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# Scenario for the evolution of atmospheric $p\text{CO}_2$ during a snowball Earth

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## ABSTRACT

The snowball Earth theory, initially proposed by J.L. Kirschvink to explain the Neoproterozoic glacial episodes, suggests that the Earth was globally ice covered at 720 Ma (Sturtian episode) and 640 Ma (Marinoan episode). The reduction of the water cycle and the growth of large ice sheets led to a collapse of  $\text{CO}_2$  consumption through continental weathering and biological carbon pumping. As a consequence, atmospheric  $\text{CO}_2$  built up linearly to levels allowing escape from a snowball Earth. In this contribution, we question this assumed linear accumulation of  $\text{CO}_2$  into the atmosphere. Using a numerical model of the carbon-alkalinity cycles, we suggest that during global glaciations, even a limited area of open waters ( $10^3 \text{ km}^2$ ) allows an efficient atmospheric  $\text{CO}_2$  diffusion into the ocean. This exchange implies that the  $\text{CO}_2$  consumption through the low-temperature alteration of the oceanic crust persists throughout the glaciation. Furthermore, our model shows that rising  $\text{CO}_2$  during the glaciation increases the efficiency of this sink through the seawater acidification. As a result, the atmospheric  $\text{CO}_2$  evolution is asymptotic, limiting the growth rate of the atmospheric carbon reservoir. Even after the maximum estimated duration of the glaciation (30 m.y.), the atmospheric  $\text{CO}_2$  is far from reaching the minimum deglaciation threshold (0.29 bar). Accounting for this previously neglected carbon sink, processes that decrease the  $\text{CO}_2$  deglaciation threshold must be further explored.

**Keywords:** carbon cycle, seafloor weathering, snowball Earth, Neoproterozoic.

## INTRODUCTION

Although processes and conditions required to trigger a snowball Earth (Kirschvink, 1992) have been intensively explored (Donnadieu et al., 2002, 2004a, 2004b; Schrag et al., 2002; Warren et al., 2002), studies related to the deglaciation of a snowball Earth remain scarce (Caldeira and Kasting, 1992; Higgins and Schrag, 2003; Pierrehumbert, 2005). The amount of atmospheric  $\text{CO}_2$  needed to trigger the deglaciation from a globally ice-covered Earth was first evaluated at 0.12 bar (Caldeira and Kasting, 1992) and then modified at 0.29 bar by Pierrehumbert (2004) to account for the decreased solar luminosity in Neoproterozoic time. Using a more complex and comprehensive model (an atmospheric general circulation model, i.e., AGCM), Pierrehumbert (2005) demonstrated that the threshold value of 0.29 bar calculated with an energy balance model (EBM) was underestimated, and suggested that this value is at the lower end of the  $\text{CO}_2$  levels required to deglaciate the snowball Earth.

In this contribution we focus on the various processes that may affect the way  $\text{CO}_2$  would accumulate in a snowball atmosphere. It has been assumed that the drastic reduction of the continental weathering and the primary productivity occurring in a snowball Earth would have left the  $\text{CO}_2$  outgassed by volcanoes free

to accumulate in the atmosphere. Hoffman et al. (1998) calculated that atmospheric  $p\text{CO}_2$  would reach 0.12 bar at the present outgassing rate after  $\sim 4$  m.y. if no air-sea gas exchange took place, but that partial gas exchange through cracks in sea ice would increase this estimate. In contrast, Higgins and Schrag (2003) assumed that the ocean and atmosphere were in equilibrium with respect to  $\text{CO}_2$  due to the air-sea gas exchange during the entire glacial event. However, in this later case an important additional factor able to modify the seawater chemistry, i.e., the low-temperature alteration of the oceanic crust, has to be considered if air-sea gas exchange took place. Because a large amount of the atmospheric  $\text{CO}_2$  could be dissolved into the ocean, the ocean acidification promotes the removal of carbon through basaltic crust dissolution. This sink may have moved the simple linear atmospheric  $\text{CO}_2$  accumulation toward an asymptotic evolution, raising the question of whether deglaciation melting can be reached.

