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1 Timing of Neoproterozoic glaciations explained by transport-limited  
2 global weathering

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9

10 **Snowball Earth glaciations are thought to be terminated by massive concentrations of CO<sub>2</sub>,**  
11 **accumulated from millions of years of volcanic degassing [1, 2]. After deglaciation, high**  
12 **temperature would increase the rate of silicate weathering, which increases the removal rate of**  
13 **CO<sub>2</sub> until a steady state is achieved [3]. It has recently been shown that the expected weathering**  
14 **rate on snowball exit could be around 10 times modern day, giving a timescale on the order of 10<sup>6</sup>**  
15 **years to restore equilibrium [4]. However, over long timescales the supply of fresh rock becomes a**  
16 **limiting factor for silicate weathering [5], constraining the maximum sustainable weathering flux.**  
17 **Here we show that this limitation could explain the pattern of greenhouse – icehouse oscillations**  
18 **during the Neoproterozoic, with long gaps between extreme glaciations. Using a modified version**  
19 **of the COPSE biogeochemical model [6], our estimated limit gives a stabilisation time of >10<sup>7</sup>**  
20 **years. With a simple ice-albedo feedback included, the model readily produces glacial-interglacial**  
21 **oscillations on this timescale, compatible with those observed in the geological record. Sustained**  
22 **above-average interglacial nutrient levels imply prolonged positive excursions in carbonate δ<sup>13</sup>C**  
23 **[7], as well as an increased flux of oxygen to the atmosphere [8], broadly consistent with data.**

24           The Neoproterozoic era (1000-542Ma) is punctuated by at least three glaciations [9], the  
25 severe low-latitude Sturtian and Marinoan episodes being proposed as examples of 'Snowball Earth'  
26 events [1, 10]. Figure 1 displays Neoproterozoic carbonate carbon isotope data [7], which shows a  
27 quasi-periodic pattern. Negative excursions associated with glaciation appear at ~50 Myr intervals  
28 between long periods of positive fractionation. The long interval between glaciations poses a puzzle  
29 given the standard model of a snowball Earth being terminated by very high CO<sub>2</sub> and temperature.  
30 The time taken to restore equilibrium after such a perturbation depends on the rate of CO<sub>2</sub>  
31 drawdown via silicate weathering, a process that would be greatly enhanced in the aftermath of  
32 snowball Earth. Highly weatherable rock flour produced by glacial grinding would likely cover a large  
33 surface area, and increased temperature and runoff should allow for an elevated weathering flux.  
34 Linked GCM and kinetic weathering models have determined the maximum weathering rate in this  
35 climate to be on the order of 10 times the modern day flux, implying a timescale of around 10<sup>6</sup> years  
36 to reduce atmospheric CO<sub>2</sub> to pre-glacial levels [4]. Based on these results, we would expect the  
37 system to establish equilibrium in a time far shorter than the interglacial periods following the  
38 Sturtian and Marinoan glaciations.

39           Here we propose that the timescale for CO<sub>2</sub> drawdown following a snowball glaciation  
40 should be extended due to transport limitation of the silicate weathering process. In a transport  
41 limited regime, silicate cations are completely leached from fresh regolith and therefore the rate of  
42 chemical weathering depends only on the physical erosion rate [11]. Modern continental cratons  
43 are transport limited, as seen by plotting the rate of denudation of silicate cations against total  
44 denudation rate [5]. In such a regime, increasing temperature or runoff does not increase the rate  
45 of CO<sub>2</sub> drawdown, because all the available silicate cations are already being processed. As global  
46 temperature and humidity rises, we would expect more weathering zones to fall into transport  
47 limitation, implying a theoretical maximum silicate weathering rate, where every available cation is  
48 leached.

