



Aftermath of a snowball Earth

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[1] Using a simple 3-box model of the ocean-atmosphere system, we simulate the cycling of carbon and strontium in the aftermath of a global glaciation. Model simulations include the delivery of alkalinity to seawater from intense carbonate and silicate weathering under high $p\text{CO}_2$ conditions as well as ocean mixing, air-sea gas exchange, and biological productivity. The $\delta^{13}\text{C}$ of the first carbonate precipitated after the glaciation depends on the $p\text{CO}_2$, temperature, the saturation state of the surface ocean, and kinetic effects associated with mineral precipitation. With no biological productivity, the model produces $\delta^{13}\text{C}$ values between +1‰ and −3‰, consistent with observations. This is in direct contradiction with arguments by *Kennedy et al.* [2001a], who suggest that the $\delta^{13}\text{C}$ value of dissolved carbon in a snowball ocean (and directly afterward) must be −5‰. Kennedy et al. assume the carbon isotope cycle is in steady state, which does not apply to a global glaciation, and also neglect any effect of high $p\text{CO}_2$ on the carbonate chemistry of seawater. A major difference between our findings and the qualitative predictions of *Hoffman et al.* [1998] is our interpretation of the cap dolostone as representing an interval dominated by carbonate weathering of exposed continental shelves. As a result, the ~2‰ drop in the $\delta^{13}\text{C}$ observed in the cap dolostone is unlikely to be the product of Rayleigh distillation of atmospheric CO_2 via silicate weathering. Instead, we interpret the ~2‰ drop in the $\delta^{13}\text{C}$ values as indicative of an increase in sea surface temperature which lowers the fractionation between CO_2 and carbonate. Kinetic isotope effects associated with rapid precipitation from a highly supersaturated surface ocean may also be important. Rayleigh distillation of atmospheric CO_2 via silicate weathering is a viable explanation for the continued drop in the $\delta^{13}\text{C}$ values in the limestone sequence above the cap dolostone, with biological productivity and carbonate weathering driving a slow increase in $\delta^{13}\text{C}$ values once $p\text{CO}_2$ levels decline. Our study also simulates the cycling of strontium in seawater. In contrast to the finding of *Jacobsen and Kaufman* [1999] and *Kennedy et al.* [2001a], model simulations show a drop in $^{87}\text{Sr}/^{86}\text{Sr}$ of less than 0.001 during 5 million years of global glaciation and an increase of less than 0.001 over the entire episode of silicate weathering. Our calculations emphasize the importance of considering the changes in seawater chemistry due to high $p\text{CO}_2$ in evaluating the Snowball Earth hypothesis.

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1. Introduction

[2] The snowball Earth hypothesis, first described by *Kirschvink* [1992] and extended by *Hoffman et al.* [1998], explains the unusual features of multiple Neoproterozoic glaciations as the result of a global climate catastrophe when a runaway ice-albedo feedback led to an ice-covered planet. The hypothesis proposes that ice persisted for millions of years, effectively shutting down the hydrological cycle and greatly reducing the rate of silicate weathering, the major sink for carbon dioxide released from volcanic and metamorphic outgassing. Eventually, the buildup of atmospheric CO_2 from volcanic outgassing was sufficient to override the high planetary albedo, and rapid deglaciation ensued. The extremely high levels of atmospheric CO_2 gave rise to a transient super-greenhouse climate during which acidic meteoric waters, combined with an intensified hydrological cycle, lead to the rapid weathering of both carbonate and silicate rocks. This weathering delivered vast quantities of alkalinity to the oceans, resulting in the rapid precipitation of carbonate. Evidence supporting the snowball Earth hypothesis arises from the geologic presence of these carbonate successions, which are globally observed “capping” glacial deposits of late Neoproterozoic age (890–580 Ma). In addition to their unusual depositional context, these cap carbonates possess unique sedimentological textures and large negative carbon isotopic excursions of $\sim -5\text{‰}$ to -6‰ that have been cited by *Hoffman et al.* [1998] as predictable consequences of a snowball event.

[3] Using a simple energy balance model, *Caldeira and Kasting* [1992] calculated that 0.12 bar of CO_2 was required to overcome the high albedo of a completely glaciated planet today, although the uncertainties on the radiative effects of high CO_2 are quite large. At such a high $p\text{CO}_2$ and at calcite saturation, the atmosphere would contain approximately 8 times as much carbon as the surface ocean. As a result, *Hoffman et al.* [1998] argued that the $\delta^{13}\text{C}$ of the surface ocean would be dominated by gas exchange with the much larger atmospheric reservoir (with $\sim 8\text{‰}$ enrichment in HCO_3^- relative to $\text{CO}_{2(\text{g})}$). The massive flux of

alkalinity to the surface ocean from silicate weathering in the transient greenhouse climate following an episode of global glaciation would draw down atmospheric CO_2 , progressively depleting the atmospheric reservoir in ^{13}C via the process of Rayleigh distillation [*Hoffman et al.*, 1998]. This progressive depletion would be mirrored in the surface ocean and consequently in the precipitated CaCO_3 . As atmospheric CO_2 declines, the effect of atmospheric distillation on the $\delta^{13}\text{C}$ of the surface ocean would weaken, eventually being overcome by the isotopic enrichment resulting from the export production and burial of organic carbon. This would drive the $\delta^{13}\text{C}$ of the surface ocean back toward positive values.

[4] *Kennedy et al.* [2001a], on the basis of geochemical observations of the glacial deposits and cap carbonates, argued that the snowball Earth hypothesis is incorrect. The snowball Earth hypothesis predicts that biological productivity during a global glaciation should be greatly reduced due to the near complete ice cover. *Kennedy et al.* [2001a] suggested that this should result in an ocean with the $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC) approaching the mantle value ($\sim -5\text{‰}$), whereas they observe significantly higher values of CaCO_3 within the glacial deposits and at the base of the cap carbonates. In addition, they argued that the cap carbonates, which they defined as the transgressive portion of the carbonate sequence, were deposited in less than 10^4 years, and that this is too fast to permit sufficient silicate weathering to draw CO_2 down from ~ 0.1 bar to more normal levels. They also argued that the strontium isotopic composition of the cap carbonates should increase due to such rapid weathering, whereas they observe roughly uniform values. This complements the arguments of *Jacobsen and Kaufman* [1999], who argued that the strontium isotopic composition of seawater during a snowball Earth, in the absence of silicate weathering, should approach the composition of hydrothermal inputs whereas the composition of the cap carbonates they measured is very similar to the composition of preglacial carbonates.

[5] A number of alternative hypotheses for the formation of the cap carbonate succession and its associated negative isotopic excursion have been



proposed. One theory is that the cap carbonates result from extreme physical stratification of the ocean during glaciation. According to *Grotzinger and Knoll* [1995], in a stratified ocean, the $\delta^{13}\text{C}$ value of the surface ocean would increase as ^{13}C -depleted organic matter is exported to the anoxic deep ocean. Bacterial sulfate reduction would then remineralize the ^{13}C -depleted organic matter, producing HCO_3^- and CO_3^{2-} depleted in ^{13}C . Upon reinitiation of ocean mixing, alkalinity-laden deep water would initiate the precipitation of carbonates whose isotopic value would reflect the $\delta^{13}\text{C}$ value of the isotopically depleted deep ocean. Possible faults of this model include 1) the tendency of glacial meltwater to reduce, not increase, ocean mixing; 2) the difficulty in stratifying the ocean for periods longer than 1.5×10^3 years [*Zhang et al.*, 2001]; and 3) the difficulty in maintaining surface ocean productivity without a nutrient-rich flux from the deep ocean [*Hotinski et al.*, 2001].

[6] A recent explanation by *Kennedy et al.* [2001b] invokes a destabilization of methane hydrates during deglaciation as the mechanism for cap carbonate formation. *Kennedy et al.* [2001b] postulated that permafrost gas hydrates, produced by bacterial methanogenesis in organic-rich marine sediments exposed by the glacial sea level fall during the extended glacial interval, destabilize upon deglaciation and submersion of the marine sediments, releasing a pulse of isotopically depleted methane ($\sim -60\text{‰}$). Sulfate reduction at the submerged methane seeps would generate alkalinity depleted in ^{13}C , initiating the precipitation of CaCO_3 whose isotopic value would correspond to mixing between the extremely depleted methane-derived alkalinity ($\delta^{13}\text{C} \sim -60\text{‰}$) and the surface ocean ($\delta^{13}\text{C} \sim 0\text{‰}$). *Hoffman et al.* [2002a] point out several problems with the cold methane seep scenario: 1) cap carbonates occur even above glacial deposits formed below ice grounding lines, which were never subaerially exposed during glaciation and consequently permafrost could not have developed; 2) cap carbonates do not show the large local variability in $\delta^{13}\text{C}$ characteristic of methane-seep carbonates; 3) cap carbonate successions are observed blanketing basement units, precluding the existence of underlying methane seeps; and 4) the methane hydrate hypoth-

esis fails to explain the additional 2‰ to 3‰ drop above the cap dolostone.

[7] In this paper, we test whether the snowball Earth hypothesis is consistent with geochemical observations by simulating the evolution of the carbon cycle following an episode of global glaciation using a simple 3-box model of the ocean-atmosphere system. We test the sensitivity of our model to various atmospheric and oceanographic parameters related to the range of plausible climatic conditions predicted by the snowball Earth hypothesis of *Hoffman et al.* [1998]. We compare our model calculations with the observed carbon and Sr isotopic evidence, discussing critiques of the current snowball hypothesis with regards to our findings.

2. Stratigraphy and Chemistry of Cap Carbonates

[8] The cap carbonate sequences that directly overlie most Neoproterozoic glacial deposits are demarcated into two principle units: an initial unit of dolostone, here referred to as a cap dolostone, and a subsequent unit predominately composed of limestone. Together, we refer to these two units as the “cap carbonate sequence.” The cap dolostone is well documented in Neoproterozoic successions on every continent [*Williams*, 1979; *Fairchild and Hambrey*, 1984; *Hoffman et al.*, 1998] and is present in many clastic-dominated successions where it frequently constitutes the lone carbonate interval.

