and funding agencies to further recognize the mutual benefits of comparative genomics.

References

1. S. Aparicio *et al.*, *Science* **297**, 1301 (2002); published online 25 July 2002 (10.1126/science.1072104).
2. J. C. Venter *et al.*, *Science* **291**, 1304 (2001).
3. S. Brenner *et al.*, *Nature* **366**, 265 (1993).
4. E. D. Green, in *The Metabolic and Molecular Basis of Inherited Disease*, C. R. Scriver, A. L. Beaudet, W. S. Sly, D. Valle, Eds. (McGraw-Hill, New York, 2000), vol. 1, pp. 259–298.
5. B. S. Abrahams *et al.*, *Genomics* **80**, 45 (2002).
6. M. S. Clark, L. Shaw, A. Kelly, P. Snell, G. Elgar, *Immunogenetics* **52**, 174 (2001).
7. M. P. Miller, S. Kumar, *Hum. Mol. Genet.* **10**, 2319 (2001).
8. S. Kumar, S. B. Hedges, *Nature* **392**, 917 (1998).
9. W. J. Murphy *et al.*, *Science* **294**, 2348 (2001).
10. J. E. Blair, K. Ikeo, T. Gojobori, S. B. Hedges, *BMC Evol. Biol.* **2**, 7 (2002).
11. M. Lynch, J. S. Conery, *Science* **290**, 1151 (2000).
12. J. W. Thomas, J. W. Touchman, *Trends Genet.* **18**, 104 (2002).
13. C. A. Bisbee, M. A. Baker, A. C. Wilson, I. Hadji-Azimi, M. Fischberg, *Science* **195**, 785 (1977).
14. B. Venkatesh, P. Gilligan, S. Brenner, *FEBS Lett.* **476**, 3 (2002).
15. J. Wittbrodt, A. Shima, M. Schartl, *Nature Rev. Genet.* **3**, 53 (2001).

PERSPECTIVES: MATERIALS SCIENCE

Dynamics in Ceramics

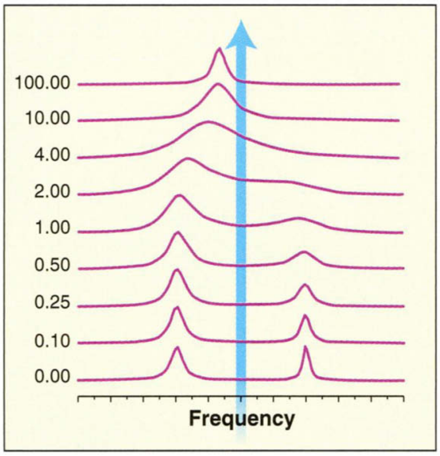
Jonathan F. Stebbins

On a macroscopic scale, oxide ceramics are hard, rigid materials. It is therefore tempting to think of them as rigid at the atomic scale as well. In particular, the oxide (O^{2-}) ions that take up much of the space in these materials seemingly ought to stay put in the crystal lattice.

It is therefore a bit surprising that these ions can be quite mobile in some ceramics. This mobility is exploited, for example, in the zirconia-based (ZrO_2) oxygen sensors that monitor the catalytic converters in most cars in the United States. The anionic electrical conductivity supplied by oxide ions is also crucial to many solid electrolytes for fuel cells, which promise more efficient use of fossil fuel and hydrogen energy resources.

Detailed knowledge of the microscopic processes underlying ionic conductance is, however, lacking. On page 1317 of this issue, Kim and Grey (*1*) bring a powerful technique to bear on this problem. They show that solid-state nuclear magnetic resonance (NMR) not only can directly determine the rate at which oxide ions hop from site to site in ionic conductors, but also can identify the sites involved in this process.

High-resolution NMR has long been an everyday tool for identifying organic molecules in liquid solutions. Since the early 1980s, NMR has also been used widely for structural studies of organic and inorganic solids. Solid-state NMR uses high-resolution methods such as magic angle spinning, in which small samples are rapidly spun at an angle of 54.7° to the external magnetic field to average out some or all orientation-dependent spectral line broadening. For oxide and silicate materials, ^{17}O NMR provides a wealth of structural detail (*2*, *3*) but requires enriched samples with ~1000 times their natural ^{17}O abundance. Enrichment sometimes necessitates tricky syntheses, but in refractory materials with mobile oxide ions, it can readily be accomplished by high-temperature gas exchange (*1*).



Merging peaks. Hypothetical NMR spectra for a material that has two distinct sites with a 2:1 occupancy ratio. The spectra were calculated at increasing ratios of site exchange frequency to frequency separation (as labeled), as expected with increasing temperature.

Complementing the high-resolution structural data, NMR can also provide unique and quantitative insights into site-specific dynamics. Many such studies have been performed on polymers (*4*), but site-specific dynamical data for inorganic materials remain limited. Spin-lattice relaxation rates are most commonly measured for nuclides such as ^{1}H, ^{7}Li, and ^{19}F, whose ions often diffuse rapidly even in solids. Such studies can be informative but are generally not site-specific. Furthermore, data analysis can be highly model-dependent, and relaxation can be strongly affected by local "rattling" within sites, which is often relatively unimportant to macroscopic transport properties.

