Review article

The snowball Earth hypothesis: testing the limits of global change

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ABSTRACT

The gradual discovery that late Neoproterozoic ice sheets extended to sea level near the equator poses a palaeoenvironmental conundrum. Was the Earth’s orbital obliquity > 60° (making the tropics colder than the poles) for 4.0 billion years following the lunar-forming impact, or did climate cool globally for some reason to the point at which runaway ice-albedo feedback created a ‘snowball’ Earth? The high-obliquity hypothesis does not account for major features of the Neoproterozoic glacial record such as the abrupt onsets and terminations of discrete glacial events, their close association with large (> 10⁶) negative δ¹³C shifts in seawater proxies, the deposition of strange carbonate layers (‘cap carbonates’) globally during post-glacial sea-level rise, and the return of large sedimentary iron formations, after a 1.1 billion year hiatus, exclusively during glacial events. A snowball event, on the other hand, should begin and end abruptly, particularly at lower latitudes. It should last for millions of years, because outgassing must amass an intense greenhouse in order to overcome the ice albedo. A largely ice-covered ocean should become anoxic and reduced iron should be widely transported in solution and precipitated as iron formation wherever oxygenic photosynthesis occurred, or upon deglaciation. The intense greenhouse ensures a transient post-glacial regime of enhanced carbonate and silicate weathering, which should drive a flux of alkalinity that could quantitatively account for the world-wide occurrence of cap carbonates. The resulting high rates of carbonate sedimentation, coupled with the kinetic isotope effect of transferring the CO₂ burden to the ocean, should drive down the δ¹³C of seawater, as is observed. If cap carbonates are the ‘smoke’ of a snowball Earth, what was the ‘gun’? In proposing the original Neoproterozoic snowball Earth hypothesis, Joe Kirschvink postulated that an unusual preponderance of land masses in the middle and low latitudes, consistent with palaeomagnetic evidence, set the stage for snowball events by raising the planetary albedo. Others had pointed out that silicate weathering would most likely be enhanced if many continents were in the tropics, resulting in lower atmospheric CO₂ and a colder climate. Negative δ¹³C shifts of 10–20‰ precede glaciation in many regions, giving rise to speculation that the climate was destabilized by a growing dependency on greenhouse methane, stemming ultimately from the same unusual continental distribution. Given the existing palaeomagnetic, geochemical and geological evidence for late Neoproterozoic climatic shocks without parallel in the Phanerozoic, it seems inevitable that the history of life was impacted, perhaps profoundly so.

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Introduction

In 1987, the Caltech biomagnetist and palaeomagnetist Joe Kirschvink gave undergraduate Dawn Sumner a rock sample to study for her senior thesis. The sample, collected by UCLA palaeontologist Bruce Runnegar, was a reddish, uncompacted, rhythmically laminated siltstone from the Elatina Formation, a late Neoproterozoic, glacial and periglacial unit widely exposed in the Flinders Ranges and elsewhere in South Australia (Preiss, 1987; Lemon and Gostin, 1990). The rhythmic laminations are interpreted to be lunar tidal bundles (Williams, 2000), implying a shallow marine depositional environment. Glaciogenic deposits (diamictites and ice-rafted dropstones) occur in most sections of the Elatina Formation (Lemon and Gostin, 1990), but previous palaeomagnetic studies suggested that the siltstone was deposited close to the equator on the basis of unusually stable remnant magnetization carried by detrital haematite (Embleton and Williams, 1986). Kirschvink was skeptical that glaciers would ever reach sea level in the tropics, so he instructed Sumner to perform a fold test (McElhinny and McFadden, 2000) on soft-sediment folds (Williams, 1996) in Runnegar’s sample. A positive fold test would prove that the natural remnant magnetization (NRM) is primary; a negative result would show that it is secondary, posing no constraint on the palaeolatitude of the Elatina glaciation. To Kirschvink’s surprise, the fold test was positive (Sumner et al., 1987), as others subsequently confirmed (Schmidt et al., 1991; Schmidt and Williams, 1995; Sohl et al., 1999). A stratigraphically consistent, polarity reversal test (Sohl et al., 1999; see also Schmidt and Williams, 1995) confirmed the primary component of NRM in the Elatina Formation, while the existence of multiple reversals (Sohl et al., 1999) suggests that the Elatina glacial epoch lasted for several 10⁵ to a few 10⁶ years.

The Elatina results refocused attention on Neoproterozoic glaciations. A critical review of the stratigraphic, geochronological and palaeomagnetic constraints on virtually all late Neoproterozoic glacial deposits (LNGD) world-wide was recently published (Evans, 2000). A total of 16 regional-scale units, known to have formed near sea level, possess primary or
near-primary NRM components giving at least ‘somewhat reliable’ palaeolatitudes (Evans, 2000). Many were apparently deposited within 10° of the equator, and none was laid down at a palaeolatitude greater than 60° (Fig. 1). Increased non-dipole components in the Proterozoic geomagnetic field (Kent and Smethurst, 1998; Bloxham, 2000) would not greatly affect those conclusions (Evans, 2000) (Fig. 1). The observations are surprising and they argue that the Elatina result is no fluke.

While LNGD (Fig. 2) closely resemble Phanerozoic glacial deposits lithologically, their distribution and mode of occurrence have never fitted comfortably into Phanerozoic stereotypes (Harland and Wilson, 1956; Schermerhorn and Stanton, 1963; Martin, 1965; Roberts, 1976; Preiss, 1987). Distinctive ‘cap’ dolostone (and rarely limestone) layers sharply overlie most LNGD without significant hiatus (Fig. 2), implying a sudden switch back to a warmer climate (Norin, 1937; Mawson, 1949b). Cap carbonates (Figs 3–5) have unusual sedimentological, geochemical and isotopic characteristics not found in other Neoproterozoic or Phanerozoic carbonates (Aitken, 1991; Fairchild, 1993; Grotzinger and Knoll, 1995; Kennedy, 1996; James et al., 2001), and they occur even in successions otherwise lacking carbonate (Spencer, 1971; Deynoux, 1980; Plumb, 1981; Myrow and Kaufman, 1999). Not surprisingly, they have long served as time markers in regional and even interregional correlation (Dunn et al., 1971; Kennedy et al., 1998; Walter et al., 2000).

The glacial origin of the Elatina Formation was first recognized by Sir Douglas Mawson – the older, thicker and more localized, Surtian LNGD in the same region were recognized much earlier by Howchin (1908), following the first described LNGD in northern Norway (Reusch, 1891) – and he discovered its cap dolostone (Mawson, 1949b). Although conservative by nature (Sprigg, 1990), Mawson was the first (to our knowledge) to argue that late Neoproterozoic glaciation was global, with large ice sheets in the tropics (Mawson, 1949a). He went on to suggest that climatic amelioration paved the way for the first metazoa (Mawson, 1949a), which had been discovered by a Mawson protegée, Reg Sprigg, in the Ediacara Hills west of the Flinders Ranges (Sprigg, 1947). Ironically (for an Adelaide resident), Mawson was opposed to continental drift, and his argument for tropical ice sheets depended critically on the occurrence of LNGD in tropical Africa today (Mawson, 1949a). [To his credit, Mawson urged students to read his

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**Fig. 1** Global distribution (a) of Neoproterozoic glaciogenic deposits with estimated palaeolatitudes based on palaeomagnetic data (modified from Evans, 2000). ‘Reliability’ takes into account not only palaeomagnetic reliability but also the confidence that the deposits represent regionally significant, low-elevation ice sheets (Evans, 2000). Histogram (b) of the same glaciogenic deposits according to palaeolatitude. The discontinuous steps show the expected density function of a uniform distribution over the sphere. Note the preponderance of low-latitude deposits and absence of high-latitude deposits. This finding would not be invalidated by plausible non-dipole components of the field, which would effectively raise the palaeolatitudes of only the mid-latitude results (Evans, 2000). The minimum in the distribution in the subtropics may reflect the meridional variation in precipitation minus evaporation due to the Hadley cells.

