film in Fig. 7, to grow it thicker and make it easier to handle.

These materials may have technological as well as fundamental implications. The hollow spheres, for instance, could be used as controlled drug-delivery systems. The membranes might be developed further for separation processes, where nanometer-scale pores are needed. From a more fundamental point of view, the process described here for structuring inorganic material might in a modified form be applicable to the formation of structured inorganic segments in living organisms. It is by now almost certain that interfaces play a crucial role in biomineralization (*18*), and the interplay of control on different length scales is certainly necessary to develop intricate structures such as diatoms.

REFERENCES AND NOTES

1. J. Israelachvili, *Colloids Surf. A* **91**, 1 (1994).
2. Q. Huo and G. Stucky, paper presented at the meeting of the Material Research Society, San Francisco, 7 to 11 April 1996.
3. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **359**, 710 (1992); J. S. Beck *et al.*, *J. Am. Chem. Soc.* **114**, 10834 (1992).
4. Q. Huo *et al.*, *Chem. Mater.* **6**, 1176 (1994).
5. Q. Huo *et al.*, *Nature* **368**, 317 (1994).
6. Q. Huo, R. Leon, P. M. Petroff, G. D. Stucky, *Science* **268**, 1324 (1995).
7. Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **8**, 1147 (1996).
8. A. Monnier *et al.*, *Science* **261**, 1299 (1993).
9. A. Firouzi *et al.*, *ibid.* **267**, 1138 (1995).
10. U. Ciesla *et al.*, *Chem. Commun.* **1994**, 1387 (1994); D. M. Antonelli and J. Y. Ying, *Angew. Chem. Int. Ed. Engl.* **34**, 2014 (1995).
11. To date, silica-base synthesis chemistry carried out above the isoelectric point of aqueous solutions of silica has not been successful for the silica composite coating of organic emulsions in water. For organic arrays supported by inorganic substrates [H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, G. A. Ozin, *Nature* **379**, 703 (1996)], surfactants at the air-water interface (G. Ozin, paper presented at the NATO Conference on Supramolecular Chemistry, Montreal, 17 to 20 May 1996), or organic liquid crystals [G. S. Attard, J. C. Glyde, C. G. Goltner, *Nature* **378**, 366 (1995)], only $S^+X^-I^+$ syntheses at a pH below the aqueous silica isoelectric point have been used.
12. The APM samples synthesized below the silica isoelectric point require a counter anion, generally a halide anion, for each surfactant molecule that is present. Terminal Si–O–groups are protonated so that the bulk compositions of M41S and APM materials made with the same surfactant starting materials are distinctly different in hydrogen and halide ion content. The ion-pair surfactants of the APM materials can be readily removed by washing with distilled water at ~70°C because the wall charge is neutral or slightly positive. Removal of surfactant from M41S samples requires ion exchange by refluxing with acidic ethanol because of the negatively charged terminal oxygen atoms. The ultimate periodic symmetry is determined in both cases by surfactant packing requirements, so that similar space groups and lattice symmetries are observed by x-ray diffraction and TEM imaging, but with different diffraction intensities. As pointed out by C. J. Brinker and G. W. Scherer [*J. Non-Cryst. Solids* **70**, 301 (1985)], APMs are prepared under conditions that give Huggins or chainlike polymerization, whereas M41S silica polymerization conditions lead to Einstein or clusterlike configurations with extensive cross-linking, so that different silica wall structures are expected. This contrast is evident in nitrogen sorption isotherm measurements, which show that APMs exhibit a sorption behavior different from that of M41S samples, with a step in the isotherm at appreciably lower p/p_0 values (p, pressure) than samples synthesized from alkaline media with a similar lattice spacing. These data and diffraction results show that the APM silica walls are effectively thicker than those of the corresponding M41S phases. Nevertheless, BET surface areas calculated for such samples can be a factor of 2 higher, indicating the presence of micropores or highly ruffled surfaces. Even taking into account the limitations of BET analysis for such materials, the difference in the values obtained indicates a major difference in the pore and wall structure of APM and MCM-41 materials.
13. D. Walsh, J. D. Hopwood, S. Mann, *Science* **264**, 1576 (1994).
14. The details of the morphology developed during such processes depend not only on the stirring rate but also on the type of stirrer used, the temperature, and the size of the reaction vessel. However, the trends reported in Fig. 1 are the same, although the numerical values of stirring rate to obtain certain morphologies might vary, depending on the other parameters.
15. S. Schacht, thesis, Universität Mainz (1995). Such siliceous fibers fall in the classification of potentially carcinogenic fibers and should thus be handled appropriately.
16. J. Kärger, private communication; in preparation.
17. Concentrations of chlorine in the product correspond to the values reported by Huo *et al.* (*6*) and are ~2 weight %.
18. C. M. Zaremba *et al.*, *Chem. Mater.* **8**, 679 (1996); G. Falini, S. Albeck, S. Weiner, L. Addadi, *Science* **271**, 67 (1996).