The clearest sign of diffusive dynamics in NMR spectra is the merging of two spectral peaks, assigned to ions or molecules in distinct chemical environments, with increasing temperature (see the figure). The merging process or "coalescence" is often attributed to chemical exchange between the sites. The exchange rate is slow at low temperature, but with increasing temperature it becomes faster than the frequency separation of the peaks. The peak separation, typically 10 to 10^6 Hz, defines the time scale of the site exchange (0.1 to 10^{-6} s).

Few studies of this kind have been performed in inorganic materials, primarily because ions of the most commonly observed nuclides (such as ^{29}Si, ^{27}Al, and ^{17}O) start hopping around at the required rates only at elevated temperatures. Alkali metal cations are more mobile but often occupy only a single site in a given crystal structure, also frustrating attempts at exchange spectroscopy, although there are exceptions (*5*, *6*). Fluoride anions can also be remarkably mobile, and high-resolution solid-state ^{19}F NMR has recently revealed F^- site hopping (*7*). The fast ion conductors described by Kim and Grey (*1*) are unusual, with oxide site exchange rates rapid enough to be observed by NMR below about 250°C (the current upper limit of fast magic angle spinning technology).

In the ionic conductive ceramic α-$Bi_4V_2O_{11}$, Kim and Grey (*1*) report rapid exchange of oxide ions among distinct sites within the vanadium oxide layers. The latter are rich in the oxygen vacancies that promote diffusive motion. No exchange is seen with the more rigid, fully occupied bismuth oxide layers. In a related, Ti-doped phase that is an even better oxide ion conductor, the authors report oxygen site hopping that is not frozen out until well below room temperature.

With some modifications, solid-state NMR can be used to observe exchange dynamics in a greater variety of materials. Slower hopping rates can be observed by two-dimensional exchange experiments (*5*, *7*). Magic angle spinning NMR can be done with special probes capable of reaching above 600°C, but with slower spinning rates and reduced resolution (*6*). Spectra can be acquired at temperatures above 2000°C on nonspinning ("static") samples (*8*) and can show distinct sites and site exchange for nuclides such as ^{27}Al, ^{29}Si, and ^{17}O (*9*). Static spectra of single crystals often have high resolution and can again be collected at high temperatures (*10*).

The prospects are thus bright for elucidating mechanisms of ionic mobility in oxide materials with high-resolution

---

The author is in the Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94025–2115, USA. E-mail: stebbins@stanford.edu

NMR. Given the role of oxygen vacancies in such diffusion (*1*) and the likelihood of such vacancies in the most common mineral in Earth's lower mantle (*11*), these mechanisms may also have key importance for understanding large-scale geophysical processes.

References

1. N. Kim, C. P. Grey, *Science* **297**, 1317 (2002); published online 18 July 2002 (10.1126/science.1074130).
2. J. F. Stebbins, P. Zhao, S. K. Lee, J. V. Oglesby, *J. Non-Cryst. Solids* **293–295**, 67 (2001).
3. C. Gervais, F. Babonneau, M. E. Smith, *J. Phys. Chem. B* **105**, 1971 (2001).
4. K. Schmidt-Rohr, H. W. Spiess, *Multidimensional Solid-State NMR and Polymers* (Academic Press, London, 1994).
5. Z. Xu, J. F. Stebbins, *Science* **270**, 1332 (1995).
6. J. F. Stebbins, I. Farnan, E. H. Williams, J. Roux, *Phys. Chem. Miner.* **16**, 763 (1989).
7. F. Wang, C. P. Grey, *J. Am. Chem. Soc.* **120**, 270 (1998).
8. D. Massiot *et al.*, *J. Phys. Chem.* **99**, 16455 (1995).
9. J. F. Stebbins, I. Farnan, X. Xue, *Chem. Geol.* **96**, 371 (1992).
10. J. F. Stebbins, *Am. Mineral.* **81**, 1315 (1996).
11. A. Navrotsky, *Science* **284**, 1788 (1999).

PERSPECTIVES: CLIMATE

An Exceptionally Long Interglacial Ahead?

A. Berger and M. F. Loutre

When paleoclimatologists gathered in 1972 to discuss how and when the present warm period would end (*1*), a slide into the next glacial seemed imminent. But more recent studies point toward a different future: a long interglacial that may last another 50,000 years.

