

Timing of Neoproterozoic glaciations linked to transport-limited global weathering: Supplementary information

Benjamin Mills^{1*}, Andrew J. Watson¹, Colin Goldblatt², Richard Boyle³ and Timothy M. Lenton³

¹School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, U.K.

²School of Earth and Ocean Sciences, University of Victoria, PO Box 3065 STN CS, Victoria, British Columbia, V8W 3V6, Canada.

³College of Life and Environmental Sciences, University of Exeter, Exeter EX4 4PS, UK, previously at School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, U.K.

* Corresponding author

SI 1. Estimating the amount of CO₂ consumed by rock flour weathering

Rapid weathering of post-glacial rock flour is an important consideration for this work. The transport limited weathering flux will not take effect until after the depletion of this reactive surface layer. We therefore attempt to calculate the maximum moles of carbon that can be buried due to rock flour weathering. In model runs, the weathering rate is set to 10 times present day when flour is present, in accordance with ref 1. This decreases via a step function to the transport limited value when no flour remains. For an initial estimate, we assume a 25cm surface layer depth¹ across the entire continental area (1.5×10^{14} m²), giving a volume of 3.75×10^{13} m³. We assume a loess density of 1.5×10^6 g m⁻³ (ref 2), therefore a total mass of 5.6×10^{19} g is calculated. Assuming a silicate cation fraction of 0.08 (ref 3) gives a cation mass of 4.5×10^{18} g. Averaging the molar masses of Ca, Mg, Na and K gives ~ 32 g mol⁻¹, therefore we calculate $\sim 10^{17}$ moles for a global depth of 25cm, meaning that this many moles of carbon can be taken up by silicate weathering. The main uncertainty in this value is in the depth of rock flour following a snowball earth. We therefore test our model with up to three orders of magnitude more rock flour to be sure of results (see main text).

SI 2. Model derivation

The 0-D Phanerozoic earth system model, COPSE⁴, uses 10 reservoirs to couple the cycles of carbon, oxygen, sulphur and ocean nutrients nitrate and phosphate. We reduce the system to 4 reservoirs: Atmosphere and ocean CO₂ (A), buried organic carbon (G), buried carbonate carbon (C) and a single limiting nutrient (P), modelled as phosphate. Full equations for this reduced model are given in tables ST1-ST3 and the text below.

Model robustness

The following changes were made to COPSE to make it robust under conditions encountered when weathering rates and temperatures are very low, as in the Neoproterozoic glaciations. The silicate weathering formulation used in the GEOCARB models is modified as follows to allow the model to remain stable at low temperature. We follow the derivation of Berner⁵ but do not make the simplifying assumption of temperature close to present day. The linear dependence of runoff on temperature results in negative values when temperature is low, and is amended by approximating the linear term with an exponential function. This gives an expression for the relative silicate weathering flux, assuming kinetic limitation:

$$W_K = \rho e^{\left(k_1 \frac{T-T_0}{T T_0}\right)} \left(e^{k_2(T-T_0)}\right)^{0.65} \sqrt{\text{NCO}_2} \quad (\text{S1})$$

Here $k_1 = 7537.69$ and $k_2 = 0.03$. T is average surface temperature in Kelvin, T_0 is present day average surface temperature (288K) and NCO_2 denotes concentration of CO₂ normalised to pre-industrial concentration. To obtain an expression for the global silicate weathering flux, equation ?? is multiplied by a factor ρ to represent possible enhancement of weathering due to continental configuration and composition. It is important to note that enhancing the kinetic weathering rate in this way does not affect the maximum transport-limited value. A higher value of ρ means that the maximum transport-limited rate can be achieved with lower temperature and/or runoff.

COPSE defines the function *anox* which takes a numerical value between 0 and 1 inclusive for the degree of ocean anoxia. The formulation used in the original model allows for negative values when ocean nutrient is extremely low. We truncate these to zero. We also add a dependence on new production to the iron-sorbed phosphorus burial flux (as is already applied to the other nutrient burial fluxes) to prevent unrealistic burial rates when nutrient concentration is low.

