

References and Notes

1. J. F. Nye, *R. Soc. London Proc. Ser. A* **219**, 477 (1953); R. LeB. Hooke, *Rev. Geophys. Space Phys.* **19**, 664 (1981); C. J. van der Veen and I. M. Whillans, *J. Glaciol.* **36**, 324 (1990).
2. Examples include velocity variations occurring over months to weeks [R. LeB. Hooke, P. Calla, *et al.*, *J. Glaciol.* **35**, 235 (1989)] and days to hours [A. Iken and R. A. Bindschadler, *ibid.* **32**, 101 (1986)].
3. S. M. Hodge, *ibid.* **13**, 349 (1974); B. Kamb *et al.*, *J. Geophys. Res.* **99**, 15231 (1994); J. Harbor *et al.*, *Geology* **25**, 739 (1997).
4. A dense array of radio-echo sounding measurements were processed with three-dimensional migration techniques. Comparisons of these measurements with borehole observations suggest that the radar is accurate to within about 8.5 m (B. C. Welch, W. T. Pfeffer, J. T. Harper, N. F. Humphrey, *J. Glaciol.*, in press).
5. J. T. Harper and N. F. Humphrey, *Geology* **23**, 901 (1995).
6. M. F. Meier, *U.S. Geol. Surv. Prof. Pap.* 351 (1960); W. S. B. Paterson and J. C. Savage, *J. Geophys. Res.* **68**, 4537 (1963); C. F. Raymond, *J. Glaciol.* **10**, 55 (1971); R. LeB. Hooke, P. Holmlund, N. R. Iverson, *ibid.* **33**, 72 (1987) were all forced to smooth inclinometry data because of high levels of noise.
7. The instrument was constructed by Slope Indicator Canada, Ltd. (Vancouver, BC). Measurement errors associated with a prototype of this instrument are discussed by E. W. Blake and G. K. C. Clarke [*J. Glaciol.* **38**, 113 (1992)]. However, analysis of actual data from the instrument used suggests that instrument errors are slightly improved from manufacturer specifications [J. T. Harper, thesis, University of Wyoming (1997); S. V. Huzurbazar, unpublished material]. Additionally, the uniformity of the borehole walls enabled a high degree of repeatability for the measurements.
8. We follow the method of C. F. Raymond, *J. Glaciol.* **10**, 39 (1971).
9. We use a cubic spline function with an iterative scheme designed to minimize the curvature of the function between data points [I. C. Briggs, *Geophysics* **1974**, 39 (1974)]. This interpolation was tested extensively with synthetic data.
10. J. T. Harper, N. F. Humphrey, W. T. Pfeffer, B. C. Welch, *U.S. Army Cold Reg. Res. Eng. Lab. Spec. Rep.* 96-27 (1996), p. 41.
11. This measurement was made within the same reach and time of year as the deformation experiments, but during a subsequent year. Sliding and surface velocities were determined by continuous filming of the base of a borehole with concurrent surveying of velocity at the surface.
12. Funded by grants from NSF (OPP-9122966 to N.F.H. and OPP-9122916 to W.T.P.). Additional funding for computer visualization was provided by NSF's EPSCoR (Experimental Program to Stimulate Competitive Research) program (EPS9550477), through the University of Wyoming's Spatial Data and Visualization Center project. D. Bahr, B. Welch, and B. Raup all made significant contributions to portions of the work presented here.

16 April 1998; accepted 28 July 1998

# A Neoproterozoic Snowball Earth

Paul F. Hoffman,\* Alan J. Kaufman, Galen P. Halverson, Daniel P. Schrag

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). Post-glacial 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  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  excursions and the existence of carbonates immediately following glaciations.

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  $743 \pm 30$  Ma and at ~39°S at  $547 \pm 4$  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  $\delta^{13}\text{C}$  values, and both units are overlain by distinctive cap carbonates, recording negative  $\delta^{13}\text{C}$  excursions (10, 11).

The younger of the two glacial units (the Ghaub Formation) is represented by unstratified diamictites, 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 diamictites 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-

P. F. Hoffman, G. P. Halverson, D. P. Schrag, Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA. A. J. Kaufman, Department of Geology, University of Maryland, College Park, MD 20742, USA.

\*To whom correspondence should be addressed. E-mail: hoffman@eps.harvard.edu

REPORTS

tropical platform, consistent with a snowball glaciation.