[9] The cap dolostone ranges in thickness from meters to tens of meters [e.g., *Grotzinger and Knoll*, 1995; *Kennedy*, 1996; *Hoffman et al.*, 1998] with a “knife-edge” basal contact that shows little evidence of subsequent reworking or a significant depositional hiatus [e.g., *Hoffman et al.*, 1998]. This abrupt juxtaposition of glacial and carbonate sequences is the source of the Neoproterozoic climate paradox, as it suggests an almost instantaneous transformation from glacial to tropical conditions [e.g., *Schermerhorn*, 1974]. It is located within a transgressive section of the stratigraphy, associated with the postglacial sea level rise. The depositional interval is constrained by the timescale of glacial-eustatic rise, which can be prescribed an upper limit of 10^4 years, based on

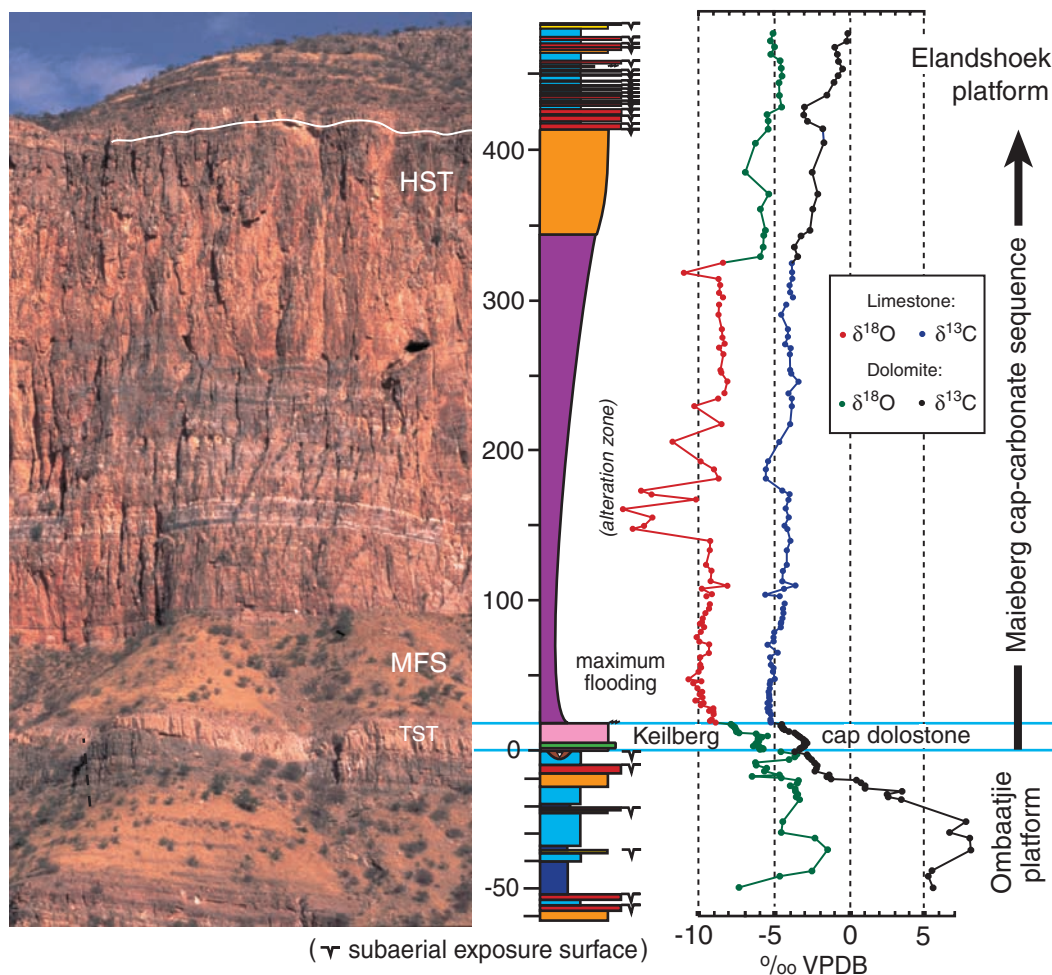


Figure 1. Stratigraphic and isotopic profile of the Maieberg cap carbonate sequence in Namibia [Hoffman and Schrag, 2002].

the duration of sea level rise in the Quaternary. The textures and lithofacies of the cap dolostone vary with locale [e.g., Spencer and Spencer, 1972; Kennedy, 1996; James et al., 2001], and include a number of unusual structures (vertically oriented tube-like pockets and oscillation mega-ripples) which suggest rapid sedimentation [Grotzinger and Knoll, 1995; Hoffman et al., 1998]. The phase of the primary precipitate is not well constrained and could reflect precipitation of primary dolomite in equilibrium with seawater or subsequent dolomitization of primary aragonite or calcite.

[10] The limestone unit that blankets the cap dolostone is locally composed of deeper water seafloor cements, which transition into flaggy, allodapic limestone (Maieberg Formation, Namibia) or black shale (Sheepbed Formation, Canada) [e.g., Grot-

zinger and Knoll, 1995; Kennedy, 1996; Soffer, 1998; James et al., 2001]. The cements form units up to 50 m in thickness and consist of aggregates of primary aragonite fans, ranging in size from meters to decameters, infilled with micritic sediments. The geometry of the growth habitat for the aragonite fans coupled with the high degree of supersaturation indicated by the presence of cements implies rapid precipitation and growth [Grotzinger and Knoll, 1995; Lasaga, 1998].

[11] The carbon isotopic profile of the cap carbonate sequence is dominated by a relatively abrupt $\sim 4\text{‰}$ drop in the $\delta^{13}\text{C}$ of CaCO_3 (Figure 1). The negative isotopic excursion is not confined to a particular unit within the cap sequence but appears relatively continuous through both the cap dolostone and limestone units. In the cap carbonate



<u>Carbonate equilibria and solubility</u>		0° C	30° C
$\text{CO}_2(\text{g}) \xrightarrow{k_0} \text{CO}_2(\text{aq})$	k_0	6.29×10^{-2}	2.52×10^{-2}
$\text{CO}_2(\text{aq}) \xrightarrow{k_1} \text{HCO}_3^- + \text{H}^+$	k_1	6.33×10^{-7}	10.47×10^{-7}
$\text{HCO}_3^- \xrightarrow{k_2} \text{CO}_3^{2-} + \text{H}^+$	k_2	3.53×10^{-10}	8.77×10^{-10}
$k_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$			
(Merbach, et al., 1973; Weiss, 1974)			
<u>Carbon Isotope fractionations</u>			
$\epsilon_{\text{CO}_2(\text{g})\text{CO}_2(\text{aq})} = -0.373 \times \frac{1000}{T} + 0.19\text{‰}^*$			
$\epsilon_{\text{CO}_2(\text{g})\text{HCO}_3^-} = 0.1141T + 10.78\text{‰}^*$			
$\epsilon_{\text{CO}_2(\text{g})\text{CO}_3^{2-}} = 0.052T + 7.22\text{‰}^*$			
$\epsilon_{\text{CO}_2(\text{g})\text{CaCO}_3(\text{calcite})} = 11.98\text{‰} - 0.12T^{**}$			
$\epsilon_{\text{CO}_2(\text{g})\text{CaCO}_3(\text{aragonite})} = 13.88\text{‰} - 0.13T^{**}$			
$\epsilon_{\text{HCO}_3^-\text{CaCO}_3(\text{dolomite})} = 2\text{‰} \text{ to } 3\text{‰}^{***}$			
$\epsilon_{\text{HCO}_3^-\text{C}_{\text{org}}} = -27\text{‰}$			
			*(Mook et al., 1974)
			** (Romanek et al., 1992)
			*** (Shepard and Schwarz, 1970)
			(Bottcher, 2000)

Figure 2. Equilibrium constants and fractionations used in model calculations.

sequence associated with the Ghaub glaciation in Namibia (i.e., the Maiberg formation), the isotopic profile of the 20 m thick cap dolostone consists of a $\sim 2\text{‰}$ drop in the $\delta^{13}\text{C}$ of CaCO_3 from an initial value of $\sim -2\text{‰}$ to a value of -4‰ at the dolostone-limestone transition. The negative excursion in the $\delta^{13}\text{C}$ of CaCO_3 continues up section into the limestone unit, reaching a minimum $\delta^{13}\text{C}$ value of -6‰ at ~ 45 m which is followed by a gradual increase in the $\delta^{13}\text{C}$ of CaCO_3 to a value of $\sim 0\text{‰}$ 480 m above the base of the sequence.

[12] The absence of the limestone unit of the cap sequence in many clastic-dominated successions has led some workers [Kennedy, 1996; Kennedy *et al.*, 2001a] to refer to the cap dolostone exclusively as the cap carbonate, assuming that it alone represents the geochemical response to the glaciation. However, the persistence of unusual sedimentological textures such as aragonitic fans and cements indicative of rapid precipitation of CaCO_3 from highly supersaturated waters as well as the continuity of the negative isotopic excursion through the dolostone and limestone units suggest that the

entire cap sequence is a product of the postglacial transient greenhouse, even if the record does not exist at all locations. Consequently, we assume in this study that the top of the cap dolostone does not signal the end of intensified carbonate and silicate weathering as argued by Kennedy *et al.* [2001a] but merely the cessation of postglacial sea level rise and the transition to alkalinity inputs from sources other than carbonate weathering of exposed carbonate platforms.

3. Model Description

[13] We simulate the evolution of the carbon cycle following a snowball deglaciation using a three-box model of the ocean-atmosphere system. The ocean is represented by a two-box reservoir consisting of a 3700 m thick deep ocean overlain by a 100 m thick surface ocean. Carbon speciation in the ocean is calculated from equilibrium constants given in Figure 2. For most of the sensitivity tests, we consider all changes in alkalinity to be driven by changes in Ca^{2+} , neglecting other cations for sim-



plicity. We explored the effects of changes in other cations such as Mg^{2+} in a smaller set of calculations. We also neglect borate and other nonconservative anions in contributing to alkalinity (i.e., $\text{Alk} = \text{HCO}_3^- + 2\text{CO}_3^{2-}$). The saturation state of the ocean is described by the product of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ with precipitation of CaCO_3 resulting when $[\text{Ca}^{2+}][\text{CO}_3^{2-}] > X \cdot K_{\text{sp}}$ where X is the degree of supersaturation and K_{sp} is the temperature dependent solubility constant of CaCO_3 given in Figure 2.

[14] The carbon isotopic compositions for species of carbon in the ocean-atmosphere system are calculated based on the equilibrium fractionation factors listed in Figure 2. Chemical and isotopic exchange occurs within each 10-year time step such that the surface ocean and atmosphere are always at chemical and isotopic equilibrium, except for the specified supersaturation of CaCO_3 . This is justified by considering the CO_2 equilibration time for the surface ocean-atmosphere system, which depends on the air-sea gas exchange as well as the amount of dissolved inorganic carbon in the surface ocean reservoir. Although the amount of carbon dissolved in the surface ocean would increase in contact with a high $p\text{CO}_2$ atmosphere, the rate of gas exchange would also increase with $p\text{CO}_2$, yielding an equilibration time similar to the modern ocean (<10 years).

