# Reports

# Antiferromagnetism in Pressure-Amorphized $Fe_2SiO_4$

M. B. KRUGER,* R. JEANLOZ, M. P. PASTERNAK,† R. D. TAYLOR,
B. S. SNYDER,‡ A. M. STACY, S. R. BOHLEN

**Amorphous $Fe_2SiO_4$ synthesized at elevated pressures exhibits a Néel transition at a temperature identical to that observed in the crystalline form, $T_N$ = 65 (±2) kelvin at zero pressure. This behavior contrasts sharply with observations on other disordered systems, such as spin glasses, which characteristically exhibit strong "frustration" of the spins and consequent marked suppression of the Néel transition.**

Amorphous materials lack the long-range order of crystal structures (*1*) but can exhibit ferromagnetic ordering (*2, 3*). Yet oxides, from which amorphous materials (glasses) have classically been made, often exhibit antiferromagnetism in the crystalline state. Although much effort has gone into their study, there has been no report to date of glasses that are clearly antiferromagnetic (*4, 5*). Even a small amount of disordering is thought to lead to "frustration," arising when it is geometrically impossible to satisfy all antiferromagnetic interactions simultaneously (*6*).

Frustration has been extensively examined in spin glasses, and it typically leads to a drastic lowering or disappearance of the antiferromagnetic ordering (Néel) temperature (*5, 7*). Indeed, spin frustration is thought to preclude true antiferromagnetism in amorphous solids (*5*). We show here that amorphous $Fe_2SiO_4$ produced at high pressures exhibits antiferromagnetic ordering that is similar to the antiferromagnetism of crystalline $Fe_2SiO_4$ fayalite. The presence of cooperative antiferromagnetic order reveals much about the glass at the microscopic level.

Our samples of $Fe_2SiO_4$ have been converted to a glassy state by pressure-induced amorphization rather than by the more conventional approach of rapid quenching from the melt (*8*). Crystalline fayalite amorphizes, upon compression to pressures exceeding 40 GPa at 300 K (*9*), and we have verified that our samples remained amorphous throughout the entire study (*10*). One aspect of using pressure-amorphized material is that conventional glasses, which are quenched from the melt, can contain microcrystalline regions and other heterogeneities caused by partial unmixing upon cooling. Such heterogeneities have plagued earlier studies of antiferromagnetism in glasses, rendering the results ambiguous (*4, 11*). In contrast, pressure-induced amorphization is less subject to unmixing because there is no thermal cycling: during preparation, the sample is always kept at kinetically low temperatures (*8*).

The magnetic susceptibilities of polycrystalline fayalite (the starting material) and of pressure-amorphized $Fe_2SiO_4$ are shown in Fig. 1 (*12*). The temperature-dependent results for the crystalline sample compare favorably with earlier results, satisfactorily reproducing both the Néel transition at $T_N$ = 65 (±2) K and a second apparent transition at $T' \sim 23$ K. For the polycrystalline samples the feature in the susceptibility at 23 K is not due to a magnetic-ordering transition but is an artifact of summing the susceptibility in the *a*, *b*, and *c* crystallographic directions (*13, 14*). At higher temperatures (>65 K), our crystalline sample behaves as a Curie-Weiss paramagnet with an effective magnetic moment (expressed in terms of the Bohr magneton, $\mu_B$) of $\mu_{eff}$ = 6.9 (±0.1) $\mu_B$ and a Weiss constant of $\theta = -99$ (±1) K (*15*).

The magnetic susceptibility of pressure-amorphized $Fe_2SiO_4$ is similar to that of crystalline fayalite, displaying the transitions at 64 (±2) and 23 (±2) K. Within our resolution, the Néel transition is no broader than that of the crystalline material, and above $T_N$ Curie-Weiss behavior is evident with $\theta = -94$ (±1) K and $\mu_{eff}$ = 4.1 (±0.3) $\mu_B$ (*16*). The sign of the Weiss constant ($\theta < 0$) is significant in proving that the magnetic interactions in the amorphous material are antiferromagnetic.

