Geochemistry
Geophysics
Geosystems
G^3
AN ELECTRONIC JOURNAL OF THE EARTH SCIENCES
Published by AGU and the Geochemical Society

Article
Volume 3, Number 6
27 June 2002
10.1029/2001GC000219
ISSN: 1525-2027

On the initiation of a snowball Earth

Daniel P. Schrag
Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, Massachusetts 02138, USA (schrag@eps.harvard.edu)

Robert A. Berner
Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520, USA (robert.berner@yale.edu)

Paul F. Hoffman and Galen P. Halverson
Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, Massachusetts 02138, USA (hoffman@eps.harvard.edu; halvers@fas.harvard.edu)

[1] The Snowball Earth hypothesis explains the development of glaciation at low latitudes in the Neoproterozoic, as well as the associated iron formations and cap carbonates, in terms of a runaway ice-albedo feedback leading to a global glaciation followed by an extreme greenhouse climate. The initiation of a snowball glaciation is linked to a variety of unusual perturbations of the carbon cycle operating over different timescales, as evidenced by unusual patterns in the carbon isotopic composition of marine carbonate. Thus a theory for why multiple glaciations happened at this time, and not in the Phanerozoic nor earlier in the Proterozoic, requires a reexamination of the carbon cycle and the controls on climate stability. We propose that the concentration of continental area in the tropics was a critical boundary condition necessary for the onset of glaciation, both because the existence of substantial continental area at high latitudes may prevent atmospheric carbon dioxide from getting too low and because a tropical concentration of continental area may lead to more efficient burial of organic carbon through increased tropical river discharge. Efficient organic carbon burial sustained over tens of millions of years, required by the high carbon isotopic compositions of preglacial carbonate, may lead to the buildup of enormous quantities of methane, presumably in hydrate reservoirs. We examine how the slow release of this methane may explain the drop in $\delta^{13}C$ values immediately before the glaciation. Moreover, the accumulation of methane in the atmosphere coupled with the response of silicate weathering to the additional greenhouse forcing can lead to a climate with methane as the major greenhouse gas. This situation is unstable because methane is not buffered by a large ocean reservoir like carbon dioxide, and so the collapse of the methane source may provide a trigger for the onset of a runaway ice-albedo feedback. A simple model of the carbon cycle is used to explore the boundary conditions that would allow this to occur.

Components: 12,960 words, 5 figures.

Keywords: Carbon cycle; snowball Earth; stable isotopes; Neoproterozoic; methane; glaciation.

Index Terms: 1030 Geochemistry: Geochemical cycles (0330); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 9619 Information Related to Geologic Time: Precambrian; 1060 Geochemistry: Planetary geochemistry (5405, 5410, 5704, 5709, 6005, 6008).

Received 27 August 2001; **Revised** 23 January 2002; **Accepted** 30 January 2002; **Published** 27 June 2002.

Schrag, D. P., R. A. Berner, P. F. Hoffman, and G. P. Halverson, On the initiation of a snowball Earth, *Geochem. Geophys. Geosyst.*, *3*(6), 10.1029/2001GC000219, 2002.

1. Introduction

[2] The end of the Proterozoic era (750–580 Ma) hosted the most spectacular glaciations in Earth history. Glacial deposits left by the retreating ice are found today on every continent [*Hambrey and Harland*, 1981]. Paleomagnetic and geological data from several of these deposits suggest that they were formed at tropical latitudes [*Evans*, 2000] and that the glaciations lasted for millions to tens of millions of years [*Sohl et al.*, 1999; *Hoffman et al.*, 1998]. In most locations the glacial deposits are overlain by "cap" carbonate sediments showing unusual textural, chemical, and isotopic patterns [*Grotzinger and Knoll*, 1995]. The Snowball Earth hypothesis [*Kirschvink*, 1992; *Hoffman et al.*, 1998] provides a single explanation for these multiple observations. The hypothesis proposes that the glacial deposits were formed by a global glaciation that occurred when ice advanced past a critical latitude (~30° North and South), creating a runaway ice-albedo feedback first theorized by *Eriksson* [1968], *Budyko* [1969], and *Sellers*, [1969]. Once frozen to the equator, the high planetary albedo locked the Earth's climate into a stable, icy state. Deglaciation required extreme levels of atmospheric CO_2 produced by millions of years of volcanic emissions [*Caldeira and Kasting*, 1992]. The cap carbonates were formed during the ultragreenhouse climate in the aftermath of the glaciation [*Hoffman et al.*, 1998].

[3] An unanswered question associated with the Snowball Earth hypothesis is what caused the Earth to plunge into this frost-thaw cycle in the first place. What was it about this particular time in Earth history that allowed such catastrophic environmental oscillations to take place? Moreover, why have such events not occurred in the Phanerozoic following the radiation of large, multicellular animals? *Hoffman et al.* [1998], following *Knoll et al.* [1986], suggested that the breakup of Rodinia, a late Proterozoic supercontinent, might have led to a global glaciation by increasing the sedimentation rate, leading to increased burial of organic matter. This suggestion was motivated by high $\delta^{13}C$ values of preglacial carbonate rocks, hinting at a link between the glaciations and some tectonically mediated perturbation of the carbon cycle [*Kaufman et al.*, 1997]. However, the breakup of Rodinia is not the only supercontinent breakup in the geologic record. Why did a global glaciation occur with the breakup of Rodinia but not with Pangea's demise? The breakup of Rodinia may have been a factor in setting the stage for the Snowball Earth, but a more detailed discussion is clearly required.

[4] One constraint on the cause of global glaciations in the Neoproterozoic is the clear evidence for multiple glaciations. At many locations, two discrete glacial intervals with cap carbonates are present in a single stratigraphic section [*Hambrey and Harland*, 1981]. Limited geochronological data and correlation based on carbon isotopes have led some to suggest that there were at least four events, two in the earlier part of the Neoproterozoic (Sturtian), approximately 730–680 Ma, and two later glaciations (Vendian) between 650 and 585 Ma [*Kaufman et al.*, 1997]. Others have tried to correlate glaciations in Australia and Africa, concluding that there were only two events [*Kennedy et al.*, 1998; *Walter et al.*, 2000]. New data from Death Valley provide evidence for two glacial episodes [*Prave*, 1999] and possibly two additional cap carbonates [*Abolins et al.*, 1999; *Corsetti and Kaufman*, 2000], giving some support to the larger number. Regardless of whether there were two, three, four, or even more individual glaciations, all workers agree that there was more than a single event. This is important in seeking an explanation for why the glaciations happened in the first place because it suggests that conditions that allowed for the initiation of a Snowball Earth must have persisted for much of the Neoproterozoic.

[5] In the Eriksson-Budyko-Sellers [*Eriksson*, 1968; *Budyko*, 1969; *Sellers*, 1969] theory for a runaway ice-albedo feedback, if ice advances past some critical latitude, the rate of increase in planetary albedo is so large that it produces a runaway positive feedback, and the ice line plunges to the equator. Budyko and Sellers placed this critical latitude at ~40° on the basis of calculations with an energy balance model (EBM). More recent work with EBMs and general circulation models (GCMs) has shown that the location of the critical latitude may be closer to 30° and depends on many factors, including ocean, atmosphere, and glacier dynamics [*Poulsen et al.*, 2001; *Chandler and Sohl*, 2000;

Hyde et al., 2000], solar luminosity, and the albedo of the ice itself, all of which have varied over geologic time. This emphasizes that a successful theory for the initiation of a Snowball Earth in the Neoproterozoic may involve two separate causes, a background condition, perhaps in the climate system or carbon cycle, that cools the climate near to the runaway state, as well as a proximate trigger for the onset of the runaway ice-albedo feedback. Regardless of exactly where one places the critical latitude, the proximate trigger for what pushed the climate system past the threshold to initiate the runaway ice-albedo feedback may be difficult to identify as it might be related to a wide variety of sources of stochastic or periodic climate variability.

[6] One factor that may have been important in promoting a global glaciation in the past is the change in solar luminosity over Earth history. Models of stellar evolution suggest that the luminosity of the Sun has increased by ~40% over Earth history [*Gough*, 1981] and was ~7% less luminous than today during the Neoproterozoic. One might hypothesize that the reduction in solar luminosity was enough to cause the Earth to plunge into the catastrophic snowball cycle and that the brightening Sun has protected the Earth since that time, preventing a global glaciation in the last ~550 million years. Although this may be a contributing factor, changes in solar luminosity cannot be the sole cause of Neoproterozoic glaciations because such a hypothesis would predict that global glaciations were common prior to the Neoproterozoic, when the Sun was even dimmer. Although some evidence exists for low-latitude glaciation in the Paleoproterozoic approximately 2.3–2.5 billion years ago [*Evans et al.*, 1997; *Williams and Schmidt*, 1997; *Kirschvink et al.*, 2000], there is no evidence for any continental-scale glaciations in the intervening 1.5 billion years. Thus a successful theory for the initiation of a Snowball Earth in the Neoproterozoic must explain not only why such glaciations have not occurred in the Phanerozoic but also why they did not happen beforehand during most of the Proterozoic.

[7] In this paper we suggest a hypothesis to explain the initiation of global glaciations in the Neoproterozoic. We propose that the Earth is susceptible to a snowball glaciation when most of the continents are located in the tropics, an unusual occurrence in Earth history. Following the work of *Marshall et al.* [1988], who explored the effects of continental distribution on climate using a simple model, we argue that this condition influences climate by removing a critical negative feedback in the carbon cycle that prevents CO_2 from reaching extremely low levels and keeps the ice line from getting close to the critical latitude for a runaway glaciation. We also show how distributing the continents at low latitudes may help explain the high $\delta^{13}C$ values observed in Neoproterozoic sediments in advance of glaciations. Finally, we discuss one possible mechanism to explain the drop in $\delta^{13}C$ values immediately prior to the onset of glaciation that may offer a direct triggering mechanism for the snowball glaciation itself. While admittedly speculative, these are testable suggestions that cast the widely observed isotopic anomalies in a new light.

2. Effect of Continental Distribution on the Global Carbon Cycle

[8] Over millions of years the amount of carbon in the ocean-atmosphere system is controlled by the fluxes of carbon between the ocean-atmosphere and the rock reservoir. The source of carbon to the ocean-atmosphere system is volcanic outgassing, which releases mantle CO_2 as well as CO_2 produced from metamorphism of carbonate sediments. Removal of CO_2 is accomplished through the conversion of CO_2 to calcium carbonate by chemical weathering of silicate rocks and through burial of organic carbon. Although the flux of carbon from volcanic sources is insignificant on the timescale of human civilization, even a slight imbalance between source and sink over millions of years would strip all the carbon out of the ocean and atmosphere, or lead to an extreme greenhouse climate. *Walker et al.* [1981] proposed that the rate of chemical weathering must respond to the level of atmospheric CO_2, providing a negative feedback on the buildup of atmospheric CO_2, keeping the sink in balance with the volcanic source. These ideas were formulated in a numerical model of the carbon cycle by *Berner et al.* [1983] (a.k.a. BLAG), who suggested that changes in volcanic outgassing over

the last 100 million years were the primary cause for the transition between greenhouse climates of the Cretaceous and ice ages of the Plio-Pleistocene. In the last two decades much attention has been given to understanding the nature of the silicate weathering feedback, and several mechanisms have been proposed that are tied to the radiative effects of CO_2 on climate. One mechanism is the direct effect of temperature on the kinetics of weathering reactions [*Berner*, 1978]. Another mechanism is the increase in precipitation rate in a greenhouse climate that may intensify weathering rates as fresh water is flushed more rapidly through soil and sedimentary rocks. Some support for temperature and precipitation both being important in regulating weathering rates comes from a recent study showing a significant correlation of bicarbonate ion in river water with mean annual temperature and precipitation for 107 individual catchments [*Ohte and Tokuchi*, 1999]. Other studies have focused on factors independent from CO_2 that may affect the rate of chemical weathering such as glaciation [*Anderson et al.*, 1997] and the effect of uplift on rates of mechanical erosion [*Harrison*, 2000] in providing fresh, silicate mineral surfaces for chemical reaction. Other complications include the evolution of land plants in the Paleozoic, leading to soils which intensified the rate of chemical weathering by making fluids more reactive with organic acids [*Retallack*, 1997; *Moulton et al.*, 2000; but see also *Keller and Wood*, 1993].