19. This research was supported by the Deutsches Forschungsgemeinschaft (Schu744/12-1), NATO (CRG 950169), NSF (DMR 95-20971, MCB 92-02775), and the Office of Naval Research (N00014-93-10584). We would like to thank S. Schunk, R. Schirach, C. Angelkort, and C. Zaremba for the SEM analyses.

22 April 1996; accepted 5 July 1996

Mongolian Tree Rings and 20th-Century Warming

Gordon C. Jacoby,* Rosanne D. D'Arrigo, Tsevegyn Davaajamts

A 450-year tree-ring width chronology of Siberian pine (*Pinus sibirica* Du Tour) growing at timberline (2450 meters) in the Tarvagatay Mountains in west central Mongolia shows wide annual growth rings for the recent century. Ecological site observations and comparisons with instrumental temperature records indicate that the ring widths of these trees are sensitive to annual temperature variations. Low-frequency variations in the Tarvagatay tree-ring record are similar to those in a reconstruction of Arctic annual temperatures, which is based on 20 tree-ring width series from northern North America, Scandinavia, and western Russia. The results indicate that recent warming is unusual relative to temperatures of the past 450 years.

Records covering a longer period of time than those that are available from instrumental measurements are essential to evaluation of the causes of climatic change, including possible anthropogenic influences on climate. Three-hundred-year annual temperature reconstructions for the Arctic (*1*) and Northern Hemisphere (*2*) based on high-latitude tree-ring data indicate that the warming during the past century seen in instrumental data (*3*) is unprecedented. However, tree rings usually reflect temperatures during the warm season, and reconstruction of annual temperatures is controversial (*4*). Records from other areas can complement the high-latitude data. The most appropriate locations are high-elevation tree-line sites where growth is also limited by temperature. During a field investigation in the summer of 1995, we sampled trees growing at timberline in the Tarvagatay Mountains of western central Mongolia (Fig. 1). Many trees in Mongolia's forests are old (300 to 500 years) and are undisturbed by human activity.

G. C. Jacoby and R. D. D'Arrigo, Tree-Ring Laboratory, Lamont-Doherty Earth Observatory, Palisades, NY 10964, USA.
T. Davaajamts, Institute of Botany, Mongolian Academy of Sciences, Ulaanbaatar 210351, Mongolia.

*To whom correspondence should be addressed.

Mongolia's climate is characterized by extreme continentality (*5*). It is dominated by the influence of the Siberian (Mongolian) high-pressure cell during the winter (Fig. 1). Rainfall occurs mainly in summer. Mean monthly temperatures in northern Mongolia are –30°C in January to 20°C in July. Daily temperatures range from –50°C to 40°C and can vary by as much as 30°C in 1 day (*6*).

The northern third of Mongolia is a montane forest-steppe zone (*7*). At lower elevations, the forests give way to grasslands or to the margins of the Gobi Desert in the south. Forests are most dense on northern shady slopes. In the high western Altai Mountains (Fig. 1), there are permanent snowfields and ice. The tree line is variously formed by Siberian pine (*Pinus sibirica* Du Tour), Siberian larch (*Larix sibirica* Ledebour), or mixed stands of these species. The most prevalent tree species is Siberian larch, with lesser amounts of spruce (*Picea*), pine

(*Pinus*), and fir (*Abies*) (*8*). Hardwoods include birch (*Betula*), willow (*Salix*), elm (*Ulmus*), poplar (*Populus*), and a halophyte, *Haloxylon ammodendron* (*8*). Several studies have shown that precipitation affects annual ring widths of Siberian larch in certain areas (*9*), and there are tree-ring data from near the northwestern border with Kazakhstan (*10*).

