From Volcanic Winter to Snowball Earth: An Alternative Explanation for Neoproterozoic Biosphere Stress

Robert J. Stern, D. Avigad, N. Miller and M. Beyth

Abstract The ~450 million years of Neoproterozoic time (1000–542 Ma) was a remarkable episode of change in the Earth system and the biosphere. Here we develop and explore the hypothesis that explosive volcanism was at least partly responsible for Neoproterozoic climate change, synopsized as the "Volcanic winter to snowball Earth" (VW2SE) hypothesis. We review how climate cools as a result of sulfuric acid aerosols injected into the stratosphere by violent volcanic eruptions. A protracted increase in explosive volcanism could disrupt Earth's radiative balance by continuously injecting sulfur aerosols into the stratosphere, causing cooling that could lead to glaciation. This mechanism would be especially effective when acting in concert with other agents for cooling. We show that the global Neoproterozoic magmatic flux was intense, so that explosive volcanism episodicly had a major effect on climate. Neoproterozoic volcanism and glacial activity happened about the same times in the Cryogenian and Ediacaran periods with no glaciation and reduced igneous activity in the Tonian Period. Glaciation followed soon after igneous activity increased as the supercontinent Rodinia broke apart, suggesting a causal relationship. The tectonic setting of climate-controlling explosive volcanism changed systematically over the Neoproterozoic supercontinent cycle, from extension-related early to arc-related late. Marinoan (~635 Ma) glaciation in particular corresponds to a peak time of subduction-related igneous activity in the Arabian-Nubian Shield and the East African Orogen. Isotopic chemostratigraphies are generally consistent with VW2SE hypothesis. These observations cumulatively support the VW2SE hypothesis as a viable explanation for what solid Earth processes caused Neoproterozoic climate oscillations.

R.J. Stern
Geosciences Dept.,
U Texas at Dallas, Richardson TX 75083-0688 USA
e-mail: rjstern@utdallas.edu

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1 Introduction

The ~450 Myr –long Neoproterozoic Era is subdivided into three periods: Tonian (1000–850 Ma), Cryogenian (850–635 Ma) and Ediacaran (635–542 Ma; Fig. 1). The first two periods are associated with microscopic biota of low complexity, but the Ediacaran Period yielded macroscopic, soft-bodied, complex metazoans. These typically were centimeters to decimeters in greatest dimension, with some giants more than a meter long. Ediacaran fossils include discs, fronds, and segmented shapes that are similar in some ways to modern animals, accompanied by fossils unlike anything seen in Phanerozoic assemblages (Narbonne 2005). By the beginning of Cambrian time all major animal phyla were established.

We are starting to delineate the Neoproterozoic record of life, and how lifeforms of increasing complexity and size evolved over this time. The rate of biological diversification was affected by changes in the physical world, including oceanic and atmospheric composition (especially rising oxygen contents; Knoll 2003), climate and tectonics. These variables interacted in ways that are still being discovered. The nexus of these Earth system changes is showcased by the controversial Snowball Earth hypothesis, which seeks to explain climate change, especially for the Cryogenian (Allen 2006; http://www.snowballearth.org/). There were several Neoproterozoic ice ages (Fig. 1), and these events give the name "Cryogenian" (greek for "birth of ice") to middle Neoproterozoic time, although more limited glaciation also occurred in the Ediacaran Period. Some scientists think that extreme biosphere stress caused by Neoproterozoic climate change stimulated biological change leading to the development of metazoa (Hoffman 1999). Others conclude that Neoproterozoic biosphere stress due to Neoproterozoic ice ages was more subtle (Corsetti et al. 2006) or that glacial extremes did not preclude photosynthesis and therefore were not analogous to the hard snowball model originally proposed by Hoffman et al. (1998).

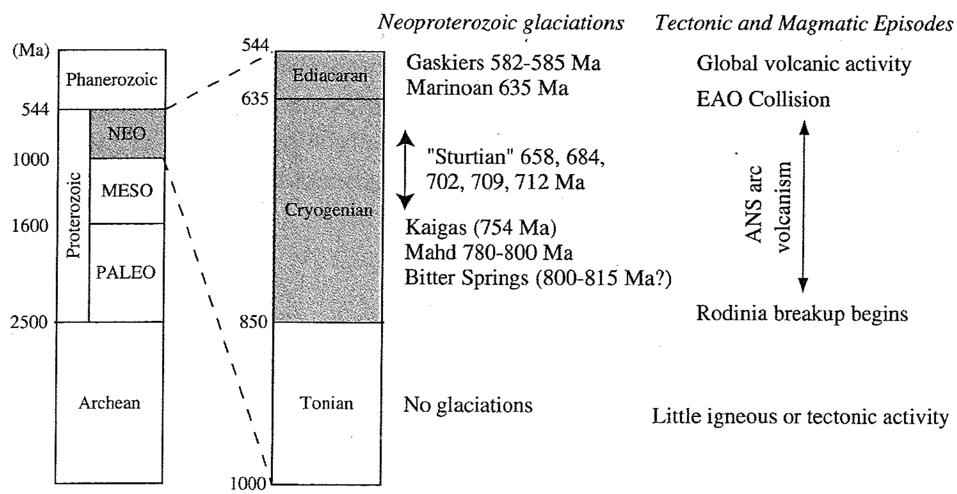

Fig. 1 Neoproterozoic time (*left*) showing the timing of glacial episodes (*center*) and timing of magmatism. Not that Tonian period has little igneous activity and no glaciation, and that glacial episodes overlap times of maximum igneous activity

The chronology of Neoproterozoic glacial episodes is still being revised as new radiometric ages are obtained. Evidence for climate change comes from direct and indirect indicators. The most direct evidence of Cryogenian glaciation is lithostratigraphic: tillites, with clear genetic indications of glacial derivation (e.g., striated or faceted clasts, dropstones), and less diagnostic diamictites, which are often considered glaciogenic. The oldest Neoproterozoic glacial deposits probably were small in extent, poorly preserved, and thus difficult to find, but the oldest may be the ~780 Ma Mahd adh Dhab tillites of Saudi Arabia (Stern et al. 2006). Another candidate for first Neoproterozoic glaciation is represented by the ~800 Ma Bitter Springs negative $\delta^{13}C$ anomaly, but the age and inferred glaciation are poorly constrained, as discussed below. With these possible exceptions, the ~754 Ma Kaigas glacial episode (Hoffmann et al. 2006) is the oldest certain Neoproterozoic glaciation.

Indirect indicators of Neoproterozoic climate change are preserved in carbonate sediments. Tillites may be abruptly overlain by distinctive carbonate successions (cap carbonates) and are typically preceded by pronounced decrease of seawater $\delta^{13}C$ (as proxied by marine carbonates). Although the specific origin of these negative $\delta^{13}C$ excursions is controversial, their common association with glacial deposits suggests an effective way to correlate carbonate units deposited in association with Neoproterozoic ice ages (Knoll et al. 1986). Yet correlation on the basis of negative $\delta^{13}C$ anomalies can be ambiguous (i.e., cf. Halverson et al. 2005 vs. in press) and a robust $\delta^{13}C$ (and $^{87}Sr/^{86}Sr$) global chemostratigraphy remains to be constructed, particularly for early Cryogenian time (Melezhik et al. 2001). Halverson et al. (in press) propose that the ~800 Ma age inferred for the Bitter Springs negative $\delta^{13}C$ anomaly in Australia correlates with similar pre-Sturtian excursions in Svalbard and NW Canada. However, none of the latter excursions are obviously associated with glaciogenic strata, and alternative correlations with pre-Sturtian excursions demonstrably younger than the Bitter Springs anomaly are possible (Miller et al., in prep.).

Until recently the Sturtian was thought to be a global episode of glaciation but these deposits range in age from ~712 Ma to ~650 Ma (Allen et al. 2002; Lund et al. 2003; Kendall et al. 2006; Fanning 2006). Only the ~635 Ma Marinoan episode still appears to have been global and long lasting (Bodiselitsch et al. 2005). The last clear Neoproterozoic glaciation occurred ~580 Ma, known as the Gaskiers or Varanger glaciation (Bowring et al. 2003). This is also about the time of the "main erosional phase" of the Arabian-Nubian Shield (Garfunkel 1999), possibly due to continental glaciation (Stern et al. 2006).

It is not surprising that our understanding of Neoproterozoic biogeological events and Earth system interactions is changing rapidly, as an international and interdisciplinary group of researchers find new pieces of the Neoproterozoic climate change puzzle. Although far removed in time from modern concerns about global warming, the stratigraphic record of these Neoproterozoic events demonstrates the "limits of global change" (Hoffman and Schrag 2002). This global search for new perspectives is one of the most interdisciplinary and international geoscientific efforts underway. It is to be expected that such an inquiry into deep time spawns controversy. The scope and significance of this controversy encourages exploration of both the broad fabric of the Neoproterozoic solid Earth-climate-life system as well as detailed examination of individual disciplinary threads. This essay follows one of these threads, namely the hypothesis that explosive volcanic activity was an important cause of Neoproterozoic climate change.

What caused Neoproterozoic ice ages is a central controversy, because we cannot pretend to understand Neoproterozoic global change if we do not understand what caused it. The sun was fainter in the Neoproterozoic than today (Tajika 2003), but this was not the principal trigger because the Sun was significantly fainter earlier in Earth history, with modest climatic effects. The oldest known glaciation is recorded by glaciogenic diamictites of the ~2.9 Ga Pongola Supergroup, and glaciation also occurred ~2.2–2.5 Ga (Kirschvink et al. 2000). There is no evidence for glaciation for the next 1.5 billion years prior to the oldest Neoproterozoic glaciations. The distribution of landmasses may also have been important. Hoffman et al. (1998) suggested that the relatively close dispersal of continents about the equator greatly enhanced continental weathering. By this scheme, carbon was buried in continental margin sediments, thereby drawing down atmospheric CO_2 and cooling climate. This ultimately led to a runaway increase in planetary albedo as glaciation spread to low latitudes, culminating in global glaciation and stopping the hydrologic cycle. This "hard snowball" interpretation has been increasingly challenged as more is learned about the number and intensity of Neoproterozoic ice ages and as we better understand the range and controls of greenhouse gas feedbacks (e.g., Hyde et al. 2000). Some researchers support the hypothesis that cooling resulted mainly from weathering-related carbon burial and CO_2 fixation (Schrag et al. 2002; Donnadieu et al. 2004), perhaps stimulated by increased clay formation (Kennedy et al. 2006). Other mechanisms include the loss of a once more significant atmospheric methane component (a much more effective greenhouse gas compared to CO_2) due to rising oxygen contents (Schrag et al. 2002), and Earth's passage through an intergalactic cloud (Pavlov et al. 2005).

