

***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.***

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Le Hir and colleagues present a model analysis of the potential global geochemical changes associated with a Neoproterozoic 'snowball Earth' like event and its aftermath. From the rate and magnitude of the changes in various environmental properties such as ocean surface pH, they speculate on the implications for snowball Earth events to provide sufficient selective pressure to drive new evolutionary innovation.

Their modelling approach represents a new analysis of the evolution of marine geo-

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chemistry through a freeze-thaw cycle and includes processes not included in previous model studies. The pH and delta-13C predictions are interesting and provocative, although by no means the 'last word' in simulating this event. The implications of the geochemical predictions, particularly (calcite) saturation state and its rate of change are important for helping develop a more complete understanding of the nature and cause of the enigmatic 'cap carbonates' found immediately overlying Neoproterozoic glacial deposits. This work can certainly achieve the criteria for publication. However, some improvements and perhaps a re-focussing need be made to the paper, detailed below. Grammar (and spellings) in many places must also be re-visited.

First, I would like to engage the authors in what to my mind is a glaring weakness in the paper - concerning the "implications for life sustainability" as per the title. Much of the abstract also concerns the implications of the rate and magnitude of environmental change (particularly ocean surface pH and dissolved oxygen concentrations), yet the authors do not provide any substantive link between their geochemical predictions and impacts (or lack of them) on life. This still-born focus on 'implications for life sustainability' is apparent later on in the paper - out of the 8-and-a-half; pages of the main body of the text, only a single page addresses the hypothesis I infer that they are testing, namely: that the global environmental changes during a late Neoproterozoic freeze-thaw cycle were of insufficient intensity (rate?) to provide a substantive filter on life. Furthermore, their conclusions on this matter are not clear, even though this seemed the intended point of the paper.

The paper would greatly benefit from a clearer statement of the hypothesis they are testing (that global environmental change was (or was not) sufficient to provide a substantive selective pressure?). I would recommend explicitly stating and discussing exactly how the paradox stated in the abstract "In this contribution we address this apparent paradox [of little change in diversity in biological records]" is resolved (or not). The authors seem to be saying that the magnitude of perturbation was insufficient to drive widespread extinction, but the rate of change was fast and important. Yet the

geological evidence (stated in the abstract) suggests that the rate wasn't important either(?) Or am I just getting confused now? Even, at the outset, it is not even clear to me exactly what the title: "implications for life sustainability" actually means. So, some considered re-writing in general in order to maximize clarity would not go amiss.

Much more substantive and interesting to me in the paper is the geochemical (and isotopic) modelling and its implications and the addition of sea-floor weathering in this study is novel and important. In fact, I see this paper as much a 'cap carbonate' paper than anything else and I think that this is where the author's most important findings lie. Indeed, the majority of the Figures relate to properties recorded in carbonates ( $\delta^{13}\text{C}$ ) or ocean environmental properties that dictate the precipitation or not of  $\text{CaCO}_3$  (pH, alkalinity, saturation). The key can be summarized so: as the authors note, "cap carbonates overlapping glacial diamictites shows a "knife-edge" contact suggesting no significant hiatus", and further, that "This abrupt juxtaposition implies an instantaneous shift from ice-house to extreme green-house conditions". (As an aside, we need some references here. A reproduced field image with scale bar would also not go amiss for illustration.) However, the authors find that it takes "20 kyr" before precipitation can commence (also, see: Figure 8). I think this is a critical point - Paul Hoffman and colleagues set up the occurrence of cap carbonates as a falsification test of the snowball Earth hypothesis in their 1998 Science paper. Yet I cannot see how if the contact between glacial diamictite and overlying carbonate truly is 'sharp' (or at least, separated by little intervening deposition) that you can fit in 20 kyr of time. After all, we have 7 times (this paper) to 40 times (if I recall correctly) in Hoffman and Schrag [2002] for the inferred enhancement in global weathering rates. Where are the resulting siliclastic deposits? Or any evidence for there having been >20 kyr of every river Worldwide being in a state of flood never seen before or since in Earth history (Noah excepting)?

I believe that the authors would do well to expand on this subject. Regardless, some issues in what they have described in this paper need addressing. Firstly, it is incorrect

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to infer that it would take 20 kyr to get the ocean from an end glacial undersaturated state with  $\text{pH} \sim 6$  to one in which the cap carbonates precipitate. This is the time from undersaturation ( $\text{oh}\omega < 1$ ) to  $\text{oh}\omega = 1$ . The modern ocean has  $\text{oh}\omega \sim 5.5$  at a global (surface) mean, yet we do not have cap carbonates forming everywhere today. The reason is that you probably need something like  $\text{oh}\omega = 10$  for substantial micritic precipitation (e.g., see summary in Ridgwell and Zeebe [2005] - EPSL 234, 299-315). In which case the interval between glacial and cap is  $\sim 100$  kyr according to the Figure 8. Is 100 kyr consistent with a "knife-edge" contact? I believe that understanding the rate of the transition from diamictite to carbonate is key to understanding the source of the alkalinity for the cap as well as potentially allowing us to distinguish between 'hard' and 'slushball' (or other) hypotheses.