We sampled Siberian pine at a timberline site near a pass through the Tarvagatay Mountains (2400 to 2500 m elevation at 48°17.51'N and 98°55.87'E). Some Siberian larch is also present at this site. Siberian pine is widely distributed in central Siberia and extends southeastward into northern Mongolia along a narrow corridor (*11*). The Tarvagatay Mountains are the southernmost limit of this species. The trees were on a northerly slope. The oldest cores (*12*) sampled for both Siberian pine and larch were over 500 years old (Fig. 2A). In the field, the low-frequency ring-width patterns in these and other cores were readily recognizable as being similar to those of temperature-sensitive white spruce trees we have sampled at the latitudinal tree line in North America (*1*, *2*).

The sampling location is that of a typical tree-line site where temperature should be the factor that limits tree growth (*13*). The vegetation is more lush here than at some (drier) high-elevation sites in the United States. This difference indicates that precipitation should not be a growth-limiting factor. Many of the pines exhibit a strip-bark morphology and partial dieback of some upper limbs (both are features indicating stress). Some trees have more live branches on their south sides, indicating stress from northerly winds. We sampled living trees at timberline. Most of the trees are separated by 10 m or more. There was no evidence of fire or other disturbance, and there was abundant subfossil wood on the surface at the site.

We processed the samples into a chronology of ring-width indices (Fig. 2B). Cores were dated by means of basic dendrochronological techniques (*14*) and were standardized with only conservative negative-exponential or straight-line fits (*1*, *2*, *14*). The resulting tree-ring series extends from 1465 to 1994, but we truncated it at 1550 because there are few samples before that year. For recent centuries, the chronology includes about 35 cores from 25 trees (Fig. 2B).

We compared the Tarvagatay Pass chronology to instrumental temperature records. The nearest long-term individual station record is at Irkutsk, in Russia just to the north of the border with Mongolia (Fig. 1). This station is about 600 km from the site and at a much lower elevation (470 m). The record begins in 1820, although there are many missing values, and the more complete record starts in 1882 and is the primary basis for gridded temperature data for the region (*15*). Although we focus on the gridded data, which encompass the sampling site (45° to 50°N, 95° to 100°E)(*15*), almost identical results were found when the individual Irkutsk record (from 1882 to 1993) was used.

Previous research has shown that ring-width indices (*16*) from the northern and elevational treeline correlate with temperatures over an extended period, including the previous fall and current growth year (*17*). In our study, the chronology and mean monthly temperatures were best correlated over the dendroclimatic year (*13*, *14*) from the prior August through the current July. Seasonally averaged temperatures for the prior fall and current spring were better correlated with the ring-width indices than were those for either winter or summer. Significantly improved results (but for lower degrees of freedom) were found by

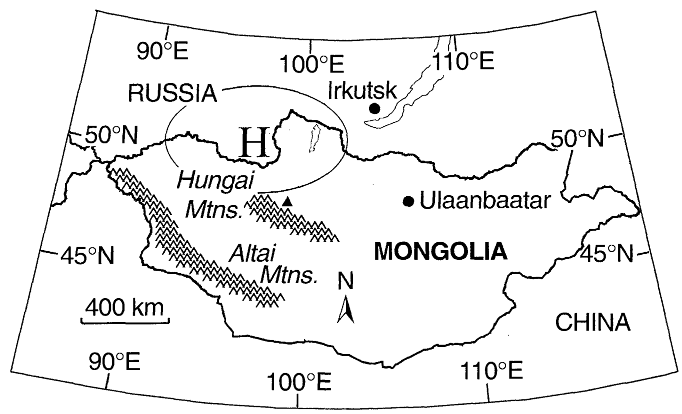
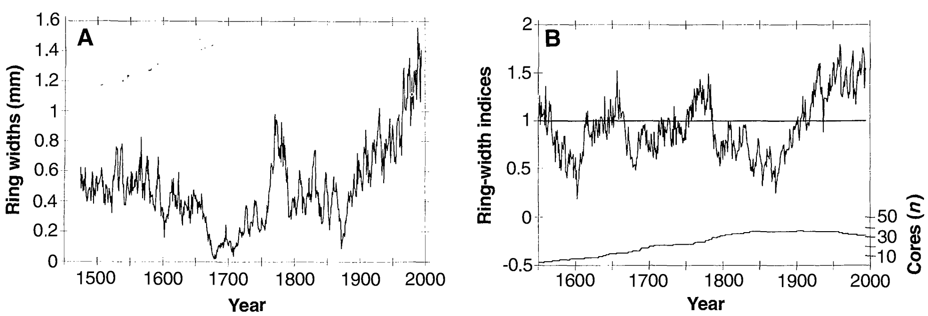