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Fig. 2 Neoproterozoic glacial features. Striated pavement (a) overlain by the Smallfjord diamictite (Table 1) at Bigganjargga, Varangerfjord, north Norway, the first recognized Neoproterozoic glacial deposit (Reusch, 1891) (G. P. Halverson photo). Faceted and multistratified stone (b) from the Jbeliat diamictite (Table 1) in Adrar, Mauritania. Rapitan diamictite (Table 1) sharply bounded (c) by carbonate strata, without transitional facies or intercalation at Stone Knife River, Mackenzie Mountains, northwest Canada. Dolomite dropstone in banded iron formation (d) within the Rapitan diamictite at Snake River, Mackenzie Mountains (G. A. Gross photo). Ice-rafted dropstone (e) of shelf-edge oolitic limestone in allodapic slope-facies carbonates of the Ghaub diamictite (Table 1) at east Fransfontein, north-west Namibia. Impact of dropstone on sea-bed caused the folded bicouple seen at 10 o’clock from coin. Typical abrupt conformable contact (f) between the upper dropstone unit of the Ghaub diamictite and its cap dolostone in slope facies at west Fransfontein, north-west Namibia. The coin, pen and hammer are 2, 15 and 33 cm in maximum dimension, respectively (same in Figs 4 and 5).
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• Mixed carbonate-dominated
textures (e.g. crystal-fan cementstones) occur above the cap dolostone in mixed (b) dolostones as the sole representatives of the post-glacial transient. However, unusual 

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distinction between ‘cap dolostone’ and ‘cap-carbonate sequence’. Workers from different times (Crawford and Daily, 1996; Kennedy et al., 2001b) regard cap dolostones as the sole representatives of the post-glacial transient. However, unusual textures (e.g. crystal-fan cementstones) occur above the cap dolostone in mixed (b) and carbonate-dominated (c) regions, and the post-glacial negative $\delta^{13}C$ anomaly may encompass the entire cap-carbonate sequence (Fig. 9). The top of the cap dolostone does not mark the end of enhanced silicate weathering (Kennedy et al., 2001b), but may reflect a change from carbonate-dominated to silicate-dominated weathering as carbonate platforms are inundated by rising sea level (Hoffman and Schrag, 2000). Base truncation (d,e) may occur if the local water mass fails to reach saturation until after post-glacial sea-level rise. Top truncation (f) occurs in regions with little background tectonic subsidence to create permanent accommodation space. Abbreviations: HST, highstand systems tract; MF, marine flooding surface; SB, sequence boundary; TST, transgressive sequence tract (van Wagener et al., 1988).

contemporary’s book (Wegener, 1922) and Sprigg, for one, identified the Adelaidean succession as a pre-Mesozoic rifted continental margin (Sprigg, 1952).] Mawson’s argument, however, collapsed in the plate tectonic revolution, with most subsequent workers attributing the extent of LNGD (Fig. 1) to rapid drift of different continents through polar regions at different times (Crawford and Daily, 1971; McElhinny et al., 1974; Crowell, 1983, 1999; Eyles, 1993).

Most, but not all. Brian Harland of Cambridge University cut his teeth in the Arctic archipelago of Svalbard, sentinel of the Barents Sea shelf, and host to a pair of LNGD (Harland et al., 1993; Harland, 1997). Harland was no fixist, but he independently reiterated Mawson’s arguments (Harland and Rudwick, 1964; Harland, 1964) and reinforced them with palaeomagnetic measurements. Low-inclination NRM in LNGD and associated strata in the North Atlantic region and elsewhere seemed initially to prove that ice sheets had indeed extended to low palaeoaltitudes (Harland and Bidgood, 1959; Bidgood and Harland, 1961; Chumakov and Elston, 1989). Later, however, with the recognition of widespread, low-temperature remagnetization (McCabe and Elmore, 1989), field tests and demagnetization procedures that constrain the age and subsequent history of magnetization became the gold-standard for acceptance of palaeomagnetic data (McElhinny and McFadden, 2000). The Elatina Formation was the first LNGD for which there were multiple field, rock-magnetic, and petrographic tests indicative of a primary, low-inclination NRM, contemporaneous with sedimentation (Embleton and Williams, 1986; Summer et al., 1987; Schmidt et al., 1991; Schmidt and Williams, 1995; Sohl et al., 1999).

Alternative theories for low-latitude glaciation

Kirschvink was not the first to wrestle with the low-latitude Elatina results. George Williams (1975, 1993, 2000) had long advocated a large (> 54°) orbital obliquity, or tilt (the angle between the Earth’s axes of rotation and orbit around the sun), to account for low-latitude glaciation in conjunction with inferred strong equatorial seasonality during the Elatina glaciation (Williams and Tonkin, 1985; Williams, 1998). In theory, obliquity could have varied chaotically within 60–90° following the early lunar-forming impact event, but a low obliquity, once achieved, is self-stabilizing through the gravitational interaction of the Moon and the Earth’s equatorial bulge (Laskar et al., 1993). Williams (1993) postulates a sharp decrease in orbital obliquity after 600 Ma, with resultant moderation of the seasonal climate cycle giving rise to the metazoa (Williams, 1993). With an obliquity > 54°, mean annual temperatures are lower around the equator than at the poles (Williams, 1975; Hunt, 1982; Oglesby and Ogg, 1999; Jenkins, 2000), making glaciation more probable at lower
latitudes (Williams, 1975). Summer insolation is so large in the polar regions (the sun staying high in the sky throughout the diurnal cycle) that surface temperatures over land areas might exceed the boiling point of water (Oglesby and Ogg, 1999). The tropics, although cooler overall, would have two hot seasons near...
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- Ombaatjie Fm
- Gruis Fm
- Rasthof Fm
- rotated basement block

- Maieberg Fm
- aeolianite
- cementstone
- conglomerate

- cap carbonate begins
- glacial sea-level fall
- pre-glacial $\delta^{13}$C drop

- platform carbonate
- tube bioherms

- Keilberg mb
- reefs
- inter-reef fill

- 100 m

- Rasthof Fm
(truncated beneath Gruis Fm)
Fig. 5 Distinctive lithofacies in the cap-carbonate sequence (Maieberg Formation) following the Ghaub glaciation (Table 1) of the Otavi platform, northwest Namibia, and possible correlatives. Section (a) near the platform margin at Tweelingskop, showing preglacial drop in δ13C, aeolian dolostone representing the glacial event, layered dolostone (Keilberg member) composed of stromatolites with tubular-like structure, and reef-like bed of sea-floor aragonite cements pseudomorphosed by calcite (Soffer, 1998). Tube-like structures (b) in hummocky cross-stratified dolostone at Khowarib Schlucht. Tubes initiated within the cap dolostone and do not tap subglacial deposits as expected if they formed by methane released from glacial permafrost as proposed by Kennedy et al. (2001a). Detail of tube-like structures (c) at Khowarib Schlucht showing meniscus-laminated micrite (tubes) filling circular pits within a honeycomb of stromatolites (arced laminae). Despite vertical continuity of tube-like structures (b), synchronous relief during growth was < 3 cm. Sheaves of former-aragonite crystal fans (d) in algal diatomite at Tweelingskop. Interlayered micrite (light) and aragonite (dark) cements (e) pseudomorphosed to calcite in the Sete Lagoas cap carbonate, Bambui platform, south-eastern Brazil. Barite crust (f) and reworked barite (Fig. 4c, d). Barite crust (f) and reworked stones (Fig. 4c, d).

Richard Sheldon (1984) postulated that orbiting ice rings episodically collapsed into the atmosphere, transiently shielding sunlight and giving rise to glaciers at low latitudes. The theory strives to explain iron formations and cap carbonates, but does not adequately account for low-latitude glaciation. Due to orbital obliquity, equatorial ice rings will cast shadows only on the winter hemisphere (see figure 2 in Sheldon, 1984). Glaciation depends critically on cool summers, not cold winters (Köppen and Wegener, 1924), as it is contingent on a fraction of the annual snowfall surviving the melting seasons.

**Snowball Earth**

Kirschvink responded to the positive Elatina fold test with a theory he first aired in 1989 (Maugh, 1989). It eventually appeared as an article, seven paragraphs long, embedded in a 1348-page book (Kirschvink, 1992). It postulated that conditions amenable to global glaciation were set up by an unusual preponderance of land masses within middle to low latitudes, a situation that has not been encountered at any subsequent time in Earth history. One effect of such a palaeo-geography would be a substantially higher albedo in the subtropics, where clouds are least important (Kirschvink, 1992). Any resultant glaciation would further increase the Earth’s albedo by lowering sea level, exposing continental shelves and inland seas (Kirschvink, 1992). Placing more continents in the tropics would also increase the silicate weathering rate (provided tectonic uplift was not mysteriously absent there), leading to a colder planet with lower atmospheric pCO2 (Marshall et al., 1988; Worsley and Kidder, 1991). In addition, the meridional heat transport by the Hadley cells would be weakened because tropical air masses would be drier on average with greater continentality. Oceanic heat transport might also be lessened, but this is less certain. These combined effects might lead to the growth of large ice caps, nucleated on islands or continents bordering the polar seas.

Ice caps create a positive feedback on climate change through ice-albedo feedback (Croll, 1867; Budyko, 1966; Manabe and Broccoli, 1985). Early energy-balance climate models revealed a fundamental instability in the climate system caused by this positive feedback (Eriksson, 1968; Budyko, 1969; Sellers, 1969; North et al., 1981), an effect reproduced in a number of GCMs (Wetherald and Manabe, 1975; Jenkins and Smith, 1999; Hyde et al., 2000; Pollard and Kasting, 2001). If more than about half the Earth’s surface area were to become ice covered, the albedo feedback would be unstoppable (Fig. 6). Surface temperatures would plummet (Fig. 7), and pack ice would quickly envelop the tropical oceans (Hyde et al., 2000; Baum and Crowley, 2001). With reduced Neoprerozoic solar forcing, the ice-albedo instability occurs in the GENESIS v2 GCM between 1.0 and 2.5 times modern pCO2 with different palaeogeographies (Baum and Crowley, 2001; Pollard and Kasting, 2001). The time scale of the sea-ice advance is uncertain – the ocean’s thermal inertia resists the ice advance initially (Poulsen et al., 2001), but the ocean is a finite heat reservoir and cooling over thousands
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...disappearance of Arctic sea ice) due to anthropogenic global warming. cap instability, which predicts a possible switch to the ice-free branch (e.g. ice-covered branch at point 7. In the 1960s, Budyko was concerned with the small ice-line latitudes at sea level) as a function of the effective solar flux (Fig. 6).

