Calibrating the Cryogenian

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The Neoproterozoic was an era of great environmental and biological change, but a paucity of direct and precise age constraints on strata from this time has prevented the complete integration of these records. We present four high-precision U-Pb ages for Neoproterozoic rocks in northwestern Canada that constrain large perturbations in the carbon cycle, a major diversification and depletion in the microfossil record, and the onset of the Sturtian glaciation. A volcanic tuff interbedded with Sturtian glacial deposits, dated at 716.5 million years ago, is synchronous with the age of the Franklin large igneous province and paleomagnetic poles that pin Laurentia to an equatorial position. Ice was therefore grounded below sea level at very low paleolatitudes, which implies that the Sturtian glaciation was global in extent.

Middle Neoproterozoic or Cryogenian strata [850 to 635 million years ago (Ma)] contain evidence for the breakup of the supercontinent Rodinia, widespread glaciation (*1*, *2*), high-amplitude fluctuations in geochemical proxy records (*3*), and the radiation of early eukaryotes (*4*); however, both relative and absolute age uncertainties have precluded a better understanding of the nature and interrelationships of these events. Several first-order questions remain: How many Neoproterozoic glaciations were there? How were they triggered? What was their duration and extent? How did the biosphere respond? Answers to all of these questions hinge on our ability to precisely correlate and calibrate data from disparate stratigraphic records around the world.

The snowball Earth hypothesis (*1*, *2*) was developed in response to strong paleomagnetic evidence for low-latitude glaciation from the Elatina Formation in Australia (*5*, *6*). The Elatina Formation and its distinct cap carbonate have been correlated with chemo- and lithostratigraphy to Marinoan-age glacial deposits in the Ghaub Formation in Namibia (635.5 ± 0.6 Ma) (*7*); the Nantuo Formation in South China (636.3 ± 4.9 Ma) (*8*), which underlies the cap carbonate of the basal Doushantuo Formation (635.2 ± 0.2 Ma) (*9*); and other glacial deposits around the globe, including the Ice Brook Formation in northwestern Canada (*10*). In contrast, a paucity of robust paleomagnetic poles and precise age constraints from volcanic rocks directly interbedded with early Cryogenian glacial deposits has precluded tests of the snowball Earth hypothesis for the Sturtian glaciation. The global nature of the Sturtian glaciation has been inferred from the ubiquitous occurrence of glacial deposits that are stratigraphically below Marinoan diamictite units (*10*) as well as banded iron formation within these deposits (*1*).

We present four high-precision U-Pb isotope dilution–thermal ionization mass spectrometry (ID-TIMS) dates from intrusive and volcanic rocks within Neoproterozoic strata of northwestern Canada. These dates, coupled with high-resolution $\delta^{13}C$ profiles (*11*), allow us to synthesize Cryogenian geological, geochemical, paleomagnetic, and paleontological data both regionally and globally. The accurate integration of these records places hard constraints on the timing and extent of the Sturtian glaciation and its relationship to the Franklin large igneous province (LIP) and the Cryogenian microfossil record.

Neoproterozoic strata are exposed in erosional windows (inliers) through Paleozoic carbonate rocks in northwestern Canada for more than 1500 km, from the Alaska border