Fig. 1. Map of Mongolia, showing locations of the Tarvagatay Mountain tree-ring sampling site (triangle) and the Irkutsk meteorological station (circle). The Tarvagatay Mountains are a smaller range extending in an easterly direction from the north side of the Hungai Mountains. The typical winter location of the Siberian-Mongolian High (H) is indicated by the stippled area.



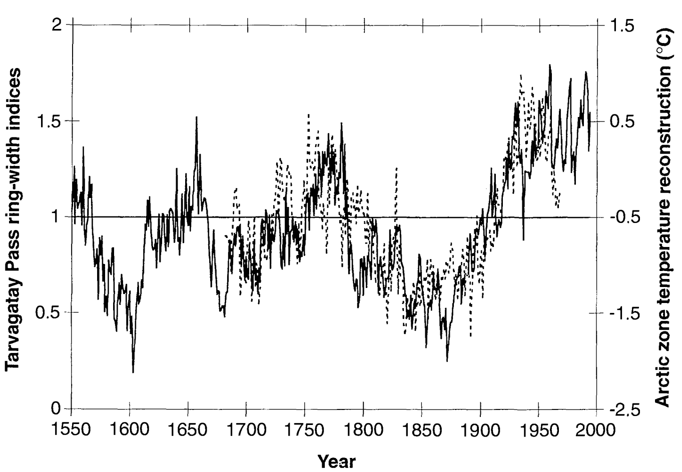


Fig. 2 (top). (**A**) Raw ring-width measurements for the first core from the first tree sampled at the Tarvagatay site. Individual cores and trees have individual variations; therefore many cores and trees are used to obtain the communal variation which, with proper site selection and sampling, is responsive to climate variations that pervade the entire site (*15*, *16*). (**B**) Tarvagatay Pass tree-ring width index chronology from 1550 to 1994 (upper line). The sample size (in number of cores) is also shown (lower line). The upper line displays the mean-value time series of ring-width indices, or common variation, for all the samples. Higher values indicate wider rings and warmer temperatures; lower values indicate narrower rings and cooler temperatures. In the mid-1500s, mid-1600s, and late 1700s, there are a few years that peak in the current range, but any multiyear mean is below that of recent decades. **Fig. 3 (bottom).** Comparison of Tarvagatay Pass ring-width chronology (solid line) and reconstruction of Arctic annual temperature departures (*1*) (dashed line).

averaging temperatures for the growth year and 1 or 2 prior years (the correlations for 1-, 2-, and 3-year averages are 0.45, 0.57, and 0.60, respectively).

Persistence or carryover effects from the growing conditions of previous years are well documented (*14*, *18*). This is especially true for evergreen conifers with long needle retention. Their photosynthetic surfaces and root systems are products of environmental conditions integrated over a longer time period than the actual season of cambial cell division (*1*, *2*, *14*, *18*). Additional evidence of the carryover effects of temperature at this site is that the correlation between the indices and averaged temperature improves from 0.45 (from the prior August through the current July) to 0.53 when averaged from the prior April through the current July.

Annual temperature records have been reconstructed for the Arctic (*1*) and Northern Hemisphere (*2*) on the basis of data from high-latitude tree-ring sites over a wide region, including North America, Scandinavia, and Russia. Many of these sites are in regions of continuous and discontinuous permafrost. The higher elevations of the Tarvagatay Mountains are also permafrost areas. The Arctic reconstruction is similar to the Tarvagatay chronology, primarily at low frequencies (Fig. 3). The correlation is 0.71 from 1682 to 1968. A principal-components analysis of the 20 original ring-width series used to reconstruct Arctic temperatures (*1*) and the Tarvagatay chronology showed strong common loading in the first eigenvector. This result implies that there is a common, coherent climatic signal among the trees from these widely separated sites.