[9] Many studies that discuss the behavior of the carbon cycle over the Phanerozoic have focused on how chemical weathering places an upper limit on atmospheric CO_2, preventing extreme greenhouse climates. Very little attention has been given to what places the lower limit on atmospheric CO_2, although this was an interest of *Walker et al.* [1981] in their discussion of the faint young Sun. The general formulation of the weathering feedback does include a decrease in weathering as CO_2 decreases, providing a negative feedback. However, this is not an effective way of regulating the carbon cycle when CO_2 is very low. Small imbalances between sources and sinks can have rapid and large impacts owing to the relatively short residence time of carbon in the ocean-atmosphere system when atmospheric CO_2 is very low. Although the focus of the original BLAG model [*Berner et al.*, 1983] was on the transition between greenhouse and icehouse climates over the last 100 million years, there exists in the BLAG model an additional negative feedback that prevents atmospheric CO_2 from getting too low. In their parameterization the rate of chemical weathering is modified by a factor (f_A) which describes the fraction of continental area available for weathering (Figure 1). This factor is linked to atmospheric CO_2 through the effect of continental ice sheets in inhibiting chemical weathering. Suppose the level of volcanic outgassing were to drop (as it likely has over the last 100 million years), causing atmospheric CO_2 to decrease. In response to lower radiative forcing, the climate would cool, and ice sheets would form over high-latitude continents. The growth of large ice sheets would then prevent or greatly reduce the rate of chemical weathering of silicate rocks, essentially reducing the land area available for weathering [*Marshall et al.*, 1988; *Kump et al.*, 1999]. Reducing the chemical weathering sink relative to the volcanic outgassing source would prevent further lowering of atmospheric CO_2. This ‘‘land area feedback’’ is much more powerful at enforcing a lower limit on CO_2 than the weathering feedback alone [*Berner et al.*, 1983].

[10] There are several aspects of this description of the carbon cycle that are, of course, gross over simplifications. First, the relationship between glaciation and weathering is not as straightforward as portrayed above. Some have argued that glaciation may actually increase rates of chemical weathering by increasing mechanical erosion through mountain glaciers or by scraping away soil cover, exposing fresh bedrock to weathering processes [*Gibbs and Kump*, 1994]. These effects are probably most important for partially glaciated regions and for regions with periodic glaciations such as North America during the Pleistocene. Certainly, such regions today have much more intense weathering than hyperarid regions in the subtropics. However, for large continental ice sheets such as those covering Antarctica and Greenland, it seems reasonable that the rate of chemical weathering is greatly reduced relative to what it would be if no ice sheets were present and there were adequate water for weathering reactions [*Anderson et al.*, 1997].

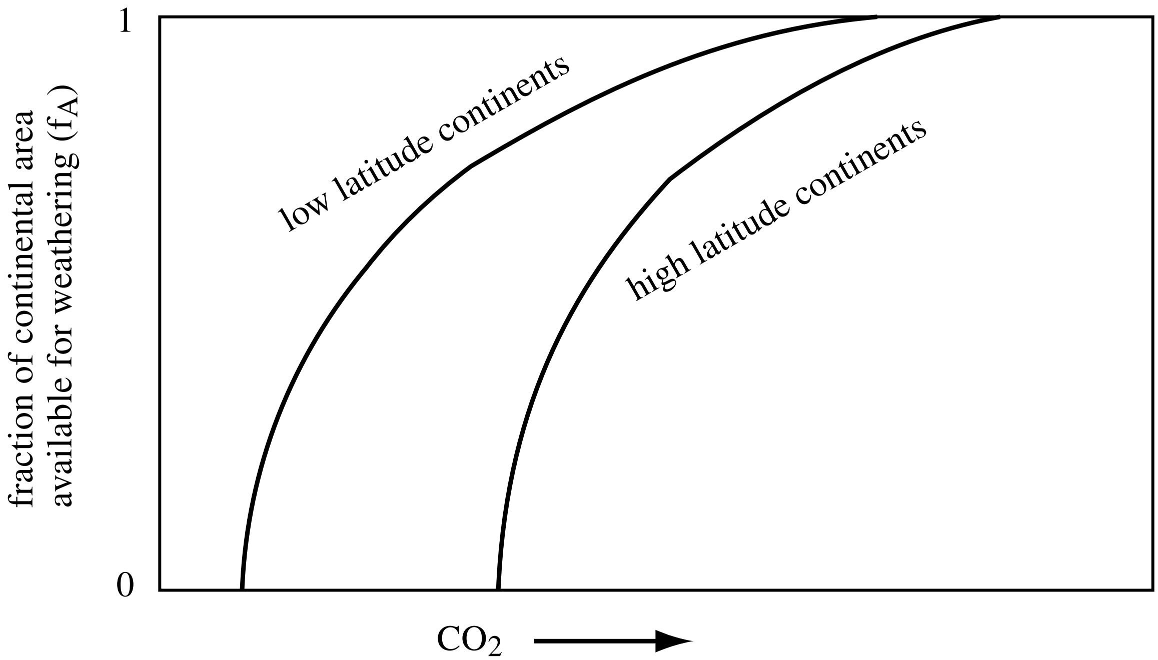

Figure 1. A schematic representation of the fraction of land area available for silicate weathering as a function of the partial pressure of atmospheric carbon dioxide for high- and low-latitude continental distributions. As carbon dioxide drops, glaciation commences on high-latitude continents, reducing the rate of silicate weathering in those areas and stabilizing the atmospheric CO_2. If most of the continents were in the tropics, this effect would not commence until CO_2 levels were substantially lower.

[11] The functional form of the land-area feedback (Figure 1) in the BLAG model [*Berner et al.*, 1983] was set for a continental distribution with substantial continental area at higher latitudes appropriate for Cretaceous and Cenozoic simulations. In the curve used in the BLAG model, the fraction of continental area available for weathering decreases as CO_2 drops to modern values; the exact shape of the low-CO_2 end of the curve was not considered in detail as it was relevant to Cretaceous and Cenozoic climate. If there were less continental area at high latitudes, the strength of the feedback would diminish; with a drop in the source, presumably the volcanic activity, a lower level of CO_2 would be required to achieve a reduction in the weathering sink to keep the carbon cycle in balance (Figure 1). In the extreme, if all continents were located in the tropics, no reduction in continental area available for weathering would happen until ice reached the tropics. Weathering might even be enhanced in tropical regions as the climate cooled if mountain glaciers provided fresh material to mature tropical soils [*Anderson et al.*, 1997].

[12] In this context, a Snowball Earth may require a continental distribution with little continental area at high latitudes [*Marshall et al.*, 1988; *Hay et al.*, 1990; *Worsley and Kidder*, 1991]. If there were substantial continental area at high latitudes, the reduction in chemical weathering from the formation of ice sheets would stabilize CO_2, arresting any further advance of the ice long before it reached the critical latitude for a runaway glaciation. A concentration of continental area in the tropics not only would contribute to lower CO_2 by putting more land area in tropical regions of high precipitation but would also disable the negative feedback. It remains possible that one could initiate a global glaciation with some extraordinary mechanism without involving the carbon cycle, for example, an abrupt and extreme drop in the effective solar flux. However, for reasons discussed above, such explanations are more difficult to reconcile with the geologic evidence for multiple low-latitude glaciations in a ~170-million-year interval but none in the previous 1500 million years or in the 580 million years since.

[13] Is the postulated continental distribution compatible with paleomagnetic data? The period between 730 and 585 Ma was a time of fragmented continents. Breakup of the early Neoproterozoic supercontinent Rodinia [*Weil et al.*, 1998] began with proto-Pacific opening between 780 and 755 Ma [*Wingate and Giddings*, 2000]. Continents were dispersed until Gondwanaland coalesced around 550 Ma [*Meert and Van der Voo*, 1997; *Alkmim et al.*, 2001]. Existing paleomagnetic data are inadequate to justify any particular continental reconstruction between 750 and 580 Ma, the period encompassing the hypothesized snowball events. Considering only those data for which the ages of natural remnant magnetization are known, the paleolatitudes of only half the major continents then in existence are constrained in this time period (Figure 2) [after *Evans*, 2000]. Those paleocontinents (Laurentia, Baltica, Siberia, South China, and Australia) all lay in low latitudes so far as is known [*Kent and Smethurst*, 1998]. Of the six glacial deposits for which "moderately reliable" paleomagnetic data exist, half formed <30° and all <50° from the equator [*Evans*, 2000]. Despite the lack of reliable paleomagnetic data from South America and Africa, the statistical low-latitude bias is so striking that nondipolar components in the Earth's magnetic field are postulated to have existed [*Kent and Smethurst*, 1998]. Laurentia migrated to the South Pole between 590 and 575 Ma [*Hyodo and Dunlop*, 1993; *Symons and Chiasson*, 1991], coincident with the last global glaciation which began soon after 596 Ma [*Thompson et al.*, 1996]. Overall, there is more evidence for low-latitude continental distribution during the Neoproterozoic, with no evidence for large continental area at high latitudes, than for any other time in Earth history [*Kirschvink*, 1992]. This is at least broadly consistent with the hypothesis discussed above.

3. Carbon Isotopes and Organic Carbon Burial in the Neoproterozoic

[14] An additional clue to the background conditions that led to a Neoproterozoic Snowball Earth comes from the unusual carbon isotopic composition of Neoproterozoic carbonates. In Neoproterozoic sections, carbonate strata not adjacent to glacial deposits are characteristically enriched in ^{13}C, with δ^{13}C values ranging from +4 to +8‰. Although absolute geochronological data are sparse, geological relationships suggest that the high values persisted for tens of millions of years [*Kaufman et al.*, 1997]. These values are substantially higher than those in the Phanerozoic, which range from 0 to +3‰. An exception is an interval in the Carboniferous and Permian, when δ^{13}C values reached +7‰. The Neoproterozoic values are also higher than for earlier parts of the Proterozoic back to ~2000 Ma [*Brasier and Lindsay*, 1998; *Kah et al.*, 1999; *Lindsay and Brasier*, 2000].

[15] A traditional interpretation for these high δ^{13}C values is that they reflect a high fraction of carbon buried as organic matter (depleted in ^{13}C), leaving the residual inorganic carbon pool (carbonate) slightly enriched [*Hayes et al.*, 1999]. A complication is the long-term storage of methane in sediments as clathrates as methane is greatly depleted in ^{13}C, but this will be discussed in more detail below. The δ^{13}C of Pleistocene carbonate is between 0 and +2‰, implying that ~20% of carbon burial to balance the volcanic source occurs as organic carbon. Neoproterozoic δ^{13}C values for carbonate rocks indicate that organic carbon burial was 30–50% of the total [*Hayes et al.*, 1999]. Although these high values need not necessarily be connected to the development of global glaciation, it seems unlikely that multiple, extraordinary events during the same interval of geologic time have no connection. At the minimum, it is worth examining possible explanations for the high carbon isotope values to see what unusual states of the carbon cycle might have existed during the Neoproterozoic.

