also showed the possibility of landmasses serving as a genesis site for ice-sheets.

2.2. GCM Simulations of Neoproterozoic Glacial Conditions

2.2.1. Fixed SST and Slab Ocean Studies. Over the last decade a number of GCM studies have been used to examine: (1) whether low-latitude glaciation is possible using boundary conditions of the Neoproterozoic, (2) if "Soft" Snowball Earth conditions are possible. The majority of the studies have used a slab ocean, which considers the thermodynamic state of the top 50–100 meters of the ocean (mixed layer). However, Jenkins and Frakes [1998] used a GCM with fixed SSTs in order to determine if year-round snow could be maintained on an idealized super-continent in low-latitudes using Neoproterozoic CO_2 and solar forcing boundary conditions. These results showed that it was not possible to maintain year-round snow in the interior of the continent with a 5% reduction and 100 ppmv CO_2 in the solar constant because of high tropical insolation and the moderating effect of the surrounding ocean.

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mixing occurs because cooler temperatures promote denser ocean water and sinking of cooler waters. Consequently, the exchange of warmer waters below and the surface leads to warming of 7°C near the sea-ice edge. This process is reasonable given what is known about the thermohaline circulation. In fact, the convective mixing could be underestimated because brine is not expelled in the simulated formation of sea-ice. The brine would increase the density of the ocean water promoting further sinking and exchanges of surface and subsurface waters.

Poulsen et al. [2002] also explored the role of paleography on Neoproterozoic low-latitude glaciation using the coupled atmosphere-ocean GCM. They used idealized low-latitude landmasses and a reconstructed landmass corresponding to 545 Ma [Dalziel, 1997]. These simulations did not yield snowball Earth conditions although the 545 Ma reconstruction did

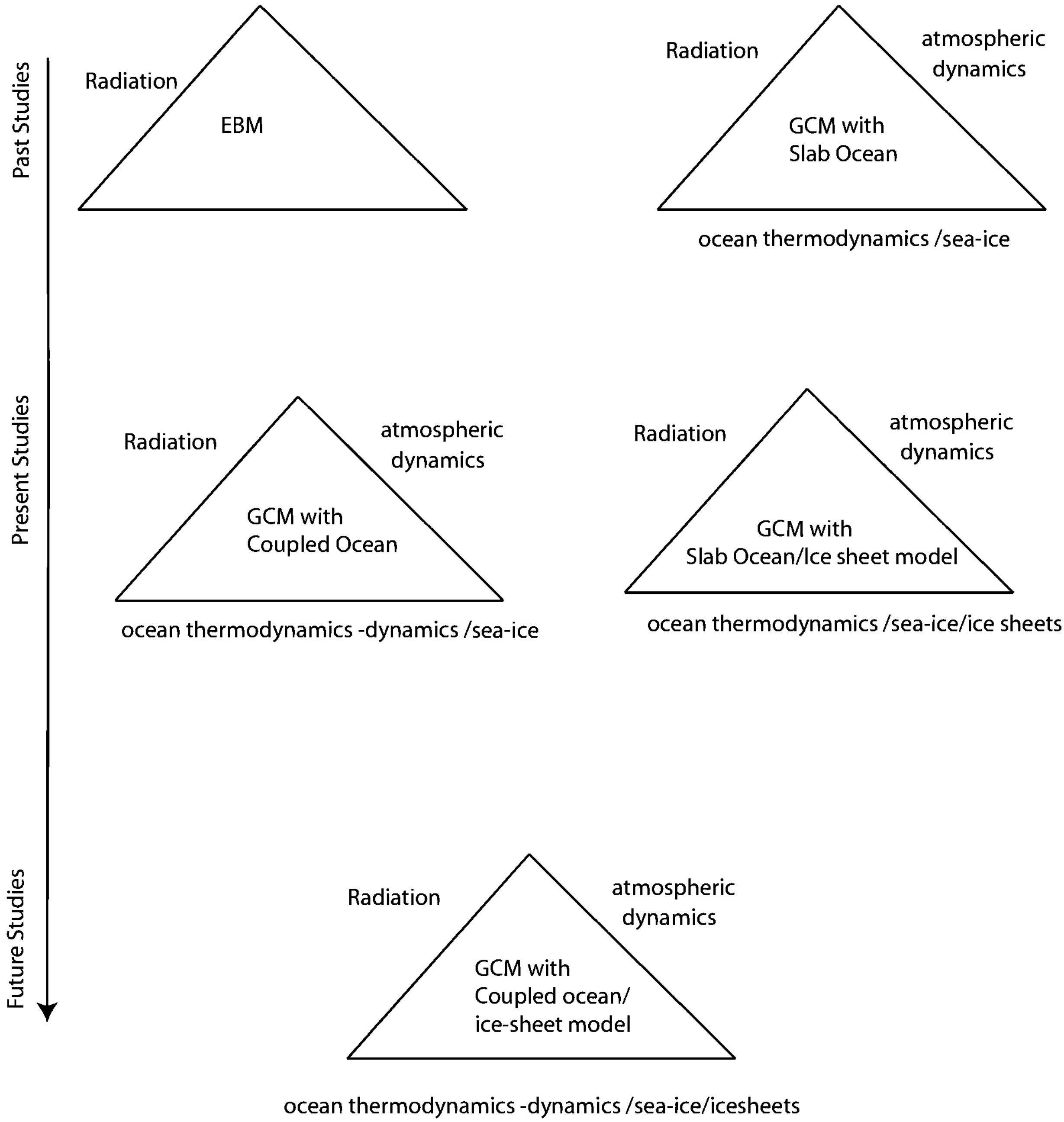

Figure 2. The evolution of climate models used in understanding Neoproterozoic low-latitude glacial conditions.

produce lower global mean temperatures (-0.58°C). The sea-ice margin in these simulations were 42° for the 545 Ma reconstruction and 51° for the idealized tropical super-continent simulations. These coupled simulations suggest that the ocean in the primary factor inhibiting the transition to "Hard" Snowball Earth conditions.

Poulsen [2003] specified ice into low-latitudes (within 10° of the Equator in both hemispheres) in order to bring about "Hard" Snowball Earth conditions in a coupled atmosphere-ocean GCM. In this simulation the boundary conditions of the Neoproterozoic were used (7% reduction in solar forcing, idealized low-latitude super-continent) and atmospheric CO_2 of 140 ppmv was specified. A sea-ice thickness of approximately 1000 meters was used at latitudes poleward of 10° and could migrate equatorward but was not allowed to melt in higher latitudes. The result shows that "Hard" Snowball Earth conditions do not occur, but rather that Equatorial latitudes remain ice-free. The tropical mixed layer ocean stores heat during the summer season and releases this heat during the winter thereby maintaining above freezing winter season low-latitude ocean temperatures. In a second experiment, the constraint of fixed sea-ice in latitudes poleward of 10° was removed. In this case, the sea-ice edge retreated poleward into middle latitudes (45°), which is similar to the mid-latitude sea-ice edge position of Poulsen et al. [2001]. In summary, these results do not support "Hard" Snowball Earth conditions at considerably lower CO_2 levels relative to the slab-ocean studies. The sea-ice edge simulated by Poulsen [2003] is poleward of Chandler and Sohl [2002], the only slab-ocean GCM study that produced "Soft" Snowball Earth conditions with CO_2 concentrations less than 140 ppmv.

2.2.3. Coupled Atmosphere-Ice Sheet GCM simulations of Neoproterozoic glacial conditions. Another area of uncertainty with respect to Neoproterozoic climate studies is the role of land-glaciers. Most GCMs do not currently incorporate ice-sheet models that can predict ice flow, mass balance and bedrock sinking. Including these components into a GCM would take thousands of model years to integrate. It is possible, however, to incorporate an ice-sheet model by running it off-line using GCM boundary conditions (temperature, precipitation). Only a few studies incorporating ice-sheet models driven by EBMs [*Hyde et al.* 2000] and GCMs [*Donnadieu et al.* 2003; *Pollard and Kasting* (this volume)] for Neoproterozoic boundary conditions have been completed.

Hyde et al. [2000] used a 2 dimensional EBM to drive an ice-sheet model with a reconstruction corresponding to 545 Ma [*Dalziel,* 1997], lower solar forcing and reduced CO_2. Snowball Earth conditions were produced with a CO_2 value of 130 ppmv and the inclusion of the ice-sheet model led to the growth of ice-sheets on land masses. These simulations suggest that there would have been a significant reduction in sea level with the building of ice-sheets on the Neoproterozoic reconstruction.

Donnadieu et al. [2000], used GCM fields from a 3 x CO_2 simulations to drive their ice-sheet model in order to examine the growth of land glaciers on a reconstructed low-latitude land mass corresponding to 750 Ma and a 6% reduction in the solar constant. At $3 \times CO_2$ the sea-ice edge is located poleward of 30° and does not lead to "Hard" Snowball Earth conditions. Under these conditions it is not possible to build ice-sheets in low-latitudes over land masses because of warm temperatures. However, Donnadieu et al. [2003] show that if "Hard" Snowball Earth conditions were to occur, then it would be possible to build ice-sheets on all land-masses including those in low-latitudes over several hundred thousand years.

3. CONCLUSION

The modeling aspects of Neoproterozoic low-latitude glacial periods are occurring at a fairly rapid pace with the number of coupled studies increasing. The majority of GCM simulations with a slab-ocean formulation suggest that "Hard" Snowball Earth conditions are possible once CO_2 concentrations are lower than approximately 2.5 time the present-day values. Recent AOGCM and atmosphere-ice-sheets GCM studies have provided new insights about the possibility of "Hard" Snowball Earth conditions and the growth of land-glaciers under "Soft" and "Hard" Snowball Earth conditions. Even with these recent advances, a fully coupled climate system model is necessary to understand feedbacks amongst the various components of the climate system (Figure 2).

Based on the recent modeling studies the ocean is the primary source of uncertainty with respect to the growth of land glaciers in low-latitudes. If the ocean remains open in low-latitudes as suggested by Poulsen et al. [2001], Poulsen et al. [2002] and Poulsen [2003] then permanent snow on land leading to the growth of ice-sheets is not likely [Jenkins and Frakes, 1998; Donnadieu et al. 2003]. It is also necessary to couple an ice-sheet model to GCMs/AOGCMs because solar radiation will interact with ice-sheets in low-latitudes leading to additional melting because of the direct input of energy. This effect cannot be simulated at present but only indirectly inferred through temperature. The coupling a GCM to an ice-sheet model remains problematic because the different time-scales necessary to reach equilibrium amongst the atmosphere (several years), oceans (hundreds of years) and ice-sheets (> 100,000 years).

Acknowledgments. I would like to thank the reviewers for their comments and the editors of this monograph. The simulations were supported by the Earth Environment Institute at Penn State University.

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Global Tectonic Setting and Climate of the Late Neoproterozoic: A Climate-Geochemical Coupled Study

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Whereas the snowball Earth hypothesis seems to account for most of the major features of the Neoproterozoic glacial records, the causes that drove the Earth into a snowball state remain largely open to debate. Most of the mechanisms leading to the initiation of a snowball Earth are based on the existence of the unusual preponderance of land masses in the tropics. However, the time of the youngest Neoproterozoic glaciation is characterised by a rather widely distributed geography from low-to-high latitudes. In the absence of reliable knowledge of Neoproterozoic topography, two series of coupled ocean-atmosphere climate model simulations were carried out with a Late Neoproterozoic paleogeography (580 Ma) and solar luminosity reduced by 6% relative to today, the first one with flat continents and the second one with mountain ranges that mimic the Pan-African Orogen occurring at this time. Those climatic simulations coupled to the long-term carbon cycle have allowed to better constrain the atmospheric pCO_2 and the associated climate by the time of the youngest late Proterozoic glaciation. The Pan-African Orogen runs result in a snow accumulation pattern compatible with a regional-scale glaciation more less extensive while the no relief runs do not succeed in initiating any glaciation. These results could give additional support to the inferences from many authors that some of the glacial deposits originally attributed to a snowball-like glaciation could in fact be the consequence of a more localised glaciation due to the important orogen occurring at the end of the Neoproterozoic.

1. INTRODUCTION

The Earth underwent at least two episodes of severe glaciation at the termination of the Proterozoic era, one around 730 Ma (Sturtian/Rapitan episode), and a second one around 600 Ma (Marinoan/Varangian episode). In 1992, Kirschvink [1992] suggested that both episodes might correspond to a complete glaciation event (the "snowball Earth" hypothesis), with total

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10.1029/146GM08

cover-up of continental and oceanic surfaces by ice. This hypothesis seems to account for most field observations, and especially for the low paleolatitudes glacial deposits inferred from paleomagnetic results (see [*Donnadieu et al.*, 2003] and [*Pollard and Kasting*, 2003]) as well as for the depletion in ^{13}C observed in the cap carbonates overlying the glacial deposits [*Donnadieu et al.*, 2003; *Hoffman et al.*, 1998a; *Hoffman et al.*, 1998b]. Hoffman and colleagues interpret this negative shift in $\delta^{13}C$ to be the consequence of prolonged low organic productivity during snowball events, high rates of carbonate sedimentation due to the high alkalinity and carbon fluxes into the ocean as a result of enhanced weathering during the "super-greenhouse" climate in the aftermath of the snowball glaciation. Whereas the snowball Earth hypothesis seems to account for most of the major features of the Neoproterozoic glacial records, the causes that drove the Earth into a snowball state remain largely open to debate. Most of the mechanisms leading to the initiation of a snowball Earth are based on the existence of the unusual preponderance of land masses in the tropics (see below the part 2). However, if a general consensus has merged favouring a low to mid latitude supercontinent named 'Rodinia' for the 1100–800 Ma period [*Dalziel*, 1997; *Meert*, 2001; *Weil et al.*, 1998] that would have broken up after 800 Ma [*Meert and Torsvik*, 2003; *Torsvik et al.*, 2001], there are no reliable paleogeographic reconstructions for the 700–600 Ma time period [*Meert and Powell*, 2001] because the paleomagnetic data are poorly constrained or entirely lacking [*Evans*, 2000]. Nevertheless, the few available recent geochronologic studies seem to indicate that the age of the last glaciation of the Neoproterozoic is most reasonably equals to 600 Ma [*Barfod et al.*, 2002; *Gorokhov et al.*, 2001; *Thompson and Bowring*, 2000]. Consequently, many climate modellers have studied the younger snowball event adopting a paleogeographic reconstruction typical of the 580 Ma time period [*Chandler and Sohl*, 2000; *Donnadieu et al.*, 2002] or even of the 545 Ma time period [*Crowley et al.*, 2001; *Hyde et al.*, 2000]. Those reconstructions, based on Laurentia migration to high latitudes by 577 Ma [*Torsvik et al.*, 1996], show the paleolatitudes of the vast majority of the continental masses range from the pole to the equator. [*Hoffman and Schrag*, 2002] suggest that those continental configurations might have ended the snowball era rather than have favoured it. It seems however interesting to test and to quantify the effect of such a paleogeography on the Neoproterozoic climate via its impact on the climate-silicate weathering feedback. Indeed, in the absence of any proxy, the critical climatic parameter, i.e. the atmospheric pCO_2, has been defined as an arbitrary boundary condition, most previous climatic and geochemical studies assuming a low pCO_2 prior to the glaciation, corresponding to an already severe cooling. However, the atmospheric CO_2 level is completely defined by the balance between the volcanic degassing and the continental silicate rock weathering [*Goddéris and François*, 1995; *Walker et al.*, 1981]. Although the volcanic degassing rate is poorly constrained for Neoproterozoic times, we will explore the impact of the continental configuration and of the presence of mountainous area (the Pan-African orogeny) on the continental weathering rates, hence on background pCO_2 and climatic setting for Marinoan times prior to any snowball event. In this contribution, we have performed two suites of global climate model experiments with a solar constant reduced by 6% relative to present day value and with various fixed values of CO_2, the first set of runs is for the 580 Ma continental reconstruction with no relief (called after NR) and the second set of runs is for the same paleogeography but with two mountain ranges resulting from the Pan-African Orogen (called after PAO). Each experiment is run for thousand years to climatic equilibrium. In this way, we have evaluated the sensitivity of the critical value of atmospheric CO_2 leading to a full glaciation to the existence of mountain ranges. Then, we have used those climatic simulations to run the global geochemical model COMBINE to calculate the steady state atmospheric CO_2 level. This modelling approach has been performed in order to answer the two following key questions: (1) Can we constrain the atmospheric pCO_2 by the time of the Marinoan glaciation? (2) Once the pCO_2 level is constrained, how does the corresponding global climate looks, and particularly what kind of glaciation can be expected (global or rather regional)?

2. SHORT REVIEW OF THE PLAUSIBLE TRIGGERS

Kirschvink [1992] was the first to postulate that conditions amenable to global glaciations were set up by an unusual preponderance of land masses within middle to low latitudes as it would lead to lower tropical temperatures, through reduced receipt of shortwave radiation and a smaller tropical greenhouse effect. In addition, placing more continents in the tropics may induce an increase of the silicate weathering rate, leading to an increase of atmospheric CO_2 consumption. Such an equatorial continental configuration turns out to be effective only for Sturtian times. In two recent studies, following these lines of evidence, Goddéris et al. [2003] and Donnadieu et al. [2004a] have quantified the possible connections between the tectonic forcing and the ice house state of the Neoproterozoic. The older snowball glaciation (730 Ma, the Sturtian one) is contemporary with the dislocation of the Rodinia supercontinent which is heralded and accompanied by intense magmatic events, including the onset of large basaltic provinces spanning the 825–755 Ma time interval ([*Goddéris et al.*, 2003], see references therein). Then, because basaltic rocks weather about eight times faster than granitic rocks [*Dessert et al.*, 2003], the global weatherability of the continental surface drastically increases following the set up of basaltic traps, resulting in an enhanced consumption of atmospheric CO_2, inducing a global long term climatic cooling. Based on the best estimates of the size and of the location of the Laurentian magmatic province, [*Goddéris et al.*, 2003] show that more than 140 ppm of atmospheric CO2 could be consumed via this mechanism which is sufficient to trigger a snowball glaciation, assuming a pre-perturbation pCO_2 value of 280 ppm. On the other hand, exploring the relationship between the paleogeographic evolution and the atmospheric CO_2 level through the coupling of the climate model CLIMBER-2 and the geochemical model COMBINE, Donnadieu et al. [2004a] demonstrate that the dislocation of the supercontinent 'Rodinia' could have promoted a CO_2 decrease of more than 1000 ppm. This is the result of the increase in continental runoff (following the dislocation) which results in an enhanced consumption of atmospheric CO_2 by the silicate weathering and subsequent trapping of carbon within carbonate sediments. Coupled to the enhanced weatherability due to the onset of large magmatic provinces, the dislocation of the Rodinia supercontinent might have driven the Earth into a snowball glaciation.

The hypothesis proposed by Schrag et al. [2002] also relies on the equatorial location of continental masses to explain the Marinoan snowball glaciation, although the continental configuration appears to be more dispersed in latitude by the time of the younger global glaciation. This hypothesis invokes methane release from organically-rich sediments accumulated within warm equatorial river deltas into a low oxygen atmosphere, ensuring a rather long residence time of CH_4 within the atmosphere, boosting consumption of atmospheric CO_2 by weathering of continental silicates through enhanced greenhouse conditions. Such methane release might explain the pre-glaciation long term decrease in seawater $\delta^{13}C$ documented prior to the Marinoan glaciation. Once methane release ends up, atmospheric methane collapses through oxidation and the remaining atmospheric CO_2 might be low enough to result in the onset of a snowball glaciation. Following this logic but using a one-dimensional photochemical model, [*Pavlov et al.*, 2003] re-explore the chemistry of the Proterozoic atmosphere. They suggest that Proterozoic O2 levels were significantly less than today's concentration based on recent studies using sedimentary sulfur isotope ratios [*Canfield*, 1998; *Canfield and Teske*, 1996] and trace sulfates in carbonates [*Hurtgen et al.*, 2002]. Then, arguing that the methane production from the oxygen-poor Proterozoic ocean could have been 10–20 times higher than the modern one, they show that it is sufficient to maintain 100–300 ppm of methane in the atmosphere. The key question to be answered is the nature of the mechanism that ends the methane release, leading to the snowball glaciation.

3. THE MODELS AND THE EXPERIMENTS

3.1. The Climate Model and the Experiments

The coupled ocean-atmosphere model CLIMBER-2 is used extensively to investigate present, future and past climates. The CLIMBER-2 model has been fully described in [*Petoukhov et al.*, 2000] and successfully simulates the last glacial/interglacial cycle [*Ganopolski et al.*, 1998b; *Ganopolski and Rahmstorf*, 2001; *Ganopolski et al.*, 1998a] as well as earlier climates [*Donnadieu et al.*, 2004b]. Briefly, the atmospheric module is a 2.5-dimensional statistical-dynamical model and has a resolution of 10° in latitude and approximately 51° in longitude (7x18 grid). The ocean module is based on the (averaged) equations of Stocker et al. [1992] and describes the zonally averaged characteristics for the ocean realm with a latitudinal resolution of 2.5°. The model also includes a thermodynamic sea-ice model. More details on the changes and on the limits of the CLIMBER-2 model when simulating very different climates, such as the Neoproterozoic one, than the present-day one can be found in Donnadieu et al. [2004b].

For the climatic simulations, shared boundary conditions are: (1) A solar luminosity 6% below present. (2) The Earth's orbit about the sun is circular (eccentricity = 0) and the Earth's obliquity is 23.5°. This setting causes an equal receipt of solar insolation for both hemispheres. (3) The land-sea distribution is the 580 Ma paleogeography used and described in Donnadieu et al. [2002]. (4) In addition, because river drainage basins are unknown for this time period, we defined a river mask in which rain falling and snow melt on land is equally redistributed to all coastal land points. The surface type, bare soil, is imposed at every land grid point of the climate model since land plants had yet to evolve. The ocean model bathymetry is a flat-bottom case (5000 m depth).

3.2. The Geochemical Model and the Coupling

The COMBINE model is an atmosphere (1 reservoir)-ocean (5 reservoirs) biogeochemical model originally coupled to an 1-D EBM [*François and Walker*, 1992] which is fully described in Goddéris and Joachimski [2003]. It includes the mathematical description of the geochemical cycles of carbon, phosphorus, alkalinity and oxygen. This model is designed to simulate long term (10^5 to 10^7 yrs) evolution of the global biogeochemical cycles.

Since a full coupling between COMBINE and CLIMBER-2 cannot be achieved due to excessive computation time, the numerical experiments were conducted in the following way: the climate model was run (with the environmental conditions described above) until equilibrium (5000 years) under an atmospheric CO_2 concentration of 5000 ppm. Then starting from the previous equilibrium state each time, we conducted a suite of simulations (5000 years for each to reach the equilibrium) in which CO_2 level is held constant but is decreased in comparison with the previous one, until we reach the CO_2level for which a global glaciation occurred. More than 40 simulations have been performed in this way in order to have, at least, a climate simulation for each 1°C of global cooling. We assume a linear behaviour in between each climatic simulations and thus, by doing an linear interpolation, we obtain the climatic variables of interest (temperature and runoff) for any pCO_2 required by the COMBINE geochemical model to calculate the consumption of CO_2 by continental weathering on a 7x18 grid. This consumption of CO_2 through silicate weathering ($F_{w,igra}$) is estimated using the following weathering law [*Oliva et al.*, 2003]:

$$F_w^{gra} = k_{gra} \cdot runoff \cdot area \cdot \exp\left(-\frac{48200}{R} \cdot \left(\frac{1}{(T+273.15)} - \frac{1}{288.15}\right)\right)$$

where *runoff*, *area* and T are respectively the continental runoff, the continental area and the air temperature at the ground level for each of the continental grid elements. This law has been determined from a compilation study of the CO_2 consumption through weathering for more than 100 small granitic catchments. The k_{gra} constant is calibrated so that the present day global CO_2 consumption through silicate weathering reaches 6.8×10^{12} moles/year ([*Gaillardet et al.*, 1999] modified by Dessert et al. [2003]). The COMBINE model also includes the calculation of the consumption of CO_2 through continental carbonate weathering, representing about 50% of the global CO_2 consumption through weathering for present day climatic conditions. Given this global consumption rate of carbon and alkalinity discharge to the ocean, COMBINE calculates the deposition flux of reef carbonates on the shelf as a function of the calculated carbonate speciation in seawater. The carbon content of the atmosphere is calculated accounting for the CO_2 consumption through weathering, for the exchange at the air-sea interface, itself controlled by the seawater carbonate speciation, and for the CO_2 degassing through volcanism. The new climate corresponding to the calculated CO_2 is then determined at each time step through the CLIMBER-2 grid interpolation procedure, COMBINE calculates new weathering rates and the iteration is performed until a steady-state pCO_2 is reached. Steady-state is achieved after several million years, and is fully characterised by the balance between the degassing flux and the consumption through silicate weathering. The organic carbon subcycle included into the COMBINE model can only produce long-lived departures from steady-state, but does not influence the final steady-state itself. For that reason, no organic carbon burial neither oxidation of continental reduced sedimentary carbon is calculated. All organic matter produced in the photic zone is assumed to be entirely recycled within the intermediate depth and deep sea reservoirs.

4. RESULTS

4.1. Overview of the Climatic Simulations

Each climatic steady-state simulation (with a fixed CO_2 value) is used to build a curve describing the evolution of the globally averaged, annual surface air temperature as a function of the atmospheric CO_2 level. In this way, two curves are plotted on figure 1a, one for the suite of NR runs and one for the suite of PAO runs. The behaviour of the CLIMBER-2 runs is consistent with other modelling studies as the ocean ice cover increases in response to the CO_2 decrease until the atmospheric CO_2 level reaches a threshold value that still yields an ice free tropical ocean. This threshold values are 57 and 78 ppm for the NR and the PAO experiments, respectively (see Fig. 2). Then, a further reduction of atmospheric pCO_2 drive the sea-ice line to the equator and the sudden transition from soft to hard snowball Earth takes a few hundreds years in both suite of experiments (Fig. 1b). These results show that the runaway ice-albedo feedback previously found in EBMs [*Budyko*, 1969; *Hyde et al.*, 2000] and in AGCMs [*Jenkins and Smith*, 1999; *Pollard and Kasting*, 2003; *Poulsen et al.*, 2001] is also a prominent feature of the coupled ocean-atmosphere climate model CLIMBER-2 but due to the thermal inertia of the intermediate and deep ocean, the time scale of the transition is a few hundreds years rather than a few years.

The large mountain range of the PAO experiments induces a higher sensitivity to the radiative greenhouse gas forcing but the difference is rather small, the collapse occurring at 77 ppm for the PAO experiments instead of 56 ppm for the NR experiments. The topography is important for the initiation of glaciation essentially because of the atmospheric lapse rate promoting colder air temperatures and less summer melt (see below for a fully description of the topographic effect in these simulations). However, the applied topography is essentially located over the mid-to-high latitudes and thus does not strongly influence the way by which the tropical ocean freezes over.

The critical values required to maintain an open water solution calculated in this study are much lower than those found with AGCM studies, 840 ppm in Pollard and Kasting [2003],

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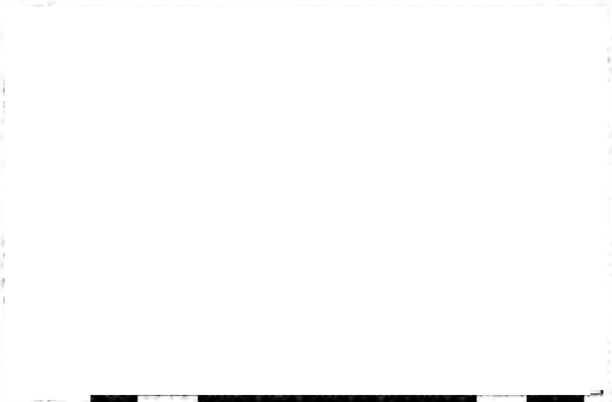

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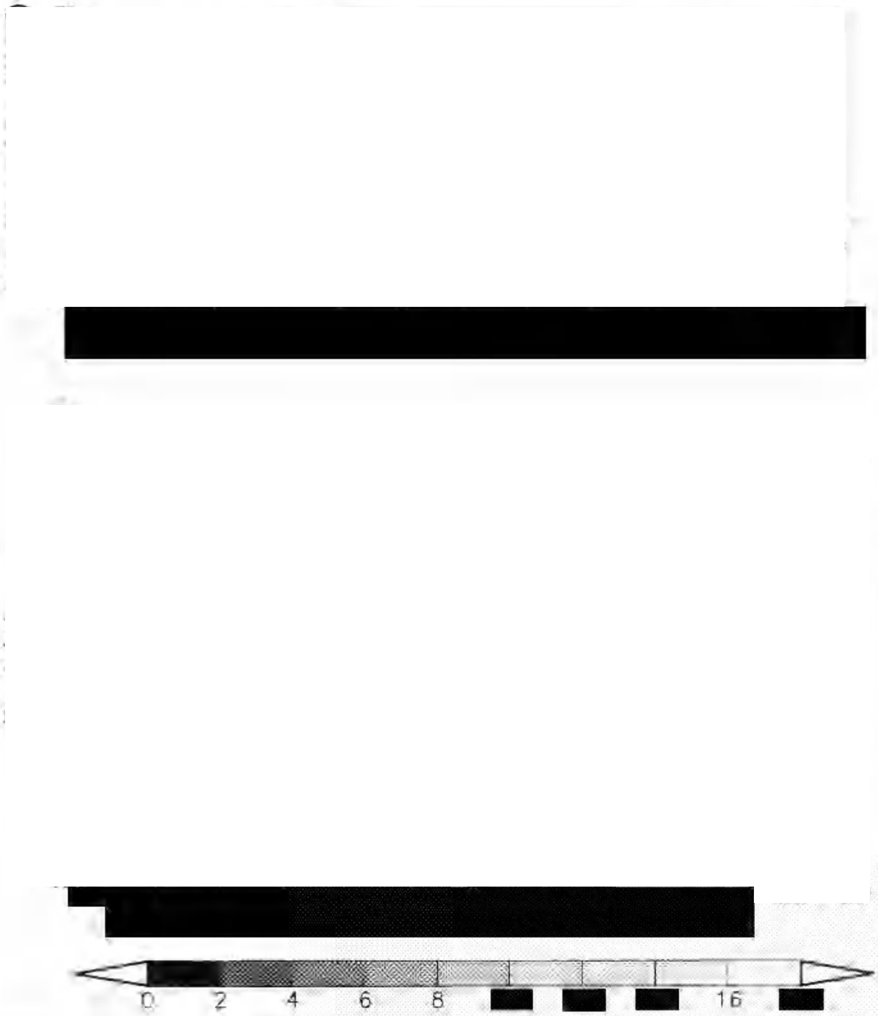

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Adopting the reconstruction of the paleo-elevations of the East African orogen and of the Brasilian orogen used in Donnadieu et al. [2002], we re-run the climate/geochemical model. A higher equilibrated atmospheric pCO_2 of 1477 ppm is found and the mean global temperature reaches a value of 10.77°C. Nevertheless, areas of snow that survive to the austral summer appear in the southern parts of the mountain chains and in the coastal areas benefiting from the marine influence that keeps continental temperatures below freezing (Plate 1-b). In contrast, the interior region of the Laurentia craton close to the South pole experiences temperatures above 5°C as there is neither high relief nor the cooling effect of the marine influence that allows snow to build up. In fact, by adding the Pan-African belts, the atmospheric circulation at the southern mid-latitude is strongly modified. The mid-latitude westerlies blowing over the West Gondwana continent bring no more hot air masses over the oceanic surface around 0° of longitude as in the NoRelief simulation (Plate 1-a). As a consequence, a strong cooling occurs over this part of the ocean and is propagated over the north-western part of Laurentia via the westerlies which increase due to the larger zonal temperature gradient at these latitudes (compared Plate 1a & Plate 1b). As a final remark, this strong cooling results in a drastic decrease of continental weathering rates in the north-western part of Laurentia and then induces a higher steady-state pCO_2 relative to the coupled climatic-geochemical NR experiments, since volcanic CO_2 degassing is assumed constant.

While we have observed the modification of climate due to the change in elevation of the land surface, the influence of the Pan-African uplift on the chemical weathering rates is more difficult to take into account as the orogen would probably increase the physical denudation of continental rocks through glacier abrasion and the development of steep slopes. A quantitative description of this mechanism is beyond the scope of this study. However, Millot et al. [2002] have established a strong positive correlation between the chemical weathering and the physical erosion for a dozen small granitic catchments, suggesting that CO_2 consumption through silicate weathering is a power law of the physical denudation rate. We thus apply a correction factor to the silicate weathering law following [*Berner and Kothaval*, 2001]:

$$F_{w,i}^{gra} = k_{gra} \cdot runoff \cdot area \cdot \exp\left(-\frac{48200}{R}\cdot\left(\frac{1}{(T+273.15)}-\frac{1}{288.15}\right)\right)\cdot fmech^{0.66}$$

The fmech factor is fixed to a constant value of 1 for pixels located outside of the Pan-African Orogen. For pixels located within the orogen, we assume a value of 3 for fmech. This latest number is based on the study of the modern analog of the Pan-African Orogen: the Himalayan uplift. Indeed Métivier et al. [1999] identified an increase of the sediment discharge originating from the Himalayan range by a factor of 3 over the course of the uplift, from the India-Asia collision 40 million years ago towards the present day. Finally, we assume that carbonate weathering is not influenced by physical erosion, because of the high solubility of carbonate minerals relative to silicate minerals.

This change in the continental weatherability drives down the atmospheric pCO_2 level to a steady-state value of 1037 ppm and results in a 2°C decrease of the global temperature that reaches 8.7°C. At mid-latitudes, the area of permanent snow cover migrates toward the south and the east of Laurentia due to the cool wind blowing over the continent (Plate 1-c). The global cooling also promotes a weak development of the perennial snow cover over the eastern part of the West Gondwana. However the high latitudes continental surfaces remain mainly influenced by a strong seasonality which prevents any accumulation of snow surviving to the austral summer except for the western part of the West Gondwana (Plate 1-c).

It appears that, under present day CO_2 degassing rate through volcanic activity, the geochemical forcing is sufficient to force the global climate into a colder state characterised by a regional extent of the permanent snow cover only if the Pan-African belts are included. Such cold conditions will facilitate the onset of a snowball event. However, the causal link existing between paleogeography, global climate and global carbon cycle may be hardly the culprit of the onset of a snowball glaciation during Marinoan times, since tropical temperatures remain well above freezing. In other terms, the atmospheric CO_2 level required to simulate a hard snowball Earth, 77 ppm, is still far away from being reached. However, nobody knows about the volcanic CO_2 degassing rate around 580 Ma. Therefore, we performed various coupled climatic-geochemical simulations by reducing the degassing rate, in order to check whether it would be possible to fall below the snowball CO_2 threshold of 77 ppm via an hypothetical decrease of this poorly constrained parameter. A CO_2 degassing rate reduced to 10% of its present day value results in a pCO_2 stabilizing around 170 ppm, corresponding to a global mean temperature of −12°C (not shown), still far above the required 77 ppm. Despite the lack of constraints on the Neoproterozoic CO_2 degassing rate, such a drastic reduction is unlikely to have occurred: the degassing rate never reached so low values during the Phanerozoic [*Engerbretson et al.*, 1992; *Gaffin*, 1987; *Rowley*, 2002], and we can furthermore expect a rough exponential decay of the CO_2 degassing flux since the formation of the Earth. This would imply higher CO_2 release from the mantle in the past, although this does not preclude periods of low degassing (related for instance to the presence of supercontinents, a configuration that does not fit the Marinoan times).

5. DISCUSSIONS AND CONCLUSIONS

A series of coupled ocean-atmosphere climate model simulations were carried out with a Late Neoproterozoic paleogeography and solar luminosity reduced by 6% relative to today. Considerations of the long-term carbon cycle of the ocean-atmosphere system, together with the variations of the climate model predictions to changes in atmospheric pCO_2, have led to the following conclusions.

First, by lowering sufficiently the atmospheric pCO_2, 56 ppm and 77 ppm for the NR and the PAO experiments respectively, it is possible to initiate an ice-covered Earth even when accounting for the ocean dynamics as this is explicitly simulated in the CLIMBER-2 model. These results are not in conflict with the studies of Poulsen et al. [2001] who do not simulate an ice-covered Earth with the coupled ocean-atmosphere model FOAM, as the lowest values of atmospheric pCO_2 they have used in their simulations is 140 ppm. In addition, the short duration of their experiments may do not allow them to account for a changes in ocean dynamics but only to the fast response of the surface layer in the tropical area.

Second, by using a geochemical-climate modelling approach to roughly estimate the atmospheric pCO_2 levels, we show that adding mountain ranges to the 580 Ma continental configuration promotes a larger equilibrated pCO_2 level (1477 ppm) than in the run with no relief (917 ppm). However, the NR run does not allow accumulation of perennial snow whereas the PAO run shows a strong modification of the atmospheric circulation due to the mountain ranges that results in a snow accumulation pattern compatible with a regional-scale glaciation. Furthermore, we have sought to test whether a large increase of the erosion flux, for instance due to physical erosion, may increase the silicate weathering sufficiently to drive the Earth to collapse into a hard snowball state. At best, we generate a regional-scale glaciation over the West Gondwana and the Laurentia cratons but the equilibrated pCO_2 are still far removed from the critical values required to initiate an ice-covered Earth. These results could give additional support to the inferences of many authors that some of the glacial deposits originally attributed to a snowball-like glaciation could in fact be the consequence of a more localised glaciation. For instance, Barfod et al. [2002] proposed that the Squantum and the Moelv glaciogenic deposits are more representative of a regionally extensive glaciation rather than of a hard snowball Earth. However, given the arbitrary assumption about the existence of a similar degassing rate at that time, and other modelling uncertainties concerning the weathering laws and the mountain ranges, these results have to be regarded as constituting only a crude sensitivity test of the sort of glaciations that may be triggered by accounting for the silicate weathering effect on the atmospheric CO_2 content at the end of the Neoproterozoic. Particularly, non steady-state effects of orogenies on the global carbon cycle should be included in future versions of the geochemical module, such as the increasing burial of carbon within reduced sediments as a result of high sedimentation rate down to the uplifted area. Such processes have been suggested to constitute a non negligible carbon sink at the million year timescale in the particular case of the Himalayan uplift [*France-Lanord and Derry*, 1997].

Acknowledgments. Y.D. acknowledges the support of CEA.

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Climate-Ice Sheet Simulations of Neoproterozoic Glaciation Before and After Collapse to Snowball Earth

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Geologic evidence of tropical sea level glaciation in the Neoproterozoic is one of the cornerstones of the Snowball Earth hypothesis. However, it is not clear during what part of the Snowball Earth cycle that land-based glaciers or ice sheets could have grown: just before the collapse with tropical oceans still open, or after the collapse with oceans completely covered with sea ice. In the former state, the tropics may still have been too warm to allow flowing ice to reach sea level; in the latter, snowfall minus sublimation may have been too small to build significant ice. These possibilities are tested with a coupled global climate model and dynamic ice sheet model, with two continental configurations (~750 Ma, 540 Ma) and two CO_2 levels bracketing the collapse to Snowball Earth (840, 420 ppmv). Prior to collapse large high-latitude ice sheets form at 750 Ma, but with flat continents, no low-latitude ice grows at 750 or 540 Ma. In the absence of reliable knowledge of Neoproterozoic topography, we apply a small-scale "test" profile in the ice sheet model, representing a coastal mountain range on which glaciers can be initiated and flow seaward. Prior to collapse, almost all low-latitude test glaciers fail to reach the coast at 750 Ma, but at 540 Ma many do reach the sea. After the collapse to full Snowball conditions, the hydrologic cycle is greatly reduced, but extensive kilometer-thick ice sheets form slowly on low-latitude continents within a few 100,000 years, both at 750 Ma and 540 Ma.

1. INTRODUCTION

A diverse array of climate models has been applied to the Neoproterozoic Snowball Earth problem [*Caldeira and Kasting,* 1992; *Oglesby and Ogg*, 1998; *Chandler and Sohl,* 2000; Jenkins, 2000; *Hyde et al.*, 2000; *Baum and Crowley,* 2001; *Crowley et al,* 2001; *Poulsen et al.*, 2001,2002; *Peltier,* 2001; *Williams and Pollard,* 2003; *Donnadieu et al.*, 2002, 2003, 2004]. Most of these studies have focused on specific parts of the hypothesized Snowball Earth cycle, when the Earth was close to or had just collapsed to a full Snowball state. Each cycle [*Hoffman et al.,* 1998; *Hoffman and Schrag,* 2000; *Schrag et al.*, 2002; *Kasting,* 2002] began with a temperate Earth that cooled over a period of ~10^7 years as a consequence of slowly falling atmospheric CO_2 levels. The CO_2 drawdown could have been caused by increasing organic carbon burial on newly created continental shelves [*Hoffman et al.,* 1998], or by silicate weathering on extensive, low-latitude, ice-free land areas [*Kasting,* 2002]. Variations involving methane have been proposed by *Schrag et al.* [2002] and *Pavlov et al.* [2003]. At some point, runaway ice albedo feedback caused a sudden transition to a full Snowball Earth, and the oceans became entirely or almost entirely covered by sea ice. The ensuing

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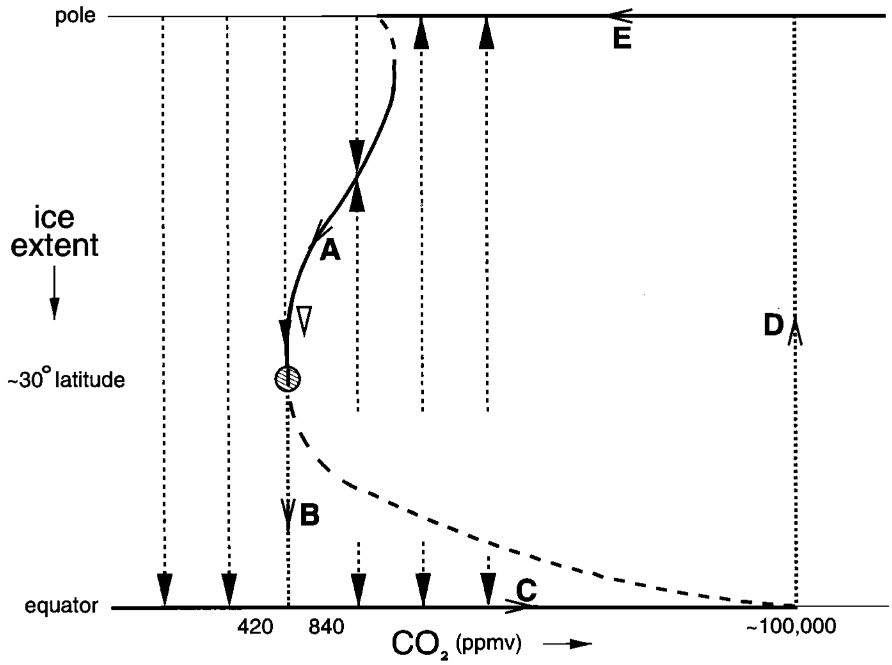

Figure 1. Stability diagram ("operating curve") of equilibrium global mean temperature, or equivalently latitude of the ice line, versus atmospheric CO_2 concentration, as established by energy-balance climate models (e.g., Caldeira and Kasting, their fig. 1). Stable solutions are shown by solid lines or curves, unstable (unrealized) solutions by dashed curves, and sudden transitions by dotted vertical lines labeled B and D. Spin-ups of GCM simulations with fixed CO_2 values are indicated in principle by unlabelled dotted arrows. The critical point from which the Earth collapses into full Snowball is shown by a large solid circle. Labels A-E identify stages of the Snowball cycle described in the text: **(A)** CO_2 slowly decreasing, ~10^7 years. **(B)** Sudden collapse to Snowball Earth, ~10^2 to 10^3 years. **(C)** Full Snowball stage, with outgassed CO_2 building up to very large values, ~10^7 years. **(D)** Sudden jump to ice-free Earth, ~10^2 to 10^3 years. **(E)** Ice-free with CO_2 decreasing rapidly, cap carbonate deposits formed, possibly ~10^3 to 10^5 years. The long time scales of stages A, C and E are controlled by carbon-cycle processes such as organic burial, weathering and outgassing, whereas the much shorter time scales of B and D are controlled by atmosphere-ocean dynamics and ocean thermal inertia.

full Snowball stage lasted for several million years, during which outgassed CO_2 built up in the atmosphere to very high levels (~0.1 bar) due to the virtual shutdown of the hydrological cycle and cessation of weathering. Ultimately, the Earth suddenly recovered to an ice-free state in a runaway reverse-albedo feedback, and the cycle began again. As described in *Caldeira and Kasting* [1992] and *Kasting* [2002], this cycle fits well into the basic global stability diagram ("operating curve") established by energy-balance models (EBMs) in the 1960s and 70s [*Budyko,* 1969; *Sellers,* 1969; *North,* 1975], shown schematically in Figure 1.

There is strong geologic evidence of substantial flowing glaciers at tropical latitudes, usually considered to be due to land ice and not abutting marine ice (but see Goodman and Pierrehumbert, 2003]. However, it is questionable when in the cycle significant land ice could have formed [*Christie-Blick et al.,* 1999; *Hoffman and Schrag,* 1999]: shortly before the collapse to full Snowball, or after the collapse in a full Snowball state. Both have unresolved questions regarding ice formation, as discussed below. In this paper we address these questions using a global climate model and dynamical ice sheet model, applied at two different stages of the Snowball Earth cycle.

We first test whether low-latitude ice sheets accumulated during the latter phase of the long slow cooling stage (labeled "A" in Figure 1). During this phase, atmospheric CO_2 had fallen to low values but still slightly above that required for the runaway transition to a Snowball Earth. The Earth would have been in this state for millions of years, and there would still have been substantial amounts of open ocean and a vigorous hydrologic cycle. Thus there would have been plenty of precipitation and time to accumulate kilometers-thick flowing ice on low-latitude highlands, *if* temperatures there were cold enough for it to fall as snow and survive through the summer. Moreover, if tropical ice formed at that stage, then there would be no need for the Earth to cool further and ever fall into full Snowball in order to explain the observed glacial deposits; that would avoid the problem of survival of life, but would require another explanation for the cap carbonate layers [*Hoffman et al.,* 1998].

To test this using a GCM, we need to identify the lowest CO_2 value that yields a climate just warmer than the unstable collapse to full Snowball. Essentially we must sketch out the GCM's operating curve in the vicinity of the critical collapse point (Figure 1), as begun by *Baum and Crowley* [2001] and *Crowley et al.* [2001]. We have done this by performing suites of GCM experiments for the Neoproterozoic with a solar constant reduced by 6% from present, and with various fixed values of CO_2 and various initial amounts of sea ice cover. Each experiment is run for multiple decades to climatic equilibrium (schematic dotted vertical arrows in Figure 1). In this way we have ascertained that the critical value of CO_2 for this GCM lies between 840 and 420 ppmv (Figure 2). The behavior of the exploratory GCM runs shown in Figure 2, and for other CO_2 values not shown, is consistent with the form of the operating curve expected from EBMs (Figure 1). Moreover, in a Neoproterozoic study using the CLIMBER Earth Model of Intermediate Complexity, *Donnadieu et al.* [2004] have verified that the stable solution does jump from ice cover to hard Snowball within just a few ppmv range of atmospheric CO_2. Since 840 ppmv is the lowest CO_2 value we tried that does not lead to full Snowball collapse, we consider the equilibrated 840-ppmv solution as "just above" the critical point, representative of climate near the end of stage A; however, we cannot of course rule out slightly lower CO_2 values and slightly colder climates still above the collapse.

The runaway transitions into and out of Snowball Earth (vertical lines labeled B and D in Figure 1) would have been very rapid, on the order of 100 to 1000 years. These unstable transitions are predicted by the EBM operating curve, and their timescale is limited only by thermal inertia and dynamics of the atmosphere and ocean; as found by *Baum and Crowley* [2001] and shown in Figure 2, most of the jump from open subtropical oceans to 100% sea-ice cover in a GCM with a slab mixed-layer ocean occurs within a couple of years. In models that include the $O(10^3)$-year thermal inertia of the deep ocean and achieve full Snowball, the transition still takes considerably less than ~5000 years, as found by *Donnadieu et al.* [2004] using the CLIMBER model. So during these transitions there would probably not have been enough time to produce the observed glacial deposits.

The full Snowball Earth stage (labeled C in Figure 1) would have lasted much longer, on the order of 10^7 years but with a vastly reduced hydrologic cycle, so it is not obvious whether snowfall minus sublimation would have been sufficient to accumulate significant ice. Also, in the absence of topography there is no obvious low-latitude "cold trap" for moisture in full Snowball, and thus no a priori reason to assume that annual snowfall minus sublimation would be negative over sea ice and positive over land, as required for continental ice sheet growth. *Donnadieu et al.* [2003] did find substantial ice growth using the LMD GCM in full Snowball state with prescribed mountain ranges. Later we test whether ice sheets could have grown shortly after collapse, with CO_2 set to the highest level

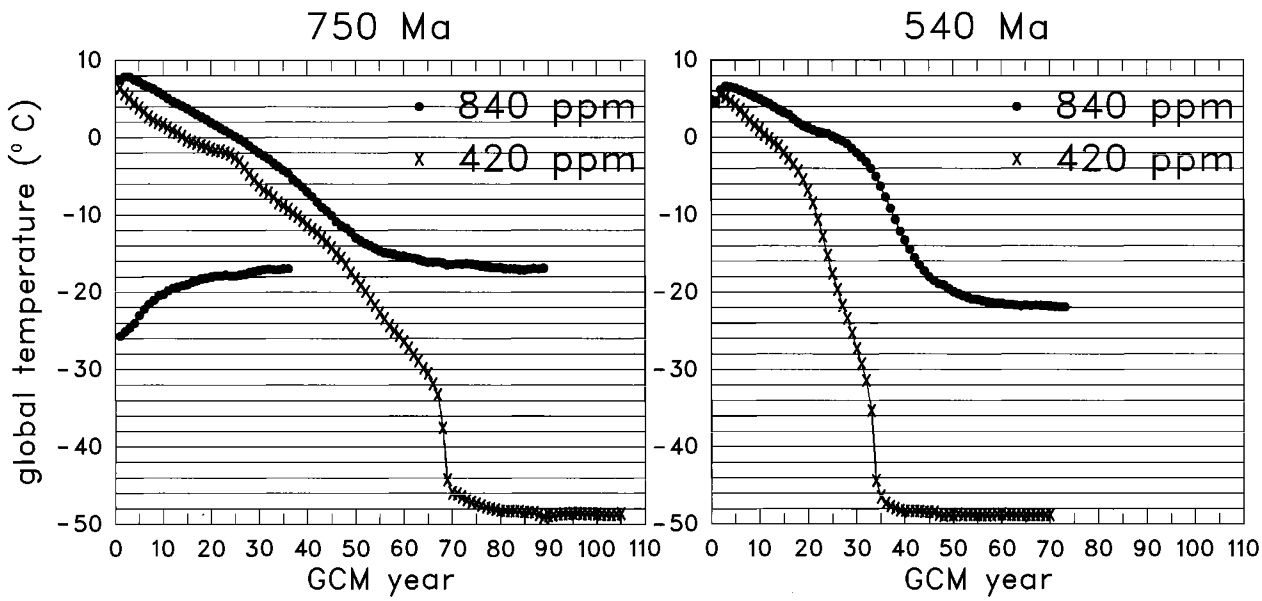

Figure 2. GCM global annual mean surface-air temperatures (°C) versus year of model run, with two values of atmospheric CO_2 (840 and 420 ppmv) and two continental configurations (750 Ma and 540 Ma). The two runs shown for 750 Ma, 840 ppmv, differ only in their initial temperature and sea ice distributions.

we tried (420 ppmv) that still yields full Snowball conditions from temperate initial conditions.

Some millions of years after collapse toward the end of the full Snowball stage, the hydrologic cycle would presumably have revived as CO_2 built up to very large values and the Earth warmed to slightly below freezing in the tropics. At that time ice sheets could well have existed that were larger and more vigorous than any modeled below. This part of the cycle is beyond the scope of our GCM due to limitations in the infrared radiation code.