## CARBON CYCLE AND SEAFLOOR WEATHERING DURING SNOWBALL EVENTS

To investigate and quantify the carbon cycle evolution in a snowball environment, we designed a simple numerical model of the

carbon-alkalinity cycles that includes the calculation of the seafloor weathering response to the acidification of the ocean (see Appendix). The model includes a box for the atmosphere, while the ocean is partitioned between a surface and a deep reservoir connected to a reservoir of water percolating through the oceanic crust, with a residence time of  $2 \times 10^4$  yr (Elderfield and Schultz, 1996). The  $\text{CO}_2$  exchange flux,  $F$ , at the ocean-atmosphere interface is calculated as a function of the gradient between the calculated atmospheric ( $p\text{CO}_2^{\text{atm}}$ ) and dissolved oceanic  $p\text{CO}_2$  ( $p\text{CO}_2^{\text{ocean}}$ ):

$$F = \alpha (p\text{CO}_2^{\text{atm}} - p\text{CO}_2^{\text{ocean}}) \text{area}_{\text{open}}, \quad (1)$$

where  $\alpha$  is the diffusion coefficient fixed at  $16 \text{ mol}/(\text{yr m}^2 \text{ PAL})$  [Present Atmospheric Level] (Etcheto et al., 1991), a value typical of high-latitude cold seawater, and  $\text{area}_{\text{open}}$  is the area of open water, a value considered as a model parameter that can be tested.  $p\text{CO}_2^{\text{ocean}}$  is estimated using Henry's law, fixing surface ocean temperature at 275 K during the snowball Earth. Carbonate speciation is calculated for each water reservoir at each time step. We assume an oceanic vertical mixing 100 times lower than the present-day thermohaline circulation (0.02 Sv) between the surface and deep ocean to account for the maximal expected overturning reduction due to the ice-covered ocean, because it seems physically improbable to completely shut down the general circulation (Zhang et al., 2001). Low-temperature seafloor alteration is calculated using laboratory kinetic laws (see Appendix). The dissolution of each mineral constitutive of the fresh basaltic crust (assumed to be a tholeiitic basalt) is modeled as a function of the temperature,  $T$ , of the water in contact with the basalt (fixed at  $40^\circ\text{C}$ ) (Brady and Gislason, 1997), and the pH of the percolating waters. The conclusions of this study partly depend on the model parameters, including the vertical mixing of the ocean, the present-day amplitude of the seafloor weathering, the water flux percolating the oceanic crust as well as its temperature, the seafloor spreading rate, the presence or absence of seafloor carbonates, and the area of open water. In the following we concentrate on the two last parameters, which are by far the most important. More details and

diagrams about sensitivity tests, regarding other important parameters such as the vertical mixing of the ocean and the efficiency of the seafloor weathering, can be found in GSA Data Repository Figures DR1 and DR2.<sup>1</sup>

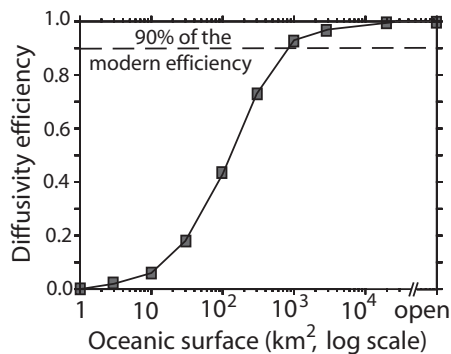
### Efficient Exchange Between the Ocean and Atmosphere