[16] Why is the fraction of carbon buried as organic matter so high in the Neoproterozoic compared to the large periods of time before and after? Moreover, what regulates the burial of organic matter and keeps the fraction relative to carbonate burial so constant over most of geologic time with the exception of the Neoproterozoic (and Permo-Carboniferous)? The answers to these questions provide interesting insights into the long-term behavior of the carbon cycle and are consistent with the hypothesis that the initiation of global glaciations

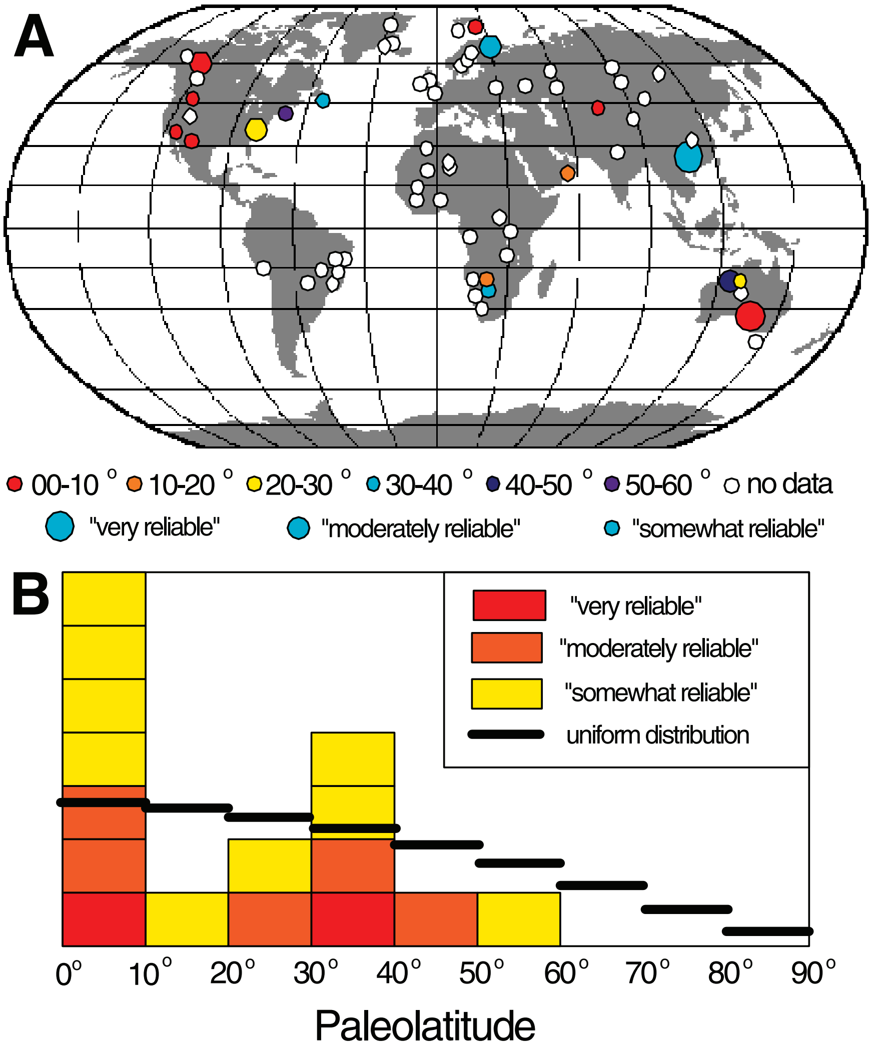

Figure 2. (a) Distribution of Neoproterozoic glaciogenic deposits with estimated paleolatitudes based on paleomagnetic data (modified from *Evans* [2000]). "Reliability" takes into account not only paleomagnetic reliability but also the confidence that the deposits represent regionally significant, low-elevation ice sheets [*Evans*, 2000]. (b) Histogram of the same glaciogenic deposits according to estimated paleolatitudes. Note the preponderance of low-latitude deposits and the absence of high-latitude deposits. The discontinuous steps show the expected density function of a uniform distribution over the sphere.

in the Neoproterozoic was encouraged by having most continents in the tropics. We suggest that high carbon isotope values are more likely to occur whenever many continents are in the tropics and that the continental distribution may help to explain the anomalous values in both the Neoproterozoic and Permo-Carboniferous.

[17] As stated above, the $\delta^{13}C$ of marine carbonate reflects the burial ratio of organic carbon to carbonate carbon. Note that for these discussions carbonate burial due to carbonate weathering is excluded from our fluxes even though this source of alkalinity may at times dominate the total carbonate burial. Over millions of years, for which a steady state assumption is reasonable, carbonate weathering merely transfers carbonates from land to ocean, resulting in no net accumulation of carbon in the ocean-atmosphere system. As the carbonate being weathered will have, in general, similar $\delta^{13}C$ values to the new carbonate being deposited, carbonate weathering has only a small effect on the carbon isotope mass balance. This simplification may not be appropriate at certain intervals of Earth

history, such as the Neoproterozoic and Permian, when the $\delta^{13}C$ of marine carbonate was most different from terrestrial limestone. In these situations, weathering of carbonate would serve to buffer the seawater composition, damping the isotopic effects of increased carbon burial. However, for our qualitative discussion the carbonate burial flux we consider is only that required to balance the alkalinity flux to seawater from silicate weathering. It is possible that changes in the major element chemistry of seawater, specifically, the calcium concentration relative to other major cations, could perturb this balance slightly, but such considerations are beyond the discussion presented here.

[18] Over millions to tens of millions of years the burial of organic carbon is controlled predominantly by two factors: the flux of phosphate from the continents to the ocean and the carbon to phosphorous ratio of the organic matter that is buried. Even when nitrate or iron limitation severely hampers productivity in many parts of the ocean, if there is no significant inorganic removal of phosphate from seawater, the phosphate levels of seawater will increase, eventually achieving a new steady state by increasing productivity in areas where iron or nitrate are abundant. If organic burial were to drop relative to riverine supply of phosphate, the total phosphate content of seawater would increase, stimulating productivity and driving higher organic burial. If organic burial were to exceed the phosphate supply, the phosphate concentration of seawater would decrease, diminishing productivity and reducing organic burial.

[19] The riverine flux of phosphate to seawater depends on the release of new phosphate from silicate rocks by weathering reactions and from weathering of soils, organic matter, and other phosphate deposits on land. Terrestrial soils and other phosphate-rich deposits such as black shales may represent significant repositories of phosphate, allowing the riverine fluxes to deviate over shorter timescales from the flux from silicate weathering. Phosphate release from sediments may even play a dominant role on million-year timescales. However, over even long timescales (i.e., tens to hundreds of millions of years) the riverine flux of phosphate must be controlled predominantly by the release of new phosphate from silicate weathering. If silicate weathering were to decrease, the riverine flux of phosphate might remain high for some time owing to sedimentary sources such as black shales (although the release from these would also vary with silicate weathering, driven by changes in climate). But the steady depletion of the sedimentary sources would eventually cause the riverine flux to drop. Additional complications may come from chemical feedbacks such as the effect of pH on phosphate mobility. Such issues are worthy of additional investigation but are beyond the present discussion.

[20] The essential point for this discussion is that both organic carbon and carbonate carbon burial (excluding the contribution from carbonate weathering) over long timescales are directly tied to the rate of silicate weathering, the former through the release of phosphate and the latter through the production of alkalinity (see a similar discussion by *Junge et al.* [1975]). If the rate of silicate weathering were to change, organic and carbonate carbon burial would be affected by approximately equal amounts, and so the ratio would not change. The $\delta^{13}C$ of carbonate rocks therefore reflects the globally averaged phosphate to alkalinity ratio of the average silicate rocks being weathered on continents. The reason that $\delta^{13}C$ values are relatively constant over most of the Phanerozoic and Proterozoic is that globally averaged composition of continental crust, in essence the average phosphorous content of granite, does not change by large amounts (i.e., factors of 2 or more) when integrated over the globe and over millions of years.

[21] Now, let us return to the question of the high $\delta^{13}C$ values in the Neoproterozoic. If the ratio of phosphate to alkalinity fluxes from silicate weathering cannot vary by large amounts over long timescales, then the only way to sustain high (i.e., 40–50%) fractional organic carbon burial for tens of millions of years is to increase the carbon to phosphorous ratio in buried organic matter. Several workers have suggested that the carbon to phosphorous ratio of organic matter in sediments is strongly affected by anoxia [*Van Cappellen and Ingall*, 1996; *Ingall and Jahnke*, 1997]. During early diagenesis in oxic sediments, phosphorous is bound up in iron phosphate minerals, and so a

relatively small fraction of phosphate is recycled into the water column. In anoxic sediments, phosphate recycling is more efficient, resulting in a substantial increase in the carbon to phosphorous ratio in the sediments. Thus one explanation for the high $\delta^{13}C$ values in the Neoproterozoic is more efficient phosphate recycling, perhaps driven by more extensive local anoxia.

[22] However, more extensive local anoxia by itself will not achieve higher rates of organic carbon burial. The burial of organic matter in the modern ocean is highly localized, occurring primarily in the deltas of large river systems in the tropics, including the Amazon and Southeast Asia (Taiwan, New Guinea, etc.) [*Berner*, 1982]. Although these regions account for a relatively small fraction of the dissolved fluxes of cations to seawater, the high discharge and suspended load, much of it organic, explains why they account for ~70% of the global organic carbon burial [*Hedges and Keil*, 1995; *Berner*, 1982]. However, for reasons discussed above, on long timescales the rate of organic carbon burial must be limited by the supply of phosphate to seawater. If one wants to increase the rate of organic carbon by increasing phosphate recycling through anoxia, it is most effective to focus on these areas with the highest carbon burial because that is where the more efficient phosphate recycling must occur. A complication is that in the Neoproterozoic, before the evolution of land plants, the suspended load of tropical rivers was unlikely to contain as much particulate organic matter. However, even without an extensive terrestrial biosphere, it seems likely that such locations, with high sedimentation rates and nutrient inputs, were dominant sites of organic carbon burial as much of the organic matter that is buried today in these deltaic environments comes from marine sources [*Aller et al.*, 1996]. A contributing factor may be the adsorption of organic matter onto clay minerals, which may enhance organic carbon burial in tropical river deltas [*Keil et al.*, 1994; *Mayer*, 1999].

[23] An intriguing possibility is that the distribution of continents may itself influence the extent of local anoxia at sites where organic carbon burial is highest. In the modern ocean most primary productivity occurs in regions of strong upwelling, including the eastern tropical Pacific and the Southern Ocean. In both these regions, far from continental sources of dust, iron is a limiting nutrient to primary productivity. Although there is some iron dissolved in oceanic intermediate waters, which can sustain some productivity, the lack of iron from aeolian sources keeps the level of primary production below the supply of phosphate and nitrate. Consider where primary productivity would occur if all the continents were located in the tropics. Given a total continental area similar to today, ~70% of the tropics would be filled with continents (in contrast to ~20% today), with two large ocean basins in the Northern and Southern Hemispheres. Upwelling in polar regions might bring phosphate and nitrate to the surface, but iron would be limiting in the large polar oceans as the weak meridional circulation of the atmosphere is ineffective at carrying continental dust to high latitudes, equivalent to the Southern Ocean today if Australia, Africa, and Patagonia were absent. Even if upwelling waters at the poles were rich enough in all nutrients, including iron, to sustain high productivity, it would be difficult to sustain deep anoxia in such large ocean basins, so organic burial rates would be low (like the eastern tropical Pacific today). Primary productivity would be focused in tropical regions, where abundant iron and other nutrients were present. The high fraction of continental area in the tropics would augment the overlap of zones of high productivity with regions of high riverine phosphorous and sediment input. However, the most important effect might be the increase in continental runoff itself, leading to larger tropical river systems. Tropical convection will always result in a large excess of precipitation over evaporation compared to the subtropics, where subsidence causes evaporation to dominate over precipitation. If most of the continental area were located in the tropics, the continental runoff could increase by a factor of 3 or 4, independent of any changes in the overall strength of the hydrologic cycle. With many large tropical river systems like the modern Amazon, a paleogeography with most continents in the tropics would be ideal for enhancing organic carbon burial combined with at least local anoxia if not broader anoxia across small, partially restricted tropical basins.

