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A Neoproterozoic Snowball Earth

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Negative carbon isotope anomalies in carbonate rocks bracketing Neoproterozoic glacial deposits in Namibia, combined with estimates of thermal subsidence history, suggest that biological productivity in the surface ocean collapsed for millions of years. This collapse can be explained by a global glaciation (that is, a snowball Earth), which ended abruptly when subaerial volcanic outgassing raised atmospheric carbon dioxide to about 350 times the modern level. The rapid termination would have resulted in a warming of the snowball Earth to extreme greenhouse conditions. The transfer of atmospheric carbon dioxide to the ocean would result in the rapid precipitation of calcium carbonate in warm surface waters, producing the cap carbonate rocks observed globally.

During the 200 million years (My) preceding the appearance of macroscopic metazoans, ~750 to 550 million years ago (Ma) (*1*), the fragmentation of a long-lived supercontinent (*2*) was accompanied by intermittent, but widespread, glaciation (*3–5*). Many of the glacial deposits contain carbonate debris or are directly overlain by carbonate rocks (*6, 7*), including inorganic sea-floor precipitates, which are normally limited to warm-water settings (*8*). Postglacial carbonate rocks (cap carbonates) occur even in terrigenous-dominated sections (*6, 7*). Certain glacial units contain large sedimentary iron formations (*9*), which reappear after a 1-billion-year hiatus in the stratigraphic record. The glacial intervals are spanned by decreases of as much as 14 per mil in the $\delta^{13}C$ value of the surface ocean (*10, 11*). These isotopic excursions are enormous in comparison with any excursions in the preceding 1.2 billion years (*12*) or in the Phanerozoic eon (*13*).

Paleomagnetic evidence suggests that the ice line reached sea level close to the equator during at least two Neoproterozoic glacial episodes (*14*). The origin of these extreme glaciations has been controversial (*1, 15, 16*). Kirschvink (*17*) proposed a snowball Earth, created by a runaway albedo feedback, in which the world ocean was virtually covered by sea ice but continental ice cover was thin and patchy because of the virtual elimination of the hydrologic cycle. Kirschvink applied this hypothesis to explain the low-paleolatitude glacial deposits as well as the occurrence of banded iron formations, suggesting that an ocean sealed by sea ice would quickly become anoxic and rich in dissolved ferrous iron (*17*). Here, we present new data on the amplitude, timing, and duration of inorganic $\delta^{13}C$ variations in Neoproterozoic rocks of northern Namibia and the relation between these variations and glaciation. We show that the snowball Earth hypothesis best explains the geological and geochemical observations, including the $\delta^{13}C$ excursions and the existence of carbonates immediately following glaciations.

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We studied the Otavi Group (Fig. 1), a carbonate platform covering the southern promontory of the Congo Craton in northern Namibia (*15, 18, 19*). In the late Neoproterozoic, the Congo Craton was a Bahama-type sea-level platform that was about the size of the conterminous United States. Paleomagnetic data from the eastern part of the craton (*20*) imply that the Otavi Group was at ~12°S paleolatitude at 743 ± 30 Ma and at ~39°S at 547 ± 4 Ma. The Otavi Group contains two discrete glacial units (Chuos and Ghaub formations) of Sturtian (~760 to 700 Ma) age (*15, 19*). Both units are underlain by thick carbonate successions with high $\delta^{13}C$ values, and both units are overlain by distinctive cap carbonates, recording negative $\delta^{13}C$ excursions (*10, 11*).

The younger of the two glacial units (the Ghaub Formation) is represented by unstratified diamictons, debris flows, and, at the top, varve-like detrital couplets crowded with ice-rafted dropstones (*15*). Both the onset and the termination of glaciogenic sedimentation were abrupt. The glacial deposits are composed predominantly of dolomite and limestone debris derived from the underlying Ombaatjie platform (Fig. 1). Clast and matrix lithologic compositions covary; thus, we interpreted the matrix as being detrital in origin and not as a seawater proxy. Glacial deposits on the platform are thin and highly discontinuous (not due to subsequent erosion). Alternately grounded and floating sea ice caused large horizontal plates to be detached from the directly underlying bedrock. The subglacial erosion surface has remarkably little relief on the platform (~50 m relative to underlying strata over a distance of 150 km), suggesting that any fall in relative sea level was limited or short-lived. Comparatively thick sections (<180 m) of diamictons and debris flows occur on the continental slope, suggesting that the ice grounding line remained close to the platform edge (Fig. 1). These observations are consistent with an abrupt development and a subsequent dissipation of grounded sea ice on a tropical or sub-

tropical platform, consistent with a snowball glaciation.