We first tested the minimal surface of open waters allowing an efficient diffusion of the atmospheric CO<sub>2</sub> into the ocean. Patches of open water were proposed in the original snowball Earth theory as refugia for living organisms (Kirschvink, 1992). Their existence has been confirmed by the study of Neoproterozoic formations (Hoffman and Maloof, 1999). To test the efficiency of the CO<sub>2</sub> diffusion from the atmosphere into the ocean, we define the diffusion efficiency *E*:

$$E = 1 - \frac{p\text{CO}_2(\text{area}_{\text{open}})}{p\text{CO}_2(\text{hard snowball})}, \quad (2)$$

where  $p\text{CO}_2(\text{area}_{\text{open}})$  is the CO<sub>2</sub> level reached after a simulation of 30 m.y., the maximum estimated duration of the snowball event (Hoffman et al., 1998), for a given free water area ( $\text{area}_{\text{open}}$ ), and  $p\text{CO}_2(\text{hard snowball})$  is the same value assuming an ocean fully covered with ice. This *E* parameter is then normalized to its present-day value ( $\text{area}_{\text{open}} = 363 \times 10^6 \text{ km}^2$ ). In our set of model simulations, wherein the ice-free surface is varied from the present-day ocean surface ( $363 \times 10^6 \text{ km}^2$ ) to 0 km<sup>2</sup>, we calculate that above 3000 km<sup>2</sup>, atmospheric CO<sub>2</sub> has enough time at the geologic time scale (here several millions of years) to dissolve within the ocean, and the area of open water is not a limiting factor for diffusion (Fig. 1). Below 3000 km<sup>2</sup>, atmospheric CO<sub>2</sub> mixing into the ocean is limited. Today the surface of emerged active hydrothermal areas largely exceeds the 10<sup>3</sup> km<sup>2</sup> scale, being equal to  $1.5 \times 10^6 \text{ km}^2$  (Dessert et al., 2003). During global glaciations, emerged geothermal environments may be associated with small open water areas, maintained by heat production and lava flows. However, the existence of thick sea ice (Goodman, 2006) may reduce the contact between the patches of free waters and the whole ocean, limiting the CO<sub>2</sub> dissolution. For that reason, we cannot firmly state that the atmospheric CO<sub>2</sub> diffusion was fully efficient, but only 3000 km<sup>2</sup> of open waters in contact with the whole ocean are enough to achieve massive CO<sub>2</sub> dissolution.

<sup>1</sup>GSA Data Repository item 2008013, Figures DR1–DR3, supplementary information on the model and additional tests, is available online at [www.geosociety.org/pubs/ft2008.htm](http://www.geosociety.org/pubs/ft2008.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1. Normalized CO<sub>2</sub> diffusion efficiency as function of the ice-free oceanic surface.**

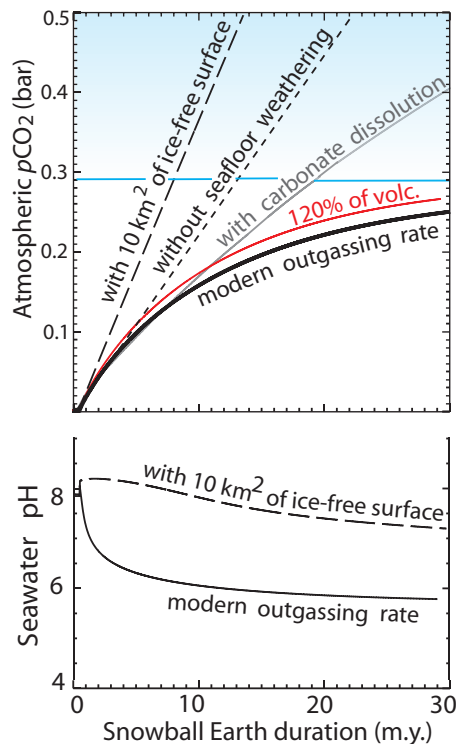
### Implications

If CO<sub>2</sub> is allowed to dissolve within the ocean during the building up of extremely high atmospheric carbon levels, seawater pH should drastically decrease and promote both deep-sea carbonates and oceanic basaltic crust dissolution.

### Seafloor Weathering and Its Implication on the pCO<sub>2</sub>

In the absence of deep seafloor sedimentary carbonates, the seawater acidification enhances the consumption of dissolved carbon through low-temperature alteration of the oceanic basaltic crust. Under the corrosive action of seawater percolating the crust at almost kilometeric depth, basalts dissolve and release alkalinity, which is then removed through carbonate precipitation in veins from highly saturated pore waters (Alt and Teagle, 1999; Brady and Gislason, 1997; Spivack and Staudigel, 1994). The CO<sub>2</sub> consumption through seafloor basaltic weathering rises until the ocean is sufficiently acidified, so that consumption of carbon through seafloor weathering balances solid Earth outgassing.