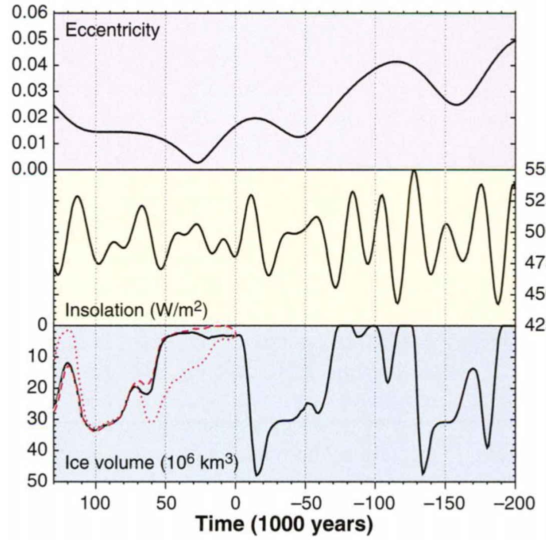
An interglacial is an uninterrupted warm interval during which global climate reaches at least the preindustrial level of warmth. Based on geological records available in 1972, the last two interglacials (including the Eemian, ~125,000 years ago) were believed to have lasted about 10,000 years. This is about the length of the current warm interval—the Holocene—to date. Assuming a similar duration for all interglacials, the scientists concluded that "it is likely that the present-day warm epoch will terminate relatively soon if man does not intervene" (*1*, p. 267).

Some assumptions made 30 years ago have since been questioned. Past interglacials may have been longer than originally assumed (*2*). Some, including marine isotope stage 11 (MIS-11, 400,000 years ago), may have been warmer than at present (*3*). We are also increasingly aware of the intensification of the greenhouse effect by human activities (*4*). But even without human perturbation, future climate may not develop as in past interglacials (*5*) because the forcings and mechanisms that produced these earlier warm periods may have been quite different from today's.

Most early attempts to predict future climate at the geological time scale (*6*, *7*) prolonged the cooling that started at the peak of the Holocene some 6000 years ago, predicting a cold interval in about 25,000 years and a glaciation in about 55,000 years. These projections were based on statistical rules or simple models that did not include any CO_2 forcing. They thus implicitly assumed a value equal to the average of the last glacial-interglacial cycles [~225 parts per million by volume (ppmv) (*8*)].

But some studies disagreed with these projections. With a simple ice-sheet model, Oerlemans and Van der Veen (*9*) predicted a long interglacial lasting another 50,000 years, followed by a first glacial maximum in about 65,000 years. Ledley also stated that an ice age is unlikely to begin in the next 70,000 years (*10*), based on the relation between the observed rate of change of ice volume and the summer solstice radiation.

Other studies were more oriented toward modeling, including the possible effects of anthropogenic CO_2 emissions on the dynamics of the ice-age cycles. For example, according to Saltzman *et al.* (*11*) an increase in atmospheric CO_2, if maintained over a long period of time, could trigger the climatic system into a stable regime with small ice sheets, if any, in the Northern Hemisphere. Loutre (*12*) also showed that a CO_2 concentration of 710 ppmv, returning to a present-day value within 5000 years, could lead to a collapse of the Greenland Ice Sheet in a few thousand years.



Orbiting the Sun. Long-term variations of eccentricity (**top**), June insolation at 65°N (**middle**), and simulated Northern Hemisphere ice volume (increasing downward) (**bottom**) for 200,000 years before the present to 130,000 from now. Time is negative in the past and positive in the future. For the future, three CO_2 scenarios were used: last glacial-interglacial values (solid line), a human-induced concentration of 750 ppmv (dashed line), and a constant concentration of 210 ppmv (dotted line). Simulation results from (*13*, *15*); eccentricity and insolation from (*19*).

On a geological time scale, climate cycles are believed to be driven by changes in insolation (solar radiation received at the top of the atmosphere) as a result of variations in Earth's orbit around the Sun. Over the next 100,000 years, the amplitude of insolation variations will be small (see the figure), much smaller than during the Eemian. For example, at 65°N in June, insolation will vary by less than 25 Wm^{-2} over the next 25,000 years, compared with 110 Wm^{-2} between 125,000 and 115,000 years ago. From the standpoint of insolation, the Eemian can hardly be taken as an analog for the next millennia, as is often assumed. The small amplitude of future insolation variations is exceptional. One of the few past analogs (*13*) occurred at about 400,000 years before the present, overlapping part of MIS-11. Then and now, very low eccentricity values coincided with the minima of the 400,000-year eccentricity cycle. Eccentricity will reach almost zero within the next 25,000 years, damping the variations of precession considerably.

Simulations with a two-dimensional climate model (*14*), forced with insolation and CO_2 variations over the next 100,000 years, provide an insight into the possible consequences of this rare phenomenon. Most CO_2 scenarios (*15*) led to an exceptionally long interglacial from 5000 years before the present to 50,000 years from now (see the bottom panel of the figure), with the next glacial maximum

---

The authors are at the Université catholique de Louvain, Institut d'Astronomie et de Géophysique G. Lemaître, 2 Chemin du Cyclotron, B-1348 Louvain-la-Neuve, Belgium. E-mail: berger@astr.ucl.ac.be