Temperature approximation

We derive a temperature approximation by first scaling for a lower solar constant, then using previously calculated climate sensitivity and radiative forcings to adjust for different carbon dioxide concentrations. To scale for a decreased solar constant, we use an energy budget model for a single layer grey atmosphere in radiative equilibrium:

$$T_{EBM} = \left(\frac{S(1 - \alpha)}{4\sigma \left(1 - \frac{\epsilon}{2}\right)} \right)^{\frac{1}{4}} \quad (\text{S2})$$

Here S is the solar constant in Wm^{-2} , α is planetary albedo, σ is Stefan's constant and ϵ represents the emissivity of the atmosphere. Assuming present day temperature of 288K, solar constant of 1368 Wm^{-2} and albedo of 0.3, we derive an emissivity $\epsilon = 0.773$. The solar constant at 650Ma was 1298 Wm^{-2} (ref 6). With a constant emissivity (i.e. Modern day greenhouse gas concentrations), equation ?? gives an average surface temperature of $T_{\text{base}} = 284.3\text{K}$ for the late Neoproterozoic. To account for increased carbon dioxide concentrations, we add a term of radiative forcing from CO_2 times climate sensitivity to T_{base}

$$T = T_{\text{base}} + \mu \cdot F_{\text{CO}_2} \quad (\text{S3})$$

Where F_{CO_2} is the radiative forcing from carbon dioxide and μ is the climate sensitivity (the ratio of change in radiative forcing to change in temperature). Our climate sensitivity is taken from previous runs of a radiative convective climate model and radiative forcings from previous runs of the AER line-by-line radiative transfer code^{7,8}, we take $\mu = 0.1815$ and $F_{\text{CO}_2} = a\lambda^4 + b\lambda^3 + c\lambda^2 + d\lambda + e$ where $a = 0.2507$, $b = 3.9216$, $c = 23.8113$, $d = 83.4113$, $e = 131.6138$ and $\lambda = \log_{10}(\text{CO}_2(\text{atm}))$.

We fit a curve for $10^{-5} < \text{CO}_2(\text{atm}) < 10^{-1}$ and extrapolate this to $5 \times 10^{-1} \text{ atm}$. Correct representation of radiative forcing above 10^{-1} atm is a rather involved problem, necessitating representation of pressure broadening from higher total pressure, CO_2 self-continuum, many weaker lines and possible line mixing. However, for the purpose of this work, it is only important that the temperature be sufficient to 'max out' the global weathering rate, which occurs at a much lower CO_2 concentration.

The COPSE model combines ocean and atmosphere carbon dioxide into a single reservoir, with a parameter ϕ to represent the fraction that exists in the atmosphere (and therefore contributes to the greenhouse effect). As more carbon dioxide accumulates in the atmosphere/ocean reservoir, a greater

fraction will reside in the atmosphere. We combine our temperature function with the CO2SYS carbon speciation model⁹ to derive a formula for ϕ in terms of A . The best fit to results is described by:

$$\phi = \frac{gA}{A + h} \quad (\text{S4})$$

Where $g = 0.78$ and $h = 1 \times 10^{20}$ mol for $\alpha = 0.3$, $h = 5.3 \times 10^{20}$ mol for $\alpha = 0.6$. This treatment contrasts to the ‘hard snowball’ model, where atmosphere and ocean are unable to exchange species. However, it has been shown that equilibrium between atmosphere and ocean during a snowball event could occur with only 100km³ of open water¹⁰, or cracks in sea ice¹¹ and thus our approach has been used in previous snowball earth simulations¹².

Weathering formulation

For this work we assume that silicate weathering is kinetically limited until the global transport limit is reached. This can be written in the form:

$$W = \begin{cases} W_K : & W_K < W_{\max} \\ W_{\max} : & W_K \geq W_{\max} \end{cases} \quad (\text{S5})$$

Where W is the overall weathering rate, W_K is the kinetically limited weathering rate and W_{\max} is the transport limited rate, expressed relative to the present day. We describe the transition from the kinetically limited curve to the transport limited value using a sigmoid function.

$$W = (W_{\max} - W_K) \left(1 + e^{-k_3(W_K - W_{\max})} \right)^{-1} + W_K \quad (\text{S6})$$

Where $k_3 = 100$. Equation ?? follows equation ?? for $W_K < W_{\max}$, but asymptotes to W_{\max} for $W_K > W_{\max}$.

