



RESEARCH LETTER

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Key Points:

- The Franklin large igneous province was coincident with onset of the Sturtian Snowball Earth glaciation
- Multiyear to decadal fissure eruptions can inject enough sulfur aerosols to the stratosphere to initiate Snowball Earth
- Cold background climate states are sensitive to ice-albedo catastrophe because tropopause height is a function of surface temperature

Supporting Information:

- Supporting Information S1

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Initiation of Snowball Earth with volcanic sulfur aerosol emissions

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Abstract We propose that the first Neoproterozoic Snowball Earth event, the Sturtian glaciation, was initiated by the injection of sulfate aerosols into the stratosphere. Geochronological data indicate that the Natkusiak magmatic assemblage of the Franklin large igneous province coincided with onset of the Sturtian glaciation. The Natkusiak was emplaced into an evaporite basin and entrained significant quantities of sulfur, which would have led to extensive SO₂ and H₂S outgassing in hot convective plumes. The largest of these plumes could have penetrated the tropopause, leading to stratospheric sulfate aerosol formation and an albedo increase sufficient to force a Snowball. Radiative forcing was maximized by the equatorial location of the Franklin and the cool Neoproterozoic background climate, which would have lowered the tropopause height, increasing the rate of stratospheric aerosol injection. Our results have implications for understanding Phanerozoic mass extinction events, exoplanet habitability, and aerosol perturbations to the present-day climate.

1. Introduction

The Neoproterozoic Era witnessed two Snowball Earth glaciations, the ~717–660 Ma Sturtian glaciation and the ~645–635 Ma Marinoan glaciation [Rooney *et al.*, 2015]. These glaciations are the largest episodes of climate change in the geological record [Hoffman and Schrag, 2002], yet we do not understand how they were initiated. Of particular importance is the transition into the first Neoproterozoic Snowball event, the Sturtian glaciation (Figure 1), which was preceded by over one billion years of apparently clement conditions.

Previously, it has been proposed that the Neoproterozoic climate was cool as a result of the predominance of equatorial continents with newly rifted margins and increased planetary weatherability [Cox *et al.*, 2016; Godderis *et al.*, 2003; Macdonald *et al.*, 2010; Rooney *et al.*, 2014; Schrag *et al.*, 2002]. The rifting of the supercontinent Rodinia occurred near the equator from ~850 to 650 Ma [Li *et al.*, 2013] and was accompanied by the emplacement of multiple large igneous provinces (LIPs), including the Franklin LIP (Figure 1a). These newly rifted margins and the emplacement of rift-related LIPs at low latitude would have increased global weatherability [Godderis *et al.*, 2003; Macdonald *et al.*, 2010; Rooney *et al.*, 2014] and phosphorous input to the oceans, which would have led to more organic carbon productivity and burial in tropical deltas [Cox *et al.*, 2016]. A low-latitude paleogeography may have also limited the “land area feedback” in which silicate weathering rates decline with the growth of ice sheets on high-latitude continents [Schrag *et al.*, 2002]. Hence, Neoproterozoic paleogeography may have been more sensitive to ice-albedo runaway. Alternatively, it has been proposed that long-term Neoproterozoic cooling was due to decreased volcanic outgassing [McKenzie *et al.*, 2016]. Whether it was a change in geological sources or sinks of CO₂, or a change in the sensitivity of the silicate weathering feedback (in the sense of Maher and Chamberlain [2014]), the fact that there were two Neoproterozoic Snowball Earth events in rapid succession suggests that background conditions played an important role.

From this cool background climate state, various proximal triggers for the Snowball transition have also been proposed to overcome the silicate weathering feedback, including short-term perturbations to the greenhouse gas inventory [Schrag *et al.*, 2002; Tziperman *et al.*, 2011] and/or the planetary albedo [Bendtsen and Bjerrum, 2002; Feulner *et al.*, 2015; Stern *et al.*, 2008]. Previous explanations invoking a short-term drawdown of CO₂ or methane were motivated by an apparent correlation between perturbations to the carbon cycle and the onset of glaciation [Schrag *et al.*, 2002; Tziperman *et al.*, 2011]. However, recent geochronology has demonstrated that the pre-Sturtian Islay carbon isotope excursion occurred more than 10 Myr before the initiation of the Sturtian by 716.5 ± 0.2 Ma [Macdonald *et al.*, 2010; Rooney *et al.*, 2014; Strauss *et al.*, 2014], ruling out a direct link. Albedo changes due to the emergence of eukaryotic algae [Feulner *et al.*, 2015] rely on the coincidence of a putative evolutionary milestone for which there is no evidence. Finally, others