[15] Each model time step simulates four concurrent processes: chemical weathering of carbonate and silicate rocks, the export production and burial of organic carbon, mixing between the surface and the deep ocean, and precipitation of calcium carbonate. Silicate weathering is simulated by a flux of alkalinity (or Ca^{2+}) from the continents to the surface ocean. This flux of alkalinity increases the saturation state of the surface ocean initiating the precipitation of CaCO_3 . Precipitation of CaCO_3 removes equal molar amounts of Ca^{2+} and carbon, lowering the total carbon in the surface ocean and atmosphere. This drop in total carbon raises the pH of the surface ocean, shifting carbon speciation toward more CO_3^{2-} and increasing the saturation state of the surface ocean, which drives additional precipitation. Thus, the net affect of silicate weathering results in the precipitation of calcium carbonate both from the direct input of alkalinity to the surface

ocean and from the draw down of CO_2 which causes additional excess supersaturation. Carbonate weathering is much simpler to simulate because carbonate weathering results in the addition of equal molar amounts of carbon and calcium to the ocean-atmosphere system. The CaCO_3 that subsequently precipitates simply represents a mass transfer of CaCO_3 from the continents to the sediment and does not affect the Ca^{2+} or carbon in the ocean or atmosphere. We do consider changes in supersaturation of the surface ocean induced by changes in rates of carbonate weathering. We model the export production of organic carbon from the surface ocean as net transfer of carbon from the surface to the deep ocean, where a fraction of that is then lost to sediment burial. This mass transfer is accompanied by an isotopic shift in both the surface and deep ocean resulting from the fractionation between HCO_3^- and photosynthate (C_{org}). The removal of carbon from the surface ocean increases the saturation state, driving precipitation of additional CaCO_3 . Mixing between the surface and deep ocean is modeled as the exchange of carbon and calcium. This exchange can shift the saturation state of the surface ocean, resulting in the precipitation or dissolution of CaCO_3 , and can change the isotopic composition of the reservoirs if some contrast exists.

[16] There are several features of the postsnowball world that are not well-constrained, and yet are critical to the model prediction for the $\delta^{13}\text{C}$ of CaCO_3 . Therefore, we perform a series of sensitivity tests for critical parameters, selecting values that cover the full range of plausible conditions. Temperature of the ocean is taken to be initially -1.5°C , corresponding to mean ocean temperatures near the freezing point during the snowball. At the onset of deglaciation, we assume a rapid temperature increase in the surface ocean of $\sim 30^\circ\text{C}$, a reasonable assumption given the severity of a greenhouse climate resulting from atmospheric CO_2 concentrations $\sim 350\times$ present atmospheric levels. According to *Caldeira and Kasting* [1992], the concentration of atmospheric CO_2 required to escape a snowball with a planetary albedo of 0.62 is ~ 0.12 bar. We assume this to be an upper limit, given the large relative uncertainties associated with greenhouse forcing at high $p\text{CO}_2$ and esti-



mates of planetary albedo, and correspondingly model additional initial values of 0.08 bar and 0.04 bar CO_2 . Significantly reduced biological productivity during a 10^6 – 10^7 year snowball event should cause the $\delta^{13}\text{C}$ of the ocean-atmosphere system to shift toward a mantle $\delta^{13}\text{C}$ value of -5‰ to -7‰ from hydrothermal and volcanic CO_2 input [Des Marais and Moore, 1984; Kump, 1991]. This $\delta^{13}\text{C}$ value would be somewhat buffered by carbonate dissolution, but the magnitude of this effect depends critically on the $\delta^{13}\text{C}$ of preglacial carbonates (see below). As the net result of any carbonate dissolution would be an increase in the $\delta^{13}\text{C}$ of the ocean-atmosphere system, we model initial $\delta^{13}\text{C}$ values for the ocean-atmosphere system of -4‰ , -5‰ and -6‰ . During a snowball episode, as $p\text{CO}_2$ increased and the atmosphere equilibrated with the ice-covered ocean through cracks in sea ice and patches of open water on continental margins, acidification of the ocean would have further promoted the dissolution of CaCO_3 . As a result, we assume that the ocean remained at or above saturation ($1\times$ to $3\times K_{\text{sp}}$) throughout the glaciation. At the onset of deglaciation, increasing temperatures and intense carbonate weathering would rapidly drive CaCO_3 saturation of the surface ocean to $10\times$ to $20\times$ supersaturation, corresponding to the degree of supersaturation coincident with precipitation of abiotic CaCO_3 in certain modern settings [e.g., Ussdowski *et al.*, 1979; Jimenez-Lopez *et al.*, 2001].

[17] The rates of both carbonate and silicate weathering in the aftermath of a snowball are limited by CaCO_3 saturation in rivers and the maximum rate of continental runoff. L. R. Kump (personal communication, 2001) calculates that for rivers saturated with CaCO_3 in equilibrium with atmospheric $p\text{CO}_2 = 0.1$ bar, the concentration of bicarbonate would be ~ 7 times modern river water. In addition, L. R. Kump (personal communication, 2001) calculates that the maximum increase in the rate of continental runoff, based on a variety of hydrological factors, would be ~ 7 times present, resulting in maximum chemical weathering rates of ~ 50 times present, or ~ 17 GtC/yr. This estimate, however, does not take into account the possibility of rivers supersaturated with CaCO_3 , or the effect of

Neoproterozoic geography (more continents in the tropics) on the intensity of the hydrological cycle, both of which would increase the maximum weathering rate. We do not explicitly calculate weathering rates using experimentally determined kinetic rate laws as global weathering rates in the aftermath of a global glaciation would be controlled primarily by the mineral surface area available for weathering. For silicate weathering, this would correspond to the abundance of glacial rock flour, while carbonate weathering would depend on the extent of exposed carbonate platforms. For the purpose of testing the sensitivity of our model to silicate and carbonate weathering, however, we neglect these considerations and use total weathering rates (carbonate and silicate) of 17 GtC/yr, 10 GtC/yr and 5 GtC/yr. The weathering of silicate rocks involves a feedback as the net removal of atmospheric CO_2 cools the Earth, reducing the intensity of the hydrological cycle, which in turn lowers the rate of silicate weathering. We model this feedback as an exponential decrease in the silicate weathering rate over time as $p\text{CO}_2$ drops. At high rates of carbonate or silicate weathering, it is conceivable that the initial delivery of alkalinity (Ca^{2+}) and bicarbonate to the surface ocean would exceed the rate of CaCO_3 precipitation, resulting in an increase in surface ocean CaCO_3 saturation. As $p\text{CO}_2$ dropped and chemical weathering subsided, precipitation of CaCO_3 would eventually outpace the delivery fluxes, resulting in a corresponding decrease in surface ocean CaCO_3 saturation. We model these changes in surface ocean CaCO_3 saturation as an increase from $15\times$ to $20\times K_{\text{sp}}$ over an initial period in the model, followed by decrease as the weathering rate is reduced. Another critical parameter for modeling carbonate weathering is the $\delta^{13}\text{C}$ of the average carbonate being weathered as it determines whether carbonate weathering raises or lowers the $\delta^{13}\text{C}$ of precipitated CaCO_3 . We selected $\delta^{13}\text{C}$ values for preglacial carbonates of -5‰ , 0‰ , and $+5\text{‰}$, representing the range (-5‰ to $+7\text{‰}$) of $\delta^{13}\text{C}$ values commonly observed for Neoproterozoic carbonates [Jacobsen and Kaufman, 1999].

[18] Given the elevated temperatures and enhanced hydrological cycle resulting from a high $p\text{CO}_2$



Table 1. Model Results for Initial $\delta^{13}\text{C}$ of Carbonate Minerals Following a Global Glaciation

$p\text{CO}_2$, bar	$\delta^{13}\text{C}$ Ocean-Atmosphere, ‰	Temperature, °C	pH	Mineralogy	Saturation ($\times K_{\text{sp}}$)	$\delta^{13}\text{C}$ of (Ca,Mg) CO_3
0.04	−5.00	−1.5	7.08	calcite	1	−0.63
0.08	−5.00	−1.5	6.90	calcite	1	0.39
0.12	−5.00	−1.5	6.79	calcite	1	1.06
0.04	−4.00	−1.5	7.08	calcite	1	0.36
0.04	−5.00	−1.5	7.08	calcite	1	−0.64
0.04	−6.00	−1.5	7.08	calcite	1	−1.64
0.04	−5.00	30	7.23	calcite	1	−3.92
0.08	−5.00	30	7.05	calcite	1	−2.99
0.12	−5.00	30	6.94	calcite	1	−2.44
0.04	−5.00	−1.5	7.08	calcite	1	−0.63
0.04	−5.00	−1.5	7.08	aragonite	1	1.07
0.04	−5.00	−1.5	7.08	dolomite	1	0.37 to 1.37
0.04	−5.00	−1.5	7.08	calcite	1	−0.63
0.04	−5.00	−1.5	7.27	calcite	3	−1.84
0.04	−5.00	−1.5	7.36	calcite	5	−1.51

greenhouse climate, we consider both rapid (surface ocean turnover rate of ~ 50 years) and suppressed (surface ocean turnover rate ~ 500 years) oceanic mixing rates. The abrupt increase in the temperature of the surface ocean (0 – 30°C) at the onset of deglaciation would create a large density contrast between the warm surface ocean ($\sim 30^\circ\text{C}$) and cold deep ocean ($\sim 0^\circ\text{C}$), severely curtailing mixing between the two reservoirs. Massive injections of glacial meltwater would increase this density contrast, further suppressing oceanic mixing for the duration of deglaciation. On the other extreme, the intense storm systems that might develop in a high $p\text{CO}_2$ climate [Emanuel *et al.*, 1995] could conceivably drive rapid mixing.

[19] The export production and burial of organic carbon are two of the least constrained parameters in modeling the $\delta^{13}\text{C}$ of CaCO_3 . The nutrient-rich ocean, a product of millions of years of hydrothermal inputs combined with suppressed biological productivity, would likely result in a massive bloom in biological productivity upon deglaciation [Kirschvink *et al.*, 2000]. We modeled this bloom by varying the rate of organic carbon burial from 0.1 GtC/yr to 0.5 GtC/yr.

4. Results

[20] The initial $\delta^{13}\text{C}$ of calcium carbonate precipitated from a surface ocean in equilibrium with a high $p\text{CO}_2$ atmosphere depends on the initial $\delta^{13}\text{C}$

of the ocean-atmosphere system, the initial $p\text{CO}_2$, and the isotopic fractionation between dissolved inorganic carbon (DIC) and carbonate minerals. Model results for different values of these parameters are listed in Table 1. Because the $\delta^{13}\text{C}$ of the initial carbonate mineral precipitated is a function of the initial $\delta^{13}\text{C}$ of the ocean-atmosphere system, changing the initial $\delta^{13}\text{C}$ of the ocean-atmosphere system will have a direct effect on the $\delta^{13}\text{C}$ of the initial carbonate mineral precipitated. For equilibrium calcite precipitation at 0°C and an initial $p\text{CO}_2 = 0.04$ bar, lowering the initial $\delta^{13}\text{C}$ of the ocean-atmosphere system from -4.0‰ to -6.0‰ drops the initial $\delta^{13}\text{C}$ from 0.4‰ to -1.6‰ .

[21] Changing the initial $p\text{CO}_2$ affects the initial $\delta^{13}\text{C}$ of carbonate minerals by changing the partitioning of carbon between ocean and atmosphere, as well as between the various species in seawater. At a $p\text{CO}_2 = 0.12$ bar and CaCO_3 at saturation, approximately 34% of the total carbon in the ocean-atmosphere system would reside in the atmosphere with 65% sequestered in the deep ocean and the remaining 1% in the surface ocean (present-day percentages are 3% atmosphere, 87% deep ocean, and 10% surface ocean). As a result, the $\delta^{13}\text{C}$ of the surface ocean would be controlled primarily by the $\delta^{13}\text{C}$ of the atmosphere, offset by the 8‰ enrichment associated with the hydration of $\text{CO}_{2(\text{g})}$. Varying initial $p\text{CO}_2$ has the effect of increasing or decreasing the fraction of total carbon present as



isotopically depleted $\text{CO}_{2(g)}$ and $\text{CO}_{2(aq)}$. To maintain isotopic mass balance, this change must be balanced by a corresponding isotopic change in all carbon species. As illustrated in Table 1, decreasing the initial $p\text{CO}_2$ from 0.12 bar to 0.04 bar lowers the $\delta^{13}\text{C}$ of the initial carbonate minerals precipitated from 1.06‰ to -0.63‰ .