We measured inorganic $\delta^{13}C$ values of carbonate rocks that spanned the glacial interval from several sections (Fig. 2) (*10, 11*). In general, $\delta^{13}C$ values are rather insensitive to diagenesis because aqueous fluids contain little carbon in comparison with carbonate rocks (*21*). This inference is supported by the overall agreement of the pattern of isotopic variations from multiple sections. The $\delta^{13}C$ data on the platform (summarized in a composite section in Fig. 3) show that (i) preglacial values are 5 to 9 per mil through >200 m of section just below the subglacial surface; (ii) values fall abruptly to as low as −5 per mil in the final regressive platformal parasequences and slope apron directly beneath the subglacial uncomformity; and (iii) immediate postglacial values are about −3 per mil (~2 per mil higher than minimum preglacial values), decline through ~40 m of section to a nadir of −6 per mil, and then rise to 0 per mil at about 480 m above the base of the cap carbonate. Lesser subglacial $\delta^{13}C$ downturns are known elsewhere on the Otavi platform (*22*) and on other continents (*10, 11*). The overall negative $\delta^{13}C$ excursion occupies ~500 m of the platformal carbonate section. Much of the lateral variance in $\delta^{13}C$ curves between sections (Fig. 2) can be accounted for in terms of subglacial erosional truncation and slope progradation.

Constraints on the duration of the isotopic excursion from a model of thermally driven subsidence of the platform (*15*) allow a maximum subsidence rate of 14 m/My (equivalent to a maximum carbonate accumulation rate, with sediment loading, of ~50 m/My). The $\delta^{13}C$ excursion begins and ends in sediments deposited near nonglacial sea level and occupies a total thickness on the platform of ~500 m (~50 m of which can be accounted for isostatically as a consequence of subglacial erosion). The remainder of the thickness (~450 m) required time-dependent thermal subsidence for its accommodation. Thus, the minimum time required to accommodate the $\delta^{13}C$ excursion (below 0 per mil) was 9 My [450 m/(50 m/My)]. Stratigraphic mapping shows that no tectonic activity occurred at the time of the $\delta^{13}C$ excursion that would affect the subsidence calculation. We cannot estimate the time span of the deposition of the cap carbonate because we do not know the water depth or the potential glacioeustatic and ice-loading effects at the onset of deposition.

If we interpret the $\delta^{13}C$ excursion in terms of carbon burial fluxes, then the proportion of organic carbon to total carbon burial changed from almost 0.5 before the glacial deposits to virtually zero immediately after. Carbonates, precipitated from an ocean in which most biological productivity had ceased for a time period greatly exceeding the carbon residence time (>10^5 years), would approach a value of −5 to −7 per mil, which is the isotopic composition of carbon entering the ocean (*23, 24*). The isotopic pattern, therefore, is consistent with the hypothesis of a snowball Earth, in which oceanic photosynthesis would be severely reduced for millions of years because the ice cover would block out sunlight. Meltwater pools and bare ground, exposed through gravitational thinning and ablation of ice sheets without much rejuvenative snowfall, might provide refugia for a variety of bacteria and simple eukaryotes.