It is remarkable in this wide-ranging discussion that explosive volcanism has not been explicitly considered as a possible cause, because this is known to affect climate on many timescales (Robock 2000), and has been suggested as a way to counteract modern "global warming" (Crutzen 2006). The fact that this possible mechanism has not been considered motivates this essay. The argument is empirical, progressing from the well-documented and modern to the speculative and ancient. We begin by reviewing the cause of volcanically-induced cooling, then examine evidence from three Holocene and Pleistocene eruptions (Pinatubo, Tambora, and Toba). We then discuss whether or not a prolonged increase in explosive volcanism could affect climate sufficiently to trigger an ice age, using Pleistocene glaciation of the N. Hemisphere as an analog. We document prolific global igneous activity during the Neoproterozoic, and link this to the scale of explosive volcanism. We note that there was elevated igneous activity during the part of Neoproterozoic time that witnessed glaciation and that explosive volcanism could have been an important cause. We conclude that explosive volcanism is a viable explanation for Neoproterozoic climate change and propose a mixed acronym for the hypothesis: VW2SE (volcanic winter to snowball Earth). It is our hope that the VW2SE hypothesis broadens discussions about the causes of Neoproterozoic climate change and about how solid Earth processes affect climate and life.

2 Explosive Volcanism and Atmospheric Cooling

Benjamin Franklin was perhaps first to note that climate was affected by intense volcanism, linking a severe winter in Europe during 1783–1784 to the euption of Laki, Iceland (Franklin 1784). Almost 200 years elapsed before the idea was resurrected by Lamb (1970), who developed the Dust-Veil Index to quantify the cooling effects of volcanic ash in the atmosphere. The idea of volcanically-induced cooling was further developed by Kennett and Thunnell (1977), who inferred that volcanic pulses at 0–2, 5, 10, and 14–16 Ma caused cooler climate. It is now widely accepted that explosive eruptions of sufficient magnitude – especially Plinian eruptions – can cause cooler climate (Robock 2004). This linkage led to development of the "Volcanic Winter" concept (Rampino et al. 1988), which focusses on short-term (1–3 years) climate cooling caused by explosive volcanism.

Explosive volcanism mainly affects climate by injecting sulfur dioxide (SO_2) into the stratosphere. Volcanic ash is also injected but this settles quickly out of the atmosphere and so causes little cooling; in contrast, sulfur aerosols can remain suspended for a year or more. A globe-encircling volcanic cloud forms in several weeks as the SO_2 is converted in the lower stratosphere (18–25 km) to frozen particles of sulfuric acid (H_2SO_4), 0.1–1 mm in diameter. Cooling of the troposphere and Earth surface results because these microdroplets reflect a significant fraction of incoming solar radiation back into space. The geographic extent of cooling resulting from volcanic aerosols depends on eruption latitude and stratospheric winds, with equatorial eruptions having the greatest effect (Self 2006)

Because S aerosols disrupt Earth's radiative balance, the short-term effect of explosive volcanism is usually cooling of the Earth's surface and troposphere. The historical relationship between injection of sulfur into the stratosphere by explosive volcanism and cooling is so strong that Sigurdsson (1990) proposed the following empirical relationship between a volcano's sulfur yield (M_S) and the ensuing maximum surface temperature anomaly, ΔT:

$$\Delta T = -5.9 \times 10^{-5} \times M_S^{0.31} . (M_S \text{ in grams}) \tag{1}$$

This relationship has been reconsidered by Blake (2003), who found that the mass of emitted SO_2 is 0.1–1 % of magma mass, with a best fit mass for SO_2:

$$\text{Megatons } SO_2 = 1.77(\text{mass of magma in gigatons})^{0.64} \tag{2}$$

Blake (2003) also concluded that the volcanic SO_2 is effectively converted into stratospheric aerosols when the ratio of eruption plume height to tropopause height is greater than $\sim$1.5. Blake (2003) also noted that of the stratospheric eruption clouds in the period 1400–1994, those $<$5 Gt magma appear to have had insignificant effects on Northern Hemisphere summer temperature whereas data for eruptions of $>$10 Gt magma suggest a mean cooling of $\sim$0.35° C.

Figure 2 shows various volcanic inputs to the atmosphere, emphasizing interactions and fates for various volcanic inputs and their impacts on Earth's radiative heat balance (after McCormick et al. 1995; Robock 2000). Apart from the formation of

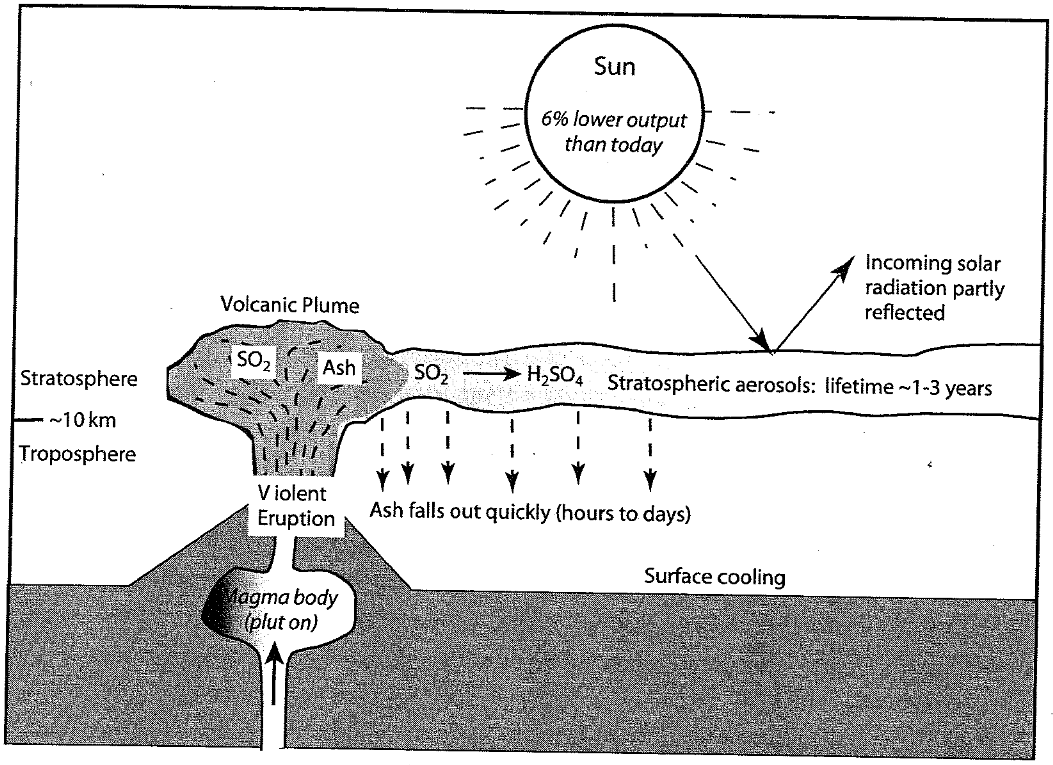

Fig. 2 Schematic diagram showing how explosive volcanism leads to climate cooling through the formation of sulphuric acid aerosols in the stratosphere. Figure is greatly simplified after Self (2006) and Robock (2000)

sulfuric acid aerosols, however, the influence of volcanic eruptions on atmospheric chemistry has not been explored in detail. Chlorine (and HCl in gaseous or aerosol form) may also be injected and this is likely to be detrimental to stratospheric ozone, but its specific climatic effects are unknown (Tabazadeh and Turco 1993; Robock 2000). Water and carbon dioxide are also injected into the atmosphere, but CO_2 in particular has warming effects that operates on a longer timescales than stratospheric cooling.

To better illustrate how explosive volcanism affects climate, three examples are presented. In this discussion we refer to the Volcanic Explosivity Index (VEI) of Newhall and Self (1982) to indicate the relative intensity of an explosive eruption. The VEI is a semi-quantitative logarithmic scale (0–8), based on a combination of erupted tephra volume and eruption plume height.

2.1 Pinatubo 1991

This eruption was relatively modest (VEI = 5–6) but is the largest to have occurred since remote sensing satellites began measuring global atmospheric sulfur and temperature. Along with petrologic investigations of eruptive products, these coupled observations provided a remarkably complete example of how one explosive eruption affected climate. Until there is a comparable or larger eruption that can be studied, testing whether or not explosive volcanism could have triggered Neoproterozoic glaciations largely requires scaling up from understanding the Pinatubo eruption.

Pinatubo's volcanic ash and lavas were unusually rich in sulfur with bulk contents of 1500–2400 ppm, and even contained anhydrite phenocrysts. Satellite-measured sulfur levels were orders of magnitude higher than that expected from simple degassing of the involved melt volume (Keppler 1999). The eruption appears to have been triggered by injection of S-rich, oxidized basalt into dacitic magma (De Hoog et al. 2004). In this scenario, the magma mixture released a S-rich fluid (possibly extracted as exsolved hydrous fluids) that may have collected at the top of the magma reservoir, and this provided the SO_2 injected into the atmosphere.

The eruption, and its effect on the stratosphere, were monitored by two important satellite systems; the Total Ozone Mapping Spectrometer (TOMS) and the Stratospheric Aerosol and Gas Experiment II (SAGE II). TOMS provided daily sulfur dioxide and ozone concentrations, and showed that Pinatubo injected a total of ~20 million tons of sulfur into the atmosphere (Bluth et al. 1992). SAGE II measured the stratospheric optical depth (D) through the atmospheric limb at sunrise and sunset. Knowing D, the vertical transmittance of the solar radiation through the atmosphere was calculated (higher D equals smaller transmittance). In general, non-transmitted solar radiation is either absorbed by the stratospheric gases and aerosols or is scattered back into space. It is through this mechanism that explosive eruptions reduce incoming solar radiation to Earth's troposphere and surface. TOMS and SAGE II thus measured Pinatubo-related volcanic ash as well as the sulfuric acid aerosols. Before Pinatubo erupted, D was globally low, $\sim 10^{-3}$. Forty days following the eruption, an aerosol cloud completely encircled the globe in a narrow zone, with maximum $D \sim 10^{-1}$, about two orders of magnitude higher than D before the eruption. Twenty months after the eruption, the aerosol cloud was dispersed globally, with D lowered to between 10^{-2} and 10^{-1}.

Global cooling caused by Pinatubo's S in the stratosphere lasted for years. Surface air temperatures over Northern Hemisphere continents were lower than normal by up to 2° C in the summer of 1992 and warmer than normal by up to 3° C in the winters of 1991–1992 and 1992–1993. Global warming may have been retarded for several years after the Pinatubo eruption because of the cooling effects of its volcanic aerosols (Robock 2000).