To confirm these results, we collected Mössbauer spectra of crystalline and pressure-amorphized $Fe_2SiO_4$ as a function of temperature (*17*). The room-temperature spectra of the crystalline and amorphous samples are clearly distinguishable (Fig. 2). In agreement with earlier studies, both sites in the polycrystalline sample were found to order antiferromagnetically, as evidenced by the appearance of hyperfine splitting at 65 K, with no transition at 23 K. The results for the pressure-amorphized sample, summarized in Fig. 3, clearly show that magnetic ordering sets in at the identical temperature for the amorphous material, 65 (±3) K,

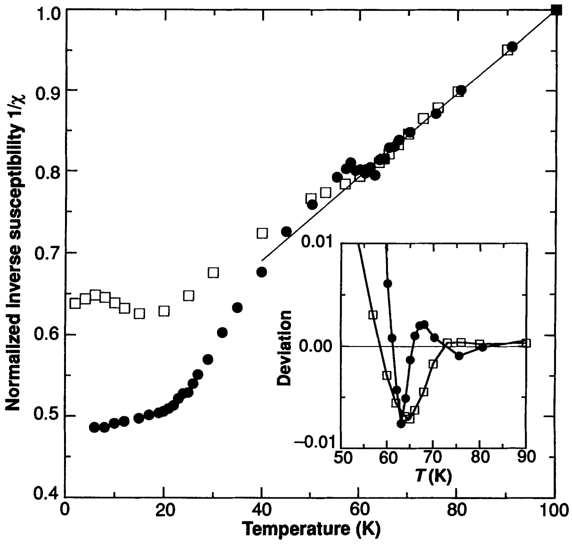


**Fig. 1.** Inverses of the magnetic susceptibilities (χ) are shown as a function of temperature for polycrystalline fayalite (open squares) and pressure-amorphized $Fe_2SiO_4$ (filled circles). The temperature is determined to 0.1 K, and the data are shown relative to the value of 1/χ at 100 K (*15, 16*). The pressure-amorphized sample was in a magnetic field of 30 kOe, and the polycrystalline sample was in a field of 50 kOe. The straight line is a least squares fit of 1/χ versus *T* for temperatures above $T_N$, confirming Curie-Weiss behavior in the paramagnetic regime ($\chi = C/(T - T_N)$, with *C* being a constant). The deviation of the observed 1/χ from the Curie-Weiss fit near $T_N$ is given in the inset (values have been interpolated and smoothed identically for both samples; consequently, temperatures are averaged over ~2 K). Both samples exhibit a Néel transition at $T_N$ ~65 K. The transition (*T'*) near 23 K in the polycrystalline sample is an artifact (*13, 14*), whereas it is a magnetic transition for the pressure-amorphized sample.

---

M. B. Kruger, Department of Physics, University of California, Berkeley, CA 94720.
R. Jeanloz, Department of Geology and Geophysics, University of California, Berkeley, CA 94720.
M. P. Pasternak and R. D. Taylor, Physics Division, Los Alamos National Laboratory, Los Alamos, NM 87545.
B. S. Snyder and A. M. Stacy, Department of Chemistry, University of California, Berkeley, CA 94720.
S. R. Bohlen, U.S. Geological Survey, Menlo Park, CA 94025.

---

*To whom correspondence should be addressed.
†Permanent address: School of Physics and Astronomy, Tel-Aviv University, Ramat Aviv 69978, Israel.
‡Present address: Rohm and Haas, Springhouse, PA 19477.