[24] The hypothesis that the high $\delta^{13}C$ values in the Neoproterozoic are the result of the unusual continental configuration of having most continents in the tropics is consistent with the observation that such high values are very unusual in the geologic record. The only times in the Phanerozoic when $\delta^{13}C$ values even approached the high values of the Neoproterozoic were the Carboniferous and Permian. The rise of large land plants as a new source of organic matter for burial was an important factor in leading to these high values at that time [*Berner*, 1998]. However, sediment fluxes into a partially restricted Tethys ocean in the tropics may have been an additional factor in promoting high organic carbon burial in tropical river deltas.

[25] The arguments presented here suggest that the high $\delta^{13}C$ values in preglacial Neoproterozoic carbonates are consistent with a concentration of continents in the tropics, supporting the discussion above on the land-area feedback. In addition, the high fractional organic carbon burial may also be important in setting the stage for a global glaciation by lowering atmospheric carbon dioxide. In the GEOCARB formulation the amount of atmospheric carbon dioxide over long timescales is driven by the rate of volcanic outgassing relative to the silicate weathering feedback. If the fraction of organic carbon burial goes up, the burial of carbon will momentarily exceed the volcanic source, reducing atmospheric CO_2 until a new steady state is achieved with lower atmospheric CO_2 and lower silicate weathering. In mathematical terms, consider, for simplicity, a formulation of the weathering feedback that is a linear function of atmospheric CO_2. In this case the conservation equation is

$$\frac{dM_{\mathrm{CO_2}}}{dt} = F_{\mathrm{volc}} - F_{\mathrm{sil}} - F_{\mathrm{org}} = F_{\mathrm{volc}} - k_{\mathrm{sil}} M_{\mathrm{CO_2}} - q_{\mathrm{org}}\left(k_{sil} M_{\mathrm{CO_2}}\right),$$

where F_{volc}, F_{sil}, and F_{org} are the rates of carbon dioxide release from volcanic outgassing, carbon dioxide uptake from silicate weathering, and organic carbon burial, respectively, k_{sil} is the slope of the weathering-CO_2 feedback, and q_{org} is the rate of organic burial as a fraction of the carbonate burial (i.e., $q_{\mathrm{org}} = X_{\mathrm{org}}/(1 - X_{\mathrm{org}})$ which is controlled by the biogeochemical cycling of phosphate discussed above. At steady state this becomes

$$M_{\mathrm{CO_2}} = \frac{F_{\mathrm{volc}}}{k_{\mathrm{sil}}\left(q_{\mathrm{org}} + 1\right)}.$$

For most of the Phanerozoic, q_{org} is $\sim$0.25, but for the Neoproterozoic, when the fraction of organic carbon burial approaches the carbonate burial, q_{org} is between 0.7 and 1, reducing the amount of carbon in the ocean-atmosphere system, and hence atmospheric CO_2, by a factor of 2. Thus it seems possible that the high fraction of organic carbon burial, which came about as a consequence of the unusual continental configuration in the Neoproterozoic, was itself responsible for cooling the Neoproterozoic climate to the point approaching the threshold for the initiation of a snowball Earth. This effect is in addition to the having higher precipitation over continents with tropical distribution, which in the parameterization used here would serve to increase k_{sil} and lower atmospheric CO_2. This could be extremely significant if continental runoff could increase by a factor of 3 or more.

4. Could Methane Be the Trigger for a Snowball Earth?

[26] The discussion of the initiation of a snowball Earth would not be complete without an explanation for the large carbon isotope excursions associated with the glacial deposits. The cap carbonates overlying the glacial deposits are depleted in ^{13}C by $\sim$5‰, which, in contrast to the enriched preglacial sediments, produce some of the most extreme carbon isotope variations observed in the entire geologic record [*Hoffman et al.*, 1998]. In the Snowball Earth hypothesis the low $\delta^{13}C$ values of the cap carbonates are caused by the rapid delivery of alkalinity to seawater in the ultragreenhouse aftermath of the glaciation. Millions to tens of millions of years of volcanism without substantial carbon burial either as organic matter or carbonate results in a calcium carbonate layer with a mean value similar to the volcanic source (approximately -5‰), although initially somewhat higher owing to the isotope fractionation associated with hydra-

tion of CO_2 [*Hoffman et al.*, 1998]. These low values in the cap carbonates are often grouped together with the high values before the glaciation as part of a carbon isotope "excursion" despite the fact that the high and low values are separated by a hiatus (i.e., the glaciation) lasting millions of years. Thus what is commonly referred to as an excursion is more accurately characterized as large differences in the carbon cycle before and after the long-lived glaciations.

[27] In Namibia, where the preglacial isotope record is recorded in a thick, carbonate platform sequence, the $\delta^{13}C$ values begin to drop several tens of meters below the glacial deposit, reaching values as low as $-5‰$ before the glacial horizon [*Hoffman et al.*, 1998; *Halverson et al.*, 2002]. There is no absolute geochronological control on the duration of this drop in $\delta^{13}C$, but tectonic subsidence modeling suggests a timescale on the order of 0.5–1.0 million years [*Halverson et al.*, 2002]. Whether this drop is a general feature of carbon isotope records globally is complicated by the possibility that glacial erosion may have eliminated much of the preglacial sediment from many sections around the world. However, such a drop has been observed in Neoproterozoic sections from other locations [e.g., *Kaufman et al.*, 1997; *McKirdy et al.*, 2001], including those in Australia and Canada. *Kennedy et al.* [1998] suggested that the preglacial excursion in Namibia is an artifact of some unusual alteration process. However, the reproducibility of the drop over hundreds kilometers at locations with different sedimentation rates and in different sedimentary facies makes a diagenetic explanation seem unlikely [*Halverson et al.*, 2002]. If the pattern is primary, and reflects a general relationship between carbon isotopes and the onset of glaciation, then such a spectacular drop in $\delta^{13}C$ values just before the initiation of tropical glaciation demands some explanation.

[28] One interpretation of a drop in $\delta^{13}C$ values over ~1 million years is that biological productivity slowed to very low levels, leaving carbonate burial as the major sink for volcanic CO_2. *Hoffman et al.* [1998] raised this possibility, suggesting that biological productivity slowed as ocean temperatures cooled prior to the runaway ice-albedo feedback drove sea ice to the equator. However, there are a number of problems with this proposal. First, as long as substantial area of oceans were ice free before the critical threshold for the runaway ice-albedo feedback, biological productivity should have been active enough to maintain substantial organic carbon burial rates. There is no reason to suspect that the tropical biota should have anticipated the onset of global glaciation and declined ~0.5 million years in advance of the deep freeze. Even if the drop in $\delta^{13}C$ does represent a drop in productivity (and hence organic carbon burial), one would expect such a drop in organic carbon burial to drive an increase in atmospheric CO_2. This is difficult to reconcile with the initiation of global glaciation. *Knoll et al.* [1986] suggested that the isotope excursions represented a rapid mixing event in a stagnant ocean, with CO_2-rich, anoxic deep waters mixing into the surface ocean. Because of wind and tidal forces, it is difficult to envision any scenario where stagnant deep ocean could be maintained for millions of years without mixing. However, even if the deep ocean were stagnant for long periods of time and if a mixing event were responsible for the preglacial drop in $\delta^{13}C$ values, the penetration of CO_2-rich waters into the mixed layer would cause atmospheric CO_2 levels to increase, inconsistent with the onset of tropical glaciation.

[29] An intriguing possibility is that the preglacial drop in $\delta^{13}C$ is driven by the release of methane to the carbon cycle. Because methane formed in deep sea sediments has very low $\delta^{13}C$ values (approximately $-70‰$), a relatively small amount of methane can have a very large effect on the average $\delta^{13}C$ value of dissolved inorganic carbon in seawater. A rapid destabilization of methane hydrates on the seafloor has been proposed to explain the carbon isotope excursion at the Paleocene-Eocene boundary [*Dickens et al.*, 1995]. For the Neoproterozoic this hypothesis is attractive as one might expect substantial amounts of methane hydrate to have formed following tens of millions of years with a high fraction of organic carbon burial and significant regions of anoxia. Indeed, a contributing factor that may help to explain the high carbon isotope ratios in the carbonate rocks underlying the

glacial deposits in addition to higher fractional organic carbon burial may be unusually high rates of methane hydrate formation in sediments. In the Paleocene, deep ocean temperatures had subsided from high values in the mid-Cretaceous but were still in excess of ∼8°C [*Miller et al.*, 1987], substantially limiting the zone of hydrate stability in deep sea sediments. However, in the Neoproterozoic, if most continents were in the tropics, and if large tropical river systems drove high rates of organic carbon burial in partially anoxic sediments over tens of millions of years, it would be the ideal factory for building up enormous reservoirs of methane hydrate, many times larger than what existed at the terminal Paleocene, particularly if ocean temperatures were relatively cool for much of this time.

[30] A problem with the idea that the drop in $\delta^{13}C$ values before the glaciation is caused by methane is that methane is a greenhouse gas, ∼25 times more potent per mole than CO_2, so one might expect that the release of methane from a large hydrate reservoir would drive a rapid warming due to enhanced radiative forcing. Indeed, such a scenario is envisioned for the Paleocene-Eocene boundary, for which there is good evidence in the oxygen isotope record for abrupt warming [*Norris and Röhl*, 1999].

[31] The residence time of methane in the modern atmosphere is <10 years and presumably similar in the latest Paleocene. Therefore methane added to the atmosphere would be oxidized rapidly to CO_2, equivalent to an increase in the rate of volcanic outgassing. The release of methane would drive an abrupt warming via the CO_2, but the large radiative forcing per molecule from methane may not be important beyond the first several decades following the abrupt release. In the Neoproterozoic, there are several important differences from the Paleocene. First, the timescale for the carbon isotope excursion is likely to have been at least two orders of magnitude longer. Thus, if the Neoproterozoic excursion were caused by release of methane, that release must have been slow and steady. In addition, the residence time of methane in the atmosphere may have been substantially longer in the Neoproterozoic than in the Phanerozoic, both because the concentration may have been higher and because the size of the sink may have been smaller. The destruction of methane in the stratosphere is limited by the availability of the hydroxyl radical, which in turn is produced via (O'D) from ozone photolysis. A variety of workers have proposed that oxygen levels were lower in the Neoproterozoic [*Derry et al.*, 1992; *Canfield and Teske*, 1996], prior to the radiation of large multicellular animals. Exactly how the residence time of methane would scale with the amount of atmospheric oxygen and with increases in the flux of methane to the atmosphere is a complex question. *Walker* [1979] used a simple chemical model to explore the effect of lower oxygen on ozone concentrations (which would scale with OH radical). He found that maximum ozone actually increased with a slight drop in atmospheric O_2 (0.5 present atmospheric level (PAL)) because of enhanced penetration of UV radiation. *Kasting et al.* [1985] explored the effects of much lower levels of oxygen with a more complete chemical model, finding that the methane residence time was slightly higher at 0.1 PAL but lower at 0.01 PAL and below. Another possibility is that the residence time of methane might increase substantially with a rise in methane flux if the tropospheric and stratospheric sinks became saturated. This possibility needs to be explored in future calculations. However, if oxygen were lower in the Neoproterozoic, and, more important, if a flux of methane to the atmosphere were sustained at much higher levels, a residence time for methane 100 times the present is not inconceivable.

