phases of both molecules have rotational potentials with fairly deep minima and (ii) above the phase transition, random orientations of neighboring molecules lead to a much smoother potential, with numerous shallow potential minima. For the rotator phase of C_{60} the extraordinary smoothness of this potential results in a rate of molecular reorientation that approaches the gas-phase rate and exceeds the value found for C_{60} in solution.

REFERENCES AND NOTES

1. C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, J. R. Salem, *J. Phys. Chem.* **95**, 9 (1991).
2. R. Tycko *et al.*, *ibid.*, p. 518.
3. P. A. Heiney *et al.*, *Phys. Rev. Lett.* **66**, 2911 (1991).
4. R. Tycko *et al.*, *ibid.*, p. 1886.
5. W. Krätschmer *et al.*, *Nature* **347**, 354 (1990).
6. R. D. Johnson, G. Meijer, J. R. Salem, D. S. Bethune, *J. Am. Chem. Soc.* **113**, 3619 (1991).
7. F. Diederich *et al.*, *Science* **252**, 548 (1991).
8. R. Freeman, in *Dynamic Nuclear Magnetic Resonance Spectroscopy*, L. M. Jackson and F. A. Cotton, Eds. (Academic Press, New York, 1975).
9. H. W. Spiess, in *NMR: Basic Principles and Progress*, P. Diehl, E. Fluck, R. Kosfeld, Eds. (Springer-Verlag, Berlin, 1978), vol. 15, p. 55.
10. F. A. L. Anet, D. J. O'Leary, C. G. Wade, R. D. Johnson, *Chem. Phys. Lett.* **171**, 401 (1990).
11. For isotropic diffusional reorientation the autocorrelation function for a tensor function of rank l of the angular coordinates decays with a time constant given by $1/l(l + 1)D$, where D is the rotational diffusion constant and τ_A and τ_S are associated with $l = 1$ and 2, respectively. See (*9*) for details.
12. P. P. Bernier *et al.*, paper presented at the Experimental NMR Conference, St. Louis, MO, 7 to 11 April 1991.
13. $S^2 = \Delta\sigma^2(1 + \eta^2/3)$, with $\Delta\sigma \equiv \sigma_{33} - (\sigma_{22} + \sigma_{11})/2$ and $\eta \equiv (\sigma_{22} - \sigma_{11})/(2\Delta\sigma/3)$. See (*9*) for details.
14. J. C. Facelli, A. M. Orendt, D. M. Grant, J. Michl, *Chem. Phys. Lett.* **112**, 147 (1984).
15. R. D. Johnson *et al.*, in preparation.
16. C. S. Yannoni *et al.*, *J. Am. Chem. Soc.* **113**, 3190 (1991).
17. K. Hedberg *et al.*, *Science* **254**, 410 (1991).
18. S. Liu *et al.*, *ibid.*, p. 408.
19. W. I. F. David *et al.*, *Nature* **353**, 147 (1991).
20. R. T. Boere and R. G. Kidd, *Annu. Rep. NMR Spectrosc.* **13**, 319 (1982).
21. W. B. Moniz, W. A. Steele, J. A. Dixon, *J. Chem. Phys.* **38**, 2418 (1963).
22. D. A. Neumann *et al.*, *Phys. Rev. Lett.*, in press.
23. A. Cheng and M. L. Klein, *J. Chem. Phys.* **95**, 6750 (1991).
24. F. Reif, *Statistical Physics* (McGraw-Hill, New York, 1975).
25. H. A. Reiley, *Mol. Cryst. Liq. Cryst.* **101**, 9 (1969).
26. C. E. Nordmann and D. L. Schmitkons, *Acta Crystallogr.* **18**, 764 (1965).
27. We acknowledge the help of L. Taylor and P. Jedrzejewski in preparing the sample, the technical assistance of G. May, and stimulating conversations with R. Tycko and F. A. L. Anet.

26 September 1991; accepted 18 November 1991

Diffusion Creep in Perovskite: Implications for the Rheology of the Lower Mantle

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High-temperature creep experiments on polycrystalline perovskite ($CaTiO_3$), an analog of $(Mg,Fe)SiO_3$ perovskite of the lower mantle, suggest that (grain size–sensitive) diffusion creep is important in the lower mantle and show that creep rate is enhanced by the transformation from the orthorhombic to the tetragonal structure. These observations suggest that grain-size reduction after a subducting slab passes through the 670-kilometer discontinuity or after a phase transformation from orthorhombic to tetragonal in perovskite will result in rheological softening in the top portions of the lower mantle.