[22] The fractionation between DIC and carbonate minerals depends on three different factors that may have varied considerably in the aftermath of a snowball: the temperature dependence of isotopic fractionation, the mineralogy of the carbonate precipitated (i.e., dolomite, calcite, or aragonite), and the possibility of kinetic isotope effects related to the precipitation of carbonate minerals from highly supersaturated waters. The temperature dependence of isotopic fractionation is such that as temperature increases, isotopic fractionation decreases. As the termination of a snowball event is relatively abrupt, the rapid transition from a glacial to a greenhouse climate would lead to significant heating of the surface ocean to temperatures in excess of 30°C from an initial state near the freezing point of water. The deep ocean, however, would remain relatively cool ($\sim 0^\circ\text{C}$) as warming of the surface ocean accompanied by massive fluxes of glacial meltwater would suppress ocean mixing, although the deep ocean would also warm up over the next several thousand years as mixing proceeded. As the $\delta^{13}\text{C}$ of a surface ocean in equilibrium with a high $p\text{CO}_2$ atmosphere is determined solely by the isotopic fractionation associated with the hydration of $\text{CO}_{2(g)}$, a large increase in temperature would significantly lower the $\delta^{13}\text{C}$ of the surface ocean. For an increase in temperature from 0 to 30°C , the enrichment associated with the hydration of $\text{CO}_{2(g)}$ drops from 8‰ to 5.5‰, lowering the $\delta^{13}\text{C}$ of the surface ocean by $\sim 2.5\text{‰}$. In addition, warming of the surface ocean results in a net transfer of CO_2 from the surface ocean to the atmosphere, as both the equilibrium constant for the reaction corresponding to the uptake of CO_2 (see above) and CO_2 solubility decrease with increasing temperature. As a result, the net effect on the $\delta^{13}\text{C}$ of CaCO_3 is a drop of $\sim 3.4\text{‰}$ for an increase in temperature from 0 to 30°C .

[23] Physical and isotopic evidence from cap carbonates [Soffer, 1998; Hoffman *et al.*, 2002b] suggest that carbonate minerals may have precipitated as either calcite, aragonite or dolomite. This is important for the $\delta^{13}\text{C}$ of the initial precipitate, as the basal unit of the cap carbonate sequence is composed primarily of dolomite. If the primary precipitate is aragonite or dolomite, this would result in a $\sim 1.0\text{‰}$ to 2.0‰ enrichment relative to calcite, ($\sim 2\text{‰}$ to 3‰ enriched relative to HCO_3^-) [Sheppard and Schwarz, 1970; Romanek *et al.*, 1992; Bottcher, 2000].

[24] According to the snowball Earth hypothesis, silicate weathering and the subsequent Rayleigh distillation of atmospheric CO_2 should result in the precipitation of carbonate minerals progressively depleted in ^{13}C [Hoffman *et al.*, 1998]. Our model profiles of the $\delta^{13}\text{C}$ as a function only of silicate weathering (Figure 3) all show the expected pattern of progressive isotopic depletion in agreement with the predictions of Hoffman *et al.* [1998]. The initial $\delta^{13}\text{C}$ equal to -2.0‰ , defined by calcite precipitation at 30°C with an initial $p\text{CO}_2$ of 0.04 bar and an initial $\delta^{13}\text{C}$ of the ocean-atmosphere system of -4.65‰ , drops to a nadir of -5.2‰ , -6.0‰ , and -6.5‰ over 10^5 yr, corresponding to initial silicate weathering rates of 5 GtC/yr, 10 GtC/yr, and 17 GtC/yr, respectively. The general geometry of the profile is the same for all calculations. While the mechanism for the progressive isotopic depletion of carbonate minerals is attributed by Hoffman *et al.* [1998] solely to the effect of Rayleigh distillation, closer examination reveals that it is actually a conjunction of two separate, yet related isotope effects. First, there is a kinetic isotope effect of Rayleigh distillation of atmospheric CO_2 . In addition, there is an equilibrium isotope effect associated with the pH dependence of carbon speciation.

[25] The precipitation of CaCO_3 removes equal molar amounts of CO_2 and Ca^{2+} from the surface ocean. The removal of Ca^{2+} from the surface ocean lowers alkalinity, generating a shift in surface ocean pH, resulting in a repartitioning of ^{13}C between the various carbon species ($\text{CO}_{2(g)}$, $\text{CO}_{2(aq)}$, HCO_3^- , CO_3^{2-}). Qualitatively, the effect of pH on the partitioning of ^{13}C between carbon species can be

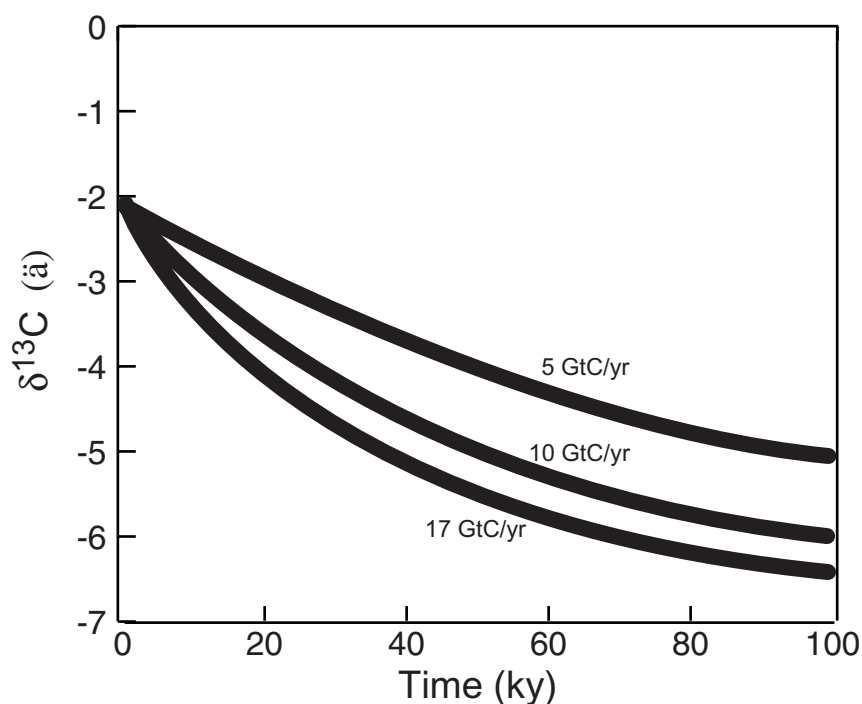


Figure 3. Model results showing the sensitivity of the $\delta^{13}\text{C}$ of carbonate to changes in silicate weathering rates.

understood as an isotopic mass balance. As pH decreases, carbon speciation is shifted toward $\text{CO}_{2(\text{aq})}$, increasing the fraction of total carbon present as the isotopically depleted carbon species ($\text{CO}_{2(\text{aq})}$ and $\text{CO}_{2(\text{g})}$). This shift must be compensated by an increase in the $\delta^{13}\text{C}$ in each of the carbon species. An increase in pH produces the opposite effect, as shifting carbon speciation toward CO_3^{2-} increases the fraction of total carbon present as the isotopically enriched carbon species (HCO_3^- and CO_3^{2-}), which must be offset by a decrease in the $\delta^{13}\text{C}$ of all carbon species. These changes in pH and their associated isotopic shifts are mirrored in the $\delta^{13}\text{C}$ of CaCO_3 . With respect to silicate weathering, because the source of alkalinity for CaCO_3 precipitation is primarily continental, the net decrease in alkalinity is much less than the net decrease in ΣCO_2 , resulting in an increase in surface ocean pH. This increase in pH is reflected in an additional drop in the $\delta^{13}\text{C}$ of CaCO_3 . The magnitude of this pH effect on the $\delta^{13}\text{C}$ of carbonate minerals can be extrapolated from Table 1. By assuming a linear relationship between changes in pH associated with variations in initial $p\text{CO}_2$ and CaCO_3 saturation state, a change in pH of ± 0.1 pH

units produces a change in the $\delta^{13}\text{C}$ of carbonate of $\sim \pm 0.3$ – 0.5% .

[26] The effect of ocean mixing rate on the progressive draw down in the $\delta^{13}\text{C}$ observed for silicate weathering is illustrated in Figure 4. As the amount of carbonate minerals precipitated during silicate weathering is dependent primarily on the flux of alkalinity from the continents, the total amount precipitated at each time step is relatively insensitive to the mixing rate. Mixing rates do, however, dictate the amount of carbon and alkalinity delivered to the surface ocean. Consequently, at slow mixing rates, the removal of carbon via CaCO_3 precipitation will significantly outpace the influx of carbon from ocean mixing, resulting in an increase in the fraction of total carbon precipitated with each time step. This fractional increase intensifies the effect of Rayleigh distillation, generating the steeper initial isotopic change observed in Figure 4.