2. MODELS AND COUPLING METHOD

The global climate model used here is GENESIS version 2 [*Thompson and Pollard,* 1997; *Pollard and Thompson,* 1995], consisting of an atmospheric general circulation model (AGCM) coupled to multilayer surface models of vegetation, soil, ice and snow. Sea-surface temperatures (SSTs) and sea ice are computed using a 50-m slab oceanic mixed layer, and a dynamic-thermodynamic sea-ice model [*Semtner,* 1976; *Flato and Hibler,* 1992]. Ocean heat transport in the slab model is diffusive depending on the local ocean slab temperature gradient. The AGCM resolution is spectral T31 (~3.75°) with 18 vertical levels, and the surface models' grid is 2x2°.

Several previous applications of this GCM have focused on the mass balance of present-day and Quaternary ice sheets, calculated by downscaling the GCM climate to finer ice sheet grids that resolve the ice sheet topography [*Pollard and Thompson, 1997*a; *Pollard et al.*, 2000]. It has also been used to drive a dynamical ice sheet model simulating the end of the last interglacial [*Pollard and Thompson,* 1997b], and the coupled model has been applied to early Antarctic evolution in the Cenozoic [*DeConto and Pollard,* 2003]. The main steps in the downscaling are (i) to interpolate stored monthly meteorological GCM variables from the GCM grid to the finer ice sheet grid, (ii) to impose simple lapse-rate corrections to certain variables such as surface-air temperature to account for errors in the GCM topography, (iii) to add a synthetic diurnal cycle, and (iv) to drive either a vertical-column snow-ice model (LSX, that of the GCM), or a more economical degree-day parameterization of ice melt neglecting evaporation, plus an allowance for refreezing of meltwater. This procedure yields the net annual ice accumulation and ablation at each ice sheet grid point, which is the surface forcing needed to drive the dynamical ice sheet model for thousands of years.

The 3-D ice model closely follows the standard lineage established by *Huybrechts* [1990], *Ritz et al.* [1997] and others. Ice thickness is predicted on a 1x1° grid by a vertically integrated flow law following the shallow ice approximation, and 3-D ice temperatures are predicted to account for their effect on ice rheology and basal sliding. There is no explicit basal hydrology, surging or sediment deformation, and the ice cannot advance into ocean points. Bedrock depression relaxes locally toward isostatic equilibrium with an e-folding time of 3000 years.

First, the GCM is run for multiple decades to climatic equilibrium with prescribed (or no) continental ice. Then stored monthly meteorological fields are downscaled to drive the ice sheet model for thousands of years or longer. During each ice sheet integration, the downscaling and surface mass balance calculations are repeated every 200 years to allow for changing ice sheet topography. In principle, the GCM could then be rerun with ice sheets prescribed from the result of the previous ice-model run, and the whole procedure could be iterated several times to converge on a final equilibrated combination of climate and ice sheet size. However, we have only performed the first step for all simulations in this paper, i.e., one GCM run with zero land ice, followed by one run of the ice sheet model, so some ice sheet albedo feedback is neglected (as opposed to sea-ice feedback, which is captured within the GCM). However, in other similar applications (Carboniferous) where several iterations were performed, we found that the first ice sheets only slightly underestimated (by ~10%) the final ice sheet size. This is probably due to the fact that within the first few years of the first GCM run, perennial snow is established on land whose area is close to the accumulation zone of the final ice sheets, and only slightly smaller than the total ice sheet size, so that the bulk of the eventual ice sheet albedo feedback is captured. This is only true for continental-scale simulations without significant topography, and not if small-scale highlands act as seeds to trigger ice sheet growth (such as Baffin Island for the Pleistocene Laurentide). Note that the "height-mass balance" feedback of the growing ice sheet itself [*Oerlemans,* 2002] *is* captured by the lapse-rate correction in the repeated surface mass balance calculations. The only feedback not captured at all by a single iteration is the effect of ice sheet topography on circulation and precipitation patterns.

3. NEOPROTEROZOIC BOUNDARY CONDITIONS AND MODEL DETAILS

For all GCM simulations in this paper, the solar constant is set to 0.94 of the present [*Gough,* 1981], neglecting changes within the Neoproterozoic as discussed further below. The Earth's rotation rate is slightly faster than present so that the day length is 22 hours, with small but noticable effects on climate [*Jenkins and Frakes,* 1998]. Since Milankovitch orbital perturbations are beyond the scope of the paper, we set the Earth's obliquity to a mid-range value of 23.5°, and eccentricity to zero to avoid an arbitrary seasonal choice for precession. The possibility of very high obliquities in the

Table 1. Global and annual means of planetary albedo, surface air temperature and precipitation, for the four Neoproterozoic GCM simulations (750 and 540 Ma, 840 and 420 ppmv CO_2). For comparison the last row is for a present-day GCM simulation [*Thompson and Pollard*, 1997].

Period (Ma)	CO_2 (ppmv)	Solar Constant (x 1365 Wm^{-2})	Planetary albedo	Temperature (°C)	Precipitation (mm/year)
750	840	0.94	0.445	-17.0	410
540	840	0.94	0.476	-21.8	312
750	420	0.94	0.665	-48.6	8.8
540	420	0.94	0.671	-48.8	9.0
0	345	1	0.302	14.1	1160

Proterozoic [*Oglesby and Ogg,* 1998; *Jenkins*, 2000; *Donnadieu et al.*, 2002; *Williams and Pollard,* 2003] is not considered here.

Global maps of continents and oceans at 2x2° have been digitized from paleogeographic reconstructions provided by *Lawver et al.* [1999]. All experiments have been performed with two continental distributions for 750 Ma and 540 Ma. The 750 Ma reconstruction represents the recognized Sturtian glaciation (~750–720 Ma). The 540 Ma reconstruction was the closest available to us to the recognized Varanger glaciation (~610–575 Ma), and is loosely termed Varanger in this paper. At 750 Ma more large landmasses are in low latitudes, whereas at 540 Ma they are mostly in high Southern latitudes, allowing us to test the sensitivity of results to very different continental distributions. Since land plants had not yet evolved in the Neoproterozoic, we prescribed bare land for all GCM land points. There is considerable uncertainty in the locations of major mountain ranges at these times [*Eyles,* 1993] and we have chosen to prescribe no topography in the GCM (200 m for all land points), and later to apply small-scale coastal "test" topographies in the ice sheet model as described below. In contrast, *Donnadieu et al.* [2003] did prescribe specific mountain ranges in their GCM-ice sheet Snowball Earth simulations, which strongly influences the locations of their predicted ice sheets.

Snow and ice albedo values are important in Snowball Earth simulations. We use the same values as in the present-day GCM: for cold snow surfaces, albedos in the visible and near-infrared wave bands are (0.90, 0.60) respectively, ramping linearly to (0.55, 0.35) as snow temperature rises from -5 to 0°C. There is also a zenith angle dependence above 60°. For sea ice, the corresponding values are (0.80, 0.50), ramping to (0.70, 0.40) as ice temperature rises from -5 to 0°C.

Minor changes to the standard GENESIS v2 GCM for the Neoproterozoic include setting the maximum allowed sea-ice fractional cover to 1.0 in both hemispheres (so leads are not enforced in full Snowball Earth), the elimination of small hard-coded hemispheric asymmetries in cloud optical properties based on present-day observations, and a uniform value for the ocean heat transport coefficient. Maximum thicknesses of snow and sea ice of 3m and 10 m respectively are imposed in the GCM; these have negligible effects on the GCM climate, and avoid long-term energy drifts than could obscure the GCM's approach to long-term equilibrium, especially for CO_2 values close to the collapse point. Sea-ice dynamics are driven only by surface winds, since ocean currents are not simulated by the slab ocean model. (Other sea-ice considerations such as penetrating solar radiation and ice-shelf dynamics with kilometer-thick ice are discussed later.)

4. CLIMATE RESULTS FOR 840 PPMV CO_2

We first present results with atmospheric CO_2 set to 840 ppmv, which yields equilibrium climates slightly above the collapse to full Snowball, in which sea ice extends to the subtropics and the tropical oceans are still open. All GCM results are annual means over the last 10 years of each run, by which time the climate has essentially reached equilibrium (Figure 2). Some global mean results are shown for all simulations in Table 1.

As expected from the extensive sea-ice cover, the high latitudes are much colder and drier than today (Figures 3 and 4). By comparison, conditions in low latitudes are more similar to the present, with temperatures well above freezing and annual precipitation and evaporation rates still on the order of several mm/day. Figure 3 shows temperatures for the warmest month of the year at each point, since that quantity is most relevant to potential summer ice melt. The predominance of polar continents at 540 Ma causes a pronounced hemispheric asymmetry due to greater summertime warming and drying of the large interior landmasses in high southern latitudes, and conversely, reduced seasonal amplitudes in the southern subtropics due to the predominance of surrounding ocean. The distributions of sea ice (Figure 3, dashed lines) are similarly shifted in latitude, and result in the global sea-ice coverage being 10% greater at 540 Ma than at 750 Ma. These factors contribute to the colder global mean temperature at 540 Ma (Table 1).

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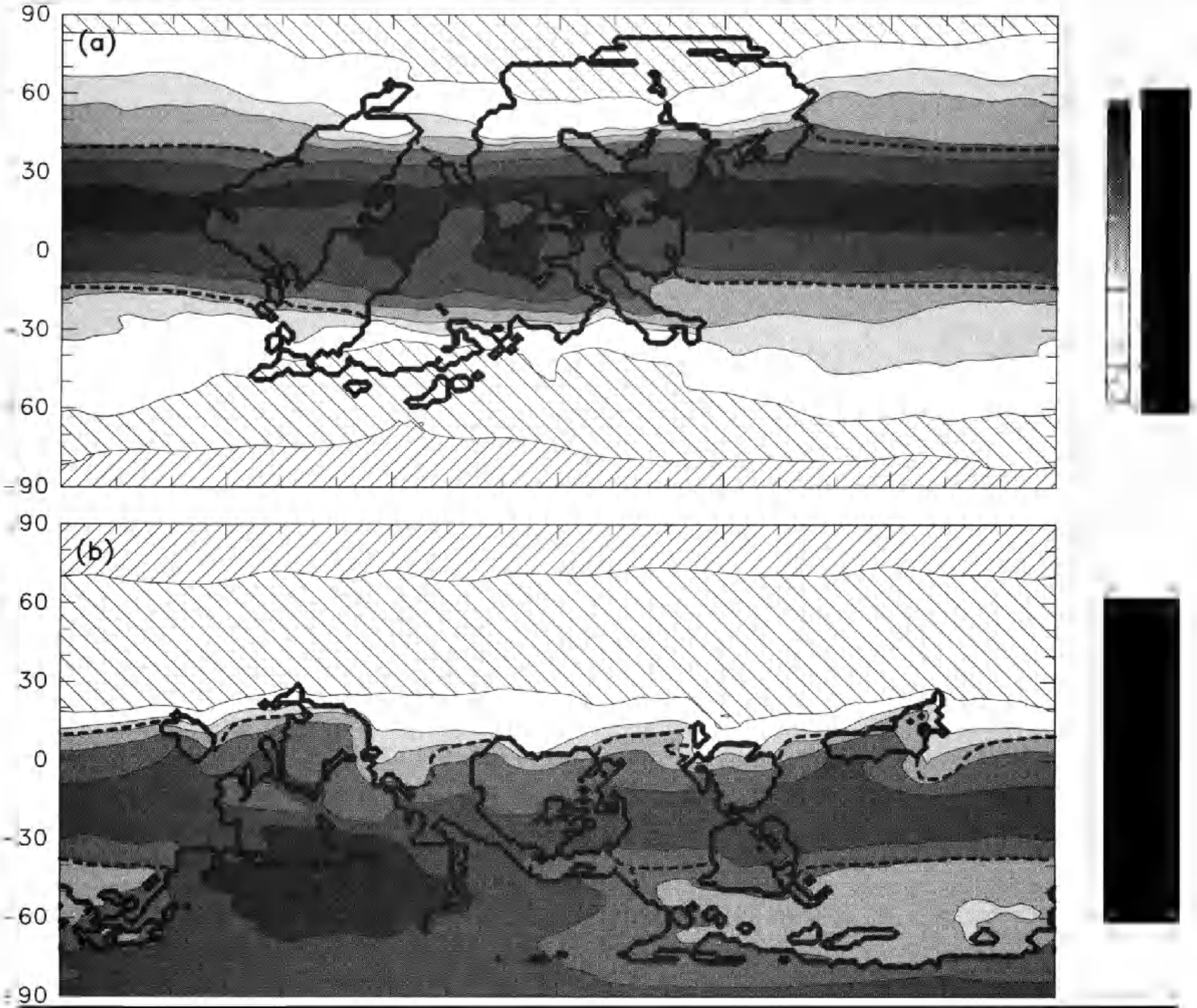

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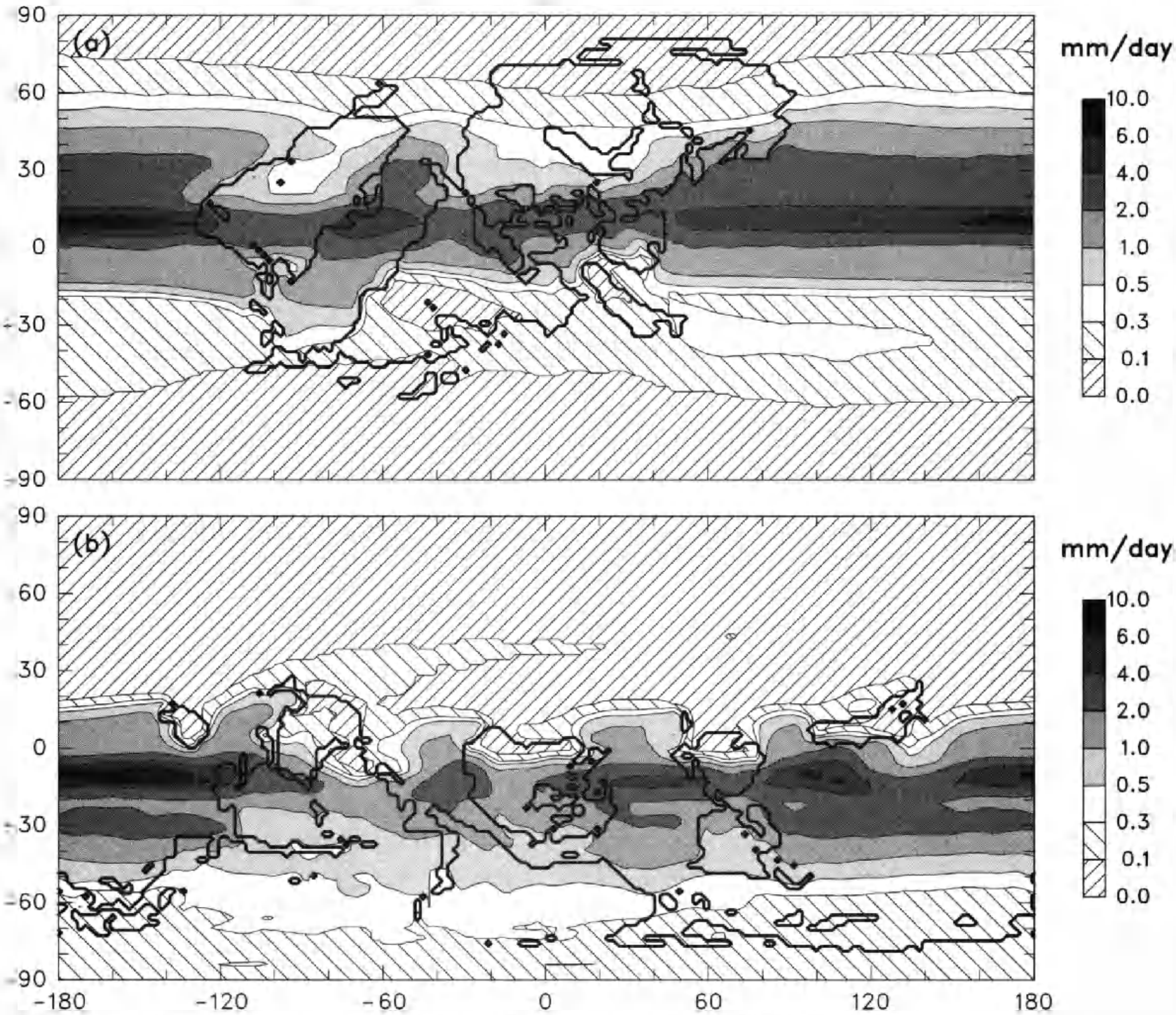

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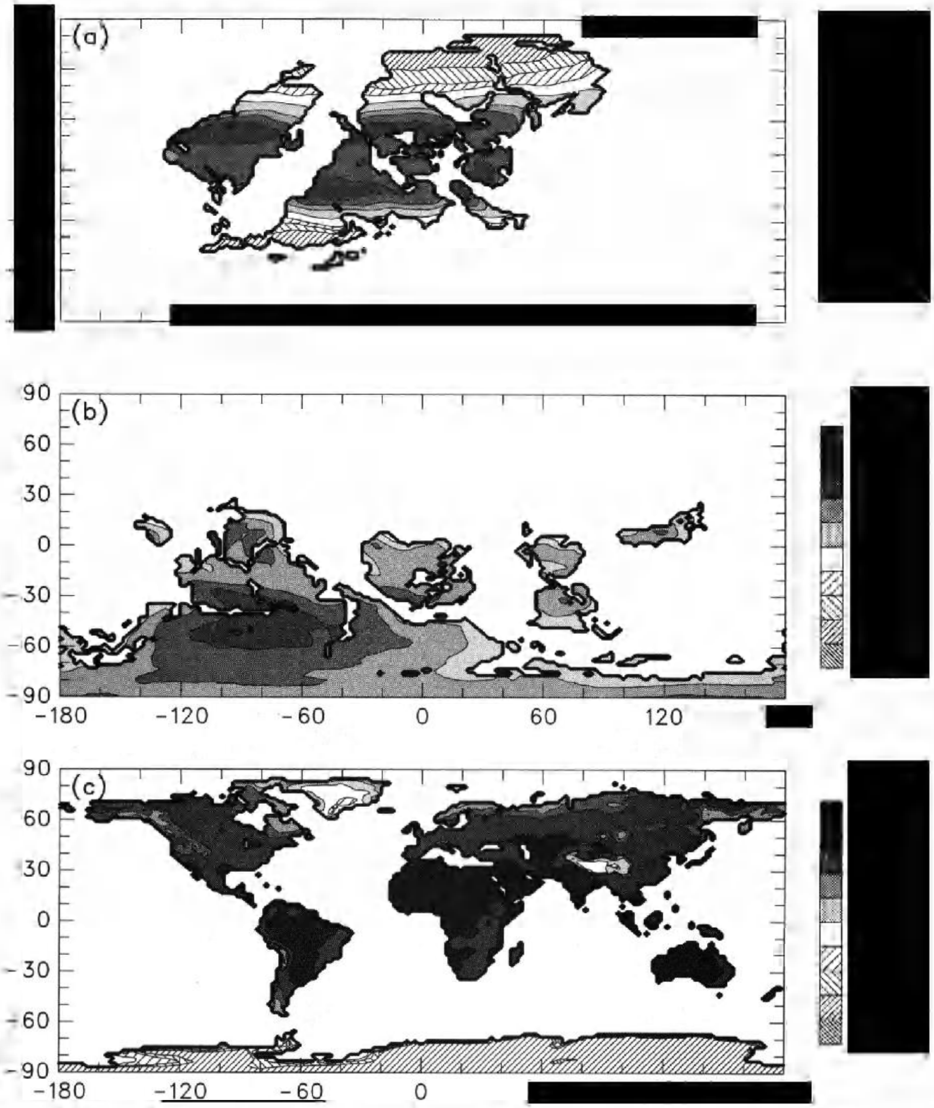

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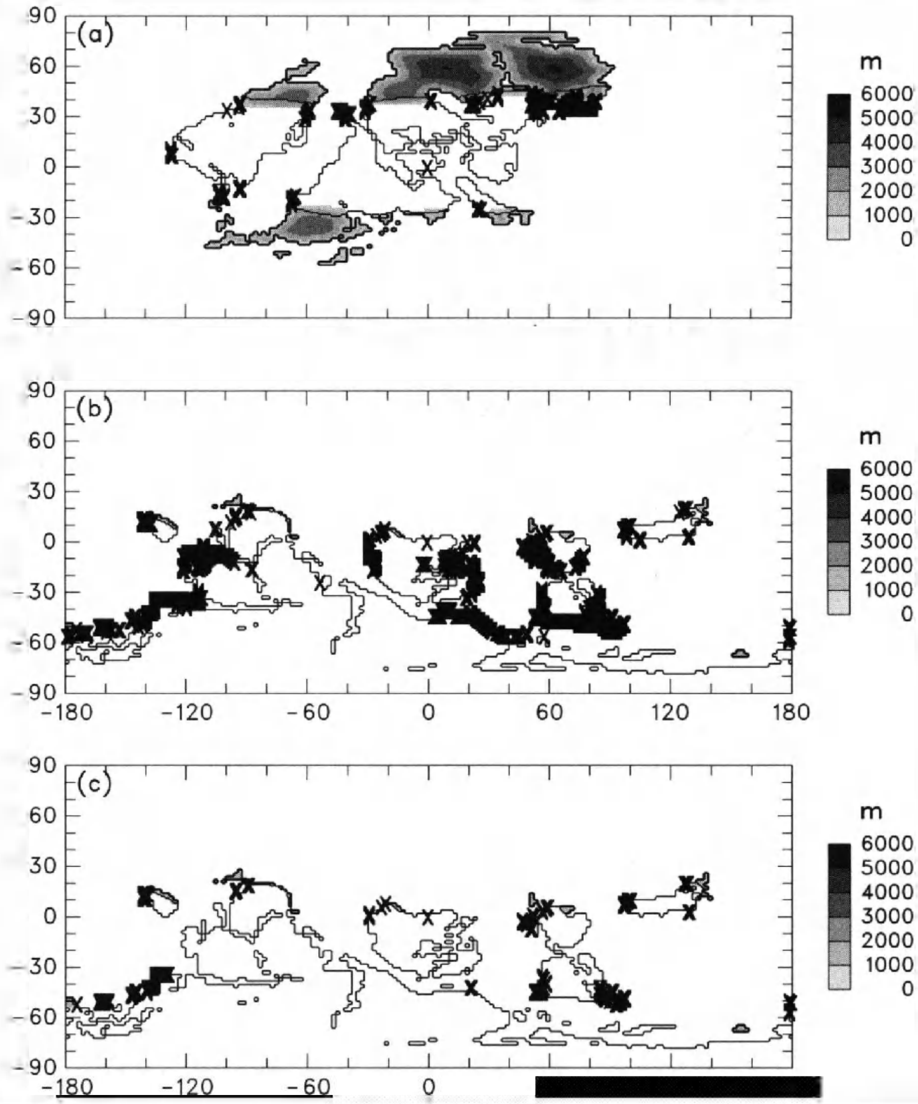

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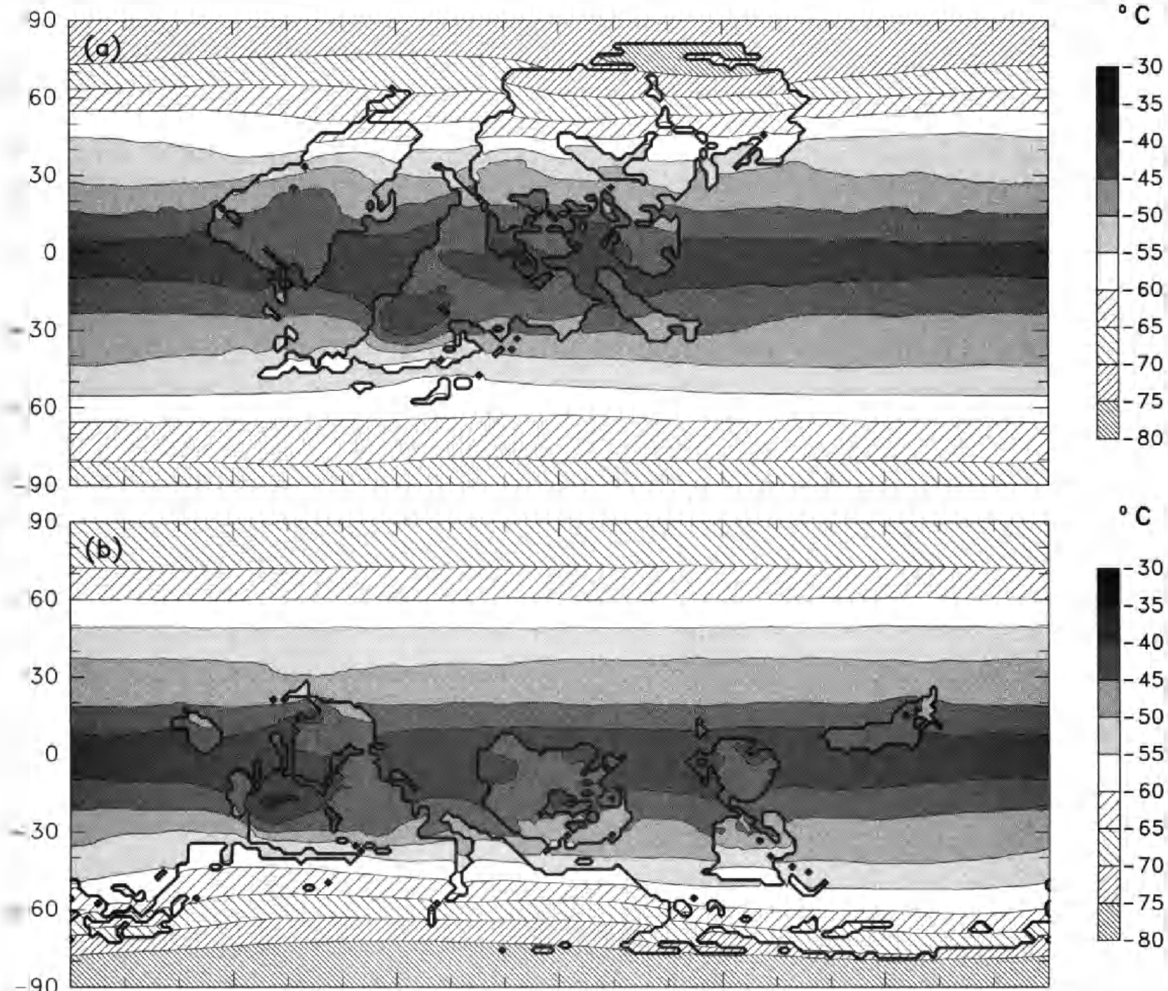

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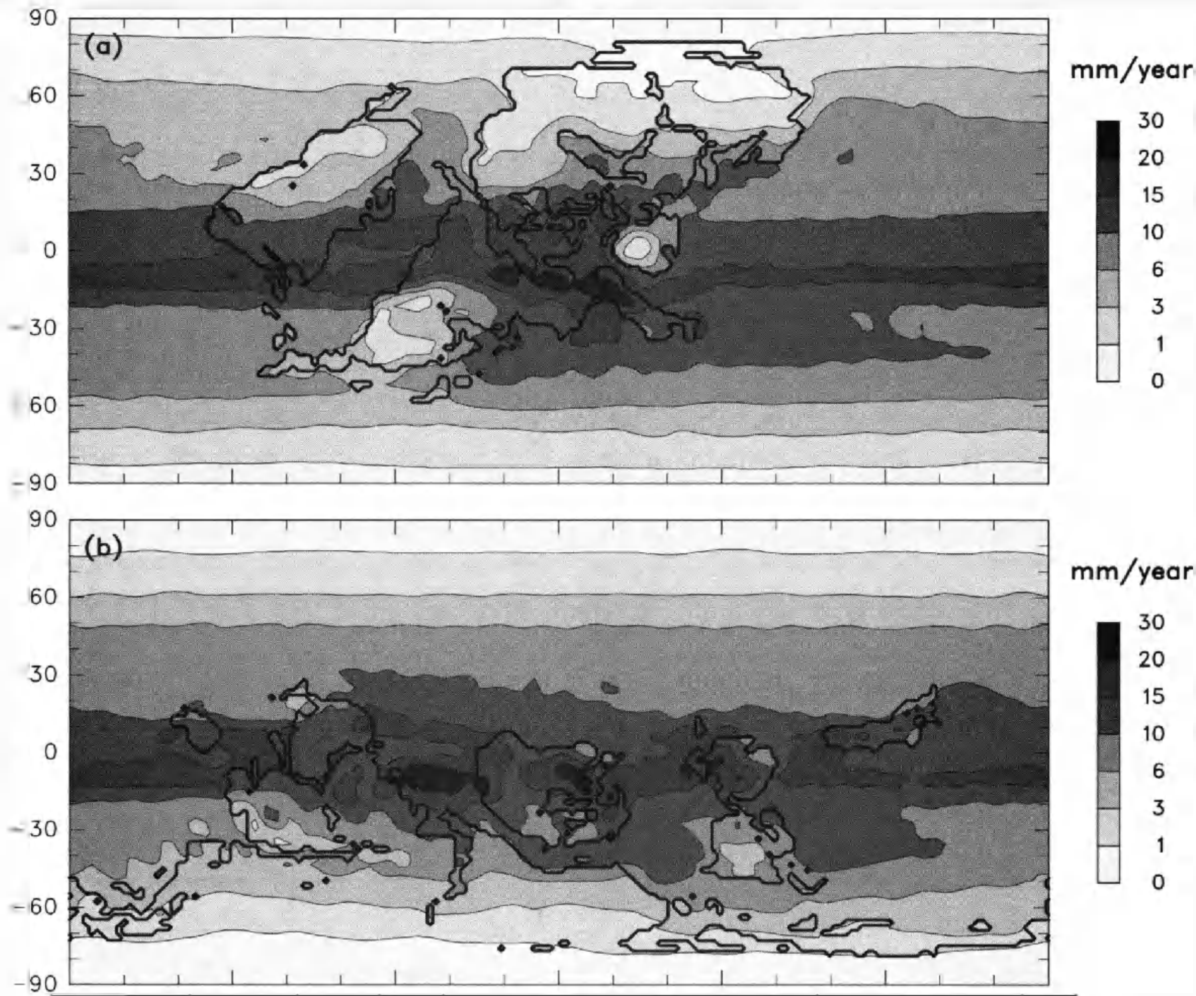

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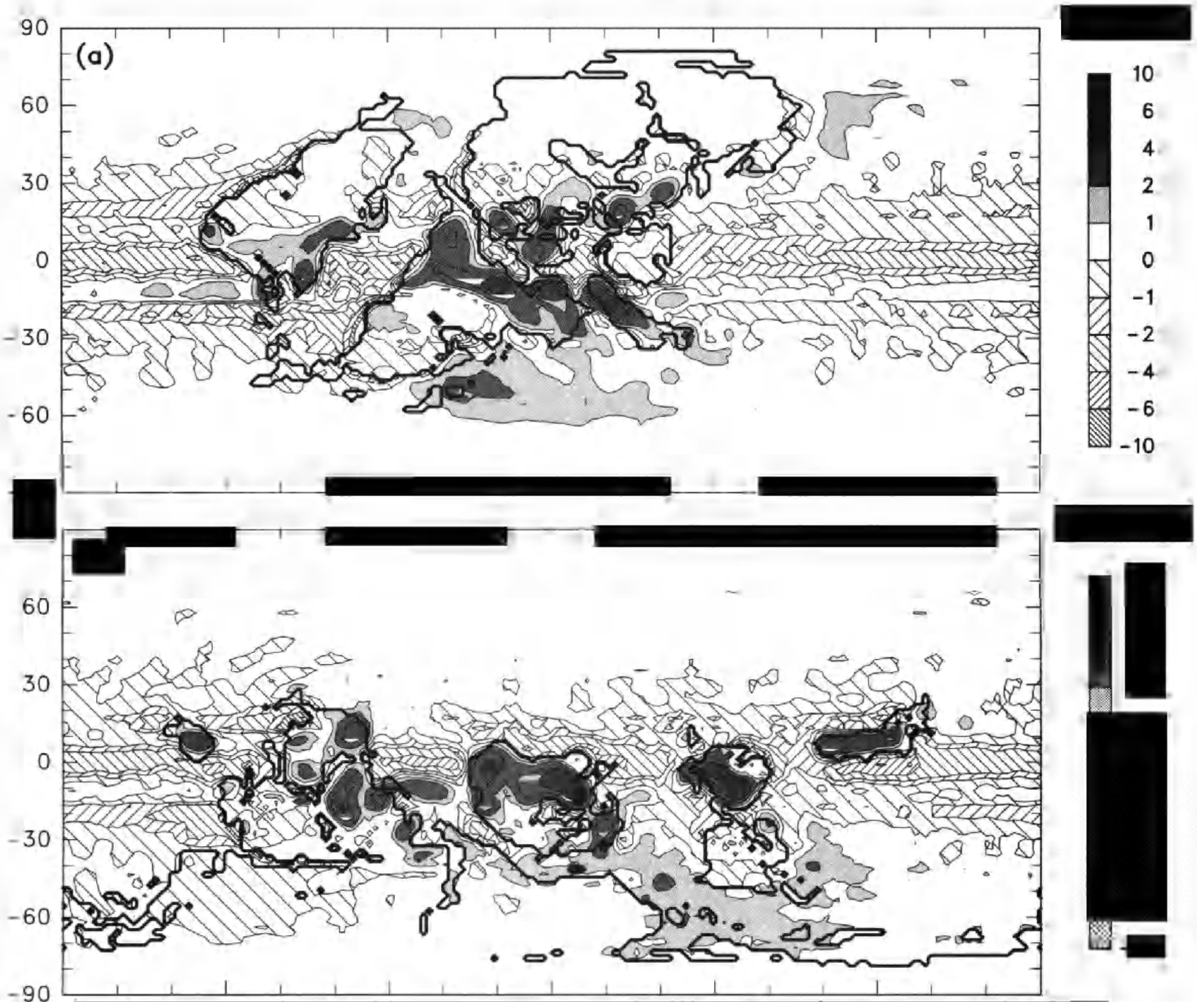

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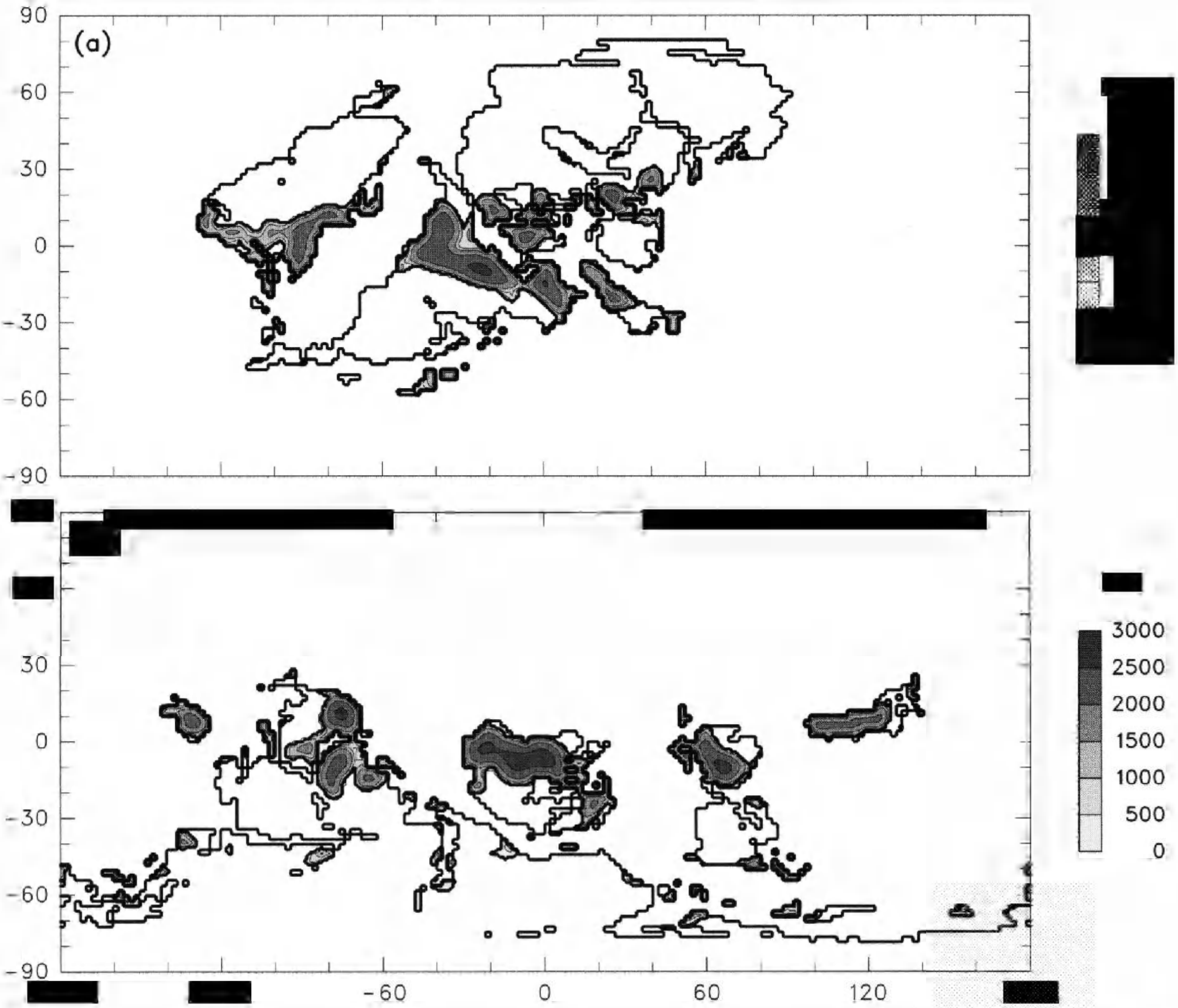

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However, there are several uncertainties and shortcomings in our models that may affect these conclusions, especially for partial ice cover. There may be somewhat lower CO_2 values and colder climates below our 840 ppmv simulation that are still above the collapse point, which could be explored by further GCM runs. More fundamentally, the position of the critical collapse point itself in CO_2 versus ice-line space (red dot in Figure 1) may be significantly affected by ocean dynamics and sea-ice meltwater effects [*Poulsen et al.,* 2001; *Donnadieu et al.,* 2004], and also simply by the GCM's sea-ice albedo values (if quite dark, they can rule out any collapse at all; *Chandler and Sohl,* 2000].

In addition, most climate models to date have neglected the physics of kilometer-thick sea ice expected in high latitudes for both partial cover and hard Snowball [*Kasting,* 2002]. For a given ice extent with no leads, this additional thickness would not affect the surface climate very much. But with partial ice cover, the thick ice would flow toward the tropical open ocean in the same way as modern ice shelves [*Goodman and Pierrehumbert,* 2003], affecting conditions at the ice line and probably changing the operating curve and the placement of the critical collapse point. In hard Snowball, the thickness of sea ice cover is currently under debate. *McKay* [2000] predicted that thin (~2 m) tropical sea ice might be stable in a hard Snowball Earth provided that the ice was clear enough to allow sufficient penetration of sunlight. If so, this could explain why photosynthetic algae survived the climate catastrophe. However, the feasibility of this solution has been questioned regarding the degree of solar penetration [*Warren et al.,* 2002] and ice flow from higher latitudes [*Goodman and Pierrehumbert,* 2003].

As in other past ice ages, Milankovitch orbital variations on $\sim 10^4$ year timescales probably affected seasonal climates and annual ice budgets enough to significantly affect ice sheet sizes, and possibly enough to trigger non-linear ice sheet thresholds of growth and decay that would cause quite different long-term behavior than those portrayed here using a single "average" orbit [*Loutre and Berger,* 2000; *DeConto and Pollard,* 2003].

We have only considered ice sheet formation just before and just after collapse to full Snowball conditions. As noted above, it seems likely that vigorous ice sheets could also have existed millions of years later in the full Snowball stage, when CO_2 had built up to very large values and tropical temperatures were only slightly below freezing. Further analysis of geologic evidence could help to constrain the timing of glacial deposits within the Snowball Earth cycle.

Acknowledgments. We thank Larry Lawver and Lisa Gahagan at the Institute for Geophysics, University of Texas, for providing paleogeographic reconstructions for 750 and 540 Ma, from which our GCM and ice sheet model continental maps were constructed. This work made use of supercomputing resources supported by the U.S. National Science Foundation grant ATM 0000545 (PMESH).

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Climate Dynamics in Deep Time: Modeling the "Snowball Bifurcation" and Assessing the Plausibility of its Occurrence

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The apparently global scale glaciation events that occurred during the Neoproterozoic era, in the interval from 750 Ma to 550 Ma, represent a significant challenge to our understanding of climate system behavior. If these episodes of glaciation were truly of "snowball" type, with the continents covered by thick ice-sheets and the oceans entirely capped by sea ice, then special pleading is required to understand the Cambrian explosion of life that occurred subsequently. Detailed models of Neoproterozoic climate, however, suggest the plausibility of preference for "equatorial refugium" or "oasis" solutions in which significant regions of open water are able to persist at the equator. We describe further analyses of such solutions in this paper, using both simple EBM coupled ice sheet models and fully articulated atmosphere-ocean-sea ice coupled models of climate evolution. Recently published analyses of the dynamics of the Neoproterozoic carbon cycle, taken together with the predictions of the models discussed herein, are strongly supportive of the equatorial refugium solutions as the most plausible form of the Neoproterozoic cooling events.

1. INTRODUCTION

The notion that the Earth was once entombed in a state of global glaciation is one that has episodically re-emerged in the geological and geophysical literature since the idea was first advocated by *Louis Agassiz* [1842]. As with the more recent proponents of the idea [*e.g. Kirschvink,* 1992; *Hoffman and Schrag,* 2002], Agassiz argued the necessity of this interpretation (die Eiszeit) on the basis of a belief [*Agassiz,* 1866] that continental glaciation had occurred at low tropical latitudes. His focus was upon the Amazon region of Brazil. As we have been reminded in the recent review of the now burgeoning "snowball literature" by *Eyles and Januszczak* [2003], Agassiz's argument was eventually shown to be invalid by *Branner* [1893]. His error of interpretation was traced to a false conclusion that a boulder laiden clay found in this geographical region was glacially produced, whereas it was in fact a simple consequence of igneous rocks having been subjected to deep weathering.

The most recent resurrection of the "snowball Earth" idea, as represented in the review by *Hoffman and Schrag* [2002], also has precedents in the work of *Harland and Herod* [1975] and *Chumakov* [1981]. It has deservedly received more serious attention than these previous formulations, however, because it has been accompanied by the elaboration of a seemingly

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plausible scenario involving climate system interactions that are not simple to dismiss on a-priori grounds. The most fundamental underpinnings of this scenario are to be found in geological data related to the carbon cycle, specifically in the time dependence of the ratio of ^{13}C to ^{12}C, denoted $\delta^{13}C$, and measured over long geological timescales in carbonates assumed to have been precipitated from the oceans and assumed to be measuring the isotopic fractionation association with photosynthesis. The measurement is therefore, in some sense, a measure of biological activity. Plate 1, based upon *Kauffman* [1997] and *Hoffman and Schrag* [1999], places these data in both a tectonophysical and a glaciological context. The Plate illustrates the temporal relationships between the very large amplitude oscillations in $\delta^{13}C$ that occurred between 750 Ma and 550 Ma in the Neopoterozoic, and the geological evidence for the times of occurrence of significant continental glaciation and the times during which supercontinents were being constructed and later "rifted" asunder. It will be noted that the Neopoterozoic era which is characterized by the large amplitude oscillations of $\delta^{13}C$ is entirely unique during the most recent 1.6 Ga of Earth history. Notable also is the fact that this era immediately preceded the beginning of the Cambrian period and the so called "Cambrian explosion of life" that occurred during it. One reason for the significant current level of interest in the snowball Earth hypothesis concerns the connection that might exist between a global freezing event and the onset of rapid evolutionary diversification that took place in its aftermath. The implausibility of this having occurred, from a biological perspective, has been stressed by Runnegar [2000] who referred to the snowball Earth hypothesis as "a script for global catastrophe".

Now the data shown on Plate 1 would appear to establish that there was indeed something rather special about the carbon cycle during the Neoproterozoic and it is equally clear that this interval in Earth history was one during which continental glaciation was extreme, if episodic. It is therefore unsurprising that the climate system interactions invoked by *Hoffman and Schrag* [2000] to support the plausibility of the occurrence of a "hard snowball" event or events have been focused upon atmospheric carbon dioxide, as well as upon the more obvious candidate for cooling based upon the secular variation in solar radiation. The latter contribution may be understood to be known on the basis of standard models of the evolution of main sequence stars such as our own Sun, models that predict the outgoing flux of energy, integrated over wavenumber, to increase at a rate of approximately 1% per 100 My as the star ages. The former contribution, however, is very much more poorly known, the best available model apparently being the GEOCARB model due to *Berner* [e.g. 1994]. This model, for which the time variation of CO_2 over the Phanerozoic period is shown on Figure 1, has been found to be difficult to

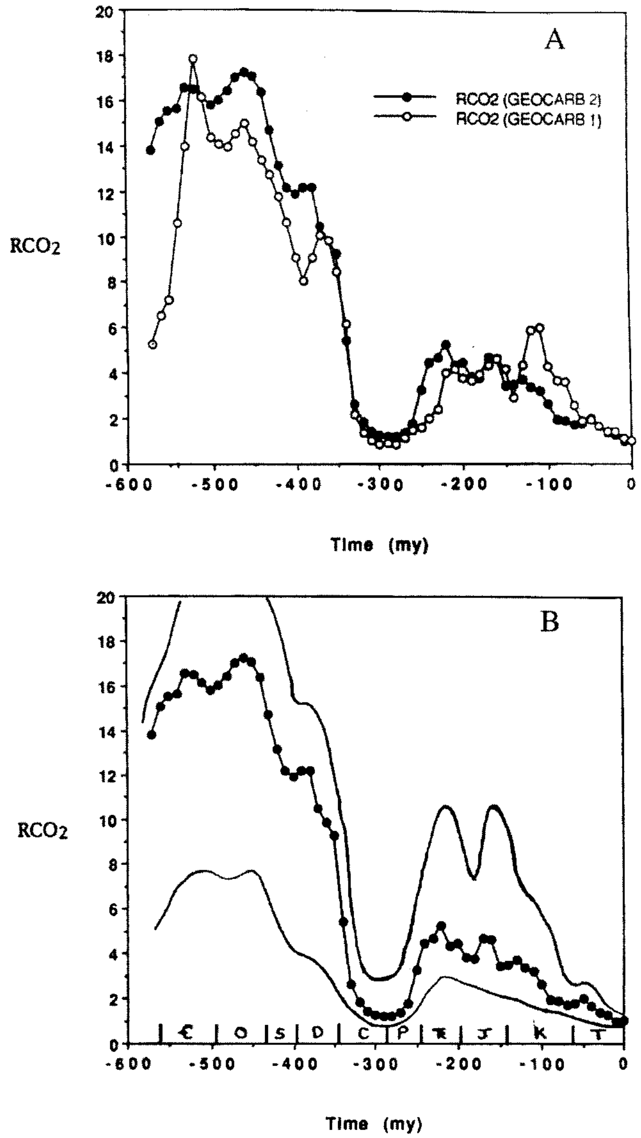
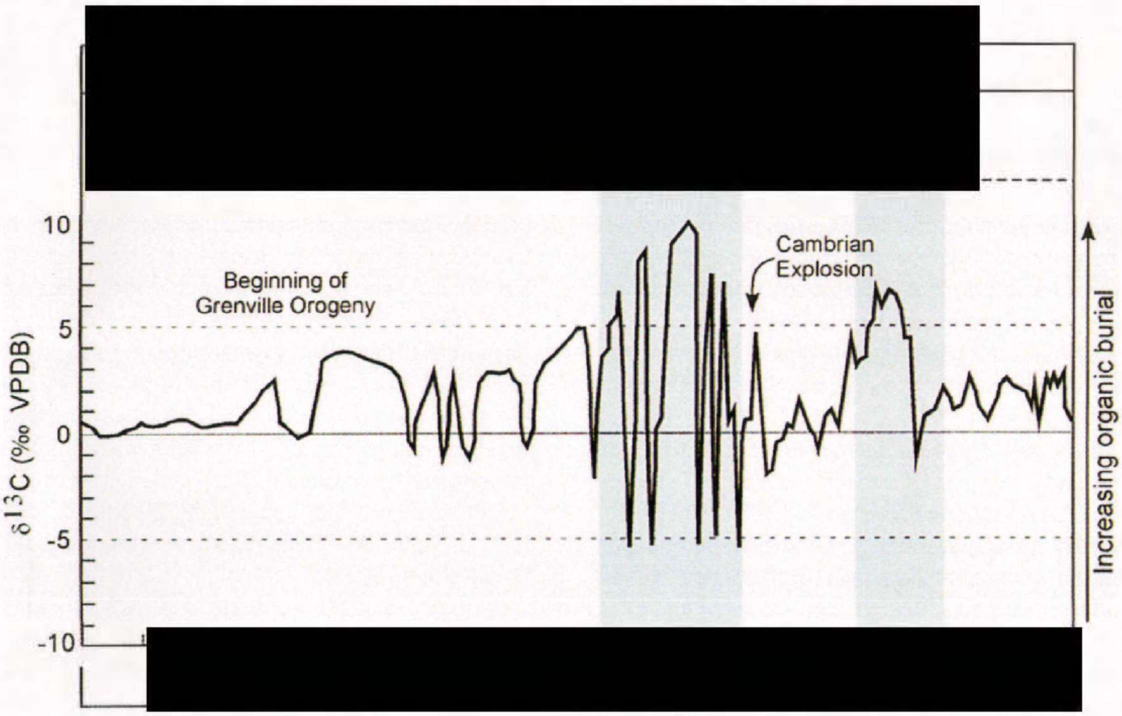


Figure 1. (A) The variation of the atmospheric concentration of carbon dioxide over the Phanerozoic era according to the GEOCARB I and GEOCARB II models of Berner [e.g. 1994]. Reproduced from Berner [1994] with permission. (B) Approximate error bounds upon the atmospheric CO_2 concentration according to the GEOCARB II reconstruction.

extend into the Neoproterozoic and so the issue of the concentration of CO_2 in the atmosphere that accompanied the $\delta^{13}C$ oscillations shown on Plate 1 remains open and has proven to provide fertile ground for speculation. During Phanerozoic time, however, it is clearly interesting and relevant to note that the minimum of atmospheric pCO_2 that occurred during the Carboniferious period at approximately 300 Ma, according to Berner, was coincident with the glacia-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tion of the supercontinent of Pangea and that the current minimum of the past few Ma has been coincident with the quasi-permanent glaciations of Greenland and Antarctica and, in the past million years, with a continuous, orbitally driven, 100 kyr oscillation of glaciation of the northern hemisphere continents near the rotation pole. To the extent that the GEOCARB model is a reasonable approximation of reality, we might therefore be forgiven for concluding that episodes of significant continental glaciation through Earth history occurred under conditions of reduced atmospheric pCO_2. It is important to recognize, however, that the GEOCARB model is not the only model of the variation of Phanerozoic atmospheric carbon dioxide concentration. In particular there are those of *Bodyko et al.* [1987] and *Rothman* [2002], models which do differ significantly from that of Berner.

Although the GEOCARB model does not extend into the Neoproterozoic, there is nevertheless good reason to believe that times of sharply varying $\delta^{13}C$ may correspond to times of sharply varying atmospheric pCO_2. Again, this is a consequence of the fact that when the photosynthetic process that is primarily responsible for the isotopic fractionation represented by $\delta^{13}C$ is active, carbon is being stored in the organic form and burial rates are high. The process of remineralization of the organic reservoir in the presence of oxygen produces CO_2 whereas the process of photosynthesis consumes it. There is therefore the possibility of occurrence of a CO_2 oscillation which has recently been suggested on the basis of entirely different lines of argument by *Crowley et al.* [2001] and *Rothman et al.* [2003], an oscillation that would have to rely upon the nonlinearity of the coupled physical-biogeochemical climate system for its existence. In this paper our goal will be to seek an understanding in terms of climate dynamics for the occurrence of these $\delta^{13}C$ oscillations that were such a prominent feature of the Neoproterozoic period of Earth history. The development of a climate dynamical interpretation of the ideas of *Crowley et al.* [2001] and *Rothman et al.* [2003] will form a prominent focus of the work to be discussed in the present paper.