DYNAMICS OF EARTH'S INTERIOR depend critically on the plastic flow properties of its constituent materials. Plastic flow in rocks occurs either by the collective motion of atoms by dislocation glide (or climb) or by the diffusive transport of individual atoms. The constitutive relation for creep between the two mechanisms is quite different, and this difference can significantly influence the dynamics of Earth's interior (*1*). Creep rate by dislocation motion is insensitive to grain size and increases nonlinearly with stress, whereas creep rate due to diffusion increases dramatically as grain size decreases and increases linearly with stress. Recent studies on crustal and upper mantle minerals show that the transition conditions between the two mechanisms are close to the conditions expected in Earth's crust and the upper mantle (*2*). Thus diffusion creep is a distinct possibility in Earth and might be a dominant mechanism of flow when a significant reduction in grain size occurs. Such a grain-size reduction is expected when a subducting slab passes through the phase transformation boundaries (*3*). For example, Ito and Sato (*4*) showed a significant grain-size reduction after the transformation of $(Mg,Fe)_2SiO_4$ into $(Mg,Fe)SiO_3$ perovskite + (Mg,Fe)O magnesiowustite (at 23 GPa or ~670 km) and suggested that rheological softening might occur if grain-size reduction occurs under differential stress. However, experimental data are lacking to examine the possibility of diffusion creep in perovskite, the mineral that makes up most of the lower mantle (670 to 2900 km).

In this study, we investigated the creep law of perovskite in the grain size–sensitive regime using $CaTiO_3$ as an analog material. Dislocation creep behavior has been studied in single crystals of analog materials of $(Mg,Fe)SiO_3$ perovskites (*5*), but understanding the process of deformation of polycrystalline aggregates is important because grain size–sensitive diffusion creep occurs only in polycrystalline specimens. $CaTiO_3$ perovskite is a good analog material of $(Mg,Fe)SiO_3$ perovskite for two reasons. First, the crystal structures are similar: both belong to the same space group *Pbnm* at ambient temperature (and pressure) (*6*) and transform to higher symmetry structures at higher temperatures (*7*). In addition, there are similarities in defect structures: the same slip systems of dislocations have been identified in both types of perovskites (*5, 8*), and the same types of point defects occur in both perovskites (*9*). A particularly attractive aspect of $CaTiO_3$ behavior is that structural phase transformations occur at high homologous temperatures ($T/T_m > 0.68$, where T_m is the melting temperature), where the material shows significant plastic flow.

We prepared dense fine-grained (5 to 27 μm) aggregates of $CaTiO_3$ perovskite by hot-pressing commercially available powder specimens. In the hot-pressing, we used a gas-medium apparatus in an iron jacket at 300 MPa and 1200°C for 1 to 2 hours. The hot-pressed specimens have densities that are better than 96% of theoretical values and uniform grain-size distributions (Fig. 1) (*10*). Transmission electron microscopy observations indicated no precipitation and no secondary phases at grain boundaries at a resolution of ~5 nm. The hot-pressed specimens were cut in a parallelepiped shape (~3 by 3 by 6 mm^3) and were deformed in

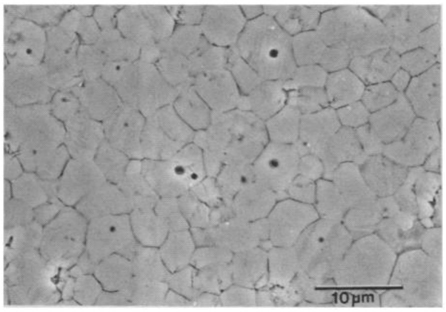

Fig. 1. A scanning electron micrograph of hot-pressed $CaTiO_3$ perovskite after etching. Note the homogeneous grain size and equilibrium grain boundaries.

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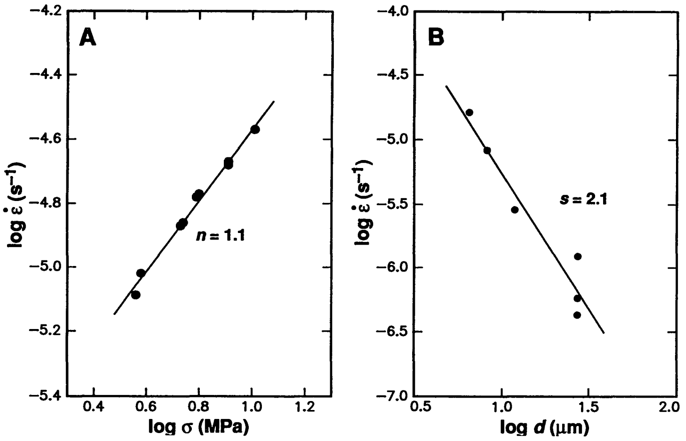

Fig. 2. (**A**) Relation between stress and strain rate in orthorhombic $CaTiO_3$ (9.4 μm, 1218°C). (**B**) The effect of grain size on creep rate in orthorhombic $CaTiO_3$ (6.2 MPa, 1218°C). A stress exponent of ~1 and a grain-size exponent of ~2 are obtained from the results of (A) and (B), respectively. These two results strongly indicate that the plastic deformation in this perovskite is due to diffusion creep.