We measured inorganic  $\delta^{13}\text{C}$  values of carbonate rocks that spanned the glacial interval from several sections (Fig. 2) (10, 11). In general,  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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 unconformity; 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  $\delta^{13}\text{C}$  downturns are known elsewhere on the Otavi platform (22) and on other continents (10, 11). The

overall negative  $\delta^{13}\text{C}$  excursion occupies ~500 m of the platformal carbonate section. Much of the lateral variance in  $\delta^{13}\text{C}$  curves between sections (Fig. 2) can be accounted for in terms of subglacial erosional truncation and slope progradation.

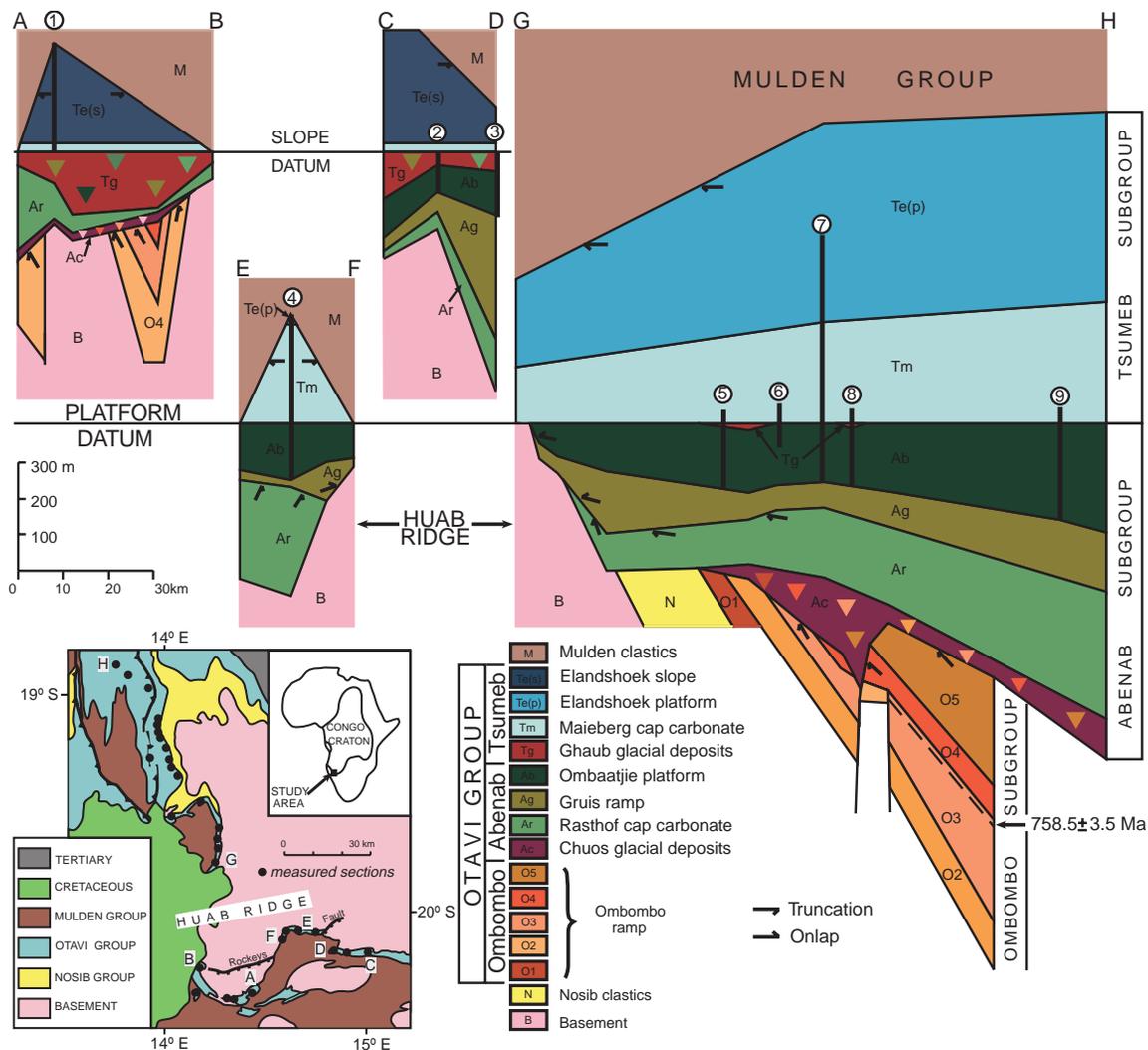
Constraints on the duration of the isotopic excursion from a model of thermally driven subsidence of the platform (15) allow a maximum subsidence rate of 14 m/My (equivalent to a maximum carbonate accumulation rate, with sediment loading, of ~50 m/My). The  $\delta^{13}\text{C}$  excursion begins and 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  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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<sup>5</sup> 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).