[32] What if the methane release to the atmosphere were slow and steady, in contrast to the rapid release proposed for the Paleocene-Eocene boundary, and the steady state concentration of methane were much higher than today? In this case the carbon cycle would have adequate time to adjust to the increased radiative forcing, leading to a very different outcome. Just as silicate weathering acts as a negative feedback for increases in atmospheric CO_2, an increase in radiative forcing from increased methane concentrations would stimulate more rapid silicate weathering with higher temperatures and more rapid precipitation. The enhanced silicate weathering would not affect the methane directly

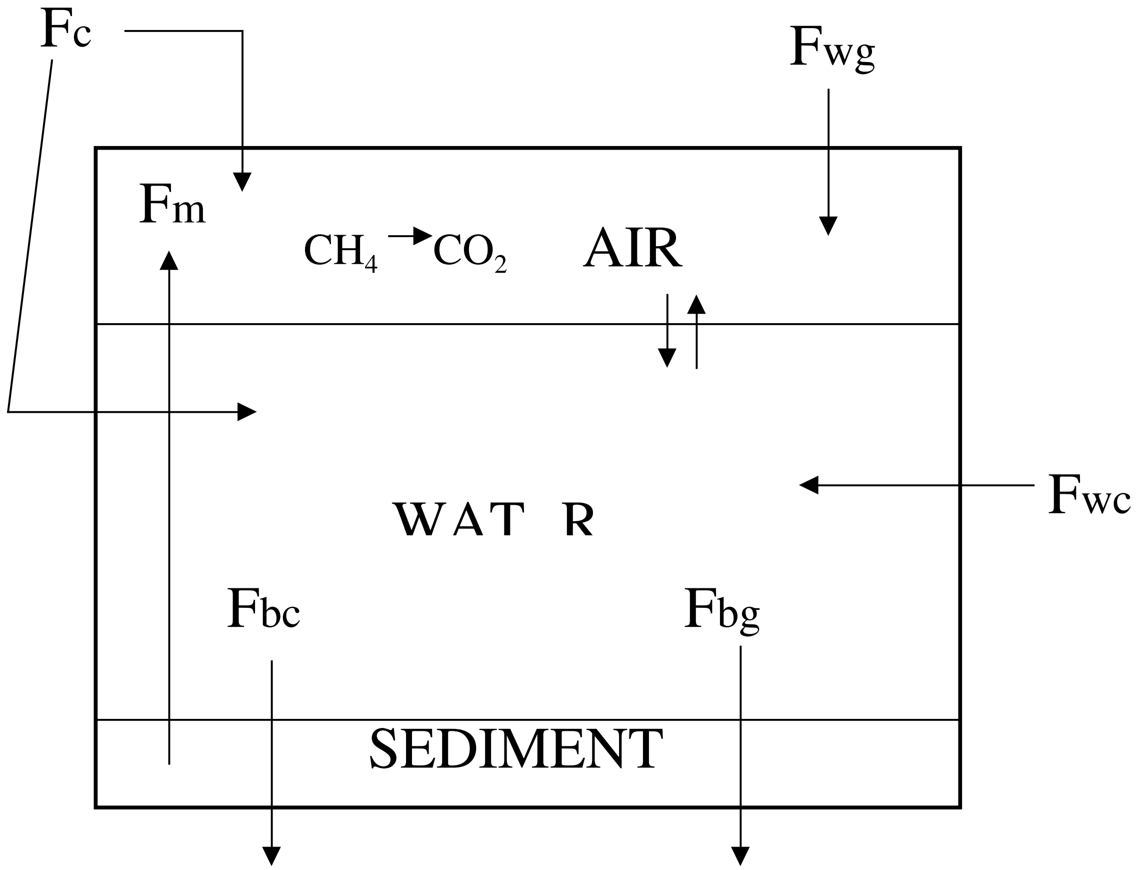

Figure 3. Schematic representation of our model of the carbon cycle with methane release and oxidation. The detailed description of the model is contained in Appendix A.

but would decrease the carbon dioxide concentrations until a new steady state was achieved. In essence, the climatic response to increased methane would be greatly dampened by the silicate weathering feedback on CO_2, reaching a steady state with similar net radiative forcing, slightly higher methane, and much lower CO_2.

[33] We have explored this using a simplified version of the GEOCARB model [*Berner*, 1991, 1994; *Berner and Kothavala*, 2001] (Figure 3). Detailed derivation of the present model is given in Appendix A. Mass balance model expressions for methane and for CO_2 are

$$dM/dt = F_{\mathrm{m}} - k_{\mathrm{m}}M,$$

$$dC/dt = \{Fc - F_{\mathrm{wsi}}(\mathrm{o})\exp\{0.09[\Gamma_{\mathrm{mc}}\ln((C + \lambda M)/(C_{\mathrm{o}} + \lambda M_{\mathrm{o}}))]\} + F_{\mathrm{m}}\}/(1{+}P)\text{'}$$

where M is mass of methane in the atmosphere, C is the mass of CO_2 in the atmosphere, F_{m} is input of methane to the atmosphere from anoxic basin sediments, F_{c} is the input of CO_2 to the atmosphere from volcanoes, metamorphism, and diagenesis, k_{m} is the decay constant for methane oxidation to CO_2 in the atmosphere due to reaction with OH radical, F_{wsi} is the uptake of CO_2 via the weathering of Ca and Mg silicates with the resulting HCO_3^- precipitated in the oceans as Ca and Mg carbonates, Γ_{mc} is the temperature sensitivity to changes in greenhouse gas concentration (assumed here to be 4°C for a doubling of both gases), λ is the radiative forcing, per molecule, for atmospheric methane relative to CO_2 ($\cong$ 25), t is time, and subscripts (o) represent the present values. The parameter P is defined as

$$P = \left[2M_{\mathrm{Ca}}K/\left(4M_{\mathrm{Ca}}^2C_{\mathrm{w}} + KC\right)\right].$$

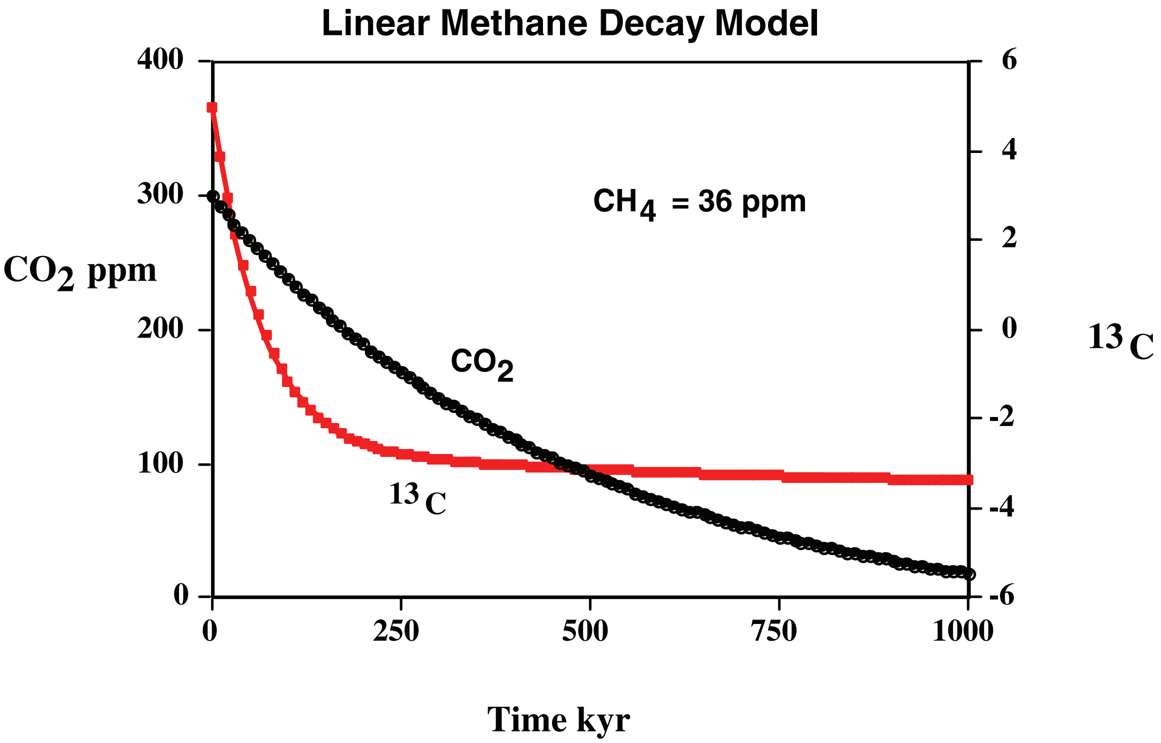

Figure 4. Model results for an initial carbon dioxide concentration of 300 ppm for the linear methane decay model. The addition of a flux of methane to the atmosphere produces a steady state concentration of 36 ppm methane, while CO_2 drops to 100 ppm in ~500,000 years owing to enhanced silicate weathering.

It represents the assumption of exchange equilibrium between the mass of atmospheric CO_2 (C) and the mass of dissolved HCO_3^- (C_w) and Ca^{++} (M_{Ca}) in the oceans. The parameter K (see Appendix A) represents the equilibrium "constant" in terms of global masses for the reaction

$$CaCO_3 + CO_2 + H_2O \leftrightarrow 2HCO_3^- + Ca^{++}.$$

Use of P allows for the degassing of CO_2 to/from the atmosphere from/to the oceans accompanying externally forced changes in atmospheric CO_2 levels. Treatment of atmosphere-ocean carbon exchange according to the dynamic model of *Berner et al.* [1983] gives similar results to this much simpler equilibrium approach.

[34] In the modeling it was assumed that methane is produced in bottom sediments, stored as methane hydrate, and then transferred to the atmosphere through an anoxic, low-sulfate ocean where little methane is consumed. The methane is oxidized to CO_2 in the atmosphere, and the resulting CO_2 is transferred partly to the oceans upon equilibration with seawater. It is also reasonable that methane should also reach a steady state concentration in the atmosphere rapidly. Thus it is assumed that $dM/dt = 0$ and $F_m = k_m M$.

[35] The rather lengthy derivation for the mass balance equations for $\delta^{13}C$ in the ocean is presented in Appendix A and includes estimated values for the flux and isotopic composition of volcanically derived CO_2, the flux and isotopic composition of carbon from the weathering of carbonates and organic matter on land, the flux and isotopic composition of methane from methanogenesis, the isotopic fractionation between seawater and both atmospheric CO_2 (−7‰) and buried organic matter (−25‰), and the flux of carbon from the atmosphere to form Ca-Mg carbonates due to Ca-Mg silicate weathering.

