Snowball prevention questioned

Arising from: W. R. Peltier, Y. Liu & J. W. Crowley *Nature* **450,** 813–818 (2007)

The 'snowball Earth' hypothesis[1] interprets geological evidence as indicating multi-million-year episodes of global glaciation near the beginning and end of the Proterozoic eon. On the basis of a coupled carbon cycle–climate model, Peltier *et al.*[2] propose that temperature-dependent remineralization of organic carbon in a Neoproterozoic ocean with 100–1,000× more dissolved organic carbon than today[3] could create a negative climate feedback, thereby preventing a snowball Earth. Their results are sensitive to initial conditions and model parameters[4]; moreover, important geological observations and components of the carbon cycle are not considered—notably the absence of sources or sinks of carbon. Their model results[2] fall short of explaining the geological evidence in the absence of global glaciation.

Peltier *et al.*[2] invoke temperature-dependent solubility of O_2 as a negative climate feedback through its control on organic carbon (or dissolved organic carbon) remineralization. Temperature-dependent solubility of CO_2 is ignored. With falling temperature, CO_2 solubility rises more rapidly than that of O_2 (ref. 5), driving a larger fraction of the total pool of dissolved inorganic carbon towards CO_2(aq.), lowering $CaCO_3$ saturation. The resulting increase in net dissolution of $CaCO_3$ turbidites on deep-sea fans[6] creates an additional sink for CO_2. If CO_2 solubility had been taken into account, the likely result would have been a positive rather than a negative climate feedback.

The model solutions presented[2] exist only for the parameter range $0 < F_{21} < F_{crit}$ (where F_{21} is the remineralization flux parameter and F_{crit} is the critical value where the system changes behaviour from slushball to snowball cycling), implying that variations in the remineralization flux must be less than 1% for the temperature changes involved. This constraint is unlikely to be met in a system with large natural variability.

Sea-ice dynamics must have featured in Neoproterozoic low-latitude glaciation; they raise the characteristic partial pressure of CO_2 at the snowball instability[7]. The model of Peltier *et al.*[2] lacks sea-ice dynamics but assumes that isotopic fractionation associated with organic carbon fixation has a strong dependence on the partial pressure of CO_2 (ref. 2). This dependence is highly nonlinear[8] and might well be negligible if sea-ice dynamics were included.

The modelled isotopic fluctuations[2] accompanying the slushball-interglacial cycle are compared with isotopic data[9] from Neoproterozoic strata. This comparison is likely to be inappropriate because the isotopic fluctuations occur mostly on shallow-water marine carbonate platforms where no deposition occurred during glacioeustatic lowerings.

The palaeogeography used in the model[2] is contrary to what has long been inferred from sedimentological and palaeomagnetic observations (see refs 10, 11 for a summary). In the model[2], a supercontinent is situated over the South Pole. This would produce a relatively warm climate if CO_2 sources and sinks were included, because low average terrestrial temperatures and moisture would reduce weathering rates, maintaining higher CO_2 levels. Conversely, palaeomagnetically informed geographies[10,11] with fragmented equatorial continents produce cold climates[12], as are observed.

Peltier *et al.*[2] remark that their point of departure was criticism[13] that a slushball glaciation would not be stable for millions of years, as inferred geologically[14]. The criticism[13] was that "with all the continents covered in ice, volcanic emissions without chemical weathering would cause atmospheric CO_2 levels to rise. But with ice-free tropical oceans, even a modest rise in CO_2 would cause the tropical glaciation to be short-lived". Consistent with this claim, it was later shown that the CO_2 required to deglaciate a slushball was ~100× less than for a snowball[15], implying that its duration should be <1% the length of a snowball glaciation. As the carbon cycle model in the present work[2] has no sources or sinks of carbon, the criticism[13] was never addressed.

The existence of sub-glacial and ice-proximal deposits at sea level close to the palaeoequator, and in carbonate-dominated successions formed in the warmest parts of the surface ocean, provide compelling evidence for two pan-glacial episodes in Cryogenian time. The extent of ice cover on the oceans is indeterminate because of sea-floor subduction and because evidence of open water on glaciated margins is equivocal—deposits could represent initial ice advance or terminal retreat, not maximum extent. However, an ice-covered ocean better explains the duration of the pan-glacial periods[14], uniquely associated Fe_2O_3 and MnO_2 ore deposits[1], and syn-deglacial cap dolostones at all palaeolatitudes[6].