which would lower the release rates of volcanic CO<sub>2</sub> 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<sub>2</sub> from mid-ocean ridge volcanism, although this flux of CO<sub>2</sub> [ $\sim 0.83 \times 10^{12}$  mol/year (24)] in the modern ocean is smaller than the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>, and a strong hydrologic cycle. Reducing atmospheric CO<sub>2</sub> 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<sup>3</sup> 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<sub>3</sub> 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  $\delta^{13}\text{C}$  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).

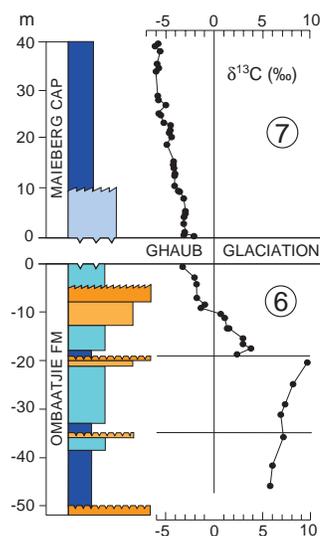
The  $\delta^{13}\text{C}$  values in the Otavi Group are consistent with the snowball hypothesis. The initial decrease in  $\delta^{13}\text{C}$  values before the glaciation on the tropical platform implies a decrease in productivity relative to carbonate deposition, perhaps because of colder conditions ( $-20$  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  $\delta^{13}\text{C}$  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<sub>2</sub> would raise the  $\delta^{13}\text{C}$  of dissolved inorganic carbon in the surface ocean, which is dominated by the large atmospheric reservoir. As the amount of CO<sub>2</sub> in the atmosphere subsided, the continued uptake of carbon with higher  $\delta^{13}\text{C}$  values would drive atmospheric  $\delta^{13}\text{C}$  down through Rayleigh distillation, while the ocean would read  $-5$  per mil because of mass balance and mixing with the deep ocean. Thus, the  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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<sub>2</sub> 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<sub>2</sub> 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  $\delta^{13}\text{C}$

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  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  data. An abrupt downturn in  $\delta^{13}\text{C}$  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).