2.2 Eighteen Hundred and Froze to Death: Tambora 1815–1816

The greatest volcanic impact on climate in historical time resulted from the eruption of Mount Tambora in Indonesia. The April 1815 explosive eruption was one of the largest in the last 10,000 years (Rampino et al. 1988). The eruption ejected ~100 km^3 of pyroclastic trachyandesite (VEI~7), forming a caldera ~7 km across and reducing the summit by 1400 m. The rapid eruption rate and the area of ash dispersal suggest that the eruption column may have reached 50 km, well into the stratosphere. An estimated 60 million tonnes of sulfur rose into the stratosphere.

Within 3 months unusual optical effects due to the volcanic cloud were observed. Spectacular sunsets and twilights were observed in England in the summer of 1815. In the spring and summer of 1816 a persistent "dry fog" was observed in the northeastern USA. Rampino et al. (1988) conclude that the haze must have been located above the troposphere, since neither surface winds nor rain dispersed it and because the total lunar eclipse of 9–10 June was extremely dark. In New York, the Sun dimmed enough that sunspots were visible to the naked eye. Some of the painter J.M.W. Turner's work, characterized by vivid orange and red skies, captured the unusual appearance of the atmosphere during this period (Oppenheimer 2003). This great climate-affecting eruption may have inspired Byron to write "Darkness", a portion of which may have attempted to capture the mood spawned by the eruption:

I had a dream, which was not all a dream.
The bright sun was extinguish'd, and the stars
Did wander darkling in the eternal space,
Rayless, and pathless, and the icy earth
Swung blind and blackening in the moonless air;
Morn came and went – and came, and brought no day,
And men forgot their passions in the dread
Of this their desolation; and all hearts
Were chill'd into a selfish prayer for light

Extract from Darkness by Lord Byron 1816

It is generally accepted that the Tambora eruption caused a brief but intense episode of cooling as a result of injecting massive quantities of sulfur into the stratosphere (Self 2006). 1816 became known as the "Year without a Summer" because of the impact on North American and European weather. Harvests were poor in the Northern Hemisphere and livestock suffered. Post (1977) characterized 1816–1819 the last great subsistence crisis to affect the Western world; 1816–1817 witnessed the worst famine in over a century. He used grain prices as a proxy for harvest outcomes through the second half of the 1810s. Prices doubled between 1815 and 1817, indicating that harvests were deficient over much of the Northern Hemisphere. This is a good indication that climatic effects associated with the Tambora eruption severely stressed the biosphere.

2.3 Toba, 74 Ka

The greatest eruption known from the past 110,000 years was at Toba, Sumatra 74 ± 2 Ka ago (Oppenheimer 2002), with VEI$\sim$8 (Zielinski et al. 1996), $\sim$3500 times greater than Tambora 1815. Not surprisingly for such an ancient eruption, estimates of the sulphur yield vary by two orders of magnitude (35–3300 million tonnes; Oppenheimer 2002). Greenland Ice Sheet Project 2 (GISP2) cores nevertheless provide indirect evidence of the importance of eruptive sulfur fluxes over the last 110 Ka, with sulfate spikes observed at 69.4, 71, 72, and 73.6 Ka (Zielinski et al. 1996). Using the latest GISP2 chronology, the 71 Ka anomaly is dated to 70 ± 5 Ka (Oppenheimer 2002). This anomaly, thought to be due to the Toba eruption, is the largest sulfate anomaly in the entire GISP2 record.

Numerical modeling of the Toba eruption indicates that the residence time of stratospheric SO_2 was two to three times longer than the observed effects of Pinatubo, requiring 5–6 years to return to normal levels (Bekki et al. 1996).

The increased atmospheric opacity caused by the eruption should have strongly cooled Earth's surface and troposphere. It might have produced a volcanic winter followed by a few years when surface-temperatures decreased by 3–5° C, inferred from equation [1]. The eruption occurred during the oxygen isotope stage 5a-4 transition, close to the beginning of the last glacial period (Wisconsin glaciation, ~70,000–10,000 years ago), thus the Toba eruption may have either triggered this glaciation, or accelerated a shift to glacial conditions already underway (Rampino and Self 1992). It has also been suggested, based on genetic RNA "clocks", that cooling caused by the Toba eruption triggered an environmental catastrophe that almost extinguished the human race (Ambrose 1998).

The paleoclimatic effects of Toba are still being investigated, with alternate interpretations regarding timing, the amount of sulfur injected into the atmosphere, the degree of cooling, and the possibility that the GISP2 sulfur spike was caused by another eruption. Oppenheimer (2002) summarizes this controversy.

3 Can Episodes of Increased Explosive Volcanism Cause Ice Ages?

The Pinatubo and Tambora examples demonstrate that individual volcanic events can cool the Earth's surface for periods of a few years, and the Toba example suggests that a single large eruption can have a greater effect. It is also recognized that several sequential eruptions can cool climate over longer intervals, up to decades (Zielinski 2000). The next temporal scale that needs to be considered is whether protracted explosive volcanism could force enough cooling to trigger an ice age. This question was answered in the affirmative by Pollock et al. (1976), but very little published work on the subject has followed. Explosive volcanism would have to be sufficiently intense and persistent to cause cooling leading to a significant increase in the annual cryosphere (the proportion of Earth's surface covered by sea ice, snowfields and glaciers). This in turn could have tipped the radiative heat balance to a runaway ice-albedo feedback, a climate instability in which the absorption of surface radiation over open-ocean regions does not balance heat loss from ice-covered regions reflected to space, thereby accelerating cooling and ice growth (Hoffman and Schrag 2002). Runaway ice-albedo feedback is recognized as a key aspect of Neoproterozoic glaciation, regardless of what initially caused cooling.

Increased explosive volcanism may have catalyzed extensive N. Hemisphere glaciation during the Late Pliocene. The beginning of the widespread N. Hemisphere "ice age" ~2.65 Ma ago is often explained as the result of closing the isthmus of Panama, drastically changing Atlantic ocean circulation or uplift of the Tibetan Plateau, but these events probably occurred too early to be the exclusive mechanism (Prueher and Rea 2001). The change from a precession-dominated orbital regime to an obliquity-dominated orbital regime may also have contributed to N. Hemisphere glaciation (Maslin et al. 1998). In contrast, Prueher and Rea (1998, 2001) suggested that N. Hemisphere glaciation was at least partly caused by a major increase in explosive volcanic activity. This idea derives from empirical observations that ash layers and glacigenic deposits in ODP Leg 145 cores coincide.

A rapid increase in Late Pliocene glacial erosion and sedimentation by ice-rafting is inferred from ODP Leg 145 cores. Evidence of deposition by ice-rafting is suggested by sand-sized or larger material on the deep sea floor that is not volcanic ash, mixed with pelagic sediments, and deposited too far from continental margins to have been transported by downslope processes (Prueher and Rea 2001). Ice-rafted debris first appeared in the North Pacific in the latest Miocene or earliest Pliocene, indicating that some glaciers around the N. Pacific reached sea level by that time, but there is little evidence of ice-rafted debris during middle Pliocene time. The resurgence of Late Pliocene ice-rafted sediments coincides with an order-of-magnitude increase in the frequency and thickness of volcanic ash layers. ODP Leg 145 shipboard scientists noted that the first ash layers always occurred just below the first dropstones, suggesting that the enhanced volcanic activity just preceded the onset of full-scale Northern Hemisphere glaciation (Prueher and Rea 2001). Magnetic susceptibility measurements of ODP Leg 145 cores indicate that the change from pre-glacial pelagic diatom ooze to glacial-age clay-rich ooze happened within a few thousand years, an interval seemingly too rapid for tectonic or orbital forcing but consistent for a sudden increase in explosive volcanism (Prueher and Rea 1998, 2001).

Prueher and Rea (2001) suggested the following scenario: the Northern Hemisphere had been cooling slowly since ~3.5 Ma. A million years of slow cooling brought it to the threshold of continental ice sheet formation, and a sudden upsurge in explosive volcanism provided the final impetus for rapid ice buildup. "The combination of widespread volcanism at climatically sensitive latitudes of 50–60°N, the natural sensitivity of the Arctic to volcanic forcing, and the coeval insolation minimum brought on full scale Northern Hemisphere glaciation quite rapidly, within the 2000 or 3000 years indicated by the sediments of the North Pacific" (Prueher and Rea 2001; p. 228).

4 Evidence that Explosive Volcanism Caused Neoproterozoic Ice Ages

The preceding discussion indicates that increased explosive volcanism can disrupt Earth's radiative balance by repeatedly injecting sulfur aerosols into the stratosphere, thereby fostering cooling that, in extreme cases, could lead to glaciation.

Explosive volcanism need not be the sole cause of cooling, but would be especially effective when coincident with other agents of cooling, such as depletion of a prior greenhouse gas source such as methane, position of continents, orbital forcing, or intergalactic dust. Explosive volcanism could also have stimulated cooling by feedbacks related to atmospheric CO_2 drawdown. Such mechanisms for cooling climate have been considered by many other researchers, but here we focus on the possibility that explosive volcanism was primarily responsible or contributed significantly. Explosive volcanism could also serve to help decrease atmospheric CO_2. Ash dispersal fertilizes the oceans by greatly increasing the supply of nutrients (i.e., P and Fe: Anbar and Knoll 2002). This would have spurred photosynthetic marine life, leading to reduced atmospheric CO_2. Abundant ash and associated lava flows on land also stimulates chemical weathering, further drawing down atmospheric CO_2 (Goddéris et al. 2003). Of course, igneous activity also adds a lot of atmospheric CO_2 which warms climate although this acts over longer time periods and could be overridden in the short term by volcanic winter effects and in the long term by weathering and fertilization.

Numerical global climate models have yet to address VW2SE, so the following discussion is qualitative and empirical. Discussion builds on the conclusion that the VW2SE hypothesis is broadly viable, and considers four related fundamental queries: How important was Neoproterozoic explosive volcanism? How did explosive volcanism intensity vary throughout the Neoproterozoic supercontinent cycle? How did the timing of peak explosive volcanism correspond with glacial episodes? Is the hypothesis consistent with Sr, C, and O isotopic chemostratigraphy?