As clearly illustrated by the data shown on Plate 1, however, the apparently oscillatory variations in the carbon cycle are not the only distinguishing feature of the Neoproterozoic period. It is clearly also important that the continents upon which glaciation was occurring during this period were being massively re-organized as the supercontinent of Rodinia underwent the two episodes of rifting that split it into a multiplicity of fragments that were then dispersed by the action of the mantle convection process. In fact, as recently discussed in some detail by *Eyles and Januszczak* [2003], the two most prominent glaciations that are supposed to have occurred in Neoproterozoic time, respectively the Sturtian ice age which occurred in the interval ~760–700 Ma and the Veranger (or Marinoan) ice age that occurred in the interval ~620–580 Ma, occurred during intervals coincident with the two stages of rifting that led to the complete breakup of Rodinia. Their work has emphasized the role that tectonics may well have played in the individual glaciation events, and in generating the sedimentological characteristics of the geological sections that are supposed by *Hoffman and Schrag* [e.g. 2000] to provide the irrefutable evidence that snowball glaciation actually occurred. An important component of the climate dynamic scenario of *Hoffman and Schrag* [2000] is the explanation of the so-called "cap carbonates" that are found, on occasion, to overlie the supposed glacial deposits of Neoproterozoic age. Their suggestion is that these rocks were formed once the influence of continuous volcanic outgassing into the atmosphere under "hard snowball" conditions had become such as to raise the atmospheric CO_2 sufficiently that the enhanced greenhouse effect was able to rapidly eliminate the global cover of sea ice. *Eyles and Januszczak* [2003] provide compelling counter argument to the effect that the diamictites that have been interpreted as glacial by the proponents of the snowball hypothesis are more likely to have been produced by debris flows driven downslope off the uplifted margins produced by rifting of the supercontinent. In arguing in this way the authors are suggesting that, just as Agassiz was misled in his interpretation of the boulder laden clay in Amazonia, Hoffman and others may also have been misled in their interpretation of the sedimentological evidence of low latitude and therefore necessarily "snowball" glaciation. These authors have also provided an alternative interpretation of the cap carbonates themselves.

One way in which we might hope to better understand the climate regime that existed during the Neoproterozoic is to employ climate system models to compute the state of the coupled atmosphere-ocean-cryosphere system that should have obtained under Neoproterozoic conditions. Although this approach to the problem of assessing the plausibility of occurrence of the snowball bifurcation is fraught with its own difficulties, such an approach is nevertheless one based upon first principles and is therefore useful counterpoint to the similarly complex process of geological inference. Issues that must be addressed involve our incomplete knowledge of the continental configuration that existed during either of the primary Neoproterozoic glacial events, our total lack of knowledge of the atmospheric concentrations of the greenhouse gases during this interval of time, as well as our total lack of knowledge of the bathymetry of the ocean basins.

The approach that we will take in the analyses to be discussed in what follows will be to employ two different models of the climate system to investigate the plausibility of occurrence of hard snowball events of the kind that have been hypothesized by Hoffman and colleagues. One of these will be the same energy balance model (EBM) coupled to a model of continental scale glaciology that has been developed at Toronto to successfully explain the 100 kyr ice age cycle of the late Pleistocene [*e.g. Deblonde and Peltier,* 1993, *Tarasov and Peltier,* 1999] as well as the Carboniferous glaciation of Pangea [*Hyde et al.* 1999]. The second model to be employed will be the complete coupled atmosphere-ocean-sea ice-land surface processes model that has been developed at the National Center for Atmospheric Research (NCAR) in Boulder, Colorado and which will be refered to herein as the Community Climate System Model (CCSM). By intercomparing the results obtained by the application of these two different representations of climate system behavior, we may hope to better understand the robustness of the predictions that models make concerning Neoproterozoic climate. As will become evident, this issue turns out to be important.

In the following Section of this paper we will briefly summarize the properties of the two models that will be employed for the purpose of subsequent analysis, as well as the design of the numerical experiments to be performed with them. Section 3 of the paper describes the new results that have been obtained using each model, whereas Section 4 provides a discussion of the climate dynamical interpretation of the $\delta^{13}C$ oscillations that follows from these model based analyses. Our conclusions are presented in Section 5.

2. MODELS OF NEOPROTEROZOIC CLIMATE AND DESIGN OF THE NUMERICAL EXPERIMENTS

Since fairly complete descriptions of both of the models to be employed for the purpose of the present work have already appeared in the literature, the level of detail concerning them to be provided here will be minimal. Interested readers should consult the citations given if they wish to read more complete discussions of technical details.

2.1. The Ice Sheet Coupled Energy Balance Model (EBM/ISM)

As previously mentioned, this model has it origins in work at Toronto directed towards the development of a theory of the 100 kyr cycle of late Pleistocene continental ice volume. The current version of this model, most recently employed to predict the evolutionary history of the North American and Eurasian ice sheets over the last glacial cycle [*Tarasov and Peltier,* 1999, *Peltier,* 2002], differs from the version of the model employed in *Hyde et al.* [2000] to investigate Neoproterozoic climate in that the ice sheet component of the model is a full three dimensional thermomechanical model rather than the simple isothermal model developed in *Deblonde and Peltier* [1991, 1993] and *Deblonde, Hyde and Peltier* [1992].

The full model consists of several individual elements for which a linked set of nonlinear partial differential equations must be solved. The global EBM is essentially that of *North et al.* [1983] to which has been added a simple thermodynamic sea ice module. This EBM is described by the following nonlinear diffusion equation:

$$C(\underline{r},t)\frac{\partial T_S(\underline{r},t)}{\partial t}=\underline{\nabla}_h\cdot(D(\theta)\underline{\nabla}_h T_S)-(A+BT_S) + a(\underline{r},t)\frac{Q}{4}S(\theta,t) \qquad (1)$$

In this equation, $C(\underline{r},t)$ is the space and time dependent heat capacity of the surface of the sphere which is employed to distinguish continental from oceanic surface and ice covered from non-ice-covered surface. $T_s(\underline{r},t)$ is the space and time dependent surface temperature, $D(\theta)$ is a latitude dependent diffusion coefficient that is inferred by tuning the model so as to enable it to fit observations of the pole-to-equator variation of temperature under modern climate conditions, the numbers A and B are obtained by linearizing the black body emission relation and tuning A and B so as to fit satellite observations of emitted radiation. The coefficient A may then be modified to represent the reduction or enhancement of the infrared forcing at the surface that arises from a change in the atmospheric carbon dioxide concentration. The space and time dependent function $S(\theta,t)$ represents the variation of the insolation incident at the top of the atmosphere (TOA) which includes the variation due to changes in the parameters that determine the geometry of Earth's orbit around the Sun. The space and time dependent parameter $a(\underline{r},t)$ is the surface albedo which is employed to distinguish a highly reflective surface such as that associated with continental ice or sea ice cover, from less reflective surfaces, either continent or non-sea-ice-covered ocean. $Q \cong 1370$ W/m^2 is the solar constant.

This model of the global energy balance is coupled to a three-dimensional thermo-mechanical model of continental ice-sheet evolution. As is the case with (1), this component of the coupled structure is also described by a non-linear diffusion equation for ice thickness H, as:

$$\frac{\partial H}{\partial t}=-\nabla_h\cdot\int_{z_b}^{h}\underline{V}(\underline{r})\,dz+G(\underline{r},T(\underline{r})) \qquad (2a)$$

where

$$\underline{V}(\underline{r})=\underline{V}_b(\underline{r})-2(\rho_i g)^m\{\nabla_h(h).\nabla_h(h)\}^{(m-1)/2}. .\nabla_h(h).f\int_{z_b}^{z}A(T(z'))\,(h-z')^m\,dz' \qquad (2b)$$

in which h is the surface elevation above present-day sea level, ρ_i is the density of ice, g is the acceleration due to gravity, T is the temperature of the ice, and G is the net mass balance. Both (1) and (2) are solved on the surface of the sphere. In (2), the function A(T) is such that

$$A(T) = f\beta\, exp(-Q/R_{gas}\, T^{\#}) \tag{3}$$

where *f* is a flow enhancement factor introduced in order to capture the increases in strain rate due to crystalline anisotropy and/or impurities and where $T^{\#}$ is the temperature of the ice in degrees Kelvin corrected for the pressure melting point, i.e. $T^{\#} = T_{ice}(z) - 8.7 \times 10^{-4}$ (°K/m) (h-z). The flow parameter ß and activation energy Q are set equal to those defined by the European EISMINT intercomparison project protocols [*Payne et al.* 2000]. The critically important mass balance function G(r,t), which consists of both accumulation and ablation components, is computed using a modification of the methodology employed in the 100 kyr cycle analyses discussed in *Tarasov and Peltier* [1999]. Ablation is computed using the two level PDD (positive degree day) method of *Huybrechts and T'siobbel* [1995] whereas precipitation, in the absence of any significant knowledge of this field for the Neopoterozoic period, will be taken to be a globally constant parameter of the model to be varied, as will be the mean elevation of the continents on which continental ice sheets may grow. For the purpose of the Neoproterozoic calculations we have assumed, explicitly, that the local precipitation rate prec(t) was computable as:

$$prec(t) = preco.(1.03)^{T_{sea\ level}(t)}$$

with the standard value for preco taken to be 0.6 m/yr.

The final component of the ice-sheet coupled EBM consists of a model of the glacial isostatic adjustment (GIA) process, a physical process that influences ice sheet topography in an important way through the so-called elevation desert effect. As the surface of the solid Earth sinks under the weight of an applied ice load, the surface of the ice-sheet itself moves to a lower elevation with respect to sea level than it would otherwise occupy, thus entering a regime of higher precipitation than would otherwise be the case. In the version of the ice-sheet coupled EBM to be employed herein, the GIA process will be described using a simple "damped return to equilibrium" model that has the following mathematical form:

$$\frac{\partial h'}{\partial t} = \frac{(h'(\underline{r},t) - h_o(\underline{r},0))}{\tau} + \frac{\rho_i}{\rho_E}\frac{H}{\tau} \tag{4}$$

in which $\tau = 4$ kyr is the assumed constant relaxation time of the adjustment process, $h_o(\underline{r},0)$ is the topography with respect to sea level of the unglaciated state, ρ_i and ρ_E are the densities of ice and Earth respectively, and h′ is the vertical bedrock deflection due to loading.

2.2. The Community Climate System Model (CCSM) of the US National Center for Atmospheric Research (v1.4)

This fully coupled atmosphere-ocean-sea ice-land surface processes model, the predictions of which we will compare to those of the ice-sheet coupled EBM, is the low resolution version of the CCSM described in *Boville and Gent* [1998]. This model consists of the above mentioned four independent components which are linked via a "flux coupler". With the exception of the ocean, which communicates with the other three components on a daily basis, the three remaining components communicate hourly. The atmospheric component is referred to as the Community Climate Model (CCM) and is described by *Kiehl et al.* [1998]. For the purpose of the application of interest to us here this model will be run in paleoclimate mode at a spectral resolution of T31 in the horizontal which corresponds to a spatial resolution of ~ 3.75 degrees. The atmospheric model has 18 non-uniformly spaced levels in the vertical. Although this model includes the capability to separately account for the radiative effects of CO_2, CH_4, N_2O and chloroflouro carbons, in the work to be described herein we will exercise only the CO_2 capability. The ocean component of the NCAR CCSM is the NCOM model described in detail in *Gent et al.* [1998], which has non-uniform horizontal and vertical resolutions which the authors refer to as x 3 degree resolution. In the horizontal, the grid increases from 0.8 degrees latitude at the equator to 1.85 degrees latitude at the poles whereas it has a uniform 3.6 degree resolution in longitude. The vertical resolution is defined by 25 non-uniformly spaced levels in the radial direction with the shallowest (12 m deep) layer at the upper surface and the deepest (450 m deep) layer in the abyssal ocean. The ocean model employs the eddy mixing parameterization of *Gent and McWilliams* [1990] and *Gent et al.* [1995] in the horizontal tracer equations but the non-local K-profile boundary layer mixing parameterization of *Large et al.* [1994], with a background value of the mixing coefficient of 1.5×10^{-5} m^2/s, is employed in the vertical. The sea ice component of the CCSM is the model of *Weatherly et al.* [1998] which consists of the three layer thermodynamic component of *Semtner* [1976] and the dynamical component of *Flato and Hibber* [1992]. Because this version of the model has no river run-off scheme, in order to ensure conservation of fresh water it continuously computes the net evaporation from the active (i.e. non sea ice covered) surface of the ocean as well as the net precipitation onto the active surface of the ocean, and then simply augments the net precipitation onto the active surface of the ocean so as to ensure conservation of the mean salinity.

This version of the CCSM has recently been subjected to a significant test by employing it to simulate the climate of Last Glacial Maximum [*Peltier and Solheim,* 2003]. For the purpose of this test the model was initialized under modern conditions of both the circulations of the atmosphere and oceans but with LGM surface, trace gas and insolation forcing conditions applied. It was then integrated forward in time until statistical equilibrium was fully achieved. The results for a variety of properties of LGM climate were then compared with paleoceanographic inferences, including the differential strength of the North Atlantic thermohaline circulation under modern and LGM conditions, the differential in sea surface temperatures across the topics and the differential strength of El Nino. As discussed in detail in *Peltier and Solheim* [2004], the results of these analyses are the first to have provided full agreement with paleoceanographic observations, especially in regards to the strength of the Atlantic THC at Last Glacial Maximum.

2.3. Design of the Numerical Experiments Concerning the Neoproterozoic Snowball Glaciations

Insofar as our experiments with the ice-sheet coupled EBM are concerned, we will make use of the high numerical efficiency of this model to explore the range of steady-state surface climates that are expected to arise under variations of the concentration of atmosphere pCO_2. For the purpose of all of these experiments we will assume, as in *Hyde et al.* [2000], that the continental configuration is one which approximates the distribution that is expected to have obtained during the most recent (Veranger/Marinoan) event in the interval from ~620 Ma to ~ 580 Ma. The continental reconstruction of *Dalziel* [1997] for 545 Ma will be employed as an approximation to the Marinoan distribution, the main characteristic of which is that the remaining main mass of Rodinia was then located in a predominantly south polar location. This interpretation of the available paleomagnetic constraints is somewhat consistent with that in *Eyles and Januszczak* [2003] (see their Figure 4b) although the latter authors have assumed a higher degree of tropical continentality to have existed at this time. All of the experiments using the ice sheet coupled EBM will be performed assuming a 6% reduction in the solar constant (unless otherwise indicated) and an orbital geometry the same as modern. Furthermore, no account will be taken of the change in the length of the day that is inferred to have been characteristic of this time in the past. The latter issue should not be a cause for concern with respect to the simulations with the ice sheet coupled EBM but could be of interest in regards to the results obtained using the NCAR CCSM.

For the purpose of the experiment to be described using this more complete model of the climate system we will employ the same continental distribution and 6% decrease of the solar constant and will start with a continental ice cover distribution equal to that predicted using the ice-sheet coupled EBM at an atmospheric pCO_2 equal to modern. The model will then be integrated forward in fully coupled mode (spun-up) until statistical equilibrium is achieved. This will allow us to test the validity of the prediction of the simple model, which includes no influence of ocean dynamics, when ocean dynamics are included, when precipitation and evaporation are computed in a self-consistent manner, and when the sea ice model includes not only thermodynamics but also dynamics. For the purpose of these complex integrations, an initial discussion of which appeared in *Peltier* [2002], the bathymetric depth of the oceans will be taken to be a constant 4000 m everywhere. As we will see, the integration of this model from a warm state into statistical equilibrium will require an integration time of approximately 425 years.

3. RESULTS FROM THE EBM/ISM AND CCSM EXPERIMENTS

Although the two models described in the previous Section of this paper are dramatically different insofar as their level of complexity is concerned, as we will see their predictions of Neoproterozoic equilibrium climate are somewhat similar.

3.1. Neoproterozoic Equilibrium Climates from the EBM/ISM and the Possible Existence of a "CO_2 Attractor"

A primary result of this paper is that shown in Figure 2 which plots the mean sea level temperature over the surface of the Earth as a function of the deviation, in Watts per square meter, of the surface radiation balance due to a decrease or increase in atmospheric pCO_2. If C_0 is the modern atmospheric concentration of CO_2 and C is the modified concentration, then the quantity dRad (W/m^2), which is the change in the surface radiative forcing due to the change in CO_2 concentration from C_0 to C, is such that (see IPCC WG-1, 1996):

$$dRad = 5.35\ x\,\ell n\left[\frac{C}{C_o}\right]. \tag{5}$$

For C = 2 C_0 this gives dRad $\cong$ 4 W/m^2. This is consistent with the results of *Ramanathan et al.* [1979] and can be re-expressed [see *Tarasov and Peltier,* 1999, equation (3)] as a perturbation (ΔA) to the parameter A in equation (1), in the form:

$$\Delta A = k\ \ell n\left[\frac{C}{C_o}\right]. \tag{6}$$

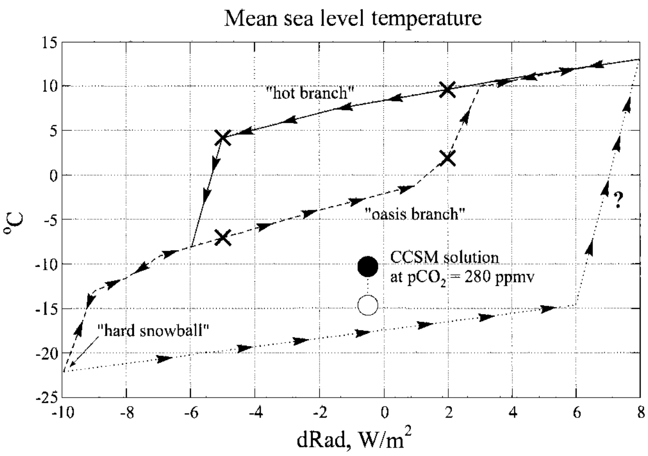


Figure 2. Mean sea level temperature as a function of atmospheric carbon dioxide concentration according to the ice sheet coupled energy balance model that has been developed at the University of Toronto. For the purpose of the computation of the large number of steady-state solutions that define the individual segments of this diagram it has been assumed that the solar constant was reduced by 6% below modern and that the parameters A and B in equation (1) that define the infrared contribution to the surface climate forcing remain fixed to modern climate values (see the text for a discussion of the implication of this assumption). The co-albedo of sea ice has been assumed to be equal to 0.55. Also shown on this Figure as the solid black circle is the mean sea level temperature solution delivered by the NCAR CCSM for an atmospheric CO_2 concentration of 280 ppmv, the continents fully glaciated and the same 6% reduction of the solar constant assumed in the integrations of the simpler model employed to construct the state-space diagram. The open circle is the result for mean surface temperature delivered by the NCAR CCSM prior to reduction of the data to sea level.

For the purpose of the results to be presented herein, we will express the changes to the surface radiation balance due to changes in atmospheric pCO_2 simply in terms of dRad. The implied concentration of CO_2 is then simply inferable by inverting (5), recognizing that the constant factor 5.35 in (5) or k in (6) may be different under Neoproterozoic conditions than it is under modern conditions. This point will turn out to be important to the understanding of the results of our analyses. Specifically it will be important to understand that when we compare climate states for different concentrations of CO_2, computed using the EBM/ISM, with those obtained for the same concentration of CO_2 using the NCAR CCSM, we should not expect to obtain precisely the same climate, even when both models are driven by a solar forcing that is 6% lower than modern. The reason for this is that the more complete model not only includes the direct effect on climate due to the change in atmospheric pCO_2 but also the indirect effect due to the fact that in the colder climate that obtains with the 6% reduction of the solar constant, there is a marked decrease in the water vapour concentration in the atmosphere and therefore a significantly further enhanced modification to the greenhouse effect.

Inspection of Figure 2 will demonstrate that the ice sheet coupled EBM exhibits hysteresis in the mean sea level temperature as a function of dRad (note that positive values of dRad indicate CO_2 concentrations higher than modern, where the modern value is taken to be equal to 300 ppmv, whereas negative values indicate decreases). For the standard values of the model parameters (mean annual precipitation rate = 0.6 m yr^{-1}, solar constant reduced by 6% from modern, sea ice co-albedo = 0.55, continental freeboard = 400 m), the region of hysteresis exists in the range dRad = - 6 W/m^2 to dRad = +3 W/m^2, on which mean sea level temperatures vary between -8°C and + 10°C. This hysteresis curve for the University of Toronto EBM coupled ice sheet model is very similar to that described in *Crowley et al.* [2001] using an earlier version of the model described in *Deblonde et al.* [1992] in which the ice sheet component of the model was assumed to be isothermal. As denoted on the Figure, the cold segment of the hysteresis loop will be referred to as comprising the "oasis branch" of solutions. We will refer to the upper branch of the hysteresis loop as the "hot branch". Also shown on this Figure, in the vicinity of dRad = -10 W/m^2, are solutions for which the mean surface temperature is less than -20°C. These are the "hard snowball" solutions called upon qualitatively by *Kirschvink* [1994] as a possible explanation for the intense low latitude glaciations that are supposed to have occurred during the Neoproterozoic. Also drawn on this Figure is a third branch of solutions that extend from dRad = - 10 W/m^2 to dRad = +6 W/m^2 which is rather flat but which, for dRad between +6 W/m^2 and dRad = +8 W/m^2, rises rapidly to reconnect with the extension to the "hot branch" of solutions. The arrows on this plot of steady-state solutions to the ice sheet coupled EBM indicate the route or routes by which climate states on the various branches of the diagram may be accessed. States on the "hot branch" of the hysteresis loop may be accessed only by cooling (by diminishing dRad) from states at higher temperature or by warming from an adjacent state on the hot branch. On the other hand states on the "oasis branch" of the hysterisis loop may only be accessed by warming from "pre-hard-snowball" cold states along the portion of the diagram in the range -10 W/m^2 < dRad < –6 W/m^2. Points on the hot branch cannot be accessed by warming from states in this range. Once a "hard snowball" climate has been achieved for dRad < -10 W/m^2, the only way to escape is by increasing dRad such that dRad > 8 W/m^2. The precise value of the CO_2 increase required to escape the "hard snowball" state is not accurately determined by this model as it does not include a detailed calculation of the influence of the thickness of the sea ice layer that must be eliminated before the system can escape its deeply frozen state. *Hoffman and Schrag* [2002] accept that escape would require an increase of CO_2 concentration to as much as 1000 times modern and suggest that this would be produced by the action of volcanism, citing the sometimes observed "cap carbonates" as evidence for the occurrence of rapid draw-down of CO_2 into the ocean that would have occurred once the global sea ice cover was eliminated. If this degassing flux were to have been equal to modern it is estimated that several million years would be required for this escape event to occur. It is important to note, a fact not discussed in *Crowley et al.* [2001], that the oasis solutions appear only in circumstances in which ice-fluxes large enough to force early glaciation occur. We find that when a standard explicit elevation-desert feedback is introduced then no hysteresis loop forms—oasis solutions do not arise. Although this paper is based upon an exploration of the implications of the existence of hysteresis, it is therefore an open issue as to whether this actually occurs in nature.

Plate 2 shows surface temperature distributions for the 4 points marked on the hysteresis curve of Plate 1. Both oasis and non-oasis solutions are shown for dRad = -5 W/m^2 and for dRad = +2 W/m^2. The non-oasis solution at dRad = +2 W/m^2 has a continental ice-sheet that is confined to the polar portion of the southern hemisphere supercontinent and a small sea ice cap covering the northern hemisphere polar ocean. At dRad = -5 W/m^2 the continental ice sheet at the south pole expands significantly as does the polar cap of northern hemisphere sea ice, but the latter only slightly. On the oasis branch at +2 W/m^2, on the other hand, the southern hemisphere supercontinent is fully glaciated, even in equatorial latitudes, and the north polar cap of sea ice has shifted to lower latitudes. At dRad = -5 W/m^2 on the oasis branch sea ice extends from the north pole and connects to the glaciated southern hemisphere supercontinent but an oasis of open water continues to persist at the equator. Climate states in the range -10 W/m^2 < dRad <-6 W/m^2 are all of oasis form, therefore suggesting from equation (5), that oasis solutions should persist down to atmospheric CO_2 concentrations as little as ~ 40 ppmv. To the extent that this ice sheet coupled EBM is an adequate representation of Neoproterozoic climate during the Veranger/Marinoan event, therefore, it is clearly incumbent upon the proponents of the hard snowball Earth scenario to provide a believable mechanism whereby the required decrease of atmospheric pCO_2 might have been produced. Although one or two suggestions of possibilities have been made in the literature, these must at present be seen as somewhat fancifull.

Plate 3 shows the results of a number of sensitivity analyses of the stability of the Neoproterozoic hysteresis loop to changes in the parameters of the base model. On the top portion of this Plate we have superimposed such loops for several variations on these parameters. Inspection will show that decreasing the annual precipitation rate from 0.6 m/yr to 0.3 m/yr shifts the centroid of the loop to a lower value of dRad (preco = 0.3). Similarly, a 20% increase in the latitude dependent thermal diffusion coefficient $D(\theta)$ (Dfac = 1.2) shifts the loop to lower dRad whereas a similar decrease Dfac = 0.8) has a slight but opposite effect. The largest influences registered on this diagram, however, are those due to changes in the extent to which the solar constant has been reduced. If, instead of the 6% reduction assumed in the base model, we assume a 7% reduction (Qfac = 0.93), then the hysteresis loop is shifted to higher dRad. On the contrary, if the reduction of the solar constant is only 5%, the loop is similarly shifted to lower values of dRad. These results imply that, during the Neoproterozoic, the region of hysteresis may exist for -9 W/m^2 < dRad < +5 W/m^2. The lower plate of Figure 2 shows "blow-ups" of the oasis branch of solutions on which the low dRad corners of the hysteresis loops are denoted by a square symbol.

3.2. A Simulation of the Climate of the Neoproterozoic Period Using the NCAR CCSM

It is prohibitively expensive of computer resources to attempt to reproduce the hysteresis loop shown on Plate 1 using a fully articulated climate model such as the NCAR CCSM. This will be clear on the basis of the analysis of LGM climate described in *Peltier and Solheim* [2004] in which it is shown that integration of the model to statistical equilibrium required a simulation in excess of 2000 calendar years duration. Although the continuing increase of CPU speed of commercially available computing systems will eventually make it possible to compute the equivalent hysteresis loop (if it exists!) for the complete CCSM, for present purposes we will content ourselves with describing a single run of the model to statistical equilibrium from a warm initial state at an atmospheric CO_2 concentration equal to preindustrial (280 ppmv), with the solar constant reduced by 6% and for the same continental configuration as that employed to compute the solutions for the ice sheet coupled energy balance model described in the last subsection. However, we will also assume that the continental ice cover at this CO_2 level is equal to that which obtains on the oasis branch of solutions of the simpler model. In this way we will be able to test the issue as to whether the equilibrium climate of the CCSM delivers a mean sea level temperature that is close to that predicted by the EBM/ISM. This may be construed to constitute a preliminary test of whether or not the same hysteresis loop might exist in the solution space of the NCAR model and whether or not the same refugium solutions exist in the full climate model as exist in the solution space of the EBM/ISM.

Figure 3 shows the results obtained for the spin-up period of the integration of the CCSM in terms of a number of global properties of the climate system that are diagnostic of climate

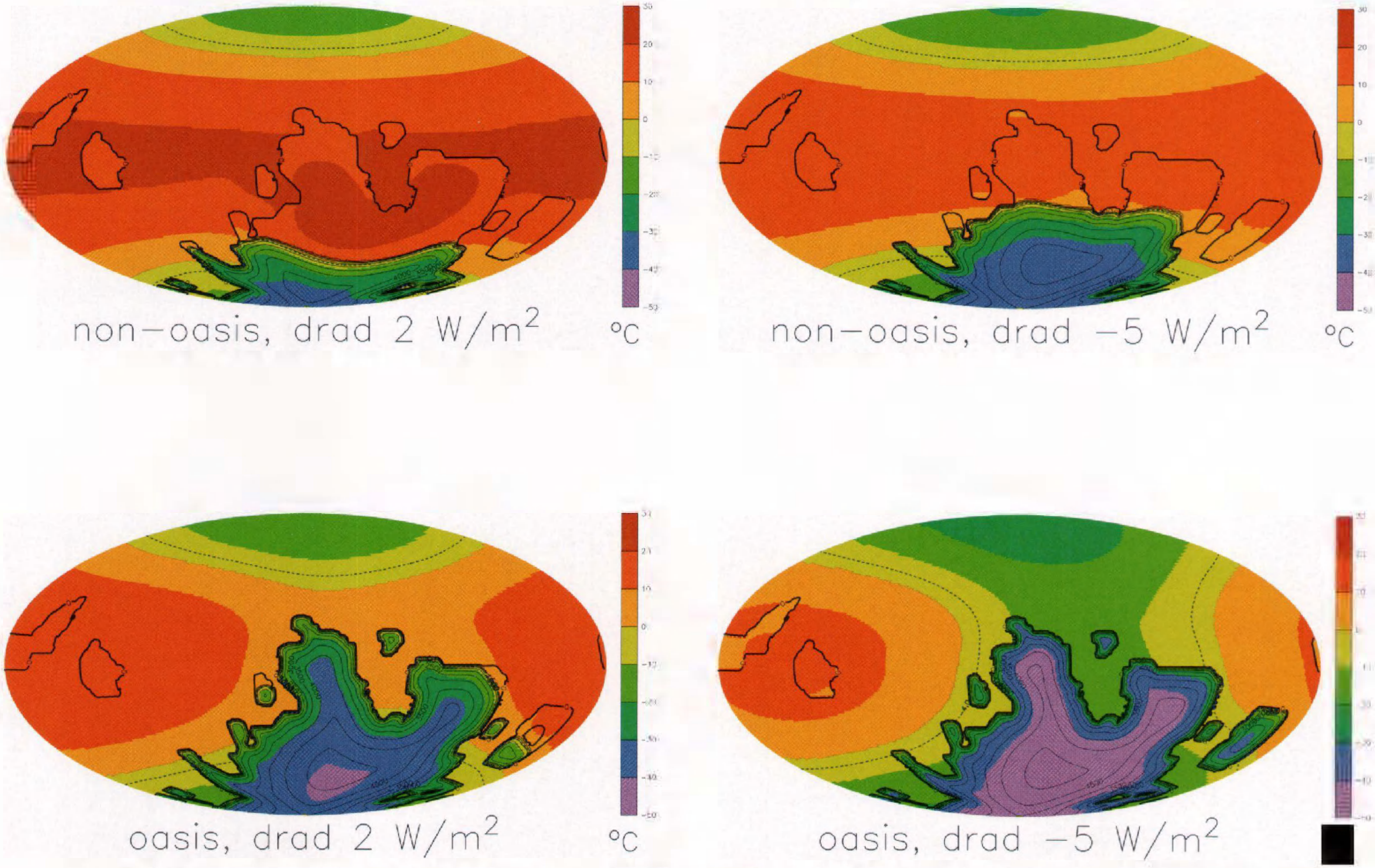
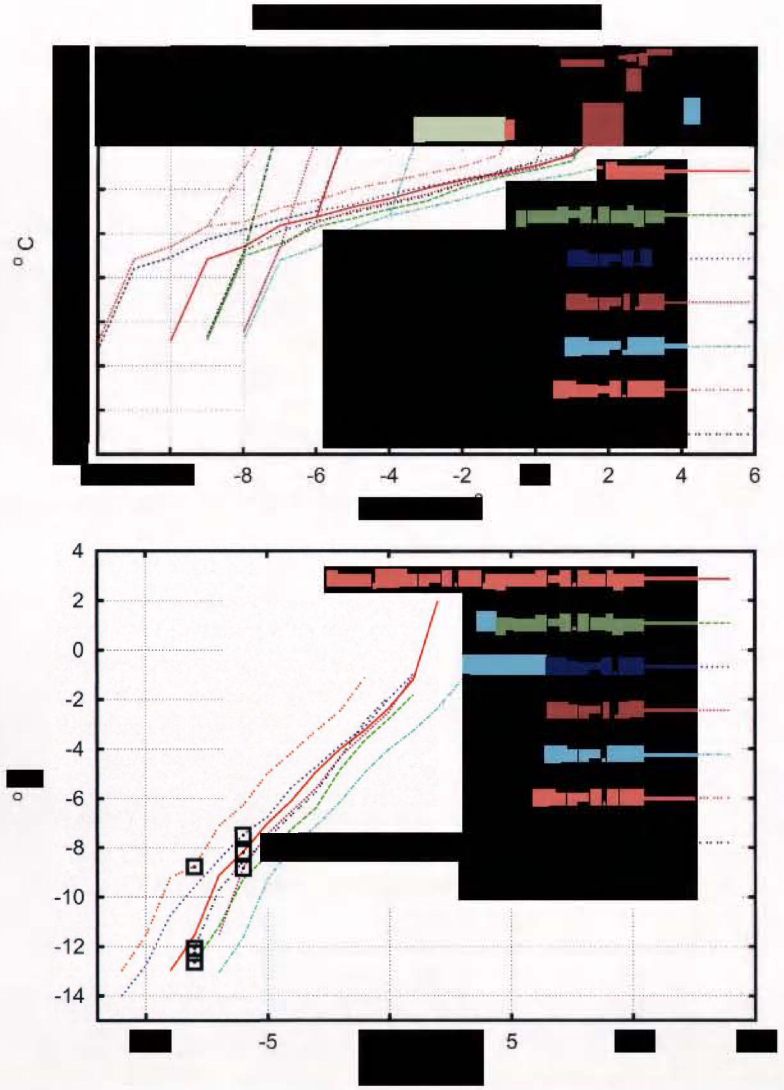


Plate 2. [redacted] fields for the four [redacted]-state so[redacted] of the EBM/IS[redacted] th[redacted] t[redacted] curve of [redacted] ted by the sy[redacted] on each of[redacted] ese p[redacted] sea level [redacted] ture is the [redacted] er[redacted] gr[redacted] rade [redacted] the [redacted] ns that are covered by sea ice. [redacted] e[redacted] xtended continental g[redacted] on is also c[redacted] depi[redacted] ther [redacted] phy contours over the [redacted] ice covered regions.



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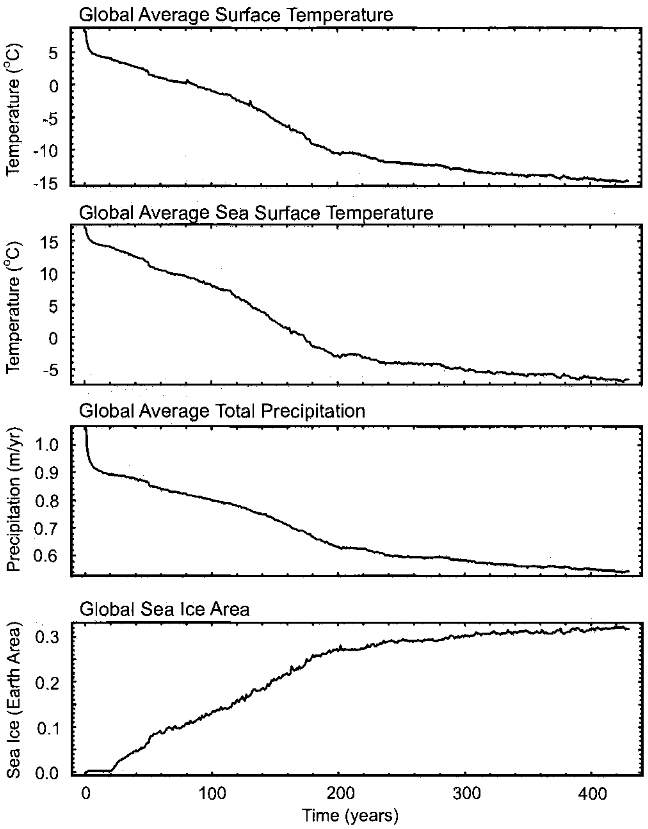

Figure 3. Spin-up to equilibrium data from the 425 year run of the NCAR CCSM for the climate of the Neoproterozoic using the same continental configuration as that employed with the EMB/ISM and the same 6% reduction of the solar constant. For the purpose of this integration the atmospheric CO_2 concentration has been fixed at the modern pre-industrial level of 280 ppmv and the continents have been assumed to be fully glaciated. Spin-up data are shown for annual and global mean surface temperature, annual and global mean sea surface temperature, annual and global mean precipitation and annually averaged sea ice area. All of these data have also been averaged for the last 50 years of model integration, a period during which the system appears to be close to statistical equilibrium.

state, including the globally averaged surface temperature, the globally averaged sea surface temperature, the globally averaged precipitation rate and the total area of sea ice cover. Inspection of the Figure will show that statistical equilibrium of the model climate has been essentially achieved after approximately 425 years of simulated evolution. That the spin-up time for the Neoproterozoic integration should be less than was required for the LGM integration of *Peltier and Solheim* [2004] is unsurprising since the geometry of the ocean basins is considerably simpler so that the complexity of the thermohaline circulation is considerably diminished. Aside from the number of simulated years required to reach a state of approximate statistical equilibrium it is important to note that the average precipitation rate that is characteristic of this eventual equilibrium is very close to the 0.6 m/yr value assumed in the integrations performed of the EBM/ISM for which results were shown on Figure 2 (Note, however, that the choice preco=0.3 myr^{-1} in the EMB/ISM gives a result that is closer to the CCSM global mean precipitation of 0.6 m yr^{-1} because of the power law dependence of prec(t) discussed in Section 2.1). It is also important to note from the final frame on Figure 3 which shows the variation with time of the area covered by sea ice, that this property of the Neoproterozoic climate state is also close to equilibration, implying that a hard snowball state will not form in a climate in which the concentration of atmospheric CO_2 is equal to the modern preindustrial level. Because the system does continue to drift very slowly towards a colder equilibrium, however, we cannot be entirely sure that a further diminution of the area of the open water refugium would not occur if the system were integrated further forward in time.

Of equal importance from the perspective of the analyses reported herein, to that demonstrating the quasi-equilibrium of the area covered by sea ice, is the quasi-equilibrium result for the globally averaged surface temperature. The equilibrated value of mean surface temperature produced by the CCSM is -14.8° C, a value which, when corrected for the topography of the ice covered continents, reduces to a mean sea level temperature of -10.3° C. The former and latter values are plotted on Figure 2 as the open circle and solid circle respectively. Inspection of this result from the CCSM relative to the result for the equivalent point on the oasis branch of the hysteresis loop delivered by the EBM/ISM, which corresponds to a value of ΔA = -0.41 W/m^2 at $[CO_2]$ = 280 ppmv, will show that the mean sea level temperature of the equilibrium predicted by the CCSM is more than 5 °C colder than that delivered by the EBM/ISM. As previously mentioned this is an entirely expected consequence of the fact that the parameters A and B employed in the representation of the infrared forcing in the simple model have not been re-calibrated so as to properly represent Neoproterozoic conditions which are characterized by a significant reduction of the IR contribution due to water vapour feedback.

Of primary interest for present purposes, however, is the nature of the equilibrium solution that the CCSM has delivered. This equilibrium is illustrated in Plate 4 on which we show, in Mollewiede projection as for Plate 2, the 50 year averaged equilibrium fields for annually averaged surface temperature, annually averaged sea surface temperature, annually averaged precipitation rate and annually averaged sea ice cover. Focusing first upon the latter field and comparing it to the results for various points on the hysteresis curve of Figure 2, it will be clear that the CCSM result is for an oasis solution that is most like the EBM/ISM result on the oasis branch for dRad = -5 W/m^2 although there is no sea ice connection to the south polar supercontinent as there is in the EBM/ISM result. Inspection of the remaining frames of Plate 4 simply illustrates the further properties of the climate that characterizes the oasis solution delivered by the CCSM. Of special note is the relatively high rate of precipitation that continues to occur along the intertropical convergence zone and the still rather warm SSTs with temperatures in excess of 15°C characteristic of this same region.

Although space will not allow us to provide a discussion of the full range of diagnostic analyses that relate to the detailed characteristics of the circulations of the atmosphere and ocean in this simulation, it proves interesting by way of summary to show some degree of further detail. To this end Plate 5 shows, in the upper and lower frames respectively, the properties of the annually averaged surface pressure and wind fields over the surface of the planet and the overturning circulation of the ocean represented by the zonally averaged meridional transport stream function. The former frame reveals strong tropical easterlies in the equatorial region over the ocean and intense midlatitude westerlies in approximate (quasi-) geostrophic balance with the surface pressure field. The nature of the overturning circulation of the oceans according to this model result is especially interesting. The lower plate of Plate 5 demonstrates this to be governed by intense mid latitude sinking in the northern hemisphere to the south of the sea ice cap and somewhat weaker sinking around the coast of the ice-covered southern hemisphere supercontinent. It appears to be the strong sinking due to brine rejection along the sea ice front which draws warm equatorial water northwards and thereby strongly inhibits the southerly extension of the northern hemisphere sea ice cap which is required in order for the system to descend into the hard snowball state. As previously discussed in *Peltier* [2002], therefore, the influence of ocean dynamics is such as to significantly inhibit the occurrence of the snowball bifurcation. Although deep water also forms along the coast of the glaciated southern hemisphere supercontinent, as it does today around Antarctica, the water mass that is formed by this process is not nearly as influential as that which forms due to sinking in the north although it also serves to impede sea ice advance by warming this southern region and drawing warm equatorial water southwards.

4. A "CO_2 ATTRACTOR" IN THE NEOPROTEROZOIC

In attempting to bring together the observational evidence for the large amplitude oscillations in $\delta^{13}C$ that are characteristic of the Neoproterozoic era and the results of the simulations of the physical climate system discussed in the last Section of this paper, we seek a mechanism or mechanisms that would strongly couple the physics to the biogeochemistry. Clearly the possible existence of hysteresis in Neoproteozoic climate evidenced in Figure 2 is highly suggestive of the possibility of the existence of a "CO_2 Attractor" as speculated upon recently in *Crowley et al.* [2001]. Their idea was simply as follows, although no attempt was made in that paper to articulate it in any detail. Suppose, for some reason, the CO_2 concentration in the atmosphere is decreasing and the system is in an initial state on the "hot branch" of the hysteresis loop in Figure 2. Eventually, as CO_2 levels continue to fall, the system will experience the sharp decrease in temperature that is precursory to its final descent into the hard snowball state. Suppose furthermore that some physical/biogeochemical process were to come into play, once the system descends from the "hot branch", which strongly opposes the continuing CO_2 decrease and in fact acts such as to reverse this initial tendency. The system would then warm along the oasis branch until finally it executes the rapid warming that takes it back onto the hot branch. If the same process that originally inhibits the descent onto the hard snowball state were then to inhibit its further ascent along the hot branch, we would have the possibility of an oscillatory system in which the atmospheric concentration of CO_2 would oscillate between the extrema that define the low concentration and high concentration edges of the hysteresis loop, simply going around the loop again and again until some additional process acts so as to allow it to escape.

What remains to be understood, if this hypothesized behaviour is to be realized, is the nature of the nonlinear process whereby entrapment onto the hysteresis loop is forced to occur. If we were able to identify such a mechanism, then we might associate the large amplitude $\delta^{13}C$ oscillations shown on Plate 1 with a limit cycle solution of a nonlinear system that included this mechanism as well as the elements of the physical climate system that support the existence of the hysteresis loop.

One suggestion of what this mechanism might involve has very recently been discussed by *Rothman et al.* [2003] although the authors were apparently unaware of the paper of *Crowley et al.* [2001] in which the idea of a Neoproterozoic "CO_2 Attractor" was first suggested. It will therefore be useful to discuss the idea of Rothman et al. in the context of the present analysis. Rothman et al. provide a very compelling argument to the effect that the oscillations of $\delta^{13}C$ that occurred during the Neoproterozoic cannot be explained by a conventional model of the carbon cycle in which equilibrium is assumed to exist between the interacting reservoirs of organic carbon and inorganic (carbonate) carbon (which includes all of the CO_2 dissolved in the oceans and all of the CO_2 in the atmosphere). They trace the necessarily disequilibrium dynamics of the Neoproterozoic interval to the existence of an extremely massive organic carbon reservoir confined to the oceans. This reservoir during the Neoproterozoic is argued to have con-

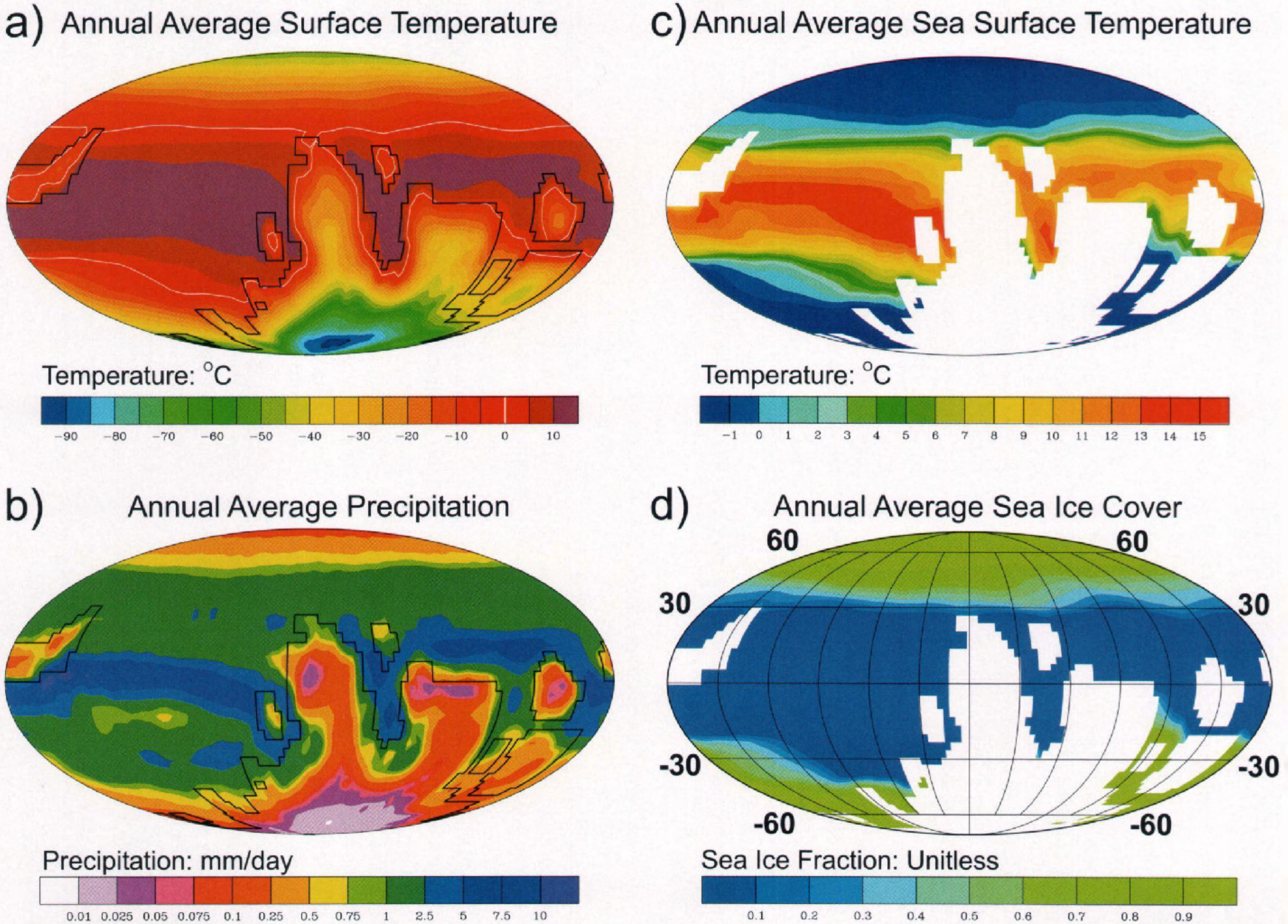

Plate 4. 50 year averaged fields for surface temperature, sea surface temperature, precipitation and sea ice area from the end of the Neoproteozoic integration.

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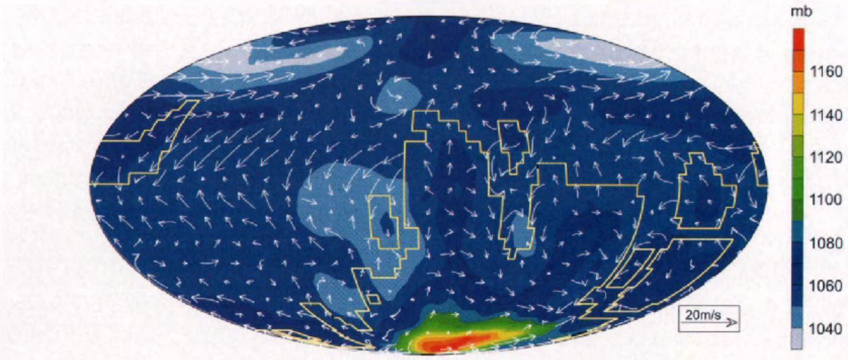

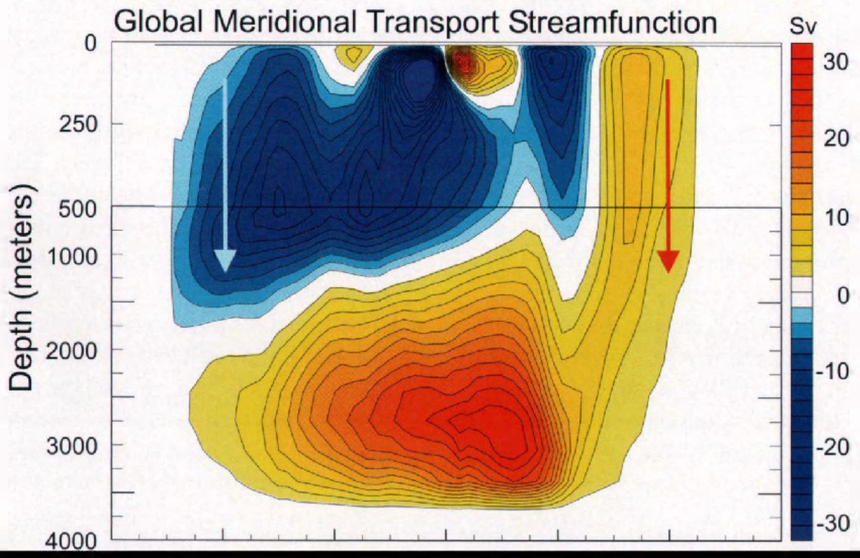

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tained as much as 100 times the organic carbon as do the present day oceans. Figure 4, which is reproduced from their paper, illustrates the 2 box model of the carbon cycle that the authors employ as basis for their analysis. In this diagram δ_1 and τ_1 are the isotopic contents and residence times in the inorganic reservoir and δ_2 and τ_2 those for the organic reservoir. Rothman et al. show that $\tau_2 >> \tau_1$ is consistent with the out of equilibrium behavior required by the observed relationship between the isotopic composition of carbonate and the difference between the isotopic compositions of carbonate and organic carbon. They show by computation on an explicit mathematical model (their equations 6–9) of the interacting reservoirs that the carbon cycle model under these conditions is able to deliver an excellent facsimile of both the positive and negative phases of the $\delta^{13}C$ oscillations shown in Plate 1.