The question is whether this theoretical steady-state CO<sub>2</sub> is higher than the required deglaciation threshold. In our scenario accounting for seafloor weathering, the atmospheric CO<sub>2</sub> build up does not rise linearly as in the classical snowball scenario (Fig. 2), but reaches an asymptotic value. Assuming a present-day total degassing rate of  $7.15 \times 10^{12} \text{ mol/yr}$  (a value fixed to balance the present continental silicate and seafloor basalt CO<sub>2</sub> consumption rates) (Brady and Gislason, 1997; Gaillardet et al., 1999), we found that the atmospheric partial pressure does not exceed 0.17 bar within the estimated snowball duration of 12 m.y. (Bodiseliitch et al., 2005), because the seawater pH goes rapidly down to 6, increasing the seafloor weathering rate by a factor slightly above 4. Even after 30 m.y., the maximal duration for the snowball event (Hoffman et al., 1998), and with a volcanic outgassing rate enhanced by 20% (which is the maximum increase recorded over the past



**Figure 2. CO<sub>2</sub> evolution as function of the snowball Earth duration; 30 m.y. is maximum estimate. One run was performed with 10 km<sup>2</sup> of ice-free surface, all others with ice-free surface of 3000 km<sup>2</sup>. Snowball earth deglaciation threshold (blue line) is 0.29 bar, estimated through an energy balance model simulation for a Neoproterozoic insolation. With a modern outgassing rate, the difference between the run with or without the seafloor weathering (black thick line and black dashed line, respectively) shows the impact of the CO<sub>2</sub> consumption by the low-temperature weathering of the basaltic seafloor. Higher volcanic degassing rate (red line) (1.2× present day; see text) would help at rising more rapidly the atmospheric CO<sub>2</sub> level but not sufficiently to overcome the deglaciation threshold. Because total degassing depends on the seafloor-spreading rate (Gaffin, 1987), the CO<sub>2</sub> consumption increases proportionally the surface of fresh seafloor basaltic rocks exposed to seawater. Below 10 km<sup>2</sup> of ice-free surface, the CO<sub>2</sub> diffusion becomes so weak that the atmosphere and ocean remain virtually isolated, the CO<sub>2</sub> accumulates in the atmosphere, and the seafloor weathering effect becomes negligible.**

160 m.y.; Cogne and Humler, 2004), the CO<sub>2</sub> threshold of 0.29 bar required to escape the snowball glaciation cannot be reached (Fig. 2).

### Buffering of Seawater pH through Carbonate Dissolution or Basaltic Weathering?

Seafloor sedimentary carbonate dissolution may have buffered seawater pH during the snowball glaciation, thus reducing the efficiency of seafloor weathering. However, maintain-

ing carbonate saturation (Higgins and Schrag, 2003) under 0.12 bar of CO<sub>2</sub> would require a calcium concentration in seawater twice its present-day level, corresponding to the dissolution of  $2.5 \times 10^{19}$  mol of carbonates if preglacial calcium concentration was close to its present-day value. If carbonate were of shelfal origin (pelagic carbonate producers being virtually absent), and considering the maximum past carbonate shelf extent of  $15 \times 10^6$  km<sup>2</sup> (Walker et al., 2002), this would correspond to the dissolution of 66 m of carbonate sediments. This value would be even greater since the 0.12 bar threshold is largely underestimated (Pierrehumbert, 2004). Because sea level fell by more than 400 m during the glacial event (Hoffman et al., 2007), these shelf carbonates might not be available for dissolution.