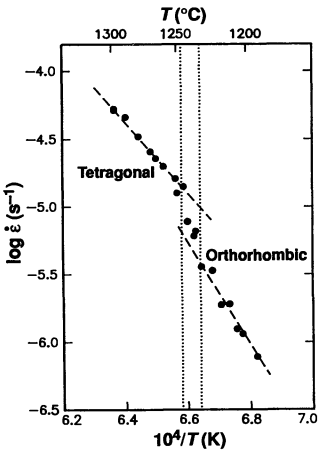

Fig. 3. The change in creep rate near the phase transformation in perovskite (5.19 MPa, 10.8 μm). $CaTiO_3$ perovskite is in the orthorhombic structure at temperatures below ~1240°C and transforms into the tetragonal structure at ~1240°C. The measurements were made both at increasing and at decreasing temperature. No hysteresis was found except for the effect of grain growth, which is corrected in this figure [see (*12*)]. This result shows that creep is significantly enhanced by the transformation from the orthorhombic to the tetragonal structure.

uniaxial compression under room pressure. The oxygen fugacity was controlled by use of a $CO\text{-}CO_2$ gas mixture or in air. The temperature was controlled by a $MoSi_2$ furnace in the range of 1180° to 1300°C. Both constant-load and constant-displacement rate tests were conducted. Steady-state creep was observed after a brief transient period. A small dependence on O_2 partial pressure was observed.

The creep law of the orthorhombic structure can be summarized by a standard formula (Fig. 2),

$$\dot{\varepsilon} = A\sigma^n \exp(-E^*/RT)/d^s$$

where $\dot{\varepsilon}$ is the strain rate, A is a constant, σ is stress, n is the stress exponent, s is the grain-size exponent, E^* is the activation energy, R is the gas constant, T is absolute temperature, and d is grain size. Our mechanical data indicate $n \approx 1$ and $s \approx 2$, values that are consistent with the volume diffusion creep model (*11*).

We also investigated the effect of structural phase transformation on creep. The structural phase transformation from the orthorhombic to the tetragonal structure occurs at $T \sim 1240°C$ (*7*). The creep rates were measured at intervals of 5° to 10°C with both increasing and decreasing temperature. No significant hysteresis was found except for a small hardening effect due to grain growth (*12*). The results indicate a significant enhancement of creep as the structure changes from the orthorhombic to the tetragonal symmetry (Fig. 3). The stress exponent in the tetragonal phase is also ~1, indicating that the deformation mechanism is diffusion creep.

Dislocation and diffusion creep have different dependences on stress, grain size, and temperature (and pressure), and therefore each mechanism dominates over the other under certain conditions. To evaluate the relative importance of diffusion and dislocation creep, one must compare these data on diffusion creep with the predictions of the dislocation creep law. Because there are no data on dislocation creep in polycrystalline perovskites, we used an approximation that the strength of a polycrystalline aggregate is the same as the strength of the hard slip system or systems (*11, 13*).

The results of such calculations (Fig. 4) indicate that diffusion creep is a dominant mechanism of deformation over a wide range of conditions. A deformation mechanism map for $CaTiO_3$ thus constructed may be used to infer the dominant mechanisms of deformation in the lower mantle, if it is assumed that a similar deformation mechanism map applies to $(Mg,Fe)SiO_3$ perovskite after an appropriate normalization (*11, 14*).

The T/T_m ratio in the lower mantle is estimated to be 0.6 to 0.8 (T_m is the melting temperature of perovskite) (*15*). The stress level σ is estimated to be in the range 1 to 10 MPa (or $\sigma/\mu = 10^{-4}$ to 10^{-5}, where μ is rigidity) (*16*). The largest uncertainty is the grain size. We might assume that the grain size of olivine in a subducting slab is similar to that in typical upper mantle rocks, that is, on the order of millimeters (*17*). This grain size will be reduced by the phase transformations, although it will eventually increase again through grain growth. Ito and Sato (*4*) reported that the grain size after the transformation to perovskite + magnesiowustite in their experiments is a few micrometers. They argued that grain growth might be slow in a perovskite + magnesiowustite mixture because the presence of a secondary phase often inhibits grain growth (*18*).