The most interesting aspect of their analysis, however, concerns a brief speculation as to how descent into a snowball glaciation event may be arrested so as to prevent entry into the hard snowball state and thereby require that the coldest achievable states are those of the oasis type first identified by *Hyde et al.* [2000], whose work Rothman et al. reference in this connection. Rothman et al. point out that as the ocean cools as a consequence of a shift to lower levels of atmospheric CO_2 concentration, "more O_2 would be partitioned into the ocean in a colder climate". As the ocean becomes more strongly ventilated the organic carbon reservoir would become re-mineralized thereby increasing the amount of CO_2 in the carbonate reservoir. They argue that this effect would be extremely important because the solubility of O_2 in sea water increases by a factor of 2 as the water temperature drops from 30°C to 0°C. If we now connect this biogeochemical effect to the physical hysteresis loop shown in Figure 2, then we clearly have the basis for the existence of the nonlinear limit cycle behavior required to understand the $\delta^{13}C$ oscillations shown on Plate 1. As the system descends to lower values of atmospheric CO_2 concentration along the hot branch of the hysteresis loop,

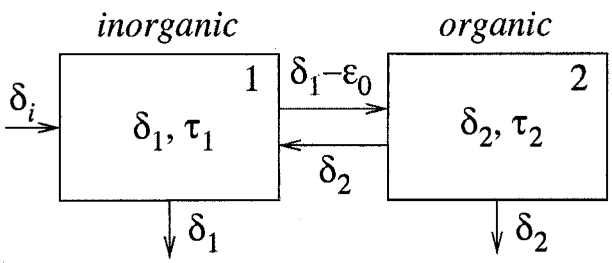

Figure 4. The 2 box model of the carbon cycle employed in the analysis of *Rothman et al.* [2003]. The box of isotopic composition δ_1 and residence time t_1 denotes the carbonate box whereas the box of isotopic composition δ_2 and residence time t_2 denotes the organic carbon box. When carbonate (CO_2) is transformed to organic carbon through photosynthesis an isotopic fractionation t_0 occurs.

eventually the system cools sufficiently that the draw down of O_2 from the atmosphere into the ocean results in the remineralization of the organic reservoir and the CO_2 concentration begins to rise again, but now along the oasis branch of the hysteresis loop of Figure 2. Eventually the system warms sufficiently as to cause it to execute the jump from the oasis branch to the hot branch. This warming exhausts the oxygen from the ocean, thereby decreasing the rate of remineralization of the organic reservoir, thereby causing the atmospheric concentration of CO_2 to begin to decrease once more. The origin of the $\delta^{13}C$ oscillations shown on Plate 1 is thereby explained by combining the fact that there is hysteresis in the physical climate system to variation of the concentration of atmospheric CO_2, together with the potential for strong negative feedback (the restoring force required to support an oscillation) due to the O_2 mediated biogeochemistry. That this suggestion is plausible follows from the fact that increased remineralization of (light) organic carbon both lowers $\delta^{13}C$ and increases pCO_2, provided that the dynamical condition identified in *Rothman et al.* [2003] is met.

Of course this model works only to the extent that the atmospheric concentration of O_2 was high enough during the Neoproterozoic to serve as the required link between the physical and biogeochemical components of the system. *Rothman et al.* [2003] provide an estimate of this requirement that suggest that a level that is only 4% of the present atmospheric O_2 concentration would be sufficient. In this regard it would appear that the early paper of *Broecker* [1970] is crucial to the success of the argument that we are presenting herein. Broecker's paper deals explicitly with the linkage between the organic and inorganic carbon reservoirs and the importance of the atmospheric oxygen concentration to this inter-connection. This idea is well captured in the following sentences which we quote directly from this paper. "The enrichment of ^{13}C in the carbonate carbon that necessarily accompanied the growth of the organic reservoir must have resulted in a shift in the $^{13}C/^{12}C$ ratios in sea water. This shift should be recorded in marine carbonates formed in the course of this transition period. Therefore, the absence of such a shift in the $^{13}C/^{12}C$ ratio in carbonates deposited from early Paleozoic to recent time [*Craig,* 1953; *Keith and Webber,* 1964] implies that the development of the organic carbon reservoir, and hence of the atmospheric O_2 reservoir, occurred prior to Paleozoic time". Here Broecker is clearly using the deep interconnection of O_2 to the two primary reservoirs, whose interaction constitutes the carbon cycle, to argue that the concentration of atmospheric O_2 must have been high early in Earth history, but the interaction he invokes is precisely that called upon in the *Rothman et al.* [2003] paper. In this scenario the hard snowball glaciations of Hoffman and colleagues are impossible to achieve. Rather, the coldest climate states that are realizable are those of "oasis" type which lie along the cold branch of the hysteresis curve in Figure 2. Even if it were to turn out that the strong hysteresis effect that we have identified herein were found not to occur in the climate system of the Earth, it may nevertheless prove possible for a strongly nonlinear oscillation of $\delta^{13}C$ to exist as a consequence of the feedbacks we are discussing.

5. CONCLUSIONS

The arguments presented herein are clearly in an early stage of development and there are several outstanding issues that will have to be resolved before we will be in a position to suggest that our hypothesis concerning the nature of Neoproterozoic glaciation is entirely sound. Among these outstanding issues, one that may be especially critical concerns the fundamental question as to whether hysteresis actually exists in a more complete climate model than that consisting of the ice sheet coupled energy balance model for which we have established it herein. In the absence of the detailed analyses that will be required to demonstrate the existence of multiple equilibria in the more complete model, the absence of this necessary analysis must stand as a caveat upon the hypothesis that we have advanced herein. If we are successful in establishing the existence of hysteresis in the fully coupled model, it will be important to extend the simpler ice sheet coupled EBM so as to explicitly incorporate the carbon cycle model of *Rothman et al.* [2003] together with the mediating influence of atmospheric O_2 as originally discussed in *Broecker* [1970]. It would appear that a biogeochemistry coupled model of the physical climate system of this kind would constitute an interesting vehicle with which to further explore the fascinating issues in Earth evolution that surround the problem of the Neoproterozoic carbon cycle.

Acknowledgments. This paper is a contribution to the Climate System History and Dynamics Programme that is sponsored by the Natural Sciences and Engineering Research Council of Canada and by the Meteorological Service of Canada. The work has also been supported by NSERC Grant A9627. Very helpful reviews of the first draft of this paper were provided by Dan Rothman and a second (anonymous) referee. We are grateful to them both.

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Interpreting the Neoproterozoic Glacial Record: The Importance of Tectonics

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The breakup of Rodinia between about 750 and 610 Ma created rifted margin basins along opposing paleo-Atlantic and paleo-Pacific margins of Laurentia. Sedimentary processes and stratigraphic successions were strongly controlled by tectonic subsidence and sediment supply. This relationship creates systematic changes in relative water depths during the rift cycle giving rise to a distinct fill stratigraphy. Lowermost synrift facies successions are dominated by coarse grained sediment, derived from faults and tectonically-uplifted topography, deposited by sediment gravity flows. Poorly-sorted debrites (*diamictites*) interbedded with sediment gravity flows such as turbidites, are a common component. These facies are often mistaken for poorly-sorted ice sheet deposits (*tillites*). Rift-related diamictites are generated regardless of paleolatitude requiring *independent evidence* of glaciation. Thick shales (principally slope turbidites) that overlie diamict-bearing synrift facies are widely regarded as recording postglacial 'glacioeustatic' flooding but instead record rapid thermal subsidence. The distribution of glacial and glacially-influenced marine strata on a simplified paleogeographic reconstruction of Rodinia, indicates that ice was widespread but regional in scope and likely related to strong tectonic uplift on the rifted margins of Laurentia. The Snowball Earth model draws heavily on fluctuations in carbon isotopes as a record of global glaciations that shut down hydrologic and biologic activity. Sedimentary and biological records instead indicate open marine conditions with a weak glacial influence and an uninterrupted hydrosphere and biosphere. Neoproterozoic glaciation was likely widespread but regional in extent, strongly controlled by tectonics and diachronous in its timing as Rodinia progressively broke apart.

INTRODUCTION

In the pursuit of globally-correlative marker horizons in otherwise unfossiliferous Neoproterozoic strata, many geologists draw simplistic interpretations from the sedimentary rock record. The use of Neoproterozoic tillites [*Chumakov*, 1981; *Narbonne* and *Gehling*, 2003] is a case in point. A widely held assumption is that most diamictite facies can be regarded as *tillites* deposited directly by continental ice sheets or glaciers, and further, that their widespread, apparently global distribution on all continents, records unique global climate events not seen since [e.g., *Lindsay* et al., 1996, p.391]. The roots of this logic are deep and can be traced back to the pre-plate tectonic era of the 1920s and 30's at a time when Wegener's model had been rejected by many English-speaking geologists. Faced with the presence of undoubted Neoproterozoic (and late Paleozoic) tillites in equatorial latitudes (and evidence of ice flow away from the equator), prominent glacial geologists argued that since the continents hadn't

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moved, glaciers must have originated in the tropics [*Coleman*, 1926]. The literature of this time period is replete with such interpretations which in fact, are anchored in the yet older proposal of a global *Eiszeit* originally made by Louis Agassiz in 1837 [1842]. According to *Agassiz* [1842] Die Eiszeit had wiped out all life on planet Earth; *Agassiz and Coutinho* [1868] claimed to have found glacial drift from such a catastrophe left in the Amazon. The concept of worldwide glaciation was elaborated by *Mawson* [1949] in his study of Sturtian tillites in Australia. It reemerged once again in the early 1960's (as the great 'infracambrian glaciation' of *Harland*, 1964) then strengthened by paleomagnetic data purporting to show that Neoproterozoic tillites had been deposited in low latitudes. In the mid-1970's, following acceptance of the plate tectonic paradigm and the emergence of sedimentology as a powerful means of interpreting paleoenvironments, the global glaciation model was rejected as a 'myth'. [*Schermerhorn*, 1974]. Nonetheless, the idea has been surprisingly resilient and has resurfaced as the 'Snowball Earth' hypothesis of Hoffman and his colleagues, supported by much additional paleomagnetic and geochemical data. These new data have unfortunately been wedded to longstanding and simplistic notions of how poorly-sorted diamictic lithofacies are generated, how sedimentary basins are formed and how they are filled. In the quest for the holy grail of global correlations, many geologists have lost sight of the importance of tectonic controls on the evolution of facies and stratigraphic successions. It is our contention that the record of glaciation and climate is encrypted in complex Neoproterozoic marine successions that cannot be read as bed-for-bed records of climate and eustatic sea level.

Purpose and Scope of This Paper

When discussing Earth's glacial record, it is important to keep in mind the distinction between periods of glaciation, *senso lato*, that last several tens of millions of years (what some have called 'glacioeras'), and short-term, high frequency glacial episodes of ice sheet expansion and contraction that almost certainly occurred *within* such episodes and akin to the glacial/interglacial cycles of the last 5 million years. This paper is primarily concerned with the broader episodes of glaciation and the associated long-term tectonic controls that appear to dictate their timing, distribution and stratigraphic record in the Neoproterozoic. Other models for Neoproterozoic glaciation, such as the Snowball Earth, essentially ignore such controls and see glacioeras as global glaciations triggered by runaway albedo effects.

The Snowball Earth model is the latest in a long line of 'global glaciation models' distinguished from its predecessors by incorporating new and exciting geochemical and paleomagnetic data. It has re-energized study of a key time period in Earth's history. Unfortunately, much that has been written of the Snowball Earth is not grounded in a thorough understanding of the sedimentologic and stratigraphic record of Neoproterozoic glacioeras; indeed, it is very evident that the results of much past work have not been been considered by the model.

First, we review contrasting approaches followed by geologists in describing and interpreting sedimentary strata. We will show that the Snowball Earth model is underpinned by an outdated and simplistic approach to interpreting the stratigraphic record. We then examine what is known of Neoproterozoic sedimentary basins, their global plate tectonic setting and the nature of their infills. This approach leads to a rather different interpretation of the extent of Neoproterozoic ice covers that is completely at odds with notions of global glaciation and a permafrozen planet.

INTERPRETATION OF SEDIMENTARY STRATA: ALLOSTRATIGRAPHY VERSUS SEQUENCE STRATIGRAPHY

As background to an examination of the Snowball Earth model, it is worth reviewing how differing groups of geologists approach the description and interpretation of sedimentary strata. For more complete reviews, the reader is referred to *Walker* [1992] and *Miall* [1995]. Sedimentologists employ a facies-based methodology where individual sedimentary *facies types* occur within thicker, genetically-related packages (*lithofacies associations*). Lithofacies associations are the product of depositional systems and geologists have formulated simple facies models for the principal clastic, carbonate and chemically dominated depositional systems found on planet Earth (e.g., glacial, aeolian, fluvial etc; *Walker* and *James*, 1992). The process of recognizing facies associations is relatively objective but the next step, that of interpretation, is not straightforward and it is here that problems abound. The central issue is identifying the main controls on the evolution of sedimentary successions; is it the ups and downs of global sea level, basin tectonics, or both acting in unison? In approaching this question, geologists follow one of two main guiding principles either *allostratigraphy* or *sequence stratigraphy*. The different routes can lead to very different interpretations.

Allostratigraphy

The term *allostratigraphy* refers to the practice of logging outcrops or core where the focus is on identification of the *bounding erosional discontinuities* that separate lithofacies associations. Implicit in this approach is recognition that the presence of such breaks highlights that important changes occurred in depositional conditions. This most commonly arises for example, by changes in water depths and associated energy levels resulting in the operation of a different set of sedimentary processes. The allostratigraphic approach recognises the wide range of geologic processes that operate within and external to the depositional system and that dictate the formation of bounding disconformities. An important control in many cases is basin tectonics, which creates changes in *relative* sea level masking any *absolute*, eustatic signal. The recognition of the latter requires very tight age or biostratigraphic dating to demonstrate that relative sea level changes in different areas of a basin were in fact, synchronous. The allostratigraphic approach has been said to allow a more 'natural' subdivision of the geologic record as against traditional 'bed by bed' lithostratigraphic approaches that tend to overemphasize the importance of individual lithologies (e.g, sandstone, shale, conglomerate etc) thereby neglecting that such facies are part of thicker, genetically-related packages [*Walker*, 1992, p. 10].

Sequence Stratigraphy

Sequence stratigraphy grew out of seismic stratigraphic methods introduced by the Exxon Production Research Company and is based on recognition of unconformity-bounded 'depositional sequences'. Sequences are attributed directly to changes in eustatic sea level often by reference to a standard chart of sea level variation through time [e.g., *Van Wagoner* et al., 1988; *Vail*, 1992]. When first introduced, if offered the real possibility of allowing global correlations between widely dispersed sedimentary basins but the assumptions behind the approach have been shown to be simplistic. As a concept, it is over-reliant on a few well-studied, mostly passive margin basins, whose fills record the specific subsidence history of that basin. At the same time, poor age dating controls has promoted force-fitting of sequences identified in different basins to notional changes in eustatic sea level. As has been pointed out at length by *Miall* [1986, 1997] whereas *some* of the inferred sea level changes may be eustatic and thus useful for global correlations, this approach ignores the often primary role of tectonics in creating relative sea level changes within individual sedimentary basins.

The distinctions made above with regard to different *modus operandi* of interpreting sedimentary rocks are of fundamental significance to interpretation of the Neoproterozoic glacial record. The Snowball Earth model, as in the classic sequence stratigraphic approach, assumes that the primary control on sedimentation was global climatic refrigeration and associated glacioeustatic sea level response [e.g., *Hoffman* et al., 1998; *Ojakangas* et al., 2001; *Christie-Blick*, 1997]. Glacioeustatic 'successions', commonly kilometres thick, are recognized and correlated globally on the basis of supposed synchronous changes in eustatic sea level reflecting the waxing and waning of ice sheets. 'Cap carbonates' are held to record postglacial glacioeustatic sea level rise [*Hoffman* and *Schrag*, 2002 and refs therein]. The model is firmly underpinned by sequence stratigraphic thinking where global climate and sea level are 'read" directly from the rock record. Diamictites are invested with glacial climatic significance and non-diamictic strata, most commonly shales that overlie diamictites, are assumed to represent interglacial climate conditions and high postglacial sea levels. The antecedents of this approach can be found in classic 'bed-for-bed' climatostratigraphic approaches [e.g., *Spencer*, 1971]. So-called 'glacioeustatic sequence boundaries' have even been proposed as a Global Stratotype Section and Point (GSSP) for the terminal Proterozoic system on the basis of the assumed world-wide synchronicity of Neoproterozoic glaciation [e.g., *Christie-Blick* et al., 1995, p. 21].

None of the above assumptions is supported by firm evidence; they are instead held to be intuitively correct by proponents of the Snowball Earth model. The following sections provide a brief critique of the principal assumptions behind the Snowball model. Alternative interpretations, based on emerging allostratigraphic approaches to the study of sedimentary basins, are indicated (Table 1).

DIAMICTITES AND TILLITES: A CASE OF MISTAKEN IDENTITY

A key weakness of the Snowball Earth model is that it is based on simplistic interpretations of diamictite facies as tillites deposited directly by ice sheets during correlative global glacial events. The term 'diamict' (lithified; 'diamictite') is a purely descriptive term for any poorly-sorted admixture of boulders, gravel, sand, silt and clay, regardless of depositional origin and where no specific sedimentary process(es) is implied. A 'till(ite)' on the other hand, is defined by glacial sedimentologists as 'a diamict that was deposited *directly* by glacier ice; usually meaning underneath the glacier or ice sheet and resulting from the melt-out and/or smearing of debris against a stiff substrate (meltout/lodgement till) or the deformation of substrate sediments (deformation till). A tillite is a diamictite, but not all diamictites are tillites.

Diamict Forming Environments

Diamict(ite)s are an example of a *common* facies type that forms in a very wide range of sedimentary environments and depositional systems regardless of climate and latitude (Fig-

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ures 1,2) . The same facies type (such as massive diamictite) occurs for example, on the slopes of volcanoes (Figure 3A), in humid tropical areas where basement rocks have experienced deep weathering (Figure 3B), as ejecta and intrusive bodies resulting from meterorite impacts (Figure 3C), in the proximal areas of submarine and subaerial fans and slopes

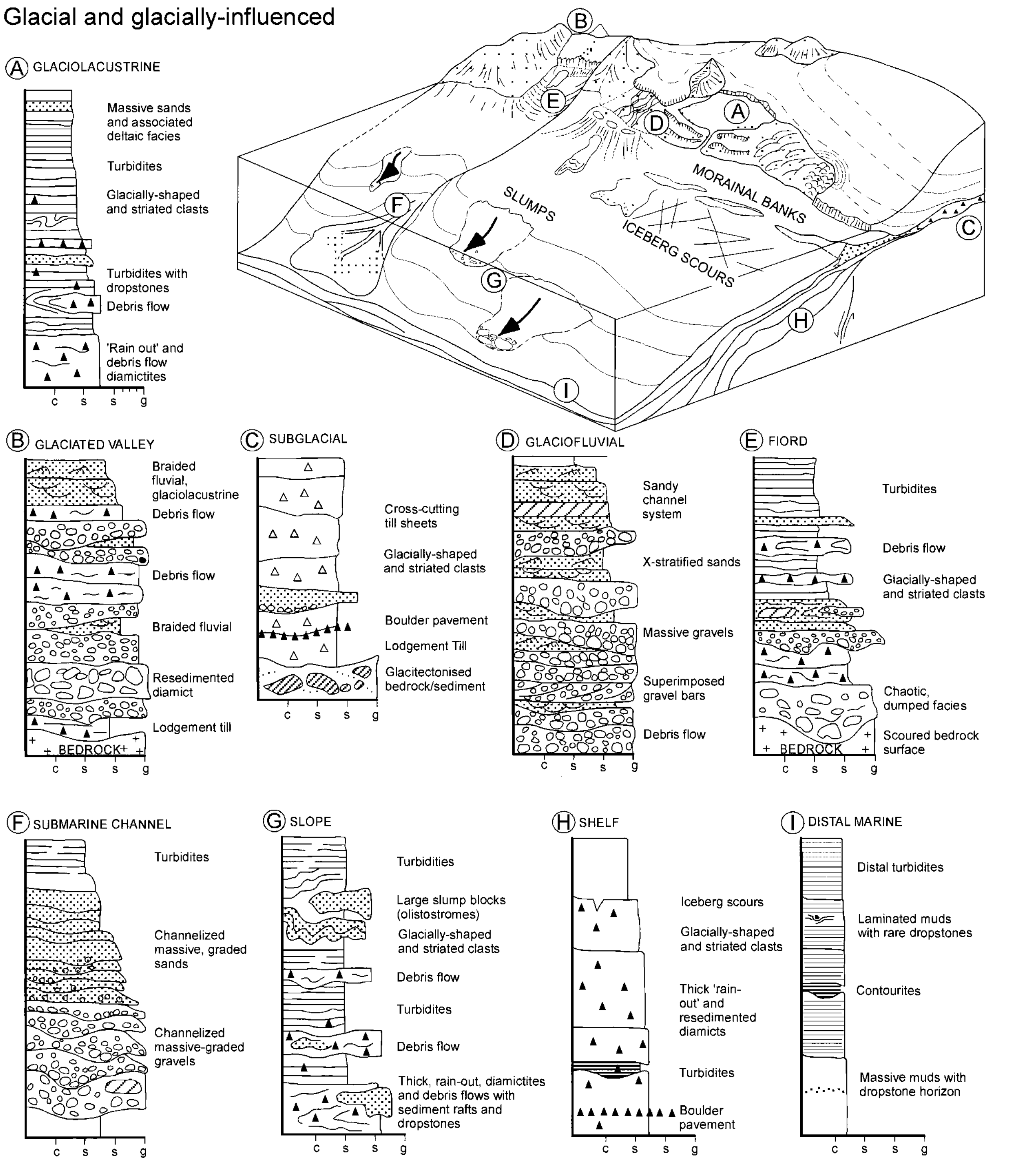

Figure 1. Glacial environments in which diamict(ite) facies are produced.

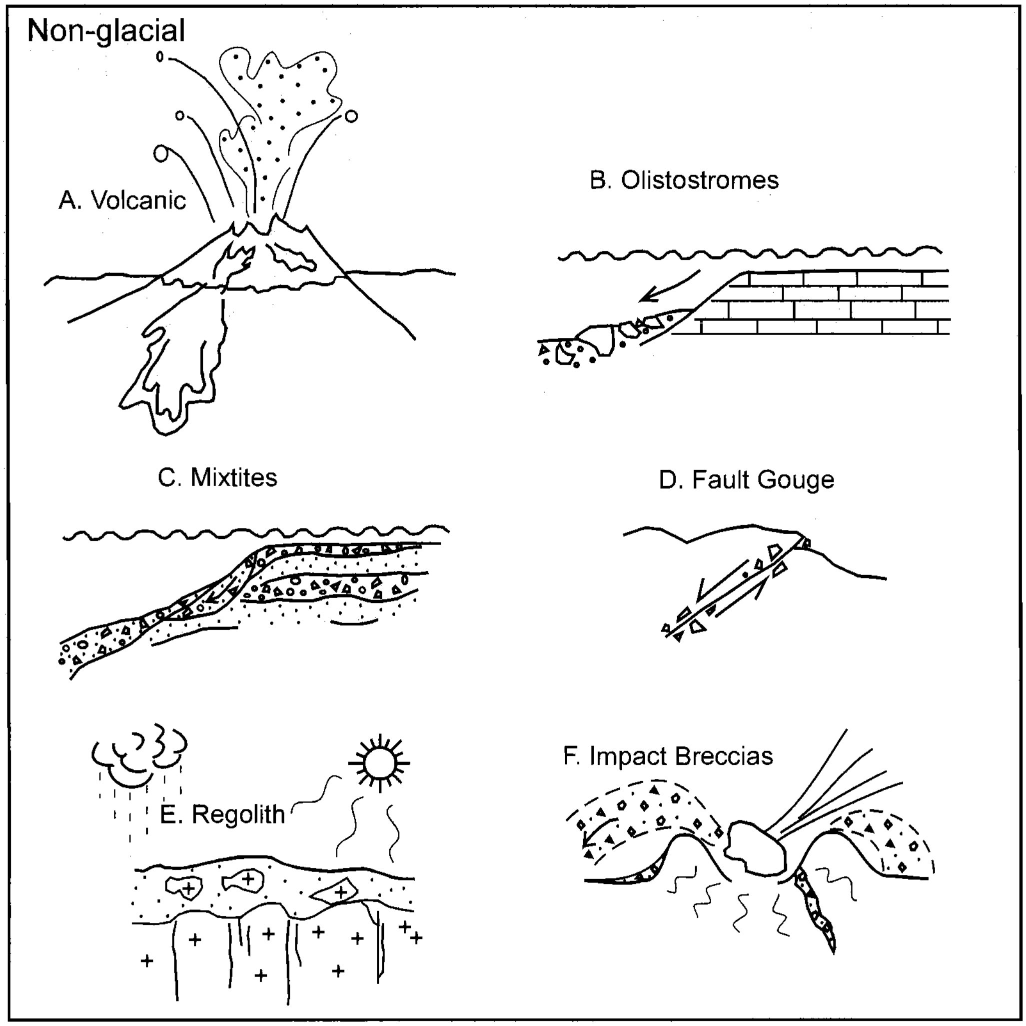

Figure 2. Non-glacial environments in which diamict(ite) facies are produced.

(Figure 3D), and in a wide range of glacial and glacially-influenced environments. In other words, the same facies types are produced by different processes. Of these processes, mass flow is the most significant such that diamictites deposited by debris flows (debrites) are arguably the most frequently occurring type in the rock record. These poorly-sorted facies are produced by the mixing of coarse and fine sediment as a result of either slope collapse [*Einsele*, 2000], the downslope transport of fault talus [*Eyles* and *Eyles*, 2000], or by the avulsion of channels transporting gravelly turbidites into areas of fine grained sediment [*Crowell*, 1957; *Nemec* et al., 1984]. By themselves, these facies have no unique distinguishing characteristics; they have the same, common appearance in outcrop or core.

There can therefore, be no unique 'glacial' environmental interpretation of diamictite facies unless there is independent evidence of glaciation (striated clasts, glacially-shaped clasts; see below). As a result of the failure to appreciate this fundamental caution, 'bogus' glaciations have been introduced into the rock record; a point made strongly by *Crowell* [1957] and *Schermerhorn* [1974, 1975].

Problems in interpreting the origin of diamictites occur because they are not *universal* facies types. These latter types are formed as a consequence of the same depositional processes (e.g., storm wave-deposited hummocky cross-stratified sands) and can be interpreted unambiguously. In the case of common or 'anonymous' facies, critical paleoenvironmental evidence must be derived from consideration of conformable and genetically associated facies found above and below. These provide the overall depositional 'context' by identifying those facies that were spatially contiguous within the then depositional system.

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noan 'Snowball' populations and does not support the hypothesis of repopulation of marine areas by extremophiles clustered around hot springs on the ocean floor [*Grey* et al., 2003]. In this record, evolutionary changes that do occur are suspected of being triggered by meteorite impact.

Part of the problem has, once again, been overly simplistic interpretations of the sedimentary strata in which organisms are preserved. Some are described for example, as being present in 'intertillite' beds implying interglacial climatic conditions [*Hoffman* et al., 1998]. The deposits in question accumulated however, in a deep marine environment (well below wave base) with only weak glacial influence on depositional conditions. This is well-illustrated by the Ediacaran faunas of the Mistaken Point Formation that occur within the 6km thick, turbidite-dominated Conception Group of eastern Canada [*Narbonne* and *Gehling*, 2003]. There, Ediacaran faunas occur stratigraphically well above (1.5 km) deep marine turbiditic strata that show a very weak glacial influence [*Eyles* and *Eyles*, 1989]; any genetic relationship between glaciation and the appearance of these faunas is unconvincing. These organisms lived in a collisional arc setting environment that was more directly influenced by volcanism (they are preserved in tuffs) (Figure 6).

The Neoproterozoic sedimentary record identifies a normal hydrologic system and restricted extent of glaciers so the lack of any link between glaciation and biological evolution is not an unexpected finding. Conditions may have been little different from that of Phanerozoic glaciations where marine life flourished throughout glacial cycles close to ice sheets.

PALEOMAGNETIC DATABASE SUPPORTS GLOBAL GLACIATION

Much emphasis has been placed on paleomagnetic data indicating low depositional paleolatitudes for Neoproterozoic glacial deposits [see *Sohl* et al., 1999; *Evans*, 1999, 2000 for important reviews]. Eyles and Januszczak [2004] concluded that precisely *how* magnetic characteristics were acquired, *when*, and the *origin* of many of the strata being sampled remain outstanding unresolved issues [see also *Meert* and *van der Voo*, 1994]. The timing of magnetic acquisition is critically important at a time of known rapid plate motions whereas the precise depositional setting of key magnetic sites remains vague (e.g., Elatina Formation of South Australia). This uncertainty greatly complicates reconstruction of Neoproterozoic paleogeographies during the assembly and breakup of Rodinia between 1000 Ma and 600 Ma [e.g. AUSWUS; *Karlstrom* et al., 1999; *Li* et al., 1996; *Li* and *Powell*, 2001; vs. AUSMEX; *Wingate* and *Giddings*, 2000; *Wingate* et al., 2002; vs. SWEAT; *Moores*, 1991; *Hoffman*, 1991; *Dalziel*, 1991, 1997].

BANDED IRON FORMATIONS REQUIRE GLOBAL GLACIATION

The limited reappearance of banded iron formations in the late Neoproterozoic has been genetically linked by proponents of the Snowball Earth model to global glaciation; the model is that anoxic seawaters form below a global cover of thick sea ice thereby enabling ferrous iron to remain in solution [*Hoffman* et al., 1998, *Hoffman* and *Schrag*, 2002]. In fact, banded iron deposits are not uniquely associated with Neoproterozoic diamictite deposits and often occur stratigraphically below such deposits, are absent outright, or are demonstrably post-depositional [*Eyles* and *Januszczak*, 2004]. The reappearance of banded iron more likely reflects widespread continental rifting in the Neoproterozoic and deposition in enclosed or restricted rift basins close to hydrothermal vents along incipient mid-ocean ridges [*Young*, 1988; *Yeo*, 1987].

CARBON ISOTOPE EXCURSIONS ARE DRIVEN BY GLOBAL GLACIATION

The Snowball Earth model requires that fluctuations in carbon isotope trends are created by global glaciation events. The model predicts positive ^{13}C values in ocean waters prior to the onset of glaciation, due to preferential incorporation of ^{12}C in biomass. As environmental conditions deteriorate prior to each Snowball event and organisms die off, the burial of organic carbon reintroduces ^{12}C into the world's oceans yielding negative ^{13}C values that persist until the postglacial re-establishment of biological activity. All this is predicated on global cold that shuts down hydrologic and biologic activity; a scenario not supported by sedimentological evidence (see above).

Additional factors that need to be considered include rapid burial of organic material in rapidly subsiding rift basins, the exposure and weathering of older carbonate and enhanced vertical gradients in seawater ^{13}C due to redox stratification of ocean waters. Isotopic excursions could also be intrabasinal in nature resulting from the breakup of Rodinia where waters in enclosed or semi-restricted rift basins were in disequilibrium with global surface oceans [see *Shields* et al., 2002]. Some carbon isotope values from carbonate interbeds and clasts within supposedly 'glacial' diamictites show unusual *positive* trends [*Kennedy* et al., 2001a]. Strontium isotope data fail to support hydrologic cycle shutdown during Snowball glaciation and any enhanced continental weathering in the succeeding very warm interglacials [*Kennedy* et al., 2001b]. Neither are the physical assumptions behind the Snowball model supported by numerical climate modeling [*Hyde* et al., 2000; *Baum* and *Crowley*, 2001].

Whereas there is good evidence for systematic carbon isotope fluctuations that might be globally correlative, they cannot be simply the product of repeated Snowball events for the reasons outlined above that negate global glaciations and any marked biological crises.

'ZIPPER-RIFT': AN ALTERNATIVE TECTONIC MODEL FOR NEOPROTEROZOIC GLACIATIONS

How do we explain the timing and distribution of Neoproterozoic glacial and glacially-influenced strata? Of paramount significance is that Neoproterozoic glaciations took place when the planet's geography, climate and ocean systems were being fundamentally reorganised by the break up and dispersal of the supercontinent Rodinia. Commencing about 750 Ma and lasting for at least 150 million years, global rifting saw the widespread formation of extensional sedimentary basins and passive margins. Break up was a protracted event which began along the paleo-Pacific margin of Laurentia at about 750 Ma and later affected Laurentia's eastern (Iapetan) margin after about 610 Ma (Figure 4 A,B). In both cases, the dominant style of sedimentation was that of thick debris flow/turbidite successions that accumulated in fan/slope settings along rifted margins. *Some* successions show a clear record of glaciation on surrounding tectonically-uplifted source areas; *many successions do not.* Neoproterozoic glaciations appear to cluster into three phases that can be directly tied to major plate tectonic events. The first phase of Neoproterozoic glaciation (Sturtian) coincides with the initial break up phase of Rodinia. Not surprisingly, this group of deposits is dominated almost exclusively by glacially-influenced marine debris flows and turbidites deposited on submarine fans and slopes. These are now found in northwest Canada [*Eisbacher*, 1985; *Young*, 1992] and conterminous USA [*Link* et al., 1994], China [*Lu* and *Zhenjia*, 1991], Australia [*Powell* et al., 1994; *Young* and *Gostin*, 1991] and Oman [*Leather* et al., 2002] (Figure 4A). The strong relationship between breakup and initial glaciation is not coincidental. Strong tectonic uplift on rift shoulders and passive margins is implicated not only in the creation and transport of large volumes of sediment but also in the nucleation of widespread but regionally-centred ice covers.

A second cluster of Neoproterozoic deposits showing a glacial influence, is restricted in space and time to the opposing margin of Laurentia when it broke away from Baltica beginning about 610 Ma. This group of deposits includes the well-known glacially-influenced and rift-related Vendian (Marinoan) deposits of Spitsbergen, Norway, Scotland and northern Australia [*Hambrey*, 1982; *Vidal* and *Moczydlowska*, 1995; *Higgins* et al., 2001; *Arnaud* and *Eyles*, 2002] (Figure 4B).

There is increasing evidence of a third, tectonically driven phase of glaciation at about 565 Ma, along the collisional arc preserved as part of the Avalonian/Cadomian Belt in Newfoundland (Gaskiers Formation) and possibly in New England (Boston Bay Group where a glacial influence has long been debated) (Figure 6). The glacial deposits of the Kimberley district of Western Australia may be related to this third and last phase of end-Neoproterozoic glaciation [*Grey* and *Corkeron*, 2003; their Figure 14]. Given the great length of the rifted margin around the periphery of Laurentia (> 25,000 km), the timing of rifting was staggered, giving rise to a markedly diachronous climatic response. This relationship has been embodied into what is called a 'Zipper-rift' model for Neoproterozoic glaciation [*Eyles* and *Januszczak*, 2004].

DISCUSSION

Our principal contention is that the bulk of the Neoproterozoic glacial record is overwhelmingly *not of terrestrial origin*, but instead, is preserved in marine strata deposited on the margins of glaciated uplands. The record of glacial climates on land is stored (or rather encrypted) within marine slope and fan deposits reflecting rift basin formation and influxes of large volumes of sediment from tectonically-uplifted topography. Marine deposits (and their included biologic record) indicate a fully functioning hydrological system and the transport of large volumes of sediment by normal sedimentary processes. The predominant control on these marine facies and facies successions is tectonics, but they continue to be simply interpreted in terms of classic sequence stratigraphic or climatostratigraphic approaches.

Eyles and Januszczak [2004] show how typical rift basin fills evident from Phanerozoic rifts can be identified in the Neoproterozoic. Fills typically can be divided into synrift, thermal subsidence and post-rift phases (Figure 5). The oldest is dominated by coarse-grained mass flow deposits (typically diamictite/turbidite facies associations), the middle phase by basin flooding (typically thick, fine-grained turbidites) and the third by shallow water facies recording reduction in subsidence rates and the progradation of sediment sources across the basin. Within such basins, the effects of eustatic sea level are difficult to identify because of the control on relative water depths resulting from varying tectonically-driven subsidence rates [*Ravnas* and *Steel*, 1998; *Ledesma* and *Johnson*, 2001]. Traditionally, in sequence stratigraphic style, 'middle' shales have been interpreted as 'glacioeustatic successions'. These however are hundreds of metres (sometimes *kilometres*) thick [*Eisbacher*, 1981, 1985; *Christie-Blick* et al., 1988; *Aitken*, 1989; *Lindsay*, 1989; *Fairchild* and *Hambrey*, 1995] and result from long term and diachronous basin subsidence not globally correlative postglacial sea level rise. In this regard, the simulation of Hyde et al. [2000] with reduced solar luminosity and decreased CO_2 levels, produces ice-covered portions of Rodinia with a total ice volume no more than during the Last Glacial Maximum in the Pleistocene at about 20,000 years ago. Such an ice volume creates geologically-brief reductions in eustatic sea level of only about 150 m [*Ruddiman*, 2001]. It can also be noted that by themselves, glacioeustatic fluctuations cannot create accommodation space since absolute sea level always returns to its preglacial position after glaciation. Accommodation space can only be created by tectonic subsidence. Possible small-scale, high frequency changes in sea level likely conditioned by glaciation are noted by some workers [*Dehler* et al., 2001; *Leather* et al., 2002].

CONCLUSIONS

The hypothesis of global glaciation (Snowball Earth) is the latest iteration of a longstanding concept introduced by Louis Agassiz in 1837. The concept was carefully tested against the Neoproterozic stratigraphic record in the mid-1970's by Schermerhorn and was shown to be deeply flawed. Since then, analyses of sedimentary basins and their fills, underscore the earlier conclusion of Schermerhorn that Neoproterozoic glaciations were regional in extent and tectonically-related.

The record of Neoproterozoic glacation is stored in deep water slope successions deposited in marine rift basins and passive margins formed during the breakup of Rodinia between about 750 Ma and 610 Ma. It cannot be coincidental that the principal episodes of rifting are directly associated in time and space with the main Neoproterozoic glacioeras. A first phase (Sturtian/Rapitan) at about 750 Ma occurs along the paleo-Pacific margin of Laurentia. A second (Marinoan/Vendian) phase of tectonically-induced glaciation occurred along Laurentia's Iapetan margin after about 610 Ma, and a third (Marinoan II?) can be possibly identified in eastern North America and Australia.

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Neoproterozoic Glaciation: Reconciling Low Paleolatitudes and the Geologic Record

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This chapter is unavailable due to technical reasons.

Earth's Earliest Extensive Glaciations: Tectonic Setting and Stratigraphic Context of Paleoproterozoic Glaciogenic Deposits

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Paleoproterozoic glaciogenic deposits have a more restricted distribution than those of the Neoproterozoic, which are thought by some to provide evidence that the surface of the entire Earth was frozen (snowball Earth hypothesis). In Laurentia, Paleoproterozoic glacial rocks appear to be associated with the breakup of a supercontinent, whereas in Vaalbara they may form part of the early fill of compressional (foreland?) basins representing ocean closure. The scattered Paleoproterozoic glacial deposits may be approximately contemporaneous but ages are poorly constrained at around 2.3 Ga. Many features ascribed to the existence of a snowball Earth in the Neoproterozoic are not developed in the Paleoproterozoic. For example most of the older glaciogenic successions lack cap carbonates. Major element geochemistry of the post-glacial sedimentary rocks of the Gowganda Formation suggests a weathering trend opposite to that predicted by the SEH. The close association between iron-formations and some glacial deposits in the Neoproterozoic, is virtually absent from the Paleoproterozoic. Thus the Paleoproterozoic glacial successions lack many of the criteria that are supposed to substantiate the snowball Earth hypothesis. These ancient glacial deposits are perhaps more appropriately compared with those of temperate glaciations. Apparent low paleolatitudes derived from some Paleoproterozoic glaciogenic deposits pose a problem for any interpretation of these rocks. Williams suggested that these odd relationships might be explained by a much higher obliquity of the Earth's ecliptic in the Precambrian but resolution of these problems must await additional geochronological and paleomagnetic work.

1. INTRODUCTION

1.1. Brief Historical Introduction

Ancient (pre-Pleistocene) glacial deposits have been under study for about 150 years. *Mawson* [1949, p. 150] referred to early discoveries of late Paleozoic glacial deposits in South Australia by A.R.C. Selwyn in 1859 and by R. Tate in 1877 but did not provide references for these discoveries. The first account of a Neoproterozoic glaciation [*Thomson*, 1871] comes from Port Askaig, on Islay in western Scotland. Twenty years later, *Reusch* [1891] published an account of a Neoproterozoic occurrence in northern Norway but its interpretation remains controversial today [*Jensen and Wulff-Pederson,* 1996; *Rice,* 2000]. Evidence of older glaciations (what is now called Paleoproterozoic) was recognized in the Huronian rocks of Ontario at the beginning of the 20th century [*Coleman,* 1908]. With the passage of time, the number of reported Precambrian glacial deposits has greatly increased. A compre-

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hensive descriptive summary of ancient (pre-Pleistocene) glacial deposits from around the world was published in the compilation edited by *Hambrey and Harland* [1981].

1.2. Are Some Diamictites Mass Flows?

Following *Bailey et al.* [1928], *Crowell* [1957] proposed that many "pebbly mudstones" and diamictites may be interpreted as submarine slumps or mudflows, rather than glaciogenic deposits. This theme was pursued by a number of authors such as *Dott* [1961] and *Condie* [1967]. *Schermerhorn* [1974] re-examined stratigraphic and sedimentological evidence from many Precambrian rocks that were considered to be glaciogenic and concluded that many of them could be equally well explained as the result of various mass flow depositional mechanisms. Such problems of interpretation are compounded by the fact that glacial deposits, like other sediments, are susceptible to "resedimentation" so that evidence for one kind of depositional mechanism does not necessarily exclude the other. These suggested alternative interpretations of diamictites and associated rocks caused a resurgence of interest in and re-examination of glaciogenic deposits. As documented in *Hambrey and Harland* [1981] a glaciogenic origin was strongly re-affirmed for many diamictites throughout the world.

1.3. An Impact Origin for Diamictites and Associated Rocks?

Since the suggestion by *Alvarez et al.* [1980] that impacts by large extra-terrestrial objects could have played a significant role in global organic extinction events, some authors [e.g. *Marshal and Oberbeck,* 1992; *Aggarwal and Oberbeck,* 1992; *Rampino,* 1992; 1994] proposed that many supposedly glaciogenic diamictites could represent unsorted ejecta that formed as a result of extra-terrestrial impacts. Striated surfaces and clasts were attributed to the forceful mass movements engendered by impact events. Isolated large "foreign" clasts in finely laminated sedimentary rocks, commonly interpreted as "dropstones" from floating ice masses, were re-interpreted as ejecta from large impacts. Although theoretically plausible, these ideas are thrown into doubt by the preservation, in some areas, of great thicknesses (several km) of glaciogenic rocks with complex stratigraphic successions. Such great thicknesses and variable lithologies are difficult to explain by short-lived catastrophic events, no matter how powerful. Likewise, the occurrence of huge thicknesses of dropstone-bearing laminites necessitates delivery of dropstones over extended periods of time and is more easily explained under a glacial than an impact hypothesis [*Young*, 1993].

These alternative interpretations of diamictites and associated rocks challenged the status quo but they have generally had a positive effect because students of glaciogenic rocks have become much more circumspect in their observations. The net result has been a re-affirmation and heightened credibility of the glacial nature of numerous ancient diamictites and associated rocks.

2. LOW LATITUDE GLACIAL DEPOSITS AT SEA LEVEL AND THE THEORY OF GLOBAL GLACIATION

With the accumulation of data on Precambrian glacial deposits came the gradual realization that these rocks are extremely widespread, especially in Neoproterozoic successions. The notion of a world-wide glacial episode, or episodes in the Neoproterozoic is attributed to early work by *Mawson* [1949]. A new piece of evidence was introduced by the pioneering paleomagnetic study of *Harland and Bidgood* [1959] who suggested that "sparagmites" in Norway (supposed to be about the same age as Neoproterozoic glacial deposits elsewhere) accumulated at low paleolatitudes. Partly because of these paleomagnetic results, *Harland* [1964] reiterated the idea that most of the Earth could have been glaciated in the Neoproterozoic. If glaciers extended to tropical regions, then it seemed reasonable to infer that most of the planet had undergone glaciation. Subsequently *Tarling* [1974] carried out a paleomagnetic investigation of the Port Askaig Tillite in western Scotland and tentatively concluded that these glacial deposits formed at a latitude of about 10°S. His interpretation was apparently strengthened by additional work on the same rocks by *Abouzakhm and Tarling* [1975], suggesting that the rocks did not contain a significant later magnetic component. It is ironic that the glacial rocks of the Port Askaig Formation, which yielded some of the first evidence of accumulation at low paleolatitudes, were later shown [*Stupavsky et al.*, 1982] to have received their low latitude magnetic signature much later, in Ordovician times. The concept of low latitude glaciation in the Neoproterozoic received a considerable boost with the publication of a paper by *Embleton and Williams* [1986], which presented convincing evidence for deposition of Neoproterozoic glaciogenic rocks in South Australia at low latitudes and altitudes (the rocks contain evidence of shallow marine influence). *Schmidt and Williams* [1995] and *Sohl et al.* [1999] presented further evidence of long-lived and widespread low latitude glaciation from late Neoproterozoic sedimentary rocks in Australia.

3. STABLE ISOTOPES IN NEOPROTEROZOIC CARBONATES ASSOCIATED WITH GLACIAL DEPOSITS

Carbonate rocks associated with Neoproterozoic glacial deposits appear to be characterized by anomalously large variations in $\delta^{13}C$. *Williams* [1979] first observed that Neoproterozoic "cap" dolostones tend to have negative $\delta^{13}C$ values and on average have lighter $\delta^{13}C$ values than Neoproterozoic dolostones that are not associated with glacial deposits. *Knoll et al.* [1986], *Kaufman et al.* [1991] and others explained the anomalous carbon isotopic signatures as the result of stratified oceanic condition during non-glacial periods and mixing associated with glacial periods. The basic idea is that during the existence of stratified oceanic conditions, descending organic matter left the upper ocean enriched in dissolved ^{13}C. The ^{13}C-depleted deep materials would have been driven to the surface when oceanic turnover was re-instated, particularly at the end of a glaciation. These alkaline waters would have released CO_2, leading to precipitation of carbonate rocks that occur above many Neoproterozoic diamictites. *Hoffman and Schrag* [2002] consider this model to be untenable because they claim that the existence of a stratified ocean for long periods of time is unlikely. They also claimed that the biological "pump" cannot be maintained in the absence of significant oceanic circulation because of the reduction in upwelling of nutrients. *Hoffman et al.* [1998] suggested that the most likely explanation for low $\delta^{13}C$ values in the "cap carbonates" was the near-extirpation of life as a result of development of a thick ice cover on most of the world oceans. *Hoffman and Schrag* [2002] preferred a more complicated model, invoking various possible causes for low $\delta^{13}C$ values below and above the glacial deposits. Pre-glacial low values were tentatively attributed to release of methane into the atmosphere from anoxic organic-rich sediments thought to have been produced as a result of special oceanic circulation patterns related to clustering of continental masses in low latitudes. By contrast the low $\delta^{13}C$ values from post-glacial cap-carbonates were explained in several ways [*Hoffman and Schrag,* 2002]. Among these was the suggestion that influx of extremely large amounts of atmospheric C into the oceans, as a result of the rejuvenated weathering cycle at the end of glaciation, would have brought about the observed fall in $\delta^{13}C$ values. The number and varying nature of the suggested explanations for these isotopic anomalies point to the remaining uncertainty as to their origin.

4. THE SNOWBALL EARTH HYPOTHESIS

Following earlier suggestions by *Mawson* [1949] and *Harland* [1964], *Kirschvink* [1992] published a short paper in which he re-visited the notion that the entire planetary surface may have been frozen and ice-covered at times in the Neoproterozoic. He coined the phrase, "snowball Earth", which has subsequently been widely used to encapsulate the hypothesis. The idea of a frozen planet, resulting from "runaway albedo" [*Budyko,* 1966] had previously foundered because of the lack of an "escape mechanism"—in other words, once the planetary surface was entirely frozen it was difficult to envisage a way of reversing the situation. *Kirschvink* [1992] and *Hoffman et al.* [1998] suggested that continuing plate tectonic activity would have brought about a gradual build-up of atmospheric CO_2 so that the consequent greenhouse effect would eventually (after several million years) have released the planet from its frozen state. Implicit in the model proposed by *Hoffman et al.* [1998] and explicit in *Hoffman* [2000] *Hoffman et al.* [2002] is the idea that both descent into and escape from global glaciation were relatively rapid occurrences, reflecting threshold values involving albedo at the initiation and high atmospheric CO_2 levels at the end.

The snowball Earth hypothesis was also used by Kirschvink as a means of explaining banded iron-formations (BIFs) that, in a number of regions, are closely associated with Neoproterozoic glaciogenic successions. The Neproterozoic iron-formations are separated by a long time gap (>1.0 b.y.) from the world-famous Superior-type iron-formations of the Great Lakes area in North America. The reappearance of BIFs in the Neoproterozoic, after such a long hiatus, has been a scientific conundrum since the younger iron-formations started to receive attention in the second half of the 20th century [*Martin,* 1965; *Whitten,* 1970; *Young,* 1976; *Yeo,* 1984, 1986; *Maynard,* 1991]. Iron-rich sedimentary rocks associated with Neoproterozoic glacial rocks are known from the western United States [*Graff,* 1984; *Miller,* 1985], South America [*Hoppe et al.,* 1987; *Urban et al.,* 1992], South West Africa [*Breitkopf,* 1988; *Buhn et al.,* 1992], South Australia [*Whitten,* 1970; *Coats and Preiss,* 1987] and south China [*Jiafu et al.,* 1987]. *Trompette et al.* [1998] considered that Fe and Mn ores and BIF of the Neoproterozoic Jacadigo Group in Brazil are not associated with glaciogenic deposits. They interpreted alleged glacial rocks as debris-flow deposits but interpretation of this region remains contentious. *Yeo* [1981; 1986] suggested that glaciation played an important role in production of these iron-rich rocks. According to this idea, glaciers debouched into a series of rift basins where hydrothermal concentration of Fe, Mn, P and other elements was taking place. The BIF precipitated when metal-charged brines were mixed with oxygenated water as a result of currents related to debouching glaciers. Support for the model comes mainly from field evidence but it is also supported by geochemistry, particularly trace element analyses [*Yeo,* 1981; 1986], which indicate a strong hydrothermal influence. Some occurrences, such as those in Alaska [*Young,* 1982], Namibia [*Martin,* 1965] and South China [*Jiafu et al.,* 1987] are associated with mafic volcanic rocks, supporting the small ocean basin model.

One of the requirements for dissolution of Fe in water is the existence of reducing conditions. Huge amounts of Fe that were dissolved in the older (anoxic) world oceans were thought by some [e.g. *Cloud,* 1976] to have been precipitated after atmospheric oxygen levels were raised in early Paleoproterozoic time. This theory poses a great problem for the occurrence of younger BIF because, once the atmosphere/hydrosphere systems were oxygenated, dissolution of large amounts of Fe should no longer have been possible. *Kirschvink* [1992] suggested an alternative mode of origin for the Neoproterozoic BIF, incorporating the snowball Earth hypothesis. He proposed that the development of a world-wide sea ice cover would have isolated the somewhat oxygenated atmosphere from the oceans, permitting a return to reducing conditions there. He suggested that precipitation of the Neoproterozoic BIF was consequent on melting of the ice and re-introduction of oxygen to the oceans at the end of the snowball condition. *Kirschvink et al.* [2000] extened the concept of a snowball Earth condition back to the Paleoproterozoic in an effort to explain glaciogenic deposits and Fe- and Mn-rich rocks in some of the older successions.

5. DISTRIBUTION OF EVIDENCE OF PALEOPROTEROZOIC GLACIATIONS

Evidence of glaciation in the Paleoproterozoic (2.5 Ga–1.6 Ga) is known from North America, NW Europe, South Africa and Western (Fig. 1). Perhaps the best known of these ancient glaciogenic deposits is the Gowganda Formation, which forms part of the Huronian Supergroup on the north shore of Lake Huron in Canada [*Coleman,* 1908; *Pettijohn and Bastron,* 1959; *Lindsey,* 1969; *Casshyap,* 1969; *Young,* 1969; *Miall,* 1983; *Young and Nesbitt,* 1999]. The Gowganda Formation (Fig. 2) includes as many as six diamictite units separated by waterlain deposits [*Lindsey,* 1969; *Young and Nesbitt,* 1999]. *Young* [1973] noted the unusual association between glacial deposits in the Gowganda Formation and supermature orthoquartzites of the overlying Lorrain Formation. Many Paleoproterozoic glacial occurrences consist of a single diamictite bearing formation but the Huronian contains three, the Ramsay Lake, Bruce and Gowganda formations (Fig. 3), suggesting that glaciation was a recurrent phenomenon in the early Paleoproterozoic of this region. The only other region with an equally complex Paleoproterozoic glacial history is in SE Wyoming, where the Snowy Pass Supergroup has a near-identical stratigraphy. The stratigraphic similarity of Paleoproterozoic rocks in these widely separated regions led *Roscoe and Card* [1993] to suggest former juxtaposition of the two areas so that they formed opposite sides of a single basin. Their separation was attributed to subsequent drifting and rotation of the Wyoming province. A more conservative interpretation is that the two regions formed part of an extensive continental margin that underwent similar tectonic and climatic histories.