However, carbonate slumps along continental slopes (Swart, 1992) or preglacial direct abiotic precipitation might have partly overlaid the deep seafloor with carbonates. We tested this hypothesis by running the model assuming that deep-sea carbonate dissolution occurs kinetically during the glacial event, forcing the seawater saturation index to 1. This corresponds to the maximum impact of carbonate dissolution on seawater chemistry, since dissolution stops when the saturation index reaches 1. We found that alkalinity rose to 18 equivalents/m<sup>3</sup> when CO<sub>2</sub> reached 0.29 bar, as a result of Ca<sup>2+</sup> release by the carbonate dissolution and Ca<sup>2+</sup>/Mg<sup>2+</sup> exchange at mid oceanic ridges (Elderfield and Schultz, 1996). Seawater pH is calculated as 6.17, close to the 5.9 calculated in the absence of seafloor sedimentary carbonates. However, oceanic crust dissolution is sensitive to small pH changes. We calculate that, accounting for the maximum effect of carbonate buffering and because basaltic seafloor weathering is reduced, 0.29 bar of CO<sub>2</sub> can be reached in 19 m.y. This maximum effect corresponds to the dissolution of a 3-m-thick sedimentary carbonate layer spread over the global seafloor surface.

A possible anoxic state of the deep ocean may increase the pH of seawater during the snowball Earth. This would also result in decreased efficiency of the seafloor weathering. All along the glacial state, sulfate reduction may have produced alkalinity if the deep ocean was anoxic. The importance of this process depends upon the SO<sub>4</sub><sup>2-</sup> level in seawater prior to the glacial event, and upon the availability of organic carbon in the water column and on the deep seafloor. A recent estimation shows that the SO<sub>4</sub><sup>2-</sup> level might have been an order of magnitude below the present-day level (Hurtgen et al., 2002), thus largely below the dissolved inorganic carbon content of a snowball ocean, itself an order of magnitude above its present-day level in our calculations due to efficient atmospheric carbon dissolution.

For that reason, we suggest that the ocean pH was still largely controlled by carbonate speciation, even during a snowball event.

## CONCLUSION

If the snowball Earth occurred, it must have deglaciated. Our study shows that if the area of surface water in contact with the deep ocean is sufficient, the dissolution of the basaltic oceanic crust during the snowball glaciation may delay the atmospheric CO<sub>2</sub> rise required to reach the melting threshold, up to unacceptable time spans. The snowball theory thus requires either an extremely efficient dissolution of a large seafloor sedimentary carbonate reservoir whose existence remains hypothetical, or additional plausible processes able to decrease the CO<sub>2</sub> threshold through, for example, an albedo decrease, such as the deposition of dark fine volcanic ash on the ice and snow as suggested by Pierrehumbert (2004), or the existence of a thin equatorial ice (Goodman, 2006; Pollard and Kasting, 2005, 2006; Warren and Brandt, 2006).

## APPENDIX: GEOCHEMICAL MODELING PROCEDURE

To simulate the evolution of the carbon content before the global glaciation, we first run the model according to Proterozoic preglacial conditions until a steady state is reached (Fig. DR3; see footnote 1). We use a standard silicate weathering law, where Ca<sup>2+</sup> and Mg<sup>2+</sup> weathering rates are proportional to global runoff and depend on mean global air temperature (Oliva et al., 2004). Continental carbonate weathering is proportional to global runoff times the concentration of Ca<sup>2+</sup> in equilibrium with calcite at the calculated mean air temperature and atmospheric CO<sub>2</sub>. Both air temperature and runoff are assumed to be a function of atmospheric CO<sub>2</sub>. Biological productivity in the surface ocean is made dependent on the input flux of phosphorus from the deep ocean (to simulate upwelling consequences) and from the weathering of continental surfaces. These dependencies are used for the calibration procedure, because continental silicate, carbonate, and phosphorus weathering are shut down during the snowball glaciation.

To apply snowball conditions we instantaneously shut down all continental weathering fluxes to reproduce the consequences of the rapid growth of continental ice sheets and the strong weakening of the hydrological cycle. Surface water temperature is forced to drop from 20 °C to 2 °C, and the vertical mixing between the surface and deep ocean decreases from  $21 \times 10^6$  m<sup>3</sup>/s to  $0.2 \times 10^6$  m<sup>3</sup>/s. The model then evolves freely.