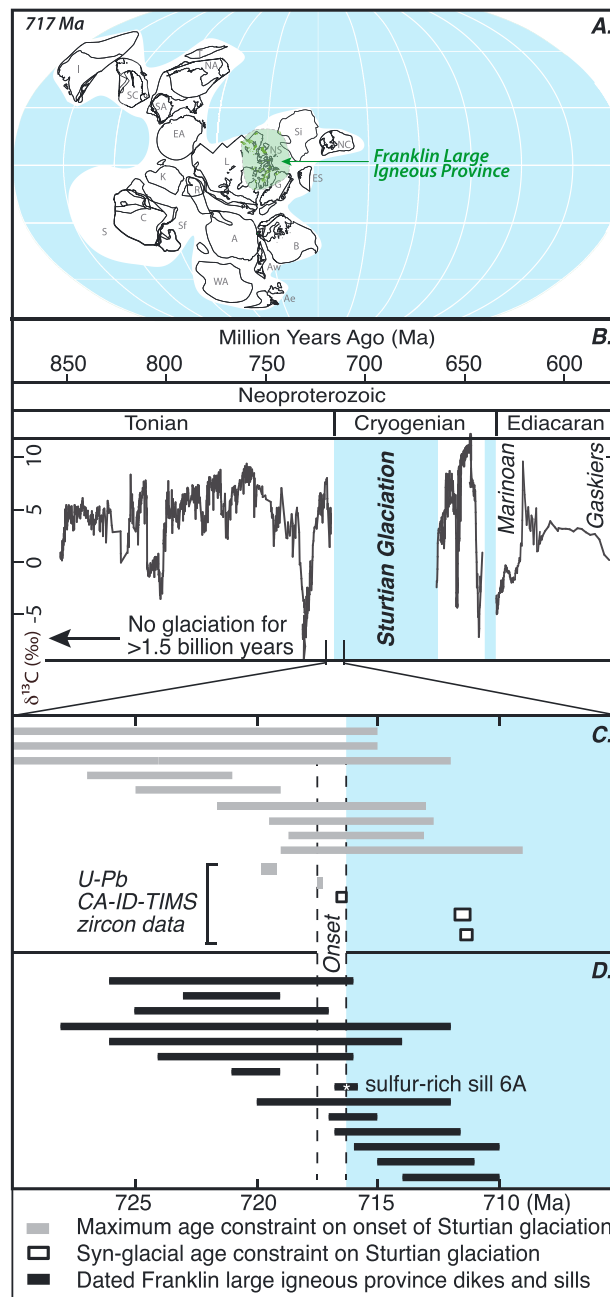


Figure 1. Paleogeographic and geochronological constraints on the onset of the Sturtian glaciation and the Franklin Large Igneous Province. (a) Neoproterozoic paleogeography modified from *Li et al.* [2013] and *Zhang et al.* [2013]. I = India; SA = southern Australia; NA = northern Australia; T = Tarim; SC = South China; M = Mongolia; EA = East Antarctica; Si = Siberia; NC = North China; L = Laurentia; NS = North Slope; ES = East Svalbard; G = Greenland; B = Baltica; A = Amazonia; WA = West Africa; Aw = western Avalonia; Ae = eastern Avalonia; Sf = So Francisco; C = Congo; K = Kalahari; R = Rio Plata. (b) Neoproterozoic timeline with carbon isotope chemostratigraphy, modified from *Cox et al.* [2016]. (c) Geochronological constraints on the onset of the Sturtian glaciation. (d) Geochronological constraints on the Franklin large igneous province. Geochronological data and sources are in Table S1 in the supporting information. Note that the Franklin large igneous province erupted at the equator, and the most precise date of sulfur-rich sills correlate with onset of the Sturtian glaciation, but the carbon isotope excursions do not.