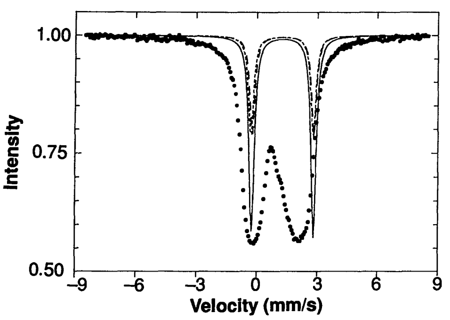


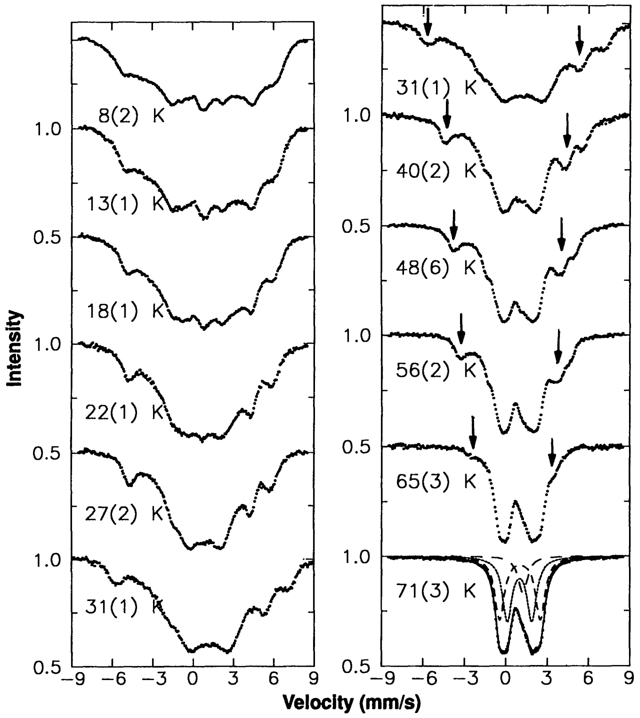
**Fig. 2.** Mössbauer spectra of $^{57}Fe_2SiO_4$ at 300 K. The points are the spectrum from the pressure-amorphized sample, and the superimposed solid line corresponds to the crystalline material fit with two doublets (shown as dashed lines).

as for crystalline fayalite (*18*). However, in contrast to the crystalline material, for the pressure-amorphized material only one of two sites orders at 65 K. The Mössbauer spectra show that the second site orders at ~28 K, the temperature of the second transition observed in the susceptibility of the amorphous material (Fig. 3). As the two materials are distinguishable both by Mössbauer and by susceptibility measurements (*16*), we believe that there is no possibility of our amorphous sample being contaminated by crystalline fayalite (*19*).

For the crystalline material, both M1 and M2 sites order at the same temperature (65 K) (*13*), whereas for the pressure-amorphized sample one site orders at 65 K and the other at 28 K. In contrast, previous studies of glasses with antiferromagnetic interactions (for example, with antiferromagnetic crystalline equivalents) have revealed that either there is no magnetic ordering over the observed temperature range (*4*, *5*) or the Néel temperature is significantly decreased by the loss of structural order (*20*). The reduction of the Néel temperature is interpreted as being due to severe frustration, with the frozen-in magnetic order actually being speromagnetic rather than antiferromagnetic (*5*). Thus, we take the fact that the Néel temperature of $Fe_2SiO_4$ is unaffected by the loss of long-range crystalline order to imply that, for one class of sites, the magnetically ordered state is antiferromagnetic rather than frustrated and speromagnetic. The large decrease in the ordering temperature (65 K → 28 K) of one of the sites is interpreted as indicating that these sites experience a certain degree of frustration, as would be expected for a noncrystalline solid.

Therefore, the final picture of pressure-amorphized $Fe_2SiO_4$ is unique among glasses. One class of sites orders antiferromagnetically, the magnetic ordering apparently being undisturbed by the structural disorder. In contrast, the second class of sites is magnetically sensitive to the geometrical disorder of the structure.

**Fig. 3.** Spectra of the pressure-amorphized sample show evidence for magnetic ordering of one site at 65 (±3) K, with the other site ordering below ~28 K. Upon magnetic ordering the spectrum exhibits hyperfine splittings indicated by the arrows. A fit of one singlet (long-dashed line) and two doublets (dashed and dotted lines) to the paramagnetic spectrum of the amorphous sample is indicated by the solid line in the 71 K spectrum.



As the M1-M2 interactions occur over distances of 0.33 to 0.37 nm in the crystal, for sites 1 to 5 and 3 to 5, respectively (*13*, *14*), we deduce that spin correlation lengths of at least 0.7 to 1.1 nm (two to three transition-metal coordination shells) are present in order to yield the observed anti-ferromagnetic behavior of amorphous $Fe_2SiO_4$. The relatively large size of the unit cell of fayalite ($a$ = 0.482 nm, $b$ = 1.047 nm, $c$ = 0.610 nm) allows such correlation lengths to be accommodated within a block of only eight unit cells, two unit cells on each side, and the longest correlation length across such a block corresponds to the seventh or eighth transition-metal coordination shell (*14*).