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1. Kirschvink, J. L. in *The Proterozoic Biosphere* (eds Schopf, J. W. & Klein, C.) 51–52 (Cambridge Univ. Press, 1992).
2. Peltier, W. R., Liu, Y. & Crowley, J. W. Snowball Earth prevention by dissolved organic carbon remineralization. *Nature* **450,** 813–818 (2007).
3. Rothman, D. H., Hayes, J. H. & Summons, R. E. Dynamics of the Neoproterozoic carbon cycle. *Proc. Natl Acad. Sci. USA* **100,** 8124–8129 (2003).
4. Crowley, J. W. *Carbon Cycle Dynamics for a Neoproterozoic Climate Model.* B.Sc. thesis, Univ. Toronto (2006); available at ⟨http://www.snowballearth.org⟩.
5. Murray, C. N. & Riley, J. P. The solubility of gases in distilled water and sea water — IV. Carbon dioxide. *Deep-Sea Res.* **18,** 533–541 (1971).
6. Hoffman, P. F. *et al.* Are basal Ediacaran (635 Ma) ''cap dolostones'' diachronous? *Earth Planet. Sci. Lett.* **258,** 114–131 (2007).
7. Lewis, J. P., Weaver, A. J. & Eby, M. Snowball versus slushball Earth: Dynamic versus nondynamic sea ice? *J. Geophys. Res.* **112,** C11014 (2007).
8. Kump, L. R. & Arthur, M. A. Interpreting carbon-isotope excursions: Carbonates and organic matter. *Chem. Geol.* **161,** 181–198 (1999).
9. Hayes, J. M., Strauss, H. & Kaufman, A. J. The abundance of ¹³C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. *Chem. Geol.* **161,** 103–125 (1999).
10. Trindade, R. I. F. & Macouin, M. Paleolatitude of glacial deposits and paleogeography of Neoproterozoic ice ages. *C.R. Geosci.* **339,** 200–211 (2007).
11. Li, Z. X. *et al.* Assembly, configuration, and break-up history of Rodinia: A synthesis. *Precambr. Res.* **160,** 179–210 (2008).
12. Donnadieu, Y., Goddéris, Y., Ramstein, G., Nédélec, A. & Meert, J. A 'snowball Earth' climate triggered by continental break-up through changes in runoff. *Nature* **428,** 303–306 (2004).
13. Schrag, D. P. & Hoffman, P. F. Life, geology and snowball Earth. *Nature* **409,** 306 (2001).
14. Hoffman, P. F., Kaufman, J. A. & Halverson, G. P. Comings and goings of global glaciations on a Neoproterozoic carbonate platform in Namibia. *GSA Today* **8,** 1–9 (1998).
15. Crowley, T. J., Hyde, W. T. & Peltier, W. R. CO_2 levels required for deglaciation of a ''near-snowball'' Earth. *Geophys. Res. Lett.* **28,** 283–286 (2001).

Carbon cycling and snowball Earth

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The possibility that Earth witnessed episodes of global glaciation during the latest Precambrian challenges our understanding of the physical processes controlling the Earth's climate. Peltier *et al.*[1] suggest that a 'hard snowball Earth' state may have been prevented owing to the release of CO_2 from the oxidation of dissolved organic carbon (DOC) in the ocean as the temperature decreased. Here we show that the model of Peltier *et al.* is not self-consistent as it implies large fluctuations of the ocean alkalinity content without providing any processes to account for it. Our findings suggest that the hard snowball Earth hypothesis is still valid.

Enhanced oxidation of a DOC reservoir at low temperature would drive the transfer of organic carbon into dissolved inorganic carbon (DIC), which would increase DIC as temperature declines, thereby increasing atmospheric CO_2. Peltier *et al.* describe a closed carbon cycle and only account for processes occurring in the oceanic and atmospheric reservoirs, while neglecting continental weathering. However, their study spans several million years, a timescale over which this process is the dominant forcing function of climate evolution[2–5]. To keep the carbon model of Peltier *et al.* physically consistent, silicate weathering has to be accounted for, which would heavily affect atmospheric CO_2.