I would strongly encourage the authors to take this opportunity to pursue this issue in more detail. For this they might like to note: Ridgwell et al. [2003] (Science 302, 859-862) and/or Ridgwell and Kennedy [2004] (Secular changes in the importance of neritic carbonate deposition as a control on the magnitude and stability of Neoproterozoic ice ages, in: The Extreme Proterozoic: Geology, Geochemistry, and Climate, Eds. Jenkins, G., et al., Geophysical Monograph Series Volume 146, American Geophysical Union, Washington DC). Indeed, in the introduction to Section 2, it is incorrect to state that "previous modelling studies were only focused on the deglaciation" - see Ridgwell et al. [2003], in which a geochemical model was used to address the ocean geochemical evolution (including terrestrial, but not sea-floor weathering) over a complete freeze-thaw cycle. As an aside, the  $< 5$  kyr prediction for the geochemical transition stated in Ridgwell et al. [2003] provides an even more extreme estimate in the model prediction inter-comparison that the authors make on page 1850/lines 16-20.

While I am excited about the carbonate geochemistry evolution (and carbonate precipitation) analysis that the authors are engaging in, I am a little uneasy about the model predictions of "extended hypoxia" (Abstract) and "development of widespread anoxia" (Conclusions), which are discussed at length in Section 3.1. The dissolved oxygen con-

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centration results arise from: "Coevally overturning reduction and oxygen consumption by hydrothermal vents [that] produce a dysoxic ocean in surface and anoxic at depth" (Conclusions). Caveats associated with this are not discussed. Critically, the assumption that: "vertical mixing, between surface and deep waters, decreases from  $21 \times 10^6$  m<sup>3</sup>/s to  $0.2 \times 10^6$  m<sup>3</sup>/s to represent a maximum oceanic circulation reduction" is neither justified nor implications of the associated uncertainties tested. We need to know on what basis the authors believe that  $21 \times 10^6$  m<sup>3</sup>/s is appropriate for the late Neoproterozoic Ocean (or is it just 'modern' in the absence of information to the contrary). More importantly: why does the ocean completely stratify during the glacial. Thinking simplistically, we are losing heat at the top (through the ice) and gaining it at the bottom (hydrothermal): hardly a great recipe for extreme stratification. It seems to me that this might be rather an important assumption, at least for the O<sub>2</sub> predictions. Perhaps the authors would like to prove me wrong in this. At the minimum we need some justification of the default assumptions and need to see the effect of constant ocean mixing throughout the duration of the freeze-thaw cycle. As an aside -  $10^6$  m<sup>3</sup>/s are the units in the body of the text, and Sv in Figure 2. Please make the equivalence between them explicit.

Also on the subject of oxygen - just how reliable is the 10% PAL (1987 Kasting) estimate that is assumed? I would be interested to learn what the implications are (if any) of making alternative valid assumptions.

Biological productivity in the ocean and the explicit suppression of its rate in order to achieve the required value of atmospheric pO<sub>2</sub> is also likely to be important. What is the assumed global export production prior to the onset of glaciation, and how does it compare to the authors previous modelling as well as to estimates of modern production?

Other points:

o Page 1841/line 2: "Oceans covered more than 75% of the Earth surface during the

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Neoproterozoic". Reference for this?

o Page 1841/line 3: "[oceans] were the only habitable environment for the Precambrian life". See: Heckman et al. [2001] (Molecular evidence for the early colonization of land by fungi and plants, Science, 293, 1129- 1133) or Horodyski and Knauth [1994] (Life on land in the Precambrian, Science, 263, 494- 498) or others.

o Page 1843/lines 20-21: I would put to the authors that their statement: "To avoid any poorly constrained parameterization of this flux, we choose to estimate the weathering rate of the basaltic crust using laboratory kinetic laws for proton" is a little bogus. Are they really trying to tell us that their estimate of Precambrian sea-floor weathering is well constrained (maybe the authors really do know the mineralogy of Precambrian ocean floor basalt and deep water temperature)? Sure - describe it as a mechanistic approach in terms of an improvement over purely empirical parameterizations. However, the equation (#1) in any case is incompletely described - what is  $R_{bas}$  (units?) and how does one derive a value for FSFW of  $1.6 \times 10^{12}$  mol/year (units? - carbon or alkalinity?) from Equation 1. Because of the importance of this equation, more detailed description and information would be extremely helpful. I for one am interested in following your work in this area!

o Page 1844/ line 25: Is the rate of phosphorous removal fixed, or does it depend in some way on the ambient concentration of dissolved  $PO_4$ ? If the former, presumably the ocean reaches a zero  $PO_4$  concentration at some point - is this realistic?

o Page 1845/lines 25-26: "This parametric relationship was obtained by running a radiative-convective climate model". Reference?

o Page 1848/lines 25-27: I would not be upset if you cited Ridgwell et al. [2003] for the hypothesis that the "absence of pelagic carbonates organisms before the Mesozoic (Bown, 2004; Kuznetsova, 2003) excludes the possibility to accumulate deep sea carbonates" :o)