Caldeira and Kasting (*25*) estimated that, at

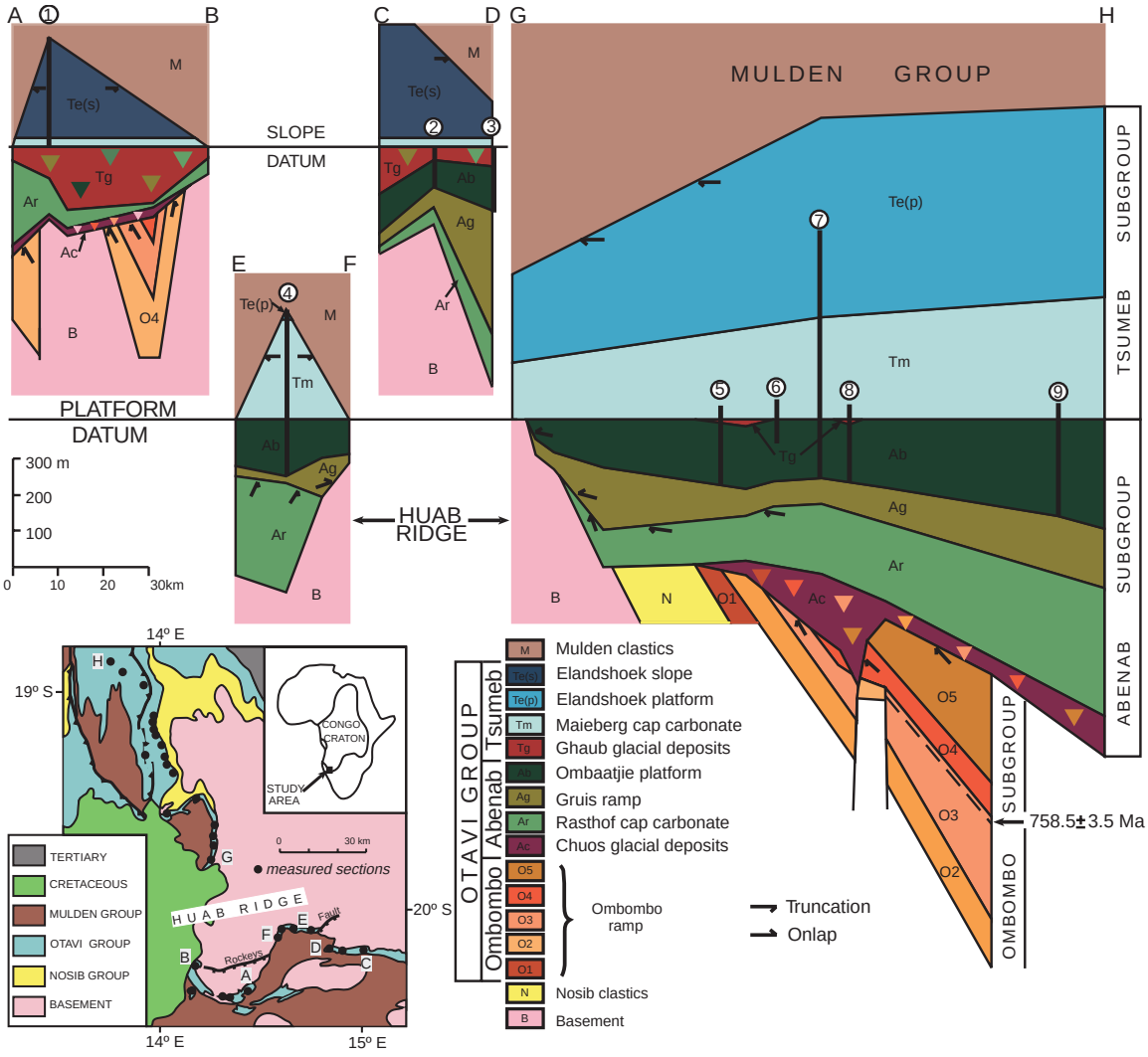

Fig. 1. Stratigraphic cross sections of the Otavi carbonate slope (A–B and C–D) and platform (E–F and G–H) in northwest Namibia, showing the measured sections in Fig. 2 (indicated by circled numbers).

present, it would take ~0.12 bar of atmospheric CO_2 from volcanic input to overcome a snowball albedo and cause meltback. This estimate implies that a snowball glaciation would last ~4 My at the modern rates of CO_2 release from subaerial volcanism [~5.4 × 10^{12} mol/year (*26*)] with no air-sea gas exchange. Partial gas exchange through cracks in sea ice would increase this estimate. In the Neoproterozoic, the duration of a snowball glaciation would be longer because of lower solar luminosity as well as reduced pelagic deposition of carbonate,

