Biogeosciences Discuss., 4, S1473–S1481, 2007
www.biogeosciences-discuss.net/4/S1473/2007/

Biogeosciences Discussions

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4, S1473–S1481, 2007

Interactive Comment

Interactive comment on “A geochemical modelling study of the evolution of the chemical composition of seawater linked to a global glaciation: implications for life sustainability” *by* G. Le Hir et al.

G. Le Hir et al.

Received and published: 24 September 2007

We first thank the three reviewers for the quality of their reviews. We divided our comment into two distinct parts. First we address the main questions, pointed by one or more reviewers. Specific questions are answered in the second part (for F. Corsetti and A. Ridgwell). We thank the anonymous referee 2 for its very useful comments, especially for its suggestions regarding the dolomite precipitation, and for the references cited. The technical corrections are now taken into account in the final draft. All scientific comments of the reviewer 2 are discussed in the General comments of the paper (hereafter).

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General comments We agree that a glaring weakness of the paper is the question of the implication for life sustainability of our geochemical results. Indeed, this question of sustainability is only superficially addressed. Nevertheless we strongly believe that relationships between climate, environmental pressure and evolution are very complex questions. Our main aim was to quantify the environmental changes to explore the consequences on the Precambrian life. However, as A. Ridgwell suggests, we do not strictly prove the link between the life evolution and global glaciation. This is a complex question that no one can fully answer up to now. We only define possible geochemical conditions during and in the aftermath of a snowball glaciation. This is the very first part of the answer to the question of life sustainability. For that reason we have changes the title of our paper, removing the last sentence regarding the life survivance, and the section dealing with the life sustainability in the main text will be rewritten somehow in the final draft.

(1) The paradox question. The paradox arises if two contradictory facts are verified: first life was not disturbed by the snowball events, second the snowball events did result in a very strong perturbation of the geochemical environment. The first assertion is controversial. Some fossils records do not show any variations in terms of biodiversity before, during and after the Marionan event (Corsetti et al., 2003; Corsetti et al., 2006; Grey et al., 2003). However, as noted by reviewer 2, this question remains open because new fossils found in Doushantuo formation (Yin et al., 2007) show a relationship between life evolution and the snowball events (note that this was published after the submission of our paper). The objective of our paper was to check whether the second assertion was true or not. And the answer is yes. We further suggest that the most important environmental pressure on life should occur during the deglaciation. The amplitude of the changes is so important that there is no doubt that only very permissive life forms, thus lowly complex (no complex animals) should be able to survive. So clearly the Yin et al. (2007) paper strengthened our conclusions, and in that case, there is no more paradox. We thus agree with reviewer 2. However the datation of the Doushantuo phosphorites remains controversial, Barfod et al (Barfod et al., 2002)

BGD

4, S1473–S1481, 2007

Interactive Comment

suggest an age around ˜599.3 +/-4.2 Ma or 584.9 +/-26 Ma. The datation by Condon et al (Condon et al., 2005) suggests that most of the Doushantuo embryos of Yin et al (2007) are younger than 580My (using the δ13C record). Only some of the Yin et al. samples (XFHB-37, XFHB-35, XFHB-30 XFHB-24, XFHB-19) are effectively dated between 632 and 580My, thus in the direct aftermath of the Marinoan glaciation. Stating that the Doushantuo embryos are located immediately after the Marinoan glacial event may be somehow overstated, because the datation remains ambiguous. Thus whether a paradox exists or not might still be an open question. We will modify the main text accordingly. But the reviewer 2 comment will be also included. So both hypotheses regarding the impact on life evolution around the snowball events will be briefly included.

(2) The surface ocean during the Neoproterozoic Indeed nobody knows exactly what was the oceanic surface at that time. The present day surface of the ocean stands for 70.8% of the Earth surface. Several crustal growth models are proposed for the crust surface evolution (linear, episodic, rapid early growth) (Origin and Evolution of Earth, by K.Condie and R. Sloan, Prentice Hall eds), but in all of them, the crustal growth is almost achieved by the time of the Neoproterozoic. The most accepted model (the episodic one) predicts that, at 0.7Ga, the continental crust surface was 7% smaller than the present day surface. 75 % of the Earth surface covered by the ocean is a reasonable assumption. Changing this value by up to 20 % does not change significantly our results.

(3) An efficient weathering during the Snowball Earth? This is a critical point applying to the whole snowball Earth theory. Indeed a recent contribution suggests that the continental weathering has remained efficient during warm periods inside the glaciation (Rieu et al., 2007). Using the chemical index of alteration observed in the Oman section, they found three intervals with evidence for extremely low rates of chemical weathering, indicating pulses of cold climate. However these intervals alternate with periods of high rates of chemical weathering, which is argued as representative of in-