have invoked albedo forcing by meteorite impacts or explosive felsic volcanism [Bendtsen and Bjerrum, 2002; Stern et al., 2008]. However, there is no evidence for a major meteorite impact at the time of the Sturtian onset, and albedo perturbations on the time-scale of less than a year are unlikely to drive runaway glaciation. Here we propose an alternative scenario, in which multiyear to decadal emissions of sulfur from the Franklin LIP were the proximal trigger that caused the Sturtian Snowball transition.

2. Synchronicity of the Sturtian Snowball Glaciation With Eruption of the Franklin LIP

While the Islay carbon isotope excursion is not synchronous with the Sturtian Snowball glaciation (Figure 1b), the emplacement of the largest Neoproterozoic LIP is. The most precise date on the initiation of the Sturtian glaciation comes from Yukon, Canada, where onset is bracketed between U/Pb zircon dates of 717.4 ± 0.1 and 716.5 ± 0.2 Ma [Macdonald et al., 2010] (Figure 1c). These dates are indistinguishable from the most precise date on the Franklin LIP of 716.3 ± 0.5 Ma [Macdonald et al., 2010] (Figure 1d). Volcanic rocks associated with the Franklin LIP cover an area of >3 Mkm² over northern Laurentia and southern Siberia [Ernst et al., 2016] (Figure 1a), which was at equatorial latitudes during its formation [Denyszyn et al., 2009b; Macdonald et al., 2010]. On Victoria Island of the Canadian Arctic, the Franklin LIP is represented by the Natkusiak magmatic assemblage, which consists of basalt and gabbroic dikes and sills that intruded carbonate, organic-rich shale, and sulfur evaporite of the Shaler Supergroup [Dostal et al., 1986]. The amount

of metamorphic CO₂ released from the emplacement of gabbroic sills of the Natkusiak assemblage was small relative to background levels and likely did not have a significant climate effect [Nabelek *et al.*, 2014]. However, due to melting and assimilation of sulfur from the evaporites, many of the sills and dikes have extremely high sulfur concentrations, ranging from 100 to 100,000 ppm [Bedard *et al.*, 2016], and sulfur isotope compositions indicative of contamination from entrained sedimentary rocks (see Figure S2 in the supporting information). Finally, these sulfur-rich sills are the same sills that have been dated at 716.3 ± 0.5 Ma, which is synchronous within error with the Sturtian glaciation onset [Macdonald *et al.*, 2010] (Figure 1c). Inspired by these observations, we propose that the emplacement of the Franklin LIP near the equator into a sulfur-rich basin and subsequent sulfur emission to the atmosphere was the critical event that initiated the Sturtian Snowball Earth.

3. Volcanic Plume, Aerosol, and Climate Modeling

During a volcanic eruption, sulfur is outgassed as a combination of SO₂ and H₂S [Textor *et al.*, 2003]. Once in the atmosphere, these gases react with O₂, H₂O, and OH to form H₂SO₄, which condenses with H₂O onto condensation nuclei to form radiatively active sulfate aerosols [Turco *et al.*, 1979a]. Weak volcanic plumes inject sulfur into the troposphere, where sulfate aerosols are consumed in days to weeks and have little long-term radiative effect [Chin *et al.*, 1996]. Conversely, strong plumes penetrate the tropopause and reach the stratosphere, where H₂SO₄ aerosols can have lifetimes of a year or more [McCormick *et al.*, 1995].

Unlike explosive volcanic eruptions such as the 1991 Pinatubo event, the eruptions associated with the Franklin LIP were basaltic in nature, leading to large fire fountains that would have driven hot convective plumes into the atmosphere [Stothers *et al.*, 1986]. This has two major consequences. First, the probability of a hot volcanic plume penetrating the tropopause is determined by the degree of thermal energy at the plume base, which can be very high given that basaltic magmas typically have temperatures of 1000 K or more. Second, and most critically, basaltic eruption sequences during LIP formation can occur over very long time periods (years to decades), potentially causing a much longer-term climate impact [Self *et al.*, 2014].