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o Page 1849/lines 2-3: "carbonates are highly soluble when pH decreases below 8" - is this true? I could devise a geochemistry with a pH of 6 but  $\omega$  of 10 if you like - would carbonates still be "highly soluble"?

o Equation 4: Please supply a reference for the value of the exponent of 1.7 or otherwise state why you assume this. I was under the impression that the calcite dissolution power could be anywhere between about 1 and 4.5 and is currently argued over. So, it could be 1.7, but I have no way of knowing from the text whether you are insightful, guessing, or simply copying the value from the precipitation reaction (Equation 3).

o Page 1852/lines 15-16: I would say that a more representative time-scale for late Quaternary ice sheet melt-back is closer to 5 kyr than 10 kyr (eye-balling the Fairbanks curve, about 100 m of sea-level rise occurs in no more than 6 kyr). And the last glacial transition mucks about and has a Younger Dryas event which represents 'lost time' in collapsing the ice sheets. So 5 kyr should be an upper limit for general ice sheet collapse of late Quaternary (Northern Hemisphere) size. I am not convinced that a ca. 4-times larger ice sheet would necessarily take 4 times longer to disappear, as the bedrock depression would be far greater under a bigger ice cube and thus deglacial ice carving presumably much more catastrophic. And the temperature rise inferred for the end of a snowball is much more than 4 times the late Quaternary change. 20 kyr would then seem like an upper limit for the duration of Neoproterozoic deglaciation and sea-level rise, which would presumably require a more rapid carbonate precipitation event than presented here? In any case, the time to reach the super-saturation required for abiotic whittings to occur ( $\omega = \text{ca. } 10$ ) is about 100 kyr from Figure 8 (discussed earlier) which would mean that closer to a 100 kyr duration of ice sheet collapse and sea-level rise is actually required?

o Page 1853/lines 12-16: Do you really mean " $\text{H}_2\text{CO}_3$ ". Or are you thinking of  $\text{CO}_2(\text{aq})$ ,?

o Page 1855/line 29 through page 1856/line 2: "If the modern biosphere has to be

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submitted to such fast environmental changes, it will be probably removed from the Earth surface". Do the authors really know this? Are there references? This looks rather like a throw-away line with little-to-no basis. And 20 kyr is far from being an unprecedentedly fast change (cd. Quaternary deglaciation in ca. 5 kyr, anthropogenic perturbation in ca. 100 years, Northern Hemisphere Dansgaard-Oeschger events in ca. 10 years, end Cretaceous bolide impact in about a 1 year?).

o Figure 2: Minor detail - it is usual to have the 'times' symbol (which I can't actually get the EGU web portal to reproduce ...) in numbers like ' $7.15 \times 10^{12}$  mol/year'. Make it clear what substances the fluxes are of (e.g., carbon (C) or alkalinity). Why do some of the fluxes have values, but not others? Please show the complete set of flux values that together give a steady-state balanced carbon cycle at the start of the transient experiments? Also, in the caption, on what basis do you judge that "3600 km<sup>2</sup>" is the "minimal surface requires for an efficient diffusion between the atmosphere and ocean"?

o Figure 2 through 8, 10 and 11: It is more common to label the y-axis parallel to the axis and to the (left) side rather than at the top, which could get confused with a title, or within the plot itself, which could get confused with a curve label. Also, where appropriate, please could the plots have a common 'look' and cover an identical time duration (e.g., Figure 3 is 0-40 Myr, Figures 4 and 5 are 0-60 Myr, Figure 6 is 0-30, but starting from a different origin, Figure 10 is ~5 to 50-ish). Having unnecessarily different scales and shapes and font sizes distracts the eye from allowing easy comparison between different experiments and environmental properties you are trying to present.

o Figure 3: Note that while the caption says "mixing ratio" (ppm), the axis label is partial pressure.

o Figure 4: What is the y-axis property? From the Figure caption it seems to be weathering flux, but it is not sufficiently clear. Please label the graph axis itself.

o Figure 5: is this surface, deep ocean, or mean global ocean pH that is shown? Are the

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two experiments with vs. completely without (any) sea-floor weathering, or responsive vs. fixed (i.e., independent of pH changes) sea-floor weathering? Please make this clearer.

o Figure 6: Poor and confusing labelling. Also: "omega 1" of surface (rather than deep or global mean) ocean?

o Figure 7: Label temperature (y-axis) in top panel outside (to the right) of axis consistent with other plots. In bottom panel - what is on the y-axis? Units? Presumably it is "Continental weathering", but you have labelled the x (time) axis with this.

o Figure 9a: Units of DIC delta-13C? Is the green line the isotopic composition of carbonate ions? Double negative charge please. Make time axis labelling consistent with the other Figures (i.e., plot in units of Myr, try and cover the same interval in time).

o Figure 9b: The Figure purports to show "comparison between modelled isotopic variations and isotopic records in Otavi Plateform carbonates" yet I cannot see any isotopic observations (data). Units of delta-13C?

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