In examining our specimens by x-ray diffraction, we can only place a limit of ~2 to 3 nm on the maximum dimension of any crystalline domains that might exist within the amorphous samples (*21*). This result, which is limited by the small size of our specimens, is sufficient to prove that none of our amorphous $Fe_2SiO_4$ was recrystallized (*10*). We emphasize, however, that previous studies of the pressure-amorphized $Fe_2SiO_4$ reveal it to be a true glass (rather than a nanocrystalline material, for example), with structural correlation lengths estimated to be less than 2 nm (*9*). The spin correlation length is therefore likely to be less than 2 nm, and, in combination with the arguments given above, we estimate it to be ~1.5 (±0.5) nm. A block of 24 unit cells (volume = 7.39 $nm^3$) accommodates such a correlation length, the average and maximum numbers of transition-metal coordination shells being ~6 and ~9, respectively. These values are close to, but somewhat less than, the number of nearest neighbor shells that have been thought necessary for anti-ferromagnetic (versus speromagnetic) ordering (*5*).

## REFERENCES AND NOTES

1. J. M. Ziman, *Models of Disorder* (Cambridge Univ. Press, Cambridge, 1979); Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980); R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
2. A. I. Gubanov, *Fiz. Tverd. Tela* **2**, 502 (1960); S. Mader and A. S. Novick, *Appl. Phys. Lett.* **7**, 57 (1965); R. Hasegawa, R. C. O'Handley, L. E. Tanner, R. Ray, S. Kavesh, *Appl. Phys. Lett.* **29**, 219 (1976); R. C. O'Handley, R. Hasegawa, R. Ray, C.-P. Chou, *ibid.*, p. 330.
3. R. Hasegawa, *Phys. Rev. B* **3**, 1631 (1971).
4. T. Egami, O. A. Sacli, A. W. Simpson, A. L. Terry, F. A. Wedgewood, in *Amorphous Magnetism*, H. O. Hooper and A. M. de Graaf, Eds. (Plenum, New York, 1973), pp. 27–43; H. O. Hooper *et al.*, *ibid.*, pp. 47–62; L. K. Wilson, E. J. Friebele, D. L. Kinser, *ibid.*, pp. 65–74.
5. K. Moorjani and J. M. D. Coey, *Magnetic Glasses* (Elsevier, Amsterdam, 1984).
6. Spin frustration can occur even in crystalline solids, a simple example being the two-dimensional triangular lattice with antiferromagnetic interactions: if atoms A and B are nearest neighbors and are both nearest neighbors of C, A–B–C forms a triangle and only two out of the three atoms can be aligned antiparallel (for example, if A and B are both antiparallel to C, then A and B must be parallel).
7. D. Chowdhury, *Spin Glasses and Other Frustrated Systems* (Princeton Univ. Press, Princeton, NJ, 1986).
8. Pressure-induced amorphization is a well-established method of producing an amorphous material: the initially crystalline material is compressed to such high pressures that it becomes unstable and collapses to the disordered state [R. Jeanloz and Q. Williams, *Nature* **350**, 659 (1991)]. Temperatures must be

kept sufficiently low during compression that equilibrium transformations are blocked kinetically.