Effect of a 30% reduction in meridional heat transport is shown, as is the estimated solar flux at ~ 600 Ma. Of three possible stable points for \( E_s = 1.0 \), the Earth actually lies on the partially ice-covered branch at point 1. An instability due to ice-albedo feedback drives any ice-line latitude < 30° onto the ice-covered branch. A \( pCO_2 = 0.12 \) bar is required for deglaciation of an ice-covered Earth, assuming the planetary albedo is 0.6 and \( E_s = 1.0 \) (Caldeira and Kasting, 1992). The snowball Earth hypothesis is qualitatively predicated on these findings and infers a hysteresis in \( pCO_2 \) and consequently surface temperature following the circuit labelled 1–7.

Starting from point 1, lowering of \( pCO_2 \) causes ice lines to migrate stably to point 2, whereupon runaway ice-albedo feedback drives ice lines to the ice-covered branch at point 3. Normal volcanic outgassing over millions of years increases \( pCO_2 \) to point 4, initiating deglaciation. Reverse ice-albedo feedback then drives ice lines rapidly to the ice-free branch at point 5, where high \( pCO_2 \) combined with low planetary albedo creates a transient ultra-greenhouse. Enhanced silicate weathering causes lowering of \( pCO_2 \) to point 6, whereupon polar ice caps reform and ice lines return to the partially ice-covered branch at point 7. In the 1960s, Budyko was concerned with the small ice-cap instability, which predicts a possible switch to the ice-free branch (e.g. disappearance of Arctic sea ice) due to anthropogenic global warming.

Climate physicists originally assumed that no ice-albedo catastrophe ever actually occurred because it would be permanent; the high planetary albedo would be irreversible. A saviour exists, however, and Kirschvink (1992) identified it as the buildup of an intense atmospheric \( CO_2 \) greenhouse through the action of plate tectonics in driving the long-term carbon cycle (Walker et al., 1981; Caldeira and Kasting, 1992; Kirschvink, 1992). On a snowball Earth, volcanoes would continue to pump \( CO_2 \) into the atmosphere (and ocean), but the sinks for \( CO_2 \) – silicate weathering and photosynthesis – would be largely eliminated (Kirschvink, 1992). Even if \( CO_2 \) ice precipitated at the poles in winter, it would likely sublime away again in summer (Walker, 2001). \( CO_2 \) levels would inexorably rise and surface temperatures would follow, most rapidly at first and more slowly later on (Fig. 7) due to the nonlinear relation between \( CO_2 \) concentration and the resultant greenhouse forcing (Caldeira and Kasting, 1992). With rising surface temperatures, sea ice thins but ground ice sheets expand in some areas due to a stronger hydrological cycle. If \( CO_2 \) outgassing rates were broadly similar to today (a reasonable assumption for 600–700 Ma), then the time needed to build up the estimated 0.12 bar \( CO_2 \) required to begin permanent melting at the equator, assuming a planetary albedo of 0.6, would be a few million years (Caldeira and Kasting, 1992; Crowley et al., 2001). This estimate (Fig. 7), while subject to large uncer-
tainties, is of the same order as the estimated time-scale of LNGD from palaeomagnetic (Sohl et al., 1999) and stratigraphic (Hoffman et al., 1998a) evidence. Once the tropical ocean begins to open up perennially, deglaciation proceeds rapidly due to reverse ice-albedo feedback (Caldeira and Kasting, 1992; Crowley et al., 2001).

**Fig. 7** Estimated changes in global mean surface temperature, based on energy-balance calculations, and ice extent through one complete snowball event. The suggested time scale of the event of ~ 5 Myr is conservative for an albedo = 0.6, based on the estimated outgassing flux of CO₂ and subsidence analysis (Hoffman et al., 1998b). The global palaeogeographical model (Powell et al., 2001) pertains to 750 Ma, ~ 30 Myr before the ‘Sturtian’ glaciation (Table 1). Palaeocontinents: Am, Amazonia; Au, Australia; Ba, Baltica; Co, Congo; In, India; K, Kalahari; M, Mawson; Si, Siberia; Ta, Tarim; WA, West Africa; Y, South China (Yangtze). The global ice-line depictions correspond approximately to points 1–7 in Fig. 2. Note the growth of terrestrial ice sheets with rising surface temperature during the snowball event. Note also the abrupt onset and termination of glacial conditions in the low and middle latitudes, consistent with geological observations, and the saw-tooth form of the temperature curve reversed to that associated with late Quaternary glacial cycles. Note finally that the estimated surface temperatures are global mean values and give no sense of the real zonal, seasonal and diurnal ranges in temperature (Walker, 2001).
The fall in planetary albedo occurs far faster than the excess atmospheric CO\textsubscript{2} can be consumed by silicate weathering, with the result that a transient heat wave must follow the ice retreat (Caldeira and Kasting, 1992; Kirschvink, 1992). Kirschvink (1992) concluded that a cold planet with many tropical continents and large polar sea-ice caps 'would be a rather unstable situation, with the potential for fluctuating rapidly between the 'ice house' and "green-house" states'.

**Testing the snowball hypothesis**

Kirschvink (1992) highlighted three implications of his theory which 'might lend themselves to geological tests'. First, 'glacial units should be more or less synchronous Harland, 1964).'. Second, 'strata from widely separate areas which preserve a record of these [rapid] climatic fluctuations [between "ice house" and "green-house" states] might bear an overall similarity in lithologic character, which would be a result of the global scale of the climatic fluctuations'. Third, 'the presence of floating pack ice should reduce evaporation, act to decouple oceanic currents from wind patterns and, by inhibiting oceanic to atmospheric exchange of O\textsubscript{2}, would enable the oceanic bottom waters to stagnate and become anoxic. Over time, ferrous iron generated at the mid-oceanic ridges or leached from the bottom sediments would build up in solution and, when circulation became reestablished toward the end of the glacial period, the iron would oxidize to form a "last-gasp" blanket of banded iron formation in upwelling areas.' Here is how these tests turned out.

**Test 1: carbon isotopes**

Direct radiometric testing of predicted glacial synchrony has not proved possible (Table 1) because of an apparent dearth of suitable material for dating (Evans, 2000). Low diversity and turnover rates of microfloral and protistan remains pose severe limits on biostratigraphic resolution until after the major Neoproterozoic glacial events (Knoll, 2000). Regardless, a sea change in favour of synchronous glaciation occurred in the 1990s, and carbon isotope stratigraphy was principally responsible.

The history of carbon isotopic variation (expressed as \( \delta^{13}C \)) the difference in per mil of \( ^{12}C/^{13}C \) with respect to standard VPDB) in marine carbonates and covarying organic matter is a robust, but ambiguous, record of biogeochemical cycling (Summons & Hayes, 1992). Despite the fact that significant spatial heterogeneity in \( \delta^{13}C \) is dynamically maintained within the ocean (Kroopnick, 1985), large secular changes in \( \delta^{13}C \) at individual sites are globally correlated (Veizer et al., 1999; Saltzman et al., 2000), reflecting the residence time of carbon ~150 times the ocean mixing time (Kump and Arthur, 1999). The \( \delta^{13}C \) of carbonate rocks is relatively immune from large diagenetic changes because pore fluids are effectively buffered by the large rock carbon reservoir (Veizer et al., 1999).

The range of secular \( \delta^{13}C \) variability of > 10‰ in the Neoproterozoic (Jacobsen and Kaufman, 1999; Walter et al., 2000) is markedly greater than for the Phanerozoic (Veizer et al., 1999) or the 1.5 billion years before the late Neoproterozoic (Brazier and Lindsay, 1998; Kah et al., 2001). The largest Neoproterozoic \( \delta^{13}C \) anomalies consistently bracket LNGD (Figs 8 and 9), with enriched values (\( \delta^{13}C_{\text{carb}} > 5\%_{\text{o}} \)) observed prior to glaciation and depleted values (\( \delta^{13}C_{\text{carb}} < 0\%_{\text{o}} \)) afterwards. A steep decline in \( \delta^{13}C \) values of 10–15‰ precedes any physical evidence of glaciation or sea-level fall in many areas (Narbonne and Aitken, 1995; Hoffman et al., 1998b; Brasier and Shields, 2000; McKirdy et al., 2001; Xiao et al., 2001; Halverson et al., 2002). Cap carbonates are universally depleted, in some cases approaching mantle values of ~6 ± 1‰ (Knoll and Walter, 1992; Kaufman and Knoll, 1995; Kennedy, 1996; Kaufman et al., 1997; Hoffman et al., 1998b; Prave, 1999a; Brasier and Shields, 2000; Walter et al., 2000; James et al., 2001). Although interpretations of these remarkable trans-glacial isotopic shifts differ widely (see below), there is consensus that they are supra-regional in nature. Even those opposed to the snowball hypothesis (Kennedy et al., 1998, 2001a;b; Prave, 1999a;b; Condon and Prave, 2000) agree on the synchrony of glacial events in widely separate areas (Africa, Australia, Canada, Europe) and base global correlation schemes upon them.