4.1 On the Importance of Neoproterozoic Explosive Volcanism

We need a quantitative assessment of how vigorous was Neoproterozoic explosive volcanism – especially compared to Mesoproterozoic and Paleozoic time - in order to test the VW2SE hypothesis. We know of no such assessment, so an indirect and qualitative assessment is developed here. Primary focus is naturally on direct evidence of explosive volcanism of great geographic extent, especially beds of airfall tuff, but this flux has not been quantified. Neoproterozoic ash beds are important targets for geochronology, especially where interbedded with carbonates (Condon et al. 2005; Hoffmann et al. 2004, 2006; Halverson et al. 2005). Because direct evidence for explosive volcanism (highly weatherable or chemically labile tuffs and pyroclastic rocks) are often obliterated by erosion, deformation, metamorphism, or in the case of VW2SE mixed with glacial deposits, we use the global distribution of Neoproterozoic igneous rocks as proxy for explosive volcanism. Plutonic rocks may not always form below explosive volcanoes, but they often do, especially if these magmas are rich in water and silica (Lipman 2007). White et al. (2006) conclude that the ratio of intrusives emplaced to extrusives erupted (I/E) ranges widely but shows no systematic variation with tectonic setting. They further suggest that an I/E $\sim$5, with considerable uncertainty, applies to a wide range of magmatic compositions and tectonic settings.

This suggests that the intensity of Neoproterozoic explosive volcanism can be inferred from relative volumes of Neoproterozoic intrusions, comprising both juvenile continental crust that formed and of older crust that was remelted during Neoproterozoic time. The area of such crust is controversial. For example, Condie (1998, 2000) infers modest Neoproterozoic crustal growth and igneous activity, whereas other estimates indicate that the Neoproterozoic was an important time of crustal growth (Reymer and Schubert 1984; Goodwin 1991; Rogers et al. 1995; Trompette 2000). Some of this disagreement may reflect a bias towards well-studied areas of N. America, Europe, and Australia. However, the greatest tracts of Neoproterozoic igneous rocks are in more poorly studied regions, especially Africa, South America, and Asia. Another complexity is common overprinting of Neoproterozoic crust in Eurasia and N. America by Phanerozoic orogens, such that even in well-studied European basement exposures it is difficult to determine how much was originally Neoproterozoic crust; all that can be stated with certainty is that much of it was. Finally, Neoproterozoic crust is often preferentially exploited by younger rifts and orogenic belts, thus complicating estimates of original distribution and abundance. Rifts related to the breakup of Gondwana preferentially exploited Neoproterozoic orogens, and much of this crust is now buried beneath subsiding passive margins. Orogenic reworking of these leading edges tectonically mixes Neoproterozoic and Phanerozoic terranes and the nonfossiliferous nature of the Neoproterozoic elements makes them difficult to recognize. This problem is particularly large for the Neoproterozoic of Eurasia, but the problem is diminishing as especially U-Pb zircon ion probe dating of this basement advances.

Disagreement about the abundance of Neoproterozoic igneous rocks also reflects different approaches: for example Condie (1998; Fig. 5) focuses on juvenile crust and subdivides Earth history in a way that neglects most of Neoproterozoic time, whereas Goodwin (1991) considers Precambrian time within four specific intervals (Early, Middle, and Late Proterozoic and Archean), and estimates areas of continental crust that formed during each time. Figure 3 presents our view of the global abundance of Neoproterozoic crust, based on a literature survey that is explained elsewhere (Stern and Stewart, in press). Comparing Goodwin's estimates or Fig. 3 to that of Condie (1998; Fig. 5) results in a very different impression about the importance of Neoproterozoic igneous activity. The contrast is especially striking for Africa, where Condie (1998; Fig. 5) shows minor Neoproterozoic crust compared with Fig. 3 and Goodwin's (1991) estimate that ~51 % of the continent consists of Neoproterozoic crust.

Disagreement about the area of Neoproterozoic crust discussed above emphasizes the challenges involved in quantifying igneous activity. This is further complicated because multiple ages are reported for tracts of continental crust, including isotopic "mantle extraction" model ages, zircon crystallization ages, and thermochronologies. These different ages provide different insights about how continental crust formed and was thermally reworked; correspondingly, what is meant by the age of a crustal tract must therefore be defined for each compilation. Progress in understanding crustal growth and how this may have affected exterior Earth subsystems (e.g., hydrosphere, climate, etc.) requires a GIS database for global crust,

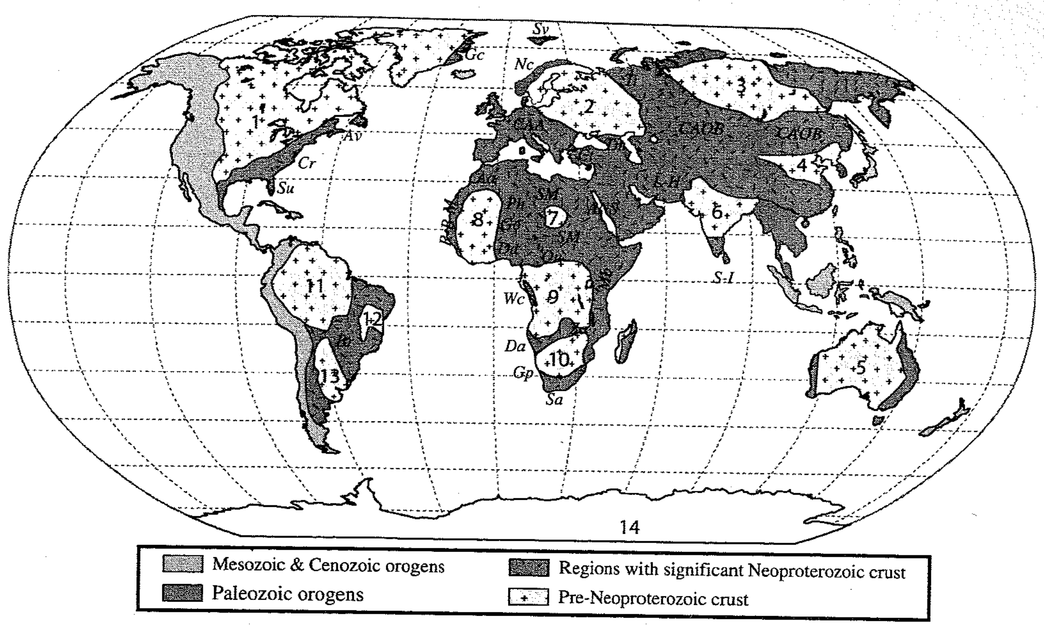

Fig. 3 Neoproterozoic crust worldwide (modified by Stern (in press), after Ernst et al. (2007)). Numbers correspond to pre-Neoproterozoic cratons: 1 = North American-Greenland craton; 2 = Baltic-East European craton; 3 = Siberian craton; 4 = N. China craton; 5 = Australia craton; 6 = Indian craton; 7 = Uweinat; 8 = West African craton; 9 = Congo craton; 10 = S. African craton; 11 = Amazon craton; 12 = Sao Francisco craton; 13 = Rio de la Plata craton; 14 = E. Antarctic craton. Italicized abbreviations are Neoproterozoic terranes (clockwise from North America: *Su* = Suwanee; *Cr* = Carolinia; *Av* = Avalonia; *Gc* = Greenland Caledonides; *Sv* = Svalbaard; *Nc* = Norwegian Caledonides; *CAA* = Cadomian, Avalonian, and Amorican; *Ct* = Cadomian of Turkey; *Tm* = Trans-caucusian massif; *Ti* = Timanides; *CAOB* = Central Asian Orogenic Belt; *L-H* = Lut and Helmut blocks; *S-I* = Southern India and Sri Lanka; *ANS* = Arabian-Nubian Shield; *Mb* = Mozambique Belt; *SM* = Saharan Metacraton; *Ou* = Oubangides; *Za* = Zambezi Belt; *Sa* = Saldanian; *Gp* = Gariep Belt; *Da* = Damaran; *Wc* = West Congo; *Dh* = Dahomides; *Go* = Gourma; *Ph* = Pharusian Belt; *Aa* = Anti-atlas; *R-B-M* = Rokelides, Bassalides, and Mauretides; *Br* = Brasiliano belts)

which does not yet exist but which would be invaluable for a wide range of fundamental geoscientific queries, including the question of Neoproterozoic igneous activity and explosive volcanism. Such a GIS will require a concerted international effort to build, update, and maintain and is far beyond the scope of this essay.

Absent such a global crustal GIS, we must nevertheless attempt to objectively estimate the volume of Neoproterozoic crust. Estimates available for this survey broadly support a concensus view that volumes of Neoproterozoic crust production were large. For example, Goodwin (1991) estimated that ~17 % of the present continental crust formed or was thermally reworked during Neoproterozoic time. Similarly, Maruyama and Liou (1998) suggested that perhaps 20 % of the area of all orogenic belts formed between 0.7 and 0.6 Ga. On a more regional scale, Reymer and Schubert (1984) concluded that 80 % of the entire Phanerozoic growth rates was required to generate the Neoproterozoic Arabian-Nubian Shield alone, although this estimate has been revised considerably (Stern 1994).

Table 1 Global Inventory of Neoproterozoic Crust

Continent	area (10^6 km^2)	% of continental area	Areal % Neoproterozoic	Neoproterozoic area (10^6Km^2)
Africa	30.37	20.36	50.60	15.37
N. America	24.49	16.42	1.60	0.39
S. America	17.84	11.96	14.90	2.66
Antarctica	13.72	9.20	8.30	1.14
Asia	43.81	29.38	9.10	3.99
Australia + NewGuin	8.5	5.70	2.80	0.24
Europe	10.4	6.97	8.40	0.87
Eurasia	52.21	35.01		
total	149.13	100		24.65

(From Table 5-1 of Goodwin, 1991)

Figure 3 shows where a significant part of the continental crust is Neoproterozoic, for all of the continents. Table 1, modified from Goodwin (1991), is to our knowledge the only areal estimate of Neoproterozoic crust. Although this estimate considers only exposed continental areas, and thus excludes perhaps an additional ~30 % of continental crust in submarine shelval areas (Cogley 1984), we use these areas to infer minimal volumes of Neoproterozoic crust production and, derivatively, as a general proxy for Neoproterozoic igneous activity likely to have been associated with explosive volcanism.

It is beyond the scope of this essay to consider in any greater detail the nature of Neoproterozoic igneous activity preserved on the continents. The interested reader is encouraged to read Stern (in press) for a more detailed overview of Neoproterozoic crustal growth.