49 Over the Phanerozoic, the mean continental erosion rate is estimated to be  $\sim 16 \text{ m Myr}^{-1}$  [12].  
50 Using the average density and area of the present day continents (area =  $1.5 \times 10^{14} \text{ m}^2$ , density =  $2.5 \times$   
51  $10^3 \text{ kg m}^{-3}$ ) yields a total mass of  $6 \times 10^{12} \text{ kg yr}^{-1}$ . Assuming a cation weight fraction of 0.08 [5], we  
52 estimate a global silicate weathering rate maximum for the Phanerozoic of around  $4.8 \times 10^{11} \text{ kg yr}^{-1}$ .  
53 This maximum transport limited rate is about 2.4 times greater than present day weathering rate  
54 [13].

55 Determining the global erosion rate in the Neoproterozoic is difficult, because it depends on  
56 the continental area and rate of uplift. Current estimates for Neoproterozoic uplift rates are close to  
57 present day values [14], and the majority of studies agree that the total continental area was  
58 probably less than it is now. Proxies for global denudation show very low values ( $< 10 \text{ m Myr}^{-1}$ ) for the  
59 early Phanerozoic, but are likely to be affected by sampling artefacts [15]. The rate of volcanic  
60 degassing in the Neoproterozoic is also important, as it is the balance between  $\text{CO}_2$  degassing and its  
61 maximum consumption rate via weathering and burial that dictates the system response time to  
62 large perturbations. In carbon cycle models, degassing is usually assumed to be proportional to the  
63 seafloor spreading rate. Accounting for different continental growth models, the Neoproterozoic  
64 outgassing rate was probably between 1 and 5 times the present day rate [14, 16]. But smaller  
65 crustal reservoirs of carbon in the Neoproterozoic [17] may have decreased the  $\text{CO}_2$  content of  
66 volcanic gas by up to 20%.

67 In figure 2, we use a modified version of the COPSE biogeochemical model [6] (see  
68 supplementary information) to investigate the effect of a weathering rate cap on the time taken to  
69 return to steady state after the suggested snowball exit concentration of 0.3 atm  $\text{CO}_2$  [1, 2] is  
70 imposed. Silicate weathering rate is fixed at a prescribed maximum value,  $W_{max}$ , which is defined  
71 relative to the present day rate. We find that choice of  $W_{max}$  has a strong effect on the system:  
72 Assuming the Phanerozoic average erosion rate ( $W_{max}=2.4$ ) yields a stabilisation time of  $\sim 10^7$  years,  
73 even for conservative estimates of the  $\text{CO}_2$  degassing rate  $D$ . A lower erosion rate, and/or a higher

74 degassing rate increases the stabilisation time greatly. For further model runs we let global  
75 weathering follow a simple kinetic equation as described by Berner [18], but asymptote to  $W_{max}$  as  
76 the kinetic weathering rate approaches the maximum transport limited value, placing a cap on  
77 global weathering rates. The choice of kinetic weathering function, and the nature of the transition  
78 to  $W_{max}$  has negligible effect on results as the rate remains at  $W_{max}$  until CO<sub>2</sub> is very close to the  
79 stable level.

80 An important consideration for this work is weathering of rock flour left on the surface after  
81 a snowball glaciation, which would be expected to increase weathering kinetics as in the quaternary  
82 glacial cycle [19]. Global weathering fluxes would not become limited by transport of fresh rock until  
83 the flour produced during the glaciation had been completely leached. Le Hir et al [4] assume a thin  
84 soil profile in their model of the snowball earth aftermath, due to evidence of persistent weathering  
85 during glaciation [20]. Following their estimate of a 25cm reactive upper layer, we derive a  
86 weatherable equivalent of  $\sim 10^{17}$  moles C (see supplementary information).

87 Figure 3 shows model sensitivity to the initial quantity of rock flour. Here we allow a global  
88 weathering rate of 10 times present day when rock flour is present [4], switching to the transport  
89 limited equation once a specified amount of carbon has been buried, analogous to the abundance of  
90 glacial flour. We find that a weatherable equivalent on the order of  $10^{20}$  moles C is required to  
91 significantly affect stabilisation time; we use a increased reactive layer depth of 2.5m ( $10^{18}$  mol C  
92 equiv.) for future model runs, due to uncertainty in estimation.