[27] The export production and burial of organic carbon is cited by Hoffman *et al.* [1998] as the primary mechanism for the isotopic rebound in the $\delta^{13}\text{C}$ of CaCO_3 globally observed in cap carbonate

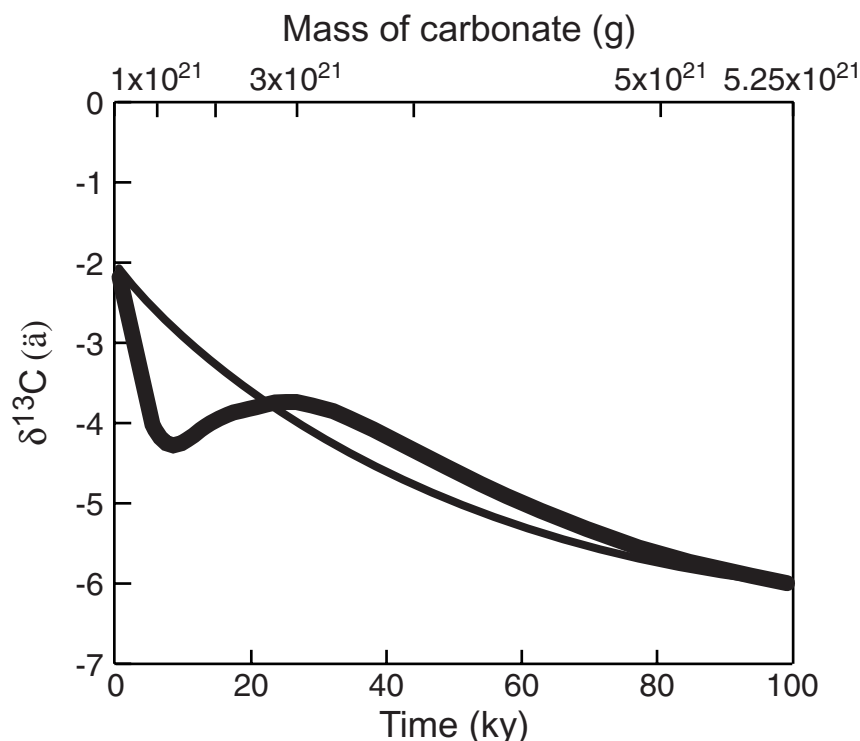


Figure 4. Model results showing the sensitivity of $\delta^{13}\text{C}$ of carbonate to ocean mixing rates of 50 years (thin line) and 500 years (heavy line).

successions. As biological carbon fixation is accompanied by a $\sim 27\%$ depletion in ^{13}C , the export production and burial of this depleted organic carbon should significantly enrich the $\delta^{13}\text{C}$ of the surface ocean and consequently the $\delta^{13}\text{C}$ of CaCO_3 . This enrichment, however, is critically dependent on two parameters, the amount of export production and the burial rate of organic carbon. Given our current imperfect knowledge of the factors controlling biological productivity and the burial of organic carbon, these parameters are virtually impossible to constrain. Figure 5 illustrates the effect of varying the rate of the burial of organic carbon on the magnitude and duration of the draw down of the $\delta^{13}\text{C}$ resulting from an initial silicate weathering rate of 10 GtC/yr. In agreement with the proposal of *Hoffman et al.* [1998], the progressive depletion of the $\delta^{13}\text{C}$ from silicate weathering is eventually overcome by the enrichment in the $\delta^{13}\text{C}$ from organic carbon burial, which drives the $\delta^{13}\text{C}$ of the carbonate precipitate back toward positive values. For organic carbon burial rates of 0.5 GtC/yr, 0.3 GtC/yr, and 0.1 GtC/yr, the

nadir of the $\delta^{13}\text{C}$ profile is attained at 3.8×10^4 years, 9.5×10^4 years, and 1.15×10^5 years, corresponding to minimum $\delta^{13}\text{C}$ values of CaCO_3 of -3.0% , -4.3% , and -6.2% , respectively (Figure 5). Increasing the rate of organic carbon burial increases the magnitude of the isotopic enrichment associated with organic carbon burial, decreasing the time necessary to initiate an isotopic reversal and consequently raising the nadir of the $\delta^{13}\text{C}$ of CaCO_3 profile.

[28] As carbonate weathering and the subsequent precipitation of carbonate minerals represents a conservative mass transfer of carbon from the continents to the sediments, the effect of carbonate weathering on the $\delta^{13}\text{C}$ is governed only by the rate of carbonate weathering and the $\delta^{13}\text{C}$ value of the weathered carbonate. Given the $\delta^{13}\text{C}$ of weathered carbonate of 0% and a surface ocean turnover time of 50 years, carbonate weathering rates of 5 GtC/yr, 10 GtC/yr, and 17 GtC/yr yield isotopic enrichments in $\delta^{13}\text{C}$ of $+0.80\%$, $+1.35\%$, and $+1.75\%$, respectively, over a 1×10^5 year interval. As

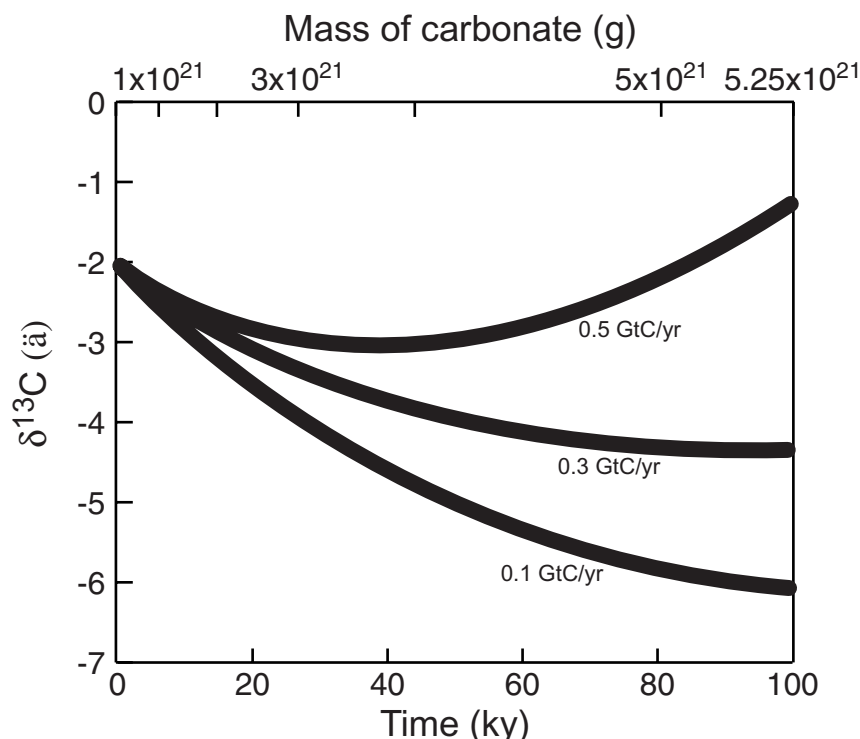


Figure 5. Model results showing the sensitivity of $\delta^{13}\text{C}$ of carbonate to organic carbon burial rates of 0.1 GtC/yr, 0.3 GtC/yr, and 0.5 GtC/yr.

expected, the intensity of carbonate weathering determines the magnitude of change in the $\delta^{13}\text{C}$ of CaCO_3 , although for the range of modeled weathering rates, the difference in isotopic enrichment is relatively small ($\sim 0.9\text{‰}$). Varying the $\delta^{13}\text{C}$ of weathered carbonate from -5‰ to $+5\text{‰}$, with a carbonate weathering rate of 10 GtC/yr and a surface ocean turnover time of 50 years, yields changes in the $\delta^{13}\text{C}$ from $+4.8\text{‰}$ to -2.0‰ . The effect of varying the $\delta^{13}\text{C}$ of weathered carbonate depends only on the difference between the $\delta^{13}\text{C}$ of the carbonate mineral precipitated and the $\delta^{13}\text{C}$ of weathered carbonate.

[29] The effect of oceanic mixing rate on the $\delta^{13}\text{C}$ of carbonate minerals precipitated from the weathering of carbonates depends on the establishment of isotopic steady state between the surface and deep ocean. At low mixing rates, the decrease in total carbon exchanged between the surface and deep ocean is balanced by an increase in the isotopic gradient between the surface ocean and the deep ocean to maintain isotopic equilibrium. Given a constant carbonate weathering rate of 17 GtC/yr

and a $\delta^{13}\text{C}$ value of weathered carbonate of 0‰ , oceanic mixing rates corresponding to surface ocean turnover times of 50 years and 500 years produce changes in the $\delta^{13}\text{C}$ of 0.4‰ and 0.75‰ , respectively. The isotopic gradient established between the surface and deep ocean as a function of oceanic mixing rate are 0.1‰ and 0.7‰ , for surface ocean turnover times of 50 years and 500 years, respectively. This isotopic difference between the surface ocean and the deep ocean represents an additional mechanism for change in the $\delta^{13}\text{C}$ as any shift in the rate of carbonate weathering or the rate of oceanic mixing would involve a re-establishment of a new isotopic steady state. However, the abrupt increase in surface ocean temperature following deglaciation would rapidly lower the $\delta^{13}\text{C}$ of the surface ocean relative to the deep ocean, offsetting any isotopic gradient due to export production, carbonate weathering or ocean mixing.

[30] If, in the aftermath of a snowball, the delivery of alkalinity and bicarbonate to the surface ocean outpaced the precipitation of carbonate minerals, supersaturation in the surface ocean would increase.



Eventually, carbonate would precipitate in excess of the alkalinity and bicarbonate fluxes, resulting in a progressive decline in supersaturation. The change in the $\delta^{13}\text{C}$ associated with these predicted changes in saturation in the surface ocean is relatively minor (0.04‰ to 0.06‰).

[31] Intensified silicate weathering in the aftermath of a global glaciation would have resulted in an increased flux of non- Ca^{2+} cations (Mg^{2+} , Na^+ , K^+) to the ocean. This flux would increase the alkalinity of the surface ocean and lead to a change in surface ocean pH and some additional carbonate precipitation. Parallel calculations accounting explicitly for the effects of other cations reveals that the effects of increased non- Ca^{2+} cation flux on the $\delta^{13}\text{C}$ results described above are minimal. Assuming relative proportions of Mg^{2+} , Na^+ , and K^+ relative to Ca^{2+} identical to modern river water, the difference in the model response is less than 0.2‰. A finding of the calculation with all major cations reveals that the Mg/Ca ratio of the ocean during and after a global glaciation remained relatively constant. During a global glaciation, hydrothermal alteration of basalts would result in a net uptake of Mg, decreasing the Mg/Ca ratio from a value of 5.5 to ~ 2.5 [Holland, 1978]. Carbonate dissolution and weathering during and after the global glaciation would further decrease the Mg/Ca ratio by ~ 0.1 to a value of 2.4. However, the decrease in the Mg/Ca ratio would not prohibit dolomite precipitation as the Mg/Ca ratios are greater than 1 [Drever, 1988].

5. Discussion

5.1. Implications for the $\delta^{13}\text{C}$ Record of Cap Carbonates

[32] Previous workers have interpreted cap carbonates and their characteristic negative shift in $\delta^{13}\text{C}$ in terms of variations in the global carbon cycle, assuming that the $\delta^{13}\text{C}$ record of cap carbonates represents changes in only one aspect of the cycling of carbon in the ocean-atmosphere system (e.g., methane hydrates [Kennedy *et al.*, 2001b], Rayleigh distillation via silicate weathering [Hoffman *et al.*, 1998], or ocean overturn [Grotzinger and Knoll, 1995]). Based on the model results presented here, the $\delta^{13}\text{C}$ record of cap carbonates likely reflects a

combination of processes including secular variations in the global carbon cycle and changes in the isotopic fractionation of carbon related to the abrupt transition from an icehouse to greenhouse climate. The salient chemical and stratigraphic features of cap carbonates that require explicit consideration are 1) the initial $\delta^{13}\text{C}$ of CaCO_3 ; 2) the stratigraphy and $\delta^{13}\text{C}$ profile of the cap dolostone; and 3) the stratigraphy and $\delta^{13}\text{C}$ profile of the cap sequence.