The conventional explanation for Neoproterozoic carbon isotopic oscillations and cap carbonates is oceanographic (Knoll et al., 1986, 1996; Kaufman et al., 1991, 1997; Derry et al., 1992; Grozinger and Knoll, 1995; Grozinger and James, 2000). The idea is roughly the following. The ocean was physically stratified for long periods pending glaciation, but switched to a turnover mode during and particularly after glacial events. In stratified mode, the biological pump (descent of organic particles from the surface) drove the \( \delta^{13}C \) of dissolved inorganic carbon (DIC) in the surface waters to higher values. Partial remineralization of the organic ‘rain’ in conjunction with bacterial sulphate reduction in the water column produced deep water laden with \( ^{13}C \)-depleted DIC. With prolonged stratification, the contrast in \( \delta^{13}C \) values between the surface and deep water DIC reservoirs (2–3‰, in the present ocean, Kroopnick, 1985) increased to > 10‰ consistent with the preglacial high \( \delta^{13}C \) values (Fig. 8). When overturn began, anoxic, alkalinity-laden, deep water upwelled to the surface, releasing \( CO_2 \) and precipitating cap carbonates with low \( \delta^{13}C \) values. Like the snowball hypothesis, the ocean ‘turnover’ model (Grozinger and Knoll, 1995; Knoll et al., 1996) seeks to explain many of the salient observations, but the basic premise is faulty. First, it is physically difficult if not impossible to shut down the overturning circulation for periods > 1.5 ky (Zhang et al., 2001). Second, organic productivity would crash if the nutrient-rich upwelling flux were removed (Hotinski et al., 2001). Consequently, stratification would not raise the \( \delta^{13}C \) in surface waters to 5–10‰, as is observed. Third, cap carbonates formed during post-glacial sea-level rise (see below), when the injection of glacial meltwater would suppressed not enhance, ocean overturn. Kennedy (1996) attributes cap carbonates and their low \( \delta^{13}C \) values simply to post-glacial sea-level rise, but his model also depends on an 8–10‰, difference in \( \delta^{13}C \) across the thermocline, compared with ~ 2.5‰ for Mesozoic–Cenozoic oceans.
In 1998, we invoked the snowball hypothesis, then in eclipse, as a possible explanation for the $\delta^{13}C$ profiles (Figs 8 and 9) of carbonates bounding glacial horizons in northern Namibia (Table 1). Hoffman et al. (1998b) gave three, mutually compatible explanations for the $\delta^{13}C$ enrichment observed in cap carbonates. First, organic productivity on snowball Earth would be greatly reduced for $10^{6}$–$10^{7}$ years, which should cause $\delta^{13}C$ values to shift towards the hydrothermal CO$_2$ input ($\delta^{13}C$ of $6\pm1\%$ VPDB, Des Marais and Moore, 1984) at mid-ocean ridges (Kump, 1991). Second, if carbonate sedimentation rates globally were very high, due to the alkalinity flux from weathering in the greenhouse transient, the organic fraction of the burial flux would be negatively effected. Consequently, carbonate would have low $\delta^{13}C$ values even if organic productivity had fully recovered from the snowball event (Hoffman and Schrag, 1999). Third, the transfer of atmospheric CO$_2$ to bicarbonate (via the weathering cycle) involves an $\approx 8\%$ isotopic fractionation favouring $^{13}C$. In transferring $>98\%$ of the built-up atmospheric CO$_2$ to the ocean and ultimately the sedimentary reservoir, the kinetic isotope effect (Rayleigh distillation) will drive the atmospheric CO$_2$ reservoir to ever lower $\delta^{13}C$ values (Hoffman et al., 1998b). To the degree that atmospheric CO$_2$ remains a major source of DIC, this would be reflected by cap-carbonate $\delta^{13}C$ values that decline with time (Fig. 8). However, the nadir in $\delta^{13}C$ (Fig. 9) does not necessarily correspond to the completion of atmospheric CO$_2$ drawdown, as Kennedy et al. (2001b) argue, but reflects the net effect of many factors, including those already mentioned, as well as methane hydrate destabilization during deglaciation (Kaufman et al., 1997; Kennedy et al., 2001a; but see Hoffman et al., 2002a) and dolomite–calcite isotopic equilibrium.

The swing to negative $\delta^{13}C$ values observed beneath the glacial deposits in many regions (Figs 8 and 9) must originate differently (Kennedy et al., 2001b; Halverson et al., 2002; Schrag et al., 2002) as they are separated in time from the cap-carbonate anomalies by the glacial periods which were of long duration (Hoffman et al.,

Table 1  Radionmetric age constraints on Neoproterozoic glacial events

<table>
<thead>
<tr>
<th>Region/Succession</th>
<th>Palaeo-continent</th>
<th>Age (Ma) Glaciation</th>
<th>Age (Ma) Glaciation</th>
<th>Age (Ma) Glaciation</th>
<th>Age (Ma) Glaciation</th>
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<tbody>
<tr>
<td>Norway (Verstertana)</td>
<td>Baltica</td>
<td>560</td>
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<tr>
<td>Svalbard (Hecla Hoek)</td>
<td>Laurentia</td>
<td>630</td>
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<tr>
<td>Scotland (Dalradian)</td>
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<td>601 ± 4</td>
<td></td>
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<tr>
<td>Appalachians (Blue Ridge)</td>
<td>Laurentia</td>
<td>570</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>New England, USA (Boston)</td>
<td>Avalon</td>
<td>590 ± 2</td>
<td></td>
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<tr>
<td>Conception (Newfoundland)</td>
<td>Avalon</td>
<td>604 ± 4.3</td>
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<tr>
<td>Mauritania (Jbeli)</td>
<td>West Africa</td>
<td>590</td>
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<tr>
<td>Oman (Huqf)</td>
<td>Arabia</td>
<td>623</td>
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<tr>
<td>China (Quruqtagh)</td>
<td>Tarim</td>
<td>777 ± 7</td>
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<tr>
<td>South China (Sinian)</td>
<td>South China</td>
<td>772 ± 5</td>
<td></td>
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<tr>
<td>Australia</td>
<td>Australia</td>
<td>714</td>
<td>6</td>
<td>741 ± 6</td>
<td></td>
</tr>
<tr>
<td>Australia (Adelaide)</td>
<td>Australia</td>
<td>778</td>
<td>± 5</td>
<td>746 ± 2</td>
<td></td>
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<tr>
<td>Canada (Windermere)</td>
<td>Laurentia</td>
<td>755</td>
<td>± 18</td>
<td>742 ± 2</td>
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<td>Canada (Rainier)</td>
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<td>± 2</td>
<td>746 ± 2</td>
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</tbody>
</table>


Conodonts by column is rather arbitrary due to limited age constraints. Glacials in bold type are discussed in the text.

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We will discuss the preglacial anomalies, both positive and negative (Fig. 8), and the larger problem of how snowball events originate, in the penultimate section of the paper.

Test 2: cap carbonates

Most LNGD are capped by continuous layers (Figs 3–5) of pure dolostone (and locally limestone), metres to tens of metres thick (Spencer and Spencer, 1972; Williams, 1979; Deynoux, 1980; Fairchild and Hambrey, 1984; Miller, 1985; Preiss, 1987; Aitken, 1991; Fairchild, 1993; Brookfield, 1994; Grotzinger and Knoll, 1995; Kennedy, 1996; Hoffman et al., 1998a; Sohl et al., 1999).

Fig. 8 Representative $\delta^{13}C$ profiles for carbonates bounding the older and younger Neoproterozoic glacials (Table 1) in the northern Canadian Cordillera (left), the Otavi platform in Namibia (centre), and the Adelaide succession in South Australia (right). Note high values ($> 5\%$) before glaciation and low values ($< 0\%$) afterwards, and the drop in values that leads the younger glaciation. Correlation follows Kennedy et al. (1998). Sources of data are (a) James et al. (2001) Redstone section, (b) unpublished Khwarib Schlucht section, (c) unpublished Parachilna Gorge section, (d) unpublished Stone Knife River section, (e) Hoffman et al. (1998b) and unpublished Keiserfontein section, (f) McKirdy et al. (2001), (g) unpublished Stone Knife River section, (h) unpublished Ombonde River section, (i) McKirdy et al. (2001), (j) unpublished Omurirapo section. Note non-uniform thickness scales in panels d–f.
Corkeron and George, 2001; James et al., 2001). Their basal contacts are characteristically abrupt (Figs 2c, 2f, 4a and 5a), with little evidence of reworking or significant hiatus (Norin, 1937; Williams, 1979; Eisbacher, 1981; Deynoux, 1982; Preiss, 1987; Hoffman et al., 1998a; Brasier et al., 2000). Cap dolostones are transgressive and they typically extend far beyond the confines of their antecedent glacial deposits, blanketing preglacial rocks disconformably (Wright et al., 1978; Preiss, 1987; Aitken, 1991; Hegenberger, 1993; Hoffmann and Prave, 1996). They range from thin, allodapic, deep-water deposits (Kennedy, 1996), through agitated shelfal facies (James et al., 2001), near-shore grainstones and stromatolites (Spencer and Spencer, 1972; Corkeron and George, 2001), to supratidal tepee beccias (Fig. 5g; Deynoux and Trompette, 1976).