The  $\alpha$  value used in equation 1 depends on wind speed (Wanninkhof, 1992). The wind

action may be more efficient on one large surface than on several small. Since the total of ice-free surface is the sum of several small surfaces, K may be overestimated in our scenario. However in the extreme case wherein K is reduced by 10, the threshold surface required for an efficient exchange reaches  $3 \times 10^4$  instead of  $3 \times 10^3$  km<sup>2</sup>, which remains very small. Note, however, that wind speed during the snowball event remains largely unknown, and the K we used is probably one of the best estimates that can be made.

## Seafloor Weathering Parameterization

The deep ocean reservoir is in contact with a water reservoir incorporated into the oceanic crust. The temperature of the deep ocean is held constant at 275 K, and based on a present-day estimation (Elderfield and Schultz, 1996), the exchange water flux between the reservoir of percolating waters and the deep ocean is  $0.2 \times 10^6$  m<sup>3</sup>/s, given that  $735 \times 10^{13}$  kg/yr of water are involved in the water circulation off axis at low temperature.

The reservoir of percolating waters is depleted in carbon through low-temperature dissolution of the basaltic crust, under the corrosive action of seawater. The release of alkalinity through this process is assumed to finally lead to the precipitation of carbonate minerals from highly saturated waters in veins, thus removing carbon from the ocean-atmosphere system at the million year time scale. The global sink of carbon is estimated as  $\sim 1.5\text{--}2.4 \times 10^{12}$  mol/yr (Alt and Teagle, 1999). Dissolution of seafloor basalts is calculated using laboratory kinetic laws to estimate the response of the H<sup>+</sup>, OH<sup>-</sup>, and H<sub>2</sub>O promoted dissolution to change in seawater pH. The mineralogical composition of the crust is taken as the mineralogy of a tholeiitic basalt, containing 54% labradorite, 32% diopside, 9% basaltic glass, 4.3% apatite, and 1.3% forsterite. Kinetic constants are taken from the WITCH model database (Godderis et al., 2006; Drever, 1997). For each mineral, the overall dissolution rate  $R_{\text{basalt}}$  (in moles of Ca<sup>2+</sup> released per m<sup>2</sup> of mineral per year) is estimated as following:

$$R_{\text{basalt}} = \sum_i d_i \exp\left(\frac{-E_i}{R \cdot T_p}\right) C_i^{n_i}, \quad (\text{A1})$$

where the sum extends up to all the dissolving species (H<sup>+</sup>, OH<sup>-</sup> and H<sub>2</sub>O), while the index  $i$  stands for the dissolving species.  $E_i$  and  $d_i$  are, respectively, the activation energy and dissolution constant for each mineral depending on the species  $i$  promoted dissolution.  $T_p$  is the temperature of the percolating waters into the oceanic crust at which dissolution occurs, here fixed at 313 K. The value  $C_i$  stands for the concentration in the species  $i$  that promotes dissolution, while  $n_i$  is the order of the dissolution reaction. We assume that carbon consumption

through seafloor weathering (hereafter swf) equals half of the alkalinity released through dissolution. The calculated overall CO<sub>2</sub> consumption flux  $F_{\text{swf}}$  is multiplied by a constant area, representing the total mineral surface area exposed to dissolution:

$$F_{\text{swf}} = \text{SR} \cdot \text{area} \cdot R_{\text{basalt}}. \quad (\text{A2})$$

This constant is in fact a calibration constant that was fixed so that the total CO<sub>2</sub> consumption rate through seafloor weathering equals  $1.6 \times 10^{12}$  mol/yr under present-day conditions, within the lower range of recent estimations (Alt and Teagle, 1999; Spivack and Staudigel, 1994). SR is the seafloor spreading, normalized to its present-day value. It is kept constant at 1 in all simulations, except when assuming higher outgassing rate, itself corresponding to a higher seafloor-spreading rate. This overall kinetic formalism predicts a minimal basaltic dissolution rate at the present value of the ocean pH of 8.2.

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