9. Q. Williams, E. Knittle, R. Reichlin, S. Martin, and R. Jeanloz [*J. Geophys. Res.* **95**, 21549 (1990)] and G. Richard and P. Richet [*Geophys. Res. Lett.* **17**, 2093 (1990)] demonstrated through a combination of x-ray diffraction, mid-infrared absorption spectroscopy, and transmission electron microscopy (TEM) that crystalline fayalite is transformed to a glass and not just crushed to a microcrystalline aggregate, upon room-temperature compression to pressures above 35 to 40 GPa. The TEM study demonstrated that amorphization was complete down to ~1 nm.
10. Samples were compressed at room temperature and to pressures >40 to 45 GPa with a gasketed Mao-Bell type diamond cell (*9*). In order to avoid contamination of the samples, no pressure medium was used. Also, different samples were prepared both with and without ruby being present for pressure calibration [see X. Li and R. Jeanloz, *Geophys. Res. Lett.* **14**, 1075 (1987)], but no difference was observed in our final results. Aliquots separated from our samples were examined by x-ray diffraction to determine that these were amorphized. We used the Debye-Scherrer method, with either filtered Cu $K_\alpha$ or monochromatized Mo $K_\alpha$ radiation, and mixed fine-grained Au with the sample to serve as an intensity standard [see M. B. Kruger and R. Jeanloz, *Science* **249**, 647 (1990); (*9*)]. By examining aliquots separated both before and after our magnetic measurements, we ensured that the samples were amorphous (that is, had not recrystallized) throughout the duration of our study.
11. F. A. Wedgwood and A. C. Wright, *J. Non-Cryst. Solids* **21**, 95 (1976).
12. The crystalline starting material is synthetic fayalite [H. Takei and S. Hosoya, in *High-Pressure Research in Geophysics*, S. Akimoto and M. H. Manghnani, Eds. (Center for Academic Publishing, Tokyo, 1982), p. 537] that has been used in numerous other studies (*9*). To verify our technique, the magnetic susceptibility of 94 (±2) μg of the crystalline sample, ground to a grain size of ~1 to 10 μm, was measured as a function of temperature. Measurements were then carried out on 34 (±5) μg of pressure-amorphized material, consisting of 18 samples that had been compressed in tungsten gaskets to over 40 GPa, and the results for the crystalline and pressure-amorphized materials are displayed in Fig. 1. All susceptibility measurements were made with a SHE superconducting quantum interference detector magnetometer operating over the temperature range 6 to 100 K. Susceptibility data were obtained at 1, 10, and 50 kOe for the polycrystalline sample, and at 20 and 30 kOe for the pressure-amorphized sample. The transition temperatures were unaffected by the different applied magnetic fields. The samples were loaded into a precalibrated container fabricated from an Al cylinder and lid, including a Kel-F (polychlorotrifluoroethylene) liner designed to minimize the contribution of the container to the measured moment of the sample. Thus, the resolution of our data is optimized by ensuring that the paramagnetism of the Al is nearly canceled by the diamagnetism of the Kel-F.
13. The structural and magnetic properties of crystalline fayalite are well known from a combination of x-ray diffraction, magnetic susceptibility, Mössbauer spectroscopy, and powder neutron diffraction measurements carried out as functions of temperature, the first three having been applied both to single-crystal and to polycrystalline samples (*14, 18*). The unit cell of fayalite is orthorhombic [*Pbnm*, *Z* (number of formula units per cell) = 4], containing eight $Fe^{2+}$ ions distributed over two crystallographically distinct sites. These are the M1 (4a) sites (numbered 1 through 4) with only a center of symmetry and the M2 (4c) sites (numbered 5 through 8) with local symmetry including a mirror plane. Thus, the Néel transition at 65 (±2) K is found to be caused by collinear antiferromagnetic ordering (parallel to the *b* crystallographic axis) of the moments on the M2 sites, along with a canted antiferromagnetic ordering of the moments on the M1 sites. In contrast, the apparent transition of crystalline fayalite at ~23 K is thought to be caused by the large anisotropy of the magnetic susceptibility, rather than by a change in magnetic ordering; specifically, the temperature dependence of the magnetization parallel to the *c* crystallographic axis changes rapidly below ~20 to 25 K (*14*). Both the canted M1 ordering and the anisotropy of the susceptibility below 65 K are due to the M1-M2 exchange interaction ($J_{15} - 2J_{35} > 0$) competing with the M1 single-ion anisotropy within the crystal.
14. H. D. Megaw, *Crystal Structures* (Saunders, Philadelphia, 1973); H. Fuess, O. Ballet, W. Lottermoser, *Adv. Phys. Geochem.* **7**, 185 (1988).
15. Our values deviate slightly from those reported by R. P. Santoro, R. E. Newnham, and S. J. Nomura [*Phys. Chem. Solids* **27**, 655 (1966)] for crystalline powders of fayalite, $\mu_{eff} = 6.03\ \mu_B$ and $\theta = -126$ K, but the discrepancy is not significant and probably results from differences in preferred orientation of the samples in the two studies. For comparison, single-crystal measurements yield Weiss constants of $\theta = -107$ K for the *a* and *b* crystallographic directions and −66 K for the *c* direction of fayalite [J. M. D. Coey and S. Ghose, *Adv. Phys. Geochem.* **7**, 162 (1988)]. Also, because of the extremely small size of our specimens, our values of $\mu_{eff}$ and $\theta$ are subject to additional uncertainties due to errors in sample mass (for example, unaccounted sample loss during handling) and to the possible presence of minor impurities (*16*).
16. The dominant source of error for our absolute values of magnetic susceptibilities, and the resulting paramagnetic moments, arises from the sample mass. The smaller moment in the amorphous state most likely arises from the quenching of the orbital contribution to the moment, thus decreasing the moment from $\mu = g[J(J + 1)]^{0.5} = 6.70\ \mu_B$ to $\mu = 2[S(S + 1)]^{0.5} = 4.9$ in reasonable agreement with our result.
17. We synthesized polycrystalline fayalite enriched in $^{57}Fe$, used as starting material for the Mössbauer studies, by heating the component oxides to 1173 K under controlled oxygen fugacity (Fe-FeO buffer) at 1.5 GPa pressure. This material was characterized by x-ray diffraction and Mössbauer spectroscopy, the results being in good agreement with previous work (*18*). Samples were then pressure-amorphized in gaskets made of Re and were examined by x-ray diffraction as described above (*10*).
18. See Coey and Ghose in (*15*); S. S. Hafner, J. Stanek, M. J. Stanek, *Phys. Chem. Solids* **51**, 203 (1990).
19. The paramagnetic ($T > T_N$) Mössbauer spectrum of crystalline $Fe_2SiO_4$ fayalite is characterized by two doublets, with isomer shifts (IS) relative to Fe, quadrupole splittings (QS), and line widths (LW) of: IS = 1.26 and 1.31 mm/s, QS = 3.09 and 3.06 mm/s, and LW = 0.33 and 0.33 mm/s at 71 K. We found that a singlet (IS = 1.22 mm/s, QS = 0, and LW = 0.84 mm/s) and two doublets (IS = 0.99 and 1.02 mm/s, QS = 1.73 and 2.95 mm/s, and LW = 0.84 and 0.84 mm/s) yield a good fit to our paramagnetic spectra of the amorphous phase.
20. J. J. Hauser, *Phys. Rev. B* **22**, 2554 (1980).
21. H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials* (Wiley, New York, ed. 2, 1974).