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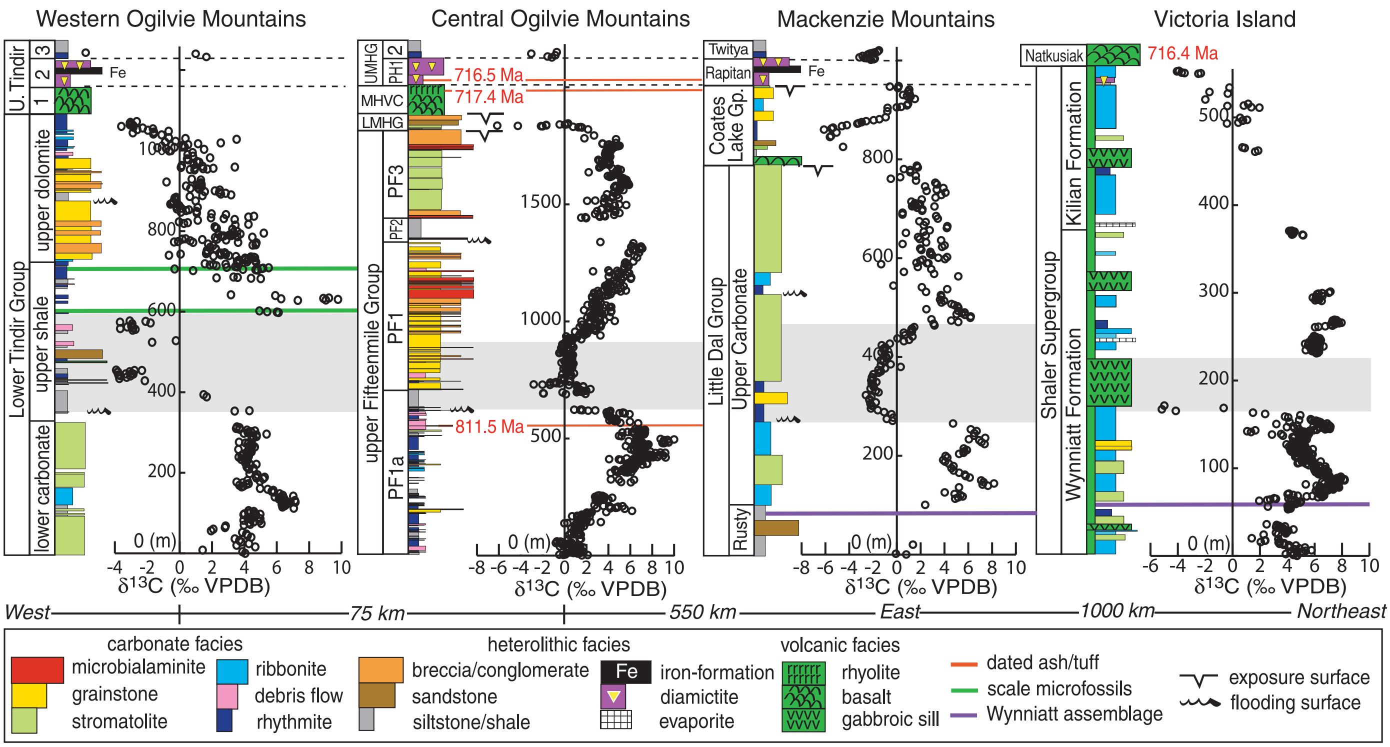

Fig. 1. Composite chemo- and lithostratigraphy of Neoproterozoic strata in northwestern Canada, including the Upper and Lower Tindir Groups (*13*), the Fifteenmile and Lower Mount Harper Group (table S2), the Little Dal Group (*3*), the Coates Lake Group (table S2), the Twitya Formation (*3*), and the Shaler Supergroup (*18*). Shaded area represents the Bitter Springs isotopic stage (*3*).

east through the Ogilvie and Wernecke Mountains of Yukon, to the Mackenzie Mountains of the Northwest Territories, and north to Victoria Island of Nunavut (fig. S1A). Exposures in the Coal Creek inlier of the central Ogilvie Mountains consist of mixed carbonate and siliciclastic rocks of the upper Fifteenmile and Lower Mount Harper Groups (LMHG), bimodal volcanic rocks of the Mount Harper volcanic complex (MHVC) (*12*), and glacial diamictite of the Upper Mount Harper Group (UMHG) (Fig. 1). A glacial origin for the UMHG is inferred from bed-penetrating dropstones with impact margins and outsized clasts in fine, laminated beds, and by striated clasts in exposures in the Hart River inlier of the eastern Ogilvie Mountains (fig. S2). Evidence for grounded ice is provided by glacial push structures and soft-sedimentary deformation (fig. S2). The UMHG and the iron-rich unit 2 of the Upper Tindir Group in the western Ogilvie Mountains are correlative with the Sturtian-age Sayunei Formation of the Rapitan Group in the Mackenzie Mountains (*13*, *14*). The broad distribution of massive diamictite and stratified glacial deposits with coarse-grained ice-rafted debris in the Rapitan Group of the Northwest Territories (*14*, *15*) and its correlatives in Yukon and Alaska (fig. S3) suggests the proximity to a marine ice grounding line.

The MHVC previously was dated with multigrain U-Pb ID-TIMS analyses at 751^{+26}_{-18} Ma (*16*). We collected a quartz-phyric rhyolite of member D from the same site (fig. S1) that yielded a weighted mean ^{206}Pb-^{238}U zircon date of 717.43 ± 0.14 Ma, interpreted as the eruptive age of this unit (fig. S4). This ~33-million-year age revision is likely due to inherited cores in the previously dated multigrain zircon fractions, resulting in an artificially old age. Below the MHVC, a green, flinty, bedded tuff within allodapic dolostone beds near the top of unit PF1a of the Fifteenmile Group yielded a weighted mean ^{206}Pb-^{238}U zircon date of 811.51 ± 0.25 Ma, interpreted as the time of deposition (fig. S4). Above the MHVC, a green to pink brecciated tuff within glacial deposits of the UMHG yielded a weighted mean ^{206}Pb-^{238}U zircon date of 716.47 ± 0.24 Ma, interpreted as the deposition age (fig. S4).