Glacial flour abundance and weathering enhancement

We represent the global reservoir of glacial rock flour, R , in terms of the number of moles of carbon it can potentially draw down via weathering. If a snowball glaciation is triggered, R is set to zero. On deglaciation we set $\frac{dR}{dt}$ equal to the silicate weathering flux. W_{\max} is dependent on the size of R , taking the maximum value of 10 for $R < R_{\max}$ and reverting to the prescribed transport limited value when

$R = R_{\max}$. Here R_{\max} is the assumed abundance of glacial flour defined by the amount of CO_2 it can potentially weather. The transition between weathering rates follows a step function. We choose this formulation in order to allow the maximum CO_2 drawdown for a given quantity of rock flour, noting that the weathering flux may actually decrease with time¹³.

Ice-albedo instability

To parameterise an ice-albedo instability we define two distinct albedos in our model and allow the value to change when a certain temperature threshold is reached. For the temperate (nonglaciated) world we let:

$$\alpha = \begin{cases} \alpha_{\text{base}} : & T > T_{\text{crit}} \\ \alpha_{\text{ice}} : & T \leq T_{\text{crit}} \end{cases} \quad (\text{S7})$$

For the glaciated world we follow ref 14 and assume a lower escape temperature, T_{escape} :

$$\alpha = \begin{cases} \alpha_{\text{base}} : & T > T_{\text{escape}} \\ \alpha_{\text{ice}} : & T \leq T_{\text{escape}} \end{cases} \quad (\text{S8})$$

Here $\alpha_{\text{base}} = 0.3$. We let $\alpha_{\text{ice}} = 0.6$, $T_{\text{crit}} = 283\text{K}$, $T_{\text{escape}} = 263\text{K}$. This allows glaciation at $\sim 150\text{ppm}$ CO_2 and deglaciation at ~ 0.25 atm, broadly in line with previous work on snowball Earth^{11,15,16}. For a simple model, α moves linearly between α_{base} and α_{ice} if temperature falls below T_{crit} , and returns to α_{base} if T_{escape} is reached whilst in a snowball glaciation.

Reduction of weathering fluxes due to glaciation is modelled using a multiplier, W_{glacial} , for global silicate and carbonate weathering fluxes. W_{glacial} depends on only the albedo, α and is modelled using a step function so that:

$$W_{\text{glacial}} = \begin{cases} 1 : & \alpha = \alpha_{\text{base}} \\ 10^{k_{\text{ice}}} : & \alpha = \alpha_{\text{ice}} \end{cases} \quad (\text{S9})$$

k_{ice} is chosen to allow temperature during the snowball glaciation to stabilise above T_{escape} in order that deglaciation can occur. This requires $k_{\text{ice}} = -2$.

Carbon isotopes

To produce results that may be compared to the geological record, we calculate the isotopic composition of carbon throughout model runs. To do this we run a duplicate carbon system that tracks the movement of the lighter isotope carbon-12. The $\delta^{13}\text{C}$ value of a sample is a measure of the ratio of carbon-13 atoms to carbon-12 atoms, and is expressed relative to a standard:

$$\delta^{13}\text{C}_{\text{sample}} = \left(\frac{R_{12\text{sample}}^{13}}{R_{12\text{PDB}}^{13}} - 1 \right) \cdot 1000 \quad (\text{S10})$$

where R_{12}^{13} is the ratio of carbon-13 atoms to carbon-12 atoms and $R_{12\text{PDB}}^{13} = 0.0112372$. If F_C is a model flux of carbon, we define the corresponding flux of carbon-12 (F_{12C}) as:

$$F_{12C} = F_C \cdot R_{12+13}^{12} \quad (\text{S11})$$

where R_{12+13}^{12} is the ratio of carbon-12 to total carbon in the parent reservoir.