[33] The initial $\delta^{13}\text{C}$ in cap carbonate sequences is consistently observed at a value of $-1.5 \pm 0.5\text{‰}$ [Kennedy *et al.*, 2001a]. Our model results show that the initial $\delta^{13}\text{C}$ depends on the $\delta^{13}\text{C}$ of the ocean-atmosphere system, the $p\text{CO}_2$ at deglaciation, the temperature of precipitation, the mineralogy of the precipitate, and to a lesser degree the saturation state of the ocean. Figure 6 illustrates the relationship between $p\text{CO}_2$ and the $\delta^{13}\text{C}$ of the ocean-atmosphere system required to generate an initial $\delta^{13}\text{C}$ of -2‰ for calcite, aragonite, and dolomite at carbonate saturation and a surface ocean temperature of 30°C . For $p\text{CO}_2$ of 0.04 bar to 0.12 bar and the $\delta^{13}\text{C}$ of the ocean-atmosphere system between -4.5‰ and -5.5‰ , the model predicts that only aragonite and dolomite could precipitate at $\sim -2\text{‰}$.

[34] Kennedy *et al.* [2001a] interpret the initial $\delta^{13}\text{C}$ of $\sim -2\text{‰}$ as well as the relatively enriched $\delta^{13}\text{C}$ ranges (-2‰ to $+5\text{‰}$) observed in CaCO_3 precipitated during the glacial interval as inconsistent with the snowball Earth hypothesis. They argued that the $\delta^{13}\text{C}$ values enriched relative to the mantle inputs imply healthy and vigorous biological productivity, incompatible with a global glaciation. However, the reasoning of Kennedy *et al.* [2001a] assume a carbon cycle in steady state, with volcanic CO_2 emissions isotopically balanced by the burial of both inorganic and organic carbon. The premise of the snowball Earth hypothesis is that volcanic emissions during glaciation are not balanced by the burial of inorganic and organic carbon. This imbalance in carbon emissions and burial is responsible for the buildup of atmospheric CO_2 , required to explain the escape from an ice-covered planet. Our model results show that the value of -2‰ for the initial carbonate precipitated after the glaciation, as well as higher values during

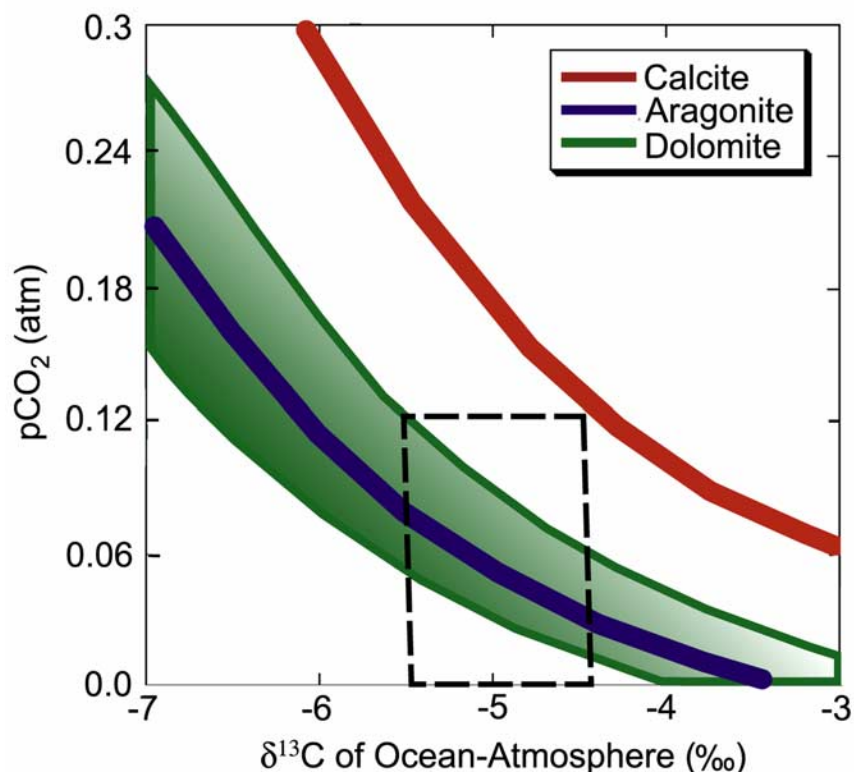


Figure 6. Combinations of $p\text{CO}_2$ and average $\delta^{13}\text{C}$ of the ocean-atmosphere system required to generate $\delta^{13}\text{C}$ of initial carbonate at -2‰ for calcite (red), aragonite (blue) and dolomite (green). Boxed area highlights the range of parameters used in the calculations presented here.

the glacial interval, are perfectly consistent with an abiotic treatment of the ocean and atmosphere during an episode of global glaciation.

[35] Although a simple model involving only silicate weathering, mixing between the surface and deep ocean, and the transport and burial of organic carbon reproduces the expected depletion and recovery of $\delta^{13}\text{C}$ values in accordance with the proposal of *Hoffman et al.* [1998] (see Figure 3), it is unlikely that this situation corresponds to a realistic weathering regime in the aftermath of a snowball Earth. The sequestration of vast amounts of water in continental glaciers during a snowball would significantly lower relative sea level, exposing the vast carbonate shelves of the continental margins. The high $p\text{CO}_2$ would drive dissolution of carbonate orders of magnitude faster than any chemical weathering of silicate rocks. Thus, carbonate weathering would dominate until sea level rise due to melting glaciers submerged the shelves,

significantly reducing the amount of carbonate available for weathering. This situation would be analogous to the Cretaceous, when high sea level reduced the area of exposed carbonate shelf by a factor of 20 relative to present [*Opdyke and Wilkinson*, 1988]. Evidence for this initial period of intense carbonate weathering comes from the ubiquitous presence of the transgressive cap dolostone unit in both terrigenous and carbonate-dominated depositional environments. The duration of this intense period of carbonate weathering is constrained to the transgressive cap dolostone unit of the cap carbonate sequence, which corresponds to a period comparable to the interval of glacioeustatic sea level rise. The timescale of sea level rise is prescribed an upper limit on the order of $\sim 10^4$ years, corresponding to the duration of sea level rise in the Quaternary, but was probably much faster given the extreme nature of a snowball deglaciation [*Kennedy et al.*, 2001a; *Hoffman et al.*, 1998].



[36] The $\delta^{13}\text{C}$ profile for the cap dolostone is punctuated by a steep $\sim 2\text{‰}$ drop in the $\delta^{13}\text{C}$ from an initial value of $\sim -2\text{‰}$, to a dolostone-limestone transition value of $\sim -4\text{‰}$. As it was originally framed, the snowball Earth hypothesis attributes this drop of $\sim 2\text{‰}$ to Rayleigh distillation of atmospheric CO_2 via silicate weathering [Hoffman *et al.*, 1998]. As we infer that the cap dolostone likely represents an interval dominated almost exclusively by the intense weathering of preglacial carbonates, it is highly unlikely that the $\sim 2\text{‰}$ drop observed in the $\delta^{13}\text{C}$ is a product of silicate weathering. The weathering of carbonates itself cannot explain the $\sim 2\text{‰}$ drop in $\delta^{13}\text{C}$ because it requires the $\delta^{13}\text{C}$ of weathered carbonates to be less than -7‰ . In fact, our calculations suggest that carbonate weathering tends to enrich the $\delta^{13}\text{C}$ of carbonate.

[37] Our model calculations suggest two possible explanations for the shift in $\delta^{13}\text{C}$ within the cap dolostone. One possibility is that the drop represents the warming of the surface ocean immediately following the glaciation, with a subsequent reduction in isotopic fractionation between CO_2 and HCO_3^- and an increase in supersaturation of the surface ocean. In this context, a drop in $\delta^{13}\text{C}$ of 2‰ represents a surface ocean warming of only $\sim 15^\circ\text{C}$. Another possibility is that the drop in $\delta^{13}\text{C}$ values is caused by a kinetic isotope effect associated with precipitation of carbonate minerals faster than the characteristic time for isotopic equilibration between HCO_3^- and CaCO_3 . Evidence from field observations of calcite precipitation in natural waters [Turner, 1982; Usdowski *et al.*, 1979] suggest a kinetic isotope effect associated with CaCO_3 precipitation from highly supersaturated waters. Synthetic precipitation experiments involving both calcite and aragonite are less conclusive [Romanek *et al.*, 1992], but they do not consider the full range of inorganic CaCO_3 precipitation kinetics (they investigate only seeded-growth heterogeneous precipitation) or the effect of seawater composition. Another possibility is that the kinetic effects are due to a smaller fractionation factor for monohydrate calcite, a metastable polymorph that forms the initial precipitate [Jimenez-Lopez *et al.*, 2001]. Together, these findings suggest that in highly supersaturated waters ($6\times -15\times K_{\text{sp}}$), the precip-

itation rate of CaCO_3 is faster than isotopic equilibrium, resulting in a decrease in the isotopic fractionation between HCO_3^- and CaCO_3 . In the most extreme cases, the fractionation between HCO_3^- and CaCO_3 virtually disappears so that the $\delta^{13}\text{C}$ of $\text{HCO}_3^- \cong$ the $\delta^{13}\text{C}$ of precipitated CaCO_3 [Turner, 1982; Usdowski *et al.*, 1979]. If we assume a kinetic isotope effect explains the drop of 2‰ in the cap dolostone, the drop would then correspond to an increase in supersaturation as carbonate weathering intensified.

[38] The rise in sea level following deglaciation would eventually flood the carbonate platforms, drastically reducing the aerial extent of carbonate available for weathering. This reduction would lead to a new weathering regime where silicate weathering dominated the total weathering flux. Our calculations can easily produce the observed 2‰ drop observed above the cap dolostone, followed by the gradual increase related to organic carbon burial. This result is consistent with the hypothesis of Hoffman *et al.* [1998], which suggests that silicate weathering and the burial of organic carbon play an important role in determining the $\delta^{13}\text{C}$ of CaCO_3 in the aftermath of a global glaciation. Our calculations also reveal that carbonate weathering, which causes an increase in $\delta^{13}\text{C}$ values, may also play a role in the gradual rise of $\delta^{13}\text{C}$ values later in the weathering sequence.

[39] Kennedy *et al.* [2001a] argued that the rate of silicate weathering required to produce the drop in the $\delta^{13}\text{C}$ of CaCO_3 observed in cap carbonates is two to three orders of magnitude too large given the maximum weathering rates calculated by L. R. Kump (personal communication, 2001). However, our model is able to produce the observed drop in the $\delta^{13}\text{C}$ of CaCO_3 with silicate weathering rates less than these rates. As discussed above, Kennedy *et al.* [2001a] assumed that the cap dolostone is the exclusive product of any intensified silicate weathering, whereas we suggest that most of the silicate weathering is accounted for by the limestone unit the cap carbonate sequence and continues even after the nadir in the $\delta^{13}\text{C}$ profile is reached.

[40] Kennedy *et al.* [2001a] also argued that equilibration between the ocean and atmosphere during

a snowball event (via cracks in the sea-ice) would significantly increase the time needed to build up the ~ 0.1 bar of atmospheric CO_2 required to initiate deglaciation and suppress the influence of the atmosphere on the $\delta^{13}\text{C}$ of the surface ocean. However, this assumes a ratio of carbon in the ocean to the atmosphere approximately equal to the modern value of 60:1, which neglects the effects of high $p\text{CO}_2$ and low pH on the speciation of carbon in the ocean-atmosphere system. Our calculations show that, at the termination of a snowball glaciation, an ocean at CaCO_3 saturation in equilibrium with an atmosphere containing ~ 0.12 bar CO_2 would result in carbon partitioning between the ocean and atmosphere in a ratio of $\sim 2:1$. This means that isotopic equilibration would be near complete during the long-lived glaciation, even if air-sea gas exchange were drastically reduced due to near complete sea ice cover.