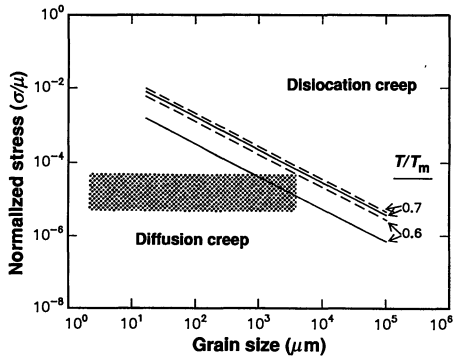

Fig. 4. The deformation mechanism map for perovskite based on this study and the inferred rate of dislocation creep. Solid lines are the boundaries between dislocation and diffusion creep for the orthorhombic structure at T/T_m = 0.7 and 0.6. Broken lines are for the tetragonal structure. Diffusion creep is the dominant deformation mechanism in perovskite over a wide range of conditions. The range of grain size and stress expected in the lower mantle is shown by the dotted region.

These considerations suggest that a wide range of grain size, say, from a few micrometers to a few millimeters, is possible in the lower mantle: relatively small grain size might occur near the leading edge of a subducting slab in the lower mantle as a result of the phase transformation from spinel to perovskite + magnesiowustite, but grain size will be larger in the lower mantle away from subducting slabs because of grain growth and the absence of continuous phase transformation. At the highest end of this grain-size range, diffusion creep is marginally important. If the grain size is smaller than this value, diffusion creep is likely to be the dominant mechanism of deformation. We conclude, therefore, that diffusion creep is a distinct possibility in the lower mantle, especially near the leading edge of a subducting slab: a subducting slab would become weak as a result of grain-size reduction as it penetrates into the lower mantle.

Our results suggest another mechanism of softening that is independent of grain size: softening due to a structural phase transformation (from the orthorhombic to the tetragonal structure). The phase transformations in perovskites are in general close to second order and involve only a small rearrangements of atoms. Thus, in contrast to the (first-order) transformation from spinel to perovskite + magnesiowustite, no grain-size reduction is found associated with the structural phase transformation from the orthorhombic to tetragonal structure. Therefore, the enhancement of creep due to this structural phase transformation must be due to the enhancement of diffusion.

Diffusion creep in fine-grained aggregates has been observed in many solids, and it is not surprising to see a similar behavior in perovskite. A real question, however, is how close are the transition conditions between diffusion and dislocation creep for perovskite to the conditions in Earth. Our results show that diffusion creep dominates in perovskite over a wide range of conditions and a linear, grain size–dependent rheology is likely to be an important deformation mechanism in a large part of the lower mantle.

Our results suggest two mechanisms of rheological softening: one due to grain-size reduction and the other due to a structural phase transformation. Both are likely to occur in the shallow portions of the lower mantle (*4, 7*). Therefore, rheologically soft layers may occur in the top portions of the lower mantle, which would act to decouple the convective motion between the upper and lower mantle (*19*).

The use of analog material to infer the lower mantle rheology has large uncertainties. We suggest that the presence or absence of seismic anisotropy in the lower mantle should provide an important clue on the dominant mechanisms of deformation: little preferred orientation of perovskite would occur and hence little seismic anisotropy would be observed if the deformation mechanism is diffusion creep, whereas dislocation creep would result in a significant preferred orientation and the resultant seismic anisotropy (*20*).