[36] The results of a sample calculation are shown in Figure 4. For this parameterization the model requires a sustained level of CH_4 of 36 ppm to

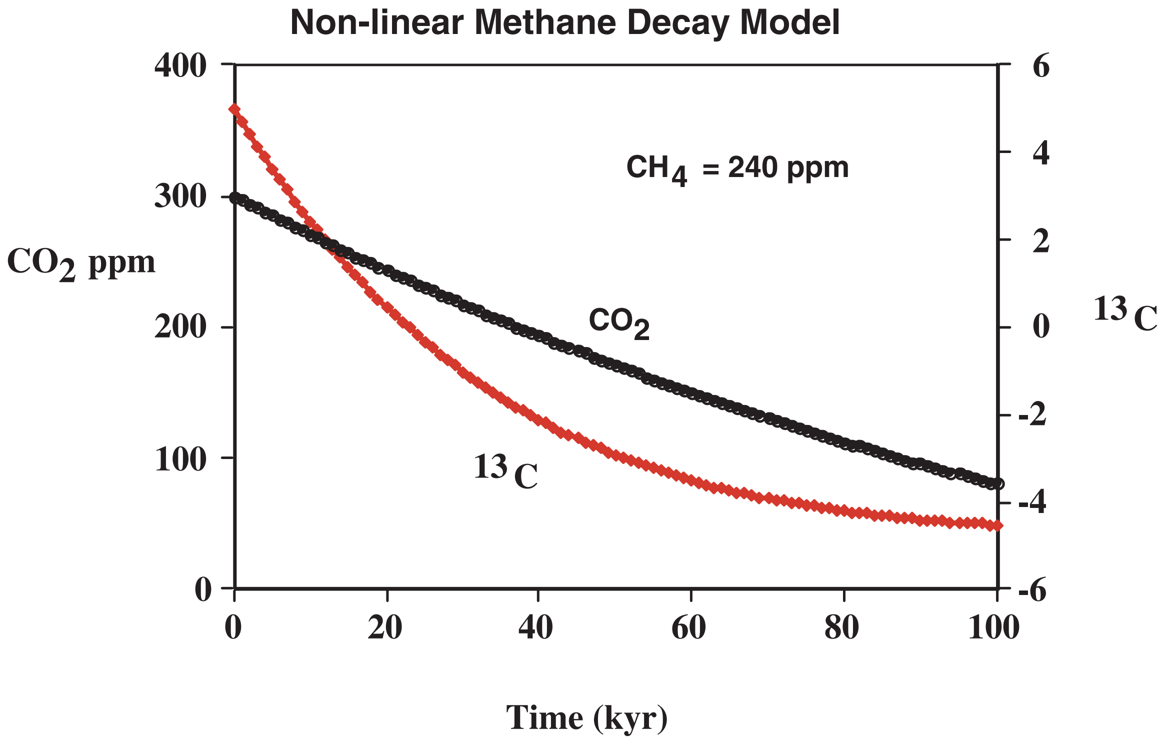

Figure 5. Model results for an initial carbon dioxide concentration of 300 ppm for the nonlinear methane decay model. The addition of a flux of methane to the atmosphere produces a steady state concentration of 240 ppm methane, while CO_2 drops to 100 ppm in ~100,000 years owing to enhanced silicate weathering.

bring about the drops both in atmospheric CO_2 and in $\delta^{13}C$ for the oceans. Values of methane flux (F_m) and methane decay constant (k_m) were varied to see how different values for atmospheric methane concentration and input flux would affect results. It was found that only limited ranges of values for F_m and k_m were possible to enable a drop in CO_2 without excessive or deficient drop in $\delta^{13}C$ of the oceans. Initial values of CO_2 (300 ppm) and $\delta^{13}C$ (5‰) were assumed in all calculations with the $\delta^{13}C$ value based on measurements of carbonates immediately underlying the glacial deposits. Use of a high k_m value appropriate for the modern atmosphere (k_m = 100,000 myr^{-1} equivalent to mean residence times of ~10 years) or even one tenth of this (equivalent to mean residence time of 100 years) resulted in too low atmospheric methane concentrations (and thus too small a greenhouse effect) and a rise in CO_2 from methane oxidation. Use of too high an F_m value resulted in an unreasonably large integrated source for the methane. The best fit values used in constructing Figure 4 are k_m = 500 myr^{-1} (2300 year mean residence time) and $F_m = 3 \times 10^{18}$ mol myr^{-1}.

[37] Other, more complex nonlinear formulations for methane oxidation are possible which may allow for the concentration of methane in the atmosphere (and the residence time) to rise more rapidly with a rise in the flux as the oxidative sink becomes saturated. Indeed, this might be expected if tropospheric sinks for methane, such as the OH radical, become saturated. To illustrate this point, an alternate, but arbitrary, sublinear half-power formulation for atmospheric methane oxidation can be employed:

$$dM/dt = F_m - k'_m M^{0.5}.$$

Using the values $k'_m = 50 \times 10^9$ $\text{mol}^{0.5}$ myr^{-1} and $F_m = 10 \times 10^{18}$ mol myr^{-1}, we obtain the results shown in Figure 5. Note that the drop in CO_2 is quicker and the standing concentration of CH_4 is much higher (240 ppm) than when using the linear decay model. The assumed value for k'_m of 50 ×

10^9 mol myr^{-1} is equivalent to an atmospheric methane half-life of 2300 years, as compared to the half-life for the linear model of 1400 years.

[38] Is the amount of methane released from methane hydrate reservoirs reasonable in terms of the storage capacity in the world oceans? The amount released from hydrate reservoirs over the time period of the linear model calculation (1 million years) is ~35,000 GtC, or 15 times what was proposed for the Paleocene-Eocene boundary [*Dickens et al.*, 1995]. For the sublinear model the amount released in 100,000 years is only 12,000 GtC. With sustained, highly efficient organic carbon burial for tens of millions of years preceding the glaciations, such quantities may not be unreasonable, as the release is not abrupt. In general, if the duration of the excursion is shorter, a smaller methane hydrate reservoir is required. Better constraints on the timing of the negative isotope excursion would help refine this hypothesis.

[39] If the carbon cycle existed in this delicate state of balance with both CO_2 and methane sharing the greenhouse gas forcing, the Earth would be vulnerable to a catastrophic destabilization of climate. Even with a lower level of atmospheric oxygen, the residence time of methane in the atmosphere-ocean is several orders of magnitude shorter than for CO_2 because carbon dioxide in the atmosphere is buffered by the large ocean reservoir of dissolved inorganic carbon. If the methane flux to the atmosphere ceased for a period on the order of the residence time of methane, oxidation would remove most of the methane from the atmosphere. The CO_2, buffered by air-sea gas exchange, cannot adjust quickly enough to replace the greenhouse forcing from the methane, and so the Earth would experience a climatic crisis, plunging the already cold planet past the threshold for the initiation of a snowball Earth. This scenario is similar to that proposed by *Pavlov et al.* [2000], who suggest that the oxidation of ~100 ppm methane in the Paleoproterozoic atmosphere due to the rise of atmospheric oxygen could initiate a snowball glaciation at that time. The critical features of the hypothesis described here are that much lower methane levels are required to develop the climate instability (i.e., ~36 ppm) and that the effect is produced by slow release of methane to the Proterozoic atmosphere, not an irreversible shift in atmospheric composition, allowing this phenomenon to happen several times in succession. This latter point makes our hypothesis consistent with the observation of at least two and possibly more glaciations in the Neoproterozoic.

[40] The idea presented here depends critically on achieving sufficient levels of methane in the atmosphere prior to the glaciations to carry a substantial portion of the total greenhouse forcing. Whether this requires lower oxygen concentrations remains unknown, depending critically on the kinetics of photochemical reactions in the stratosphere and the response of atmospheric methane concentrations to a rise in methane flux. One possibility is that an enhanced and sustained flux of methane could contribute to the lowering of atmospheric oxygen itself, leading to its slow accumulation in the atmosphere and the reduction of CO_2 through silicate weathering as described above [*Halverson et al.*, 2002]. In this scenario the drop in $\delta^{13}C$ would commence as methane was released from hydrates but would have a minimal effect on climate forcing until oxygen levels were low enough to allow atmospheric methane levels to rise. The problem with this idea is that it depends on methane reducing atmospheric oxygen by overwhelming any other buffering capacity in the system. If other biogeochemical cycles involved in the regulation of atmospheric oxygen had a faster response time to a reduction in oxygen, an increase in flux of methane to the atmosphere would have no effect on atmospheric oxygen. However, as there is no widely accepted theory for what buffers oxygen levels either today or in the Proterozoic, this idea warrants further attention.

[41] What would drive the release of methane from a large hydrate reservoir, and what would cause that release to end, triggering the climatic crisis? As the drop in $\delta^{13}C$, and hence the release of methane, is not abrupt but occurs over at least 100,000 years, a tectonic mechanism, such as the slow uplift of a hydrate reservoir to shallower depth, is a possibility. Such a mechanism could be enhanced by the ocean warming driven by the accumulation of methane in the atmosphere. The cessation of the methane flux might be simply due to the exhaustion of the existing

methane hydrate reservoir, as the amount of methane released over hundreds of thousands of years is substantial. Once the slow methane release began from such a large hydrate reservoir, it was only a matter of time until the supply of methane was exhausted and a greenhouse crisis ensued.

[42] The strength of the methane hypothesis described here is that it connects the ~10‰ drop in $\delta^{13}C$ of marine carbonate with the onset of a global glaciation. It is counterintuitive in that the release of methane, a powerful greenhouse gas, leads to a global cooling, not a warming. All other hypotheses for lowering the $\delta^{13}C$ of marine carbonate so precipitously imply an increase in atmospheric CO_2 and a warmer climate [*Halverson et al.*, 2002]. The idea is admittedly speculative and may be difficult to test as direct evidence for slow, sustained methane release may be difficult to find. However, additional modeling efforts with more complete atmospheric chemical kinetics will help determine whether this mechanism can be sustained. One would also expect to see similarly large negative carbon isotope excursions beneath other Neoproterozoic glacial deposits, although glacial erosion may make this difficult to find.

5. Conclusion

[43] The initiation of a snowball glaciation is linked to a variety of unusual perturbations of the carbon cycle operating over different timescales. The concentration of continental area in the tropics was a critical boundary condition necessary for the onset of glaciation, both because the existence of substantial continental area at high latitudes may prevent atmospheric carbon dioxide from getting too low and because a tropical concentration of continental area may lower atmospheric carbon dioxide by intensifying the weathering feedback and by enhancing the efficiency of organic carbon burial. Efficient organic carbon burial sustained over tens of millions of years, required by the high carbon isotopic compositions of preglacial carbonate, may lead to the buildup of enormous quantities of methane, presumably in hydrate reservoirs. The release of this methane may explain the drop in $\delta^{13}C$ values immediately before the glaciation and may provide a trigger for the onset of a runaway ice-albedo feedback through the interaction of atmospheric methane, carbon dioxide, and silicate weathering.

Appendix A: Model for Snowball Initiation

[44] The model is summarized in Figure 3. It consists of mass balance expressions for (1) atmospheric methane, (2) combined atmospheric + oceanic carbon, and (3) isotope mass balance for combined atmospheric + oceanic carbon.

A1. Total Carbon Mass Balance

[45] The total carbon mass balance expressions are

$$dM/dt = F_m - F_{om}, \tag{A1}$$

$$d(C + C_w)/dt = F_c + F_{wc} + F_{wg} - F_{bc} - F_{bg} + F_{om}, \tag{A2}$$

where

M mass of methane-C in atmosphere;
C mass of CO_2-C in atmosphere;
C_w mass of inorganic-C in the oceans;
F_m input of methane to the atmosphere from anoxic basin sediments;
F_{om} oxidation of methane to CO_2 in the atmosphere;
F_c input of CO_2 to the atmosphere from volcanoes, metamorphism and diagenesis;
F_{wc} input of bicarbonate to the oceans from carbonate weathering on land;
F_{wg} input of CO_2 to the atmosphere from organic weathering on land;
F_{bc} burial of calcium carbonate in oceanic sediments;
F_{bg} burial of organic carbon in oceanic sediments;
t time.

Several simplifications can be made. The first is

$$F_{wsi} = F_{bc} - F_{wc}, \tag{A3}$$

where F_{wsi} is the rate of atmospheric CO_2 uptake via weathering of Ca and Mg silicates followed by precipitation of the Ca and Mg in marine sediments as carbonates [*Berner*, 1991].