22. We thank G. E. Brown, M. E. Fischer, B. K. Godwal, E. Knittle, H. E. Lorenzana, and Q. Williams for helpful discussions. This work was supported by the University of California Institute of Geophysics and Planetary Physics (Los Alamos National Laboratory), the National Science Foundation, and Exxon Research and Engineering Company. A.M.S. was supported by the Sloan Foundation and the Dreyfus Foundation.

4 October 1991; accepted 23 November 1991

---

# Modeling 100,000-Year Climate Fluctuations in Pre-Pleistocene Time Series

THOMAS J. CROWLEY, KWANG-YUL KIM, JOHN G. MENGEL,
DAVID A. SHORT

**A number of pre-Pleistocene climate records exhibit significant fluctuations at the 100,000-year (100-ky) eccentricity period, before the time of such fluctuations in global ice volume. The origin of these fluctuations has been obscure. Results reported here from a modeling study suggest that such a response can occur over low-latitude land areas involved in monsoon fluctuations. The twice yearly passage of the sun across the equator and the seasonal timing of perihelion interact to increase both 100-ky and 400-ky power in the modeled temperature field. The magnitude of the temperature response is sufficiently large to leave an imprint on the geologic record, and simulated fluctuations resemble those found in records of Triassic lake levels.**

SINCE THE PUBLICATION OF THE HISTORIC Hays, Imbrie, and Shackleton paper in 1976 (*1*), a great deal of attention has been given to the origin of the dominant 100-ky orbital eccentricity signal in late Pleistocene time series of ice volume. Additional studies (*2*) demonstrated that 100-ky fluctuations also occur in other late Pleistocene climate series. Although most modeling studies have linked the 100-ky ice volume fluctuations to nonlinear interactions between the climate system and ice sheets (*3*), a puzzling dilemma arises from examination of climate time series from periods earlier than the late Pleistocene. Records from the Pliocene and early Pleistocene (~1.0 to 2.4 Ma, million years ago), Miocene (~15 Ma), Cretaceous (~100 Ma), and Triassic (~200 Ma) also indicate that 100-ky and sometimes 400-ky climate fluctuations were occurring, but either there is little evidence for the presence of extensive ice sheets during these times or the ice sheets were fluctuating at other dominant periods (*4*). Astronomical times series (*5*) indicate that the most important term in the series expansion for eccentricity is at 413 ky. Furthermore, many of the proxy records are from tropical regions,

---

T. J. Crowley and K.-Y. Kim, Applied Research Corporation, 305 Arguello Drive, College Station, TX 77840.
J. G. Mengel, Applied Research Corporation, 8201 Corporate Drive, Landover, MD 20785.
D. A. Short, Laboratory for Atmospheres, Code 913, National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, MD 20771.