In the Minto inlier on Victoria Island (fig. S1), zircon and baddeleyite from gabbroic sills and dikes from the Franklin LIP previously were dated at 723^{+4}_{-2} Ma and 718 ± 2 Ma (*17*). Our Franklin LIP sample is from a coarse-grained diabase sill, >20 m thick, intruding the middle of the Wynniatt Formation (*18*), which yielded a weighted mean ^{206}Pb-^{238}U baddeleyite date of 716.33 ± 0.54 Ma (fig. S4). We interpret the apparent discrepancy between our result and previous ages (*17*) as an artifact of comparing upper intercept and ^{207}Pb/^{206}Pb dates with our ^{206}Pb/^{238}U dates in light of recently recognized systematic error in the U decay constant ratio (*11*, *19*).

This geochronology reveals the >3000-km extent of the Franklin LIP (~716.5 Ma), from the Yukon-Alaska border to Ellesmere Island, where mafic dikes have been dated at 716 ± 1 Ma (*20*). Although no evidence for prevolcanic extension and rifting is present on Victoria Island (*21*), conspicuous normal faulting exists within the LMHG and the lower suite of the MHVC (*12*), temporally linking the Franklin LIP to extension on the northwestern Laurentian margin.

Several paleomagnetic studies on strongly magnetized mafic dikes, sills, and lavas have demonstrated that the Franklin LIP was emplaced when northwestern Laurentia was within 10° of the equator (*6*, *22*, *23*). The dated sill and the sediments that it intrudes on Victoria Island yield paleomagnetic data that are consistent with the previous low-latitude results (*18*). The age of the tuff interbedded with glacial deposits of the UMHC, 716.47 ± 0.24 Ma, is indistinguishable from the date of the Franklin LIP, 716.33 ± 0.54 Ma. Therefore, grounded ice was present on the northwestern margin of Laurentia at ~716.5 Ma, when it was situated at equatorial latitudes. Climate models have long predicted that if the ice line advanced equatorward of ~30° to 40°, an ice-albedo feedback would drive global glaciation (*24*, *25*). Thus, we conclude that the Sturtian glaciation at ~716.5 Ma was global in nature.

It is uncertain whether the Sturtian glacial epoch consisted of one discrete glaciation that lasted tens of millions of years, or multiple glacial episodes including the low-latitude glaciation at ~716.5 Ma. Prior to this study, minimum and maximum age constraints on the Sturtian glaciation were provided by a sample from South China dated at 662.9 ± 4.3 Ma (*26*) and the Leger Granite in Oman dated at 726 ± 1 Ma (*27*), respectively. We suggest that our age from member D of the MHVC, 717.43 ± 0.14 Ma, provides a maximum age constraint on the low-latitude Sturtian glaciation not only because glacial deposits have not been identified below member D, but also because models suggest extremely rapid ice advance once ice is below 30° latitude (*24*, *25*), such that glaciation of equatorial latitudes should be synchronous around the globe. Evidence for a pre-Sturtian glaciation at ~750 Ma (referred to as the Kaigas glaciation) was reported in southern Namibia (*28*), Zambia (*29*), and northwestern China (*30*). However, at these localities the contact relationship of the purported glacial deposit with the dated unit and the glacial origin of the deposit are sus-