[46] If the organic subcycle is balanced we may also assume

$$F_{\mathrm{wg}} = F_{\mathrm{bg}}, \tag{A4}$$

and because of the short residence time of methane in the atmosphere, the mass of atmospheric methane reaches steady state rapidly:

$$F_{\mathrm{om}} = F_{\mathrm{m}}. \tag{A5}$$

From equations (A2)–(A5),

$$d(C + C_{\mathrm{w}})/dt = F_{\mathrm{c}} - F_{\mathrm{wsi}} + F_{\mathrm{m}}. \tag{A6}$$

In terms of atmospheric CO_2,

$$dC/dt = (F_{\mathrm{c}} - F_{\mathrm{wsi}} + F_{\mathrm{m}}) - dC_{\mathrm{w}}/dt. \tag{A7}$$

To quantify dC_{w}/dt, a simplification to the problem can be done by assuming, reasonably, that oceanic and atmospheric carbon are in exchange equilibrium with one another and that the oceans are saturated with calcium carbonate. This is done by using a global equilibrium expression for the reaction

$$\mathrm{CaCO_3} + \mathrm{CO_2} + \mathrm{H_2O} \leftrightarrow 2\mathrm{HCO_3^-} + \mathrm{Ca^{++}},$$

which is [see *Berner et al.*, 1983]

$$M_{\mathrm{Ca}} C_{\mathrm{w}}^2 / C = K, \tag{A8}$$

where M_{Ca} is the mass of calcium in the oceans.

[47] We can assume from the above reaction that $dM_{\mathrm{Ca}}/dt = 0.5\ dC_{\mathrm{w}}/dt$ if we make the first-order assumption of the approximate equivalence of carbonate alkalinity and C_{w}. In this way, dC/dt and dC_{w}/dt can be related to one another. By differentiation and substitution we obtain

$$dC_{\mathrm{w}}/dt = \left[2M_{\mathrm{Ca}}K/\left(4M_{\mathrm{Ca}}^2 C_{\mathrm{w}} + KC\right)\right] dC/dt. \tag{A9}$$

Letting $P = [2M_{\mathrm{Ca}}K/(4M_{\mathrm{Ca}}{}^2 C_{\mathrm{w}} + KC)]$, we obtain from (A7) and (A9)

$$dC/dt = (F_{\mathrm{c}} - F_{\mathrm{wsi}} + F_{\mathrm{m}})/(1 + P). \tag{A10}$$

Now, silicate weathering rate can be assumed to be a simple function of temperature, which is, in turn, a function of the CO_2 and CH_4 contents of the atmosphere. From *Berner* [1991, 1994],

$$F_{\mathrm{wsi}}(T)/F_{\mathrm{wsi}}(T_{\mathrm{o}}) = \exp\{0.09(T - T_{\mathrm{o}})\}, \tag{A11}$$

where T is temperature and subscript o refers to the initial state.

[48] A simple representation of greenhouse warming is (modified from *Berner* [1991, 1994])

$$T - T_{\mathrm{o}} = \Gamma_{\mathrm{mc}} \ln[(C + \lambda M)/Co + \lambda Mo], \tag{A12}$$

where Γ_{mc} refers to the combined methane plus CO_2 greenhouse response and λ is the ratio of the greenhouse response of methane per molecule to that of CO_2.

[49] From GCM results applied to a cold climate, Γ_{c} = 6°C; also, λ = 25. Combining equations (A10)–(A12),

$$\begin{aligned} dC/dt = \{&F_{\mathrm{c}} - F_{\mathrm{wsi}}(T_{\mathrm{o}})\exp\{0.09[\Gamma_{\mathrm{mc}}\ln((C + \lambda M) \\ &/(Co + \lambda M))]\} + F_{\mathrm{m}}\}/(1 + P). \end{aligned} \tag{A3}$$

For the oxidation of methane to CO_2 in the atmosphere a simple first approximation is that of first-order decay with the rate constant being a function of the OH and O_2 level of the atmosphere. At steady state,

$$F_{\mathrm{om}} = F_{\mathrm{m}} = k_{\mathrm{m}} M. \tag{A14}$$

Or, alternatively (see text),

$$F_{\mathrm{om}} = F_{\mathrm{m}} = k'_{\mathrm{m}} M^{0.5}. \tag{A15a}$$

One can assume that k_{m} and k'_{m} vary with time or hold them constant as a first approximation.

[50] By numerical integration, for fixed $F_{\mathrm{wsi}}(T_{\mathrm{o}})$, M_{o}, C_{o}, λ, F_{c}, and P, using equations (A13) and (A14), one can calculate C as a function of time for different values of F_{m} and M for a fixed k_{m} or k'_{m}. For initial conditions the value of P (equation (A10)) is calculated from current values for C, C_{w}, and M_{Ca} although use of a different ocean chemistry and atmospheric CO_2 level (but still

maintaining equilibrium via equation (A8)) is possible. In this way, CO_2 evolution can be calculated for changes in methane input.

A2. Isotope Mass Balance

[51] The analogous expression for atmosphere plus ocean isotope mass balance is

$$d(R_aC + R_wC_w)/dt = R_vF_c + R_gF_{wg} + R_cF_{wc} + R_mF_m - R_{bc}F_{bc} - R_{bg}F_{bg}, \tag{A15b}$$

where

R	$^{13}C/^{12}C$ ratio
R_a	R for atmospheric CO_2
R_w	R for oceanic carbon
R_v	R for volcanic input
R_g	R for organic matter undergoing weathering
R_c	R for $CaCO_3$ weathering
R_m	R for methane input
R_{bc}	R for marine carbonate burial (assumed equal to the value for seawater R_w)
R_{bg}	R for marine organic carbon burial

Again, because $F_{bc} = F_{wsi} + F_{wc}$ and assuming that $F_{wg} = F_{bg}$, equation (A15a, A15b) simplifies to

$$d(R_aC + R_wC_w)/dt = R_vF_c + (R_c - R_{bc})F_{wc} + \left(R_g - R_{bg}\right)F_{wg} + R_mF_m - R_{bc}F_m - R_{bc}F_{wsi}. \tag{A16}$$

Introducing δ‰ terminology, equation (A16) can be rewritten as

$$Cd(\delta_a)/dt + (\delta_a)dC/dt + C_wd(\delta_w)/\delta t + (\delta_w)dC_w/dt = \delta_vF_c + (\delta_c - \delta_{bc})F_c + \left(\delta_g - \delta_{bg}\right)F_{wg} + \delta_mF_m - \delta_wF_{wsi}. \tag{A17}$$

A great simplifying assumption is that of isotopic equilibrium between the atmosphere and the ocean, such that

$$\delta_a = \delta_w - 7 \tag{A18}$$

and

$$d(\delta_a)dt = d(\delta_w)/dt. \tag{A19}$$

Also, the δ_{bg} value for organic matter being buried can be represented by a constant frationation with respect to the δ value for seawater [e.g., see *Garrels and Lerman*, 1984]:

$$\delta_{bg} = \delta_w - 25. \tag{A20}$$

With these assumptions and substituting equations (A3), (A9), and (A10) for F_{bc}, dC_w/dt, and dC/dt, we obtain the final expression:

$$(C_w + C)d(\delta_w)/\delta t = (\delta_vF_c + (\delta_g - \delta_w + 25)F_{wg} + \delta_mF_m + (\delta_c - \delta_w)F_{wc} - \delta_wF_{wsi} - [(\delta_w - 7)/(1 + P)](F_c - F_{wsi} + F_m) - [\delta_wP/(1 + P)](F_c - F_{wsi} + F_m). \tag{A21}$$

From equation (A21) the value of δw, the carbon isotopic composition of seawater, is obtained by numerical integration. For this purpose the following values (in 10^{18} mol myr^{-1} or ‰) were used: $F_c = 6$; $F_{wc} = 13\exp\{0.09\ [\Gamma_{mc} \ln((C + \lambda M)/(Co + \lambda Mo))]\}\}$; $F_{wg} = 5$, $\delta_v = -6$, $\delta_c = 5.4$ (representing the weathering of just previously deposited isotopically heavy carbonates and providing isotopic mass balance prior to perturbation by methane release); $\delta_g = -25$; $\delta_m = -70$; $P = 26.67$ at start based on $C = 0.05$, $C_w = 2.8$, $M_{Ca} = 14$, and $K = 2195.2$ (values for the present atmosphere and ocean).

Acknowledgments

[52] The authors thank Lee Kump, Jim Kasting, and Jerry Dickens for comments that greatly improved the manuscript. This work was supported by NSF awards OCE-9733688 and EAR-9905495 and by the NASA/Harvard Astrobiology Institute.

References

Abolins, M. J., R. L. Charlton, B. P. Wernicke, and R. L. Ripperdan, Three distinct Neoproterozoic glacial intervals recorded in Western Laurentia and Australia, *Geol. Soc. Am. Abstr. Programs*, *31*, A–485, 1999.

Alkmim, F. F., S. Marshak, and M. A. Fonseca, Assembling West Gondwana in the Neoproterozoic: Clues from the São Francisco Craton region, Brazil, *Geology*, *29*, 319–322, 2001.

Aller, R. C., N. E. Blair, Q. Xia, and P. D. Rude, Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments, *Cont. Shelf Res.*, *16*, 753–786, 1996.

Anderson, S. P., J. I. Drever, and N. F. Humphrey, Chemical weathering in glacial environments, *Geology*, *25*, 399–402, 1997.

Berner, R. A., Rate control of mineral dissolution under Earth surface conditions, *Am. J. Sci.*, *278*, 1235–1252, 1978.

Berner, R. A., Burial of organic carbon and pyrite sulfur in the modern ocean: Its geochemical and environmental significance, *Am. J. Sci.*, *282*, 451–473, 1982.

Berner, R. A., A model for atmospheric CO (sub 2) over Phanerozoic time, *Am. J. Sci.*, *291*, 339–376, 1991.

Berner, R. A., GEOCARB II: A revised model of atmospheric CO (sub 2) over Phanerozoic time [modified], *Am. J. Sci.*, *294*, 56–91, 1994.

Berner, R. A., The carbon cycle and CO(sub 2) over Phanerozoic time: The role of land plants, *Philos. Trans. R. Soc. London, Ser. B*, *353*, 75–82, 1998.

Berner, R. A., and Z. Kothavala, GEOCARB III: A revised model of atmospheric CO^2 over phanerozoic time, *Am. J. Sci.*, *301*(2), 182–204, 2001.

Berner, R. A., A. C. Lasaga, and R. M. Garrels, The carbonate-silicate geochemical cycle and its effects on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci.*, *283*, 641–683, 1983.

Brasier, M. D., and J. F. Lindsay, A billion years of environmental stability and the emergence of eukaryotes: New data from northern Australia, *Geology*, *26*, 555–558, 1998.

Budyko, M. I., The effect of solar radiation variations on the climate on the Earth, *Tellus*, *21*, 611–619, 1969.

Caldeira, K., and J. F. Kasting, Susceptibility of the early Earth to irreversible glaciation caused by carbon dioxide clouds, *Nature*, *359*, 226–228, 1992.

Canfield, D. E., and A. Teske, Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies, *Nature*, *382*, 127–132, 1996.

Chandler, M. A., and L. E. Sohl, Climate forcings and the initiation of low-latitude ice sheets during the Neoproterozoic Varanger glacial interval, *J. Geophys. Res.*, *105*, 20,737–20,756, 2000.

Corsetti, F. A., and A. J. Kaufman, High resolution chemostratigraphy of the Neoproterozoic Beck Spring dolomite, Great Basin, USA, *Geol. Soc. Am. Abstr. Programs*, *32*, A–144, 2000.

Derry, L. A., A. J. Kaufman, and S. B. Jacobsen, Sedimentary cycling and environmental change in the late Proterozoic: Evidence from stable and radiogenic isotopes, *Geochim. Cosmochim. Acta*, *56*, 1317–1329, 1992.

Dickens, G. R., J. R. O'Neil, D. K. Rea, and R. M. Owen, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene, *Paleoceanography*, *10*, 965–971, 1995.