4.2 Neoproterozoic Igneous Activity and the Supercontinent Cycle

Modern plate tectonic processes form and rejuvenate continental crust largely by igneous activity within the context of a supercontinent cycle, and similar processes operated in Neoproterozoic time (Murphy and Nance 2003). The Neoproterozoic witnessed the breakup of the supercontinent Rodinia and the reassembly of its fragments into a new supercontinent, known as Greater Gondwana or Pannotia, by the end of the era. Rodinia remained intact during the Tonian period (*tonos* is Greek for tension or stretching) and the first 150 Ma of Neoproterozoic time witnessed little igneous activity. In contrast, the Cryogenian period – when Rodinia broke up beginning ~830 Ma ago (Li et al. 1999; Torsvik 2003) – experienced intense magmatic activity. Early Cryogenian igneous rocks related to Rodinia breakup are well preserved in western N. America, China, Australia, and Siberia, leading to the inference that some of these were adjacent crustal tracts prior to early Cryogenian rifting (Burret and Berry 2000; Sears and Price 2003; Wang and Li 2003). Rodinia fragmentation required formation of new subduction zones, and Cryogenian magmatism reflected the increasing vigor of volcanic activity at rifts, volcanic rifted margins, and island arcs. Breakup continued throughout the rest of Neoproterozoic time. Completion of the Neoproterozoic supercontinent cycle during Ediacaran time was associated with orogenic collapse and the start of a new cycle of rifting.

Progression from breakup of Rodinia to assembly of Greater Gondwana represents a ~300 Ma long supercontinent cycle (Nance et al. 1988), over which time the efficacy of divergent- and convergent-margin volcanism to inject S into the stratosphere and thus affect climate would have evolved (Fig. 4). Fragmentation of Rodinia was protracted and continued throughout the rest of Neoproterozoic time (Hoffman 1999; Goodge et al. 2002; Lund et al. 2003). Increased igneous activity was an inevitable result of Rodinia breakup, both in and around the widening rifts and at new subduction zones and island arcs that formed to allow the rifts to widen into oceans. Explosive volcanism is associated with both convergent and divergent plate boundaries (Mason et al. 2004), but eruptions must be subaerial or nearly so

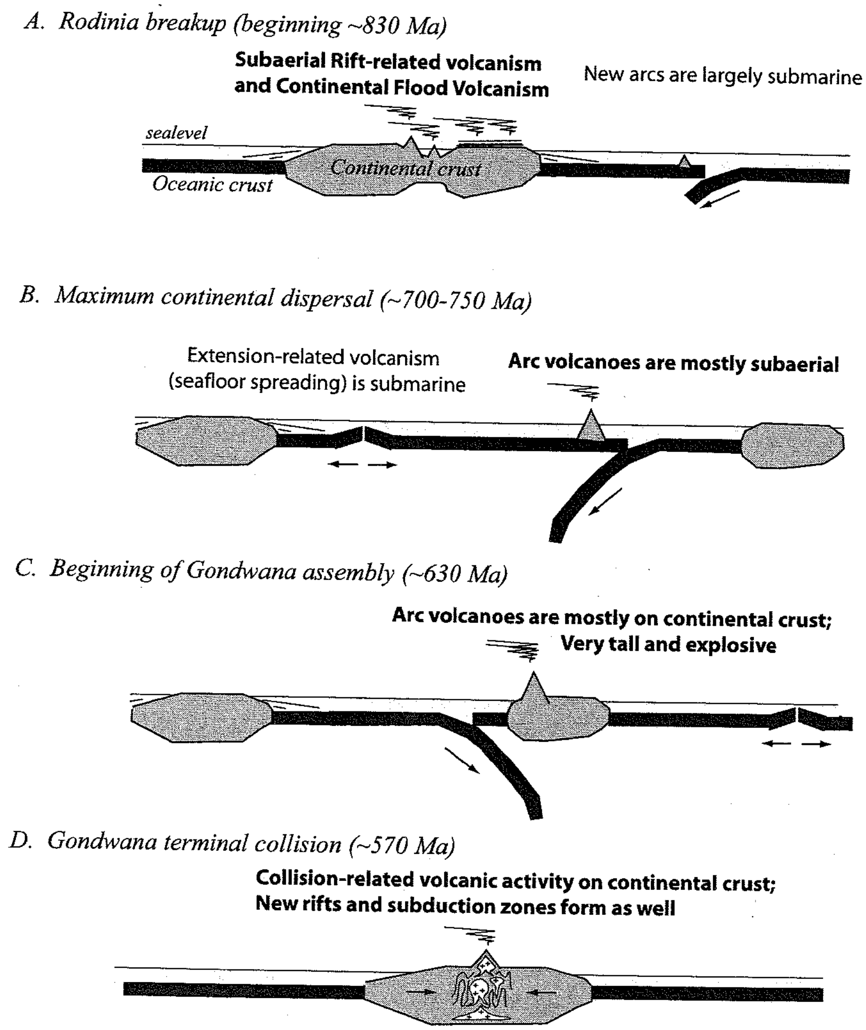

Fig. 4 Progressions in volcanic activity during the Neoproterozoic supercontinent cycle, greatly simplified. Figure is greatly simplified after Stern (in press). Important styles of volcanism for controlling climate are shown in bold letters

for volcanic plumes to rise into the stratosphere. Over the Neoproterozoic supercontinent cycle, explosive volcanism would at first have been dominated by rifts, with arcs and collision-related igneous activity becoming progresively more important. This progression can be inferred because maturing rifts tend to subside below sealevel as rifting progresses to seafloor spreading whereas arc volcanoes and the crust on which they are built become increasingly emergent (subaerial). Continental rifting volcanism could inject SO_4 into the stratosphere, but the extent to which this could cause cooling is controversial (see different views of Wignall 2001 and Self et al. 2005). Convergent margin igneous activity is likely to become increasingly subaerial over the Neoproterozoic supercontinent cycle, as submarine and barely emergent island arc volcanoes are replaced by continental Andean-type arc volcanoes. Arc volcanoes, near sealevel when they formed at the start of the cycle, would have been dominated by low-K tholeiitic and medium-K calc-alkaline magmas. Because of their relatively low explosivity, injection of S into the stratosphere is less likely, thus these volcanoes would have modest effects on climate. Submarine volcanoes could not inject S into the stratosphere in any case, and emergent arc volcanoes would have been relatively low, further making it difficult to inject S into the stratosphere. The effect of arc volcanism on climate should progressively increase over the supercontinent cycle, as juvenile arcs coalesced to produce thicker crust, and arc volcanoes became taller and erupted more fractionated and thus explosive magmas. In summary, extension-related volcanism would have been a more important agent of climate change in early Cryogenian time whereas arc volcanism should have become more important in the late Cryogenian and Ediacaran periods (Fig. 4). This progression may be part of the reason why the first significant Neoproterozoic glaciations followed a few tens of millions of years after Rodinia began to break up ~830 Ma.

The Ediacaran period witnessed significant glaciation and igneous activity at diverse tectonic settings, reflecting magmatic activity associated with collision and post-orogenic collapse. Such a transition is observed in the Arabian-Nubian Shield at ~600Ma, when convergent margin magmatism was replaced by post-tectonic or anorogenic magmatism (e.g., Beyth et al. 1994); a similar transition is inferred for Neoproterozoic crust of eastern North America and western Europe (Nance et al., in press). The end-Neoproterozoic supercontinent started to breakup almost immediately, with transtension and rifting on its northern and western margins (Nance et al., in press) along with formation of new subduction zones with Andean-type arcs along its southern margins (Terra Australis Orogen of Cawood 2005).

4.3 Synchroneity of Neoproterozoic Glaciation and Igneous Activity

Indirect support for the VW2SE hypothesis comes from the overlapping ages of igneous activity and glaciation, and from the observation that both are missing from the 150 Ma long Tonian record (Fig. 1). We agree with the conclusion of Fairchild and Kennedy (2007, in press): "The most plausible root causes for long-term change in the surface Earth System are deep-earth processes and biological innovation . . ." Other resesearchers have also inferred a causal relationship between Neoproterozoic tectonics and magmatism on the one hand and glaciation on the other. Hoffman et al. (1998) concluded that cooling began about the time of Rodinia breakup ~830 Ma, and inferred a link between breakup and cooling. Widespread igneous activity began globally about this time, especially in China, Africa, and western N. American. Flood basalt volcanism related to Rodinia breakup, forming especially the Laurentian magmatic province at ~780Ma, was inferred by Goddéris et al. (2003) to have caused climate cooling, due to decreased atmospheric CO_2 resulting from accelerated weathering of basalt. Donnadieu et al. (2004) also linked cooling to reduced atmospheric CO_2 caused by Rodinia breakup, but emphasized the role of increased runoff. Further support for the idea that vigorous tectonic movements are associated with glaciation is found in the distribution of Neoproterozoic Banded Iron Formation (BIF) – one of the hallmarks of the Snowball Earth Hypothesis. Young (2003) noted that Neoproterozoic BIFs were generally deposited in tectonically active (rift) settings. Most Neoproterozoic BIFs are broadly Sturtian (700 ± 30 Ma), recording an important episode of tectonic and perhaps seafloor hydrothermal activity. The observation that Neoproterozoic glacial sediments were deposited during times of strong tectonic movements is consistent with the VW2SE hypothesis.

Below we consider a very interesting line of evidence in support of the VW2SE hypothesis: the similar timing of Marinoan glaciation and peak igneous activity in the Arabian-Nubian Shield (ANS) and East African Orogen (EAO). Among the Neoproterozoic glacial episodes, the comparatively well-studied ~635 Ma Marinoan glaciation displays evidence that best supports a truly global glaciation (Allen 2006). Thus, if the VW2SE hypothesis has any merit, evidence for it should be apparent in association with the Marinoan glaciation. Figure 5 compares the timing of major Neoproterozoic glaciations with igneous rock ages in the ANS (Fig. 5A) and the entire EAO (Fig. 5B,C). We recognize that the EAO (including the ANS) preserves only a fraction, perhaps 30 %, of total global Neoproterozoic igneous activity, that geochronologic results are partly biased toward datable units (zircon-bearing or high Rb-Sr plutonic rocks), and that the relationship between age distributions of dominantly plutonic rocks and the record of explosive volcanism is not resolved. Nevertheless, taken at face value, the comparison suggests that Marinoan glaciation closely corresponded to a time of peak igneous activity in the EAO and ANS, providing specific if coincidental support for the VW2SE hypothesis.

Detrital zircon U-Pb SHRIMP ages from Cambrian and Ordovician strata deposited on various segments of the Arabian-Nubian Shield (N. Ethiopia, southern Israel) provide an additional perspective on the timing of igneous activity along the EAO. A preponderance of the detrital zircon ages are concentrated at 650–600 Ma (Avigad et al. 2003, 2007; Kolodner et al. 2006) strengthening the notion that Marinoan glaciation coalesced with intense igneous activity along the EAO.