The partial pressure of atmospheric CO_2 (p_{CO_2}) is dependent on the DIC content of the ocean and on alkalinity. Peltier *et al.* assume that atmospheric carbon content is related to the DIC content of the ocean to the power X ($X = 2$ being the standard case; equation (2) in ref. 6). However, Kump and Arthur[6] arrived at this mathematical expression by assuming that sea water was saturated with respect to the mineral calcite. Peltier *et al.* suggest that the ocean DIC content rose markedly in response to the oxidation of a DOC reservoir. Consequently, keeping the validity of the equation of Kump and Arthur implicitly requires that seawater alkalinity also rose drastically (to maintain the saturation with respect to carbonate minerals and to ensure the validity of the key equation of their model). Using equations defining seawater carbonate speciation, we calculated the concomitant change in alkalinity implied by Peltier *et al.* (Fig. 1a). We find that carbonate alkalinity has to rise by 40% when calculated atmospheric CO_2 rises from 100 to 450 parts per million by volume (p.p.m.v.). Values other than 2 for X are meaningless; X is not a free parameter and depends on the equilibrium constants of the carbonate speciation.

The additional alkalinity cannot come from either the dissolution of seafloor carbonates (because the model of Peltier *et al.* implicitly assumes permanent saturation of seawater with respect to calcite) or from the oxidation of DOC by oxygen (because this process does not supply alkalinity). Anoxic recycling of organic matter may provide alkalinity, but this process is overlooked by Peltier *et al.* This leaves continental weathering as the only remaining source of the additional alkalinity. The weathering of exposed carbonate platforms cannot be the culprit, as sea level also rises by several hundred metres in the model of Peltier *et al.* when CO_2 increases from 100 to 450 p.p.m.v. Carbonate platforms should therefore be water-covered, and this source of alkalinity should actually decrease with rising CO_2 (ref. 7). The ultimate source of alkalinity is continental silicate and intracratonic carbonate weathering which is a function of climate and atmospheric CO_2.

Using the GEOCLIM numerical model describing continental weathering under Neoproterozoic conditions[4], we calculated that the fluctuations in continental weathering implicitly required by Peltier *et al.* force the atmospheric CO_2 to fluctuate between 320 and 800 p.p.m.v. (Fig. 1b), markedly above their CO_2 reconstruction. The model of Peltier *et al.* arrives at a paradox. The equation that underpins their study requires that continental weathering changed markedly during their calculated carbon cycle oscillations, whereas Peltier *et al.* state that continental weathering is negligible because air temperature is low and land plants are absent in the Proterozoic. Our
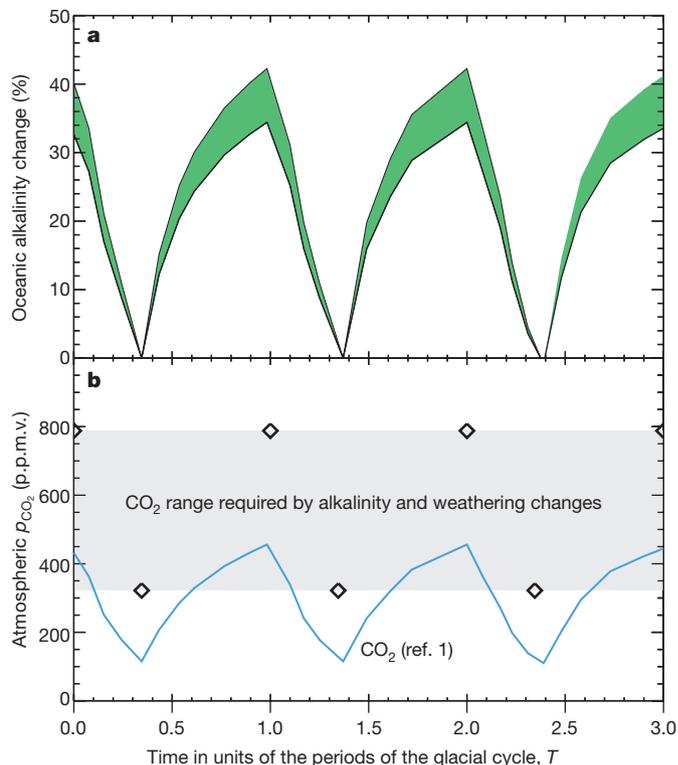

Figure 1 | Oceanic carbonate alkalinity changes required by the Peltier *et al.* scenario and consequences for the calculated atmospheric CO_2. a, The increase in carbonate alkalinity concentration in sea water as a function of atmospheric partial pressure of CO_2 (p_{CO_2}) required by the Peltier *et al.*[1] scenario for snowball Earth prevention. It is expressed in percentage increase from the alkalinity content at 100 p.p.m.v. The green shading corresponds to calculations performed at 4 and 25 °C. We use equations defining seawater carbonate speciation when equilibrated with the atmospheric CO_2 level. As boundary conditions, we use the oscillating p_{CO_2} of the Peltier *et al.* study[1] (between 100 and 450 p.p.m.v.). **b,** Comparison between the atmospheric p_{CO_2} calculated by Peltier *et al.* (ref. 1; blue line) and the range of CO_2 change required by the carbonate alkalinity fluctuations implied by the Peltier *et al.* model (grey shaded area; optima are represented by diamonds).

calculations indicate that overly simplistic descriptions of the geological carbon cycle can result in misinterpretations.