A widespread Paleoproterozoic glaciation in North America was proposed by *Young* [1970] because of the preservation of glaciogenic diamictites in the Ontario and Wyoming regions,

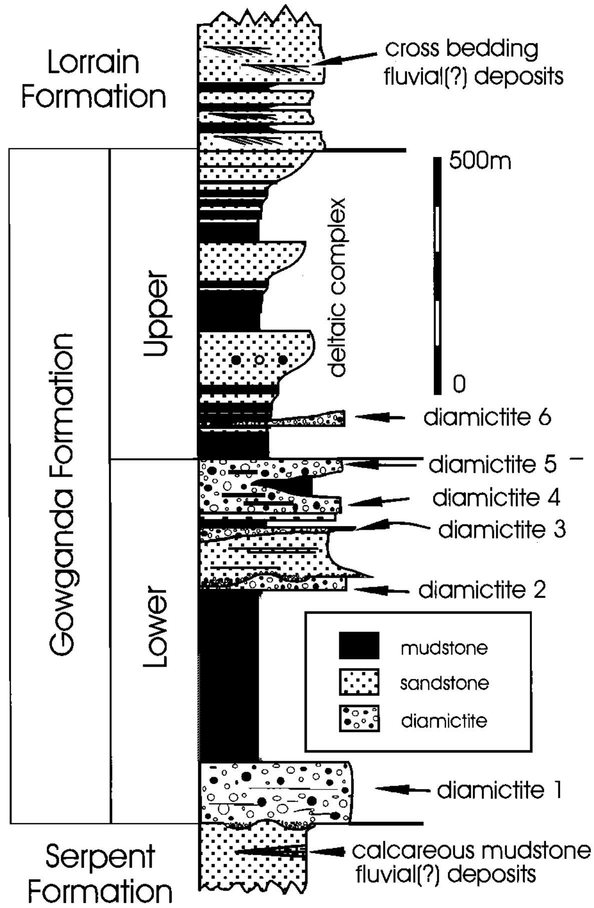

Figure 2. Generalized stratigraphic succession of the Paleoproterozoic Gowganda Formation (~2.3 Ga) in the southern part of the Huronian outcrop belt, north shore of Lake Huron. Note the complex stratigraphy, with at least six major diamictite units separated by waterlain sediments such as mudstones and sandstones.

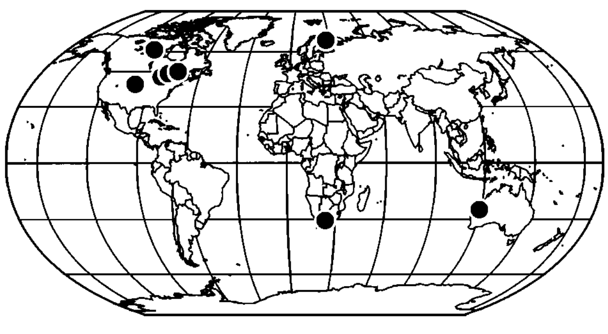

Figure 1. Known global distribution of Paleoproterozoic glaciogenic deposits (black dots).

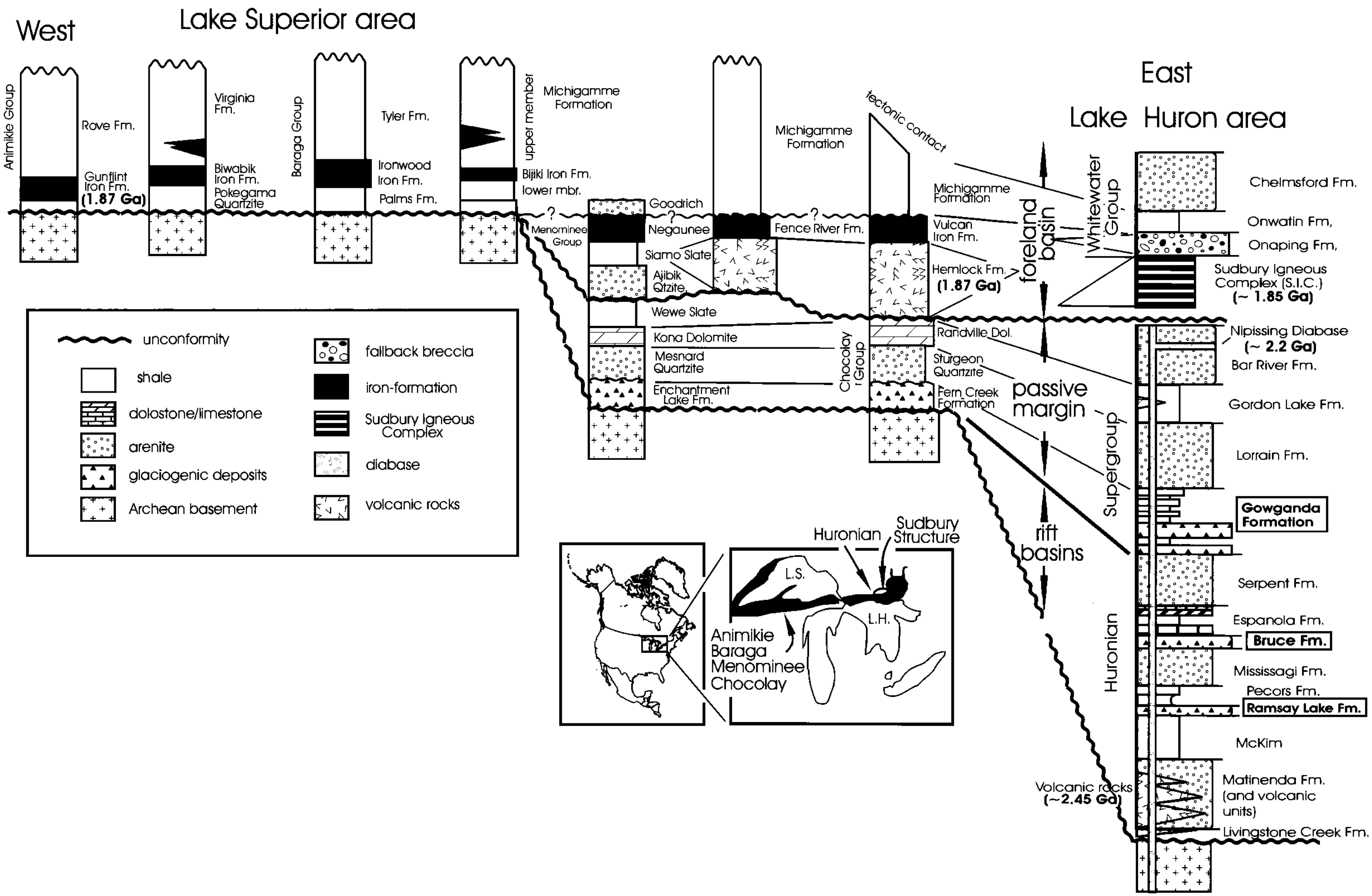

Figure 3. Generalized stratigraphic sections for Paleoproterozoic rocks of the Great Lakes region, North America. Sections from the Lake Superior area have been modified from *Ojakangas et al.* [2001a]. Note the three glaciogenic formations in the Huronian succession (in boxes at right side of the figure). The youngest glaciogenic rocks of the Gowganda Formation are separated from the overlying BIF-rich successions by about 250 m.y. See text for discussion.

near Chibougamau in Quebec and in the Hurwitz Group on the west side of Hudson Bay. Subsequently, similar, broadly correlative glaciogenic successions have been described from Finland [*Marmo and Ojakangas,* 1984], South Africa [*Visser,* 1971] and Western Australia [*Trendall,* 1981; *Martin,* 1999].

6. TECTONIC SETTING OF PALEOPROTEROZOIC ROCKS OF NORTH AMERICA

Young and Nesbitt [1985] proposed that the lower Huronian (formations below the Gowganda in Fig. 3), which has a much more limited distribution than overlying Huronian rocks, accumulated in a rift basin, strongly influenced by contemporaneous faults. By contrast, the upper Huronian, beginning with the glaciogenic Gowganda Formation, was considered to have been deposited on a continental margin. This interpretation of the Gowganda Formation is supported by the fact that it has a much wider distribution than the underlying units, suggesting a transgressive regime, typical of a subsiding, newly-formed, continental margin. In the absence of a subsident basin the transgressive nature of the glacial deposits would have been unlikely, for widespread glaciation is normally accompanied by lowering of sea level and a regressive sedimentary regime. It may, however, be explained by depression of the crust by an extensive ice sheet and deposition of the glaciogenic sediments prior to isostatic uplift. Such uplift would presumably have brought about removal of much of the sedimentary cover by erosion but widespread preservation of the Gowganda and succeeding formations suggests a more long-lived basin depression, perhaps related to plate tectonic phenomena. This interpretation is also supported by the occurrence of extensive quartzarenites in the upper Huronian (Lorrain and Bar River Formations) and evidence of marine influence (tidal activity) in the Gordon Lake Formation [*Chandler,* 1986]. The two lower diamictite-bearing units (Ramsay Lake and Bruce Formations) formed in a restricted, rift environment whereas the much more extensive Gowganda Formation is considered to have been deposited on a newly-formed passive margin.

Correlation of Paleoproterozoic successions between the Lake Huron region and SE Wyoming has proved to be much more convincing than between the Huronian and the much closer Lake Superior area. *Young and Church* [1966] suggested that formations in the upper part of the Huronian Supergroup might be correlated with the oldest Paleoproterozoic units in Michigan and neighbouring states on the south shore of Lake Superior but, mainly because of spurious geochronological results, these correlations were rejected by most workers until quite recently [*Southwick,* 1995; *Ojakangas et al.,* 2001a]. The proposed stratigraphic relations between Paleoproterozoic successions of these two areas are illustrated in Fig. 3. The Chocolay Group begins with locally developed glaciogenic diamictites (Fern Creek, Reany Creek, Enchantment Lake formations) that are considered to be equivalent to the Gowganda Formation in Ontario. These rocks form part of the Chocolay Group, which is overlain, following a long (~300 m.y.) hiatus, by the iron-formation-bearing successions of the Lake Superior area. The iron-rich succession is considered to have been deposited in a foreland basin representing the closure of the "Huronian" ocean [*Hoffman,* 1987; *Schneider et al.,* 2002; *Young,* 2003]. The Menominee Group was thought to be younger than the Baraga and Animikie groups [*Ojakangas et al.,* 2001a] but recent geochronological investigations have shown that they have near-identical ages of ~ 1.87 Ga [*Schneider et al.,* 2002; *Fralick et al.,* 2002] and their superposition is probably due to tectonic processes. These dates are important because they show that the thick and extensive BIFs of the Lake Superior region formed about 300 Ma after the Gowganda glaciation and therefore are in no way related to a "snowball Earth" condition in the Paleoproterozoic.

Chown and Gobeil [1990] described clastic dykes filled with diamicite material from areas of the Archean shield between the Huronian and outcrops of Paleoproterozoic glaciogenic rocks in the Chibougamau area of Quebec, supporting the idea that the glaciogenic deposits were formerly quite extensive. As pointed out by *Young* [1970] Paloeproterozoic glaciogenic rocks outcrop sporadically in a roughly NE-SW line from Chibougamau in Quebec to the Medicine Bow Mountains in SE Wyoming. In spite of apparently contradictory geochronological evidence [*Wanless and Eade,* 1975], *Young* [1975] suggested a stratigraphic correlation among the Paleoproterozoic rocks of the Ontario Huronian, SE Wyoming and a similar succession (Hurwitz Group) on the west side of Hudson Bay. This correlation was based, in part, on the recognition of glaciogenic deposits in all three areas.

The succession of Paleoproterozoic rocks of the Hurwitz Group (Fig. 4) was studied by the Geological Survey of Canada as part of large scale reconnaissance mapping projects [e.g. *Eade,* 1966; *Bell,* 1970]. *Bell* (1970) concluded that the lower parts of the Hurwitz succession (including diamictites of the Padlei Formation) were deposited in "terrestrial basins" and the succeeding mature quartzites formed on a stable platform. The upper part of the Hurwitz Group was attributed to a "geosynclinal" stage. Deposition was concluded with a "molassic" stage involving cannibalization of the older Hurwitz units into a late stage basin-filling succession. *Pettijohn* [1970] considered the Hurwitz succession to be too thin to fit the "geosynclinal" model. *Young* [1973; 1975] suggested the Hurwitz Group is correlative with both the Huronian and Snowy Pass supergroups. The Huronian-Snowy Pass correlations have been further refined by *Karlstrom et al.* [1984] and *Houston et al.* [1992]. The tectonic setting of the Hurwitz Group has

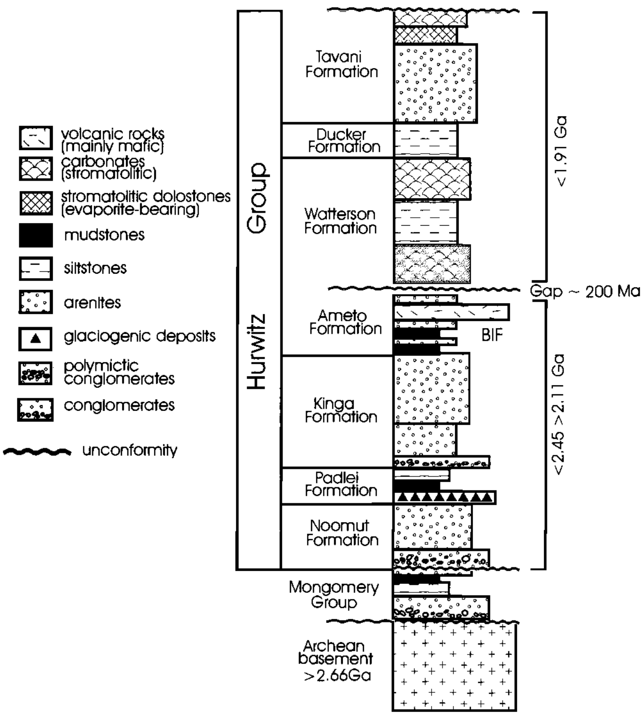

Figure 4. Schematic section to represent the stratigraphy of the Hurwitz Group and associated rocks on the west side of Hudson Bay, Canada [after *Aspler et al.,* 2001]. Note the 200 m.y. gap separating the upper and lower parts of the Hurwitz Group.

been the subject of much discussion. The Huronian and Snowy Pass supergroups are juxtaposed between Archean basement on one side and Paleoproterozoic orogenic belts on the other but the Hurwitz Group lies in the central part of a huge structural province [Churchill province of Stockwell, 1964]. It has, subsequently become apparent that orogenic events have obscured a fundamental subdivision of the Churchill province into an Archean part to the NW (Rae and Hearne provinces) and a largely juvenile portion to the SE—the Trans-Hudson orogen [*Hoffman,* 1988]. This reinterpretation lends credence to *Bell's* [1970] and *Young's* [1988] suggestion that the Hurwitz Group evolved through a classical rift basin to passive margin and foreland basin.

If these stratigraphic correlations are accepted (and they are supported in a general way by available geochronological results) then the widespread Paleoproterozoic glaciogenic deposits of North America appear to have been coincident with a period of transition from rift to a passive margins, during the breakup of the supercontinent Kenorland [*Williams et al.,* 1991]. If the breakup was comparable to the opening of the Atlantic Ocean, it could have involved over 100 m.y. In some successions (Huronian and Snowy Pass supergroups) there is evidence of two earlier glacial episodes but these appear to be locally developed and preserved in rift-type settings.

7. PALEOPROTEROZOIC GLACIAL DEPOSITS IN FENNOSCANDIA

In Fennoscandia Paleoproterozoic rocks are represented in the Karelian Supergroup [*Ojakangas et al.,* 2001b] which formed between 2.45 and 1.9 Ga. These rocks lie on an Archean basement consisting of granitoid rocks and erosional remnants of greenstone belts. The oldest Proterozoic succession (the Sumian) unconformably overlies Archean basement and is characterized by volcanic and immature sedimentary rocks (Fig. 5). The basal part of the Sariolian is made up mainly of conglomerates and arkoses, which probably accumulated in fault-bounded basins (rifts?). These rocks are overlain by a 200–260m-thick succession of diamictites and associated rocks that are interpreted as glaciomarine [*Marmo and Ojakangas,* 1984; *Kohonen and Marmo,* 1992]. *Ojakangas et al.* [2001b] suggested that these glaciomarine deposits signaled a marine transgression during Sariolian time (2.4–2.3 Ga). This interpretation is similar to that proposed for the Huronian [*Young and Nesbitt,* 1985]. Deposition of the Finnish Paleoproterozoic glaciomarine rocks was followed by a period of intense weathering and development of paleosols [*Pekkarinen,* 1979; *Marmo,* 1986; *Ojakangas et al.,* 2001b]. Deposition of the thick (possibly up to 2500m) Jatulian Group took place following paleosol development. The Jatulian includes mafic lavas and tuffs but is characterized by conglomerates and quartzites attributed to braided stream environments. This is followed by development of more arkosic sediments and finally, development of thick extensive orthoquartzites considered to be shallow marine. Paleocurrent studies suggest that these sandstones were mainly transported towards the west and southwest [*Ojakangas,* 1965] although *Marmo et al.* [1988] reported more complex paleocurrent directions with modes in the north, northwest and southern quadrants. The topmost Jatulian includes dolomites, carbonaceous mudstones and volcanic rocks.

The Jatulian is overlain by the Kalevian Group, which is dominantly a thick (variously estimated at 3–10km) turbidite-mudstone sequence but also includes some iron-formation near the base. These rocks are considered to be autochthonous in the east but they are allochthonous and associated with ophiolites in the west. Fragments in Kalevian conglomerates include Jatulian quartzites, suggesting partial derivation by cannibalization of the underlying succession. These rocks are younger than 1970 Ma, the age of the youngest detrital zircon discovered within them [*Claesson et al.,* 1993]. In Karelia these rocks are thought to have undergone metamorphism at 1.87–1.88 Ga [*Ojakangas et al.,* 2001b].

The Sariolian glacial deposits may have formed in a series of separate basins (like the structural basins in which they are now preserved) but *Ojakangas et al.* [2001b] suggested that

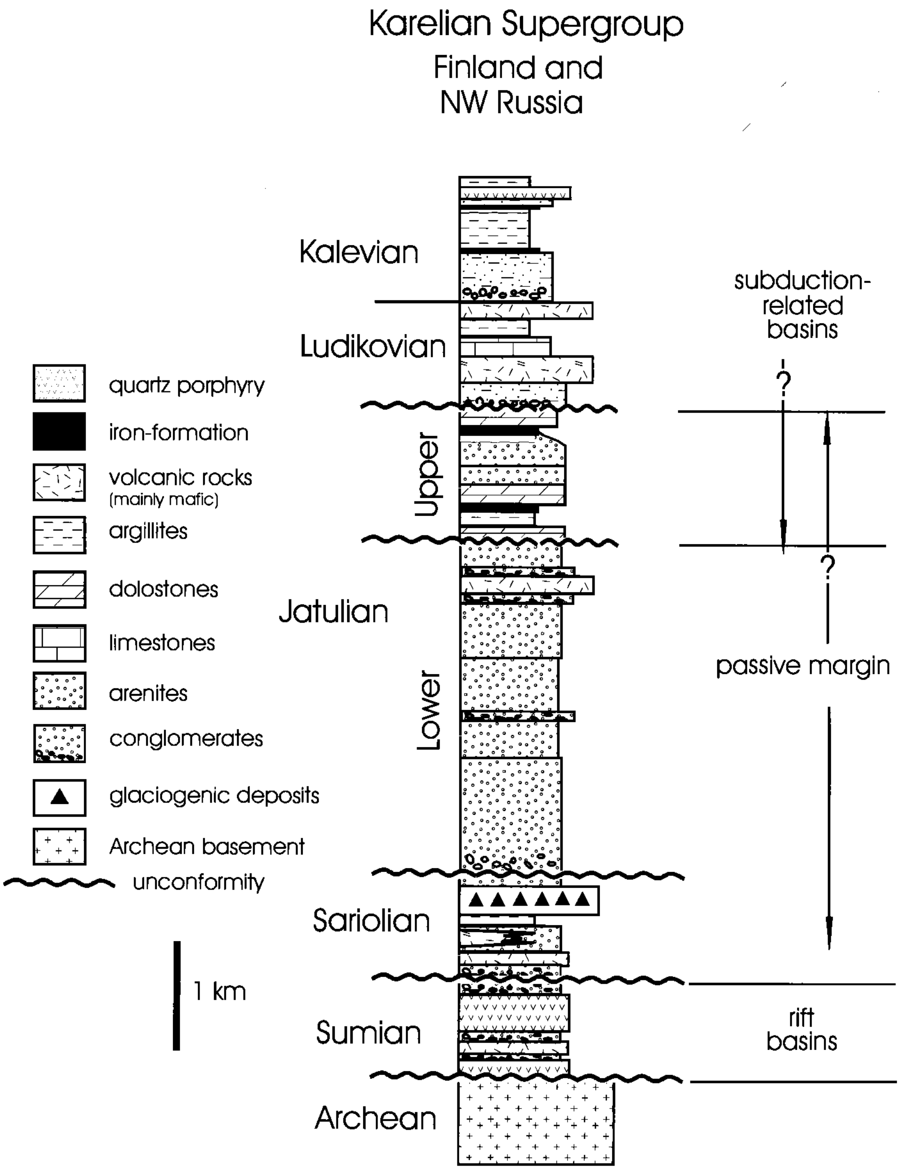

Figure 5. Generalized stratigraphy of Paleoproterozoic supra-crustal rocks in the Karelian region of Finland and Russia [after *Ojakangas et al.*, 2001b].

the marine deposits formed in extensive near shore environments during a transgression. The overlying marine Jatulian includes orthoquartzites, followed by stromatolitic carbonates, some evaporites and iron-formations. The succeeding Ludicovian Group and the probably equivalent Marine Jatulian of Finland show evidence of deeper water environments, with deposition of carbonaceous shales (shungites), turbidites and some BIF. These deposits possibly represent basin subsidence, reflecting initiation of foreland basin conditions during ocean closure. The flyschoid Kalevian Group further testifies to foreland basin development. Provenance of the thick succession of Kalevian sedimentary rocks is not known but a high proportion of these rocks could have been derived from an orogen that advanced towards the craton.

8. PALEOGEOGRAPHY AND PLATE TECTONIC SETTING OF NORTH AMERICAN AND FENNOSCANDIAN PALEOPROTEROZOIC GLACIOGENIC ROCKS

Using the continental reconstruction of *Karlstrom et al.* [1999] an attempt was made to reconstruct Paleo-proterozoic paleogeography. It is suggested that the breakup of the supercontinent Kenorland [*Williams et al.,* 1991] resulted in formation of a continental margin (Fig. 6) that extended for almost 10,000 km, from present day SW United States to Finland and NW Russia. See *Young et al.* [1977] and *Ojakangas et al.* [2001b] for discussions of intercontinental correlations of Paleoproterozoic rocks in the North Atlantic region. Possible stratigraphic relation-ships among the Paleoproterozoic units of this large region are shown in Fig. 7. According to the reconstruction shown in Fig. 6, glaciogenic deposits are preserved as a linear array, close to the proposed continental margin. Some of the glaciogenic rocks are preserved in rift environments (lower parts of the Huronian and Snowy Pass supergroups) but the most widespread (Gowganda Formation and equivalents) are interpreted as passive margin deposits. Preservation of glaciogenic deposits appears to be linked to sur-

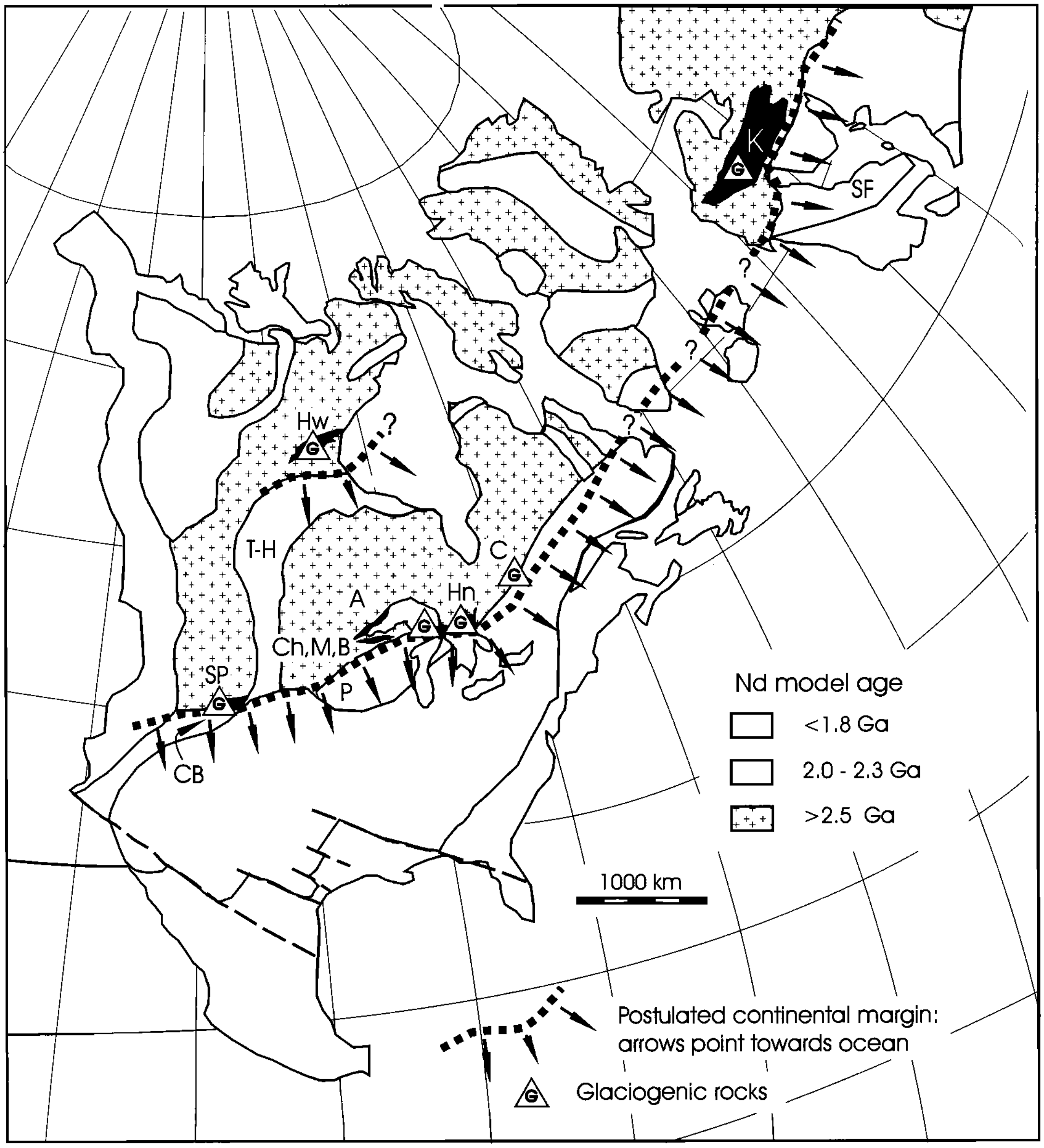

Figure 6. Reconstruction of Laurentian supercontinent in the Paleoproterozoic to show the approximate location of an extensive continental margin on which Paleoproterozoic glaciogenic rocks may have acumulated. Abbreviations representing stratigraphic units are as follows: A–Animikie Group; C–Chibougamau Formation: Ch,M,B–Chocolay, Menominee, Baraga groups; Hn–Huronian Supergroup; Hw–Hurwitz Group; K–Karelian Supergroup. Abbreviations representing orogenies are as follows: CB–Cheyenne Belt; P–Penokean; SF–Svecofennian; T-H–Trans-Hudson.

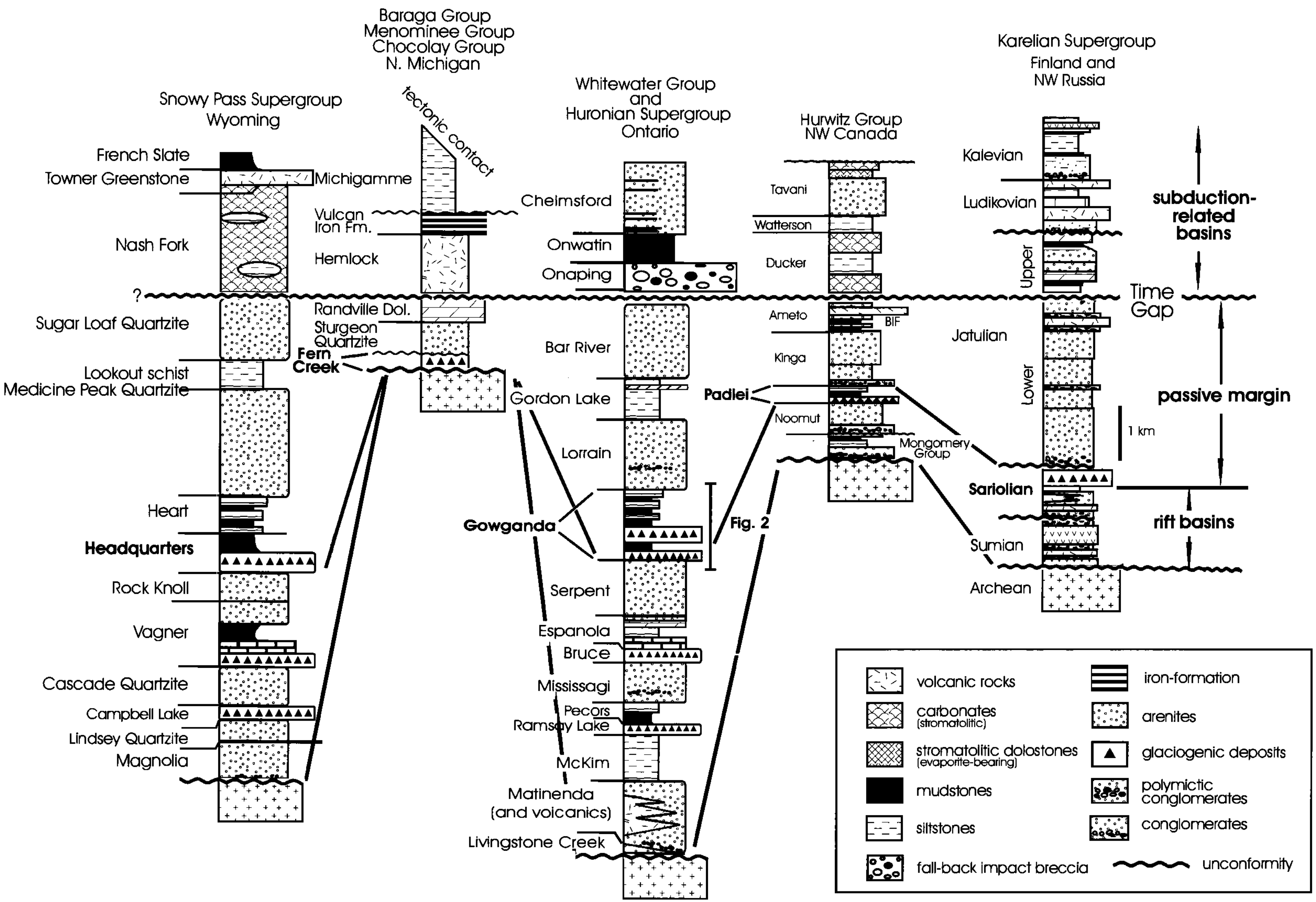

Figure 7. Representative lithostratigraphic successions for five regions extending from SE Wyoming to Finland and NW Russia (see text for sources of data). The successions have been divided into those attributed to rift basins, passive margins and subduction-related basins. Note the "time gap" between passive margin successions and those attributed to deposition in subduction-related basins. In some areas this hiatus represents as much as 300 m.y. Relationships between the two successions range from an angular unconformity (Huronian Supergroup and Whitewater Group) to an apparently concordant contact (Hurwitz Group) These structural differences probably respectively reflect proximity to or distance from an advancing orogen during basin closure. The approximate locations of the sections are shown in Fig. 6. The stratigraphic position of the section shown in Fig. 2 is indicated on the central column.

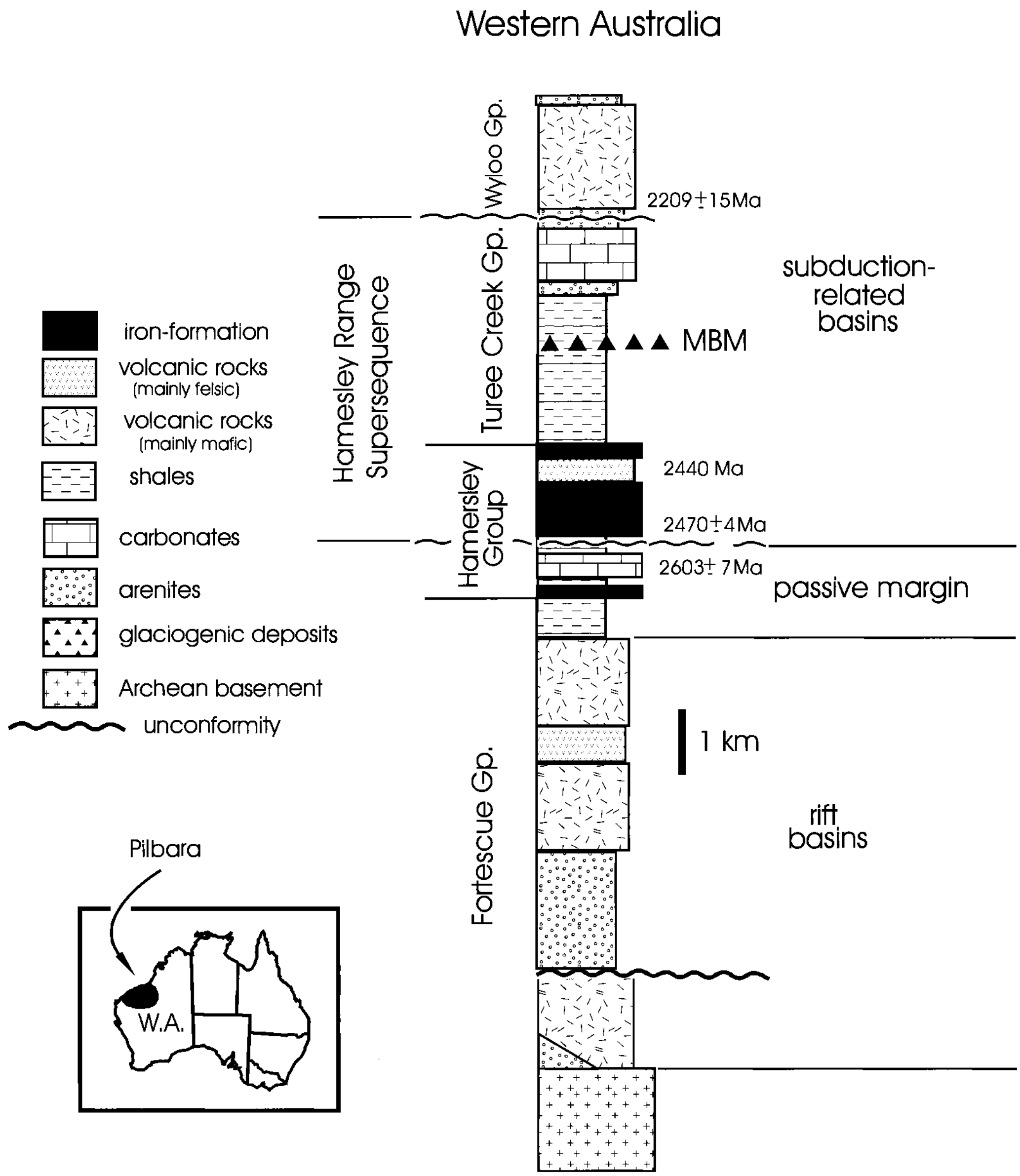

Figure 8. Stratigraphic column [after *Blake and Barley,* 1992 and *Martin,* 1999] to represent some of the Archean-Paleoproterozoic stratigraphy of the Pilbara region in Western Australia. Note the stratigraphic and inferred tectonic setting of the glaciogenic Meteorite Bore Member (MBM) and the possible hiatus in the Hamersley Group, as noted by *Blake and Barley* [1992].

vival of parts of the orogenic belt (Cheyenne belt, Penokean orogen, Svecofennian orogen) that developed after closure of the Paleoproterozoic ocean. Such deposits are absent (presumably uplifted and eroded or metamorphosed beyond recognition) in a large area extending from Chibougamau (C on Fig.6) to Scandinavia—an area that was affected by younger orogenies, notably the Grenville.

Glacial deposits of the Hurwitz Group (Padlei Formation) appear to have formed in a separate depositional basin. It has been suggested [*Aspler and Chiarenzelli,* 1997] that these rocks formed in an intracratonic basin but striking stratigraphic similarities with other Paleoproterozoic successions [*Young,* 1975; 1988; *Aspler et al.*, 2001] are perhaps better accommodated if the Hurwitz basin were affected by marine influences. *Young* [1970] suggested that the Hurwitz glacial deposits were derived from the same ice sheet as the Huronian Gowganda Formation but it now seems likely that the Padlei Formation was derived from a separate ice sheet located on the Rae-Hearne provinces to the NW (present co-ordinates) of the Hurwitz exposures. The proposed paleogeographic reconstruction is shown in Fig. 6. It is suggested that the glaciogenic Padlei Formation was deposited close to the southeasterly-facing continental margin of a Paleoproterozoic ocean [Manikewan ocean of *Stauffer,* 1984] that lay in the region now occupied by the Trans-Hudson orogen. Extensive Paleoproterozoic glaciation appears to have followed breakup of the end-Archean supercontinent, Kenorland and glacial deposits are preserved on the SE (present co-ordinates) margins of two Paleoproterozoic oceans.

Paleomagnetic data from the Paleoproterozoic glaciogenic rocks of North America and NW Europe are sparse. *Williams and Schmidt* [1997] and *Schmidt and Williams* [1999] ascribed some Huronian paleomagnetic directions to early CRM (chemical remanent magnetization) acquired fairly soon after deposition, as opposed to some of the paleomagnetic data from the Neoproterozoic Elatina Formation in south Australia which are DRM (detrital remanent magnetization). They obtained remanent magnetic data from the glaciogenic Gowganda Formation, indicating that glaciation took place at about 11 degrees (and possible as little as 4) removed from the equator. *Schmidt and Williams* [1999] also reported paleomagnetic results from hematitic breccias at the base of the Lorrain Formation and interpreted them to indicate a near-equatorial position at the time of their formation. These data suggest that at least a portion of the Paleoproterozoic glaciation of the Kenorland margins took place at low latitudes.

9. PALEOPROTEROZOIC GLACIATION IN WESTERN AUSTRALIA

In Western Australia the ancient granite-greenstone terrane of the Pilbara craton is overlain by a thick supracrustal succession that includes Paleoproterozoic glaciogenic diamictites and related deposits. These rocks are known as the Meteorite Bore Member and form part of the Turee Creek Group (Fig. 8). Their glaciogenic nature was noted by *Trendall* [1981] and a detailed description was given by *Martin* [1999]. According to *Blake and Barley* [1992], the Turee Creek Group formed in a backarc basin, that developed in relation to subduction to the SW (present co-ordinates). The glaciogenic Meteorite Bore Member is about 270m thick and forms part of a thick succession of supracrustal rocks that ranges in age from almost 2.8 Ga to just over 2.2 Ga.

The volcanic and sedimentary rocks of the Fortescue Group, [*Blake and Barley,* 1992] are considered to have formed in a rift environment. The upper part of the Fortescue Group and the lower part of the Hamersley Group [Marra Mamba Supersequence of *Blake and Barley,* 1992] have been interpreted as a passive margin succession. divided The Hamersley Group has been divided by *Blake and Barley* [1992] into two parts, separated by a "condensed section" or an unconformity. Geochronological results support the existence of a considerable time gap (>100 m.y.) between these two subdivisions. The world famous iron-formations of the Hamersley Group [*Trendall,* 2002] occur in the upper package and are overlain by the Turee Creek Group, which includes the Kungarra Formation with its glaciogenic Meteorite Bore Member.

Blake and Barley [1992] and *Powell et al.* [1999] interpreted the plate tectonic setting of these rocks as a starved back-arc basin or a back-arc compressive basin. The hiatus at the base of the Marra Mamba Supersequence may be comparable to that between the Huronian Supergroup and the Whitewater Group within the Sudbury Basin or between sequences 2 and 3 of the Hurwitz Group [*Aspler et al.,* 2001]. It may therefore represent part of the period of time between development and destruction, by subduction, of ancient oceanic crust. *Horwitz* [1982] suggested that the rocks of the Turee Creek Group were derived from the southwest and pointed to the presence of clasts derived from the older Hamersley and Fortescue groups. The basal unit of the Turee Creek Supersequence of *Blake and Barley* [1992] is the Boolgeeda Iron Formation, which is succeeded by a thick siliciclastic succession that includes the glaciogenic deposits of the Meteorite Bore Formation. A date of 2209±15 Ma was obtained from the Cheela Springs Basalt, which is ~ 2000 m stratigraphically above the glaciogenic rocks [see *Martin,* 1999]. The glacial deposits are loosely bracketed between about 2.45 Ga and 2.2 Ga. Paleoproterozoic Glaciogenic deposits preserved in North America and NW Europe formed on passive margins of a fragmenting supercontinent. They were followed by a long hiatus before the appearance of detritus in a foreland basin. The Australian Paleoproterozoic glacial deposits appear to be part of the fill of a foreland basin, formed after a significant break in deposition.

10. PALEOPROTEROZOIC GLACIAL DEPOSITS OF SOUTH AFRICA

The Transvaal region is characterized by the presence of a thick supracrustal succession that spans the Archean-Proterozoic boundary. These rocks are disposed in two major regions known as the Transvaal and Griqualand West basins. Glaciogenic rocks have been reported from both basins and form part of the Transvaal Supergroup. In the more westerly Griqualand West Basin they are known as the Makganyene Formation and in the Transvaal basin glaciogenic rocks have been reported from two stratigraphic levels, the Duitschland Formation and the Upper Timeball Hill (Fig. 9). There are different opinions concerning the tectonic setting and stratigraphic correlations [*Moore et al.,* 2001] of these rocks. *Visser*

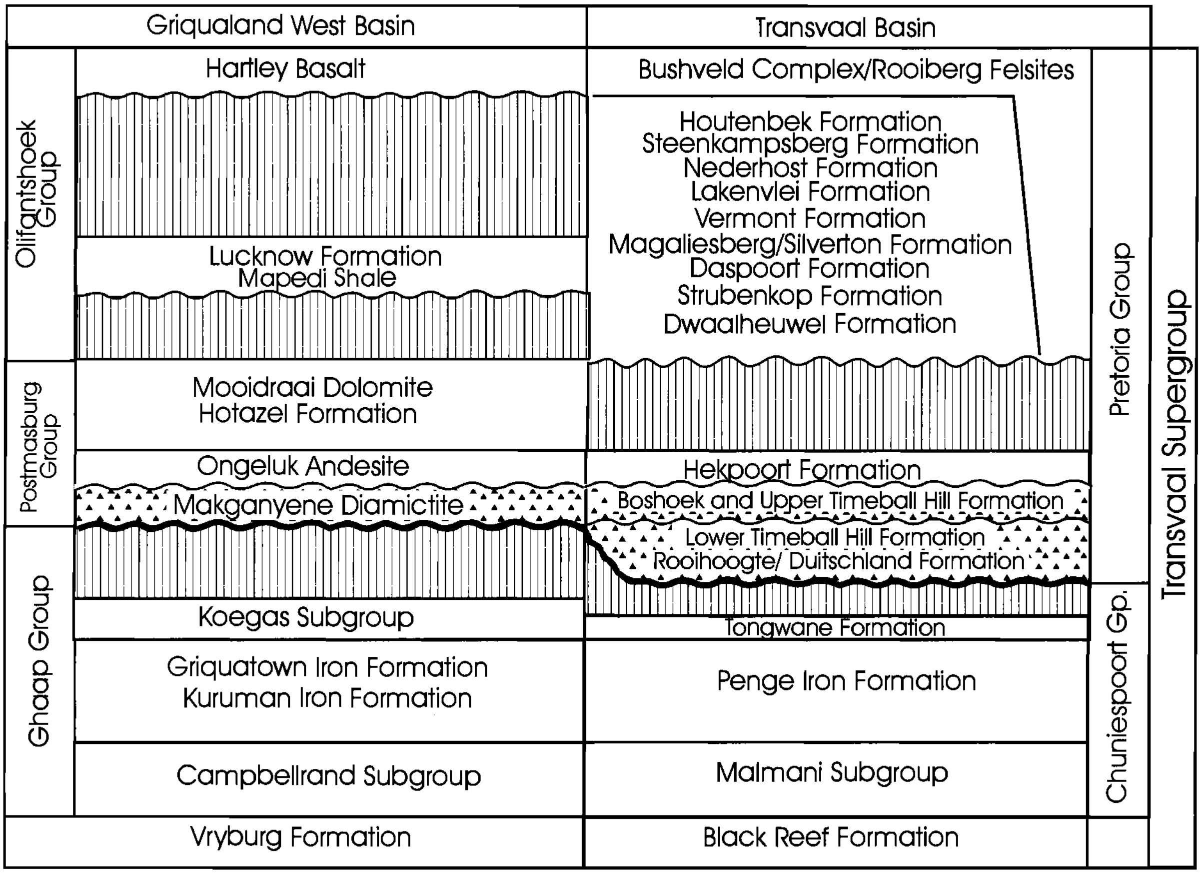

Figure 9. Schematic representation of stratigraphy of Archean-Paleoproterozoic rocks in the Transvaal and Griqualand West basins of South Africa [slightly modified from *Bekker et al.,* 2001]. Gaps in the stratigraphic record are represented by vertical striped ornament. Units containing glaciogenic deposits are show by triangular ornament. Wavy lines represent unconformities. See text for discussion.

[1981] considered the Makganyene to be equivalent to part of the Timeball Hill Fm. in the Transvaal basin. The Makganyene is unconformably overlain by the Ongeluk lavas [*Altermann and Nelson,* 1998], which have yielded a 2222 Ma age (Pb-Pb isochron).

The Makganyene is underlain by shales and quartzites that form part of the Koegas Subgroup but in places these are missing and the glacial beds lie on banded iron-formations. *Visser* [1981] and *Altermann and Nelson* [1998] stated that, in the Griqualand West basin, the basal contact of the glaciogenic rocks is unconformable. Some diamictite beds have a ferruginous sandy matrix and iron-rich chert and carbonate beds are interbedded with some diamictites. Dropstones are reported from the chemical sediments. Visser reported six regressive(?) cycles, involving diamictites, conglomerates, sandstones shales and carbonates in upward succession. The complexity and scale of these cycles are reminiscent of glacial advance-retreat cycles of temperate glaciations such as those recorded in the Pleistocene of the northern hemisphere. *Visser* [1981] inferred an origin from the SE and invoked erosion of the basement and underlying formations of the Transvaal and Griqualand sequences to explain the nature of the clasts in the diamictites. Because of associated waterlaid deposits, he considered deposition to have occurred near sea level under temperate glacial conditions. The underlying Ghaap Group was considered by Visser to have been deposited on a stable platform but he noted a paleocurrent reversal in the overlying beds in Griqualand West Basin and inferred that these were harbingers of an approaching orogen from the west. *Altermann and Halbich* [1990; 1991] presented structural and stratigraphic evidence indicating that the rocks of the lower part of the Transvaal along the SW margin of the Kaapvaal craton were subjected to multiple folding and thrusting. The first tectonic phase predates the Makganyene diamictite and, according to *Altermann and Nelson* [1998], is unconformably overlain by the 2.2 Ga Ongeluk lava. Crustal stress was directed towards the NE. It post-dates deposition of the Koegas Subgroup (Fig. 9) but not the Ongeluk lavas. There are also younger tectonic episodes (~2.07–1.88 Ga) and the area was later affected by Namaquan deformation events (1100 Ma) with right and left lateral components. Tectonic effects extended as much as 130 km into the craton to the east. These structural studies appear to support Visser's claim that the diamictites and succeeding rocks of the Postmasburg Group were deposited in a foreland basin setting.

Cheney [1996] likewise interpreted the Pretoria-Postmasburg groups as a clastic wedge but he proposed that the siliciclastic rocks were derived from the Limpopo Orogenic Belt, which welded the Zimbabwe Province to the Transvaal craton. He claimed that the Limpopo Belt was younger than the 2.67 Ga date previously assigned to it. This interpretation is supported by *Button's* [1975] paleocurrent study of the Dwaalheuwel Formation (Fig. 9) in the eastern Transvaaal, suggesting that the sediments making up the formation were transported to the W and SW. The Dwaalheuwel Formation lies on sericitized volcanics (paleosol) and has a sharp to gradational contact with overlying shales. In northern exposures the Dwaalheuwel Formation it is over 100m thick but it disappears to the SW, where it passes into shales and shaley sediments with lenses of oolitic iron-formation. The base may represent a transgression, followed by a regressive phase due either to deltaic progradation or marine regression.

Eriksson et al. [2001] considered that the Transvaal basin was mainly intracratonic and more strongly affected by thermal subsidence than plate tectonics throughout most of its history.

Thus the tectonic setting and paleogeography of Paleoproterozoic glaciogenic rocks in South Africa remain uncertain but, by analogy with the North American Paleoproterozoic [e.g. *Young et al.*, 2001] it is possible that the region went through a Wilson Cycle, involving rifting, development of a passive margin, then production of subduction-related (foreland?) basins. Derivation of sediments from both sides of a foreland basin has also been documented for the Great Lakes Paleoproterozoic [e.g. *Hemming et al,* 1995].

11. VAALBARA

It has been suggested by several authors [*Cheney et al.*, 1988; *Cheney,* 1996; *Aspler and Chiarenzelli,* 1998] that the Kaapvaal and Pilbara cratons were formerly juxtaposed in a fashion similar to that shown in Fig. 10. This interpretation is not universally accepted. For example, *Nelson et al.* [1999] pointed out geochronological discrepancies between the two areas and stated that the many stratigraphic similarities may be explained by global sea level changes and do not necessarily indicate former contiguity of the two regions. *Dawson et al.* [2002] preferred a reconstruction in which the Kaapvaal is placed on the other side of the Pilbara region. When the two cratons are juxtaposed (one possibility is depicted in Fig. 10) then the Archean-Paleoproterozoic stratigraphic successions of both regions can be interpreted in terms of a Wilson Cycle. The volcanic and siliciclastic rocks that dominate the "Older rocks" in Fig. 10 (Ventersdorp and Fortescue groups) are interpreted as rift deposits. The overlying siliciclastic and chemical deposits of the Hamersley, Ghaap and Chuniespoort groups are thought to represent deposition in passive margin settings, formed when an (unknown) western continental region drifted away. In some areas of North America a large time break has been recognized between deposits of Paleoproterozoic passive margins and succeeding foreland basins. e.g. between the Huronian Supergroup and Animikie Group *Young,* [2003] and *Aspler et al.* [2001] called attention to a similar time break in the Hurwitz Group in northern Canada. Geochronological results from Western Australia led Cheney [1996] to propose a similar hiatus at the base of the major BIF of the Hamersley Group (Fig. 8). Thus the Turee Creek Group, which contains glaciogenic deposits of the Meteorite Bore Member, and possibly the underlying iron-formations, are thought to represent foreland basin deposits derived from a rising orogen to the southwest [*Horwitz,* 1982]. The break in the Australian succession may correspond to the unconformities noted in the Griqualand West and Transvaal basins of South Africa (dark wavy line on Fig. 9) and in both regions this gap is thought to signal the transition from passive margin to compressional basin settings. *Myers* [1990] and *Myers et al.* [1996] have suggested dates between about 2.0 Ga and 1.6 Ga for the Capricorn orogeny but the stratigraphically based and now geochronologically constrained interpretations of *Horwitz* [1982, his Fig. 3] and *Blake and Barley* [1992, their Fig. 3] suggest that stratigraphic and sedimentological manifestations of compression, and development of a foreland basin were considerably earlier and that the younger dates may reflect the terminal phases of the orogeny.