To evaluate our hypothesis that the Sturtian glaciation was initiated by the creation of sulfate aerosols from equatorial basaltic volcanism, we modeled the height to which hot, buoyant sulfur-bearing plumes from fire fountains could reach in the atmosphere, the chemical and microphysical evolution of sulfur in the atmosphere, and the radiative effects of sulfate aerosols once they formed. To simulate the volcanic plumes, we used a one-dimensional steady state model incorporating turbulent entrainment. This relatively simple approach is justified based on extensive previous comparisons with observations and laboratory experiments (see discussion in the supporting information). Our sulfur aerosol microphysics model is sectional (82 bins total) and incorporates particle growth, coagulation, sedimentation, and mixing. Sulfate aerosol radiative forcing was calculated using Mie theory and a one-dimensional radiative-convective correlated-*k* model [Wordsworth *et al.*, 2010; Wordsworth *et al.*, 2013]. We also used this model to provide atmospheric temperature-pressure profiles as input to the volcanic plume model. A complete description of our modeling approach is given in the supporting information.

4. Results

First, we investigated the dependence of the maximum thermal volcanic plume height on the strength of an individual Franklin LIP eruption and on the background climate. Our modeling indicates that plume height is a strong function of volume eruption rate, with eruption rates of 10^4 – 10^5 m³/s leading to plume heights greater than the present-day tropical tropopause (~12 km) under Neoproterozoic atmospheric conditions (Figure 2). We estimate these rates to be representative of the peak values produced during eruptions associated with the Franklin LIP (see supporting information). Furthermore, our climate modeling shows that tropopause height is a strong function of surface temperature (Figure 2a). This is because a warmer surface injects more water vapor into the atmosphere, reducing the lapse rate. Hence, very warm climates can “shield” the Earth from stratospheric aerosol injection by even the largest volcanic plumes [see also Glaze *et al.*, 2017]. Conversely, a cool background climate in the Neoproterozoic would have made it a particularly dangerous time for a sequence of large basaltic eruptions to occur.

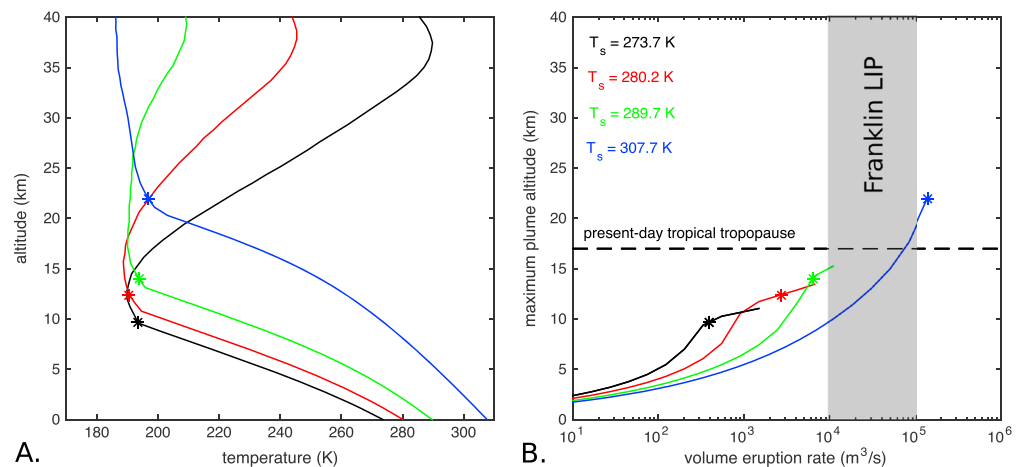


Figure 2. (a) Equilibrium atmospheric temperature profiles produced from the radiative-convective climate model for varying CO₂ concentrations under Neoproterozoic conditions. The black, red, green, and blue lines correspond to simulations where the background CO₂ levels were 30, 300, 3000, and 30,000 ppm, respectively. (b) Maximum Franklin LIP plume height as a function of volume eruption rate. In both panels, asterisks indicate tropopause height, defined as where the lapse rate first drops below 2 K/km. The grey box brackets the maximum plausible volume eruption rate during formation of the Franklin LIP (see the supporting information).