BGD

4, S1473–S1481, 2007

Interactive Comment

EGU

terglacial periods with warmer climates. We think that if periods of intense weathering occurred inside the Neoproterozoic glacial event, then the glacial pulses cannot be assimilated to snowball event for two main reasons. First, Rieu et al. (2007) identified 3 to 4 intense weathering episodes inside a 10Ma period, alternating with glacial pulse. As a consequence glacial pulses cannot be snowball glaciations because time is too short to allow for the accumulation of up to 0.29 bars of CO2 into the atmosphere tom mel it. Second, assuming that warm periods occurred during a snowball glacial episode is controversial in terms of climate. Indeed, Pierrehumbert (Pierrehumbert, 2005) has shown that with 0.2bar the equatorial temperature remains far below the melting point, the annual mean temperature reaching ˜230K. Therefore the climate remains dramatically cold all along the snowball, until the melting threshold is reached. We conclude that the Rieu et al. (2007) data are not compatible with the snowball theory, as strongly suggested by Rieu et al. themselves. However, BIFs, δ13C shift, Ir accumulation, and the cause of cap carbonate deposition must still be explained, and the datation of the Fiq formation remains unknown (Leather et al., 2002). Furthermore, in the Oman section (Rieu et al 2007) high weathering rates seem to be associated with sandstone banks, not with diamictites. In this context sediments may come from several sources with different initial weathering degrees. Since the chemical weathering drops, in a cold environment (Tranter et al., 2002), the glacial transport would not affect its index. In this case variations in weathering index represent a variation in the source, without a climate origin (as suggested P.Hoffman on his website, http://www.snowballearth.org/), although the reason why it should be cyclic remains obscure. Furthermore, the Fiq formation may have recorded either the inception or the melting phase of a snowball event, as suggested by reviewer 2, in case there is no contradiction with the snowball Earth theory. Finally, Leather et al. (2002) and Rieu et al. (2007) do not mention any datation for the Fiq formation. Our model was designed to test the hard snowball scenario. The objective is to answer the question: what is the geochemical impact of a hard snowball glaciation? Rieu et al. (2007) suggest a totally different glacial environment, and testing it is beyond the scope of this paper. If the chemical weathering remains efficient during the glaciation, then the Snowball theory needs to be deeply reformulated.

Note finally that the existence of a dynamic ice cycle is not in contradiction with a collapse of weathering, since what is needed for weathering is liquid water. A dynamic ice cycle may be maintained through sublimation and ice formation only, without transient liquid water. Hence, if a chemical weathering is maintained below glaciers then it is certainly extremely low (Tranter et al., 2002).

(4) The sharp contact between the diamictites and cap carbonates Reviewer 1 suggests that a knife sharp contact does not have a solid significance in term of timing, and it is our opinion too. But the question is what happened during the hiatus, if any.

Duration of a possible hiatus in carbonate sedimentation. A. Ridgwell points at a very good question. In our study, if cap carbonates precipitate when the ocean become saturated (omega=1), the duration of the hiatus is 20kyr (figure 8). If a threshold of omega=10 is required, then the hiatus reaches 100kyrs (Figure 8). First, we do not feel that the exact value of the saturation threshold is so important. Cap carbonates are indeed cap dolomites, and nobody knows how they formed. We have no kinetic laws describing accurately dolomite precipitation. So, the saturation threshold is only indicative of the existence of a threshold, but its exact value is not known. However, the question is the compatibility between the timing of the hiatus and the melting phase. If this duration of the hiatus exceeds the deglaciation duration, then cap carbonates should start to precipitate after the transgression, and this is not the case (Higgins and Schrag, 2003; Hoffman et al., 2007). But is the deglaciation really fast? Nobody can precisely constrain the melting duration, but geological evidences (several paleomagnetic inversions in cap dolostones, (Font et al., 2006; Sohl et al., 1999)) suggest that the cap dolostones are precipitated during at least 250kyrs, and probably more. Therefore a hiatus of up to 100kyrs is not in contradiction with the precipitation of cap carbonates during the transgression.

BGD

4, S1473–S1481, 2007

Hiatus and the presence of siliclastic sediments Andy Ridgwell asks the question about the absence of siliclastic sediments in the hiatus between diamictites and the cap carbonate (Fig 9b). First, our results suggest that this is a carbonate sedimentation hiatus, not a total sedimentation hiatus. Cap carbonates cannot accumulate in the direct vicinity of the glacial phase because of calculated undersaturation. But diamictites were mostly accumulated during the melting phase, and prior to the restart of the carbonate sedimentation (Hoffman et al., 2007). The siliclastic sediments are thus not missing: there are parts of the diamictite sequence accumulated during the melting phase. So there might be no sedimentation hiatus at all. We suggest to modify fig. 9b, which was confusing, by replacing the hiatus by diamictites.

Second, the sedimentary record shows that diamictites were generally not accumulated at the same location than the cap carbonates, but in the deep sea environment (Hoffman et al., 2007). This suggest that siliclastic sediments were removed in the early phase of the melting, when sea-level was very low, thus during our calculated carbonate sedimentation hiatus. And cap carbonate accumulation occurs in shallower environments (Hoffman et al., 2007), thus at the end of the flooding.

Anyway, a modelling of the melting phase is highly needed, but not easy to perform. This should be a priority for the modelling community working on the snowball Earth.