Other proxy series from northern latitudes show trends similar to those of the Mongolian chronology and Arctic reconstruction. Specifically, these general trends are (i) cooler conditions (more narrow rings) in the early 1700s, followed by warming (wider rings) for the mid- to late 1700s; (ii) abrupt cooling and continued cool conditions for much of the 1800s; and (iii) a warming trend for the late 1800s and much of the 1900s (Fig. 2B and Fig. 3). Of the larch series from northwestern Mongolia developed by Chistyakov, the chronology from the highest elevation site shows similar growth variations (*10*). A chronology developed from Hinoki cypress growing on a montane site (1550 m) in central Japan evidently reflects winter temperatures (*19*). It also shows low-frequency trends that are similar to those of the Mongolian chronology and Arctic reconstruction. Some high-elevation chronologies from timberline sites in the Canadian Rockies (*20*) and southwestern United States (*21*) also show similar trends. Tree-ring density records for eastern Siberia correlate primarily with summer temperatures and thus are not directly comparable to the Arctic or Tarvagatay series (*22*). Winter temperature curves for China based on historical data (*23*) and an oxygen isotope ratio ($\delta^{18}O$) curve from the Dunde Ice Cap (*24*) also show these common trends since 1700 but differ before 1700.

Both the Arctic reconstruction and the Mongolian data indicate that the 20th century has been a time of unusual warmth relative to the past several centuries. After regression with temperatures, there is no trend in the residuals in this or the Arctic study (*1*) that would indicate possible CO_2 or N fertilization. Growth for the period from 1944 to 1968 was the highest of any 25-year growth interval over the entire length of the chronology. The 10 highest (overlapping) growth intervals are all after 1920. The interval from 1852 through 1876 was the coldest, corresponding to the Neoglacial maximum of the Little Ice Age in some areas (*25*).

Many efforts are under way to define the influence of forcing factors (such as solar effects, volcanism, and greenhouse gases) for climatic variations in the Holocene (*26*). Of these, a reconstruction of solar irradiance (*27*) shows a strong similarity to the tree-ring curves. The warming trend starts in the late 1800s, which is in agreement with the solar curve and before significant increases in trace gases. The greatest departures from the solar curve are in the middle 1800s, a time of several major volcanic events (*28*); and in recent decades, when the solar irradiance does not fully account for the warming (*27*).