In addition to evidence of near-equatorial glaciation at sea level (Sohl et al. 1999), the global extent inferred for the Marinoan glaciation is supported by identical ages retrieved from ash beds associated with Neoproterozoic glacigenic sediments in

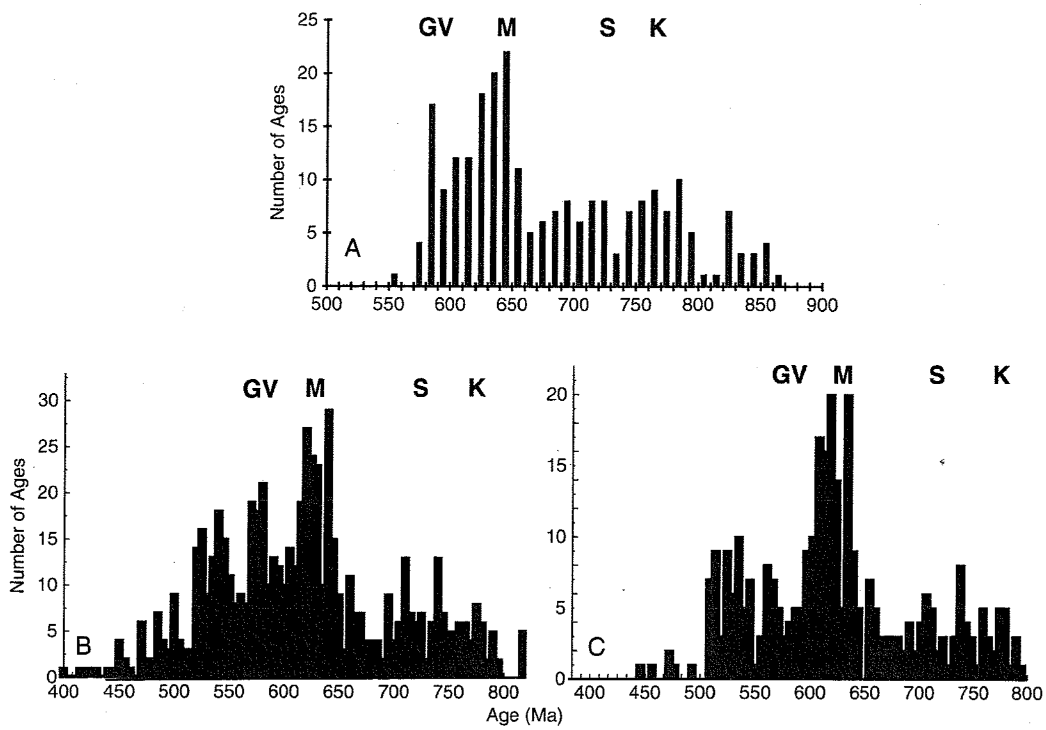

Fig. 5 Relationship between Neoproterozoic glaciations and igneous activity in the Arabian-Nubian Shield. (**A**) Robust radiometric ages of the ANS (Johnson and Kattan 2007). (**B**) Ages for East Africa and Madagascar (n = 695; Meert 2003). (**C**) Eastern Africa and Madagascar, zircon ages only (Meert 2003). Bold letters signify major Neoproterozoic glaciations: KM = Kaigan-Mahd (~ 780 – 750 Ma); S = Sturtian (~ 680 – 750 Ma); M = Marinoan (635 Ma); GV = Gaskiers/Varager (580 Ma)

Namibia and China (ash bed at top of Nantuo tillite in south China is 635.2 ± 0.6 Ma (Condon et al. 2005); ash bed in Ghaub dropstone beds in Namibia is 635.5 ± 1.2 Ma (Hoffmann et al. 2004); the Marinoan Flinders Range glaciogenic sequence has not been similarly constrained by high precision dating. We do not know if these geographically disparate ash beds were derived from the same eruption or from the ANS, but these results demonstrate that explosive volcanism and glaciation were then intimately associated and nearly synchronous (if not coeval) on a widespread (if not global) scale. Regardless, the strong correlation between peak Neoproterozoic magmatic activity in the ANS-EAO and ~635 Ma ashes associated with geographically disparate Marinoan glacial deposits currently forms a strong argument for further considering the VW2SE hypothesis.

A secondary peak in the ANS and EAO igneous rock record at ~580 Ma could similarly indicate an episode of increased explosive volcanism that was coincident with the Gaskiers/Varanger glaciation. We also note that there are no clear peaks in the histograms that correspond to the times of pre-Marinoan glacial episodes (Mahd, Kaigas, and Sturtian). This may partly reflect the under-representation of older Neoproterozoic igneous rocks on these histograms. This in turn suggests that tests of this hypothesis should focus initially on the Marinoan glaciation. Some potentially corroborating studies already exist. For example, Bodiselitsch et al. (2005) found Ir anomalies at the base of post-Marinoan cap carbonates from the Eastern Congo craton. Although attributed to an extraterrestrial origin, Ir anomalies could also result from enhanced volcanism at 635Ma. Ir has been found in airborne particulates from Kilauea eruptions (Zoller et al. 1983) and in ashes of the British Tertiary province (Elliot et al. 1992; Schmitz and Asaro 1996). Furthermore, Bodiselitsch et al. (2005) also found very high element/Al ratios of Th, Ta, Hf, K, and Ti, consistent with inclusion of a silicic or Hawaiian-like volcanic component.

4.4 Isotopic Constraints

Sr, C, and S isotopes provide environmental constraints. The $^{87}Sr/^{86}Sr$ record of marine carbonate sediments, which proxy for seawater, reveal an ocean with sources of Sr that changed from dominantly oceanic ~800 Ma to dominantly continental ~600 Ma (Walter et al. 2000; Melezhik et al. 2001; Halverson et al., in press). It must be noted that, although low seawater $^{87}Sr/^{86}Sr$ indicates mantle activity, it does not proxy for explosive volcanism because major, climate-affecting eruptions may involve remelted older crust at Andean-type margins and continental collision zones. Such magmas will have elevated $^{87}Sr/^{86}Sr$, so that increased igneous activity and explosive volcanism could in different circumstances act to raise or lower seawater $^{87}Sr/^{86}Sr$. For this reason, Sr isotopic data provides a relativley weak test of the VW2SE hypothesis.

Carbon isotopes provide a better test of the VW2SE hypothesis. It is well known that Neoproterozoic glacial episodes are associated with negative $\delta^{13}C$ excursions, which often begin before the glacial episode itself and endure after glacial recovery, as recorded in cap carbonate successions (Halverson et al. 2002, 2005). Negative $\delta^{13}C$ excursions are variously explained (e.g., large scale methane release, collapse of biosphere, etc.), but it is also possible that these $\delta^{13}C$ excursions at least partly reflect increased addition of mantle CO_2 ($\delta^{13}C \sim -6$ ‰), released by volcanic activity. Estimates of C flux from the solid Earth suggests that inputs from arc volcanoes today are about twice that from mid-ocean ridges and that hot spot contributions are insignificant (Sano and Williams 1996), although major flood basalt eruptions introduce massive amounts of CO_2 (Wignall 2001). Volcanic inputs will have variously negative $\delta^{13}C$ (~ -1 to -10‰), in the range appropriate for the negative $\delta^{13}C$ excursions. Of course the addition of large amounts of CO_2 should warm climate, not cool it, unless sufficient SO_4 was also injected into the stratosphere to overcome the greenhouse warming effect of volcanic CO_2 until Earth's ice-covered surface was extensive enough and planetary albedo low enough for runaway cooling. This would have been most likely when explosive, S-rich arc volcanism was important, as would be expected during the middle of the Neoproterozoic supercontinent during the Cryogenian Period. Arc volcanism would have been less important at the beginning and end of the Neoproterozoic cycle, thus the ~800 Ma Bitter Springs and ~ 600–540 Ma Shuram anomaly (Halverson et al. 2005; Le Guerroué et al. 2006) may have been associated with subordinate arc volcanism, stratospheric sulfur, and climate cooling.

Sulfur isotopic compositions of Neoproterozoic sedimentary rocks may provide a key test for the VW2SE hypothesis. Mantle inputs should have $\delta^{34}S \sim 0‰$ (Holser et al. 1988) but the effect of significant inputs of such sulfur on the composition of sedimentary sulfate and sulfide is not clear. This is because coexisting sulfide and sulfate strongly fractionate sulfur isotopes, given by $\Delta^{34}S$ ($= \delta^{34}S_{sulfate} - \delta^{34}S_{sulfide}$), the difference for the Phanerozoic being >46‰ (Canfield and Teske 1996). The $\delta^{34}S$ for pyrite decreases by several tens per mil during Sturtian and Marinoan glaciations; the $\delta^{34}S$ sulfate record is less complete but significant $\delta^{34}S$ decreases are also suggested by the compilation of Hurtgen et al. (2005) and is expected from equilibrium with coexisting sulfides (Hurtgen et al. 2005).

Could the large negative excursions observed for $\delta^{34}S$ during glacial episodes be due to magmatic inputs of S? Variations in $\delta^{34}S$ for sedimentary sulfate and sulfide are generally explained as a change in the balance between removal of sulfur from seawater as sulfide vs. sulfate (Hurtgen et al. 2002). This variable is significant because ^{32}S is preferentially removed by sulfide burial. Positive $\delta^{34}S$ excursions thus reflect a greater ratio of sulfide to sulfate burial, whereas negative excursions result when a greater fraction of total sulfur is buried as sulfate. Neoproterozoic negative $\delta^{34}S$ excursions could reflect increased sulfate burial, but it is difficult to imagine why more sulfate – which is most commonly found in evaporates – would be preferentially deposited during the cold climate of a glaciation; furthermore, some models for Neoproterozoic glacial episodes predict oceanic anoxia, which should result in much more sulfide than sulfate deposition (Hurtgen et al. 2002). However, it is by no means agreed that the oceans during Neoproterozoic glacial episodes were anoxic. Using the S isotopic chemostratigraphy of Neoproterozoic rocks to test the VW2SE hypothesis is thus difficult because we do not yet understand what effect increased volcanic S would have on the marine S cycle. Hurtgen et al. (2002) suggested $\delta^{34}S$ inputs from rivers are ~6‰ but this is poorly constrained. What would volcanic arc input be? Bulk Earth and MORB-like $\delta^{34}S$ ~0‰ or like modern arc volcanics, which range widely: 0 to +10‰ (De Hoog et al. 2001). In summary we conclude that although the S isotope system was greatly disrupted about the time of Neoproterozoic glaciations, there is not currently a sufficient basis to interpret the cause of variations, including the possibility of a VW2SE hypothesis.