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1. Peltier, W. R., Liu, Y. & Crowley, J. W. Snowball Earth prevention by dissolved organic carbon remineralization. *Nature* **450,** 813–818 (2007).
2. Berner, R. A. & Caldeira, K. The need for mass balance and feedback in the geochemical carbon cycle. *Geology* **25,** 955–956 (1997).
3. Donnadieu, Y. *et al.* A GEOCLIM simulation of climatic and biogeochemical consequences of Pangea breakup. *Geochem. Geophys. Geosyst.* **7,** doi:10.1029/2006GC001278 (2006).
4. Donnadieu, Y. *et al.* A 'snowball Earth' climate triggered by continental break-up through changes in runoff. *Nature* **428,** 303–306 (2004).
5. Walker, J. C. G., Hays, P. B. & Kasting, J. F. A negative feedback mechanism for the long term stabilization of Earth's surface temperature. *J. Geophys. Res.* **86,** 9776–9782 (1981).
6. Kump, L. R. & Arthur, M. A. Interpreting carbon-isotope excursions: Carbonates and organic matter. *Chem. Geol.* **161,** 181–198 (1999).
7. Ridgwell, A. J., Kennedy, M. J. & Caldeira, K. Carbonate deposition, climate stability, and Neoproterozoic ice ages. *Science* **302,** 859–862 (2003).

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Peltier & Liu reply

The first of several questionable assertions in the Comment of Hoffman *et al.*[1] on our paper[2] is that our results are ''sensitive to initial conditions and model parameters''. This references an undergraduate report[3] in which this issue was not addressed. Figure 1 illustrates a sequence of trajectories of the nonlinear system. These are 'attracted to' the set of steady state solutions such that, following transient adjustment, the system locks-on to the oscillatory 'slushball' solution unless the initial CO_2 concentration is extremely low or F_{21}, the control variable of the model that determines the sensitivity of the rate of remineralization to temperature changes, is supercritical. This first assertion is therefore misleading.

The second concerns our neglect of CO_2 solubility relative to that of oxygen. Our model assumes a biogeochemically mediated partitioning of CO_2 between atmosphere and ocean that depends solely on ocean dissolved inorganic carbon (DIC; the concentration of which is M_1) relative to an equilibrium level (M_{1_e}), namely:

$$\frac{p_{CO_2}(t)}{p_{CO_{2e}}} = \left[\frac{M_1(t)}{M_{1_e}}\right]^X$$

Here p_{CO_2} is the partial pressure of CO_2 and subscript "e" indicates its equilibrium value. With $X = 2$, this is from Kump and Arthur[4] and relies on the assumption that the ocean remains saturated with respect to carbonate. This appears to have been overlooked by Hoffman *et al.*[1]. Goddéris and Donnadieu[5], in their Comment, question the internal self-consistency of its application but recognize its central importance. Because Neoproterozoic glacial events terminate in massive 'cap carbonate' precipitation, the assumption of (super?) saturation for the glacial periods (see also ref. 6) would appear to be well founded. Furthermore, because DIC rises as the system cools, leading to the exhaust of CO_2 into the atmosphere, and because the cooling-induced drawdown of the CO_2 due to solubility also causes DIC to rise, this influence would be self-limiting and thus trumped by the buffering action of biogeochemistry. Oxygen uptake by the oceans is not similarly buffered.

The argument of Goddéris and Donnadieu focuses on the alkalinity change needed to maintain ocean carbonate saturation given the predicted variation of p_{CO_2}/DIC. The claim is that silicate weathering is the only source of this alkalinity. We would like to point out, however, that: (1) alkalinity is also available from microbial respiratory activity in sub-oxic/anoxic settings (see, for example, ref. 7) which is not accounted for; (2) the assertion that ''exposed carbonate platforms cannot be the culprit, as sea level also rises by several hundred metres…… when CO_2 increases from 100 to 450 p.p.m.v.'' is incorrect. During the phase of the cycle when CO_2 is increasing (see original Fig. 3), continental ice volume remains high and therefore such platforms remain exposed and susceptible to intense weathering. This source delivers alkalinity when and only when the ocean needs it and involves no net p_{CO_2} drawdown. (3) The authors seem to neglect volcanic outgassing entirely. In our view, there is therefore no ''paradox'' in the scenario we have proposed.