REFERENCES AND NOTES

1. R. D. D'Arrigo and G. C. Jacoby, *Clim. Change* **25**, 163 (1993).
2. G. C. Jacoby and R. D. D'Arrigo, *ibid*. **14**, 39 (1989).
3. J. Hansen and S. Lebedeff, *J. Geophys. Res.* **92**, 345 (1987); P. D. Jones and K. R. Briffa, *The Holocene* **2**, 174 (1992).
4. D. W. Stahle, in *Tree Rings, Environment and Humanity*, J. S. Dean, D. M. Meko, T. W. Swetnam, Eds. (Radiocarbon, Tucson, AZ, 1996), pp. 119–126.
5. J. Zhang and Z. Lin, *Climate of China* (Wiley, New York, 1992).
6. Mongolian Academy of Sciences (MAS) (formerly the Academy of Sciences of Mongolia), *National Atlas of Mongolian People's Republic* (Ulaanbaatar, Mongolia, 1990).
7. H. Barthel, *Land Zwischen Taiga & Wuste* (Geographische Bausteine, VEB Hermann Haack, Leipzig, Germany, 1971).
8. The distribution of tree species is from the map *Forests of Mongolia* (1983) (scale, 1:1,500,000).
9. N. V. Lovelius, Ts. Davaajamts, P. D. Gunin, *Dendrochronological Indications of Forest Growth Conditions in Mongolia and Possibilities of Forecasting* (Russian Academy of Sciences, Puschino, Moscow, 1992), pp. 32–49; R. Mijiddorj and A. Namhay, in *The First PRC-Mongolia Workshop on Climate Change in Arid and Semi-Arid Regions over the Central Asia*, Mongolia Hydrometeorological Service and China Meteorological Administration, Beijing, 1993, pp. 11–16; R. Mijiddorj and D. Enkhbat, in *The Second PRC-Mongolia Workshop on Climate Change in Arid and Semi-Arid Regions over the Central Asia*, Mongolia Hydrometeorological Service and China Meteorological Administration, Ulaanbaatar, Mongolia, 1995, pp. 68–73; D. V. Sevast'yanov, A. N. Yegerov, Zh. Tserensodnom, *Izv. Vses. Geogr. Ova*. **122**, 535 (1990) (English translation by Plenum, New York, 1993).
10. Six tree-ring chronologies from Mongolia were placed in the International Tree-Ring Data Bank in February 1996 by K. V. Chistyakov of St. Petersburg Univ. in Russia. They are all larch and are from lower elevations than the Tarvagatay Pass series. The chronology from the highest elevation (2380 m) is somewhat similar to our series, with an increase in indices in the mid- to late 1700s, a decrease in the early 1800s, and an increase since the mid-1800s. Larch, a deciduous conifer, tends to have more of a warm-season–only response than evergreens [see, for example, (*24*)].
11. N. T. Mirov, *The Genus Pinus* (Ronald Press, New York, 1967).
12. All sampling of living trees was done by coring, leaving only a small wound. The trees will continue to grow and record environmental changes.
13. H. C. Fritts, *Tree Rings and Climate* (Academic Press, New York, 1976); W. Tranquillini, *Physiological Ecology of the Alpine Timberline* (Springer-Verlag, New York, 1979).
14. E. R. Cook and L. A. Kairiukstis, Eds., *Methods of Dendrochronology* (Kluwer, Boston, 1990).
15. The temperature data set was obtained from P. D. Jones, Climatic Research Unit, Univ. of East Anglia. Data for 1927 are missing for the grid box and the Irkutsk record, and there are eight other missing monthly values. All these values (1.5% of data) were estimated by averaging values for 10 years before and 10 years after the missing value for the same month. The mean of the 20 values was substituted for the missing value.
16. Raw ring-width measurements are standardized to remove age-related growth trends and produce a chronology of annual mean values of dimensionless indices (*14*).
17. G. C. Jacoby and R. D. D'Arrigo, *Global Biogeochem. Cycles* **9**, 227 (1995). By northern and elevational tree line, we mean at the limits of survival, not just in the general area of the tree line.
18. P. J. Kramer and T. T. Kozlowski, *Physiology of Woody Plants* (Academic Press, New York, 1979).
19. T. Sweda, *Terr. Atmos. Ocean. Sci.* **5**, 431 (1994).
20. B. Luckman, in *Report of 1995 Dendroecological Fieldweek*, P. Brown and P. Krusic, Eds.; University of Arizona, University of Arkansas, and Columbia University, sponsors; Alberta, Canada, 1 to 8 July 1995 (not paginated).
21. V. C. LaMarche Jr. and C. W. Stockton, *Tree-Ring Bull.* **34**, 21 (1974); V. C. LaMarche Jr., *Science* **183**, 1043 (1974).
22. K. R. Briffa, P. D. Jones, F. H. Schweingraber, S. G. Shiyatov, E. A. Vaganov, in *Tree Rings, Environment and Humanity*, J. S. Dean, D. M. Meko, T. W. Swetnam, Eds. (Radiocarbon, Tucson, AZ, 1996), pp. 25–41.
23. D. Zang, *Kexue Tongbao* **25**, 497 (1980).
24. T. Yao, Z. Xie, X. Wu, L. G. Thompson, *Sci. China Ser. B Chem. Life Sci. Earth Sci.* **34**, 760 (1991); L. G. Thompson, in *Climate since A.D. 1500*, R. S. Bradley and P. D. Jones, Eds. (Routledge, London, 1992), pp. 517–548.
25. J. M. Grove, *The Little Ice Age* (Methuen, London, 1988).
26. T. J. Crowley and K. Y. Kim, *Geophys. Res. Lett.* **23**, 359 (1996); D. Rind and J. Overpeck, *Quat. Sci. Rev.* **12**, 357 (1993).
27. J. J. Lean, J. Beer, R. Bradley, *Geophys. Res. Lett.* **22**, 3195 (1995).
28. T. Simkin and L. Siebert, *Volcanoes of the World* (Geoscience Press, Tucson, AZ, ed. 2, 1994).

29. We thank D. Baatar, R. Mijiddorj, S. Erdembileg, Dondov, D. Lawrence, D. Stahle, the American Museum of Natural History, and C. Goulden. Supported by NSF grant ATM94-06372. This is Lamont-Doherty Earth Observatory contribution number 5522.

8 April 1996; accepted 3 June 1996