Eriksson, E., Air-ocean-icecap interactions in relation to climatic fluctuations and glaciation cycles, *Meteorol. Monogr.*, *8*, 68–92, 1968.

Evans, D. A. D., Stratigraphic, geochronological, and paleomagnetic constraints upon the Neoproterozoic climatic paradox, *Am. J. Sci.*, *300*, 347–433, 2000.

Evans, D. A., N. J. Beukes, and J. L. Kirschvink, Low-latitude glaciation in the Palaeoproterozoic era, *Nature*, *386*, 262–266, 1997.

Garrels, R. M., and A. Lerman, Coupling of the sedimentary sulfur and carbon cycles—An improved model, *Am. J. Sci.*, *284*(9), 989–1007, 1984.

Gibbs, M. T., and L. R. Kump, Global chemical erosion during the last glacial maximum and the present: Sensitivity to changes in lithology and hydrology, *Paleoceanography*, *9*, 529–543, 1994.

Gough, D. O., Solar interior structure and luminosity variations, *Sol. Phys.*, *74*, 21–34, 1981.

Grotzinger, J. P., and A. H. Knoll, Anomalous carbonate precipitates: Is the Precambrian the key to the Permian?, *Palaios*, *10*, 578–596, 1995.

Halverson, G. P., P. F. Hoffman, D. P. Schrag, and A. J. Kaufman, A major perturbation of the carbon cycle before the Ghaub glaciation (Neoproterozoic) in Namibia: Prelude to snowball Earth?, *Geochem. Geophys. Geosyst.*, *3*(5), 10.1029/2001GC000244, 2002.

Hambrey, M. J., and W. B. Harland, *Earth's Pre-Pleistocene Glacial Record*, Cambridge Univ. Press, New York, 1981.

Harrison, C. G. A., What factors control mechanical erosion rates?, *Int. J. Earth Sci.*, *88*, 752–763, 2000.

Hay, W. W., E. J. Barron, and S. L. Thompson, Global atmospheric circulation experiments on an Earth with polar and tropical continents, *J. Geol. Soc. London*, *147*, 749–757, 1990.

Hayes, J. M., H. Strauss, and A. J. Kaufman, The abundance of (super 13) C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma, *Chem. Geol.*, *161*, 103–125, 1999.

Hedges, J. I., and R. G. Keil, Sedimentary organic-matter preservation—An assessment and speculative synthesis, *Mar. Chem.*, *49*, 81–115, 1995.

Hoffman, P. F., A. J. Kaufman, G. P. Halverson, and D. P. Schrag, A Neoproterozoic snowball Earth, *Science*, *281*, 1342–1346, 1998.

Hyde, W. T., T. J. Crowley, S. K. Baum, and W. R. Peltier, Neoproterozoic "snowball Earth" simulations with a coupled climatic/ice-sheet model, *Nature*, *405*, 425–429, 2000.

Hyodo, H., and D. J. Dunlop, Effect of anisotropy on the paleomagnetic contact test for a Grenville Dike, *J. Geophys. Res.*, *98*, 7997–8017, 1993.

Ingall, E., and R. A. Jahnke, Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis, *Mar. Geol.*, *139*, 219–229, 1997.

Junge, C. E., M. Schidlowski, R. Eichmann, and H. Pietrek, Model calculations for the terrestrial carbon cycle: Carbon isotope geochemistry and evolution of photosynthetic oxygen, *J. Geophys. Res.*, *80*, 4542–4552, 1975.

Kah, L. C., A. G. Sherman, G. M. Narbonne, A. H. Knoll, and A. J. Kaufman, Delta (super 13) C stratigraphy of the Proterozoic Bylot Supergroup, Baffin Island, Canada: Implications for regional lithostratigraphic correlations, *Can. J. Earth Sci.*, *36*, 313–332, 1999.

Kasting, J. F., H. D. Holland, and J. P. Pinto, Oxidant abundances in rainwater and the evolution of atmospheric oxygen, *J. Geophys. Res.*, *90*, 10,497–10,510, 1985.

Kaufman, A. J., A. H. Knoll, and G. M. Narbonne, Isotopes, ice ages, and terminal Proterozoic earth history, *Proc. Natl. Acad. Sci.*, *94*, 6600–6605, 1997.

Keil, R. G., D. B. Montluçon, F. G. Prahl, and J. I. Hedges, Sorptive preservation of labile organic matter in marine sediments, *Nature*, *370*, 549–552, 1994.

Keller, C. K., and B. D. Wood, Possibility of chemical weathering before the advent of vascular land plants, *Nature*, *364*, 223–225, 1993.

Kennedy, M. J., B. Runnegar, A. R. Prave, K. H. Hoffmann, and M. A. Arthur, Two or four Neoproterozoic glaciations?, *Geology*, *36*, 1059–1063, 1998.

Kent, D. V., and M. A. Smethurst, Shallow bias of paleomagnetic inclinations in the Paleozoic and Precambrian, *Earth Planet. Sci. Lett.*, *160*, 391–402, 1998.

Kirschvink, J. L., Late Proterozoic low-latitude global glaciation: The snowball Earth, in *The Proterozoic Biosphere*, edited by J. W. Schopf and C. Klein, pp. 51–52, Cambridge Univ. Press, New York, 1992.

Kirschvink, J. L., E. J. Gaidos, L. E. Bertani, N. J. Beukes, J. Gutzmer, L. N. Maepa, and R. E. Steinberger, Paleoproterozoic snowball Earth: Extreme climatic and geochemical global change and its biological consequences, *Proc. Natl. Acad. Sci.*, *97*, 1400–1405, 2000.

Knoll, A. H., J. M. Hayes, A. J. Kaufman, K. Swett, and I. B. Lambert, Secular variation in carbon isotope ratios from upper Proterozoic successions of Svalbard and East Greenland, *Nature*, *321*, 832–838, 1986.

Kump, L. R., M. Arthur, M. Patzkowsky, M. Gibbs, D. S. Pinkus, and P. Sheehan, A weathering hypothesis for glaciation at high atmospheric pCO_2 in the Late Ordovician, *Palaeoclimatol. Palaeoecol. Palaeogeogr.*, *152*, 173–187, 1999.

Lindsay, J. F., and M. D. Brasier, A carbon isotope reference curve for ca. 1700–1575 Ma, McArthur and Mount Isa basins, northern Australia, *Precambrian Res.*, *99*, 271–308, 2000.

Marshall, H. G., J. C. G. Walker, and W. R. Kuhn, Long-term climate change and the geochemical cycle of carbon, *J. Geophys. Res.*, *93*, 791–801, 1988.

Mayer, L. M., Extent of coverage of mineral surfaces by organic matter in marine sediments, *Geochim. Cosmochim. Acta*, *63*, 207–215, 1999.

McKirdy, D. M., J. M. Burgess, N. M. Lemon, X. Yu, A. M. Cooper, V. A. Gustin, R. J. F. Jenkins, and R. A. Booth, A chemostratigraphic overview of the Cryogenian Interglacial Sequence in the Adelaide Fold-Thrust Belt, South Australia, *Precambrian Res.*, *106*, 149–186, 2001.

Meert, J. G., and R. Van der Voo, The assembly of Gondwana 800–550 Ma, *J. Geodyn.*, *23*, 223–235, 1997.

Miller, K. G., R. G. Fairbanks, and G. S. Mountain, Tertiary oxygen isotope synthesis, sea-level history, and continental margin erosion, *Paleoceanography*, *2*, 741–761, 1987.

Moulton, K. L., J. West, and R. A. Berner, Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering, *Am. J. Sci.*, *300*, 539–570, 2000.

Norris, R. D., and U. Röhl, Carbon cycling and chronology of climate warming during the Palaeocene/Eocene transition, *Nature*, *401*, 775–778, 1999.

Ohte, N., and N. Tokuchi, Geographical variation of the acid buffering of vegetated catchments: Factors determining the bicarbonate leaching, *Global Biogeochem. Cycles*, *13*, 969–996, 1999.

Pavlov, A. A., J. F. Kasting, L. L. Brown, K. A. Rages, and R. Freedman, Greenhouse warming by CH (sub 4) in the atmosphere of early Earth, *J. Geophys. Res.*, *105*, 11,981–11,990, 2000.

Poulsen, C. J., R. T. Pierrehumbert, and R. L. Jacob, Impact of ocean dynamics on the simulation of the Neoproterozoic ‘‘snowball Earth,’’*Geophys. Res. Lett.*, *28*, 1575–1578, 2001.

Prave, A. R., Two diamictites, two cap carbonates, two $\delta^{13}C$ excursions, two rifts: The Neoproterozoic Kingston Peak Formation, Death Valley, California, *Geology*, *27*, 339–342, 1999.

Retallack, G. J., Early forest soils and their role in Devonian global change, *Science*, *276*, 583–585, 1997.

Sellers, W. D., A global climatic model based on the energy balance of the Earth-atmosphere system, *J. Appl. Meteorol.*, *8*, 392–400, 1969.

Sohl, L. E., N. Christie-Blick, and D. V. Kent, Paleomagentic polarity reversals in Marinoan (ca. 600 Ma) glacial deposits of Australia: Implications for the duration of low-latitude glaciation in Neoproterozoic time, *Geol. Soc. Am. Bull.*, *111*, 1120–1139, 1999.

Symons, D. T. A., and A. D. Chiasson, Paleomagnetism of the Callander Complex and the Cambrian apparent polar wander path for North America, *Can. J. Earth Sci.*, *28*, 355–363, 1991.

Thompson, M. D., O. D. Hermes, S. A. Bowring, C. E. Isachsen, J. R. Bescancon, K. L. Kelly, Tectonostratigraphic implications of late Proterozoic U-Pb zircon ages in the Avalon Zone of southeastern New England, in *Avalonian and Related Peri-Gondwanan Terranes of the Circum-North Atlantic*, edited by R. D. Nance and M. D. Thompson, *Spec. Pap. Geol. Soc. Am.*, *304*, 179–191, 1996.

Van Cappellen, P., and E. D. Ingall, Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity, *Science*, *271*, 493–496, 1996.

Walker, J. C. G., The early history of oxygen and ozone in the atmosphere, *Pure Appl. Geophys.*, *117*, 498–512, 1979.

Walker, J. C. G., P. B. Hays, and J. F. Kasting, A negative feedback mechanism for the long-term stabilization of Earth's surface, *J. Geophys. Res.*, *86*, 9776–9782, 1981.

Walter, M. R., J. J. Veevers, C. R. Calver, P. Gorjan, and A. C. Hill, Dating the 840-544 Ma Neoproterozoic intervalby isotopes of strontium, carbon, sulfur in seawater, and some interpretative models, *Precambrian Res.*, *100*, 371–433, 2000.

Weil, A. B., R. Van der Voo, C. Mac Niocaill, and J. G. Meert, The Proterozoic supercontinent Rodinia: Paleomagnetically derived reconstructions for 1100 to 800 Ma, *Earth Planet. Sci. Lett.*, *154*, 13–24, 1998.

Williams, G. E., and P. W. Schmidt, Paleomagnetism of the Paleoproterozoic Gowganda and Lorrain formations, Ontario: Low paleoaltitude for Huronian glaciation, *Earth Planet. Sci. Lett.*, *153*, 157–169, 1997.

Wingate, M. T. D., and J. W. Giddings, Age and paleomagnetism of the Mundine Well dyke swarm, Western Australia: Implications for an Australian-Laurentia connection at 755 Ma, *Precambrian Res.*, *100*, 335–357, 2000.

Worsley, T. R., and D. L. Kidder, First-order coupling of paleogeography and CO (sub 2), with global surface temperature and its latitudinal contrast, *Geology*, *19*, 1161–1164, 1991.