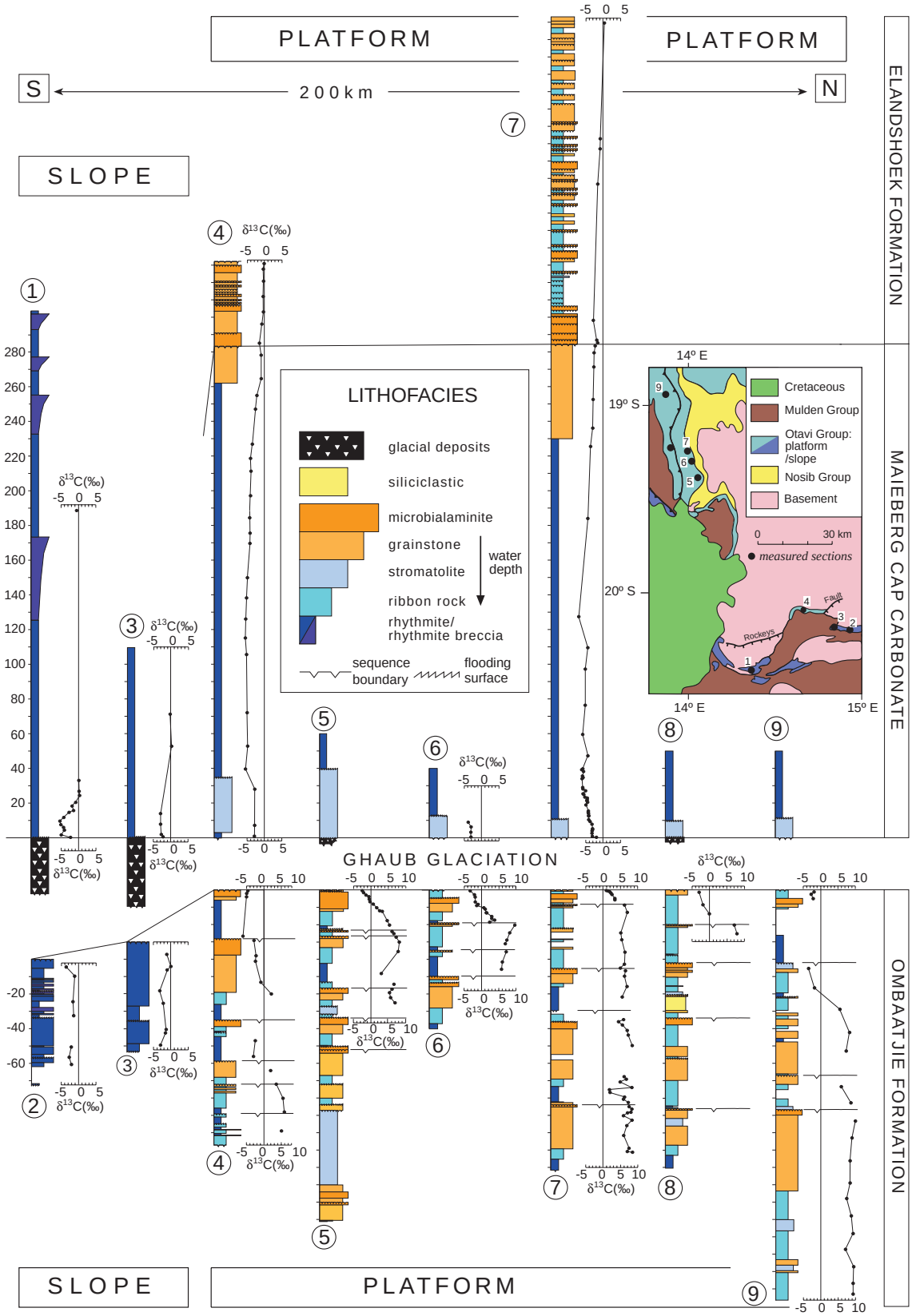

Fig. 2. Measured sections of carbonates bracketing the Ghaub glaciation in a south-north profile across the Otavi platform and slope. The extended negative $\delta^{13}C$ excursion is centered on the Maieberg cap carbonate on the platform, and its condensed stratigraphic equivalent is on the continental slope. The $\delta^{13}C$ values decline from positive preglacial values that are stratigraphically beneath Ghaub glacial deposits or the bare glaciated surface. The crossover from positive to negative values occurs in a 25-m-thick parasequence, which can be correlated regionally and which is variably truncated by the subglacial surface.

which would lower the release rates of volcanic CO_2 at convergent margins (*27*). A minimum value of 4 My and a maximum estimate of 30 My (*25*) are broadly consistent with the 9 My duration of the isotopic excursion in the Otavi Group.