[41] The total amount of CaCO_3 precipitated using the maximum weathering rates of L. R. Kump (personal communication, 2001) and an initial $p\text{CO}_2$ of 0.04 bar to 0.12 bar ranges from $\sim 6 \times 10^5$ to 1×10^6 GtC. This corresponds to a total cap thickness ranging from 8–15 m for an area corresponding to the entire ocean floor, or 50–100 m for an area corresponding only to the continental shelves. The thickness of the cap dolostone can be inferred from the amount of CaCO_3 precipitated during the first 10^4 years of each model run. For the range of initial conditions listed above, the thickness of the cap dolostone ranged from 1.5–2 m for an area corresponding to the entire ocean floor, or 10–14 m for an area corresponding to the continental shelves, a value that is broadly in agreement with observations.

[42] We summarize our results in Figure 7, which represents our best estimate for isotopic evolution of a cap carbonate sequence following an episode of global glaciation. At an initial $p\text{CO}_2$ of 0.04 bar, an initial $\delta^{13}\text{C}$ of the ocean-atmosphere system of -5‰ , and a surface ocean temperature of 30°C , primary dolomite precipitates at -2‰ . Rapid weathering of exposed carbonate platforms increases both CaCO_3 supersaturation and the $\delta^{13}\text{C}$ of CaCO_3 . However, an increase in surface ocean temperature as well as

the possibility of reduced fractionation between dolomite and HCO_3^- due to a kinetic isotope effect (also driven by the increase in temperature), drives the $\delta^{13}\text{C}$ lower by 2‰. Glacial-eustatic sea level rise eventually submerges the vast carbonate platforms, resulting in a significant relative increase in the silicate weathering rate, which draws down the $\delta^{13}\text{C}$ of carbonate via Rayleigh distillation by an additional 2‰. Eventually, as $p\text{CO}_2$ and total chemical weathering rate decrease, the burial of organic carbon and carbonate weathering become significant, resulting in the reversal of the $\delta^{13}\text{C}$ profile at a nadir of $\sim -6\text{‰}$.

5.2. Sr Isotopes and the Snowball Earth

[43] The absence of large variations in Sr isotopes over Neoproterozoic glacial intervals has been cited by *Kennedy et al.* [2001a] and *Jacobsen and Kaufman* [1999] as incompatible with the snowball Earth hypothesis of *Hoffman et al.* [1998]. According to *Jacobsen and Kaufman* [1999], the shutdown of the hydrological cycle during a $\sim 10^6$ year glaciation should generate a shift in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio toward a hydrothermal value of 0.7035. However, the observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the cap carbonates are only ~ 0.001 lower than the preglacial carbonates, suggesting that the maximum duration of the glaciation was only 10^6 years, as opposed to the 10^7 years proposed by *Hoffman et al.* [1998]. *Kennedy et al.* [2001a] argue that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the cap carbonates should increase due to intensified silicate weathering in the aftermath of a global glaciation, whereas they observe roughly uniform values throughout the cap carbonate succession. We explored the effect of an episode of global glaciation lasting $\sim 5 \times 10^6$ years and the subsequent rapid weathering of both carbonate and silicate rocks on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of cap carbonates by adding Sr isotopes and Sr chemistry to our model. The key factors in evaluating the response of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to climate forcing are 1) the inventory of Sr in Neoproterozoic oceans; 2) the mean concentration of Sr in abiotic aragonite and calcite; 3) the mean concentration of Sr of silicate rocks; and 4) the fluxes of Sr from chemical weathering and hydrothermal inputs. We assume hydrothermal

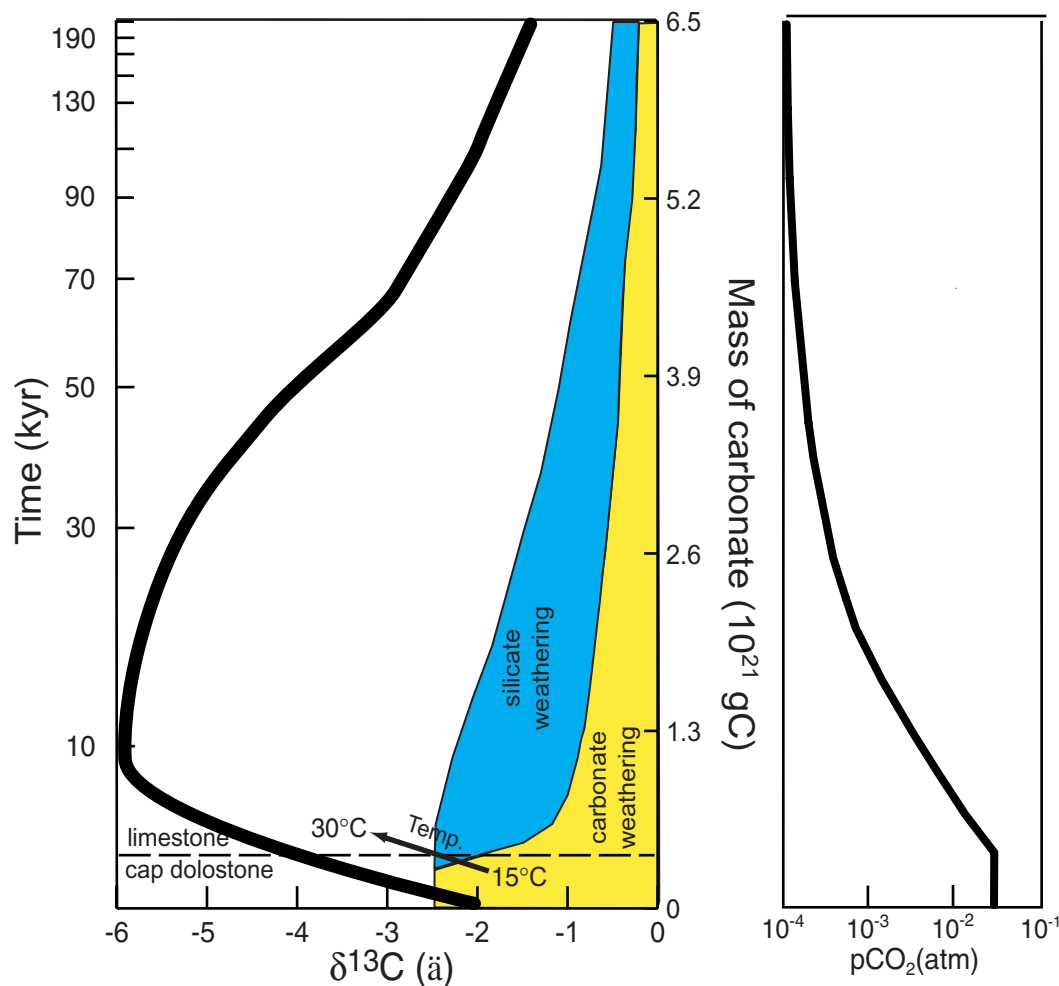


Figure 7. Modeled $\delta^{13}\text{C}$ profile for a cap carbonate sequence. Cap dolostone is formed from intense carbonate weathering with a drop in $\delta^{13}\text{C}$ values due to increasing sea surface temperature following deglaciation. The limestone sequence is dominated by silicate weathering which lowers $p\text{CO}_2$. The increase in $\delta^{13}\text{C}$ values at 100 ky is due to organic carbon burial and carbonate weathering.

inputs of 9×10^9 mol Sr/yr, equal to 25% of the total present-day Sr flux (3.6×10^{10} mol Sr/yr) [Stoll and Schrag, 1998]. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for continental inputs we calculate to be 0.7089, which is consistent with preglacial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7075 when the Sr cycle was in steady state. Weathering inputs were obtained from our previous model calculations, assuming an initial maximum weathering rate of 17 GtC/yr. As the mineralogy of the primary precipitate of cap carbonates is unconstrained, we model Sr concentrations corresponding to the partitioning of Sr in abiotic aragonite (~ 500 ppm Sr) [Carpenter *et al.*, 1992]. Additionally, we assume Sr concentrations in silicate rocks of 1000 ppm. As the

concentration of Sr in inorganically precipitated carbonates is, in general, lower than the concentration of Sr in biogenic carbonates, we would expect higher Sr concentrations and a longer Sr residence time for Neoproterozoic oceans [Hoffman *et al.*, 1998]. The concentrations would be further increased during and after an episode of global glaciation because of the relationship between high $p\text{CO}_2$ and the Ca^{2+} concentration of the ocean at CaCO_3 saturation. Consequently, we estimate model Sr inventories to be $3 \times$ present ($\sim 1.2 \times 10^{17}$ mol Sr).

[44] The results of our model calculations for both syn and postglacial Sr isotopes are illustrated in

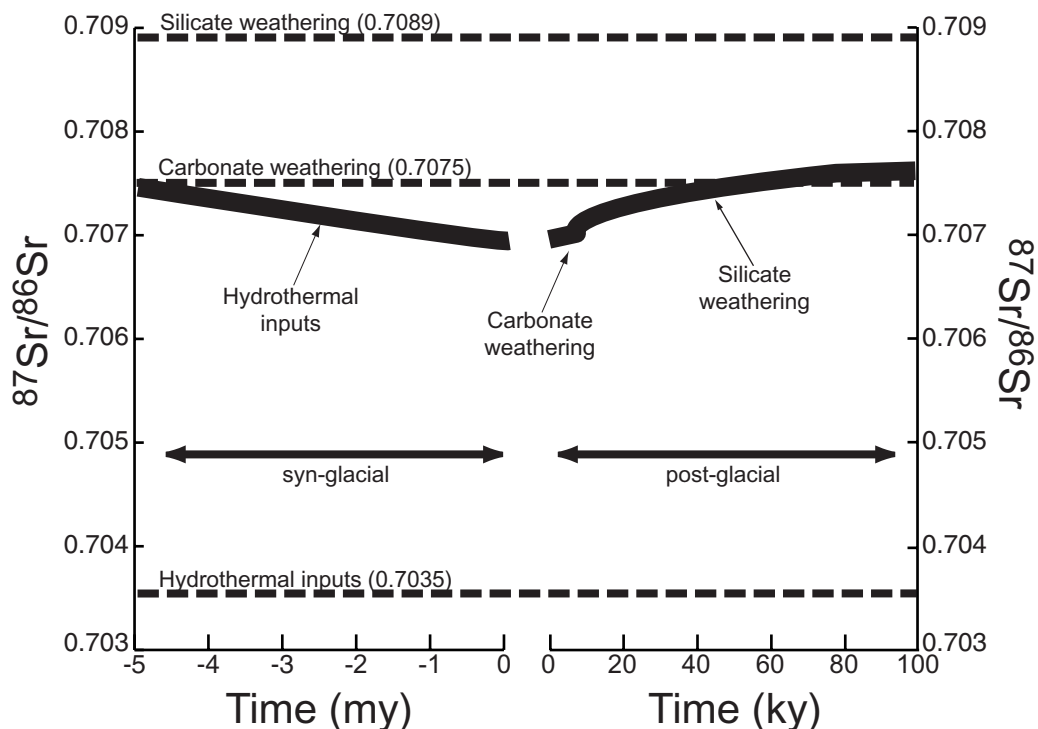


Figure 8. Model results for Sr isotope evolution of seawater during and after a global glaciation.