5 Conclusions

The hypothesis that explosive volcanism was at least partly responsible for Neoproterozoic climate change is viable if not proven. The mechanism of cooling by sulfuric acid aerosols in the stratosphere is well-established from studies of recent volcanic eruptions. It is possible – as demonstrated by recent analogs – that a persistent episode of plinian eruptions alone could cause ice ages. A qualitative inventory of Neoproterozoic igneous rocks shows that these are very abundant, so that the derivative Neoproterozoic explosive magmatic flux could have seriously impacted climate. The general timing of Neoproterozoic volcanism and glacial activity correspond, with no glaciation and reduced igneous activity in the Tonian era. Glaciation followed soon after increased igneous activity began as Rodinia broke apart. The Marinoan (~635 Ma) glaciation in particular corresponds to a peak time of igneous activity in the Arabian-Nubian Shield and the East African Orogen. Explosive volcanism need not be the sole cause of cooling, and would be especially effective when happening in concert with other agents of cooling, such as lowered atmospheric CO_2 due to enhanced weathering, methane oxidation, latitudinal position and configuration of continents, orbital forcing, intergalactic dust, etc. These observations indicate that the hypothesis that some if not all of the Neoproterozoic ice ages were at least partly caused by increased explosive volcanism warrants further testing.

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References

Allen PA (2006) Snowball Earth on trial. EOS 87 45:495–496

Allen PA, Bowring SA, Leather J, Brasier M, Cozzi A, Grotzinger JP, McCarron G, Amthor J (2002) Chronology of Neoproterozoic glaciations: new insights from Oman. 16th International Sedimentological Congress, Johannesburg, International Association of Sedimentologists, pp 7–8 (abs)

Ambrose SH (1998) Late Pleistocene human population bottlenecks, volcanic winter, and differentiation of modern humans. J Hum Evol 34:623–651

Anbar AD, Knoll AH (2002) Proterozoic Ocean Chemistry and Evolution: A Bioinorganic Bridge? Science 297:1137–1142

Avigad D, Kolodner K, McWilliams M, Persing H, Weissbrod T (2003) Origin of northern Gondwana Cambrian sandstone revealed by detrital zircon SHRIMP dating. Geology 31: 227–230

Avigad D, Stern RJ, Beyth M, Miller N, McWilliams MO (2007) Detrital zircon geochronology of Cryogenian diamictites and Lower Paleozoic sandstone in Ethiopia (Tigrai): age constraints on Neoproterozoic glaciation and crustal evolution of the southern Arabian-Nubian Shield. Precambrian Res 154:88–106

Bekki S, Pyle JA, Zhong W, Toumi R, Haigh JD, Pyle DM (1996) The role of microphysical and chemical processes in prolonging the climate forcing of the Toba eruption. Geophys Res Lett 23:2669–2672

Beyth M, Stern RJ, Altherr R, Kröner A (1994) The Late Precambrian Timna Igneous Complex, southern Israel: evidence for comagmatic-type sanukitoid monzodiorite and alkali granite magma. Lithos 31:103–124

Blake S (2003) Part IV: Atmospheric, climatic and environmental impacts of volcanic emissions. Correlations between eruption magnitude, SO_2 yield, and surface cooling. In: Oppenheimer C, Pyle DM, Barclay J (eds) Volcanic Degassing, Geological Society, London, Special Publication 213, pp 371–380

Bluth GJS, Doiron SD, Schnetzler SC, Krueger AJ, Walter LS (1992) Global tracking of the SO clouds from the June 1991 Mount Pinatubo eruptions. Geophys Res Lett 19:151

Bodiselitsch B, Koeberl C, Master S, Reimold WU (2005) Estimating duration and intensity of Neoproterozoic snowball glaciations from Ir Anomalies. Science 308(5719):239–242

Bowring SA, Myrow PM, Landing E, Ramezani J, Grotzinger J (2003) Geochronological constraints on terminal Neoproterozoic events and the rise of metazoans. Geophys Res 5:13219 (abs)

Burret C, Berry R (2000) Proterozoic Australia-Western United States (AUSWUS) fit between Laurentia and Australia. Geology 28:103–106

Canfield DE, Teske A (1996) Late Proterozoic rise in atmosphere oxygen concentration inferred from phylogenetic and sulfhur-isotope studies. Nature 382:127–132

Cawood PA (2005) Terra Australis Orogen: Rodinia breakup and development of the Pacific and Iapetus margins of Gondwana during the Neoproterozoic and Paleozoic. Earth-Sci Rev 69:249–279

Cogley JG (1984) Continental margins and the extent and number of continents. Rev Geophys Space Phys 22:101–122

Condie KC (1998) Episodic continental growth and supercontinents: a mantle avalanche connection? Earth Planet Sci Lett 163:97–108

Condie KC (2000) Episodic continental growth models: afterthoughts and extensions. Tectonophysics 322:153–162

Condon D, Zhu M, Bowring S, Wang W, Yang A, Jin Y (2005) U-Pb ages from the Neoproterozoic Doushantuo Formation, China, Science 308:95–98

Corsetti FA, Olcott AN, Bakermans C (2006) The biotic response to Neoproterozoic snowball Earth. Palaeogeogr Palaeoclimatol Palaeoecol 232:114–130

Crutzen PJ (2006) Albedo enhancement by stratospheric sulfur injections: a contribution to resolve a policy dilemma? Clim Change 77:211–219

De Hoog JCM, Hattori KH, Hoblitt RP (2004) Oxidized sulfer-rich mafic magma at Mount Pinatubo, Philippines. Contrib Mineral Petrol 146:750–761

De Hoog JCM, Talor BE, van Bergen MJ (2001) Sulfur isotope systematices of basaltic lavas from Indonesia: Implications for the sulfur cycle in subduction zones. Earth Planet Sci Lett 189:237–252

Donnadieu Y, Goddéris Y, Ramstein G, Nédelec A, Meert, J (2004) A 'snowball Earth' climate triggered by continental break-up through changes in runoff. Nature 428:303–306

Elliot WC, Aronson JL, Millard HT Jr (1992) Iridium content of basaltic tuffs and enclosing black shales of the balder formation, North Sea. Geochim Cosmochim Acta 56:2955–2961

Ernst WG, Hacker BR, Liou JG (2007) Petrotectonics of ultrahigh-pressure crustal and upper mantle rocks-implications for Phanerozoic collisional orogens. In: Sears J, Harms T, Evenchick C (eds) Whence the mountains? Inquiries into the evolution of orogenic systems: a volume in honor of Raymond A. Price, Geological Society of America, Special Paper No. 433, 27–49

Fairchild IJ, Kennedy MJ (2007) Neoproterozoic glaciation in the Earth system. J Geol Soc London 164:895–921

Fanning CM (2006) Constraints on the timing of the Sturtian glaciation from southern Australia; i.e., for the true Sturtian, Geological Society of America Abstracts with Programs 38:115 (abs)

Franklin B (1784) Meteorological imaginations and conjectures. Memoirs of the Literary and Philosophical Society of Manchester 2:357–361

Garfunkel Z (1999) History and paleogeography during the Pan-African orogen to stable platform transition: reappraisal of the evidence from the Elat area and the northern Arabian-Nubian Shield. Isr J Earth Sci 48:135–157

Goddéris Y, Donnadieu Y, Nédélec A, Dupré B, Dessert C, Grard A, Ramstein G, François LM (2003) The Sturtian 'snowball' glaciation: fire and ice. Earth Planet Sci Lett 211:1–12

Goodge J, Myrow P, Williams IS, Bowring SA (2002) Age and provenance of the Beardmore group, Antarctica: constraints on Rodinia Supercontinent breakup. J Geol 110:393–406

Goodwin AM (1991) Precambrian geology: the dynamic evolution of the continental crust. Academic Press, London, 666pp

Halverson GP, Dudas F, Maloof AC, Bowring SA (2007) Evolution of the $^{87}Sr/^{86}Sr$ composition of Neoproterozoic seawater. Palaeogeogr Palaeoclimatol Palaeoecol 256:103–129
Halverson GP, Hoffman P, Schrag D (2002) A major perturbation of the carbon cycle before the Ghaub glaciation (Neoproterozoic) in Namibia: prelude to snowball Earth? Geochem Geophys Geosyst 3(6). doi:10.1029/2001GC000244
Halverson GP, Hoffman PF, Schrag DP, Maloof AC, Rice AHN (2005) Toward a Neoproterozoic composite carbon-isotope record. Geol Soc Am Bull 117:1181–1207
Hoffman PF (1999) The break-up of Rodinia, birth of Gondwana, true polar wander and the snowball Earth. J Afr Earth Sci 28:17–33
Hoffman PF, Kaufman AJ, Halverson GP, Schrag DP (1998) A Neoproterozoic snowball Earth. Science 281:1342–1346
Hoffmann K-H, Condon DJ, Bowring SA, Crowley JL (2004) U-Pb zircon date from the Neoproterozoic Ghaub Formation, Namibia: constraints on Marinoan glaciation. Geology 32:817–820
Hoffmann K-H, Condon DJ, Bowring SA, Prave AR, Fallick A (2006) Lithostratigraphic, carbon ($\delta^{13}C$) isotope and U-Pb zircon age constraints on early Neoproterozoic (ca. 755 Ma) glaciation in the Gariep Belt, southern Namibia. Snowball Earth Conference,, 2006, Ascona, Switzerland p 51 (abs), 16–21 July 2006
Hoffman PF, Schrag DP (2002) The snowball Earth hypothesis: testing the limits of global change. Terra Nova 14:129–155
Holser WT, Schidlowski M, McKenzie FT, Maynard JB (1988) Geochemical cycles of carbon and sulfur, In: Gregor CB, Garrels RM, McKenzie FT, Maynard JB (eds) Chemical cycles in the evolution of the Earth, Wiley, New York, pp 105–173
Hurtgen MT, Arthur MT, Suits NS, Kaufman AJ (2002) The sulfur isotopic composition of Neoproterozoic seawater sulfate: implications for a snowball Earth? Earth Planet Sci Lett 203:413–429
Hurtgen MT, Arthur MT, Halverson GP (2005) Neoproterozoic sulfur isotopes, the evolution of microbial sulfur species, and the burial efficiency of sulfide as sedimentary pyrite. Geology 33:41–44
Hyde WT, Crowley TJ, Baum SK, Peltier WR (2000) Neoproterozoic 'snowball Earth' simulations with a coupled climate/ice-sheet model. Nature 405:425–429
Johnson PR, Kattan FH (2007) Geochronologic dataset for Precambrian rocks in the Arabian Peninsula: a catalog of U-Pb, Rb-Sr, Ar-Ar, and Sm-Nd ages, Saudi Arabian Deputy Ministry for Mineral Resources Open-File Report USGS-OF-2007-3, 40pp
Kendall BS, Creaser RA, Selby D (2006) Re-Os geochronology of postglacial black shales in Australia: constraints on the timing of the 'Sturtian' glaciation. Geology 34:729–732
Kennedy M, Drosser M, Mayer LM, Pevear D, Mrofka D (2006) Late precambrian oxygenation; inception of the clay mineral factory. Science 311:1446–1449
Kennett JP, Thunnell RC (1977) Global increase in Quaternary explosive volcanic eruptions. Science 187:1231–1234
Keppler H (1999) Experimental evidence for the source of excess sulfur in explosive volcanic eruptions. Science 284:1652–1654
Kirschvink JL, Gaidos EJ, Bertani LE, Beukes NJ, Gutzmer J, Maepa LN, Steinberger RE (2000) Paleoproterozoic snowball Earth: extreme climatic and geochemical global change and its biological consequences. Proc Natl Acad Sci 97:1400–1405
Knoll AH (2003) Life on a young planet; The first three billion year of evolution on Earth, Princeton University Press, Princeton/Oxford, 277pp
Knoll AH, Hayes JM, Kaufman AJ, Swett K, Labert IB (1986) Secular variation in carbon isotope ratios from upper Proterozoic successions of Svalbard and East Greenland. Nature 321:832–838
Kolodner K, Avigad D, McWilliams M, Wooden JL, Weissbrod T, Feinstein S (2006) Provenance of north Gondwana Cambrian-Ordovician sandstone: U-Pb SHRIMP dating of detrital zircons from Israel and Jordan. Geol Mag 143:367–391
Lamb HH (1970) Volcanic dust in the atmosphere; with a chronology and assessment of its meteorological significance. Philos Trans R Soc Lond A 266:425–533
Le Guerroué E, Allen PA, Cozzi A, Etienne JL, Fanning M (2006) 50 Myr recovery from the largest negative $\delta^{13}C$ excursion in the Ediacaran ocean. Terra Nova 18:147–153