Our microphysical model converts SO₂ and H₂S gas to H₂SO₄ aerosols on a time scale of 30–40 days. Once formed, the aerosols remain in the stratosphere for 1–2 years, with the aerosol loading peaking in the first 3–6 months, in agreement with observations of the 1991 Pinatubo eruption (see the supporting information). We find that the radiative forcing caused by episodic injections of SO₂ into the equatorial stratosphere increases with the quantity of SO₂ injected (Figure 3a), but the increase is sublinear due to particle coagulation, which increases mean particle size and sedimentation rate for large eruptions [Pinto *et al.*, 1989]. For a single eruption, mean global forcing in the following year increases from -2.7 W/m^2 given 20 Mt SO₂ injection (cf. Pinatubo [McCormick *et al.*, 1995]) to -12 W/m^2 for 500 Mt SO₂ (sensitivity to parameters described in the supporting information). Estimating the rate at which sulfur was released from the Franklin LIP on a decadal time scale is challenging, but 500 Mt/yr is similar to estimates of SO₂ release rate from more recent LIPs [Self *et al.*, 2014]. For comparison, the radiative forcing due to CO₂ doubling on the present-day Earth is around 3.7 W/m^2 [Myhre *et al.*, 1998].

The eruption sequence of fissure eruptions associated with a LIP is poorly constrained. The best historical analog is the 1783–1784 Laki fissure eruption in Iceland, which emitted $\sim 122 \text{ Mt SO}_2$ over 8 months with ~ 10 pulses that produced eruptive columns extending 9–13 km [Thordarson and Self, 2003]. However, many larger flow fields have been identified in the geological record, which require longer total durations [Self *et al.*, 2014]. If these eruptions had higher magma output rates than Laki, different types of lava would have been produced. For example, using peak output rates from Hawaii and Laki, Thordarson and Self [1998] estimated that the 1300 km^3 Roza flow field of the Columbia River Basalt Group formed in ~ 10 –20 years. Larger flows, such as those associated with the Deccan and Siberian Traps, may have lasted an order of magnitude longer [Self *et al.*, 2014] and had multiple eruptive centers. Nonetheless, because a robust eruption time series for a multiyear fissure eruption does not exist, particularly for the sulfur release from an fissure eruption through a sulfur-rich basin, we model the radiative effect of pulsed yearly equatorial volcanic eruptions under Neoproterozoic conditions assuming 20, 100, and 500 Mt of SO₂ injection to the stratosphere (Figure 3a). This covers the range of SO₂ emissions from the historical Pinatubo and Laki eruptions over longer time periods and also explores the larger SO₂ concentrations estimated for the Franklin LIP.

The ability of volcanic aerosols to force a Snowball transition depends on both the starting climate state and on the rate at which the upper layers of the tropical ocean can cool. Based on radiative-convective modeling, we estimate that a -10 W/m^2 global mean aerosol radiative forcing would be sufficient to cause runaway glaciation for CO₂ levels of 3000 ppm (Figure 3b). These CO₂ levels yield approximately present-day global mean temperatures in our model given the fainter Neoproterozoic Sun. For lower background CO₂ levels, as might