Figure 8. For syn-glacial Sr isotopes, we observe a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from an initial value of 0.7075 to a final value of 0.7067. These values fall within the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed ($0.707 \pm .001$) at the base of the cap sequence. *Jacobsen and Kaufman* [1999] calculated that their value would be much lower (0.7035), neglecting any change in ocean chemistry due to the progressive increase of atmospheric CO_2 and subsequent dissolution of carbonate. The difference between our model calculations and the predictions of *Jacobsen and Kaufman* [1999] stem from the added effects of CaCO_3 dissolution and the larger inventory of Sr in Neoproterozoic oceans which tend to buffer the effect of hydrothermal input.

[45] The buffering effect of CaCO_3 dissolution and a larger Sr inventory are also evident for our model calculation of postglacial Sr isotopes. *Kennedy et al.* [2001a] argue that, due to the intense silicate weathering rates predicted by the snowball Earth hypothesis, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of cap carbonate sequences should shift significantly toward a continental $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. However, our model pre-

dicts only small changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7067 to 0.7076) following an episode of global glaciation, in good agreement with the observed range of 0.7072 to 0.7081 [*Kennedy et al.*, 2001a]. Precise determination of the Sr isotope curve is obstructed by the presence of significant amounts of Rb in many postglacial carbonates and the difficulty of correcting for Rb decay. For example, a study of Namibian rocks from the cap carbonate sequence found that most rocks had Rb concentrations between 10 and 20 ppm (G. P. Halverson and D. P. Schrag, personal communication, 2002). Because these rocks are so old, the presence of only 8 ppm Rb, if uncorrected, would raise the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio by 0.001.

[46] An additional difference in our calculations from those of *Kennedy et al.* [2001a] is that they use a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for continental weathering of 0.7135, a value significantly higher than even the modern riverine estimate [*Palmer and Edmond*, 1992], as opposed to our estimate of 0.7089. The modern $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.711 to 0.712) is strongly influenced by the uplift of the Himalayas, resulting in the modern ocean value of 0.7092. This would



not be the case in the Neoproterozoic when the preglacial values for the ocean was ~ 0.707 .

6. Conclusions

[47] Our calculations show that the observed patterns of carbon isotopic variations in Neoproterozoic cap carbonate sequences can be explained in the context of the geochemical evolution of the carbon cycle following a period of extended global glaciation. We suggest that the basal unit of the cap carbonate sequence, the cap dolostone, represents an interval dominated by carbonate weathering of exposed continental shelves. The initial $\delta^{13}\text{C}$ value of the dolostone, observed to be approximately -2‰ , is controlled by $p\text{CO}_2$, temperature, the $\delta^{13}\text{C}$ of the ocean-atmosphere system and the saturation state of the surface ocean. For an abiotic ocean, our model calculations can produce initial values between $+1\text{‰}$ and -3‰ , in contradiction with the suggestion of Kennedy *et al.* [2001a] who suggested that these values require vigorous biological productivity. The 2‰ drop in $\delta^{13}\text{C}$ values observed within the cap dolostone itself is unlikely to be a product of Rayleigh distillation of atmospheric CO_2 via silicate weathering as suggested by Hoffman *et al.* [1998]. We show that this drop can be explained by the precipitation of carbonate while sea surface temperature is rising, although kinetic isotope effects may play an important role as well. The rest of the isotopic variations can be explained by the competing effects of silicate weathering, carbonate weathering, and burial of organic carbon. Our model predicts that strontium isotope variations would be very small during and after the glaciation, less than the range of existing observations. In general, our modeling emphasizes the need to properly consider the geochemical consequences of elevated $p\text{CO}_2$ on the carbon and strontium cycles when considering the Snowball Earth hypothesis.

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References

- Bottcher, M., Stable isotope fractionation during experimental formation of Norsethite ($\text{BaMg}[\text{CO}_3]_2$): A mineral analogue of dolomite, *Aquat. Geochem.*, **6**, 201–212, 2000.
- Caldeira, K., and J. F. Kasting, Susceptibility of the early Earth to irreversible glaciation caused by carbon dioxide clouds, *Nature*, **359**, 226–228, 1992.
- Carpenter, S. J., K. C. Lohmann, P. Holden, L. M. Walter, T. J. Huston, and A. N. Halliday, $\delta^{18}\text{O}$ values, $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Mg ratios of Late Devonian abiotic marine calcite: Implications for the composition of ancient seawater, *Geochim. Cosmochim. Acta*, **55**, 1991–2010, 1992.
- Des Marais, D. J., and J. G. Moore, Carbon and its isotopes in mid-oceanic basaltic glasses, *Earth Planet. Sci. Lett.*, **69**, 43–57, 1984.
- Drever, J. I., *The Geochemistry of Natural Waters*, Prentice-Hall, Old Tappan, N. J., 1988.
- Emanuel, K. A., K. Speer, R. Rotunno, R. Srivastava, and M. Molina, Hypercanes: A possible link in global extinction scenarios, *J. Geophys. Res.*, **100**, 13,755–13,765, 1995.
- Fairchild, I. J., and M. J. Hambrey, The Vendian succession of northeastern Spitsbergen: Petrogenesis of a dolomite-tillite association, *Precambrian Res.*, **26**, 111–167, 1984.
- Grotzinger, J. P., and A. H. Knoll, Anomalous carbonate precipitates: Is the Precambrian the key to the Permian?, *Palaaios*, **10**, 3–20, 1995.
- Hoffman, P. F., and D. P. Schrag, The snowball Earth hypothesis: Testing the limits of global change, *Terra Nova*, **14**, 129–155, 2002.
- Hoffman, P. F., A. J. Kaufman, G. P. Halverson, and D. P. Schrag, A Neoproterozoic snowball Earth, *Science*, **281**, 1342–1346, 1998.
- Hoffman, P. F., G. P. Halverson, and J. P. Grotzinger, Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals?: Comment, *Geology*, **30**, 286–287, 2002a.
- Hoffman, P. F., A. Van Dusen, G. P. Halverson, J. Saenz, A. J. Kaufman, and D. P. Schrag, Significance of sea-floor barite cements in Marinoan-age post-glacial cap carbonates, *Geochim. Cosmochim. Acta*, **66**, A335, 2002b.
- Holland, H. D., *The Chemistry of the Atmosphere and Oceans*, Wiley-Interscience, New York, 1978.
- Hotinski, R. M., K. L. Bice, L. R. Kump, and R. G. Najjar, Ocean stagnation and end-Permian anoxia, *Geology*, **29**, 7–10, 2001.
- Jacobsen, S. B., and A. J. Kaufman, The Sr, C and O isotopic evolution of Neoproterozoic seawater, *Chem. Geol.*, **161**, 37–57, 1999.
- James, N. P., G. M. Narbonne, and T. K. Kyser, Late Neoproterozoic cap carbonates: Mackenzie Mountains, northwestern Canada: Precipitation and global glacial meltdown, *Can. J. Earth Sci.*, **38**, 1229–1262, 2001.
- Jimenez-Lopez, C., E. Caballero, F. J. Huertas, and C. S. Romanek, Chemical, mineralogical and isotope behavior, and



- phase transformation during the precipitation of calcium carbonate minerals from intermediate ionic solution at 25 C, *Geochim. Cosmochim. Acta*, 65, 3219–3231, 2001.
- Kennedy, M. J., Stratigraphy, sedimentology, and isotope geochemistry of Australian Neoproterozoic postglacial cap dolostones: Deglaciation, $\delta^{13}\text{C}$ excursions, and carbonate precipitation, *J. Sediment. Res.*, 66, 1050–1064, 1996.
- Kennedy, M. J., N. Christie-Blick, and A. R. Prave, Carbon isotopic composition of Neoproterozoic glacial carbonates as a test of paleoceanographic models for snowball Earth phenomena, *Geology*, 29, 1135–1138, 2001a.
- Kennedy, M. J., N. Christie-Blick, and L. E. Sohl, Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals?, *Geology*, 29, 443–446, 2001b.
- 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. U. S. A.*, 97(4), 1400–1405, 2000.
- Kump, L. R., Interpreting carbon-isotopic excursions: Strange-love oceans, *Geology*, 19, 299–302, 1991.
- Lasaga, A. C., *Kinetic Theory in Earth Sciences*, Princeton Univ. Press, Princeton, N. J., 1998.
- Opdyke, B. N., and B. H. Wilkinson, Surface area control of shallow cratonic to deep marine carbonate accumulation, *Paleoceanography*, 3, 685–703, 1988.
- Palmer, M. R., and J. M. Edmond, Controls over the strontium isotope composition of river water, *Geochim. Cosmochim. Acta*, 56, 2099–2111, 1992.
- Romanek, C. S., E. L. Grossman, and J. Morse, Carbon isotope fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate, *Geochim. Cosmochim. Acta*, 56, 419–430, 1992.
- Schermerhorn, L. J. C., Later Precambrian mixtites: Glacial and/or non-glacial?, *Am. J. Sci.*, 274, 673–824, 1974.
- Sheppard, S., and H. Schwarcz, Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite, *Contrib. Mineral. Petrol.*, 26, 161–198, 1970.
- Soffer, G., Evolution of a Neoproterozoic continental margin subject to tropical glaciation, Senior Honors Thesis, Harvard Coll., Cambridge, Mass., 1998.
- Spencer, A. M., and M. O. Spencer, The Later Precambrian/Lower Cambrian Bonahaven Dolomite of Islay and its stromatolites, *Scott. J. Geol.*, 8, 269–282, 1972.
- Stoll, H. M., and D. P. Schrag, Effects of Quaternary sea level cycles on strontium in seawater, *Geochim. Cosmochim. Acta*, 62, 1107–1118, 1998.
- Turner, J. V., Kinetic fractionation of carbon-13 during calcium carbonate precipitation, *Geochim. Cosmochim. Acta*, 46, 1183–1191, 1982.
- Usdowski, E., J. Hoefs, and G. Menschel, Relationship between ^{13}C and ^{18}O fractionation and changes in major element composition in a recent calcite-depositing spring—A model of chemical variations with inorganic CaCO_3 precipitation, *Earth Planet. Sci. Lett.*, 42, 267–276, 1979.
- Williams, G. E., Sedimentology, stable-isotope geochemistry and palaeoenvironment of dolostones capping late Precambrian glacial sequences in Australia, *J. Geol. Soc. Aust.*, 26, 377–386, 1979.
- Zhang, R., M. J. Follows, J. P. Grotzinger, and J. Marshall, Could the Late Permian deep ocean have been anoxic?, *Paleoceanography*, 16, 317–329, 2001.