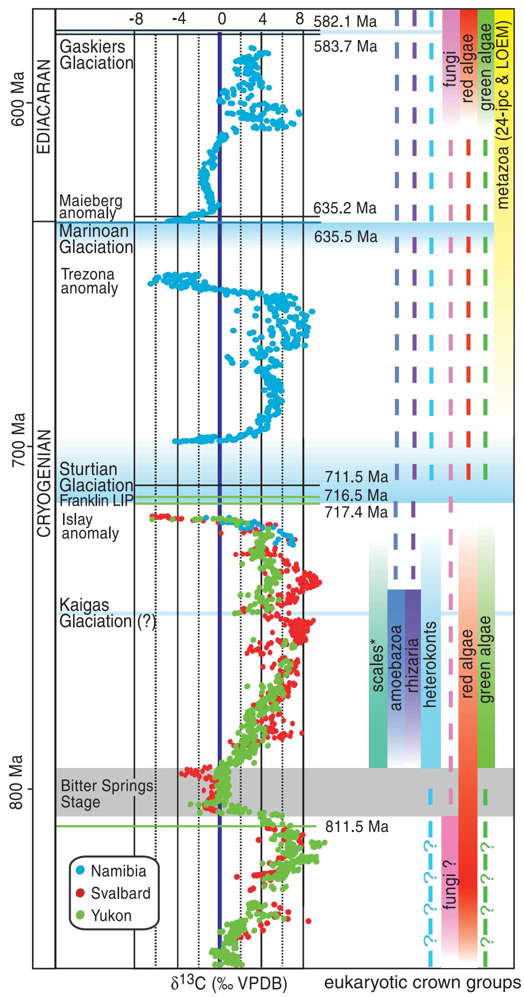

Fig. 2. Neoproterozoic composite carbonate δ^{13}C chemostratigraphy with U-Pb ID-TIMS ages that are directly linked to isotopic profiles (*11*). Bars indicate the time spans of fossil assemblages representing eukaryotic crown groups. Asterisks indicate fossil groups of uncertain taxonomic affinity. Bars faded upward reflect uncertainty in the minimum age constraint; bars faded downward reflect uncertainty in the maximum age constraint. Dashes represent the time span where a fossil record has not been identified but for which the eukaryotic group's presence is inferred from its occurrence in Ediacaran or Phanerozoic strata. Dashes with question marks indicate that earlier records have been proposed but the relationships between these fossils and the crown groups are uncertain.

pect (*10*). Moreover, because there are no robust paleolatitude constraints on these rocks, the Kaigas glaciation may have been regional in extent. Previous Sturtian synglacial constraints at ~685 Ma were reported from Idaho (*31*, *32*). However, these results have been questioned because the glacial nature of these deposits is uncertain, contacts between dated volcanic rocks and diamictites are tectonic, and repeated analyses have given different results (*10*). A ^{206}Pb-^{238}U ID-TIMS date of 711.52 ± 0.20 Ma was reported from volcaniclastic rocks interbedded with glacigenic deposits within the Ghubrah Formation in Oman (*27*). Thus, if the Ghubrah Formation is recording the same glacial episode as the UMHG, the Sturtian glaciation lasted a minimum of 5 million years.

Using a recalibrated and expanded $\delta^{13}C$ record, we can place the record of eukaryotic evolution in the context of geochemical perturbations and global glaciation (Fig. 2). The tuff dated at 811.5 Ma provides a maximum constraint on the Bitter Springs isotopic stage (*3*) and a useful benchmark for the calibration of early Neoproterozoic microfossil record. For instance, the chemostratigraphic position of the mineralized scale microfossils in the Lower Tindir Group of the western Ogilvie Mountains is above the Bitter Springs isotopic stage and below glacial deposits with banded iron formation that were previously correlated with the Rapitan Group (*13*). The Tindir microfossils are thus broadly coeval with complex microbiota described from the Chuar Formation in the Grand Canyon (older than 742 ± 6 Ma), the preglacial Beck Spring Formation of Death Valley, and the Svanbergfjellet Formation of Spitsbergen (*11*). Collectively, the calibration of these diverse microfossil records indicates that between the onset of the Bitter Springs isotopic stage (~811.5 Ma) and the Sturtian glaciation (~716.5 Ma), many major eukaryotic crown groups—members of Rhizaria, Amoebozoa, green and red algae, and vaucheriacean algae—had diverged and diversified. In contrast, the microfossil record between the Sturtian glaciation and the Marinoan glaciation (i.e., between ~716.5 and ~635 Ma) is depauperate; only simple acritarchs of unknown phylogenic affinity have been described (*4*, *11*). This apparent bottleneck might be due in part to poor preservation and limited sampling, and/or the survival of some groups as cryptic forms. It is clear that a diverse biosphere persisted through the Neoproterozoic glaciations (*4*), but the impact of global glaciation on eukaryotic evolution remains unresolved.