The Paleoproterozoic glaciogenic rocks of South Africa and Western Australia may therefore have been deposited in foreland basin settings close to an extensive continental margin that developed along the edge of the Transvaal and Pilbara cratons. This tectonic setting is in marked contrast to that of glaciogenic deposits of similar age in North America and Fennoscandia, which appear to have formed shortly after continental fragmentation and development of a passive margin.

12. SUMMARY AND DISCUSSION

Apart from the glaciogenic deposits of the Hurwitz Group, virtually all the known Paleoproterozoic glaciogenic rocks may have formed close to the margins of two Archean supercontinents, Kenorland (or Laurentia) and Vaalbara. The Hur-

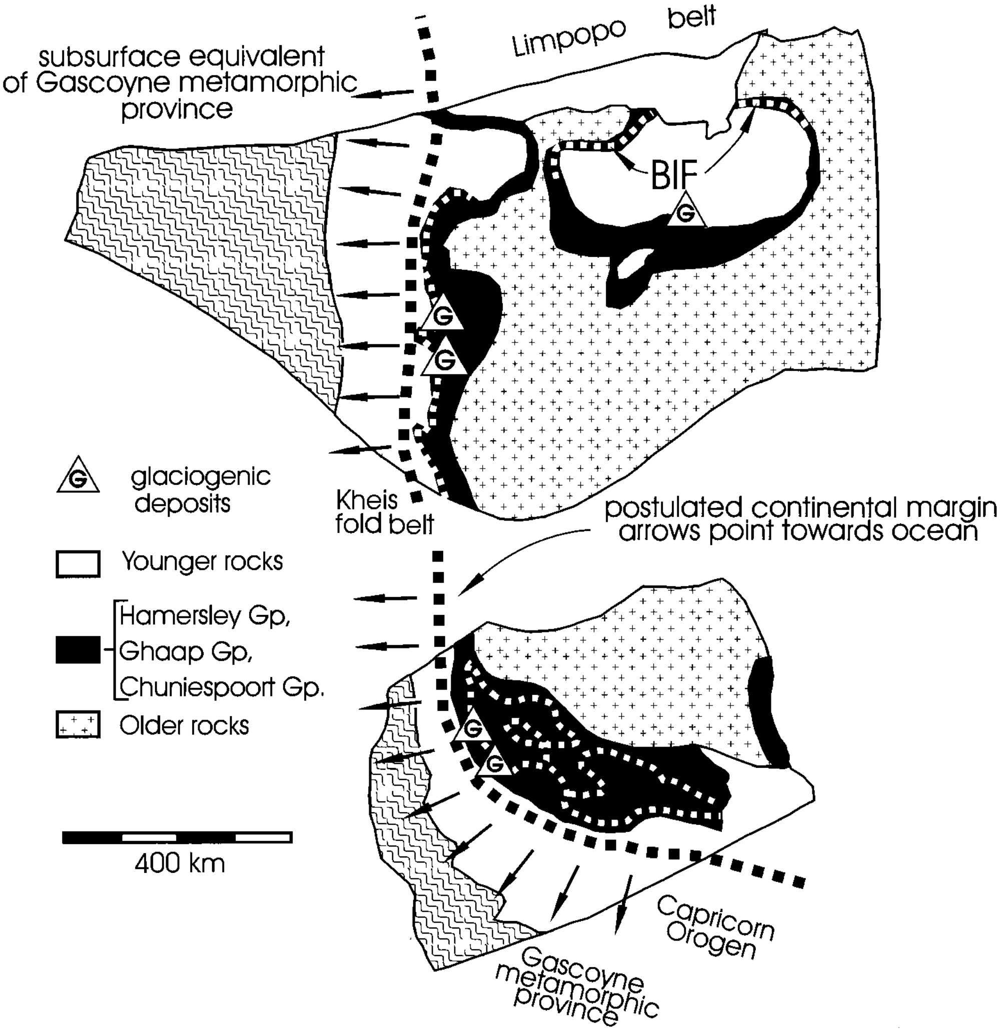

Figure 10. Sketch map showing one possible configuration of the proposed supercontinent, Vaalbara [*Cheney et al.,* 1988]. Whereas the relative positions of the Transvaal and Pilbara cratons are not unique, the diagram serves to illustrate the similar paleogeographic relationships that existed in both areas during Archean-Paleoproterozoic times. Note that most of the glacio-genic deposits are close to the proposed continental margin. See text for discussion.

witz Group appears to occupy a similar stratigraphic and tectonic position to those of Paleo-proterozoic successions on the SE margin (present co-ordinates) of Kenorland (Fig. 6) but it is likely that the Hurwitz Group was deposited close to the margins of a separate smaller (?) ocean basin (Fig. 6). The ages of most of these deposits are only loosely constrained but allow the possibility that they are all contemporaneous. The Laurentian glaciogenic deposits all appear to have accumulated in passive margin settings, whereas those preserved on the western margin of Vaalbara may represent foreland basin deposits. When considered on a global scale, these deposits are relatively locally developed but it is not known whether the present distribution reflects preservation rather than original distribution.

Recent paleomagnetic results both from the Huronian [*Williams and Schmidt,* 1997; *Schmidt and Williams,* 1999] and from volcanic rocks associated with the Makganyene Formation in South Africa [*Evans et al.,* 1997] may indicate deposition at low paleolatitudes. Since the glaciogenic rocks probably formed at sea level, then their low paleolatitudes have been taken by some to indicate that the entire Earth may have been frozen at that time (snowball Earth condition). The presence of varve-like deposits in some of these glacial successions [*Coleman,* 1908; *Jackson,* 1967; *Young,* 2001; *Hughes,* 2003] and possible fossil ice-wedge structures [*Young and Long,* 1976] suggest large seasonal temperature variations, unlike tropical regions today. These characteristics of Paleoproterozoic glaciogenic deposits are not explained under the snowball Earth hypothesis, nor are the abundant associated waterlaid sediments and complex stratigraphic successions [*Young and Nesbitt*, 1995; *Visser*, 1981] which are suggestive of temperate glaciation, rather than the extreme conditions envisaged under the SEH. Based on computer simulations, *Jenkins* [2003] proposed that glaciation at low latitudes would have been possible with an increased obliquity [cf. *Williams*, 1975], reduced solar luminosity and migration of a supercontinent into low paleolatitudes.

The reappearance of banded iron-formations, associated with some Neoproterozoic glaciogenic deposits, after a gap of ~1.5 b.y. led Kirschvink [1992] to suggest that they formed as a result of complete freezing of the surface of the planet. The iron-formations were thought to have precipitated at the end of the snowball Earth condition when the oceanic ice cover disappeared and oxygenation of the oceans took place. In the Paleoproterozoic of Laurentia the classical banded iron-formations of Lake Superior type are about 300 m.y. younger than the glaciogenic rocks so that the genetic association predicted by the SEH clearly does not apply. In the Vaalbara successions there is a much closer stratigraphic relationship between iron-formations and glaciogenic deposits. Both rock types appear in compressional (foreland basin?) settings and the Makganyene Formation (South Africa) is closely associated with Fe and Mn-rich sediments. *Kirschvink et al.* [2002] suggested that this association supported snow-ball Earth conditions in the Paleoproterozoic but this is the only known co-occurrence of Paleoproterozoic glaciogenic deposits and iron-formation. In the Pilbara region glaciogenic deposits occur well above the iron-formations (Fig. 8).

Bekker et al. [2001] considered the Timeball Hill and Duitschland formations in South Africa to be between 2486 and 2368 Ma. The age of the Gowganda Formation in Ontario was estimated by *Fairbairn et al.* [1969] as 2288+-87 Ma (Rb-Sr whole-rock isochron). This gives a possible range between 2375 and 2201. These dates suggest that the Gowganda is younger than the S. African occurrences and if the younger limit for the Gowganda is accepted, then as much as 167 Ma younger. The younger date may be more accurate as there is some evidence that the sediments of the Gowganda Formation were not completely consolidated at the time of intrusion of diabases, that are possibly part of the 2.2 Ga Nipissing diabase suite [*Shaw et al.*, 1999]. These admittedly loosely constrained dates may indicate that the South African glaciogenic rocks are not contemporaneous with those in North America, thus negating one of the requirements of the SEH but clearly more precise geochronological data are required.

Bekker et al. [2001] compared the South African glaciogenic deposits with those of the Huronian. Based partly on $\delta^{13}C$ values from associated carbonates, they suggested that two of the Huronian glaciogenic formations (Bruce and Gowganda) might be equivalent to two glacial units (Duitschland and upper Timeball Hill) in South Africa. The geochronological evidence cited above may, however, negate these proposed correlations. These authors also suggested that, at beginning and end of the Proterozoic Eon, reduced atmospheric CO_2 levels (due to increased organic activity/burial or increased weathering) may have caused glaciations. There is, however, no known significant $\delta^{13}C$ enrichment in carbonates below the Duitschland diamictite nor is the end of the Paleoproterozoic C-isotope excursion (between 2.2 and 2.1 Ga) marked by known glacial phenomena.

It has been proposed [*Hoffman et al.*, 1998] that cap carbonates are the result of extreme alkalization of the oceans at the end of the snowball Earth condition. A corollary of this idea is that siliciclastic sediments deposited after the glaciation should exhibit chemical evidence of extreme weathering since vast amounts of Ca, Na and K should have been removed from surficial sediments and older rocks to bring about alkalization of the global oceans. This is clearly not the case in the Gowganda Formation since sedimentary rocks immediately following the end of glaciation show a gradual upward increase in CIA values [*Young and Nesbitt*, 1999; *Young*, 2003], indicating a gradual amelioration of climate at the end of glaciation, rather than the opposite trend (due to normalization of atmospheric CO_2 levels) as predicted by the SEH. An additional argument against snowball Earth conditions in the Paleoproterozoic is the absence of cap carbonates above most glaciogenic deposits of that age, with the possible exception of the Espanola Formation [*Bekker et al.*, 2001].

13. CONCLUSIONS

Paleoproterozoic glaciogenic deposits appear to have developed close to two continental margins—one on the east side of Laurentia and the other forming the western margin of the supercontinent Vaalbara (as depicted in Figs. 6 and 10). On the southeastern side of the supercontinent Kenorland and contiguous Baltica, glaciogenic rocks were deposited on a newly-formed passive margin at about 2.3 Ga. They may have extended for over 8000 km along a continental margin from present day Wyoming to the Karelian region. By analogy with the opening of the Atlantic Ocean, formation of such a long continental margin may have involved over 100 m.y. Glaciogenic deposits of the Padlei Formation in the Hurwitz Group formed near a continental margin on the NW side of a separate Paleoproterozoic ocean that occupied the region now underlain by the Trans-Hudson orogen. A somewhat older continental margin developed on the west side of the supercontinent Vaalbara. In contrast to Kenorland, Paleoproterozoic glaciogenic deposits in Vaalbara appear to be part of the fill of compressional basins (foreland and associated basins), formed by closure of an ancient ocean.

Paleoproterozoic glaciogenic rocks are much less widespread than those of the Neoproterozoic, which have been ascribed by some to a snowball Earth condition. Most also lack cap carbonates, which occur above many Neoproterozoic glaciogenic successions. Major element geochemistry of the post-glacial sedimentary rocks of the Gowganda Formation suggests a weathering trend opposite to that predicted by the SEH. Iron-formations are commonly associated with Neoproterozoic glaciogenic deposits but this relationship is observed in few Paleoproterozoic occurrences. In the Lake Huron-Lake Superior region Paleoproterozoic iron-formations are separated by ~300 Ma from glacial deposits (formed on a much older passive margin). The iron-formations are part of the fill of a foreland basin that developed during ocean closure. In South Africa iron-formations are found together with glaciogenic rocks of the Makganyene Formation but in the Pilbara region of Western Australia glacial deposits of the Meteorite Bore Member lie about 1800 m stratigraphically above banded iron-formation. Thus the Paleoproterozoic glacial deposits lack many of the characteristics thought by some to support the snowball Earth hypothesis and are perhaps more easily explained as "normal" glaciations comparable to those of the Tertiary and Quaternary. This interpretation appears to be compromised by the low paleolatitudes at which Paleoproterozoic glaciogenic deposits in Ontario, and possibly in South Africa, appear to have accumulated. One possibility, proposed by *Williams* [1975; 1993] and supported by modeling [*Jenkins,* 2003] is that the Earth's obliquity was significantly different throughout the Precambrian so that when the Earth entered a glacial phase, continental areas lying in equatorial areas were more susceptible to glaciation than those at high latitudes. Resolution of these problems must await additional geochronological and paleomagnetic work but the available data do not appear to support the suggestion that the Earth's surface was completely frozen (snowball Earth condition) during the Paleoproterozoic glaciations.

Acknowledgments. I am grateful for financial support from the National Science and Engineering Research Council of Canada (NSERC), which supported my investigations of ancient glacial deposits over many years. I would also like to thank the many individuals who have stimulated and shared my interest in these fascinating rocks. In particular I acknowledge inspiration and insight from former "glacial" students Darrel Long, Gary Yeo and Kathy Neale and colleagues John Crowell, Vic Gostin and Roland Trompette. The manuscript benefitted from a careful review by George Williams and Greg Jenkins is thanked for thoughtful and careful editorial handling.

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High Obliquity as an Alternative Hypothesis to Early and Late Proterozoic Extreme Climate Conditions

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Climate model simulations are used to assess the high obliquity hypothesis as a solution to Palaeoproterozoic and Neoproterozoic low-latitude glacial conditions. Climate model simulations show that if a low-latitude land mass is assembled it can explain the Paleoproterozoic glacial deposits. In the Neoproterozoic, the High Obliquity hypothesis can explain the Sturtian low-latitude glacial deposits when the supercontinent Rodinia was located in low-latitudes. The High Obliquity hypothesis cannot explain Varangian high-latitude glacial deposits because of the high amounts of incident solar radiation, which will not allow for the accumulation of snow. However the high-latitude Varangian glacial deposits are the least reliable and should be viewed with caution. Moreover, if the majority of glacial deposits are in low-latitudes in support of the high obliquity hypothesis it is possible that local environmental conditions such as elevated topography may have been responsible for high latitude glacial deposits. The most problematic issue for high obliquity is the mechanism responsible for significantly reducing obliquity on a 100-million year time-scale.

1. INTRODUCTION

The Proterozoic Era (2.5 Ga–544 Ma) is a unique period in Earth's history from a climatological perspective. This period can be characterized as one of climate extremes with evidence of severe glaciation at the beginning (Palaeoproterozoic) and end (Neoproterozoic) with implied warmth due a lack of glacial evidence in the MesoProterozoic. The early or Palaeoproterozoic period (~2.5–2.0 Ga) represents the first clear evidence of glacial conditions in Earth's history [*Evans et al.* 1997; *Williams and Schmidt,* 1997]. Surprisingly the geologic evidence shows that this was a low-latitude event (<20°) representing one of the most extreme climatic conditions (Snowball Earth) in Earth's history assuming the present-day orbital parameters (obliquity ~ 23.5°). Near or soon after this extreme event oxygen levels rose [*Kasting*, 1987; *Pavlov et. al.* 2000; *Holland*, 1994].

After the Palaeoproterozoic there is a lack of glacial deposits for approximately 1 billion years, which parallels the warm Archean Era. In the Neoproterozoic period (850–544 Ma), there is evidence of at least two periods of widespread low-latitude glaciation at approximately 725 Ma and 600 Ma [*Schmidt and Williams*, 1995; *Hoffman et al.* 1998; *Evans*, 2000]. At least some of the deposits were formed near sea level and in close proximity to the present-day Equator [*William and Schmidt*, 1995; *Hoffman et al.* 1998].

Two primary candidates could explain the causes of the variable Proterozoic climate conditions: the Snowball Earth hypothesis [*Kirschvink*, 1992; *Hoffman et al.* 1998], and the High Obliquity hypothesis [*Williams*, 1975]. Neither of these hypotheses has been tested completely and both have problems associated with them. In the Snowball Earth hypothesis, atmospheric greenhouse gases levels are responsible for

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triggering low latitude glacial conditions and for the warm, ice-free conditions that follow. In the High Obliquity hypothesis, the obliquity of the Earth was considerably larger than present and triggered low latitude glaciation when landmasses were assembled in low latitudes. Warm conditions returned when the land mass either broke into smaller pieces or migrated into higher latitudes.

The series of events in the Proterozoic based on the Snowball Earth hypothesis may have gone as follows: in the late Archean, rising oxygen levels lead to a significant reduction in anaerobic methanogenic bacteria causing a reduction in atmospheric methane (CH_4). The reduction in atmospheric CH_4 cooled global mean temperatures while increasing sea-ice and snow amounts triggering global glaciation, thereby explaining the glacial deposits in the Palaeoproterozoic [*Pavlov et al.*, 2000; *Pavlov et al.*, 2003; *Jenkins*, 2003]. In order to end global glacial conditions, atmospheric CO_2 levels increase because of low silicate weathering rates under Snowball Earth conditions. In the MesoProterozoic, CO_2 levels would have remained relatively high, thereby explaining the warm conditions and the lack of glacial deposits. In the Neoproterozoic, some processes such as excessive silicate weathering on tropical landmasses would have reduced atmospheric CO_2 levels, leading to an increase in sea-ice and snow amounts triggering global glaciation.

The stellar evolution of our Sun complicates the climate of the Proterozoic Era. During Earth's history the solar luminosity has increased by approximately 30% [*Endal and Schatten*, 1982]. During the Proterozoic Era the solar forcing was reduced by 6–18% relative to the present. Hence, an increase in atmospheric greenhouse gases would have been required to offset the lower solar constant. Figure 1a shows that if atmospheric CO_2 were the primary greenhouse gas, then in order to compensate the lower solar constant, its values would have been 5–142 present atmospheric levels (PAL) (1,414–48,320 ppmv) throughout the Proterozoic [*Kiehl and Dickinson*, 1987]. If the Snowball Earth events are now incorporated into this context, then CO_2 levels spiked at the end of each event in order to terminate glacial conditions. A minimum of 0.3 bars of CO_2 is required in the Palaeoproterozoic and Neoproterozoic to terminate glacial conditions (Figure 1b). In order to explain the lack of glacial deposits in the MesoProterozoic, 7–69 PAL of CO_2 (2, 515–23, 552 ppmv) would be required to compensate the lower solar constant.

The evidence to support Snowball Earth conditions includes: low-latitude glacial deposits, the formation of banded iron formations, negative excursions in δC^{13} and carbonate caps representing the termination of Snowball Earth. The Snowball Earth hypothesis, however, faces numerous challenges: (1) the synchronicity of the glacial deposits has been question. (2)

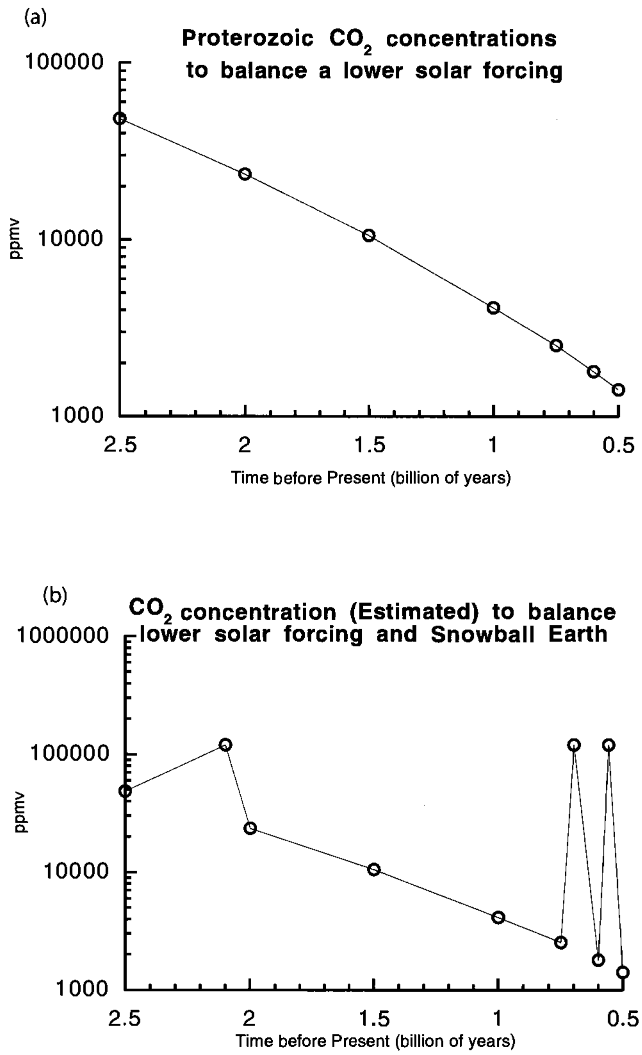

Figure 1. (a) Atmospheric CO_2 concentrations required to balance the lower solar forcing during the Proterozoic. Based on *Kiehl and Dickinson*, [1987]. (b) Same as Figure a but now assuming Snowball Earth condition in the Proterozoic.

The Snowball Earth hypothesis does not explain how life survived under several hundred meters of ice for millions of years. (3) The Snowball Earth hypothesis does not explain why glacial deposits are found primarily in latitudes less than 60° when high latitudes should have been the first to glaciate. (4) GCM studies with a fully coupled atmosphere-ocean model can not produce Snowball Earth conditions using boundary conditions of the Neoproterozoic [*Poulsen et al.* 2001. *Poulsen et al.*, 2002, *Poulsen*, 2003].

The primary goal of this study is to examine if a change in Earth's orbital tilt from a low value (23.45°) to a high value (70°) can help to explain the low-latitude glacial event of both the Palaeoproterozoic and Neoproterozoic periods. In Section 2 a brief description of how obliquity affects climate is examined, while in Section 3 GCM simulations using boundary conditions for the Palaeoproterozoic and Neoproterozoic periods are shown. In Section 4, some remarks are given on the strengths and weaknesses of the High Obliquity hypothesis in the Proterozoic Era.

2. THE ROLE OF OBLIQUITY IN EARTH'S CLIMATE

Obliquity controls the latitudinal distribution of solar radiation at the top of the atmosphere, which determines the amount of solar radiation reaching the surface and hence surface temperatures. For the present day obliquity of approximately 23.45° the mean annual insolation is highest in the low latitudes with small variations throughout the year. The insolation is reduced with latitude and the lowest values are found in the highest latitudes. The largest variations in insolation are found in the high latitudes with no solar radiation received poleward of the Arctic or Antarctic Circles during the winter season and the highest values on Earth found during the summer season (24 hrs of sunlight). On times-scales of 100,000 years the Earth's obliquity has variations between 22–24°. Here, the effects of high obliquity (> 54°) on climatic conditions are explored.

Williams [1975] proposed that high obliquity was a solution to low-latitude Proterozoic glacial conditions. Williams [1975, 1993] suggests that high obliquity on Earth could have obtained because of a collision with another planetesimal. Such an event may have been associated with the formation of the moon [*Canup and Asphaug*, 2001]. If the Earth's obliquity were greater than 54° the high latitudes would have received more insolation than the low latitudes (Figure 2). Consequently, the low latitudes would have been cooler than high latitudes. In order to explain low-latitude glacial conditions during the Proterozoic Era, the Earth's obliquity must have been high for at least 2 billion years. However it is likely that the Earth's obliquity would have been high prior to the Proterozoic Era in order to be consistent with the proposed mechanism for creating high obliquity.

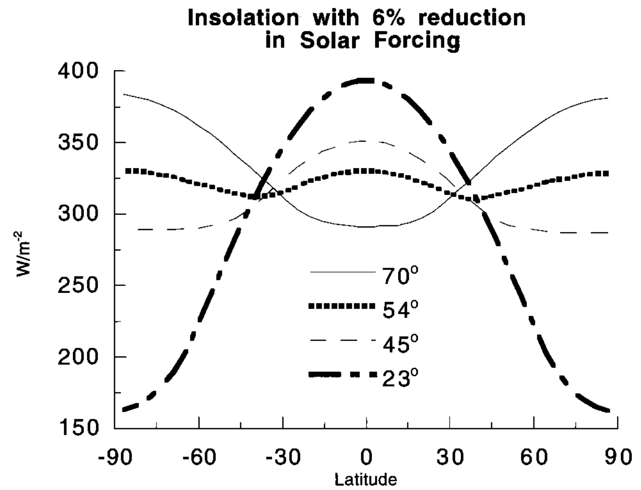

Figure 2. Zonally averaged Insolation with varying obliquity using boundary conditions of a 6% reduction in the solar constant. Units are W-m^{-2}

The Earth would have been returned to the present-day obliquity at the end of the Proterozoic through some mechanism such as core-mantle dissipation or obliquity-oblateness feedback when most of Earth's landmass was centered near the South Pole [*Williams*, 1993; *Bills*, 1994; *Williams et al.*, 1998]. *Vanyo and Awramik*, [1982] suggest that the obliquity was much lower in the late Proterozoic and Pais et al. [1999] have suggested that that the core-mantle dissipation is not a viable mechanism for reducing the Earth's obliquity from high to present-day conditions. Recently, Levrard and Laskar, [2003] have shown that climate friction is not a viable mechanism for reducing high obliquity back to present-day values at the end of the Proterozoic. This area of geophysics should be explored further due to the lack of published studies on internal mechanisms to reduce obliquity from high to low values on a 100 million year time-scale.

3. THE CLIMATIC IMPACT OF HIGH OBLIQUITY

3.1. High Obliquity and Simulations of Early Proterozoic low-latitude glaciation

The first clear evidence of low-latitude glaciation occured at approximately 2.4–2.2 Ga just before or near the rise of oxygen levels. The sedimentological evidence points to glacial conditions within 20° of the Equator. Under present day obliquity, low latitude glacial conditions would suggest that near "Snowball Earth" conditions occurred in the Early Proterozoic. *Pavlov et al.* [2000], *Pavlov et al.* [2003] suggests that methane levels were considerably higher than present prior to the low-latitude Proterozoic glacial conditions. They suggest that a rise in oxygen levels led to a reduction in biogenic sources of methane levels thereby triggering low-latitude glaciation.

GCM simulations of low latitude glaciation [*Jenkins*, 2003] due to a reduction in atmospheric CH_4 from 10 ppmv to 0.1 ppmv support the hypothesis by *Pavlov et al.* [2000]. However, a reduction in oceanic heat transport can produce similar results suggesting that the ocean or a reduction CH_4 could initiate early Proterozoic glacial conditions [*Jenkins*, 2003]. A key question is whether the Palaeoproterozoic glacial events occurred prior to the rise of oxygen or after a rise in oxygen levels. If glacial conditions occurred prior to the rise of oxygen it suggests that there was some factor that triggered low-

[redacted]

[redacted]

[redacted]

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[redacted] and

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[redacted]

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200

[redacted]

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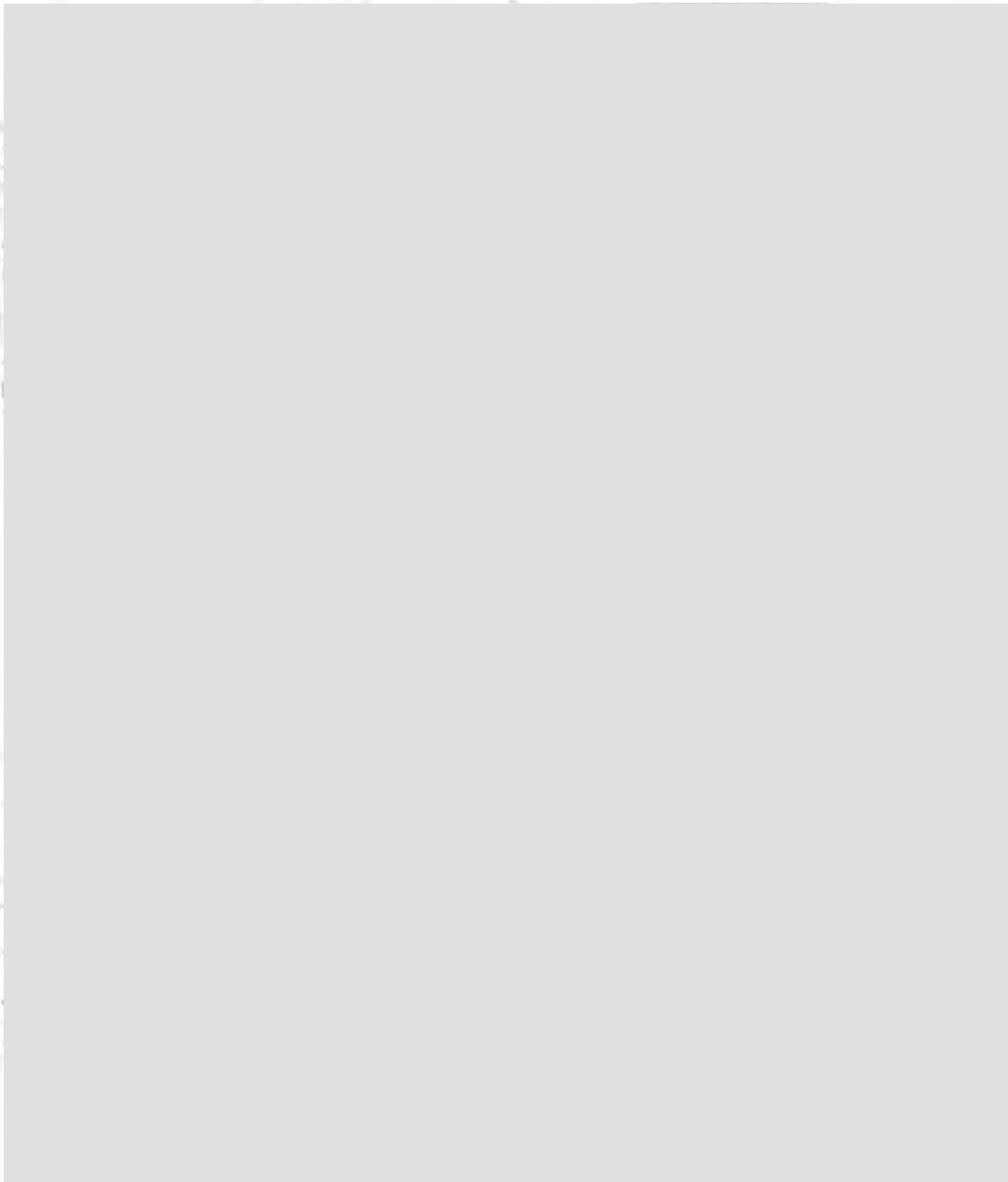

Table 1. Simulations of Low Latitude Super-Continent for Neoproterozoic Boundary Conditions.

Simulation	S/So	CO_2 (ppmv)	Obliquity
MLAT1	0.94	170	70
MLAT2	0.94	170	54
MLAT3	0.94	690	54
MLAT4	0.94	690	45

mean temperatures with ice-free conditions over the ocean. A 65° obliquity leads to permanent snow over land-areas but primarily in elevated regions. But, an obliquity of 70° leads to the growth of sea ice at all latitudes less than 45°. The growth of sea-ice in this case begins near the Equator and migrates poleward. However, the ice does not migrate to the poles because the high incident of solar radiation in high latitudes. It is the 2 km mountains on the idealized super-continent serves as the genesis site for permanent snow [*Jenkins*, 2000].

The idealized super-continent used in GCM simulations [*Jenkins*, 2000] is representative of the Sturtian period reconstruction, when the super-continent of Rodinia was located in Equatorial latitudes. *Donnadieu et al.* [2002], using a reconstruction for the Sturtian glacial period found that high obliquity is a solution to low-latitude glaciation. However, when using a reconstruction corresponding to the Varangian glacial period (620–580 Ma), which includes mid/high latitude land-masses, they were not able to produce mid to high latitude permanent snow that would correspond to suspected glacial deposits. Consequently, they have suggested that the high obliquity hypothesis has been invalidated because of the inability to reproduce the spatial patterns of glacial deposits in the Varanger glacial period.

To examine this question further, GENESIS v2.0 simulations [*Pollard and Thompson*, 1997; *Jenkins*, 2003] using idealized low and high latitude Southern Hemisphere continents have been undertaken using the boundary conditions of a 6% reduction in the solar forcing. The atmospheric CO_2 is varied from 170 ppmv to 690 ppmv and sea ice is prescribed in the lowest latitudes in order to ensure that growth of sea-ice into high latitudes is a possibility. The GCM has a grid spacing corresponding to approximately 4.5° × 7.5°, 12 vertical levels and a 50-meter slab ocean for computing sea surface temperatures is used. The obliquity is varied from 45° to 70° in these simulations (Table 1). In these simulations a small, idealized continent is placed in low latitudes, to trigger the growth of sea-ice and a larger idealized super-continent is placed in high latitudes.

Figures 5 and 6 show NH winter season (DJF) and summer (JJA) 2-meter air temperatures. During DJF above freezing temperatures over the ocean are found poleward of approximately 50°N with a 70° obliquity (Figure 5). However with a lower obliquity (54°, 45°) sub-freezing air temperatures are found at all latitudes in the Northern Hemisphere. In the Southern Hemisphere air temperatures over the ocean in all of the simulations are approximately 273°K as the ocean is completely ice-covered. Over land areas 2-meter air temperatures are above freezing in all cases with the warmest temperatures (>325°K) found for a 70° obliquity. Land areas between 30°S and 40°S are subfreezing and snow-covered year round. During DJF all snow over the Southern Hemisphere high latitude landmass is melted away because of the high values of incident solar radiation.

During JJA, the mid to high latitude land-mass in the southern hemisphere is below freezing with much of the continent being less than 210°K (Figure 6). In the 70° obliquity simulation the high latitudes of the Northern Hemisphere remains above freezing and ice-free while only a small portion of the Southern Hemisphere ocean remains above freezing. With an obliquity of 54° or 45° the entire Southern Hemisphere is below freezing and essentially in a Snowball Earth state. The seasonal range of land-temperatures over the Southern Hemisphere is more than 100°K for each simulation. The global mean temperatures for the four simulations are 234.6° K (MLAT1), 223.9° K (MLAT2), 226.3° K (MLAT3), 225.3° K (MLAT4). One interesting feature in these simulations is the growth and migration of sea-ice in the simulations. For an obliquity of 70°, sea-ice migrates from low-latitudes into higher latitudes in the evolution of the simulation. However, as obliquity is lowered to 45°, sea ice growth occurs in the high latitudes as well as low latitudes. Consequently, the evolution to "Hard" Snowball Earth conditions occurs rapidly.

4. CONCLUSION

The Proterozoic Era is the only time period in Earth's history with recorded glacial deposits in low latitudes. Our limited understanding of the climate system along with an incomplete geologic record leads to two hypotheses to explain these low latitude glacial periods. If present-day obliquity is assumed then, some factor led to a reduction in greenhouse gases and triggered the growth of sea-ice and snow in middle/high latitudes. Sea-ice migrates equatorward through a positive ice-albedo feedback and ultimately led to a snow and ice covered earth (Snowball Earth hypothesis). If on the other hand the obliquity of Earth was considerably higher than present during the Precambrian, then the assemblage or migration of a large landmass could have triggered low-latitude glaciation (High Obliquity hypothesis). Both hypotheses have limitations that could lead to their invalidation.

In the Snowball Earth hypothesis, the triggering mechanism for Neoproterozoic glaciation remains problematic. While, silicate weathering of a low-latitude super-continent thereby reducing atmospheric CO_2 is a viable mechanism for the Sturtian low-latitude glacial event, this mechanism fails for the Varanger low-latitude glacial event since a smaller fraction of Earth's landmasses occupied low-latitudes. Moreover, fully coupled atmosphere/ocean GCMs have shown that sea-ice is confined to middle latitudes when using boundary conditions corresponding to the Neoproterozoic [*Poulsen et al.* 2001, *Poulsen et al.* 2002; *Poulsen*, 2003]. Finally, only "Soft" Snowball Earth conditions would have provided refuge for the majority of life during these extreme conditions. *Warren et al.* [2002] show that at least several hundred meters of sea-ice would have existed under "Hard" Snowball Earth condition bringing a cessation to photosynthetic processes. However, Soft" Snowball Earth conditions tend to disagree with the geologic rock record which show glacial deposits near the Equator.

Several problems also exist with the High Obliquity hypothesis. In particular, the hypothesis must address the return to low obliquity values at the of the Proterozoic and the possible occurrence of mid to high latitude glacial deposits. Several mechanisms have been identified as a means of reducing high obliquity at the end of the NeoProterozoic, including core-mantle dissipation [*Williams*, 1993] and obliquity-oblateness feedback [*Williams et al.* 1998]. However the viability for each of these mechanisms has been challenged. More research is required in each of these areas of geophysics to determine the viability of each mechanism. *Donnadieu et al.* [2002] also have shown that high latitude deposits associated with the Varanger glacial period invalidates the High Obliquity hypothesis because year-round snow cannot be simulated.

The results of *Donnadieu et al.* [2002] may be a bit premature for several reasons: the reliability of the high latitude glacial deposits have been questioned, the timing of the glacial deposits, and mechanisms for building Varanger ice-sheets. The high-latitude Varanger glacial deposits used for invalidating the High Obliquity hypothesis are considered the least reliable [*Evans*, 2000]. Another uncertainty is the synchronicity of the glacial deposits in middle/high latitudes relative to those in low-latitudes. Does the timing of the glacial deposits in high latitudes correspond to those in low latitudes as would be expected in Snowball Earth hypothesis. Since landmasses were distributed over a larger latitudinal zone, there should be approximately synchronicity in the deposits for "Hard" Snowball Earth conditions, with high latitude deposits forming first. The Varanger reconstruction used by *Donnadieu et al.* [2002] also suggests that there would be difficulty in growing or maintaining ice-sheets associated with the high latitude glacial deposits using present-day or high obliquity because of the lack of moisture. This reconstruction shows the super-continent centered over the South Pole with closest moisture source the mid-latitude ocean. It is difficult to imagine how moisture could penetrate into the super-continents without an unfrozen ocean.

However there is a fundamental question: does the evidence of one high latitude glacial deposit invalidate the High Obliquity hypothesis? I am not convinced that it does, because of the uncertainty associated with high latitude glacial deposits. Even if there is evidence of several glacial deposits in the high latitudes, it may suggest some unique environmental conditions associated with the glacial deposits especially if the majority of glacial deposits are found in low latitudes. For example, *Eyles* [1993] has suggested that many of the Neoproterozoic deoposits are found near elevated regions.

The climate simulations presented here, suggest that if high obliquity were present, then glacial deposits at latitudes greater than 60° would be unlikely, because of the high incidence of solar radiation during the summer. However, sub-freezing summer temperatures are found at latitudes less than 40° and temperatures are moderately warm in the latitude band between 40° and 50°. Consequently, one may take the view that because the geologic record shows that the majority of glacial deposits are found at low latitudes it would not invalidate the High obliquity hypothesis, rather it would strengthen it. The Varanger glacial period may have been unique because the formation of the high-latitude super-continent (Pannotia) was underway and high latitude deposits may have been associated with mountain building or other local/regional environmental conditions.

When viewed from a Precambrian perspective, the High Obliquity hypothesis is a solution to both the Archean and Proterozoic climate paradoxes [*Jenkins*, 2000, *Jenkins*, 2001; *Jenkins*, 2003] even if the mechanisms for restoring high obliquity to near present-day values is still unknown. Simulations show that the high obliquity hypothesis provides a basis for understanding the Palaeoproterozoic and Neoproterozoic low-latitude glacial events and the warm MesoProterozoic [*Jenkins*, 2003]. Further research using reconstructions for Sturtian and Varanger periods and high obliquity boundary conditions exploring boundary conditions (continental position, greenhouse gases,) are required.

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Thin Ice on the Snowball Earth

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Global ice-covered conditions during a Neoproterozoic snowball Earth seem inconsistent with the survival of eukaryotic algae. The presence of thin ice in the tropics remains a viable alternative to resolve this paradox. The simple method of *McKay* [2000] for computing ice thickness has been improved by considering separately a short wavelength interval (<700 nm) and a long wavelength interval (>700 nm). The key to determining the plausibility of thin ice models on the snowball Earth is a better determination of the relationship between optical properties of sea ice and freezing rate. If slowly freezing sea ice is optically clear, as field evidence suggests, then mean equatorial temperatures on the snowball Earth warmer than about -45°C imply thin ice that can support photosynthesis.

1. INTRODUCTION

There is considerable geological evidence that indicates that at several times during the Neoproterozoic (about 550 to 830 Myr ago) there was extensive glaciation in the tropics—the "Snowball Earth" model [*Kirschvink*, 1992; *Hoffman et al.*, 1998; *Hoffman and Schrag*, 2000]. If the oceans were covered by a thick covering of ice, then photosynthesis would be greatly reduced, a possibility consistent with the negative carbon isotope anomalies in carbonate rocks [*Hoffman et al.*, 1998; *Higgins and Schrag*, 2003; *Kennedy et al.*, 2001], although *Kennedy et al.* [2001] argue that the carbon isotope data are not consistent with the snowball Earth scenario outlined by *Hoffman et al.* [1998].

However, from a biological evolution point of view, an ice-covered Earth poses significant challenges. This is especially true since the ice would have been long-lived. The geological data [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2000] as well as climate simulations [*Caldeira and Kasting*, 1992] both suggest that the snowball Earth state would persist for about 5 Myr. Thus ecosystems would have equilibrated with the ice-covered conditions. If thick ice covered the oceans for millions of years it is puzzling that many eukaryotic algae (including red, green, and chromophytic algae) survived these snowball events [*Knoll*, 1992; 2003; *Williams et al.*, 1998] as well as complex microbial communities of prokaryotes and eukaryotes [*Corsetti et al.*, 2003].

McKay [2000] suggested a resolution to this paradox might be that the thickness of the ice in the tropical regions of the snowball Earth would have been thin enough to support photosynthesis under the ice cover. Photosynthesis under perennial ice occurs in the Antarctic dry valley lakes [*Parker et al.*, 1982; *McKay et al.*, 1985]. In the dry valleys, the mean annual temperature is −20°C but the thickness of the ice cover on the large closed lakes in these valleys is only about 5 m [*McKay et al.*, 1985]. The thin ice is not due to geothermal heat flow which alone would imply an ice thickness of 300 m [*McKay et al.*, 1985]. The explanation lies in the fact that heat flows many times larger than the geothermal heat flow are present in these ice covers due to sunlight penetrating the ice cover and to latent heat released by freezing at the bottom of the ice cover.

In the Antarctic dry valley lakes the transmissivity of sunlight through the ice cover varies from about 1 to 5% for wavelengths less then 700 nm [*McKay et al.*, 1994]. This corresponds to an annual average energy deposition of 0.5 to 2.5 W m^{-2}. The latent heat release can be determined from the ablation plus the melting rate, which together are from 35 cm yr^{-1} to 100 cm yr^{-1} corresponding to an annual average energy release of 3.3 to 9.4 W m^{-2}. Thus both solar and latent heat

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terms must be included but latent heat is 5 times larger. However, when applied to the tropical regions of the snowball Earth, the average sunlight is about 3 times that in the dry valleys. This higher sunlight might be expected to sustain thin ice even in the case that the ablation rate was negligible. This was reported by *McKay* [2000] and is an important factor in determining the possibility of thin ice in the tropical regions of the snowball Earth.

2. THIN ICE CALCULATIONS

It is useful to review in some detail how the thickness of perennial ice has been computed. *McKay et al.* [1985] developed a simple method for computing the thickness of a perennial ice cover. The method assumes that all heat and mass flows are vertical and that the ice cover is thick enough that its thickness can be determined from the annual average energy balance. The ice cover in the dry valley lakes does persist all year but the extreme seasonality of the polar regions implies that an annual average energy balance is only an approximation. In summer the sun is shining and the lake ice is warmed reaching 0°C throughout the ice cover forming a substantial liquid water fraction [*Fritsen et al.*, 1998]. The liquid water fraction is highest in the upper two meters of the ice cover with typical values of 10 to 20% but with values reaching as high as 60% [*Fritsen et al.*, 1998]. During the summer the ice becomes thiner as both ablation and melting remove ice from the surface. The total amount removed varies with summer conditions but is between 0.35 and 1 m [*Wharton et al.*, 1992]. With the coming of winter the ice cover refreezes and temperatures drop. The water at the bottom of the ice cover begins to freeze and the ice cover thickens as heat is carried from the warm ice-water interface (always at 0°C) to the cold winter atmosphere (~ −20°C). Thus the ice cover thickens in the winter and thins in the summer. The seasonal variability is about 20% so the assumption of an annual average is approximate and valid at this 20% level.

With the caveat of seasonal variability in mind we can consider the energy balance equation for a thick ice cover in terms of the equilibrium annually averaged thickness of the ice [*McKay et al.*, 1985].

Figure 1 shows the conceptual diagram for constructing the energy balance of the ice cover. Consider a level in the ice at depth z (with z increasing downward). The energy flows across this level include upward (positive) conduction through the ice cover from the warm bottom (0 °C) to the cold top (−20°C), advection of latent and sensible heat by the ice (due the transport of liquid water downward and ice upward), and solar energy. The advection of latent heat is equivalent to considering the freezing of water at the bottom of the ice cover as

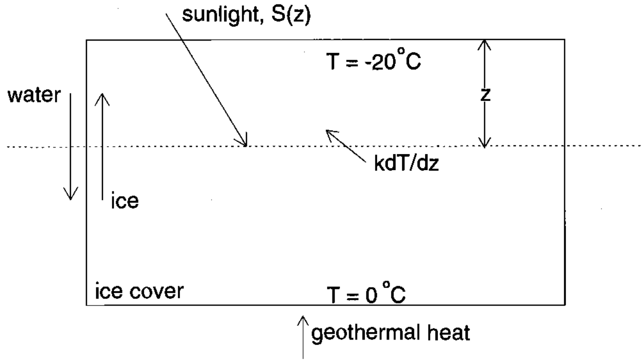

Figure 1. Energy balance diagram for an arbitrary level within the ice of perennial ice-covered lake. Liquid water flows down around the ice cover and ice flows back up. Energy diffuses upward by conduction through the ice cover. Sunlight enters the lake and may be absorbed or scattered. *S(z)* is the downward net flux at the level in consideration. The geothermal heat is coming up from deep below the lake.

a source of energy. In equilibrium, the net upward flux of energy at the level z must equal the geothermal heat flow. Thus we can write

$$k\frac{dT}{dz} - v\rho[L + c_W T_W - c_i T(z)] - S(z) = F_g \tag{1}$$

where k is the thermal conductivity, T is the mean annual temperature in the ice at the depth z, v is the ablation rate, ρ is the density of ice, L is the latent heat of fusion of water, c_w and T_w are the specific heat and temperature of the downflowing liquid water and c_i and $T(z)$ are the corresponding values for the upward flowing ice, $S(z)$ is the net solar flux penetrating below level z, and F_g is the geothermal heat flux from deep below the lake.

The assumption of steady state implies that the downward mass flow of water is equal to the upward mass flow of ice and hence we use the mass flow ($v\rho$) only for the ice. The term *v?L* is the latent heat content of the liquid water flowing downward (hence negative). The term $v\rho[c_w T_w - c_i T(z)]$ is the difference between the sensible heat content of the downward flowing water and the upward flowing ice. Since $L > c_i[T_w - T(z)]$ (80 compared to 10) we ignore the advection of sensible heat and consider only the latent heat term.

Note that in this model the ablation rate v is equivalent to the upward velocity of the ice cover and that ablation here can also refer to melting of the surface of the ice cover and the subsequent flow of the liquid to beneath the ice as shown in Figure 1. The internal melt fraction of the ice cover that forms in summer and refreezes at the start of winter cannot be represented accurately with this simple steady state model. A time dependent version of this model would be needed to represent this seasonal effect.

Following *McKay et al.* [1985], the attenuation of sunlight in the ice cover is expressed with an exponential. Thus, $S(z) = (1-a)(1-r)S_o \exp(-z/h)$, where a is the albedo of the ice averaged over the solar spectrum, r represents a fraction of the ice surface that is covered with dark absorbing material such as sand or silt, S_o is the solar radiation, and h is the effective attenuation coefficient and includes the cosine of the averaged solar zenith angle; h is the average of the cosine of the solar zenith angle divided by the extinction coefficient. Thus Eq. 1 can be expressed as:

$$k\frac{dT}{dz} = (1-a)(1-r)S_O \exp(-z/h) + \nu\rho L + F_g \qquad (2)$$

This is the approximation used by *McKay* [2000], *Warren et al.* [2002], *Goodman and Pierrehumbert* [2003], and *Pollard and Kasting* [2004] to compute the ice thickness on the snowball Earth.

The thermal conductivity of ice can be treated as constant or more accurately approximated by $k=b/T - c$, where b and c are constants given by 780 W m^{-1} and 0.615 W m^{-1} K^{-1}, respectively. Using these relations and integrating Eq. 2 from the ice-water interface to the surface gives [*McKay et al.*, 1985]:

$$Z = \frac{c(T_S+T_O) - b\ln(T_S/T_O) - S_O h(1-a)(1-r)[1-\exp(-Z/h)]}{\nu\rho L + F_g} \qquad (3)$$

where T_o is the temperature of ice in equilibrium with the water beneath it, T_s is the yearly averaged temperature at the surface (both in K), and Z is the equilibrium thickness of the ice cover. For very cold ($T_s < -40$°C) surface conditions the non-constancy of the thermal conductivity between the surface and the warm ice-water interface is significant (20% change in k).

Previous models [*McKay et al.*, 1985; *McKay*, 2000] treated the solar radiation as a single average over the entire spectrum. For the Antarctic dry valley lakes the corresponding parameter values were: a=0.6, h=1 m, r=0.1, and S_o = 104 W m^{-2}. This gives reasonable results but as pointed out by *Warren et al.* [2002], the albedo assumed is too high. Measurements and theory indicate that the albedo of the ice cover is about 0.3 in the visible and drops to smaller values in the infra red [*McKay et al.*, 1994]. More importantly, the transmission of light through the ice is high and fairly uniform for light in wavelengths less than 700 nm but drops sharply to virtually zero for wavelengths longer than 700 nm [*McKay et al.*, 1994]. This led *Warren et al.* [2002] to suggest approximating the solar radiation using two intervals: visible (<700 nm) and near-infrared (>700 nm). Roughly half the solar energy is contained within each interval. Thus a two band model for the Antarctic dry valley lakes can be constructed with parameters for the visible of a = 0.3, h = 1.2 m, r = 0.1, and S_o = 52 W m^{-2} (half of the sunlight) while for the infrared a = 0.0, h = 0 m, r = 0.1, and S_o = 52 W m^{-2} (half of the sunlight). Because the infrared radiation does not penetrate the ice cover (h=0) it does not appear in the energy balance.

To summarize, Eq. 2 can be used with a simple two-band solar model by allowing the albedo and transmission to represent the values averaged only over wavelengths less than 700 nm, and also replacing the incident sunlight, S_o, by 1/2 the full value. This approach was used by *Doran et al.* [2003] to model the ice cover on Lake Vida. *Warren et al.* [2002] have presented a 60-band scheme for computing the transmission of the ice with an idealized model of bubbles in ice. The simplification of the uniform bubble model and the complexity of real ice [*McKay et al.*, 1994] suggests that this is probably over computation.