Li ZX, Li XH, Kinny PD, Wan J (1999) The breakup of Rodinia: did it start with a mantle plume beneath South China? Earth Planet Sci Lett 173:171–181

Lipman PW (2007) Incremental assembly and prolonged consolidation of Cordilleran magma chambers: evidence from the Southern Rocky Mountain volcanic field. Geospheres 3:42–70

Lund K, Aleinkoff JA, Evans KV, Fanning CM (2003) SHRIMP U-Pb geochronology of Neoproterozoic Windermere Supergroup, central Idaho: implications for rifting of western Laurentia and synchroneity of Sturtian glacial deposits. Geol Soc Am Bull 115:349–372

Maruyama S, Liou JG (1998) Initiation of ultrahigh-pressure metamorphism and its significance on the Proterozoic-Phanerozoic boundary. IslArc 7:6–35

Maslin MA, Li XS, Loutre M-F, Berger A (1998) The contribution of orbital forcing to the progressive intensification of Northern Hemisphere glaciation. Quaternary Sci Rev 17:411–426

Mason BG, Pyle DM, Oppenheimer C (2004) The size and frequency of the largest explosive eruptions on Earth. B Volcanol 66:735–748

McCormick MP, Thomason LW, Trepte CR (1995) Atmospheric effects of the Mt. Pinatubo eruption. Nature 373:399–404. doi:10.1038/373399a0

Meert JG (2003) A synopsis of events related to the assembly of eastern Gondwana. Tectonophysics 362:1–40

Melezhik VA, Gorokhov IM, Kuznetsov AB, Fallick AE (2001) Chemostratigraphy of Neoproterozoic carbonates: implications for 'blind dating'. Terra Nova 13:1–11

Murphy JB and Nance RD (2003) Do supercontinents turn inside-in or inside-out? Int Geol Rev 47:591–619

Nance D, Worsley TR, Moody JR (1988) The supercontinent cycle. Sci Am 259(1):72

Nance RD, Murphy RD, Strachan RA, Keppie JD, Gutiérez-Alonson G, Fernández-Suárez J, Quesada C, Linnemann U, D'Lemos R, Pisarevsky SA (in press) Neoproterozoic-early Palaeozoic tectonostratigraphy and palaeogeography of the peri-Gondwanan terranes: Amazonian versus West African connections. In: Nasser, E Liégeois, J-P (eds) The boundaries of the West African craton, Geological Society of London Special Publication

Narbonne GM (2005) The Ediacara Biota: Neoproterozoic origin of animals and their ecosystems. Annu Rev Earth Planet Sci 33:421–442

Newhall CG, Self S (1982) The volcanic explosivity index (VEI): an estimate of explosive magnitude for historical volcanism. J Geophys Res 87:1231–1238

Oppenheimer C (2002) Limited global change due to the largest known Quaternary eruption, Toba~74 kyr BP? Quaternary Sci Rev 21:1593–1609

Oppenheimer C (2003) Climatic, environmental and human consequences of the largest known historic eruption: Tambora volcano (Indonesia) 1815. Prog Phys Geog 27:230–259

Pavlov AA, Toon OB, Pavlov AK, Bally J, Pollard D (2005) Passing through a giant molecular cloud: "Snowball" glaciations produced by interstellar dust. Geophys Res Lett 32:L03705, doi:10.1029/2004GL021890

Pollock JB, Toon OB, Sagan C, Summers A, Balwin B, van Camp W (1976) Volcanic explosions and climate change: a theoretical assessment. J Geophys Res 81:1071–1083

Post JD (1977) The last great subsistence crisis in the Western World. Johns Hopkins University Press, Baltimore, MD, 240pp

Prueher LM, Rea DK (1998) Rapid onset of glacial conditions in the subarctic North Pacific at 2.67 Ma: clues to causality. Geology 26:1027–1030

Prueher LM, Rea DK (2001) Volcanic triggering of late Pliocene glaciation: evidence from the volcanic glass and ice-rafted debris to the North Pacific Ocean. Palaeogeogr Palaeoclimatol Palaeoecol 173:215–230

Rampino MR, Self S (1992) Volcanic winter and accelerated glaciation following the Toba super-eruption. Nature 359:50–52

Rampino MR, Self S, Stothers RB (1988) Volcanic winters. Annu Rev Earth Planet Sci 16:73–99

Reymer A, Schubert G (1984) Phanerozoic addition rates to the continental crust and crustal growth. Tectonics 3:63–77

Robock A (2000) Volcanic eruptions and climate. Rev Geophy 38:191–219

Robock A (2004) Climatic impact of volcanic emissions. In: Sparks RSJ, Hawkesworth CJ, The state of the planet: frontiers and challenges in geophysics, Geophysical Monograph Series, American Geophysical Union, Washington, DC 150:125–134

Rogers JJW, Unrug R, Sultan M (1995) Tectonic assembly of Gondwana. J Geodynamics 19:1–34

Sano Y, Williams SN (1996) Fluxes of mantle and subducted carbon along convergent plate boundaries. Geophys Res Lett 23:2749–2752

Schmitz B, Asaro F (1996) Iridium geochemistry of volcanic ash layers from early Eocene rifting of the northeastern North Atlantic and some other Phanerozoic events. Geol Soc Am Bull 115:349–372

Schrag DP, Berner RA, Hoffman PF, Halverson GP (2002) On the initiation of a snowball Earth. Geochem Geophy Geosyst 3(6):1036. doi:10.1029/2001GC000219

Sears JW, Price RA (2003) Tightening the Siberian connection to western Laurentia. Geol Soc Am Bull 115:943–953

Self S (2006) The effects and consequences of very large explosive volcanic eruptions. Phil Trans R Soc A 364:2073–2097

Self S, Thordarson T, Widdowson M (2005) Gas fluxes from flood basalt eruptions. Elements 1:283–287

Sigurdsson H (1990) Evidence of volcanic loading of the atmosphere and climate response. Palaeogeogr Palaeoclimatol Palaeoecol 89:277–289

Sohl LE, Christie-Blick N, Kent DV (1999) Paleomagnetic polarity reversals in Marinoan (ca. 600 Ma) glacial deposits of Australia: implications for the duration of low-latitude glaciation in Neoproterozoic time. Geol Soc Am Bull 111:1120–1139

Stern RJ (1994) Arc assembly and continental collision in the Neoproterozoic East African Orogen: implications for the consolidation of Gondwanaland. Annu Rev Earth Planet Sci 22:319–335

Stern RJ, Avigad D, Miller NR, Beyth M (2006) Geological Society of Africa Presidential Review, No. 10: evidence for the snowball Earth hypothesis in the Arabian-Nubian Shield and East African Orogen. J Afr Earth Sci 44:1–20

Stern RJ (in press) Neoproterozoic crustal growth: The solid Earth system during a critical episode of Earth history. Gondwana Research doi: 10.1016/j.gr. 2007.08.006

Tabazadeh A, Turco RP (1993) Stratospheric chlorine injection by volcanic eruptions: HCl scavenging and implications for ozone. Science 260:1082–1084

Tajika E (2003) Faint young Sun and the carbon cycle: implication for the Proterozoic global glaciations. Earth Planet Sci Lett 214:443–453

Torsvik T (2003) The Rodinia jigsaw puzzle. Science 300:1379–1381

Trompette R (2000) Gondwana evolution; its assembly at around 600 Ma. C R Acad Sci Paris, Sci de la Terre et des Planets 330:305–315

Walter MR, Veevers JJ, Calver CR, Gorjan P, Hill AC (2000) Dating the 840–544 Ma Neoproterozoic interval by isotopes of strontium, carbon and sulfur in seawater, and some interpretative models. Precambrian Res 100:371–433

Wang J, Li Z-X (2003) History of Neoproterozoic rift basins in South China: Implications for Rodinia break-up 122:141–158

White SM, Crips JA, Spera FJ (2006) Long-term volumetric eruption rates and magma budgets. Geochem Geophys Geosyst 7(3). doi:10.1029/2005GC001002

Wignall PB (2001) Large igneous provinces and mass extinctions. Earth-Sci Rev 53:1–33

Young GM (2003) Stratigraphic and tectonic settings of Proterozoic glaciogenic rocks and banded iron-formations: relevance to the snowball Earth debate. J Afr Earth Sci 35:451–466

Zielinski GA (2000) Use of paleo-records in determining variability within the volcanism-climate system. Quaternary Sci Rev 19:417–438

Zielinski GA, Mayewski PA, Meeker LD, Whitlow S, Twickler MS, Taylor K (1996) Potential atmospheric impact of the Toba mega-eruption ~71,000 years ago. Geophys Res Lett 23:837–840

Zoller WH, Parrington JR, Kotra JMP (1983) Iridium Enrichment in Airborne Particles from Kilauea Volcano: January 1983. Science 222:1118–1121