If a flux undergoes a fractionation effect of ι parts per thousand, the modified ratio of carbon-12 to total carbon in the flux is calculated:

$$R_{12+13}^{12} = \frac{1}{1 + R_{12}^{13}} = \frac{1}{1 + R_{12\text{PDB}}^{13} \left(\frac{\delta^{13}\text{C} + \iota}{1000} + 1 \right)} \quad (\text{S12})$$

where $\delta^{13}\text{C}$ is the fractionation relative to PDB of the parent reservoir. We assume a photosynthetic fractionation effect of -30‰. For fractionation due to carbonate burial we consider both a constant effect (+1‰) and a temperature-dependent function as used in COPSE:

$$\delta_{mccb} = \phi \left(\frac{9483}{T} - 23.89 \right) - \frac{4232}{T} + 15.1 \quad (\text{S13})$$

Here δ_{mccb} represents the difference in composition between atmosphere/ocean CO_2 and buried carbonate in units of per mil (‰) relative to PDB. T is temperature in degrees Kelvin and ϕ is the fraction of total CO_2 that is in the atmosphere.

Full model equations

Reservoirs and fluxes are taken directly from the COPSE model with the following exceptions: Land organic carbon burial (*locb*) is removed to reflect the absence of plants in the Neoproterozoic. Iron sorbed

phosphate burial (f_{epb}) is amended as described above. The weathering fluxes $silw$ and $oxidw$ are redefined to include the glacial limitation, $W_{glacial}$, and transport limitation in the case of $silw$. We hold oxygen concentration (denoted O) constant at an assumed Neoproterozoic value of 1% of the atmosphere, and therefore assume no dependence of $oxidw$ on oxygen concentration. Carbonate weathering is assumed to follow the silicate weathering equation for this analysis, as it has no net effect on CO_2 . The crustal reservoirs of organic and carbonate carbon (G and C) are held constant. Table ST1 displays model fluxes, ST2 shows the reservoir calculations, ST3 defines the forcing parameters and ST4 shows model constants.

References

1. Le Hir, G. et al. The snowball Earth aftermath: Exploring the limits of continental weathering processes. *Earth Planet. Sci. Lett.* **277**, 453-463 (2009).
2. Bettis, E.A., Muhs, D.R., Roberts, H.M. & Wintle, A.G. Last Glacial loess in the conterminous USA. *Quart. Sci. Rev.* **22**, 1907-1946 (2003).
3. West, A.J., Galy, A. & Bickle, M. Tectonic and climatic controls on silicate weathering. *Earth Planet. Sci. Lett.* **235**, 211-228 (2005).
4. Bergman, N.M., Lenton, T.M. & Watson, A.J. COPSE: A new model of biogeochemical cycling over phanerozoic time. *Am. J. Sci.* **304**, 397-437 (2004).
5. Berner, R.A. Geocarb II: A revised model of atmospheric CO_2 over phanerozoic time. *Am. J. Sci.* **294**, 56-91 (1994).
6. Caldeira, K. and Kasting, J.F. The life span of the biosphere revisited. *Nature* **360**, 721-723 (1992).
7. Clough, S.A. et al. Atmospheric radiative transfer modeling: a summary of the AER codes. *J. Quant. Spectrosc. Ra.* **91**, 233-244 (2005).
8. Goldblatt, C., Lenton, T.M., & Watson, A.J. An evaluation of the long-wave radiative transfer code used in the Met Office Unified Model. *Q. J. R. Meteorol. Soc.* **135**, 619-633 (2009).
9. Lewis, E. & Wallace, D.W.R. Program developed for CO_2 system calculations. Report no. ORNL/CDIAC 105, Carbon dioxide Information and Analysis Center, Oak Ridge National Laboratory, Oak Ridge, TN USA (1998).
10. Le Hir, G., Ramstein, G., Donnadieu, Y. & Godderis, Y. Scenario for the evolution of atmospheric pCO_2 during a snowball Earth. *Geology* **36**, 47-50 (2008).

11. Hoffman, P.F., Kaufman, A.J., Halverson, G.P., & Schrag, D.P. A Neoproterozoic Snowball Earth. *Science* **281**, 1342-1346 (1998).
12. Higgins, J.A. & Schrag, D.P. Aftermath of a snowball Earth. *G3* **4**, 1028 (2003).
13. Vance, D., Teagle, D.A.H. & Foster, G.L. Variable Quaternary chemical weathering fluxes and imbalances in marine geochemical budgets. *Nature* **458**, 493-496 (2009).
14. Hoffman, P.F. & Schrag, D.P. The snowball Earth hypothesis: testing the limits of global change. *Terra Nova* **14**, 129-155 (2002).
15. Pierrehumbert, R.T. Climate dynamics of a hard snowball Earth. *J. Geophys. Res.* **110**, D01111 (2005).
16. Donnadieu, Y., Godderis, Y., Ramstein, G., Nedelec, A. & Meert, J. A 'snowball Earth' climate triggered by continental break-up through changes in runoff. *Nature* **428**, 303-306 (2004).