The agreement between the simple two-band method and the 60-band method for snowball Earth conditions is shown in Figure 2. The comparison is based on Figure 7 of *Warren et al.* [2002] in which ν (ablation) and r are set to zero, the solar flux is set to 320 W m^{-2} (the average equatorial sunlight on the snowball Earth), and the mean temperature is set to –30°C. The squares are points taken from the spectral model in that figure. For comparison to these points, the dotted line shows the simple two-band calculation for h=1.2 m—the value determined for wavelengths less than 700 nm for the dry valley lakes based on the transmissivity data in *McKay et al.* [1994]. The solid lines labeled $h(a)$ and 2 X $h(a)$ refer to computations using the expression for h as a function of albedo given in Eq. 7 of *Warren et al.* [2002]. The two-band model with constant h is in reasonable agreement with the *Warren et al.* [2002] spectral results in that it predicts the transition from thin ice to thick ice at similar values of the albedo. However, the variable expression for $h(a)$ given by *Warren et al.* [2002] when put in the simple model does not give good agreement but multiplying the h value by two produces very good agreement. This factor of two probably arises because *Warren et al.* [2002] computed the value of h by averaging over all wavelengths. As discussed above, h is approximately zero for half the solar spectrum. Thus the value of $h(a)$ to be used in the visible spectrum (<700 nm) is expected to be twice the value of *Warren et al.* [2002]. This comparison supports the use of the two-band model for computing the ice thickness on the snowball Earth.

3. APPLICATION TO SNOWBALL EARTH

Because of the lack of seasonal variability, the tropical regions of the snowball Earth are better suited to the energy balance model of Eq. 2 than are the lakes of the dry valleys of

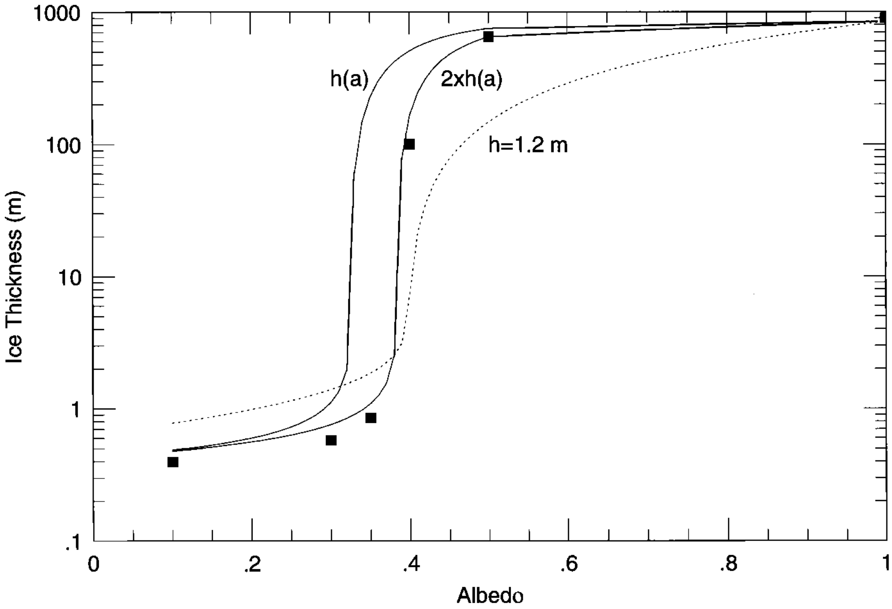

Figure 2. Comparison between the two-band model (lines) and the 60 band model (squares) of *Warren et al.* [2002]. Ablation, *v*, and dust loading, *r*, are set to zero and the solar flux is set to 320 W m^{-2} and the mean temperature is set to -30°C. The squares are points taken from the spectral model from Figure 7 of *Warren et al.* [2002]. The dotted line shows the simple two-band calculation for h=1.2 m. The solid lines labeled *h(a)* and 2 X *h(a)* refer to computations using the expression for h as a function of albedo given in Eq. 7 of *Warren et al.* [2002].

Antarctica. Figure 3 shows the thickness of the ice on the tropical snowball Earth as a function of the mean annual air temperature. The albedo and light penetration are treated as parameters. The ablation rate (melting is neglected) varies with temperature following the vapor pressure of ice [*Clow et al.*, 1988; *Moore et al.*, 1995] and is determined in these calculations by scaling from the measured value in the Antarctic dry valleys (35 cm yr^{-1} for temperature of −20°C). Thus at −40°C the ablation rate is 4 cm yr^{-1} and is 0.4 cm yr^{-1} at −60°C. Interestingly, the ice thickness falls to low values for temperatures warmer than about −45°C. This is similar to the results of *McKay* [2000] and seems to be incompatible with the results presented by *Warren et al.* [2002].

The explanation for this difference is in the physical assumptions of the different models not the mathematical treatment. A key physical difference between the model presented here and that presented in *Warren et al.* [2002] is the relationship between h and a. *Warren et al.* [2002] compute the optical properties of the ice by considering spherical bubbles within the ice. The values of h and a vary as the concentration of bubbles changes. High values of the albedo are only achieved by having high concentrations of bubbles and this in turn drives the value of h down to below 10 cm (see for example Figure 10 of *Warren et al.* [2002]). *Goodman and Pierrehumbert* [2002], attempting to adapt the *Warren et al.* [2002] results to the simple model of *McKay* [2000], cite a value of h = 0.05 m, which may be appropriate for glacial ice but is clearly at odds with measurements of light transmission through thick lake ice [*McKay et al.*, 1994].

Unrealistically small values of h cause the model of *Warren et al.* [2002]) to always predict thick ice covers for large values of the albedo. Our value of h (1.2 m) corresponds to the value *Warren et al.* [2002]) determine for an albedo of about 0.3. Thus we should expect that the ice thickness we obtain for this value of albedo to be in agreement with *Warren et al.* [2002]. Comparison of Figure 3 with Figure 9 of *Warren et al.* [2002] shows that this is the case. Both models predict thin ice when the albedo is 0.3 for temperatures as cold as −50°C.

It is hard to reconcile high bubble density with slowly forming, thick ice. It is well known that as the rate of ice formation slows the concentration of bubbles decreases. Evidence from the Antarctic dry valley lakes suggest —albeit in fresh water— that the bubbles become large at low freezing rates [*Wharton et al.*, 1992]. Data for slowly growing sea ice is lacking and for sea ice, brine pockets as well as bubbles contribute to scattering. *Wettlaufer* [1998] has shown theoretically that the fingering instability which leads to the incorporation of brine pockets does not occur for growth rates less than 6 mm/yr. Thus if sea ice forms slowly enough it is likely to be "black ice" not bubbly ice. Further modeling and field observations are needed to establish how freezing rate correlates with optical properties in sea ice.

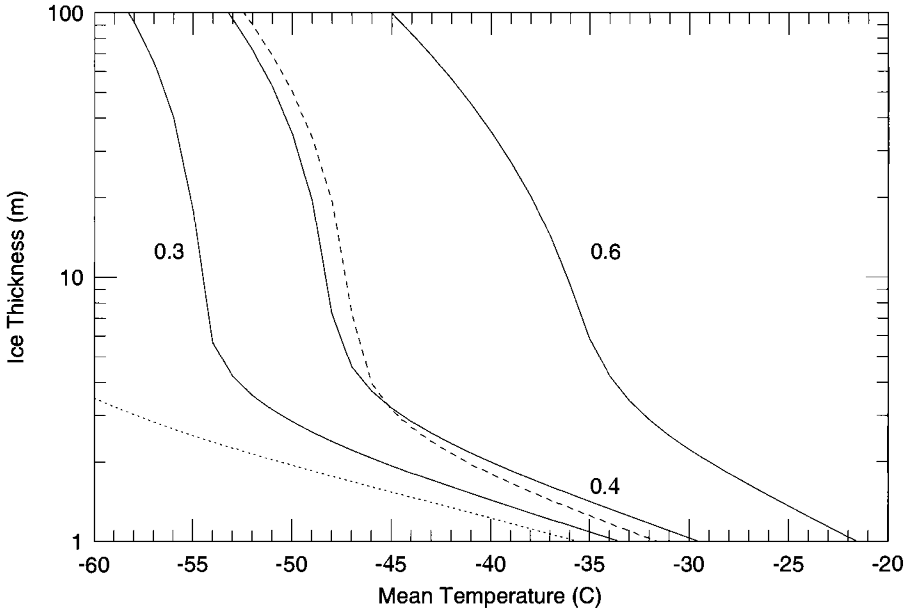

Figure 3. Thickness of ice in the tropical regions for a snowball Earth computed using Eq. 2 for a range of mean annual surface temperatures and with ablation rate equal to 35 cm yr^{-1} at -20°C and proportional to the vapor pressure of ice. Solid curves are computed with a=0.3, 0.4, and 0.6, r=0.0, S_o=320 W m^{-2}, and h=1.2 m. The dotted line is for a=0.3, r=0.0, and h=1.5; dashed line is for a=0.3, r=0, and h=1 m. This curve corresponds to Figure 4 in *McKay* [2000].

Note that the calculations presented in Figure 2 are averages over diurnal cycles and therefore are not applicable to very thin ice (<5 m). Ice covers thinner than a few meters probably imply a partly open sea surface. Note also that the analysis presented here does not consider the lateral flow of sea ice. This may be an important effect and could invalidate the one dimensional approach used here.

4. DISCUSSION

We have reconsidered the thin ice model for tropical ice on the snowball Earth. The analysis presented here suggests that even if Earth was largely covered with ice during the Neoproterozoic, if mean annual equatorial temperatures were warmer than –45°C, and if sea ice that forms from slow freezing is optically clear, then there would likely remain some regions in the tropics that would be covered with ice thin enough (<30 m, [*McKay*, 2000]) to allow for photosynthesis. Even in this case the total flux of sunlight available for primary productivity would be greatly reduced compared to ice-free conditions. This reduction in total productivity is consistent with the geological data which implies that, globally, the proportion of organic carbon to total carbon burial changed from almost 0.5 before the glaciation to virtually zero during it [*Kirschvink*, 1992]. In the tropics, however, photosynthesis through thin ice could have allowed for the survival of photosynthetic marine algae and supported a reduced but still complete ecosystem. As the ice receded, these localized regions of production would have spread to recolonize the ocean.

Based on the work presented here we can present the following specific conclusions regarding the thin ice model:

1. The simple method for computing ice thickness of *McKay et al.* [1985] can be improved by separating the sunlight into a short wavelength interval (<700 nm), which penetrates the ice, and a long wavelength interval (>700 nm), which does not. For the same physical assumptions regarding ice optical properties, this two-band model agrees with more detailed spectrally resolved calculations.
2. The key to determining the plausibility of thin ice models on the snowball Earth is a better determination of the relationship between optical properties of sea ice and freezing rate.
3. The primary environmental variable for determining if a thin ice solution is possible for the snowball Earth is the mean equatorial temperature. For optically clear ice (as assumed in this paper) mean equatorial temperatures warmer than about –45°C are required. For bubbly ice [*Warren et al.*, 2002] mean equatorial temperatures must be warmer than about –25°C for thin ice to be possible.
4. The thin ice model provides a plausible, but not yet adequately proven, mechanism for allowing the survival of photosynthetic eukaryotic algae during snowball Earth conditions.

Acknowledgments. This work was supported by the NASA Astrobiology Program.

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Neoproterozoic Glaciations and the Fossil Record

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Sedimentary, geochronological, and $\delta^{13}C$ chemostratigraphic data require that at least three glaciations—the Sturtian, Marinoan, and Gaskiers in geochronological order—occurred in the Neoproterozoic glacial interval (NGI; ca. 750–580 Ma); at least the Gaskiers glaciation has not been demonstrated global in nature. Available radiometric and $\delta^{13}C$ chemostratigraphic data also suggest that the fossil-rich Doushantuo Formation may have been deposited after the Marinoan but before the Gaskiers glaciation, thus representing a window between two glaciations. A review of the fossil record under this geochronological framework reveals the following patterns: 1) a broad decline in stromatolites and acritarchs occurred in the Cryogenian (ca. 750–600 Ma); 2) a taxonomically unique assemblage of large acanthomorphic acritarchs occurs between the Marinoan and Gaskiers glaciations; 3) multicellular algae diversified after the Marinoan glaciation, although they evolved earlier; 4) animals, probably in microscopic forms, evolved before the Gaskiers glaciation if not earlier; and 5) post-Gaskiers diversification of complex Ediacaran organisms/animals may have begun in deep-water slope environments and later expanded to shallow-water shelf environments where macrobilaterians and biomineralized animals first appeared. It is hypothesized that 1) the Cryogenian decline in stromatolites and acritarchs may have been causally related to glaciations; and 2) acanthomorphic acritarchs, algae, and animals may have suffered diversity loss related to the Gaskiers glaciation. The fossil record also implies that 1) at least some lineages of different algal clades survived all Neoproterozoic glaciations; and 2) some members of the animal clade survived the Gaskiers glaciation, probably in non-glaciated refugia.

1. INTRODUCTION

The causes, consequences, magnitude, and number of Neoproterozoic glaciations have been controversial [*Kirschvink*, 1992; *Kaufman et al.*, 1997; *Hoffman et al.*, 1998; *Kennedy et al.*, 1998; *Hyde et al.*, 2000; *Kennedy et al.*, 2001a; *Kennedy et al.*, 2001b; *Hoffman and Schrag*, 2002]. Nonetheless, the global distribution of Sturtian and Marinoan glaciogenic deposits [*Hambrey and Harland*, 1981; *Deynoux et al.*, 1994] and the demonstrably low paleolatitude of some glaciated continents [*Schmidt and Williams*, 1995; *Evans*, 2000] indicate that these glaciations dwarf their Phanerozoic counterparts. Glaciation events of such magnitude are expected to have had significant impacts on biological evolution, causing biological extinctions followed by post-extinction recoveries and radiations. As yet, however, no carefully designed paleontological tests for these extinctions have been carried out. The delay stems from several obstacles. First, the geochronological resolution of many Neoproterozoic successions is poor, and as a result the precise temporal relationship between Neoproterozoic glaciations and evolutionary events has been elu-

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sive. Second, the Neoproterozoic fossil record is sketchy, and the phylogenetic interpretations of many Neoproterozoic fossils have been controversial. In the past few years, however, both the Neoproterozoic fossil record and geochronological resolution have been significantly improved, allowing a closer examination of the paleontological record in the broad context of climate changes. In this paper, I attempt to review currently available stratigraphic, geochronological, and paleontological data to bear on the relationship between Neoproterozoic glaciations and biological evolution. It is not the purpose of this paper, however, to differentiate among the end-member scenarios of Neoproterozoic glaciations [*Hoffman et al.*, 1998; *Hyde et al.*, 2000], although the proposed glaciation scenarios will have to eventually account for the paleontological record.

2. NEOPROTEROZOIC GLACIATIONS

As mentioned above, one of the key obstacles in the current analysis is the poor understanding of the temporal relationship between Neoproterozoic glaciations and the fossil record. In particular, the number of Neoproterozoic glaciogenic has been controversial [*Kaufman et al.*, 1997; *Kennedy et al.*, 1998; *Halverson*, 2002; *Hoffman and Schrag*, 2002; *Bowring et al.*, 2003; *Rice et al.*, 2003]. *Kaufman et al.* [1997], for example, argue that there may have been as many as five Neoproterozoic glaciations. *Kennedy et al.* [1998], on the other hand, recognize only two Neoproterozoic glaciations—the older Sturtian and younger Marinoan glaciation. Others [*Brasier et al.*, 2000; *Brasier and Shields*, 2000; *Knoll*, 2000; *Corkeron and George*, 2001; *Zhou et al.*, 2001; *Halverson*, 2002; *Hoffman and Schrag*, 2002; *Bowring et al.*, 2003; *Rice et al.*, 2003] suggest that at least three glaciations occurred in the Neoproterozoic. Below, I summarize our recent work in the Quruqtagh area [*Xiao et al., in press a*] and in South China [*Xiao et al.*, 2003] that bears on the number of Neoproterozoic glaciations.

2.1. Quruqtagh

The Neoproterozoic Quruqtagh Group [*Norin*, 1937] in the Quruqtagh area, eastern Chinese Tianshan, is a >3 km thick, predominately siliciclastic succession. It consists of, in ascending order, the Bayisi, Zhaobishan, Altungol, Tereeken, Zhamoketi, Yukkengol, Shuiquan, and Hankalchough formations (Figure 1; [*Gao and Zhu*, 1984]). The Quruqtagh Group is bracketed between early Neoproterozoic stromatolitic dolomite and Early Cambrian (pre-trilobite Meishucunian to be exact) cherts and phosphorites. Diamictites exist in the Bayisi/Altungol, Tereeken, and Hankalchough formations. Large boulders set in silty matrix are common in all three diamictite formations, but unambiguous evidence for glacial activities only occurs in the Tereeken and Hankalchough diamictites. Previous investigators interpreted these diamictite intervals as recording three Neoproterozoic ice ages in Quruqtagh [*Gao and Zhu*, 1984; *Gao and Qian*, 1985; *Brookfield*, 1994]. Our field investigation only confirms the glaciogenic nature of the Tereeken and Hankalchough diamictites; the Bayisi/Altungol diamictites may or may not be glaciogenic, but deformation and metamorphism make it difficult to identify unambiguous glaciogenic features.

Our $\delta^{13}C$ chemostratigraphic data from sporadic carbonate units within the Quruqtagh Group suggest that the Hankalchough glaciation likely postdates the Marinoan glaciation [*Brookfield*, 1994]. This conclusion is supported by several lines of evidence. First, carbonate units between the Bayisi Formation and the Tereeken glacial interval have extremely positive $\delta^{13}C$ values up to +10.4‰ PDB but very negative $\delta^{18}O$ values (as low as –16‰ PDB). Such highly positive $\delta^{13}C$ values are characteristic of post-Sturtian but pre-Marinoan carbonates, such as the Etina Formation in the Adelaide Rift Complex [*Walter et al.*, 2000; *McKirdy et al.*, 2001], the middle Ombaatjie Formation in Namibia [*Kennedy et al.*, 1998; *Halverson et al.*, 2002; *Hoffman and Schrag*, 2002], the Keele Formation in NW Canada [*Narbonne et al.*, 1994; *Kaufman et al.*, 1997], and the lower Tsagan Oloom Formation in southwest Mongolia [*Brasier et al.*, 1996]. Neoproterozoic carbonate units characterized by similar magnitude of positive $\delta^{13}C$ excursion and interpreted of similar age also occur in Brazil [*Iyer et al.*, 1995], Scotland [*Brasier and Shields*, 2000], and western United States [*Smith et al.*, 1994]. The ~+10‰ $\delta^{13}C$ excursion in Quruqtagh is suggestive, although not compelling, evidence that the Tereeken and Hankalchough diamictites represent two post-Sturtian glacial deposits.

Second, a 10-m-thick cap carbonate sharply overlying the Tereeken diamictite shows sedimentary and geochemical similarities to Marinoan cap carbonates. The Tereeken cap consists of pinkish, macropeloidal dolomite and has a negative $\delta^{13}C$ profile, evolving from –4 ~ –5‰ near the base upward to more negative values. Declining $\delta^{13}C$ profile and macropeloidal dolomite are characteristic of Marinoan caps [*Kennedy et al.*, 1998; *James et al.*, 2001; *Hoffman and Schrag*, 2002], suggesting that the Tereeken is Marinoan and the Hankalchough, post-Marinoan.

Third, a strong positive $\delta^{13}C$ shift occurs in the Shuiquan Formation immediately below the Hankalchough diamictite (see also [*Xu et al.*, 2002]). This *positive* trend is in sharp contrast to the pronounced *negative* trend observed in carbonates immediately preceding the Marinoan glaciation [*Halverson et al.*, 2002; *Hoffman and Schrag*, 2002], indicating that the Hankalchough glaciation is probably not Marinoan in age.

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Fourth, *Gao et al.* [1980] reported vendotaenid fossils from the Shuiquan Formation. True vendotaenid fossils typically occur in post-Marinoan Neoproterozoic rocks, again suggesting that the overlying Hankalchough glaciation is younger than the Marinoan.

Fifth, the Hankalchough diamictite is overlain by a non-classic cap carbonate. Homogenous dolomicrite of the Hankalchough cap is characterized by extremely light and regionally variable $\delta^{13}C$ values (0 to –17‰) but normal $\delta^{18}O$ values (0 to –6‰). Part of the wide $\delta^{13}C$ range may be related to transgressive onlapping and spatial geochemical heterogeneity. Diagenetic alteration alone cannot satisfactorily explain the extremely light $\delta^{13}C$ values, given the normal $\delta^{18}O$ values. However, it is interesting to note that several post-Marinoan (and probably pre-Ediacaran) carbonate units in Australia (the Wonoka Formation; [*Calver*, 2000]), Oman (the Shuram Formation; [*Burns and Matter*, 1993; *Brasier et al.*, 2000]), and possibly Lesser Himalaya [*Jiang et al.*, 2002], are characterized by very negative $\delta^{13}C$ values.

Therefore, our preferred interpretation is that the Tereeken and Hankalchough are respectively Marinoan and post-Marinoan in age, regardless whether the Bayisi/Altungol diamictites are glaciogenic. It is also possible that the Hankalchough glaciation predates Ediacaran animals if we push the chemostratigraphic significance of the extremely negative $\delta^{13}C$ excursion immediately overlying the Hankalchough diamictite. Of course, an ultimate test of the proposed age for the Hankalchough diamictite critically depends on reliable radiometric ages of the Quruqtagh deposits.

2.2. Other Post-Marinoan Diamictites

Although controversial, evidence for post-Marinoan Neoproterozoic glaciation(s) (sometimes referred to as the younger Varanger glaciation) has also been reported from South Australia [*Di Bona*, 1991], NW Australia [*Grey and Corkeron*, 1998; *Corkeron and George*, 2001], NW Canada [*Kaufman et al.*, 1997], southern Namibia [*Saylor et al.*, 1998], Death Valley [*Corsetti and Kaufman*, 2003], and southern Norway [*Brasier et al.*, 2000; *Knoll*, 2000]. The Fersiga diamictite in western Africa is said to be Early Cambrian [*Bertrand-Sarfati et al.*, 1995], but the dated granite (556 +/– 12 Ma) in the Ahaggar inlier only provides an imprecise maximum age constraint for the Fersiga diamictite in the Taoudenni Basin.

The most unambiguously post-Marinoan diamictites are the Squantum [*Thompson and Bowring*, 2000], Gaskiers [*Bowring et al.*, 2003], and Fauquier diamictites [*Aleinikoff et al.*, 1995; *Kaufman and Hebert*, 2003] in eastern North America. The Squantum diamictite is constrained between 595.5 +/– 2 Ma and 570 Ma [*Thompson and Bowring*, 2000], and the Gaskiers glaciation occurred around 580 Ma [*Bowring et al.*, 2003]. Cap carbonates overlying the Fauquier diamictite are interlayered with basalts of 564 +/– 9 Ma [*Aleinikoff et al.*, 1995; *Kaufman and Hebert*, 2003]. These diamictites were likely deposited after the Marinoan glaciation that ended before 599 +/- 4 Ma [*Barfod et al.*, 2002].

So far there is no paleomagnetic evidence suggesting that any of these post-Marinoan diamictites were deposited in the tropical ocean. And it is unclear whether all post-Marinoan Neoproterozoic diamictites record a single, widespread Gaskiers glaciation. But chemostratigraphic and radiometric data allow us to conclude that at least three glaciations—the Sturtian, Marinoan, and Gaskiers in geochronological order—occurred in the Neoproterozoic, although the Gaskiers glaciation may have been much less extreme than the other two.

2.3. South China

In South China, the Nantuo diamictite underlies the fossil-rich Doushantuo and Dengying formations and overlies siltstone, shale, and rhodochrosite of the Datangpo Formation (Figure 2B). The Nantuo is believed by most to be Marinoan in age and this is supported by a Marinoan-like cap dolostone atop the Nantuo diamictite. The Nantuo cap dolostone is characterized by tepee-like structures, barite precipitates, sheet cracks, and a declining $\delta^{13}C$ profile—features known to occur in many Marinoan caps but not common in Sturtian caps.

Two recently available radiometric dates help to constrain the age of the Nantuo (and Marinoan) glaciation. Phosphorites of the Doushantuo Formation are dated from 599 +/– 4 Ma (Pb–Pb isochron; n=5) [*Barfod et al.*, 2002], and an ash bed from the Datangpo Formation is dated from 663 +/– 4 Ma (U–Pb zircon) [*Xiao et al.*, 2003]. Together, these dates suggest that the Nantuo glaciation began after 663 +/– 4 Ma and ended before 599 +/– 4 Ma. This is consistent with other age constraints for the Marinoan glaciation. Detrital zircons put a maximum depositional age of ca. 650 Ma for the Marinoan glaciation in southern Australia [*Ireland et al.*, 1998]. A maximum depositional age for the Laplandian (probably Marinoan) glaciation in southern Urals is provided by a U–Pb zircon age of 660 +/– 15 Ma [*Semikhatov*, 1991]. The new radiometric dates from South China not only support a Marinoan age for the Nantuo diamictite, but also make it difficult to equate the Nantuo with either the Gaskiers [*Bowring et al.*, 2003] or the Sturtian glaciations [*Brasier et al.*, 2000].

2.4. Correlation

Since the goal of this paper is to evaluate the evolutionary patterns in the context of Neoproterozoic glaciations, the following discussion on stratigraphic correlation will be based on physical stratigraphic, chemostratigraphic, and radiometric

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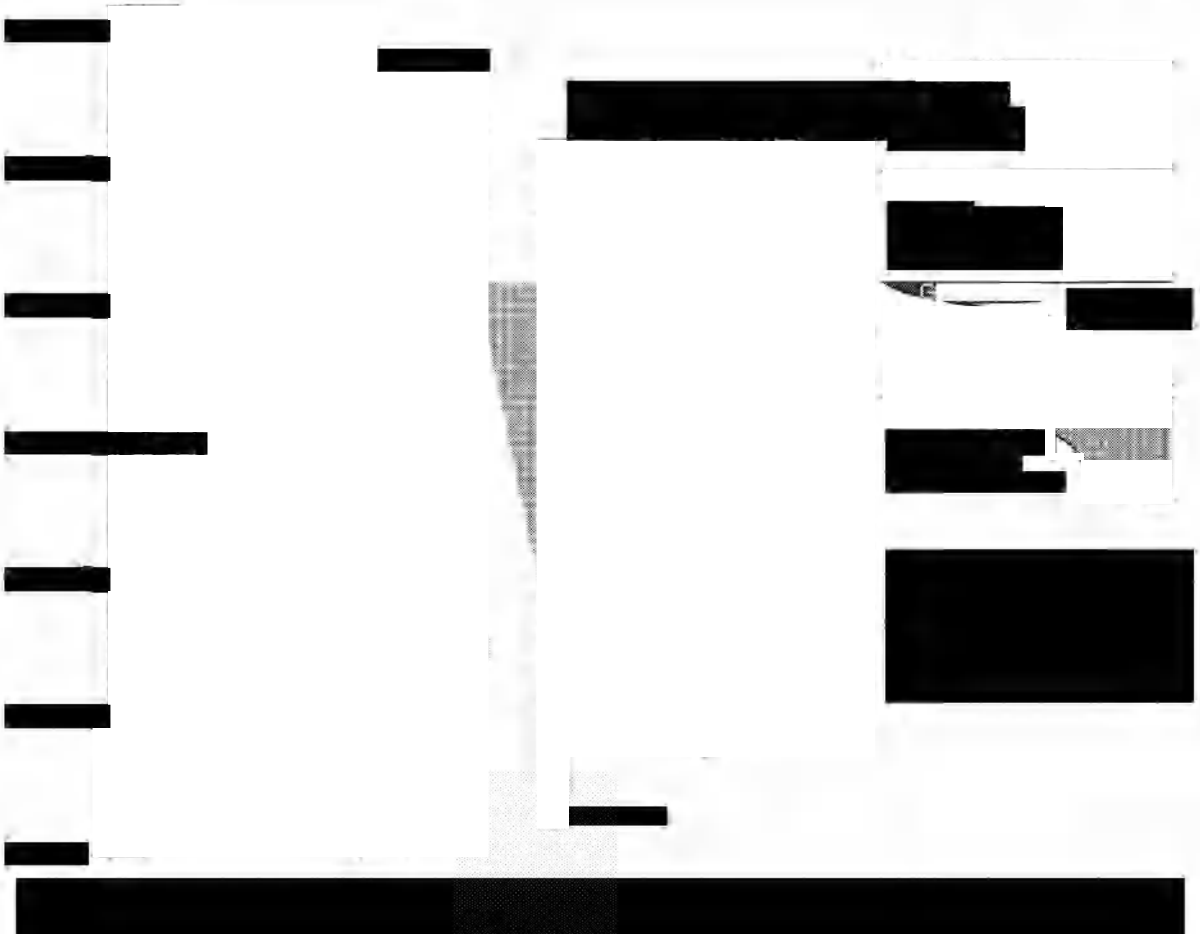

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is equivalent to the Gaskiers [*Brasier et al.*, 2000; *Brasier and Shields*, 2000; *Knoll*, 2000]. Their argument is based on the occurrence of large (>100 μm in diameter) acanthomorphic acritarchs (Doushantuo–Pertatataka microflora, or DPM; [*Zhou et al.*, 2001]). In both South China and the Amadeus Basin, Australia, DPM occurs in rocks deposited after the Marinoan (or Nantuo) glaciation but before the radiation of complex Ediacaran organisms [*Zang and Walter*, 1992; *Zhang et al.*, 1998a; *Knoll and Xiao*, 1999]. Several elements of the DPM also occur in the Biskopås Conglomerate below the Moelv diamictite [*Vidal*, 1990]. This led *Zhou et al.* [2002] to conclude that the Doushantuo was deposited after the Marinoan but before the Moelv glaciation.

If we ignore the acritarch biostratigraphic data to avoid circularity, circumstantial chemostratigraphic evidence is consistent with the proposition that the Doushantuo probably predates the Gaskiers. Carbonates in the uppermost Doushantuo Formation are characterized by a negative $\delta^{13}C$ excursion [*Yang et al.*, 1999; *Wang et al.*, 2002a; *Wang et al.*, 2002b], possibly equivalent to negative $\delta 13^{C}$ excursions in the Gaskiers cap carbonate [*Myrow and Kaufman*, 1999; *Bowring et al.*, 2003] and other post-Marinoan but pre-Ediacaran successions discussed above. In some sections, the uppermost Doushantuo beds are characterized by $\delta^{13}C$ values as low as –8‰ but normal $\delta^{18}O$ values around 0‰ to –2‰ [*Wang et al.*, 2002a], reminiscent of the cap carbonate overlying the Hankalchough diamictite that is interpreted as post-Marinoan in age (see above).

If the Gaskiers glaciation occurs near the Doushantuo–Dengying boundary, then the Doushantuo Formation represents a window between two Neoproterozoic glaciations, while the overlying Dengying Formation and other classic Ediacaran successions record post-Gaskiers evolution (Figure 2).

3. NEOPROTEROZOIC FOSSIL RECORD AND GLACIATIONS

It has been proposed that the beginning and end of the Cryogenian Period be defined by, respectively, the initiation of the Sturtian and the conclusion of the Marinoan glaciation [*Knoll*, 2000]. This may be justifiable because the Marinoan diamictites are the most widespread and covered by a well-developed cap carbonate. A precise definition of the Cryogenian–terminal Proterozoic boundary is pending upon the ratification of a GSSP section. For the sake of simplicity and convenience, however, in the following discussion I use the term "Neoproterozoic glacial interval" (NGI; Figure 2A) to encompass all three Neoproterozoic glaciations: Sturtian, Marinoan, and Gaskiers; this would be a geological interval about 140 myr, longer than any Phanerozoic periods.

3.1. Stromatolites

Cyanobacteria and stromatolites clearly survived all Neoproterozoic glaciations. The survival of photoautotrophic groups, particularly the presence of stromatolites in carbonates interbedded with diamictites [*Corsetti et al.*, 2003], places a limit on the nature of NGI glaciations. The survival of high-ranking taxonomic groups, however, does not invalidate biotic perturbation or extinction events that occurred at lower taxonomic level.

Indeed, the abundance and morphological "diversity" of stromatolites began to decline in late Neoproterozoic, before the NGI [*Awramik*, 1971; *Walter and Heys*, 1985; *Awramik*, 1990; *Awramik*, 1992; *Semikhatov and Raaben*, 1994; *Semikhatov and Raaben*, 1996; *Awramik and Sprinkle*, 1999; *Grotzinger and Knoll*, 1999]. This decline has been traditionally related to the appearance of grazing and burrowing animals [*Awramik*, 1971; *Walter and Heys*, 1985], but significant grazing and burrowing did not occur until after the NGI [*Droser et al.*, 2002]. In addition, Phanerozoic stromatolites commonly coexisted with grazing and burrowing animals [*Pratt*, 1982; *Farmer*, 1992]. Grotzinger [*Grotzinger*, 1990; *Grotzinger and Knoll*, 1999] proposed that the stromatolite decline was caused by decreasing carbonate saturation of seawater (and hence probability of stromatolite preservation) throughout the Proterozoic. An additional, and more obvious, culprit of the stromatolite decline is Neoproterozoic glaciations, because the most significant decline in stromatolite abundance and "diversity" occurred during the NGI. Glacioeustatic sea level drop could greatly reduce the carbonate platform environments available to phototrophic microbial mats. Glaciations would also initiate other environmental changes affecting, directly or indirectly, microbial habitats, abundance, or diversity. The stratigraphic resolution is still insufficient for us to determine whether the broad declining trend starting before the NGI is a mega-Signor–Lipps artifact [*Signor and Lipps*, 1982] and whether stromatolites briefly recovered between glaciations.

3.2. Acritarchs

At the broad scale, acritarchs (traditionally interpreted as resting cysts of photoautotrophic eukaryotes but likely including heterogeneous groups) also suffered significant diversity loss between the Sturtian and Marinoan glaciations [*Knoll*, 1994; *Vidal and Moczydlowska-Vidal*, 1997]. The global diversity pattern is supported by assemblage-level data; the α–diversity of all described Cryogenian assemblages is extremely low [*Knoll et al.*, 1981; *Vidal*, 1981; *Vidal and Nystuen*, 1990; *Yin*, 1990], suggesting that the Cryogenian diversity decline is real at both local and global scales.

A taxonomically unique acritarchs assemblage, characterized by large acanthomorphs, diversified shortly after the Marinoan glaciation. In South China, this acritarchs assemblage occurs in the Doushantuo Formation and includes such forms as *Asterocapsoides sinensis*, *Bacatisphaera baokangensis, Castaneasphaera speciosa, Dicrospinasphaera zhangii*, *Distosphaera speciosa*, *Echinosphaeridium maximum*, *Eotylotopalla delicata*, *Eo. dactylos*, *Ericiasphaera magna*, *Er. rigida*, *Er. sparsa*, *Mastosphaera changyangensis*, *Meghystricosphaeridium chadianensis*, *Me. magnificum*, *Me. reticulatum*, *Papillomembrana compta*, *Pustulisphaera membranacea*, *Sinosphaera rupina*, and *Tianzhushania spinosa* [*Yuan and Hofmann*, 1998; *Zhang et al.*, 1998a; *Yin*, 1999]. Elements of the Doushantuo acritarch assemblage have also been reported in the Pertatataka Formation, Amadeus Basin, central Australia [*Zang and Walter*, 1992], the Scotia Group, Svalbard [*Knoll*, 1992b], the lower Krol Group (Krol A), Less Himalaya [*Tiwari and Knoll*, 1994], and lower Vendian rocks in eastern Siberia [*Moczydlowska et al.*, 1993]. All these units locally overlie glacial deposits interpreted as Marinoan in age.

In the Yangtze Gorges area, large acanthomorphic acritarchs first appear within meters above the Nantuo cap carbonate [*Yin et al.*, 2001]. Accepting the Pb-Pb date from the upper Doushantuo Formation [*Barfod et al.*, 2002], Doushantuo acritarchs first appeared before 599 +/− 4 Ma. In South Australia, however, similar acritarchs radiated after the ca. 580 Ma Acraman impact ejecta layer [*Grey et al.*, 2003]. The apparent delay in South Australia may be related to unsuitable taphonomic or paleoenvironmental conditions.

Available evidence also suggests that the Doushantuo acritarch assemblage disappeared around the Gaskiers glaciation. Many Doushantuo acritarchs are preserved in both cherts and phosphorites [*Xiao*, in press]. The overlying Dengying Formation contains beautifully phosphatized fossils [*Ding et al.*, 1992], but no Doushantuo-type acritarchs. Basal Cambrian acritarchs [*Moczydlowska*, 1991] are entirely different from those preserved in the Doushantuo Formation. Accepting that the Gaskiers glaciation occurred near the Doushantuo–Dengying boundary, the simplest interpretation is that most Doushantuo-type acritarchs are restricted between the Marinoan and Gaskiers glaciations.

Acritarchs from the Biskopås Conglomerate in southern Norway [*Vidal*, 1990] share similarities to those from the Doushantuo Formation, but the Biskopås Conglomerate is stratigraphically below the Moelv diamictite. This leads to one of the following two conclusions: either the Moelv represents a Marinoan diamictite and several genera (e.g. *Papillomembrana* and *Ericiasphaera*) of the Doushantuo assemblage sailed through the Marinoan glaciation, or the Moelv is equivalent to the Gaskiers and the entire Doushantuo assemblage is restricted between the Marinoan and Gaskiers glaciations. Because of the uncertain age of the Moelv diamictite, it is difficult to distinguish these two alternatives. However, that the Pertatataka assemblage may be bracketed by the Marinoan and Egan (?=Gaskiers) glaciations [*Grey and Corkeron*, 1998] lends support to the latter alternative.

More systematic paleontological sampling of the Doushantuo and other units is required to refine the picture and to distinguish the signals of environmental heterogeneity, preservational bias, and evolutionary trend in the observed fossil record. If it can be confirmed that the Doushantuo acritarch assemblage is restricted between the Marinoan and Gaskiers glaciations, it raises the question whether the appearance and disappearance of this assemblage were related to glaciations.

3.3. Algae

Various eukaryotic clades, including both photoautotrophic and heterotrophic protists such as red algae, green algae, stramenopiles, alveolates, and both lobose and filose amoebae, also diverged before the NGI [*Knoll*, 1992a; *Butterfield et al.*, 1994; *Butterfield*, 2000; *Porter and Knoll*, 2000]. Obviously, these high-ranking groups also survived all NGI glaciations.

The history of algal evolution broadly parallels to that of acritarchs. Multicellular algae are poorly known between the Sturtian and Marinoan, but are abundant and diverse in Doushantuo shales, phosphorites, and cherts [*Zhang*, 1989; *Zhang and Yuan*, 1992; *Zhang et al.*, 1998a; *Xiao et al.*, 1998; 2002; in press b; *Xiao*, in press]. Cellular preservation in Doushantuo phosphorites allows us to understand the possible phylogenetic relationships of phosphatized Doushantuo algae; most can be interpreted as stem group florideophyte red algae or stem group coralline algae [*Xiao et al.*, in press b]. It is possible that these stem groups went extinct at the same time when Doushantuo-type acritarchs disappeared. But the conclusion is less secure in this case because, unlike acritarchs, post-Doushantuo algal fossils are rare or poorly preserved for meaningful comparison.

3.4. Animals Before or During the NGI

3.4.1. Molecular clock studies. Molecular clock studies indicate that animals, plants, and fungi may have diverged from each other in the Mesoproterozoic [*Doolittle et al.*, 1996; *Wang et al.*, 1999; *Heckman et al.*, 2001; *Nei et al.*, 2001; *Hedges*, 2002]. Similar studies also suggest that the deepest (protostomes–deuterostomes) divergence within the crown-group bilaterian animals probably occurred either before or within the NGI, although the range and uncertainty of these estimates are large [*Runnegar*, 1982; *Doolittle et al.*, 1996;

Wray et al., 1996; *Ayala et al.*, 1998; *Bromham et al.*, 1998; *Gu*, 1998; *Lee*, 1999; *Lynch*, 1999; *Wang et al.*, 1999; *Smith and Peterson*, 2002]. If correct, they indicate that minimally one lineage each of the protostome, deuterostome, and non-bilaterian clades survived one or more glaciations. While the survival of ancestral animals puts limits on the extreme nature of Neoproterozoic glaciations, the molecular clock studies themselves say nothing about the physiological and ecological selectivity of the survivors. Nor do they provide any insights into the morphology, diversity, and phylogeny of early diverging but subsequently extinct stem lineages. Hence, molecular clock studies alone are not sufficient to understand the dynamic relationship between environmental perturbations and biological turnovers in the NGI. We will have to depend on the fossil record, however sketchy or biased it is, to determine the morphology (e.g. body size and related physiological constraints) and ecology (e.g. shallow-water shelf *vs.* deep-water slope environments) of ancestral animals. The currently available fossil record does not allow us to answer all these questions, but some general patterns can be learned.

3.4.2. Pre-NGI animals. Reports of millimeter-wide bedding plane traces in the Paleo- and Mesoproterozoic rocks [*Seilacher et al.*, 1998; *Rasmussen et al.*, 2002a; *Rasmussen et al.*, 2002b; *Ray et al.*, 2002] are attractive, but interpretations of these markings as animal traces remain controversial. The often-cited pre-NGI worm-like fossil, *Protoarenicola*, from North China [*Sun et al.*, 1986] has been shown to be a holdfast-bearing benthic alga [*Qian et al.*, 2000]. At the present, there do not appear to be any unequivocal body or trace fossils of pre-NGI animals.

3.4.3. Discoidal fossils. There are several reports of discoidal or circular fossils from rocks underlying Neoproterozoic diamictites. Discoidal fossils from the Twitya Formation in the Mackenzie Mountains, northwestern Canada, are bracketed by the Rapitan (=Sturtian) and Ice Brook (=Marinoan) glaciations [*Hofmann et al.*, 1990]. Simple discoidal fossils from the Cheikhia Group in the Taoudenni Basin, Algeria, predate the Fersiga diamictite [*Bertrand-Sarfati et al.*, 1995], whose age is poorly constrained but possibly equivalent to the Gaskiers glaciation. Assemblages dominated by discoidal or circular fossils also occur in other Neoproterozoic (e.g. [*Narbonne and Hofmann*, 1987; *Farmer et al.*, 1992; *Zhang and Shu*, 2002]) and possibly Cambrian deposits [*Crimes et al.*, 1995]. The biological interpretation of such simple forms is challenging. Some have been interpreted as cnidarian animals [*Glaessner*, 1984; *Hofmann et al.*, 1990; *Bertrand-Sarfati et al.*, 1995], coenocytic algae [*Xiao et al.*, 2002; *Knoll and Xiao*, 2003], holdfasts of frondose Ediacaran organisms [*Gehling et al.*, 2000], or scratch marks [*Jensen et al.*, 2002]. Each interpretation makes its own predictions: coenocytic algae lived (but were not necessarily preserved) in the photic zone, and frondose Ediacaran organisms must occur in the same geological interval as their holdfasts.

If the Twitya discs are correctly interpreted as stem-group cnidarians [*Hofmann et al.*, 1990], they imply that at least stem-group sponges and possibly stem-group bilaterians, depending on the exact phylogenetic relationships between cnidarians and bilaterians [*Collins*, 1998; *Kim et al.*, 1999; *Medina et al.*, 2001], existed before the Marinoan glaciation.

3.4.4. Doushantuo animals. The Doushantuo Formation contains multiple taphonomic windows of exceptional preservational quality, in its cherts, shales, and phosphorites. Doushantuo chert nodules, deposited in subtidal environments in the Yangtze Gorges area and elsewhere in South China, preserve abundant cyanobacteria, acanthomorphic acritarchs, as well as multicellular algae [*Zhang et al.*, 1998a; *Xiao*, in press]. Rare triaxonal spicules preserved in Doushantuo chert nodules have been interpreted as hexactinellid spicules ([*Tang et al.*, 1978; *Ding et al.*, 1985; *Zhao et al.*, 1988]; but see [*Steiner et al.*, 1993]). No other animals have been reported from the chert nodules.

Subtidal (below wave-base) shales in the uppermost Doushantuo Formation in the Yangtze Gorges area preserve carbonaceous compressions, many of which can be unambiguously interpreted as macroscopic (centimeter- to decimeter-sized) algae [*Xiao et al.*, 2002]. The preservational style and quality of these algae is comparable to that of Burgess Shale and Chengjiang algae [*Briggs et al.*, 1994; *Butterfield*, 1995; *Chen et al.*, 1996; *Butterfield*, 2003]. A taphonomic test can be therefore carried out: if there existed in subtidal environments macroscopic animals with reasonably recalcitrant structures such as extracellular cuticles, they should be preserved in Doushantuo shales. A couple of Doushantuo fossils resemble and may be equivocally interpreted as sponges or cnidarians. But no macrobilaterians have been documented in Doushantuo shales. Nor are there any macroscopic resting traces or crawling tracks on Doushantuo bedding planes. This leads to one of the following hypotheses: 1) macrobilaterians (and their pattern formation mechanisms) had not evolved; 2) macrobilaterians with extracellular cuticles had not evolved; 3) macrobilaterians with extracellular cuticles had not invaded into subtidal platform environments. This leaves several possibilities of NGI bilaterians: microbilaterians [*Davidson et al.*, 1995], bilaterians without any recalcitrant structures, or bilaterians living in offshore pelagic environments [*Runnegar*, 2000]. Expanding our search into deeper paleoenvironments and into taphonomic windows that can preserve microscopic and more labile organic structures will provide key tests of these possibilities.

Doushantuo phosphorites, deposited in shallow subtidal (above wavebase) environments at Weng'an and several other localities in South China, represent a NGI taphonomic window that has the potential to preserve labile micrometazoans. At Weng'an, phosphatic horizons occur in both the lower and upper Doushantuo Formation, separated by a subaerial exposure surface [*Xiao and Knoll*, 2000a]. Rare earth element patterns in the lower Doushantuo phosphorite are consistent with phosphatization in an anoxic sedimentary/diagenetic environment [*Chen et al.*, 2003]. The absence of not only algal and animal fossils but also cyanobacteria and acritarchs in the lower phosphorite horizon is probably related to the anoxic preservational and/or paleoenvironmental conditions.

The best-preserved and most diverse fossils come from the upper Doushantuo Formation. In addition to filamentous and coccoidal cyanobacteria, acanthomorphic acritarchs, and multicellular algae, sub-millimeter-sized animal embryos at successive cleavage stages also occur in the upper phosphorite horizon [*Xiao et al.*, 1998; *Xiao and Knoll*, 2000b; Xiao, 2002]. It is difficult to determine which animal clade(s) these fossil embryos belong to. But they display a chimeric combination of features that individually occur in crown group sponges, cnidarians, and bilaterians, suggesting that these embryos may belong to stem groups at the animal, eumetazoan, or bilaterian levels [*Xiao and Knoll*, 2000b]. Phosphorites of the upper Doushantuo Formation also yield sub-millimeter-sized, tabulated tubes [*Xue et al.*, 1992; *Li et al.*, 1997]. These tubular fossils can be interpreted as either stem-group eumetazoans or stem-group cnidarians [*Xiao et al.*, 2000] or crown group anthozoans [*Chen et al.*, 2002]. Finally, microscopic sponge body fossils and putative gastrulas have been reported from the upper Doushantuo Formation [*Li et al.*, 1998; *Chen et al.*, 2000; 2002], although the interpretation of such forms are highly debatable [*Zhang et al.*, 1998b; *Xiao et al.*, 2000].

Despite the interpretative uncertainties surrounding the Doushantuo fossils, the important messages from Doushantuo phosphorites are 1) animals evolved before the Gaskiers glaciation; 2) none of them can be unambiguously interpreted as macroscopic bilaterians; and 3) many of them can be regarded as stem groups at deep phylogenetic levels.

3.5. Post-NGI Radiation

3.5.1. Complex Ediacaran fossils. Post-NGI evolution is characterized by the arrival of complex Ediacaran fossils. Some Ediacaran fossils have been interpreted as lichens, possible fungi, or extinct groups phylogenetically unrelated to animals [*McMenamin*, 1986; *Seilacher*, 1989; *Seilacher*, 1992; *Zhuravlev*, 1993; *Retallack*, 1994; *Peterson et al.*, 2003]. The Ediacaran biotas as a consortium, however, represent merely a sampling of the Neoproterozoic biodiversity (Figure 2B; [*Runnegar*, 1995; *Waggoner*, 2003]) that includes, among others, animals such as sponges [*Gehling and Rigby*, 1996], stem-group eumetazoans [*Buss and Seilacher*, 1994], cnidarians or cnidarian-grade animals [*Glaessner*, 1984; *Conway Morris*, 1993b], and bilaterians [*Fedonkin and Waggoner*, 1997].

Among the best-known Ediacaran fossils, the Newfoundland assemblage is probably the oldest [*Benus*, 1988; *Gehling and Narbonne*, 2002; *Bowring et al.*, 2003; *Narbonne and Gehling*, 2003]. The White Sea and South Australia assemblages are younger [*Martin et al.*, 2000], and the Namibia assemblage is the youngest in the Neoproterozoic [*Grotzinger et al.*, 1995]. A few Ediacaran fossils may extend into the Cambrian [*Conway Morris*, 1993a; *Jensen et al.*, 1998; *Hagadorn et al.*, 2000]. Quantitative analysis also delineates the Newfoundland, White Sea–South Australia, and Namibia assemblages [*Waggoner*, 2003].

The temporal succession of Ediacaran assemblages is accompanied by paleoenvironmental shift and evolutionary progress. The Newfoundland assemblage occurs in a deep-water slope environment [*Myrow*, 1995], while the younger assemblages in White Sea, South Australia, and Namibia are from shallow-water (within photic zone) platform environments. There do not appear to be any unambiguous macrobilaterians in the Newfoundland assemblage [*Clapham and Narbonne*, 2002; Guy Narbonne, personal communication, 2003]. The White Sea and Namibia assemblages, on the other hand, include body and trace fossils of macrobilaterians, and the latter also includes partially biomineralized animals (e.g. *Cloudina*, *Namapoikia*, *Namacalathus* in Namibia) [*Fedonkin*, 1994; *Grotzinger et al.*, 1995; 2000; *Jenkins*, 1995; *Fedonkin and Waggoner*, 1997; *Jensen et al.*, 2000; *Droser et al.*, 2002; *Gehling*, 2002; *Wood et al.*, 2002]. The difference in macrobilaterian diversity unlikely represents poorer preservation in the Newfoundland assemblage, considering its *in-situ* preservation beneath volcanic ash covering [*Clapham and Narbonne*, 2002; *Narbonne and Gehling*, 2003]. Rather, the diversity difference probably results from evolutionary (temporal) change and/or ecological (spatial) heterogeneity.

Taken at face value, the temporal succession of Ediacaran assemblages indicates that post-NGI radiation of macroscopic, complex Ediacaran organisms began in deep-water slope environments and later expanded into shallow-water shelf environments where macrobilaterians first evolved. This hypothesis predicts that the oldest shallow-water assemblage post-dates the oldest deep-water assemblage, although it does not preclude Ediacaran organisms persisting in deep-water environments. Key tests of this hypothesis include more precise dating of additional complex Ediacaran assemblages from both shallow- and deep-water environments (e.g., shallow-water: South Australia, South China, Siberia; deep-water: Mackenzie Mountains, North Carolina, Charnwood Forest; [*Ford*, 1958; *Sun*, 1986; *Fedonkin*, 1990; *Narbonne and Aitken*, 1990; *Narbonne*, 1994; *Gehling*, 2000; *MacNaughton et al.*, 2000; *Compston et al.*, 2002]).

Available paleontological evidence does not allow us to tell whether ancestors of complex Ediacaran organisms survived the Gaskiers glaciation in deep-sea refugia, although the moderate phylogenetic diversity, ecological complexity, and morphological disparity of the Newfoundland assemblage [*Clapham and Narbonne*, 2002; *Narbonne and Gehling*, 2003] do suggest that there may have been some Ediacaran forerunners in pre-Gaskiers oceans.