‘Cap-carbonate sequences’ (see below and Fig. 3) share a distinct set of unusual sedimentary structures (Cloud et al., 1974; Peryt et al., 1990; Aitken, 1991; Fairchild, 1993; Grotzinger and Knoll, 1995; Kennedy, 1996; Hoffman et al., 1998a; James et al., 2001), and they are consistently depleted in $^{13}$C relative to other Neoproterozoic carbonates (Knoll and Walter, 1992; Kaufman and Knoll, 1995; Kaufman et al., 1997; Hoffman et al., 1998a; Corkeron and George, 2001; James et al., 2001).
et al., 1998b; Kennedy et al., 1998; Myrow and Kaufman, 1999; Brasier and Shields, 2000; Walter et al., 2000). They share certain features with Archean and some pre-Neoprotobiotic carbonates (Grotzinger and Knoll, 1995; Grotzinger and James, 2000; Sumner, in press), but they are without parallel in the Phanerozoic. They have long been considered paradoxical because they suggest that an abrupt transformation from glacial to tropical conditions took place virtually everywhere (Spencer, 1971; Schermerhorn, 1974; Williams, 1979; Fairchild, 1993). Kirschvink (1992) did not foresee cap carbonates as consequential to snowball events – he was unaware of their existence (personal communication, 1999) – but they are a striking affirmation of the second testable implication (see above) of his theory. In cap carbonates, we see the ‘smoke’, if not the ‘gun’, of the snowball Earth.

‘Cap dolostones’ (Fig. 3) are the transgressive systems tracts (Van Wagoner et al., 1988) of depositional sequences (‘cap-carbonate sequences’) associated with post-glacial sea-level rise. They typically grade across a marine flooding surface (Fig. 3) into deeper water limestone or shale, which gradually shoals upward through carbonate or siliciclastic lutites and arenites to an exposure surface 100s of metres above the base of the sequence (Figs 4a and 9). The great thickness and deep-water aspect of many cap-carbonate sequences (von der Borch et al., 1988; Narbonne and Aitken, 1995; Dalrymple and Narbonne, 1996; Hoffman et al., 1998b) is anomalous within their overall stratigraphic context (Fig. 9). This is commonly ascribed to post-glacial sea-level rise, but long-term tectonic subsidence is required to preserve the sequence from isostatically driven erosion, because the glacio-eustatic cycle alone creates no permanent accommodation space. On the Otavi carbonate platform in northern Namibia, an estimated background tectonic subsidence rate equivalent to ~ 0.065 mm yr⁻¹ of isostatically adjusted carbonate (Halverson et al., 2002) implies a timescale on the order of 5 million years to create the accommodation space occupied by the younger cap carbonate sequence (Fig. 9), which is 300–400 m thick. Hoffman et al. (1998a) suggested that that the snowball event occupied the vast majority of this time, when the average sedimentation rate on the platform was very low. By the end of the event, substantial net subsidence had occurred, although masked at that time by relative sea-level fall. Upon deglaciation, sea level rose and chemical and/or detrital sediments rapidly filled in the accommodation space provided, making up for ‘lost time’, so to speak. High sedimentation rates in cap dolostones and overlying limestones are consistent with their low δ¹³C values (see above) and with their petrological characteristics (see below).

Petrologists, being fascinated by the unusual, have had a field day with cap carbonates (Peryt et al., 1990; Aitken, 1991; Fairchild, 1993; Grotzinger and Knoll, 1995; Kennedy, 1996; Hoffman et al., 1998b; James et al., 2001; Kennedy et al., 2001a; Corsetti and Kaufman in press; Sumner, in press). The Elatina, Ghaub, Ice Brook, Landrigan and Numees glacial deposits (Table 1) are directly overlain by pale, flinty, very pure, cap dolostones (Fig. 3), generally 3–30 m thick (Aitken, 1991; Kennedy, 1996; James et al., 2001). They are invariably well laminated and, at proper palaeodepths, hummocky cross-laminated with laminae defined by sets of reverse-graded peloids (Fig. 4b) (Aitken, 1991; Kennedy, 1996; James et al., 2001). Structures referred to as ‘tepees’ (Fig. 4c) occur in all the above but they have neither the geometry nor associations of conventional supratidal tepees (Kendall and Warren, 1987). In plan, they are linear and parallel, orientated subparallel to the regional palaeoslope (Williams, 1979; Eibach, 1981; Aitken, 1991; Kennedy, 1996; James et al., 2001), not polygonal like conventional tepees (Fig. 5g), which result from lateral expansion due to the force of crystallization (Kendall and Warren, 1987). Inspection of their cuspatate axial zones (Fig. 4d) reveals that they formed by continuous aggradation in a highly oscillatory flow regime. Microbial bioherms (Fig. 5a–c) and biostrates (stromatolites) occur within some cap dolostones (Spencer and Spencer, 1972; Cloud et al., 1974; Wright et al., 1978; Walter and Baud, 1983; Bertrand-Sarfati et al., 1997; Hoffman et al., 1998a; Corkeron and George, 2001; James et al., 2001). In Namibia and the North American Cordillera, stromatolites in cap dolostones of the Ghaub, Numees (and correlative Bilddah), Wildrose, and Ice Brook glaciations (Table 1) are distinguished by internal, vertically orientated, tube-like or sheet-like pockets of infilled micritic sediment and cement (Cloud et al., 1974; Hegenberger, 1988; 1993; Hoffman et al., 1998a, 2002a). The tube-like variety (Fig. 5b) has been attributed to gas escape (Cloud et al., 1974; Hegenberger, 1987; Kennedy et al., 2001a), but close inspection of well-preserved examples (Fig. 5c) reveals a stromatolitic (microbial) origin (Hoffman et al., 1998a, 2002a; James et al., 2001). The micritic sediment gathered in shallow pits or gutters on the stromatolitic surface, which aggraded with remarkably little change in morphology (Fig. 5b). As a result, the sediment-filled pits and gutters became vertical tubes and sheets, respectively. The pitted stromatolitic surfaces must have resembled giant golf balls (so designed to reduce drag). Cap dolostones have much more to reveal (Hoffman et al., 2002b), but the whole ensemble of structures suggests rapid aggradation on storm-dominated ramps.

Locally, cap dolostones are overlain by limestone buildups composed largely of sea-floor cements (Peryt et al., 1990; Aitken, 1991; Grotzinger and Knoll, 1995; Kennedy, 1996; Soffer, 1998; James et al., 2001). The cements consist of upward-fanning, prismatic crystals pseudomorphosed by calcite (Figs 4f and 5e). The square-tipped, pseudo-hexagonal habit of the crystals indicates that the primary phase was aragonite. Although individual crystal fans are small (~ 1 cm), they aggregate into reef-like masses (pseudostromatolites) that range from metres to decimetres in scale (Fig. 5a,d). The cements did not precipitate slowly in the absence of particulate sediment, but grew rapidly in a race against micritic burial (Figs 4f and 5e). The cementstone buildups are up to 50 m thick, but eventually they give way to flaggy, alodapic, pink limestone with large-scale hummocky cross-bedding (Maieberg Formation, Namibia), or to black, organic-rich shale (Sheepbed Formation, Canada). The cements imply a high degree of carbonate...
oversaturation (Grotzinger and Knoll, 1995; Sumner, in press) and the denritic-prismatic growth habit suggests rapid, diffusion-limited, growth rates (Lasaga, 1998). The presence of dissolved Fe(II) may have inhibited carbonate nucleation in anoxic waters below the mixed layer, thereby promoting the growth of crystal fans on the sea floor (Sumner and Grotzinger, 1996) while the micritic component nucleated in oxic surface waters. Deep-water anoxia is inevitable if the ocean was ice-covered for long periods (see below) and is consistent with dolomitization of cap dolostones on the sea floor (Baker and Kastner, 1981) and with the co-occurrence of sea-floor barite precipitates (Fig. 4e). The localization of these cementstone buildups at ancient shelf breaks (Soffer, 1998; James et al., 2001) suggests that their occurrence may be dictated by upwellings.