References and Notes

1. A. H. Knoll, *Sci. Am.* **265**, 64 (October 1991); ——— and M. R. Walter, *Nature* **356**, 673 (1992); A. H. Knoll, in *Origin and Evolution of the Metazoa*, J. H. Lipps and P. W. Signor, Eds. (Plenum, New York, 1992), pp. 53–84.
2. G. C. Bond, P. A. Nickeson, M. A. Kominz, *Earth Planet. Sci. Lett.* **70**, 325 (1984); P. F. Hoffman, *Science* **252**, 1409 (1991); I. W. D. Dalziel, *Annu. Rev. Earth Planet. Sci.* **20**, 501 (1992); C. M. Powell, Z. X. Li, M. W. McElhinny, J. G. Meert, G. K. Park, *Geology* **21**, 889 (1993); A. B. Weil, R. Van der Voo, C. Mac Niocall, J. G. Meert, *Earth Planet. Sci. Lett.* **154**, 13 (1998).
3. W. B. Harland, *Geol. Rundsch.* **54**, 45 (1964).
4. M. J. Hambrey and W. B. Harland, *Earth's Pre-Pleistocene Glacial Record* (Cambridge Univ. Press, Cambridge, 1981).
5. G. M. Young, *Geology* **23**, 153 (1995).
6. J. D. Roberts, *J. Geol.* **84**, 47 (1974); J. D. Aitken, *Bull. Geol. Surv. Can.* **404**, 1 (1991); I. J. Fairchild, in *Sedimentology Review 1*, V. P. Wright, Ed. (Blackwell, Oxford, 1993), pp. 1–16.
7. M. J. Kennedy, *J. Sediment. Res.* **66**, 1050 (1996).
8. Although Phanerozoic cool-water skeletal carbonates are not uncommon [N. P. James and J. A. D. Clarke, *Cool-Water Carbonates* (Society for Sedimentary Geology, Tulsa, OK, 1997)], the inverse solubility of CaCO<sub>3</sub> with temperature mitigates against such an origin for inorganic carbonates with abundant aragonitic sea-floor cements, which are typical of Neoproterozoic postglacial cap carbonates [T. M. Peryt *et al.*, *Sedimentology* **37**, 279 (1990); (7)].
9. H. Martin, *The Precambrian Geology of South West Africa and Namaqualand* (Precambrian Research Unit, University of Cape Town, Cape Town, South Africa, 1965); J. V. N. Dorr Jr., *Econ. Geol.* **68**, 1005 (1973); G. M. Young, *Precambrian Res.* **3**, 137 (1976).
10. A. H. Knoll, J. M. Hayes, A. J. Kaufman, K. Swett, I. B. Lambert, *Nature* **321**, 832 (1986); A. J. Kaufman, J. M. Hayes, A. H. Knoll, G. J. B. Germs, *Precambrian Res.* **49**, 301 (1991); A. J. Kaufman and A. H. Knoll, *ibid.* **73**, 27 (1995). The carbon isotopic compositions of carbonates were determined according to procedures described in these references and in (11) and were reported as δ<sup>13</sup>C values relative to Vienna Pee Dee belemnite in units per mil defined as [(R<sub>sample</sub>/R<sub>standard</sub>) - 1] × 10<sup>3</sup>, where R = <sup>13</sup>C/<sup>12</sup>C.
11. A. J. Kaufman, A. H. Knoll, G. M. Narbonne, *Proc. Natl. Acad. Sci. U.S.A.* **94**, 6600 (1997).
12. R. Buick, D. J. Des Marais, A. H. Knoll, *Chem. Geol.* **123**, 153 (1995); L. C. Kah and J. K. Bartley, *Geol. Soc. Am. Abstr. Programs* **29**, 115 (1997); M. D. Brasier and J. F. Lindsay, *Geology* **26**, 555 (1998).
13. W. T. Holsler, in *Patterns of Change in Earth Evolution*, H. D. Holland and A. F. Trendall, Eds. (Springer-Verlag, Berlin, 1984), pp. 123–143.
14. P. W. Schmidt and G. E. Williams, *Earth Planet. Sci. Lett.* **134**, 107 (1995); L. E. Sohl, *Geol. Soc. Am. Abstr. Programs* **29**, 195 (1997); J. K. Park, *Can. J. Earth Sci.* **34**, 34 (1997).
15. P. F. Hoffman, A. J. Kaufman, G. P. Halverson, *GSA Today* **8**(5), 1 (1998).
16. M. R. Rampino, *J. Geol.* **102**, 439 (1994); G. E. Williams, *Geol. Mag.* **112**, 441 (1975); *Earth Sci. Rev.* **34**, 1 (1993).
17. J. L. Kirschvink [in *The Proterozoic Biosphere*, J. W. Schopf and C. Klein, Eds. (Cambridge Univ. Press, New

- York, 1992), pp. 51–52] extended an idea originally proposed by W. B. Harland (3).
18. R. M. Miller, in *African Basins*, vol. 3 of *Sedimentary Basins of the World*, R. C. Selley, Ed. (Elsevier, Amsterdam, 1997), pp. 237–268.
19. K. H. Hoffmann and A. R. Prave, *Communs. Geol. Surv. Namibia* **11**, 47 (1996).
20. J. G. Meert, R. Van der Voo, S. Ayub, *Precambrian Res.* **74**, 225 (1995); J. G. Meert and R. Van der Voo, *J. Geol.* **104**, 131 (1996).
21. Discussions of diagenesis in Neoproterozoic carbonates and descriptions of methods for screening samples before isotopic analysis are contained in (10) and (11).
22. M. J. Kennedy, A. R. Prave, K. H. Hoffmann, *Geol. Soc. Am. Abstr. Programs* **29**, 196 (1997).
23. L. R. Kump, *Geology* **19**, 299 (1991).
24. D. J. Des Marais and J. G. Moore, *Earth Planet. Sci. Lett.* **69**, 43 (1984).
25. K. Caldeira and J. F. Kasting, *Nature* **359**, 226 (1992). The time required to achieve meltback would be less if the ice surface became darkened by volcanic ash. However, the effect of ash accumulation would be countered by hoarfrost formation that originated from volcanic outgassed H<sub>2</sub>O. Caldeira and Kasting reported the possibility of irreversible icehouse conditions due to the formation of CO<sub>2</sub> clouds, as did Kirschvink (17), but it now appears that cooling actually may be limited by CO<sub>2</sub> clouds [F. Forget and R. T. Pierrehumbert, *Science* **278**, 1273 (1997)].
26. S. N. Williams, S. J. Schaefer, V. Calvache, M. D. Lopez, *Geochim. Cosmochim. Acta* **36**, 1765 (1992).
27. K. Caldeira, *Geology* **19**, 204 (1991).
28. H. Elderfield and A. Schultz, *Annu. Rev. Earth Planet. Sci.* **24**, 191 (1996); R. E. McDuff and J. M. Gieskes, *Earth Planet. Sci. Lett.* **33**, 1 (1976).
29. J. W. Morse and M. L. Bender, *Chem. Geol.* **82**, 265 (1990).
30. Sea-floor crystal fans, pseudomorphic after aragonite (not ikaite) and reeflike in overall construction, occur locally in the Maieberg cap carbonate (G. Soffer, personal communication).
31. Analysis of tidal rhythmites indicates ~400 solar days in the late Neoproterozoic year [G. E. Williams, *J. Phys. Earth* **38**, 475 (1990); C. P. Sonett, E. P. Kvale, A. Zakharian, M. A. Chan, T. M. Demko, *Science* **273**, 100 (1996)].