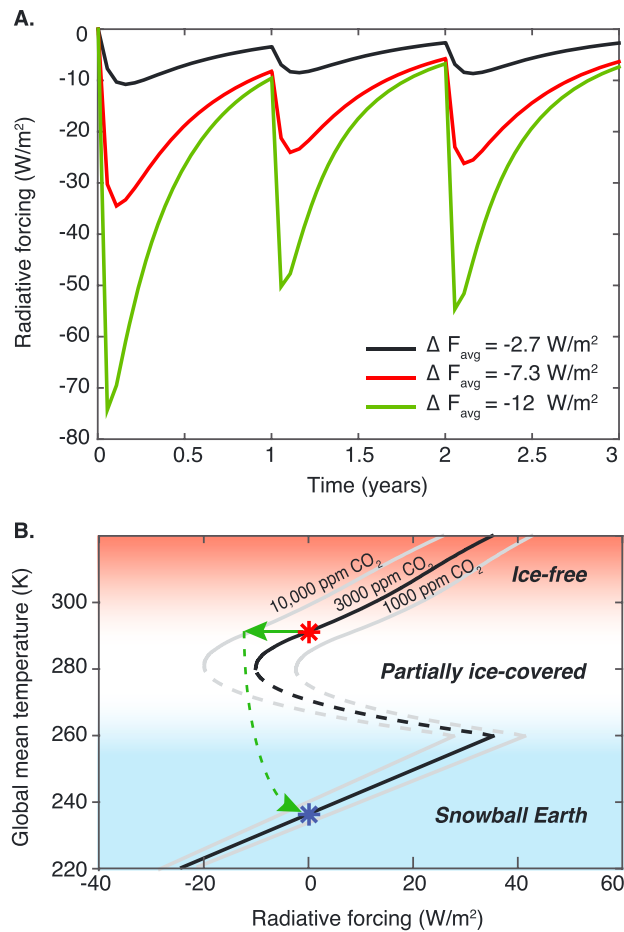


Figure 3. The effect of volcanic sulfate aerosol emission on global climate. (a) Equatorial radiative forcing due to yearly equatorial volcanic eruptions under Neoproterozoic conditions. The black, red, and green lines show simulations assuming 20, 100, and 500 Mt of SO₂ injection to the stratosphere. Annual global mean forcings are also displayed. (b) Bifurcation diagram of global mean temperature versus radiative forcing defined as the difference between outgoing longwave radiation and absorbed solar radiation. The dashed lines are unstable states. Starting from a mean surface temperature close to present day (red star), a negative radiative forcing of $< -10 \text{ W/m}^2$ is sufficient to push the Neoproterozoic Earth (green line) into a Snowball state (blue star). Starting from a colder initial state, the required radiative forcing is lower.

5. Discussion

If the Franklin LIP caused a Snowball Earth, then why are other LIPs not also associated with Snowball Earth events? The Siberian Traps, which erupted around 250 Ma at the end of the Permian, are similar in size to the Franklin LIP, but instead of cooling, they appear to be associated with warming and extinction [Ganino and Arndt, 2009]. Another LIP, the Central Atlantic Magmatic Province (CAMP), may have caused temporary cooling followed by warming [Schoene et al., 2010]. The different outcomes are likely related to several factors: the background climate conditions, changes in background planetary albedo with different paleogeography, the latitude of the eruptions, the composition of the country rock that the LIPs were emplaced into (a sulfate-rich basin, coal deposits, and an ancient mountain belt for the Franklin, Siberian Traps, and CAMP, respectively), and timing of SO₂ injection relative to the cumulative release of gases such as CO₂. Although Neoproterozoic paleogeography likely favored a cool climate [Li et al., 2013; Marshall et al., 1988], the Siberian Traps and CAMP erupted during the ice-free Late Permian and Late Triassic, respectively, when warm conditions

be expected in a cool background climate, a Snowball transition could have been caused by a correspondingly lower radiative forcing. A simple calculation assuming an ocean mixing layer depth of 50 m yields a time scale of order 3 years to drive equatorial sea surface temperatures to the freezing point of water and commence a Snowball transition (see the supporting information). Hence, a sequence of large, sulfur-rich eruptions of the type shown in Figure 3a may have been sufficient to drive a runaway ice-albedo event.

Estimates of the Snowball cooling time scale from present-day conditions using general circulation models coupled to a dynamic ocean yield longer time scales (decades to several hundred years, depending on the initial climate state), due to the enhanced vertical ocean mixing driven by surface cooling in those models [Voigt et al., 2011]. Many aspects of mixing in the present-day ocean remain poorly captured by numerical models [Wunsch and Ferrari, 2004], so the extrapolation to the Snowball regime is challenging. Nonetheless, if these estimates are robust, they suggest that the climate state before the Franklin LIP erupted would have needed to be colder than that of present-day Earth to allow sulfate aerosol forcing to drive a transition. They also suggest that another reason the 14.98 Ma Roza flow failed to initiate a Snowball was because it erupted during the Miocene climatic optimum, when higher temperatures would have required a significantly longer time scale to freeze the surface ocean.