During a snowball glaciation, the Ca/Mg ratio of seawater would have increased because of hydrothermal activity at mid-ocean ridges and low-temperature alteration of basalt (*28*). Without the input of alkalinity from rivers, carbonate would dissolve in the deep sea, driven by the input of CO_2 from mid-ocean ridge volcanism, although this flux of CO_2 [$\sim 0.83 \times 10^{12}$ mol/year (*24*)] in the modern ocean is smaller than the CO_2 input to the atmosphere from subaerial volcanism. Air-sea gas exchange through cracks in the sea ice would intensify the carbonate dissolution. Hydrothermal activity without continental weathering would also decrease the Sr isotopic composition of seawater, although this effect might be small considering the buffering effect of carbonate dissolution during the glaciation as well as the lower Sr/Ca partitioning in inorganically precipitated carbonates (*29*) and, therefore, the higher Sr concentrations and the longer Sr residence time in Proterozoic oceans.

Once atmospheric CO_2 reached the critical concentration [$\sim$120,000 parts per million (ppm) (*25*)], a transformation from icehouse to greenhouse conditions would occur quickly, as the albedo and water vapor feedbacks would enhance the warming with the opening of low-latitude oceans. This abrupt climate change would make Pleistocene glacial terminations seem slow in comparison. On meltback, gas exchange between the surface ocean and the high-CO_2 atmosphere would first drive carbonate dissolution and then drive precipitation as cold deep waters with high concentrations of calcium and dissolved inorganic carbon mixed with warm tropical surface waters. Additional sources of alkalinity would come from intense continental weathering that was driven by warm temperatures, high levels of CO_2, and a strong hydrologic cycle. Reducing atmospheric CO_2 pressure from 0.12 to 0.001 bar [that is, from terminal snowball conditions to normal Neoproterozoic values (*25*)] would provide $\sim 2.5 \times 10^{20}$ g of carbon, sufficient to produce $\sim 8 \times 10^5$ km^3 of carbonate, which is enough to cover the entire present-day continental crust with a layer $\sim$5 m thick. The space that was created by thermal subsidence during a prolonged glacial period could be rapidly filled by the cap carbonate sequence, which is consistent with textural evidence in the Maieberg and other Neoproterozoic cap carbonates suggesting rapid deposition (*6, 7, 30*). Precipitation would be strongly localized on warm shallow-water platforms, where $CaCO_3$ solubility is minimized, which is in agreement with the regional variation in cap carbonate thickness (*6, 7*) and the observed increase in thickness of the negative $\delta^{13}C$ excursion from the slope to the platform (Fig. 2). If the observed millimeter-scale laminations in cap carbonates are diurnal (the dominant cycle in the tropics), accumulation rates were $\sim$40 cm/year (*31*).

The $\delta^{13}C$ values in the Otavi Group are consistent with the snowball hypothesis. The initial decrease in $\delta^{13}C$ values before the glaciation on the tropical platform implies a decrease in productivity relative to carbonate deposition, perhaps because of colder conditions (-20 to 0 m; Fig. 3). During the glaciation, if there was no air-sea gas exchange, both the ocean and the atmosphere would have similar $\delta^{13}C$ values, equivalent to the hydrothermal or the volcanic input (-5 to -7 per mil). At the termination, isotopic fractionation associated with the hydration of CO_2 would raise the $\delta^{13}C$ of dissolved inorganic carbon in the surface ocean, which is dominated by the large atmospheric reservoir. As the amount of CO_2 in the atmosphere subsided, the continued uptake of carbon with higher $\delta^{13}C$ values would drive atmospheric $\delta^{13}C$ down through Rayleigh distillation, while the ocean would read -5 per mil because of mass balance and mixing with the deep ocean. Thus, the $\delta^{13}C$ values of the cap carbonate start out somewhat higher than -5 per mil but quickly decrease to the low values of the glacial atmosphere (0 to 40 m; Fig. 3). The reestablishment of the biological pump drove values back up toward preglacial levels over a stratigraphic thickness determined by sedimentation rate, which is much higher on the platform than on the continental slope (Fig. 2).

A review of the alternative hypotheses that attempt to explain various aspects of Neoproterozoic isotopic excursions and glacial events reveals contradictions between each of the hypotheses and our data from Namibia (*15*). A popular model asserts that the isotopic anomalies were driven by alternating periods of ocean stagnation and overturn, corresponding to positive and negative surface-water $\delta^{13}C$ values, respectively (*10, 11, 32*). The model predicts that the duration of the negative excursion should be limited by the residence time of carbon in the ocean [$<10^5$ years) (*6, 7, 23*)], which is inconsistent with our estimate of the duration of the excursion in the Otavi Group.