Differences among cap-carbonate sequences have elicited debate as to temporal vs. spatial control (Kennedy et al., 1998; Brasier and Shields, 2000). Some examples (Fig. 3d,e) lack transgressive systems tracts and their isotopic profiles also appear base truncated – the descending phase of the $^{813}$C anomaly is missing (Hoffman et al., 2001). This could result from undersaturation of the local water mass until after the post-glacial sea-level rise was complete, bearing in mind the large alkalinity input required to maintain saturation if atmospheric $p$CO$_2$ rose to high levels (Fig. 10) during the hypothesized snowball event. Base truncation appears more typical of ‘Sturtian’ (Table 1) cap-carbonate sequences (Kennedy et al., 1998), and could mean that the glacial ocean was less well buffered by carbonate dissolution and/or that less carbonate was available for weathering during deglaciation (see below). While actively subsiding areas (Kimberley, Adelaide, Cordillera, Otavi) have thick (200–1200 m) post-glacial sequences (Plumb, 1981; von der Borch et al., 1988; Christie-Blick et al., 1995; Narbonne and Aitken, 1995; Hoffman et al., 1998a), the Jbélait cap-carbonate sequence in the cratonic Taoudeni basin (Deynoux and Trompette, 1976) is highly condensed (Figs 3 and 11). After isostatic adjustments, minimal accommodation space remained after post-glacial sea-level rise because the background tectonic subsidence rate was very low. The cap carbonate built rapidly to sea level, resulting in the formation of spectacular supratidal tepee structures (Fig. 5g) and associated, early diagenetic (phreatic), barite crusts (Fig. 5f). We speculate the latter may have formed in a meteoric-marine groundwater mixing zone beneath a surface exposed to the hypothesized transient greenhouse atmosphere. Where the sequence expands to fill palaeovalleys (Fig. 11), the transgressive nature of the basal cap dolostone which drapes the palaeotopography is apparent. The Jbélait example is also interesting inasmuch as the glacial deposits (continental tillites and outwash) preceded the hypothesized snowball event, which is apparently represented by a regolith horizon (Fig. 11) with well-developed polygonal sand wedges (Deynoux, 1982, 1985). This horizon separates the glacial deposits from the cap dolostone, and marks a period when ablation exceeded precipitation in the region. Cap carbonates also thin basinward: the Maieberg Formation is 300–400 m thick on the Otavi platform (Fig. 9), but its equivalent (correlated isotopically) thins to \(<25 \text{ m}\) within 30 km downslope from the shelf break (Hoffman et al., 1998b; Kennedy et al., 1998).

We are not burdened by an over-abundance of explanations for cap carbonates. Fairchild (1993) suggested that they were precipitated from glacial meltwaters saturated with alkalinity due to interaction with carbonate-rich glacial debris and rock powder. This does not adequately explain the presence of cap carbonates in areas where the glacial deposits have little carbonate, for example the Kimberleys in Australia (Plumb, 1981). Grotzinger and Knoll (1995) proposed that cap carbonates record the turnover of a previously stratified ocean (see above), with upwelling of alkalinity-laden deepwater driving precipitation of $^{13}$C-depleted carbonates. This model dovetails with Kirschvink’s (1992) post-glacial interpretation of Neoproterozoic BIF (Klein and Beukes, 1993), but the premise is questionable for reasons already given. Kennedy (1996) related cap carbonates to post-glacial flooding of continental shelves and seas, analogous to the ‘coral reef’ hypothesis for the Quaternary (Berger, 1982), and Kennedy et al. (2001a) hypothesized that cap carbonates are byproducts of methane released from permafrost on continental shelves globally during post-glacial flooding. But methane oxidized aerobically in the water column produces CO$_2$, causing carbonate dissolution; only methane oxidized anaerobically in conjunction with bacterial sulphate reduction in pore waters yields bicarbonate (Boeiu, 2000). If very large amounts of methane were released rapidly (Kennedy et al., 2001a), sulphate limitation would likely prevent substantially increased rates of anaerobic methane oxidation. Moreover, the characteristic spatial variability in $^{813}$C$_{\text{Carb}}$ (−40 to 0‰) observed in Phanerozoic methane-seep carbonates (Kaufman et al., 1996) is not found in cap carbonates. Tube-like structures purportedly conduits for methane release (Kennedy et al., 2001a) are strictly internal to cap carbonates (Fig. 5b): they do not tap the conjugated methane source rocks (Hoffman et al., 2002a). They occur only within microbial boundstones (Fig. 5c), even in cap dolostones deposited directly on metamorphic or granitic rocks (Cloud et al., 1974; Wright et al., 1978), unlikely to be prolific sources of methane.

Once we realized that the snowball hypothesis could explain the $^{813}$C anomalies associated with LNGD, we took as a test that it should also account for cap carbonates. Recall the deglaciation of a snowball Earth, sea ice and glaciers disappearing rapidly due to reverse ice-albedo feedback in an intense greenhouse with > 10% CO$_2$ (Caldeira and Kasting, 1992). As surface temperatures soar, carbonic (and initially sulphuric) acid rain beats down on a landscape dominated by frost-shattered rock and rock powder from glacial action, not to mention millions of years’ worth of unaltered volcanic material (Hoffman et al., 1998b; Hoffman and Schrag, 2000). Intense chemical (and physical) weathering ensues. Initially, where former carbonate platforms are exposed, carbonate weathering dominates. Later, after sea level has risen, silicate weathering becomes proportionally more important, and over time, draws down the atmospheric
The snowball Earth hypothesis

The internal stratigraphy is alkalinity-laden from carbonate weathering. The internal stratigraphy is alkalinity-laden from carbonate weathering; silicate weathering is too slow, given a deglaciation time of \(10^4–10^6\) years [not \(< 10^4\) years as suggested by Kennedy et al. (2001b)]. The alkalinity flux driving cap carbonate deposition during post-glacial sea level rise (i.e. below ‘maximum flooding’ in Figs 3, 9) came from carbonate weathering; silicate weathering is too slow, given a deglaciation time of \(< 10^4\) years (Kennedy et al., 2001b).

Large inputs of alkalinity are required to maintain seawater saturation if atmospheric \(p\text{CO}_2\) greatly increased in a snowball event (Fig. 10). The hydrothermal dominance of the snowball ocean will drive down seawater \(p\text{H}\) unless it is buffered by dissolution of carbonate, supplied for example by glacial action. Buffering would enable cap carbonates to form immediately upon deglaciation. This is consistent with the inference (see above) that many cap carbonates formed during post-glacial transgression (Fig. 3) and with the absence of post-glacial karst beneath cap carbonates. The deglaciation of a snowball Earth involves the rapid generation and mixing of warm, oxic, surface water with cold, saline deepwater, the latter dominated hydrothermally and the former by melting and runoff that is alkalinity-laden from carbonate weathering. The internal stratigraphy of complex cap carbonates may reflect, in addition to changing water depth, the mixing of contrasting water masses (Hoffman et al., 2002).

**Test 3: iron formations**

For Joe Kirschvink, iron is the element of choice. Iron formations are extensive deposits of sedimentary Fe(III) oxide and chert, not directly associated with volcanoes or hydrothermal vents. Common in the early stratigraphic record (Fig. 12), they virtually disappear after 1.85 Ga (Isley and Abbott, 1999). The only major reappearances of iron formation since that time (barring Clinton-type oolitic ironstones) occur strictly within LNGD (Fig. 2d), notably in Canada (Young, 1976; Yeo, 1981, 1986; Klein and Beukes, 1993), Brazil (Urban et al., 1992; Graf et al., 1994; Trompette et al., 1998), Namibia–South Africa (Martin, 1965) and Australia (Preiss, 1987; Lottermoser and Ashley, 2000).

The prerequisites for iron formation are three (Drever, 1974; Holland, 1984): (1) ocean anoxia to allow extensive transport of dissolved Fe(II); (2) an \(H_2S:Fe(II)\) flux ratio < 2, so that not all Fe(II) is scavenged by sulphide (FeS\(_2\)) burial, and (3) a local oxidant to drive the precipitation of an iron-formation precursor. Before the first atmospheric oxidation event around 2.4 Ga (Karhu and Holland, 1996), deep waters were anoxic and riverine sulphate input was low (Walker and Brimblecombe, 1985; Canfield et al., 2000; Farquhar et al., 2000). After 2.4 Ga, deepwater anoxia arguably persisted, but not until 1.8 Ga did oxidative weathering drive sulphate reduction in the ocean to levels sufficient to bury all Fe(II) as FeS\(_2\) (Canfield, 1998). The reappearance of iron formation in LNGD, after a 1.5-billion-year absence, is consistent with ocean anoxia due to stagnation beneath near-global sea-ice cover (Kirschvink, 1992), and also with an attenuated flux of reduced sulphur due to the frozen surface (Canfield and Raiswell, 1999).

Kirschvink (1992) and his early supporters (Klein and Beukes, 1993) suggested that Neoproterozoic iron formations were deposited at the end of snowball events, when renewed thermohaline circulation would have driven Fe(II)-rich deepwater into the oxic zone in upwelling areas. This model has been criticized on the grounds that iron formation occurs stratigraphically within or below, rather than above, certain LNGD (Williams and Schmidt, 2000). However, glacial erosion at low latitudes will itself be strongly biased toward the end of a snowball event, when the hydrological cycle has strengthened (Fig. 7). Alternatively, iron formation may have been deposited beneath the tropical ice pack if sea ice was thin (< 20 m) or discontinuous (McKay, 2000; but see Warren et al., 2002). Oxogenic photosynthesis would drive precipitation, given an anoxic ocean rich in dissolved iron. The giant Rapitan iron formations in the northern Canadian Cordillera, for example, were deposited close to the equator (Park, 1997) and are overlain by < 600 m of glacial diamicite and outwash (Yeo, 1981). (Young (1988) attributes the Rapitan iron formation to regional (but cryptic), rift-related, hydrothermal activity, but this is not supported by its trace-element geochemistry (Klein and Beukes, 1993; Graf et al., 1994) and ignores the complete absence of volcanics in the Rapitan belt and the age distribution of iron formations globally (Fig. 12).)