32. J. P. Grotzinger and A. H. Knoll, *Palaio* **10**, 578 (1995); A. H. Knoll, R. K. Bambach, D. E. Canfield, J. P. Grotzinger, *Science* **273**, 452 (1996).
33. H. G. Marshall, J. C. G. Walker, W. R. Kuhn, *J. Geophys. Res.* **93**, 791 (1988); W. W. Hay, E. J. Barron, S. L. Thompson, *J. Geol. Soc. London* **147**, 749 (1990); T. J. Crowley and S. K. Baum, *J. Geophys. Res.* **98**, 16723 (1993).
34. J. I. Hedges and R. G. Keil, *Mar. Chem.* **49**, 81 (1995).
35. V. A. Melezhik and A. E. Fallick, *Mineral. Mag.* **58A**, 593 (1994); D. A. Evans, N. J. Beukes, J. L. Kirschvink, *Nature* **386**, 262 (1997).
36. P. Van Cappellen and E. D. Ingall, *Paleoceanography* **9**, 677 (1994).
37. D. E. Canfield and A. Teske, *Nature* **382**, 127 (1996); S. J. Carpenter and K. C. Lohmann, *Geochim. Cosmochim. Acta* **61**, 4831 (1997).
38. G. Vidal and M. Moczydlowska-Vidal, *Paleobiology* **23**, 230 (1997); A. H. Knoll, *Proc. Natl. Acad. Sci. U.S.A.* **91**, 6743 (1994).
39. W. J. Green and E. I. Friedmann, Eds., *Physical and Biogeochemical Processes in Antarctic Lakes*, vol. 59 of *Antarctic Research Series* (American Geophysical Union, Washington, DC, 1993); K. H. Nealson, *J. Geophys. Res.* **102**, 23675 (1997).
40. A. H. Knoll, *Science* **256**, 622 (1992).
41. H. L. Carson, *Annu. Rev. Genet.* **21**, 405 (1987); K. J. Niklas, *The Evolutionary Biology of Plants* (Univ. of Chicago Press, Chicago, 1997).
42. H. J. Hofmann, G. M. Narbonne, J. D. Aitken, *Geology* **18**, 1199 (1990).
43. We thank S. Bowring, J. Edmond, B. Farrell, M. Delaney, J. Grotzinger, A. Knoll, J. Marshall, M. McElroy, and P. Myrow for discussions. B. Holtzman, G. Hu, A. Maloof, A. Prave, G. Soffer, and D. Sumner contributed to fieldwork. The manuscript benefited from comments by K. Caldeira, L. Derry, D. Erwin, L. Kump, and an anonymous reviewer. This work was supported by NSF grants EAR 95-06769, EAR 95-10339, EAR 96-30928, EAR 96-14070, and OCE 97-33688; the National Sciences and Engineering Research Council of Canada; the Canadian Institute of Advanced Research; Harvard University; the University of Maryland; and the Geological Survey of Namibia.

21 April 1998; accepted 21 July 1998

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

T. Peter Rakitzis, S. Alex Kandel, Andrew J. Alexander, Zee Hwan Kim, Richard N. Zare\*

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