Name	Shorthand	Equation
Marine organic carbon burial	<i>mocb</i>	$k_1 \left(\frac{P}{P_0} \right)^2$
Nutrient weathering	<i>phosw</i>	$k_8 \left(\frac{2}{12} \frac{silw}{silw_0} + \frac{5}{12} \frac{carbw}{carbw_0} + \frac{5}{12} \frac{oxidw}{oxidw_0} \right)$
Marine organic phosphate burial	<i>mopb</i>	$\frac{mocb}{CP_{sea}}$
Calcium-bound phosphate burial	<i>capb</i>	$k_2 \frac{mocb}{mocb_0}$
Iron-sorbed phosphate burial*	<i>fepb</i>	$\frac{k_3}{k_4} (1 - anox(O, P)) \frac{mocb}{mocb_0}$ where $anox = 1 - k_4 \left(\frac{O}{O_0} \frac{P_0}{P} \right)$
Silicate weathering*	<i>silw</i>	$k_5 \left\{ (W_{max} - W_K) (1 + e^{-k_3(W_K - W_{max})})^{-1} + W_K \right\}$ where $W_K = W_{glacial} \rho e^{\left(k_1 \frac{T - T_0}{T T_0} \right)} (e^{k_2(T - T_0)})^{0.65} \sqrt{NCO_2}$
Oxidative weathering*	<i>oxidw</i>	$k_7 W_{glacial}$
Organic carbon degassing	<i>ocdeg</i>	$k_9 D$
Carbonate carbon degassing	<i>ccdeg</i>	$k_{10} D$

Table ST1: List of fluxes: (* indicates a flux that has been modified for this work)

Name	Equation
Phosphate	$\frac{dP}{dt} = phosw - mopb - capb - fepb$
Atmosphere/ocean CO ₂	$\frac{dA}{dt} = -mocb - silw + oxidw - carbw + ocdeg + ccdeg + carbw$
Buried organic carbon	$\frac{dG}{dt} = 0$
Buried carbonate carbon	$\frac{dC}{dt} = 0$

Table ST2: Reservoir calculations

Name	Meaning
D	Relative CO ₂ degassing rate
ρ	Rock weatherability

Table ST3: Model forcings

Name	Meaning	Size	Source
k_1	Total organic carbon burial	$9 \times 10^{15} \text{ mol C yr}^{-1}$	COPSE
k_2	Ca associated phosphorus burial	$1.5 \times 10^{10} \text{ mol P yr}^{-1}$	COPSE
k_3	Fe associated phosphorus burial	$6 \times 10^9 \text{ mol P yr}^{-1}$	COPSE
k_4	Initial oxic fraction	0.86	COPSE
k_5	Silicate weathering	$6.65 \times 10^{12} \text{ mol C yr}^{-1}$	for steady state
k_6	Carbonate weathering	$1.335 \times 10^{13} \text{ mol C yr}^{-1}$	COPSE
k_7	Oxidative weathering	$7.75 \times 10^{12} \text{ mol C yr}^{-1}$	for steady state
k_8	Reactive phosphorus weathering	$5.7 \times 10^{10} \text{ mol P yr}^{-1}$	for steady state
k_9	Organic carbon degassing	$1.25 \times 10^{12} \text{ mol C yr}^{-1}$	COPSE
k_{10}	Carbonate carbon degassing	$6.65 \times 10^{12} \text{ mol C yr}^{-1}$	COPSE
CP_{sea}	C:P burial ratio	250 mol:mol	COPSE
A_0	Present day atmosphere/ocean CO_2	$3.193 \times 10^{18} \text{ mol}$	COPSE
P_0	Present day ocean phosphate	$3.1 \times 10^{15} \text{ mol}$	COPSE
O_0	Present day atmosphere/ocean O_2	$3.7 \times 10^{19} \text{ mol}$	COPSE

Table ST4: Table of constants