3.5.2. Bilaterian animals. One of the important tie points in the Proterozoic animal fossil record is the presence of millimeter- to centimeter-sized body and trace fossils of macrobilaterians in younger, shallow-water Ediacaran assemblages in White Sea, Australia, and Namibia [*Fedonkin*, 1994; *Grotzinger et al.*, 1995; *Fedonkin and Waggoner*, 1997; *Jensen et al.*, 2000; *Droser et al.*, 2002; *Gehling*, 2002], suggesting that bilaterian animals diverged no later than 555 Ma [*Martin et al.*, 2000].

3.5.3. Animal biomineralization. Partially biomineralized tubular fossils have been known in the youngest Ediacaran assemblage—the shallow-water Namibia assemblage [*Grant*, 1990; *Grotzinger et al.*, 2000; *Waggoner*, 2003]. Similar fossils also occur in the upper Miette Group in British Columbia [*Hofmann and Mountjoy*, 2001] and the middle Dengying Formation in South China [*Chen et al.*, 1981; *Conway Morris et al.*, 1990; *Ding et al.*, 1992; *Bengtson and Zhao*, 1992; *Chen and Sun*, 2001]. The middle Dengying Formation also yields a rare frondose Ediacaran fossil identified as *Paracharnia dengyingensis* [*Sun*, 1986]. It would be interesting to learn whether the upper Miette Group and middle Dengying Formation have depositional ages similar to that of the Kuibis and Schwarzrand subgroups where *Cloudina* and *Namacalathus* occur in Namibia.

To summarize, the post-Gaskiers fossil record suggests that complex Ediacaran organisms, at least some of which were animals, emerged from deep-water slope environments shortly after the Gaskiers glaciation. Although animals evolved during the NGI, it is not until the later stage of Ediacaran diversification when macroscopic bilaterian animals evolved and colonized the shallow-water shelf environments. And animal biomineralization evolved still later—very close to the Precambrian–Cambrian boundary (Figure 2).

4. DISCUSSION AND CONCLUSIONS

The above analysis suggests that the marine communities did respond to climate changes associated with Neoproterozoic glaciations. The Cryogenian decline in stromatolites and acritarchs may have been causally related to the Sturtian and Marinoan glaciations. The brief diversification and eventual disappearance of Doushantuo-type acritarchs near the Doushantuo–Dengying boundary points to a possible extinct event caused by the Gaskiers glaciation. The prevalence of many stem group red algae and animals in the Doushantuo Formation is also consistent with a Gaskiers extinction event; stochastic and massive trimming of a phylogenetic tree is expected leave many twigs as stem groups.

On the other hand, the intensity of these possible extinction events is less than what would be expected from hard snowball Earth events [*Hoffman et al.*, 1998]. At least some members of several photoautotrophic groups (e.g., cyanobacteria and algae) survived all Neoproterozoic glaciations. Some animals must have survived the Gaskiers glaciation if post-Gaskiers animals did not evolve *de novo*.

Perhaps more can be learned by studying the paleoenvironmental distribution of Neoproterozoic biodiversity before and after each glaciation. Did organisms lived in the photic zone suffer more during Neoproterozoic glaciations? Did deep-sea environments or other non-glaciated areas serve as effective refugia during the glaciations? Did post-glacial radiation indeed begin in deep-sea refugia? Answers to these questions would provide paleobiological constraints on the nature of Neoproterozoic glaciations.

To answer these questions and further test the ideas expressed in this paper, future work should be aimed 1) to sharpen the geochronological resolution of Neoproterozoic successions; 2) to improve the stratigraphic and phylogenetic resolution of Neoproterozoic fossils; 3) to better understand the environmental distribution and taphonomic biases embedded in the Neoproterozoic fossil record. To achieve these requires more paleontological, stratigraphic, paleoenvironmental, and taphonomic analyses of carefully measured successions. The current Neoproterozoic fossil record is mostly based on sporadic sampling of cherts, phosphorites, or carbonaceous shales, rather than bed-by-bed sampling as practiced in the Phanerozoic. There are of course taphonomic issues in the Neoproterozoic because virtually all Neoproterozoic organisms are non-biomineralized and their preservation requires unusual taphonomic conditions. But there are Neoproterozoic sections with abundant shales or chert nodules, allowing high-resolution paleontological sampling. Such data will allow us to obtain a high-resolution picture of the Neoproterozoic diversity dynamics at local, regional, and global levels.

Acknowledgments. I would like to thank Gregory Jenkins for inviting me to contribute. I would also like to thank Huiming Bao, Frank Corsetti, Whitey Hagadorn, Paul F. Hoffman, Ganqing Jiang, Alan. J. Kaufman, Andrew H. Knoll, Guy M. Narbonne, Zhanxiong Peng, Curt Pueschel, Bob Tucker, Leiming Yin, Xunlai Yuan, and Chuanming Zhou for sharing data and ideas. My research on the Neoproterozoic geobiology is supported by National Science Foundation and National Geographic Society.

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Climate, Paleoecology and Abrupt Change During the Late Proterozoic: A Consideration of Causes and Effects

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This chapter examines the influence of the biosphere on the initiation, and termination of, the glaciations of the late Proterozoic. Recent considerations suggest that the biosphere controlled the timing of the onset of glaciation and also controlled the timing of the end of glaciation. Massive carbonate accumulation and giant stromatolites of the Late Proterozoic, combined with major blooms of phytoplankton, led to significant drops in the carbon dioxide content of the atmosphere, and forced climate from greenhouse to icehouse conditions. Cryoconites and hyperscums, each with a distinctively adapted cryophilic microbiota, developed during the Proterozoic ice ages and may have been a factor in melting the ice. The Proterozoic Tindir Group, Alaska provides evidence for such a cryophilic microbiota. Only by invoking the activity of such organisms can we explain the rapidity of deglaciation. A propensity to accumulate massive carbonates was present before the glaciation as well as after the deposition of the cap carbonates. Substrate disturbance by burrowing metazoa after the ice ages disrupted the microbial mat component of Proterozoic carbonate sequestration. Stromatolites after the glaciation tend to have porous, clotted and thrombolitic textures instead of evenly laminated textures and would therefore be less effective at retaining carbon dioxide (as carbonate and organic matter) and keeping it out of marine circulation. Newly emergent, burrowing metazoa of the Late Proterozoic eventually halted the development of ice-age inducing conditions, and may have prevented even worse glaciations by releasing hydrocarbons sequestered in seafloor sediment.

1. INTRODUCTION

Ever since Peter Dobson's interpretation [*Dobson,* 1826; *McMenamin,* 2001a] of boulders in the Connecticut Valley as glacial erratics, Ignace Venetz's exposition in 1833 of the classic theory of glaciation [*Hallam,* 1992], and Louis Agassiz's 1837 presidential address to the Swiss Society of Natural Sciences of Neuchâtel promoting the concept of *die Eiszeit* [*Corozzi,* 1967], ice ages have become a widely accepted fact of Earth history. The severity of some of these glacial intervals has been less well known until more recently [*Walker,* 2003]. With the development of white earth or snowball earth theory, it has become clear that particular intervals during pre-Phanerozoic Earth history were marked by episodes of severe glaciation.

Much of this volume has been devoted to assessing the severity and extent of the late Proterozoic glacial events (LPGES). Although certain concepts, such as the possibility of extensive sea ice at the equator during LPGES may be difficult to test, it now seems clear that continental-scale glaciers occurred on land at the equator near sea level during these glaciations. Understandable reluctance to accept the low-latitude paleomagnetic results [*Cloud,* 1988] has given

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way to widespread acceptance of the fact of major glaciation at low latitude.

Such a phenomenon would be remarkable enough by itself, but to this must now be added evidence for breathtakingly sudden climate change from extreme glaciation (as recorded by the LPGES glacial debris) to presumably warm climate (as recorded by the cap carbonates deposited immediately above the glacial tills). In order to interpret the influence of these extraordinary events on the history of the biosphere, and the influence of the biosphere on these events, it is best to begin by describing what is known of the Earth's biota and its paleoecology before the onset of LPGES.

2. PROTEROZOIC BIOTA

At 850–800 my, Earth was richly populated with bacteria and eukaryotic microbes and sparsely populated with larger eukaryotic organisms. The microbes of the time took advantage of broad expanses of continental shelf to form extensive microbial mats. These mats were subsequently expressed in the rock record as organo-sedimentary structures called stromatolites, and as unusual primary sedimentary structures in fine-grained siliciclastic rocks. Stromatolites of the time were abundant, well-developed [*Vanyo and Awramik,* 1985], and capable of reaching enormous size in the late Proterozoic. Some stromatolites in eastern California and Canada attained the sizes of hills and small mountains [*Cloud et al.* 1974].

The eukaryotic grade of organization has a history extending perhaps as far back as two billion years, but the interpretation of megascopic fossils of this age (such as *Grypania)* has been controversial, with some researchers contending that the fossils are large bacteria or clustered bacterial colonies. Acritarchs presumed to have been formed by eukaryotes appear by about 1.8 billion years ago, but the eukaryote fossil record remains comparatively sparse (primarily acritarchs and macroalgae such as *Chuaria* and related forms) until approximately a billion years ago. At this time there appears to be a radiation of eukaryotes, and forms such as bangiopyte algae [*Butterfield,* 2000] and cysts belonging to presumed heterotrophic protists [*Porter and Knoll,* 2000] appear in the fossil record. The trigger or triggers for this burst of eukaryotic radiation are not well understood, but in the same way that the evolution of whales may be linked to the closure of Tethys and an exceptionally fertile, short-lived seaway that formed between India and Asia just before the Himalayan orogeny [*Gingerich et al.,* 1983], diversification of early eukaryotes may have been favored by evolution in narrow, nutrient-rich seaways formed by oceanic closure during the amalgamation of Rodinia.

3. CONTINENTAL POSITIONS AND GLACIATION

As what Cloud [1988, p. 298] called the "long Umberatanan winter" descended on the planet, beginning about 750 my, the biosphere was thrust into an extended episode of global freeze. The cause of the glaciation is contentious, although there is a continuing school of thought that invokes continental position to explain the ice ages. In its first iteration, the continental position hypothesis emphasized the possibility of elevated terrains near the equator. In wrestling with the implications of low latitude glaciation during the LPGES, it was noted by some [*McMenamin and McMenamin,* 1990] that glaciers form today at the equator in the 5200 m high Ruwenzori Mountains of Ethiopia. The elevation of these mountains is a result of the crustal buoyancy associated with the thermal effects of East African rifting. Preston Cloud conjectured [1988, p. 304]: "Could a clustering of sufficiently elevated continents at low paleolatitudes account for meteorological conditions that would lead to extensive equatorial and low-latitude glaciation?" Alternately, the continents themselves might have moved into polar regions. McMenamin and McMenamin [1990, p. 104] noted two possible causes of extensive glaciation: "if parts of Rodinia were at high latitude or if global climate were severe."

In the second iteration of the continental position hypothesis as a cause of LPGES, Kirschvink [1992] and subsequently Hoffman and Schrag [2002, p. 148] inferred that "a preponderance of continents in middle to low latitudes created conditions favorable for snowball events." This concept of the disposition of the continents is in accord with the best current evidence for continental positions in the Late Proterozoic; in other words, continents do indeed appear to have been at middle to low latitudes rather than at high latitudes [*Donnadieu et al.*, 2003]. This, however, brings us to a curious juncture in the progress of scientific thought. At first an explanation for the glaciation was sought in the possibility of continents being either topographically elevated or displaced to high latitudes. Failing this, an explanation is now sought in the likelihood of continents occurring at middle to low latitudes, a remarkably counterintuitive explanation as these regions are considerably warmer than the poles! Poulsen et al. [2002], using a fully coupled ocean-atmosphere general circulation model (FOAM), were able to show that concentrations of continents in low latitudes actually *did* lower equatorial (tropical) temperatures. In none of their three model simulations (each with different continental dispositions), however, were Poulsen et al [2002] able to generate fully white earth conditions.

One could fall back on what Cloud [1988, p. 303] refers to as John Crowell's Eclectic Hypothesis, the concept that many different types of processes interact to cause the glaciations [*Crowell,* 1999]. Hoffman and Schrag [2002, p. 148] allude to a version of this Eclectic Hypothesis: "Perhaps each event was triggered differently." I find this approach scientifically unsatisfying—it merely appeals to a diversity of causes rather than encouraging a search for necessary and sufficient causes. When considering such events as the worst glaciations on record and, say, the worst known mass extinction, appeals to many different causes [e. g., *Erwin,* 1993] may be politically safe (i. e., no one's favorite hypothesis gets left out) but scientifically unsound as they can obscure our search for what really happened. As pointed out by Cloud [1983], such attempts at explanation represent an unwelcome type of substantive uniformitarianism smacking of gradualism. Great and catastrophic events of earth history will in many cases require bold explanations if we hope to further our understanding. There is nothing to be gained by cowering before the task. It seems likely that the answer to the cause of LPGES, rather than being found in a series of multiple causes all of which in some way contribute to glaciation, resides in some single overriding factor.

I believe that a primary problem with current attempts to explain the LPGES is that most efforts have focused too intently on a strictly physical explanation for the onset of glaciation. This tendency reaches its extreme in the case of the low-obliquity models, where a thoroughly physical mechanism [tilting Earth's rotation axis; *Williams,* 1975] is invoked to explain the low-latitude ice. While I applaud the boldness of this hypothesis (and indeed Mars' rotation axis can tilt 60°), it unfortunately runs afoul of evidence in the terrestrial sedimentary record. For example, rhythmic sedimentation patterns [*Hughes et al.* 2003; *Williams,* 1975; see especially the rhythmic varvite with dropstone from northeast of Port Augusta, South Australia. *Cloud,* 1988, p. 298] and the morphology of sine wave columns of the Proterozoic stromatolite *Anabaria juvensis* [*Vanyo and Awramik,* 1985] is in accordance with the hypothesis of an essentially normal earth tilt during the growth of the stromatolites. These types of both biotic and abiotic periodic structures indicate that the obliquity of the Proterozoic ecliptic was not significantly different from current values.

Consideration of causes of the end of glaciation are beset by similar problems that are nearly as intractable as the problems associated with consideration of the factors causing the onset of glaciation. Much recent research focuses on the global geochemical changes associated with the "cap carbonates" occurring immediately upsection from the glacial deposits. Cap carbonates are thin but very widespread limestone/dolostone rock units that are usually interpreted as evidence for sudden and massive carbonate deposition in warm climate. Hoffman and Schrag [2002] prefer division of these units into a lower "cap dolostone" and an upper "cap limestone/cementstone" to reflect the dual nature of some of these deposits (particularly in Namibia and Canada).

Compounding the difficulties associated with low latitude glaciation is evidence for cap carbonate deposition immediately above the glacial deposits. This juxtaposition is a major geological anomaly. Williams [1979, p. 385] noted in prescient fashion the climatic significance of the juxtaposition of cap carbonates above the glacial strata:

"The sedimentological and oxygen-isotope data are consistent with relatively high formation-temperatures from the cap [carbonates]. Abrupt climatic warming from cold glacial to at least seasonally high temperatures at the close of the late Precambrian glacial epochs is implied."

These unusual carbonates have three signal characteristics. First, they are depleted in heavy carbon (they have a $\delta^{13}C$ value of approximately -5, indicating a low $\delta^{13}C$ /^{12}C ratio). A low $\delta^{13}C$ /^{12}C ratio is usually interpreted as representing low marine biotic productivity (as indicated by a low ratio of buried organic carbon to carbonate carbon), as organisms preferentially take up the lighter isotope and leave seawater (from which the marine carbonates are precipitated) enriched in heavy carbon. Second, these deposits characteristically extend over vast map areas, having been deposited in both shallow water and relatively deep-water environments. As such they provide a useful tool for lithostratographic correlation. Third, they contain in their lower parts primary dolostones, a highly unusual rock type [*Woods,* 1999] owing to the rarity of primary precipitation of the mineral dolomite (i. e., dolomite usually forms as a secondary mineral). New cap carbonate occurrences are being described as more stratigraphic sections receive scrutiny.

Kirschvink [1992] and Hoffman and Schrag [2002] relied on an abiotic geochemical model to explain the snowball earth/cap carbonate juxtaposition. Kirschvink's original hypothesis [1992] for the mechanism of escape from snowball earth conditions involved the accumulation of carbon dioxide in the atmosphere as a result of volcanic input, the near cessation of photosynthesis, and the inhibition of silicate weathering via the Urey reaction [*McMenamin,* 2001b]. Neoproterozoic marine iron formations were explained as buildup of dissolved iron in the water under the ice, followed by sudden oxydation and precipitation during the debacle (i. e., as the ice broke up). Renewed photosynthesis could then begin again to generate appreciable quantities of oxygen.

Hoffman and Schrag [2002] added that cap carbonates would be an expected outcome of "extreme greenhouse conditions unique to the transient aftermath of a snowball earth." In this view the sudden leap from white earth climate to cap carbonate climate is attributable to hothouse conditions resulting from unprecedented atmospheric CO_2 buildup.

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deposits of the Kingston Peak Formation. Thus the diamictites of the Kingston Peak Formation [several have been identified, the upper Wildrose Diamictite and the lower Surprise Diamictite; *Prave,* 1999] are sandwiched between the carbonates of the Beck Spring Dolomite and the Crystal Spring Formation below, and the presumed cap carbonate [*Woods,* 1999] of the Noonday Dolomite above. Cyclothem-like cyclic bedding in the stromatolitic Algal member of the Crystal Spring Formation [*Roberts,* 1982] may suggest biotic influence (by drawdown of greenhouse gases) in a rapidly deteriorating global climate with continental ice already beginning to influence eustatic sea level.

The Beck Spring Dolomite of eastern California provides a fascinating glimpse into carbon isotope dynamics just before the glaciation. The lower part of the formation has carbon isotopes varying from +2 to -2 per mil $\delta^{13}C$. The middle part of the Beck Springs Formation shows strongly positive $\delta^{13}C$ values (up to +6), with values falling to as low as -4 just before the Kingston Peak glaciation [*Corsetti and Kaufman,* 2000]. This isotopic curve agrees with those from the Keele in Canada (Ice Brook Glaciation), the Ombaatije in Namibia (Ghaub Glaciation), and the Etina in Australia [Elatina Glaciation; *Hoffman and Schrag,* 2002]. The Kingston Peak, Ice Brook, Ghaub and Elatina glaciations are all considered here to be synchronous and Marinoan in age (but see Lund et al. [2003] for an alternate interpretation of glacial syncroneity). Lund et al. [2003] do, however, hold the Ice Brook and upper Kingston Peak (Wildrose) diamictites to be synchronous). The high $\delta^{13}C$ values in these sections are interpreted here to represent an active seafloor microbiota that sequestered great amounts of isotopically fractionated organic carbon in sea floor sediments, triggering a decline into icehouse conditions. The sudden drop in $\delta^{13}C$ in the Beck Spring, Keele, Ombaatije and Enorma/Trezona (Etina Group) formations, respectively, represents a secular cooling in climate regime that immediately preceded the glaciation and the associated die-off in microbe populations. Probable fungal fossils, consisting of branched filaments belonging to the species *Paleosiphonella cloudii,* occur in Beck Spring chert [*Licari,* 1978], providing evidence for abundant organic matter which, along with the carbonate rock that entombed it, is hypothesized here as having been responsible for drawing down atmospheric carbon dioxide levels.

Gaucher [2000] attributes the drawdown of carbon dioxide to phytoplankton blooms preceding the glaciation. Gaucher et al. [2003] proposed the following scenario for slippage into an icehouse climate. First, enhanced volcanic and hydrothermal activity associated with the Rodinia breakup injects large amounts of silica, iron and other nutrients into seawater, and these accumulate in the deep sea, forming a eutrophic bottom layer in a stratified ocean. Second, fortuitous combinations of wind and water circulation trigger upwelling on a massive scale, leading to great blooms of phytoplankton and deposition of both phosphorites and banded iron formations on the sea floor below. The anoxic bottom water conditions encourage sulfate-reducing bacteria, triggering a positive shift in $\delta^{34}S$ values. Carbon removed from the atmosphere and sent to the seafloor by the phytoplankton blooms trigger the icehouse conditions. It is interesting to note that in the Arroyo del Soldado Group of Uruguay, banded iron formations occur in positive $\delta^{13}C$ intervals [*Gaucher et al.*, in press]. Furthermore, the highest concentrations of organic-walled microfossils occur in the iron oxide-bands of banded iron formation [*Gaucher,* 2000]. Interestingly, iron fertilization of equatorial Pacific surface waters has resulted in both phytoplankton blooms and carbon fractionation [*Bidigare et al.,* 1999].

Note the fascinating similarity between the carbon isotopic curves of the Kingston Peak, Ice Brook, Ghaub and Elatina glaciations (or more concisely, the Marinoan glaciation) and the drop in carbon isotope values (from +6 in the Kinderhookian/Mississippian to -2 in the Morrowan/basal Pennsylvanian) followed by moderate glacial/postglacial rise in $\delta^{13}C$ in the Arrow Canyon Range of southern Nevada [*Saltzman,* 2003]. Evidence for Pennsylvanian glacio-eustacy and cyclothems begins immediately after the nadir in carbon isotope values [base of the Morrowan stage; *Saltzman,* 2003], just as the nadir in the Marinoan sections occurs just before the first sedimentological evidence for glaciation. The Late Paleozoic glaciation was not nearly as extreme of course, and hence the carbon isotopic results do not seem to correlate as well from continent to continent [*Saltzman,* 2003], but nevertheless the message seems clear enough. Wang et al. [2003] have also shown that carbon reservoir changes preceded ice-sheet expansion at the mid-Brunhes event during the Pleistocene glaciations. Sufficient expansion of carbon- sequestering, primary-producing organisms will be followed (after a suitable lag period) by climate deterioration (and die off in primary production, thus accounting for the drop in carbon isotope values to -2 to -4 per mil from a previous high of +6–7) and then glaciation. For the Pennsylvanian, the coal forests of Hypersea [*McMenamin and McMenamin,* 1994] acted as the sequestering agent after overcoming the challenges of nutrient acquisition, desiccation and oxydation on land. For the latest Proterozoic glaciation, the carbonate-sequestering stromatolitic microbiotas acted as the climate culprit. In both cases, organic (over)productivity generated a carbon sink that eventually nudged global climate across a threshold from greenhouse to icehouse conditions. Incidentally, the telltale drop in $\delta^{13}C$ *before* the glaciation effectively rules out a bolide impact [*Rampino,* 1994] or other instantaneous event as a cause of the glaciation. The biomatter overproduction hypothesis advocated here may be tested by a careful comparison of the global carbon budgets before and after glaciation, using cubic kilo-

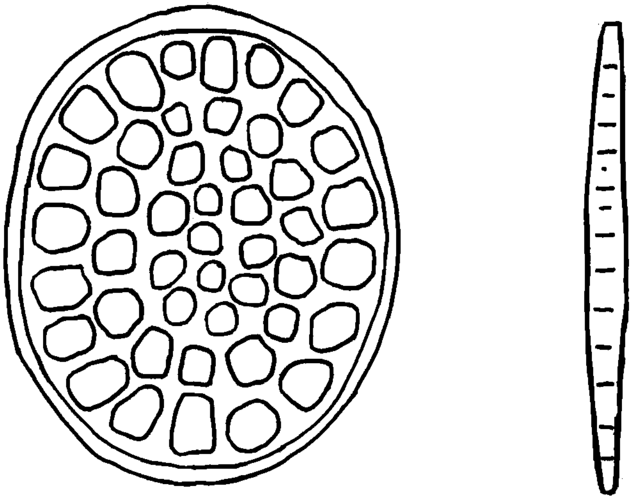

Figure 2. *Chilodictyon caliporum* [*Allison and Hilgert,* 1986] from chert in the Tindir Group of northwestern Canada. The scale microfossil is shown in plan view (right) and profile (left). This scale represents one element of a multi-scale test. Greatest dimension of individual scale 22 microns.

meters of carbonate rock (or coal) deposited as proxies for variation in atmospheric carbon dioxide.

It is worth considering ways in which the biota might respond to end a glaciation. In other words, it is well worth considering how organisms might exploit a snowball earth environment and how any resulting modes of life might hasten the end of the glaciation. Ice diatoms form a thick brown layer at the base of the ice in modern polar environments. As light can pass through thick layers of ice, a dark algal layer at the bottom of a floating ice sheet could lead to considerable warming of the underside of the ice, and contribute to ice melt. Although diatoms had not yet appeared by the Late Proterozoic to form the light-catching brown layer, other types of microbes evolved to fill extremophile niches similar to those occupied by modern ice diatoms, and might have provided a feedback mechanism for melting the ice.

5. TINDIR GROUP MICROFOSSILS: A RELICT ICE MICROBIOTA

A microbial community of chrysophyte and chlorophyte algae and their bacterial neighbors, preserved in Proterozoic cherts of the Tindir Group (Alaska) are apparently descended from a cryophilic microbiota. This microbiota apparently formed a dark-colored biofilm underneath Proterozoic ice sheets wherever they were thin enough to allow light penetration [*McMenamin,* 2004].

The Tindir sequence of Alaska and Yukon Territory provides a battery of potential tests of the hypotheses associated with snowball earth. Unit 1 of the upper Tindir consists of volcanic rocks and pillow lavas associated with the final stages of the breakup of Rodinia. Units 2 and 3 consist of purple mudstones interbedded with Marinoan glaciomarine diamictites. Unit 4 is a dolostone that presumably represents a cap carbonate. Unit 5 consists of resedimented limestones (possibly derived from a cap limestone/cementstone) interbedded with clastic sediments.

A curious biota of siliceous chrysophyte algae and bacteria were discovered in the late 1970s in cherts of the fetid (i.e., organic-rich) limestone in unit 5 of the Tindir Group in western Yukon Territory [*Allison and Hilgert,* 1986]. Originally thought to belong to the Cambrian System, the fossils are now known to be Late Proterozoic. Sponge spicules in the Tindir are among the earliest sponge spicules known. The algal fossils occur in small chert nodules in limestone.

The fossil chrysophytes are of great interest as they represent the first appearance of siliceous microfossils in the fossil record and the earliest known fossils of chrysophyte algae. The fossils consist of tiny, oval, opaline scales that in life formed an imbricate outer plating of each microbe's surface. The eukaryotic Tindir taxa are extinct, and they occur nowhere else in the rock record. The microbiota includes seventeen genera (including *Archeoxybaphon, Hyaloxybaphon, Chilodictyon* and *Altarmilla).* Several of the genera, particularly *Chilodictyon* (Figure 2) and *Characodictyon* (Figure 3), have a superficially diatom-like aspect. Allison and Hilgert [1986, p. 979] noted that many of the Tindir chrysophytes most closely resemble modern species known "largely or exclusively from fresh water rather than marine environments." Interestingly, modern scaled chrysophytes are commonly encountered in Arctic pond environments.

The fossil alga *Spirotindulus kryofili* (Figure 4) from the Tindir represents a large, elongate resting zygospore of a chlorophyte green alga [*McMenamin,* 2004]. Its grooved outer surface is quite similar to the flanges extending the full length of the cell in the elongate zygospores of the cryophilic chlorophyte algae *Chloromonas nivalis* and *Chloromonas polyptera. Spirotindulus kryofili* and *Chloromonas nivalis* zygospores have the same number of flange groove pairs (11 each).

These fossil chrysophyte and chlorophyte algae, plus their unique bacterial neighbors (including the cyanobacterial genera *Yukonosphaeridion, Microagglomeratus* and *Phacelogeminus* and the species *Cephalophytarion grande*), are hypothesized [*McMenamin,* 2004] to be descended from the cryophilic microbiota that formed a brown biotic undercoat to snowball earth ice wherever it was thin enough to allow light penetration. Exceptional populations of modern *Chlamydomonas nivalis* show optimum photosynthesis at 0° to -3°C, although most populations do best at 10°-20°C. Such microbes can catalyze melting of ice, both by withdrawing fresh water

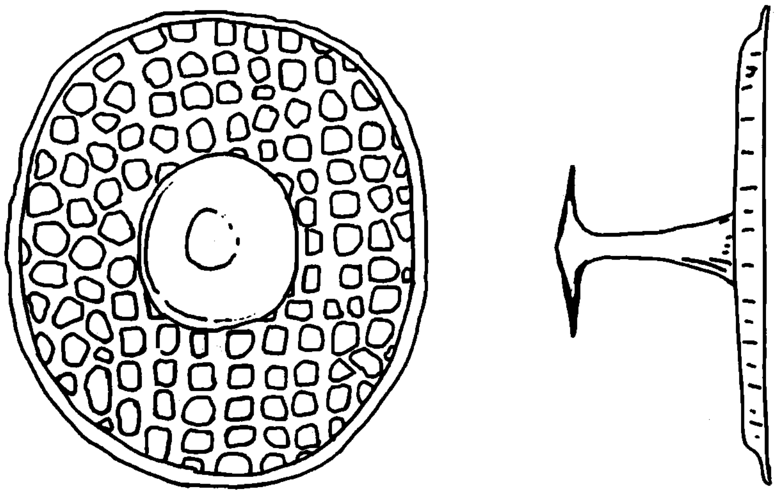

Figure 3. *Caracodictyon diskolopium* [*Allison and Hilgert*, 1986] from chert in the Tindir Group of northwestern Canada. The scale microfossil is shown in plan view (right) and profile (left). Note trumpet-like process extending from the surface of the scale. In an intact test (composed of a number of scales), the processes would project from the outer surfaces of the scales. Greatest dimension of individual scale 19 microns.

from the ice (and forming ice-corroding brine pockets) and by trapping heat in the brown sub-ice mat or "hyposcum."

Much of a white earth glaciation would occur in low and even equatorial latitudes, where light levels are intense and light penetration through ice is greatest. Organisms can thrive in such conditions; for example, Campen et al. [2003] have reported evidence for microbial metabolism within a low-latitude glacier. The upper Tindir microbiota may largely represent a relict biota adapted for the tenebrous conditions beneath the ice. This biota, as a result of its albedo-altering characteristics, melted the ice and was subsequently thrust into moderate climate after deposition of the dolostones of upper Tindir unit 4. The marine environment, at last having returned to "normal," led to deposition of the fetid (=petroliferous odor) Tindir carbonate with its fossiliferous chert inclusions. The microbiota of the Tindir, with its preponderance of scaled chrysophytes, still carried with it the signature of its icy origin.

The spirally grooved zygospore *Spirotindulus kryofili* is another member of this holdover community from glacial times [*McMenamin*, 2004]. The spiral grooves on *Spirotindulus,* like those of the modern chlorophyte *Chloromonas,* were probably used to anchor these cells to a frigid substrate. The hypothesized ice microbiota may have existed as a stratified community at the base of the snowball earth ice, analogous to modern ice algae, Antarctic rock-dwelling lichens, or the farbstreifensandwatt of North Atlantic coastlines. The similarities between the Tindir chrysophytes and modern ice diatoms and Arctic lake chrysophytes are no coincidence, as all these microbes evolved to occupy frigid habitats. It might even be argued that the unique ice biota ancestral to the biota of the Tindir fetid limestone evolved specifically to take advantage of the sub-ice environment. One could also infer that the pre-Tindir brown layer consisted largely of euryhaline species that could also colonize periglacial freshwater environments.

At first the pre-Tindir brown layer may have been restricted in extent, but with continued ice thinning the habitat of the pre-Tindir microbes would have expanded rapidly. Ice edges seem to be a particularly favorable habitat [*Leck and Persson,* 1996]. Special phytopigments and protective phenolic compounds, such as those found in the snow alga *Chlamydomonas nivalis,* could have developed to cope with increased amounts of incom-

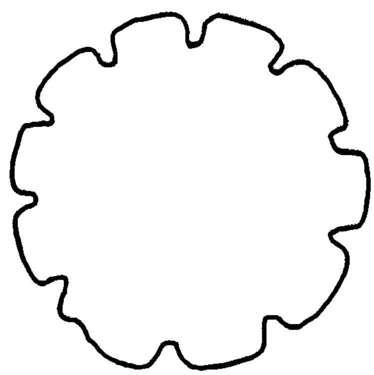

Figure 4. *Spirotindulus kryofili* [*McMenamin*, 2004] from the upper Tindir Group unit 5, Yukon Territories, Canada. Transverse section through fossil. Diameter of fossil 43 microns.

ing radiation [*Duval et al.*, 2000] after millions of years life in a habitat of faint light and limited UV exposure. Clay coatings may have also played a similar role [*Tazaki et al.*, 1994].

6. A PROTEROZOIC CRYOCONITE

Cryoconite is a term applied to dark-colored material that forms on glacier ice, formed primarily of wind-borne dust and microbial mat material [*McMenamin,* 2001b]. Cryoconite has been implicated in the acceleration of melting of Himalayan glaciers, and recent studies show that Alpine and Himalayan cryoconites consist of microbial mats formed by cyanobacteria and heterotrophic microbes [*Sharp et al.*, 1999; *Takeuchi et al.*, 2001; *Margeson et al.*, 2002]. Cryoconite microbes play a role in reduction of glacier albedo, and are known to colonize open areas after the ice melts. Interestingly, the distribution of individual microbes in granules of granular cryoconite [*Takeuchi et al., 2*001, their Figures 4–6] bear a curious resemblance to the spatial distribution of Proterozoic microbes in silicifed granules from the El Arpa Formation, Sonora, Mexico. The resemblance is seen both in granule morphology and arrangement of the spherical microbial mat of filamentous cyanobacteria [*McMenamin,* 2004]. This resemblance may not be merely coincidental.

If the El Arpa Formation is correlated to the Canadian Tepee Dolostone and to the Noonday Dolomite, as seems reasonable [*McMenamin,* 1996], the El Arpa would qualify as a cap carbonate. The Tepee Dolostone serves as the cap carbonate for the underlying, glaciogenic Ice Brook Formation. Taking the correlations a step further, the microfossiliferous part of the Tindir has been correlated with the Keele and Sheepbed Formations of northwestern Canada [*Young,* 1982] suggesting that this part of the Tindir correlates to the "cap limestone/cementstone" of the basal Sheepbed [*Hoffman and Schrag,* 2002, their Figure 3]. These proposed correlations are speculative, however, and need to be backed up by further study of the biostratigraphy, lithostratigraphy, and chemostratigraphy of the sections involved.

Wind-blown sediments alone, be they volcanigenic or otherwise, do not greatly alter the albedo of ice surfaces, as they are generally light tan or gray in color. But detrital cryoconites do begin to alter ice surface albedo when colonized by mat-forming microbes. Cryoconite microbial mats are known for forming dark humic acid accumulations that accelerate ice melting [T*akeuchi et al.,* 2001]. The microbes involved are able to use almost anything as a food source. The Arctic psychrophile bacterium *Polaromonas vacuolata* is able to form biofilms on a wide variety of substrates, including dichloroethane as the sole carbon source [*Coleman et al.,* 2002] and is even able to utilize the polycyclic aromatic hydrocarbons pyrene and phenanthrene [*Eriksson et al.,* 2002].

7. A BIOSPHERE-INDUCED MELTDOWN

The ice of a snowball earth would be biotically thawed from both above (cryoconite microbial mats) and below (sub-ice algal/bacterial brown layer), thus accelerating the meltdown by amplifying the abiotic factors (particularly volcanic emission of atmospheric carbon dioxide) driving global warming. A dark, humic acid-rich cryoconite layer would tend to block light from reaching any brown layer below, but this would be compensated for by cryoconite-induced thinning of the ice sheet above the brown layer. Furthermore, light entering the ice laterally from some distance away could become trapped in the ice between the upper and lower dark layers, further contributing to meltdown. All of this would be accelerated by the high light intensities at low latitudes.

It would be to the immediate advantage of cryoconite microbes and brown layer microbes to expand their range and influence, thus melting more ice and expanding the areal extent of the band-shaped zone between the ice margin and the limit of light penetration through the ice. There would be but few limits to growth, especially for a cold-adapted biota, as the chemical composition of the oceans of the time may have resembled "the nutrient media typically used for growing cyanobacteria in pure culture" [*Duval et al.*, 2000] and a steep nutricline may not yet have been re-established in the oceans. In Vernadskian fashion, uncontrolled growth of the Tindir microorganisms might well have catalyzed rapid collapse of the ice sheets, heating them, as it were, from above, below and within (internally) by passive solar gain. The organisms would also begin penetrating into the ice itself by means of brine pockets and cryoconite holes [*Wharton et al., 1*985].

The oceans could thus become "prematurely" free of ice; that is, clear of ice before the normal operation of biogeochemical cycles could resume. The accumulated levels of atmospheric carbon dioxide would then represent a highly metastable situation, and carbon dioxide would literally collapse out of the atmosphere as the Urey reaction kicked in with full force in an anomalously hot climate, causing the "freeze-fry" transition. Carbon stripped from the atmosphere and sequestered as dissolved calcium carbonate would be delivered in massive amounts to the ocean basins. Although the actual duration of the Proterozoic glacial episodes is not known, it is possible that they lasted for millions of years rather than the tens to hundreds of thousands of years for the Pleistocene glaciations. Without the influence of life, the Proterozoic glaciations might have lasted considerably longer than was actually the case.

The atmospheric component of meltdown may have had a significant biotic component as well. Leck et al. [2004] presented research results showing that atmospheric particulates generated by microbes associated with high-Arctic (89°N, 1°E) pack ice and microbe activity in nearby open ocean areas have potentially important climate implications. Leck et al. [2004] hypothesized that the particulates (curious virus-like particles that act as centers for the condensation of dimethylsulfide oxydation products) influence low altitude cloud formation and are thus important in the melting of Arctic pack ice. The particulate centers seem to be mostly associated with the thin surface layers of open water, whereas the dimethylsulfide gas was mostly formed by microbes living around the edges of the pack ice [*Leck et al.*, 2004; *Leck and Persson, 1996]*.

The odd radiating crystal textures and unusual dolostones of the cap carbonates are evidence for precipitation as a result of what could be called oceanic supersaturation with respect to calcium carbonate. The depletion in heavy carbon (low $\delta^{13}C$ values) of the cap carbonates is also considered evidence for a chemical oceanographic origin [*Kennedy et al.*, 2001], although the source of this carbon is not entirely clear. Atmospheric carbon and carbon in methane from gas hydrates undergoing decomposition as global climate warmed have been suggested as sources. Newly described gas hydrate chimneys could have profound effects on the stability of gas hydrates (*Wood et al.*, 2002).

8. CLIMATE IMPLICATIONS

Some type of runaway biotic feedback must be responsible for the rapid transition from snowball conditions to tropical cap carbonate deposition. Conventional abiotic geochemical systems simply cannot respond with the requisite speed. Caldeira and Kasting [1992] estimated that it would require an atmospheric carbon dioxide content (pCO_2) of 0.12 bar to rescue the earth from hard snowball conditions. This estimate was assumed by Higgins and Schrag [2003] in the initiation of their climate model at values of 0.04, 0.08 and 0.12 bar, respectively. I suspect that these pCO_2 values are far too low. Note that the greenhouse effect is not going to work very well on a pearly white planet because the incoming solar radiation will simply bounce off the ice rather than being transformed into infrared (heat) radiation to be trapped by what greenhouse gases may exist in the atmosphere at the time. Joseph Kirschvink (personal communication, 2001) has calculated that the atmosphere requires 0.6 bar CO_2 to end hard snowball earth conditions, and that it takes 70 million years to thaw the earth once this level of atmospheric carbon dioxide has been attained. The rock record suggests that the transition out of glacial conditions took less (and perhaps much less) than a million years (judging from the conformable contact at the base of the cap carbonates), in which case Kirschvink's estimate is more than seventy times the amount of time allowed by the rock record to accomplish the transition. Snowball earth thus provides a challenge for anyone wishing to rely exclusively on abiotic mechanisms to explain climate change. Abiotic geochemistry alone is inadequate to explain the rapid deglaciation (or for that matter, the onset of glaciation).

The rapid onset of Cenozoic glaciation in Antarctica (the ice cap begins to form in the Early Oligocene, 33.5 million years ago) is thought to have been a result of declining atmospheric carbon dioxide [*DeConto and Pollard,* 2003]. The reason for this decline is often attributed to falling amounts of carbon dioxide from mantle sources as the breakup of Pangea and the tectonic dispersion of its fragments began to slow down. Life processes, such as the changing productivity of the southern oceans and transistions from forest to peatland, possibly on Antarctica itself (R. DeConto, personal communication, 2004), may also have played an important role in helping to cool climate by pulling carbon dioxide out of the atmosphere. Even though they only account for about one percent of the land surface area today, peatlands (mires) are thought to contain about a third of the organic carbon stored in soil [*Gorham,* 1991; *Turunen et al.*, 2002].

Life processes, for Vernadsky *the* geological force [*Vernadsky,* 1998], can certainly impact global climate. Such influence, however, must always be considered in Vernadskian terms. The Vernadskian "pressure of life" will expand explosively at unexpected times and places, as with the Cambrian Explosion that ended the Proterozoic [*McMenamin,* 2003a]. Microbes flourished even under glacial conditions, and prokaryotic and eukaryotic microbes (primarily cyanobacteria and vase-shaped microfossils) did not suffer mass extinctions due to the glaciations [*Corsetti et al.*, 2003]. Explosive blooms of *Bavlinella faveolata* are known to occur globally in post-Varangerian deposits [*Gaucher et al.*, 2003]. The inferred growth of the cryoconites and the pre-Tindir microbe brown layer, hypothesized here to have assisted the collapse of the Neoproterozoic ice sheets, provides further examples of the opportunistic potential of life.

Yet another problem involves the calcium required to balance the massive accumulation of carbon in the cap carbonates. Hoffman and Schrag [2002] calculate that to sustain the marine calcium saturation needed to maintain the cap carbonate deposition, a five-fold increase in marine calcium ion concentration is required. The question arises of how this much calcium was delivered to the sea. Glacial flour (rock powder) and frost-shattered silicate rock would rapidly weather via the Urey reaction, thus putting calcium in solution (while at the same time drawing down atmospheric carbon dioxide). But Higgins and Schrag [2003] and Hoffman (written communication, January 2003) argue that oceanic supersaturation was achieved by rapid weathering of carbonates. Marine shelves were extensively exposed to weathering as deglaciation began, and some of these terranes consisted of exposed carbonate rock. Carbonate weathering proceeds hundreds of times faster than silicate weathering, and this would have been especially enhanced by high pCO_2 levels which would have boosted levels of carbonic acid in rainwater. But the question remains—was there sufficient carbonate rock exposed to rapid weathering to maintain supersaturation and sustain the cap carbonate precipitation? The five-fold increase in concentration required is huge. Such a hypothetical erosive unconformity (eroded downward into the carbonates) should be expressed in the rock record by a karst zone of unprecedented proportions. Intriguingly, Neoproterozoic karsts are known from several sequences, including the Sierras Bayas Group, Argentina [*Barrio et al.,* 1991] and the Arroyo del Soldado Group, Uruguay, at the contact between the Polanco and Barriga Negra Formations [*Gaucher,* 2000]. However, whether the extent of this karsting can account for the missing calcium is unknown, and furthermore, the post-glacial erosion would first be directed to the blanket of till covering the proximal parts of the exposed continental shelves. This blanket would presumably be dominated by siliciclastic debris, and it would tend to protect the shelfal carbonates from the acid rain.

Part of the problem here, once again, is over-reliance on physical science models that do not sufficiently account for the influence of the biota. We should not underestimate the influence of the Vernadsky's [1998] pressure of life. Runaway expansions of the biota eventually run out of space on a spherical planet, forcing a new and eventually stable climate equilibrium. Perhaps the two levels of stasis in $\delta^{13}C$ levels in Namibia before the Ghaub Glaciation [at about +6 per mil before the big drop in values, and at about -4 per mil after the drop and shortly before deposition of the diamictite; *Hoffman and Schrag,* 2002] represent biotic response (in the direction of reestablishing climate equilibrium) in the face of declining levels of a critical greenhouse gas.

Note that many of the cap dolostones are distinguished by impressive evidence for life. Some of the largest stromatolites known [*Cloud et al.,* 1974; *Hoffman and Schrag,* 2002 and references therein] occur within the cap dolostone. Carbonate bioherms formed of tubular stromatolites ("stromatolitic pipe rock") occur in the dolostone part (Keilberg member) of the Maieberg Formation in Namibia and represent biotic trapping of carbonate on a tremendous scale [*Hoffman and Schrag,* 2002]. As the sediment trapping and binding activities of filamentous mat-forming microbes are well-known, it may be safe to assume that such a great (five-fold) supersaturation with respect to calcium concentration was not required to form the cap carbonates. The filamentous seafloor microbes trapped and bound lime mud, and this action provided a biological pump for calcium carbonate, taking it from seawater (with elevated but not necessarily supersaturated concentrations of calcium) and sequestering it to the sea floor as cap carbonate. Indeed, the mountainous sizes of some of these stromatolites indicate that the stromatolite carbonate pump was working overtime, indicating a strong biotic [again more Vernadskian than Gaian; *McMenamin,* 2004] signature to cap carbonate formation. The fetid odor of the Tindir cap limestone indicates that, at least locally, the cap carbonate interval was also a time of continued organic productivity and sequestering of isotopically fractionated carbon.

The next generation of general circulation models should (in addition to improving their treatment of cloud cover in light of the results of Leck et al. [2004]) consider parameters designed to describe the surge aspect of biotic influence on global climate. Another good example of the phenomenon already mentioned is the expansion of Hypersea in the Devonian [*McMenamin and McMenamin,* 1994] and associated climate instability later in the Paleozoic [another glaciation; *Saltzman,* 2003]. Certainly our species could be considered responsible for a similar type of geologically sudden perturbation, only this time via addition rather than subtraction of carbon dioxide from the atmosphere.

The intensity of white earth conditions during the Marinoan and Sturtian ice ages needs to be better understood if we hope to present a more complete description of extreme climate dynamics and their influence on Neoproterozoic sedimentation [*Miller et al.,* 2003]. For example, carbonate sediments (peloids, oncolites and marine cements) occurring within the glacial strata and presumably precipitated directly from glacial seawater of ancient Australia and Namibia have relatively high $\delta^{13}C$ values. These high values suggest to some that the global biological carbon pump *during the glaciation* was functioning normally, an interpretation that argues against ice-covered oceans [*Kennedy et al.,* 2001]. Paul F. Hoffman and Adam C. Maloof (written communication, 2001) argue that these high values would be consistent with a detrital origin for the intra-glacial diamictite carbonates, in which case the carbonates would have a heavy carbon signature inherited from more ancient carbonates. This would also avoid the difficulty of having to deposit newly formed carbonate in mid-glaciation. Or perhaps the intra-glacial sediment carbonates are indeed primary, but result from an unusual ecosystem at the base of the ice or on the seafloor below the ice.

Strange and innovative biology seems to be associated with the sub-ice biota. The hyposcum habitat would have been a suitable proving ground for a tenebrous proto-Garden of Ediacara ecology. Many palaeontologists have assigned the Ediacaran fossils to conventional animal phyla such as the Cnidaria, Echinodermata or Annelida, but the arguments supporting these assignments have not convinced everyone. This is primarily so because of the bizarre morphology of the fossils. The stramge shapes of these creatures have inspired comparisons to metacellular algae [*McMenamin,* 1998] and even fungi [*Peterson et al.,* 2003]. Until recently, skeptics (with regard to the animal affinity hypothesis) pointed out that not a single uniquely animalian trait had been identified on any of the thousands of Ediacaran fossils collected so far. A consensus interpretation for at least some of the fossils may be emerging, however, with recent new evidence showing trilobitoid arthropod features in *Spriggina* [*McMenamin,* 2003b] and with the association of *Kimberella* with grazing traces [*Fedonkin,* 2003].

The biota of the latest Proterozoic can be modeled as a relict cryophile ecosystem experiencing normal marine conditions for the first time. Ecological analogs to such an ecosystem are seen among modern protists. Giant branching foraminifera (*Notodendroides antarctikos)* live under semi-permanent sea ice in McMurdo Sound, Antarctica [*Delaca and Lipps,* 1980]. They take up dissolved organic matter largely as a function of their surface area, a mode of feeding that has been inferred for the Ediacarans. When large predators appeared near the beginning of the Cambrian [*McMenamin,* 2003a], the Garden of Ediacara ecosystem (an overgrown cryophilic microbiota?) was lost to the voracious Cambrian predators such as *Anomalocaris.*

To what then shall we attribute the post-glacial Proterozoic diversification of complex eukaryotes such as Ediacarans and animals? Grey et al. [2003] consider linkages to both snowball earth events and the Acraman impact event. The Acraman impact site (570 my) of South Australia, associated with 160 km diameter crater, shock metamorphism and shattercone development, is comparable in size to the 214 my Manicouagan impact structure of Canada and thus might plausibly be linked to an episode of mass extinction and evolutionary change.

Clapham and Narbonne [2002] argue that Ediacarans were tiered filter feeders living in a conventional cnidarian-dominated ecosystem. This argument is called into question by later results [*Narbonne and Gehling,* 2003] indicating that among the earliest Ediacarans were the largest known. Some other evolutionary mechanism besides tiering among filter feeders, such as improved light capture for photosymbiosis, must be invoked to explain large early Ediacarans such as *Charnia wardi.* This species approaches 580 million years age and is up to 2 meters long [*Narbonne and Gehling,* 2003]. Narbonne has described this fossil as being "too complex to have arisen in 10 million years," that is, in the time elapsed between the end of the snowball glaciation (represented in Newfoundland by the Gaskiers Formation till, a Marinoan deposit) and the deposition of the fossils [*Hecht,* 2003]. Narbonne [in *Hecht,* 2003] thus concludes that either the Ediacarans evolved extremely rapidly or, more likely, that the ice did not entirely cover the oceans, allowing polynyas where organisms could thrive and evolve *during* the ice age. Although rapid evolution for the Ediacarans cannot be ruled out, and indeed their strange [and perhaps metacellular; *McMenamin,* 1998] body plan provides a relatively "quick and cheap" way of attaining large body size, it does seem plausible that they existed before the end of the glaciation. Compelling fossil evidence of their presence at that time should be sought.

In conclusion, it seems reasonable to infer that an extremophile biota could exert a major influence on white earth conditions, and that white earth conditions in turn could have a significant impact on the evolution of ecosystems. Likewise, the perplexing cap carbonate deposition bears a signature of biotic influence on a massive scale, comparable to the Oxygen Event represented by the early Proterozoic banded iron formations [*Johnson et al.,* 2003]. The first inference could be tested by scalable experiments on modern ice microbes associated with floating, grounded or anchored ice. Certainly the extreme fluctuation in carbon isotope values of Late Proterozoic time implies substantive changes in the global and local biogeochemistry of microorganisms. Similarly, the *rôle* of microorganisms in the formation of cap carbonates could be tested by a series of experiments involving rates of artificial stromatolite growth under a variety of simulated marine chemistries, including of course marine water supersaturation with regard to the calcium ion.

Ever since Mawson [1949] and Harland and Rudwick [1949] drew attention to the severity of the Proterozoic glaciations, there have been concerns about the "bizarre potential, and possible past states of Earth's climate" [*Fairchild,* 2001]. In particular, there are fears that alteration of the northward course of the Gulf Stream and shutdown of North Atlantic bottom water generation could threaten the mild climate of northwestern Europe. We need to combine analysis of ocean dynamics [*Pulse et al.,* 2001] with analysis of biotic feedback mechanisms to arrive at an understanding of the constraints (or lack thereof) associated with extreme climatic fluctuations of the past. For a century and a half our species has been trying to retrodict (as opposed to predict) evolutionary changes and predict the course of future change as a function of carbon dioxide content of the atmosphere [*Koene,* 1856]. It may not matter much for bacteria, however, as there is evidence suggesting that Proterozoic pre-glacial bacterial communities were much the same as the syn-glacial bacterial communities [the oscillatoracean cyanobacterium *Cephalophytarion grande* passes through the Marinoan glaciation unchanged; *McMenamin,* 2004; see also *Fairchild,* 2001], a fact not in accord with arguments that snowball earth had catastrophic effects on the entire biosphere [*Runnegar,* 2000]. Conversely, a component of the modern biosphere in the guise of *Homo sapiens* appears to be having a major and perhaps soon to be catastrophic influence on the stability of polar ice sheets. If so, we may be merely following a trajectory blazed by our Proterozoic microbial forebears.

In conclusion, it seems likely that the biosphere, simply by exercising its Vernadskian prerogative—the pressure of life—

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