93 Our results indicate that the sequence of deep glaciations in the Neoproterozoic could be  
94 the result of a change of state in the long-term carbon-climate system to a regime which exhibits  
95 self-sustaining oscillations. If there was a long period in which global steady state temperature  
96 remained below the value required to trigger a snowball glaciation, this would be manifest as an  
97 oscillatory regime, with snowball glaciations alternating with warm phases. Such a temperature  
98 forcing may well be attributed to the continental configuration at this time. It has been shown that

100 the position of the continents at low latitudes at 750Ma, along with the prevalence of basaltic  
101 lithologies, could provide the necessary cooling to trigger the first snowball event [21]. It is thought  
102 that the continents would have remained near low latitudes until 600Ma [22], after which they begin  
103 to drift to higher latitudes, relaxing the forcing.

104 To investigate this possible mechanism we parameterise a runaway ice-albedo feedback in  
105 our model by imposing a change in albedo when temperature falls below a given value  $T_{crit}$ .  
106 Assuming the classic snowball scenario [23], we choose  $T_{crit} = 283\text{K}$  and allow deglaciation at 263K.  
107 Because deglaciation begins in the tropics, it is assumed to occur at lower temperature than is  
108 required for the ice sheets to initially advance. Throughout this work we assume a solar constant for  
109 650Ma ( $1298 \text{ Wm}^{-2}$  [24]), broadly representing the timeframe of interest. This allows glaciation at  
110  $\sim 150\text{ppm CO}_2$ , close to other estimates [21].

111 We impose the described cooling scenario in the model, adding a parameter  $\rho$  to represent  
112 enhancement of kinetic weathering. This follows the treatment of vascular plant colonisation in the  
113 Phanerozoic COPSE model runs [6], acting as a multiplier on the kinetic weathering rate equation. To  
114 trigger oscillations we increase  $\rho$  by a factor of three for a period of 150Myrs. The magnitude of this  
115 enhancement is roughly analogous to the increase in basaltic surface area and mid-latitude runoff  
116 calculated in ref [21]. For present day  $\text{CO}_2$  degassing rate ( $D = 1$ ), we require  $W_{max} = 1.4$  to produce a  
117 rough analogue of the Neoproterozoic record. This parameter choice is shown in figure 4. Assuming  
118 a higher  $\text{CO}_2$  degassing rate shortens glacial duration and allows for larger values of  $W_{max}$  to produce  
119 the observed timing, in line with figure 2.

120 We use output from the CO2SYS model [25] to approximate the atmospheric fraction of  
121 total ocean and atmosphere  $\text{CO}_2$ , assuming that there is gas exchange between atmosphere and  
122 ocean during glaciation [1]. The total solubility of  $\text{CO}_2$  is higher in cold water than warm water,  
123 therefore deglaciation causes a large transfer of  $\text{CO}_2$  from ocean to atmosphere.

123           The solid line for  $\delta^{13}\text{C}$  shows the isotopic fractionation of marine carbonates, assuming the  
124 fractionation effect on burial takes into account the equilibrium fractionation between oceanic and  
125 atmospheric carbon, and a dependence on temperature, as in the full COPSE model [6]. The dashed  
126 line shows an alternative solution where fractionation effects are constant. Both treatments yield a  
127 continued positive fractionation during the interglacial period due to elevated burial of light organic  
128 carbon, due in turn to sustained above-average nutrient fluxes from weathering. Higher assumption  
129 of  $W_{max}$  increases nutrient delivery and therefore also increases fractionation. Low productivity  
130 during glaciations causes a negative excursion. We do not expect a simple model such as this to  
131 replicate exactly the isotope record. Negative excursions preceding glaciation are not reproduced by  
132 our model, and may be due to direct temperature effects on productivity, which are not included.  
133 Our aim is to demonstrate that the extended period of system disequilibrium following a snowball  
134 glaciation should contribute to prolonged positive excursions in  $\delta^{13}\text{C}$ , more complex analysis is  
135 required to fully understand the Neoproterozoic carbon cycle.