Kennedy et al. (1998) pointed out that iron formation is more common in (but not limited to) ‘Sturtian’
ice sheets. This would have caused a larger sea-level fall and, according to Kump and Seyfried (2001), a greater propensity for iron formation.

**Questioning the snowball Earth**

The snowball hypothesis has properly been questioned and the sharpest questions to date concern the terrestrial glacial regime, the isotopic evolution of snowball seawater and the fate of eukaryotic organisms. These and other questions highlight the central difficulty with the hypothesis, which is our limited conception of a snowball event itself. With postulated conditions lying far outside familiar parameter space, there is danger that the hypothesis we question is a caricature of a snowball Earth.

**Would glaciers flow?**

Geological evidence for the existence of dynamic glaciers is uncontroversial. Many LNGDs contain faceted and striated clasts (Fig. 2b), some far-travelled, and deformation structures caused by glacial flow (Cahen, 1963; Eisbacher, 1981; Wang et al., 1981; Edwards, 1984; Deynoux, 1985; McMechan, 2000). Associated subglacial pavements (Fig. 2a) are indelibly shaped, scratched, cracked and polished by glacial motion (Reusch, 1891; Perry and Roberts, 1968; Deynoux, 1980; Rice and Hofmann, 2000). Are these observations compatible with the cold, dry atmosphere and limited hydrological cycle of a snowball Earth (Christie-Blick et al., 1999; McMechan, 2000)? A major difficulty with this question is that we do not generally know which phase of the glacial cycle (Fig. 7) the glacial deposits represent. The magnetic reversal record in the Elatina (Sohl et al., 1999), however, indicates that a significant part of the hypothesized snowball event is represented.

Climate models suggest that an ice-albedo runaway might occur very rapidly (Hyde et al., 2000), freezing the tropical oceans before ice sheets had time to develop on low-latitude continents (Hoffman et al., 1998b; Pollard and Kasting, 2001). During a snowball event, mean temperatures slowly rise (Fig. 7) in response to atmospheric CO₂ and this will cause an exponential increase in saturation...
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Neoproterozoic snowball events

Palaeoproterozoic snowball events

Metazoa

Eukarya

Bacteria

\[ pO_2 > 0.2 \text{ bar} \]

\[ pO_2 > 0.03 \text{ bar} \]

\[ pO_2 < 0.002 \text{ bar} \]

Proterozoic glacial gap

banded iron formations

\[ \text{Age (x10^9 years before present)} \]

0.0  0.5  1.0  1.5  2.0  2.5  3.0  3.5

Fig. 12 Frequency of occurrence of iron formations (purple) (modified from Isley and Abbott, 1999), major glacial periods (blue) (Crowell, 1999), constraints on atmospheric oxygen levels (Rye and Holland, 1998), and steps in the history of life. Note the two eras of snowball events separated by a 1.5 billion year gap when evidence is lacking for glaciation at any latitude.

vapour pressures. Moisture sources include subaerial volcanic outgassing, sublimation of tropical sea ice (Warren et al., 2002), and evaporation of transient melt ponds (Walker, 2001) and polynyas within the tropical ice pack (Kirschvink, 1992). Given large seasonal and diurnal fluctuations in surface temperature (Walker, 2001), water vapour would be advected to topographic highs on summer afternoons and moisture would condense there forming glaciers (Walker, 2001). Due to the weak hydrological cycle, snow accumulation rates would be extremely low, but a positive feedback would develop between surface elevation and snow accumulation if glaciers thickened. Over sufficient time, these glaciers must become wet-based and flow, possibly in localized ice streams or as episodic ice surges (Bentley, 1987; MacAyeal, 1993). The observed zonal distribution of LNGD (Fig. 1) might broadly reflect the zonal pattern of precipitation minus ablation on the snowball Earth. On the regional scale, the importance of topography, particularly coastal topography, in capturing the limited precipitation is not inconsistent with the common observation that thicker glacial deposits occur in tectonically more active areas and times (Young, 1995). They commonly overlie preglacial strata with angular unconformity, consistent with a prolonged hiatus (with ongoing block rotation) between the ice-albedo runaway and the onset of glacialic sedimentation (Fig. 7). Where LNGD are absent, without evidence for removal by erosion, or where their position is occupied by aeolianite (Deynoux et al., 1989; Moussine-Pouchkine and Bertrand-Sarfati, 1997; Williams, 1998; Fig. 5a), ablation evidently exceeded precipitation over the full glacial cycle.

Would seawater change?

The elemental and isotopic composition of seawater should change in a snowball event. Decimated organic productivity and hydrothermal dominance should cause \( \delta^{13}C \) and \( {^{87}Sr/^{86}Sr} \), respectively, to fall (Kump, 1991; Jacobsen and Kaufman, 1999). The trajectories of the changes depend on the C and Sr residence times, and are sensitive to buffering by carbonate dissolution (Jacobsen and Kaufman, 1999) in response to submarine volcanic exhalations of CO\(_2\) and other acids. Consequently, few \( \delta^{13}C \) or \( {^{87}Sr/^{86}Sr} \) values have been reported for the glacial ocean because primary synglacial carbonates are rare. Kennedy et al. (2001b) report positive \( \delta^{13}C \) values from purported examples in Australia, Namibia and California, whereas Xiao et al. (2001) find that thin calcareous crusts in the Tereeken glacials (Table 1) of NW China have \( \delta^{13}C \) close to \( -5\% \).

Cap carbonates have been substituted as proxies for seawater \( {^{87}Sr/^{86}Sr} \) during snowball events (Jacobsen and Kaufman, 1999; Kennedy et al., 2001b), justified by the Sr residence time of \( \sim 3.5 \) Myr in the present ocean. Neoproterozoic Sr isotope data are not very reliable because strontium is a mobile trace element and most carbonates of that age are totally recrystallized (Derry et al., 1992). Nevertheless, the ‘least altered’ \( {^{87}Sr/^{86}Sr} \) ratios in cap limestones (dolomites have very low Sr concentrations) are not significantly different from preglacial values (Jacobsen and Kaufman, 1999; Kennedy et al., 2001b). This may be interpreted in two ways. Either the \( {^{87}Sr/^{86}Sr} \) ratio of seawater changed little because the glaciation was short-lived (Jacobsen and Kaufman, 1999), contrary to palaeomagnetic (Sohl et al., 1999) and subsidence (Hoffman et al., 1999a) data, or else the ratio was buffered by carbonate dissolution during the hypothesized snowball event and enhanced weathering in the greenhouse aftermath (Hoffman et al., 1998b). If atmospheric \( pCO_2 \) rose from a preglacial value of 0.0003 bar to 0.12 bar over the course of a snowball event (Caldeira and Kasting, 1992), then the Ca ion concentration of seawater would have to increase five-fold simply to maintain carbonate saturation (Fig. 10). This enormous Ca input would be accompanied by a flux of isotopically conservative Sr from carbonate dissolution and radiogenic Sr from silicate weathering. These inputs might greatly reduce or even eliminate the predicted lowering of \( {^{87}Sr/^{86}Sr} \) during a snowball event of any given duration (Jacobsen and Kaufman, 1999). The large magnitude of the resulting seawater Sr reservoir, plus the rapid weathering of carbonates and young volcanics, would damp any increase in seawater \( {^{87}Sr/^{86}Sr} \) due to silicate weathering, consistent with available data (Jacobsen and Kaufman, 1999; Kennedy et al., 2001b). Contrary to Kennedy et al. (2001b), the transient weathering flux is not limited to the time-scale of the sea-level rise (\( < 10^4 \) years) but continued long after as indicated by the negative \( \delta^{13}C \) anomaly (Fig. 9) which encompasses the entire transgressive-
regressive post-glacial sequence. According to, $^{87}$Sr/$^{86}$Sr ratios in cap carbonates are broadly similar to preglacial values but should rise thereafter due to silicate weathering, as is observed (Shields et al., 1997).

Would eukaryotes survive?

Few biologists doubt that prokaryotic organisms could survive snowball events (Priscu et al., 1998; Gaidos et al., 1999; Vincent and Howard-Williams, 2000; Thomas and Dieckmann, 2002), but many extant clades of eukaryotic algae, protists and tests (Butterfield, 2002), but many extant clades of eukaryotic algae, protists and tests (Butterfield, 2002), but many extant clades of eukaryotic algae, protists and tests (Butterfield, 2002), but many extant clades of eukaryotic algae, protists and tests (Butterfield, 2002), but many extant clades of eukaryotic algae, protists and tests (Butterfield, 2002) could survive snowball events (Priscu et al., 2000; Thomas and Dieckmann, 2002). Would eukaryotes survive?