With high-precision ages directly tied to the stratigraphic record we can begin to address the mechanisms behind Neoproterozoic environmental change. The presence of the Islay $\delta^{13}C$ anomaly in the pre-Sturtian LMHG suggests a relationship between global carbon cycling and climate degradation (Figs. 1 and 2). Moreover, the synchrony among continental extension, the Franklin LIP, and the Sturtian glaciation is consistent with the hypothesis that the drawdown of CO_2 via rifting and weathering of the low-latitude Franklin basalts could have produced a climate state that was more susceptible to glaciation (*25*, *33*). However, even with the updated age constraints, it is unclear whether the bulk of the magmatism preceded or occurred during the glaciation.

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34. We thank the Yukon Geological Survey for assistance with logistics and helicopter support, T. Petach and S. Petersen for assistance in the field, and D. Pearce and H. Yntema for preparing samples. Supported by the Polar Continental Shelf Project and NSF Geobiology and Environmental Geochemistry Program grant EAR 0417422.

Supporting Online Material

www.sciencemag.org/cgi/content/full/327/5970/1241/DC1
Materials and Methods
Figs. S1 to S4
Tables S1 and S2
References

14 October 2009; accepted 11 December 2009
10.1126/science.1183325

The Role of Sulfuric Acid in Atmospheric Nucleation

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Nucleation is a fundamental step in atmospheric new-particle formation. However, laboratory experiments on nucleation have systematically failed to demonstrate sulfuric acid particle formation rates as high as those necessary to account for ambient atmospheric concentrations, and the role of sulfuric acid in atmospheric nucleation has remained a mystery. Here, we report measurements of new particles (with diameters of approximately 1.5 nanometers) observed immediately after their formation at atmospherically relevant sulfuric acid concentrations. Furthermore, we show that correlations between measured nucleation rates and sulfuric acid concentrations suggest that freshly formed particles contain one to two sulfuric acid molecules, a number consistent with assumptions that are based on atmospheric observations. Incorporation of these findings into global models should improve the understanding of the impact of secondary particle formation on climate.

Nucleation of particles in the atmosphere has been observed to be strongly dependent on the abundance of sulfuric acid (H_2SO_4) (*1*–*4*). Sulfur dioxide (SO_2), the precursor of H_2SO_4, has both natural and anthropogenic sources. Anthropogenic SO_2 emissions can have large indirect effects on climate if H_2SO_4 is responsible for atmospheric nucleation, but laboratory experiments have systematically failed to reproduce ambient new-particle formation rates as well as the nucleation rate dependence on the H_2SO_4 concentration (Table 1) (*5*–*15*).

PALEOCLIMATOLOGY

Snowball Earth Has Melted Back To a Profound Wintry Mix

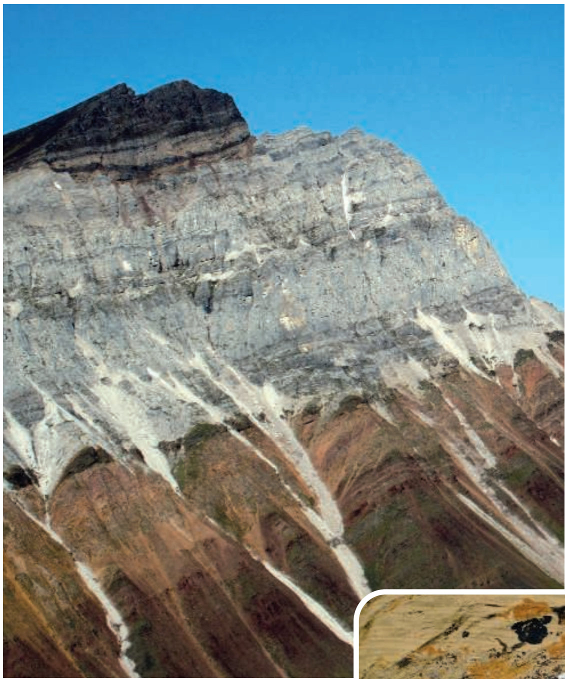
In 1998, a handful of geoscientists at Harvard University breathed new life into a daring idea: that Earth froze over from pole to pole more than a half-billion years ago, threatening life with extinction but perhaps prodding it to greater evolutionary heights (*Science*, 28 August 1998, p. 1342). On page 1241 of this issue, geoscientists report evidence that the tropics also hosted glaciers more than 100 million years before that supposed global freeze. Such low-latitude glaciation is a hallmark of so-called hard snowball Earth scenarios, in which a kilometer of ice sealed off the world ocean.