136           With the imposition of a suitable long term maximum weathering rate, oscillations in this  
137 simple carbon – climate model can provide a qualitative fit to the sequence of glaciations and carbon  
138 isotope variations in the Neoproterozoic. The globally transport limited scenario presents a  
139 prolonged period of elevated primary productivity, which would support suggested increases in  
140 oxygen concentration and phosphorous deposition over this time [7, 8, 26-29]. There is evidence for  
141 phosphorous deposition after the Marinoan glaciation but not after the Sturtian.

142           It is important to note that the mechanism we describe relies on a particular interpretation  
143 of the Neoproterozoic period, namely the Snowball Earth hypothesis [1, 10]. It is possible that the  
144 Neoproterozoic actually contained more frequent smaller glaciations, which would not terminate via  
145 a high  $\text{CO}_2$  ‘super greenhouse’. Due to our extreme timeframe for  $\text{CO}_2$  drawdown, our prediction is  
146 highly testable, with for example one recent study proposing a rapid decline in  $\text{CO}_2$  following the

147 Marinoan glaciation [30]. Further work to establish the duration of any post-glacial greenhouse may  
148 thus enable validation or falsification of mechanisms to explain these fascinating events.

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229  
230

231 **Author Contributions:**

232 BM and AJW suggested the study. BM wrote the model, results were analysed by BM and AJW.

233 Discussion with CG helped improve the method. RB and TML contributed to the manuscript.

234 **Competing financial interests statement**

235 The authors declare that they have no competing financial interests.

236 **Figure captions**

237 **Figure 1:  $\delta^{13}\text{C}$  record for the late Neoproterozoic.** Isotopic composition of carbonates from ref. [7].

238 The vertical grey bars from left to right denote the Sturtian, Marinoan and Gaskiers glaciations.

239

240 **Figure 2: Phase portrait: stabilisation time versus maximum weathering rate,  $W_{max}$ .** Here we

241 assume an initial  $\text{CO}_2$  concentration of 0.3 atmospheres, and fix the global weathering rate at  $W_{max}$ .

242 The three lines show different choices of the relative  $\text{CO}_2$  degassing rate,  $D$ .  $W_{max}$  is defined relative

243 to present day silicate weathering rate, with the grey vertical line showing our estimate of  $W_{max} = 2.4$

244 for the Phanerozoic. Increasing the weathering rate enhances nutrient delivery and therefore

245 increases the organic burial fraction, allowing stability when  $W_{max}$  is somewhat smaller than  $D$ ,

246 providing  $W_{max} > 1$ . See supplementary information for full model description.

247

248 **Figure 3: Stabilisation time after 0.3 atm  $\text{CO}_2$  perturbation for different initial abundances of rock**

249 **flour.** Here  $R_{max}$  denotes the maximum amount of carbon (in moles) that can be drawn down via

250 weathering of glacial rock flour before it is depleted. This is set to  $10^{18}$  (solid line),  $10^{19}$  (dashed line)

251 and  $10^{20}$  (dash-dot line). This figure shows the situation where  $D = 1$ ,  $W_{max} = 2.4$ . The grey vertical

252 line shows the stabilisation time when no flour is present (as in fig2). The second drop in weathering

253 rate here occurs as  $\text{CO}_2$  returns to a stable concentration.

254 **Figure 4: Cyclic solution when steady state temperature is forced below the ice-albedo runaway**  
255 **value for 150Myr.** Here we let  $D = 1$  and  $W_{max} = 1.4$  to produce glacial timing on the order observed  
256 in the Neoproterozoic. The imposed kinetic weathering enhancement ( $\rho$ ) is shown in grey in panel 1;  
257 in black is the weathering rate relative to present. Panel 2 shows total atmosphere/ocean carbon  
258 (grey), and atmospheric  $\text{CO}_2$  (black). Panel 3 shows temperature alongside snowball entry/exit  
259 thresholds. Panel 4 shows  $\delta^{13}\text{C}$ . Solid line shows temperature/ $\text{CO}_2$  dependent fractionation [6],  
260 dashed line shows solution when fractionation effects are constant.