To simulate a snowball Earth, coupled energy-balance models require that atmospheric CO_2 levels be lowered dramatically ($\sim 10^{-4}$ bar), even with lower-than-present solar luminosity (*33*). Fragmentation of the Rodinia supercontinent may have contributed to the CO_2 drawdown (*1, 2*) by creating many new continental margins, which are major repositories for organic carbon in the modern ocean (*34*), consistent with the high $\delta^{13}C$ values observed before the glaciation. This is also consistent with the observation that Sturtian ($\sim$760 to 700 Ma) and Varangian ($\sim$620 to 550 Ma) glaciations accompanied the opening of the Pacific and Iapetus oceans, respectively (*5*), and might explain why the only known older examples of similar carbon isotope excursions and low-latitude glaciations (*35*) accompanied the fragmentation of a late Archean megacontinent. We speculate that higher solar luminosity, less efficient burial of organic carbon due to bioturbation, and limits on primary productivity due to lower levels of nutrient iron and phosphorus (*36*) in the more oxic Phanerozoic ocean (*37*) prevented Phanerozoic snowball Earth conditions.

Postglacial cap carbonates are predictable consequences of the recovery from a snowball Earth. Accordingly, the succession of late Neoproterozoic glaciations characterized by cap carbonates and large $\delta^{13}C$ excursions (*10, 11*) should represent multiple episodes of runaway ice albedo. These episodes (cryochrons) should be useful for global correlation (*3–5*). A snowball Earth followed by extreme greenhouse conditions represents a strong source of selective pressure on the evolution of life in the Neoproterozoic. Although the absence of skeletal organisms makes any extinction difficult to evaluate, there is some evidence for a substantial turnover among acritarchs (*38*). Many prokaryotic organisms, which dominated the Neoproterozoic biosphere, are able to survive ex-

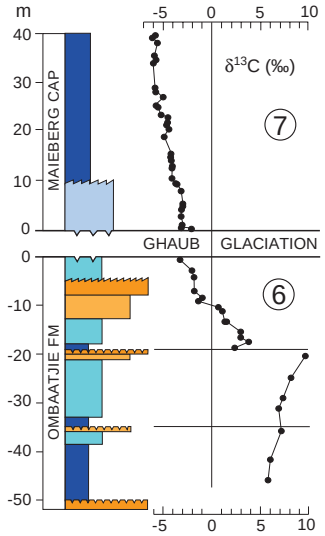

Fig. 3. Composite section across the Ghaub glacial surface on the platform, showing high-resolution $\delta^{13}C$ data. An abrupt downturn in $\delta^{13}C$ occurs at the base of the penultimate preglacial parasequence, and there is a postglacial descent to a nadir of -6 per mil, $\sim$40 m above the glacial surface and $\sim$20 m above the maximum flooding interval. In the snowball Earth model, the glacial surface would represent $\sim$10 My, but the 400-m-thick cap carbonate would only represent thousands of years.

treme and prolonged environmental stress (*39*) and were likely unaffected. Many eukaryotic phyla (including red, green, and chromophytic algae) evolved before the late Neoproterozoic glaciations and also must have survived the environmental stress (*40*). However, a succession of snowball glaciations must have imposed an intense environmental filter, resulting in a series of genetic "bottleneck and flush" cycles (*41*), possibly leading to an initial metazoan radiation before the terminal glaciation (*42*) and an Ediacaran radiation in its aftermath (*11*).

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Photofragment Helicity Caused by Matter-Wave Interference from Multiple Dissociative States

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Isolated diatomic molecules of iodine monochloride (ICl) were photodissociated by a beam of linearly polarized light, and the resulting ground-state Cl atom photofragments were detected by a method that is sensitive to the handedness (helicity) of the electronic angular momentum. It was found that this helicity oscillates between "topspin" and "backspin" as a function of the wavelength of the dissociating light. The helicity originates solely from the (de Broglie) matter-wave interference of multiple dissociating pathways of the electronic excited states of ICl. These measurements can be related to the identity and to the detailed shapes of the dissociating pathways, thus demonstrating that it is possible to probe repulsive states by spectroscopic means.

The photodissociation of a diatomic molecule occurs, in the simplest case, as the breakup of an excited molecule on a single potential energy surface (*1*). The molecule then dissociates under the influence of a force directed along the bond axis. The photodissociation