Limitations for evolution? A variety of refugia would have existed and their relative isolation and selective stresses could have contributed to evolutionary diversification. They include brine channels in new sea ice (Thomas and Dieckmann, 2002), polynyas in the tropical ice pack (Kirschvink, 1992; Lemke, 2001), tidal cracks along ice-grounding lines (Gaidos et al., 1999), transient meltwater ponds (Walker, 2001), beneath clear sea or lake ice < 20 m thick (McKay, 2000), and shallow hot springs around volcanic islands (Hoffman and Schrag, 2000). Snowball seawater would be laden with nutrients due to hydrothermal activity and limited organic productivity (Kirschvink et al., 2000) particularly in the younger Neoproterozoic glaciations when iron formation, a major sink for phosphorus, was rare (see above). Enhanced productivity and burial of organic matter when snowball oceans were uncorked would have released oxygen to the atmosphere (Kirschvink et al., 2000; Walter et al., 2000), consistent with evidence of increased environmental oxygenation roughly coincident with the Neoproterozoic glaciations (Prasad and Roscoe, 1996; Rye and Holland, 1998; Farquhar et al., 2000; Murakami et al., 2001) and Neoproterozoic (Des Marais et al., 1992; Logan et al., 1995; Canfield and Teske, 1996) snowball eras (Fig. 12). The isotopic signal of such organic-burial events might be muted if they were accompanied by a high carbonate burial flux, driven by weathering as we have argued. The appearance of particular Ediacaran fossils has long been attributed to a rise in free oxygen (Runnegar, 1982; Knoll and Carroll, 1999). Speculatively, snowball events may have acted not only as an environmental filter on the evolution of life, but also as a biogeochemical pump that permanently changed the environment itself.

Snowball events in Earth history

Any viable explanation for snowball events must also explain why they are rare. Extensive low-latitude glaciation occurred only near the beginning (2.45–2.22 Ga) and the end (0.73–0.58 Ga) of the Proterozoic eon (Fig. 12). The former include the Makganyene glacials in South Africa (Evans et al., 1997; Tsikos and Moore, 1998; Kirschvink et al., 2000), three discrete Huronian glaciations in central Canada (Williams and Schmidt, 1997; Schmidt and Williams, 1999), and equivalents in Wyoming and Finland (Ojakangas, 1988). The Makganyene and Huronian glacials have similar age brackets, > 2.22 and < 2.45 Ga (see references in Williams and Schmidt, 1997; Bekker et al., 2001). The Makganyene glaciation was preceded by carbonates with unusually high $^13$C values, similar to LNGD (Bekker et al., 2001), and succeeded by a major Fe–Mn sedimentary formation (Tsikos and Moore, 1998; Kirschvink et al., 2000). The middle Huronian and equivalent glacial units have cap carbonates (the only carbonate in the 14-km-thick Huronian succession) with negative $^13$C (Veizer et al., 1992; Bekker et al., 2001), and the ultimate Huronian glaciation was followed by an intense lateritic weathering regime (Young, 1973). Remarkably, there is virtually no evidence for large ice sheets at any palaeolatitude during the 1.5 billion years in between the two snowball eras (Fig. 12). Two things need to be explained (Schrag et al., 2002): what special conditions set those two eras apart (allowing snowball events to occur), and what triggered the individual snowball events?

The length of both eras, 100–200 Myr, is of the time-scale of global palaeogeographical reorganizations due to plate tectonics. Kirschvink (1992) proposed that a preponderance of land masses in the middle and low latitudes set the stage for snowball events, consistent with existing palaeomagnetic data for LNGD (Fig. 1). This is broadly in line with global reconstructions for 750 Ma (Fig. 7), prior to the ‘Sturtian’ (Table 1) glaciation(s), but ‘Varanger–Marinoan’ (Table 1) palaeogeography is quite uncertain, primarily because of poor age control. Reconstructions in which land masses are centred on the (south) pole (e.g. Hyde et al., 2000; Baum and Crowley, 2001; Crowley et al., 2001) hinge on Laurentia’s migration to high latitudes by 577 Ma (Torsvik et al., 1996), after the last snowball event (Table 1), a migration which could have ended the snowball era rather than being a precondition for it (Hyde et al., 2000). Placing continents at tangent to the tropics results in a colder Earth for a variety of reasons.
It raises the surface albedo (Kirschvink, 1992) and it enhances silicate weathering, unless tectonic activity is mysteriously absent there (Marshall et al., 1988; Worsley and Kidder, 1991; Schrag et al., 2002). Weathering rates are greater on small continents because they are wetter than large ones. The Neoproterozoic snowball era was a period of continental dispersal, involving the breakup of supercontinent Rodinia and the aggregation of megacontinent Gondwana (Hoffman, 1999). Polar ice caps may reduce global weathering rates and mitigate against snowball events if large land areas exist at high latitudes (Schrag et al., 2002), as in the Phanerozoic. An absence of high-latitude continents and a preponderance of tropical and subtropical land masses would be an unusual situation in Earth history, and might give rise to polar sea-ice caps large enough to threaten runaway ice-albedo feedback (Kirschvink, 1992; Schrag et al., 2002).

Clues regarding the triggering of individual snowball events may be found in preglacial $\delta^{13}$C records (Figs 8 and 9). Snowball events generally follow long stages (> 10$^7$ years) of high $\delta^{13}$C (> 5$\%_o$ PDB in shallow marine carbonates) (Kaufman et al., 1997; Brasier and Shields, 2000; Walter et al., 2000; Halverson et al., 2002). This likely signifies that organic matter was disproportionately represented in the global carbon burial flux ($f_{org}$ $\geq$ 0.4). We speculate (Schrag et al., 2002) that a preponderance of middle- and low-latitude continents would produce this effect. Nutrient transport patterns will cause marine biological productivity to be focused in the congested mid-latitude and low latitudes where high rates of organic production will drive some basins to become anoxic (Schrag et al., 2002). Anoxic bottom waters cause high C:P ratios in the organic burial flux (Van Cappellen and Ingall, 1994; Colman and Holland, 2000), which greatly increases phosphorus availability for recycling, which in turn allows high sustained rates of organic production and burial.

Spectacular declines in $\delta^{13}$C (Figs 8 and 9) have been discovered directly beneath the younger LNGD in northwest Canada (Narbonne and Aitken, 1995), north-west Namibia (Hoffman et al., 1998b; Halverson et al., 2002), South Australia (Walter et al., 2000; McKirdy et al., 2001) and north-west China (Xiao et al., 2001), and also beneath the older LNGD in Scotland (Brasier and Shields, 2000) and northeast Svalbard (Halverson and Maloof, 2001). The time-scale of the isotopic anomaly in Namibia is estimated to be on the order of 0.5 Myr (Halverson et al., 2002). We argue that this anomaly is most likely the result of a sustained release of $^{13}$C-enriched carbon, possibly methane generated in the organic-rich sediments previously deposited (Halverson et al., 2002; Schrag et al., 2002). A prolonged release of methane into the atmosphere, engendered by the unusual continental distribution, would not only drive down marine $\delta^{13}$C but might also destabilize the climate. Because atmospheric methane is not equilibrated with the ocean, as is CO$_2$, any substantial dependence on methane greenhouse could counter-intuitively trigger a snowball event if the methane supply was interrupted for any reason (Pavlov et al., 2000; Schrag et al., 2002). These ideas are highly speculative and it remains to be seen if any or all snowball events were initiated in this way. Perhaps each event was triggered differently, a possibility that highlights the glaring uncertainty regarding the number and correlation of LNGD (Kaufman et al., 1997; Grey and Corkeron, 1998; Kennedy et al., 1998; Saylor et al., 1998; Prave, 1999b; Brasier and Shields, 2000; Walter et al., 2000; Corsetti and Kaufman, in press).

Conclusions

The appeal of the snowball hypothesis (Kirschvink, 1992) is that it provides credible explanations for many previously enigmatic features of Neoproterozoic Earth history. It explains: (1) the widespread distribution of LNGD on virtually every continent; (2) the palaeomagnetic evidence that glacial ice lines reached sea level close to the equator for long periods; (3) the stratigraphic evidence that glacial events began and ended abruptly; (4) the reappearance of iron formations, exclusively within glacial units, after an absence of 1.2 billion years; (5) the world-wide occurrence of cap carbonates with unusual features, resting sharply above successive LNGD; (6) the existence of very large positive and negative $\delta^{13}$C anomalies, before and after each glacial event, respectively. The alternative ‘loop-hole’ model (Hyde et al., 2000; Runnegar, 2000) compromises many of these explanations (Schrag and Hoffman, 2001), and is therefore less attractive. As the observations have no parallel in the Phanerozoic, it should not be surprising that the events responsible for them have no Phanerozoic counterparts.

Following Kirschvink (1992), we speculate that a preponderance of continents in middle to low latitudes created conditions favourable for snowball events. Such conditions would be rarely met in Earth history overall, but could persist for intervals long enough to engender repeated snowball events, as is observed. A possible trigger for individual snowball events, suggested by carbon isotopic data in many areas (Halverson et al., 2002), arises counter-intuitively from a dependence on greenhouse methane, engendered by the same unusual continental distribution (Schrag et al., 2002).

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