extended to Earth's polar regions [Taylor *et al.*, 1992]. Consequently, there would have been a higher tropopause that would have prevented stratospheric aerosol injection by all but the most powerful volcanic eruptions (Figure 2). Moreover, the Siberian Traps erupted at high latitude, whereas the CAMP and Franklin LIP erupted at equatorial latitudes [Denyszyn *et al.*, 2009b]. Consequently, albedo changes associated with the Siberian Traps would have primarily affected mid-to-high latitudes in one hemisphere, whereas the CAMP and Franklin LIP would have maximized albedo at low latitude, where solar forcing is highest. Because aerosol radiative forcing is most negative when surface albedo is low, and a high-latitude eruption in a cold climate occurs over snow or sea ice, an equatorial eruption is far more effective at forcing a Snowball transition than a high latitude one (see the supporting information). Deeper in Earth's past, in the Archean and Proterozoic, a warmer climate caused by elevated levels of CO₂ or other greenhouse gases [e.g., Feulner, 2012; Wordsworth and Pierrehumbert, 2013b] may have elevated the tropopause sufficiently to shield the Earth continuously from significant stratospheric sulfate aerosol injection.

The geological record preserves evidence for two Cryogenian glaciations, the Sturtian and the Marinoan. Although there is not evidence for a LIP during the onset of the Marinoan glaciation, this may be a matter of preservation. The low-latitude rifting of Rodinia continued throughout the Neoproterozoic, and it is likely that this was associated with additional LIPs. Geochronological constraints suggest that the Sturtian glaciation lasted ~58 Myr and that the nonglacial interlude before the Marinoan started was short, between 8.6 and 19.4 Myr [Rooney *et al.*, 2014]. If planetary weatherability remained high during the Cryogenian due to continued low-latitude paleogeography and recently emplaced continental flood basalt provinces [Cox *et al.*, 2016], transport-limited weathering in the aftermath of the Sturtian glaciation may have returned the Earth on a 10 Myr time scale to a climate state sensitive to further short-term perturbations in the planetary albedo [Mills *et al.*, 2011]. After the Marinoan glaciation, the removal of a basaltic carapace and drift of continents to higher latitudes [Li *et al.*, 2013] likely reduced global weatherability and climate sensitivity.

6. Conclusion

Based on a combination of geological evidence and atmospheric modeling, we have proposed that the proximal trigger for the Sturtian Snowball Earth was a sudden increase in planetary albedo caused by the emission of sulfate aerosols from basaltic volcanism. Further tests of our hypothesis will be possible via tighter constraints on the geochronology of the Sturtian glaciation and the Franklin LIP, and better estimates of sulfur release with melt inclusion studies along with three-dimensional coupled ocean-atmosphere modeling of the climate effect of stratospheric aerosol emissions. Mercury anomalies have been observed in sedimentary records that span the Permian-Triassic and Triassic-Jurassic boundaries and have been attributed to the Siberian Traps and CAMP, respectively [Thibodeau and Bergquist, 2017, and references therein]. Our model predicts that similar mercury signals will be present in sedimentary successions deposited during onset of the Sturtian glaciation.

Our proposed scenario for initiation of the Sturtian has several important implications beyond the Neoproterozoic. In the Phanerozoic, the correlation of LIPs and meteorite impacts with both glaciations and mass extinction events has long suggested a causal link. However, our results imply that the timing and location of major volcanic and impact events may matter as much as, or more than, their overall magnitude. For exoplanets, our results indicate that volcanically active planets may be much more vulnerable to Snowball transitions than traditional habitable zone ideas based on the carbonate-silicate cycle [Kasting *et al.*, 1993] would suggest. Finally, if the largest known glaciation event in Earth's history was indeed triggered by stratospheric sulfate aerosols, this should give some caution to similar geo-engineering strategies proposed recently to decrease or eliminate anthropogenic climate change [Rasch *et al.*, 2008].

Acknowledgments

The supporting information describes the materials and methods used, and model validation and sensitivity tests; includes four tables and 10 figures, and cites the additional references.

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