Concerning silicate weathering, our model has been specifically designed to isolate the influence due to temperature dependence of the rate of remineralization of dissolved organic carbon. We assume that the silicate weathering sink precisely balances the volcanic outgassing source, and therefore have not neglected sources and sinks as claimed by Hoffman *et al.*[1]. The impact of imprecision in this balance may be captured qualitatively by noting that the control parameter F_{21} determines the rate at which the system traverses the hysteresis loop. Assuming that weathering is less efficient at moderating outgassing in the glacial phase leads to relative contraction of the ice-free phase (Fig. 2). The additional concern of Hoffman *et al.*[1] regarding the timescale of glacial episodes is therefore unfounded as weathering continues during them (see also ref. 6).

It will be noted that we have neglected the orbital forcing that would have caused multiple advances and retreats of land ice (see, for example, ref. 8). The suggestion by Hoffman *et al.*[1] that our explicitly predicted low frequency variability should be susceptible to noise misses the point that the variations in flux are in its average over the entire volume of the oceans. Its stability may be tested using newly developed methods[9].

The assertion by Hoffman *et al.*[1] that dynamic sea-ice processes would eliminate the 'slushball' is based on an inconsistent model[10] (no explicit atmospheric dynamics or radiative transfer). In ref. 11, complete Neoproterozoic integrations of the NCAR CSM 1.4 model with dynamic sea ice were performed, starting with fully glaciated
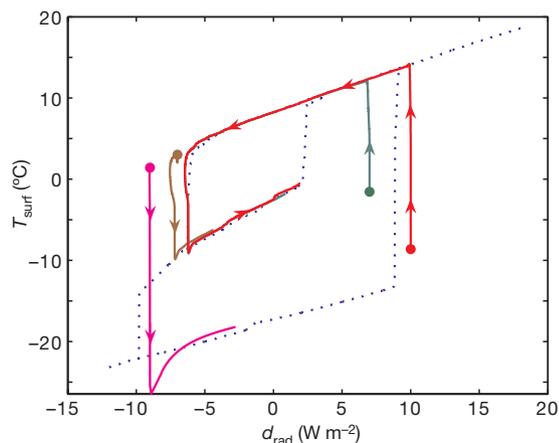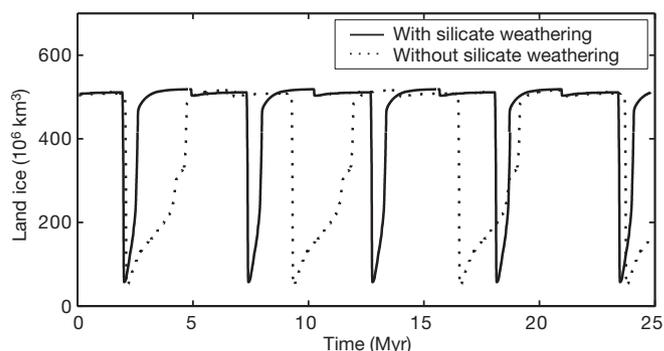

Figure 1 | Trajectories of the solution for the coupled carbon cycle and climate model started from different initial conditions, indicated by filled circles of different colours. The dotted line represents the set of steady state solutions of the climate model; this set includes the hysteresis loop on the cold branch of which the 'slushball' forms. The parameter d_{rad} denotes the increase in infrared radiative forcing at the surface of the Earth due to the increasing concentration of carbon dioxide in the overlying atmosphere. The variable T_{surf} is the annual mean surface temperature of the planet.

Figure 2 | Influence of silicate weathering on the evolution of the coupled model. The influence of weathering is qualitatively simulated by increasing the value of F_{21} by a factor of 5 from the base value of 8×10^{-5} per °C on the glacial branch of the hysteresis loop to the higher value of 4×10^{-4} per °C on the hot branch. The consequence of this parameterization of the diminished influence of weathering relative to outgassing in the glacial phase of the cycle is that the length of the warm period of the cycle is correspondingly reduced.

continents to optimize the probability of 'hard snowball' development. With a 6% decrease in solar insolation, a Marinoan-like distribution of the continents, and a p_{CO_2} of 280 p.p.m.v., the near equilibrium climate maintained significant open water at the Equator.