(4) Carbonates in a acidic ocean The carbonates are dissolved when the ocean becomes undersaturated (omega$<$1), not when the ocean becomes acidic. This was a misprint. In one of our simulation, we maintain carbonate saturation in the ocean under more than 0.2 bars of CO2. The pH goes down to 6, so the acidic ocean stays saturated (Figure 5 corrected and Figure 6). The only limitation to this process (carbonate dissolution) is the mass of carbonate available for dissolution.

About the presence of carbonate debris in the diamictites: if the part of the diamictites were deposited during the melting phase of the snowball, they experienced a maximum of 20kyrs of carbonate undersaturation, from the deglaciation threshold up to the

BGD

4, S1473–S1481, 2007

Interactive Comment

carbonate sedimentation start, according to the model results. According to the above discussion, there might be still at least 80kyrs of diamictites accumulation under saturated conditions. As a result, our model does not exclude the existence of fine grained carbonates inside the diamictites.

(5) The seafloor weathering Andy Ridgwell asks for more information about equation 1. This equation is a kinetic description of the dissolution rate of a silicate mineral, inferred from the transition state theory (Eyring, 1937; Godderis et al., 2006). Rbas is the total dissolution of the basaltic rock in mol of main cation/m2 of rock/yr. We will modify the text accordingly. This Rbas rate has to be multiplied by a reactive surface. The total reactive surface of the oceanic crust cannot be estimated, but we use this surface as proportionality constant to calibrate the total CO2 consumption by seafloor weathering on the published estimates (Alt and Teagle, 1999). The kinetic constants are given in table 1 (included in the final draft).

For sure, we are not arguing that our estimate of the seafloor weathering in the Precambrian is safe, because of poorly known environmental boundary conditions. But kinetics is the same in the Precambrian and today. It is safer to use kinetic laws than extrapolating parametric laws calibrated on the present day conditions. Furthermore, the deep sea temperature is not the ultimate temperature controlling the seafloor weathering process. The temperature of interaction depends on the thermal gradient of the crust, and we fixed it at 40°C (Brady and Gislason, 1997). This temperature is at least partly decoupled from the deep sea temperature. Finally, the mineralogical composition of the oceanic crust at the very end of the Precambrian can be reasonably fixed at its present day mean value.

The seafloor weathering efficiency is of course dependent on several parameters. The most important of them are the vertical mixing of the ocean, and the mid-oceanic ridge spreading rate. Indeed the vertical mixing brings the carbon from the atmosphere and the surface ocean in contact with the oceanic crust. Cutting down completely the vertical mixing during the snowball will leave the seafloor weathering without any impact on the carbon content of the atmosphere. This point is further discussed in the next section. Regarding the seafloor spreading rate, we might expect that seafloor weathering linearly increases with spreading rate (Wallmann, 2003). But this is also the case of the mid-oceanic ridge degassing. Changing by 20 % the spreading rate (this is the maximum amplitude of the spreading rate change during the last 200 million years (Cogne and Humler, 2004) does not change significantly our result, the change in the CO2 sink being largely compensated for by the change in the CO2 source.

(6) Vertical oceanic mixing Nobody knows about the mixing of the ocean prior to the snowball event. However, we might expect that an almost fully ice covered ocean will experience less mixing. Indeed, this is already the case for the ocean mixing during the last glacial maximum. There is no doubt that the thermohaline circulation will be strongly affected by the presence of a worldwide sea ice cover. Hence, we have drastically reduced the vertical mixing during the glaciation (down to 0.21Sv)(21Sv being the present assumption for the oceanic circulation intensity (IPCC report). We argue that 0.21 Sv is really the minimum value because tidal forces weakly mix yet the ocean (Garrett, 2003) and that a fully stratified ocean cannot be physically maintained during a long period of time (Zhang et al., 2001). Reducing the vertical mixing, our objective was to test the reliability of our CO2 consumption mechanism through seafloor weathering. Any higher value of the vertical mixing will facilitate the consumption of CO2 by seafloor weathering, by bringing more CO2 from the atmosphere and surface ocean in contact with the oceanic crust. The stratification of the ocean was chosen to test the limit of our model, we did not choose this minimal value relative to O2 consideration. But with a low overturning, one consequence is, indeed, the decrease in O2 concentration of the deep waters, because the O2 consumption at mid-oceanic ridges remains efficient. Note that the O2 level is already in the dysoxic domain prior to the glaciation (due to low atmospheric levels), and is divided by two during the glacial phase in the deep ocean. To match the reviewer requirement, we performed two additional sensitivity tests, assuming a decrease in vertical mixing by 10 and by 50. The corresponding O2 levels in the deep ocean after 30 Ma of simulation are 0.011 mol/m3 and 0.010

BGD

4, S1473–S1481, 2007

Interactive Comment

EGU

mol/m3, compared to the 0.009 of the reference run. Thus reducing the vertical mixing by 10 is already enough to drive the deep ocean to deep dysoxia.

(4) Technical point The reference list will be updated including all references cited by referees. A special attention will be paid to cite the initial papers instead of reviews papers. Regarding the Figures, the corrections will be included in the final draft, and the complementary information in the figure caption.

Interactive comment on Biogeosciences Discuss., 4, 1839, 2007.