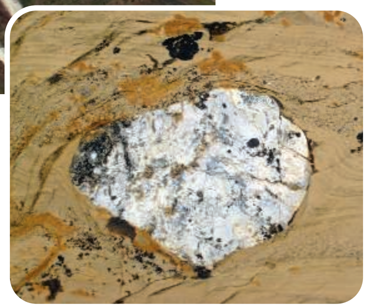
But despite the new work, the much-studied hypothesis has fallen on hard times. "In many people's minds, the hard snowball is dead," says geochemist Michael Arthur of Pennsylvania State University (PSU), University Park, who was not involved in the new work. Earth was profoundly cold in those geologically weird days, many agree—a "slushball" of a planet, perhaps. But sealed in ice? Unlikely.

The new contribution to the snowball debate comes from Harvard geologist Francis Macdonald and colleagues at Harvard and elsewhere. They dated volcanic ash layered within deposits of the so-called Sturtian glacial era to an age of 716.5 million years. That's the same age as rocks whose paleomagnetic record places them and the Sturtian glaciers in the tropics.

Researchers speculated about possible ancient tropical glaciers for several decades before geobiologist Joseph Kirschvink of the California Institute of Technology in Pasadena coined the term "snowball Earth" in 1992. But the hard-snowball concept gained ground only after geologist Paul Hoffman—then at Harvard University and now retired—and three colleagues boosted it in the 1998 *Science* paper. Drawing on simple climate modeling, the authors concluded that any ice that reached tropical latitudes during the Marinoan glaciation, about 650 million years ago, would not have stopped there. Instead, once the highly reflective ice covered enough area, a climatic feedback would inevitably drive the ice to the equator and create global glaciation: a hard snowball.

Some more-recent paleoclimate modeling, however, suggests that the leap from low-latitude glaciation to a hard snowball may be difficult or even impossible. "We can get ice on land," says climate modeler Mark Chandler of the Goddard Institute for Space Studies in New York City. "It's the ocean we can't freeze over." Model oceans can hold lots of heat and move it around in currents, frustrating a complete freeze-over, Chandler says. A few years ago, "the pattern was that the more sophisticated the model, the less likely you'd get a hard snowball result," he says. Discouraged, Chandler and others moved on to other projects.





Definitely chilly. Clear signs of glaciation, such as rocks dropped to the sea floor from icebergs (*inset*), show up in tropical deposits (dark peak).

Atmospheric physicist James Kasting of PSU now favors a slightly more modest "thin ice" snowball. He and climate modeler David Pollard of PSU have considered how a continent poleward of an inland sea might hold off thick ice intruding from higher latitudes and preserve small areas of thin ocean ice, thin enough to let sunlight through for marine plants. "We think the thin-ice solution satisfies all the constraints better than the other models."

But almost all geologists now reject any worldwide freeze, says geologist Philip Allen of Imperial College London. "When the snowball came up, the [geological] community was very open to it," he says. Now, "it's my impression that 90% of the geological community is quite hostile to the idea."

Allen and other geologists went to the field to study glacial deposits from about the time of the proposed Marinoan hard snowball. Instead of stagnation, the sediments recorded signs of water and ice in motion: ice moving, ocean currents flowing, and waves moving on an open sea. "We do not have a hard snowball Earth," says Allen. Hoffman hasn't disputed such interpretations, but he has argued that they could reflect conditions either just before or after a hard snowball.

Most geochemists aren't sold on a hard snowball either. Key to the Harvard group's argument was the contention that a bizarre chemical deposit found on the top of glacial deposits—the cap carbonate formation—could have formed after a glacial period only if the world ocean had been sealed off from the atmosphere for millions of years. Only rare cracks in the ice or open water maintained by volcanic hot spots kept the biota going, the group maintained. Geologist Alan Jay Kaufman of the University of Maryland, College Park, a co-author of the 1998 *Science* paper, has shifted his stance. After studying the isotopic records of carbon, strontium, and sulfur, he now supports the slushball view. The sulfur isotopes in particular, he says, suggest "that there was more than cracks in the ice."

Hoffman is unperturbed. Resistance to the hard snowball "is really typical of scientific controversy," he says. "The problem is the experts reach a quick judgment and dig themselves into a position." The idea of a recent ice age, he notes, took 40 years and a new generation of scientists to win acceptance in the 19th century. In his view, "the evidence [for a hard snowball] is getting stronger and stronger." He cites oxygen isotope findings published last year supporting the existence of extremely high atmospheric carbon dioxide concentrations predicted by the hard snowball. Still, Hoffman says, "I don't expect to live to see the conclusion on Snowball Earth, though I think I know how it will turn out."

–RICHARD A. KERR

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Published by AAAS