Concerning the issue of palaeogeography, we note the recent suggestion[12,13] that the appearance of heavy glaciation at sea level in the tropics could have resulted from an inertial interchange true polar wander (IITPW) event. Before the Sturtian ice age, Rodinia was positioned near the north magnetic pole[14]. Subsequently, it came to be positioned near the Equator. If IITPW had occurred, an already glaciated polar supercontinent would have shifted to low latitude. Apparently this possibility is not ruled out by the palaeomagnetic and dating constraints (J. Kirschvink, personal communication to W.R.P.; we note this author has previously argued for a similar IITPW event during the Cambrian[15]). The palaeogeography-based argument could be the ultimate 'red herring' in the snowball debate.

Our carbon cycle coupled climate model has been used to explore the efficacy of a particular negative feedback which was plausibly active during the Neoproterozoic. This feedback may work to prevent the occurrence of hard snowball conditions while allowing very severe glaciation of the continents. It is an influence not previously considered and warrants further analysis. All of us interested in the science of climate variability in deep geological time would be well advised to accept the limitations on our ability to divine the truth due to the paucity and ambiguity of the observational constraints available to us.

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1. Hoffman, P. H., Crowley, J. W., Johnston, D. T., Jones, D. S. & Schrag, D. P. Snowball prevention questioned. *Nature* **456**, 10.1038/nature07655 (2008).
2. Peltier, W. R., Liu, Y. & Crowley, J. W. Snowball Earth prevention by dissolved organic carbon remineralization. *Nature* **450**, 813–818 (2007).
3. Crowley, J. W. *Carbon Cycle Dynamics for a Neoproterozoic Climate Model.* B.Sc. thesis, Univ. Toronto (2006).
4. Kump, L. R. & Arthur, M. A. Interpreting carbon-isotope excursions: Carbonates and organic matter. *Chem. Geol.* **161**, 181–198 (1999).
5. Goddéris, Y. & Donnadieu, Y. Carbon cycling and snowball Earth. *Nature* **456**, 10.1038/nature07653 (2008).
6. Ridgwell, A. J., Kennedy, M. J. & Caldeira, K. Carbonate deposition, climate stability, and Neoproterozoic ice-ages. *Science* **302**, 859–862 (2003).
7. Kaufman, A. J., Corsetii, F. A. & Varni, M. A. The effect of rising atmospheric oxygen on carbon and sulphur isotope anomalies in the Neoproterozoic Johnie Formation, Death Valley, USA. *Chem. Geol.* **237**, 47–63 (2007).
8. Etienne, J. L., Allen, P. A., Rieu, R. & Le Guerroue, E. in *Glacial Sedimentary Processes and Products* (eds Hambrey, M. J., Christoffersen, P., Glasser, N. F. &Hubbard, B.) 343–399 (Special Publication 39, Association of Sedimentologists, 2008).
9. Stastna, M. & Peltier, W. R. On box models of the North Atlantic thermohaline circulation: Intrinsic and extrinsic millennial timescale variability in response to deterministic and stochastic forcing. *J. Geophys. Res.* **112**, C10023, doi:10.1029/2006JC003938 (2007).
10. Lewis, J. P., Weaver, A. J. & Eby, M. Snowball versus slushball Earth: Dynamic versus nondynamic sea ice? *J. Geophys. Res.* **112**, C11014, doi:10.1029/2006JC004037 (2007).
11. Peltier, W. R., Tarasov, L., Vetteretti, G. & Solheim, L. P. in *The Extreme Proterozoic: Geology, Geochemistry and Climate* (eds Jenkins, G. S., McMenamin, M. A., McKay, C. & Sohl, L.) 107–124 (Geophysical Monograph 146, American Geophysical Union, 2004).
12. Li, Z. X., Evans, D. V. D. & Zhang, S. A 90° spin on Rodinia: Possible causal links between the Neoproterozoic supercontinent, superplume, true polar wander and low-latitude glaciation. *Earth Planet. Sci. Lett.* **220**, 409–420 (2004).
13. Peltier, W. R. in *Treatise on Geophysics* Vol. 9 (ed. Schubert, G.) 243–294 (Elsevier, 2007).
14. Li, Z. X. *et al.* Assembly, configuration, and break-up history of Rodinia: A synthesis. *Precambr. Res.* **160**, 179–210 (2008).
15. Kirschvink, J. L., Ripperdan, R. L. & Evans, D. A. Evidence for a large scale re-organization of early continental masses by inertial interchange true polar wander. *Science* **277**, 541–545 (1997).