REFERENCES AND NOTES

1. U. R. Christensen and D. A. Yuen, *J. Geophys. Res.* **94**, 814 (1989); A. P. van den Berg, D. A. Yuen, P. E. van Keken, *Geophys. Res. Lett.* **18**, 2197 (1992).
2. S. M. Schmid, J. N. Boland, M. S. Paterson, *Tectonophysics* **43**, 257 (1977); S. Karato, M. S. Paterson, J. D. Fitz Gerald, *J. Geophys. Res.* **91**, 8151 (1986); J. Tullis and R. A. Yund, *J. Struct. Geol.* **13**, 987 (1991).
3. D. C. Rubie, *Nature* **308**, 505 (1984).
4. E. Ito and H. Sato, *ibid.* **351**, 140 (1991).
5. N. Doukhan and J. C. Doukhan, *Phys. Chem. Minerals* **13**, 403 (1986); J. P. Poirier, S. Beauchesne, F. Guyot, in *Perovskite: A Structure of Great Importance to Geophysics and Materials Science*, A. Navrotsky and D. J. Weidner, Eds. (American Geophysical Union, Washington, DC, 1989), pp. 119–123.
6. E. Ito and Y. Matsui, *Earth Planet. Sci. Lett.* **38**, 443 (1978); T. Yagi, H.-K. Mao, P. M. Bell, *Phys. Chem. Minerals* **3**, 97 (1978).
7. G. H. Wolf and M. S. T. Bukowinski, in *High Pressure Research in Mineral Physics*, Y. Syono and M. H. Manghnani, Eds. (American Geophysical Union, Washington, DC, 1987), pp. 313–331; Y. Wang, F. Guyot, A. Yeganeh-Haeri, R. C. Liebermann, *Science* **248**, 468 (1990); X. Liu and R. C. Liebermann, *Eos* **69**, 1451 (1988).
8. S. Karato, K. Fujino, E. Ito, *Geophys. Res. Lett.* **17**, 13 (1990).
9. U. Balachandran, B. Odekirk, N. G. Eror, *J. Solid State Chem.* **41**, 185 (1982); G. V. Lewis and C. R. A. Catlow, *J. Phys. Chem. Solids* **47**, 89 (1986); A. Wall and G. D. Price, *Phys. Earth Planet. Inter.* **58**, 192 (1989).
10. Pores occur both inside the grains and at grain boundaries. Deformation experiments were carried out at up to 30% strain without fracture. Also, the results on specimens with different porosities are indistinguishable. Thus we believe that the mechanical data are largely free from the effects of porosity.
11. H. J. Frost and M. F. Ashby, *Deformation Mechanism Maps* (Pergamon, Oxford, 1982), chaps. 2 and 18.
12. Grain growth from ~11 to ~13 μm occurred during the course of the deformation experiment, which accounts for an ~40% change in creep rate. The grain size shown in Fig. 3 is the starting grain size.
13. Both the $\{110\}\langle 1\bar{1}0\rangle$ and $\{100\}\langle 001\rangle$ slip systems operate in perovskites [the slip systems are referred to the corresponding cubic lattice (*5*)]. At high temperatures, the $\{110\}\langle 1\bar{1}0\rangle$ slip system is stronger than the $\{100\}\langle 001\rangle$ slip system [*5*; K. Wright, thesis, University of London (1991)]. Therefore, the $\{110\}\langle 1\bar{1}0\rangle$ slip system is assumed to control the creep strength of a polycrystal (*11*). Wright observed no significant effect of phase transformations on dislocation creep, and her dislocation creep data apply to both orthorhombic and tetragonal phases.
14. Frost and Ashby (*11*) and S. Karato [*Phys. Earth Planet. Inter.* **55**, 234 (1989)] discussed the systematics of creep properties. A. M. Brown and M. F. Ashby [*Acta Metall.* **28**, 1085 (1980)] examined the correlation in diffusion coefficients with crystal structure and bonding. These studies suggest that creep properties of materials with the same crystal structure and chemical bonding will be similar at the same homologous temperatures (T/T_m).
15. R. Jeanloz and S. Morris, *Annu. Rev. Earth Planet. Sci.* **14**, 377 (1986); E. Ito and T. Katsura, *Geophys. Res. Lett.* **16**, 425 (1989).
16. The stress magnitude σ in the mantle may be estimated from the viscosity η and the strain rate $\dot{\varepsilon}$ from $\sigma \sim \dot{\varepsilon}$. Choosing $\eta = 10^{21}$ to 10^{22} Pa·s [W. R. Peltier, in *Mantle Convection*, W. R. Peltier, Ed. (Gordon and Breach, New York, 1989), pp. 389–478] and $\dot{\varepsilon} = 10^{-15}\ \mathrm{s}^{-1}$ (estimated from the velocity of plates and the depth of the mantle), one gets $\sigma = 1$ to 10 MPa (or $\sigma/\mu = 10^{-4}$ to 10^{-5}).
17. H. G. Ave' Lallemant, J. C. Mercier, N. L. Carter, J. V. Ross, *Tectonophysics* **70**, 85 (1980); S. Karato, *ibid.* **104**, 155 (1984).
18. I-W. Chen and L. A. Xue, *J. Am. Ceram. Soc.* **73**, 2585 (1990).
19. The presence of a low-viscosity layer at the top of the lower mantle or at the base of the upper mantle is suggested by the theoretical analysis of geoid by A. M. Forte, A. M. Dziewonski, and R. L. Woodward [in *Proceedings of IUGG Symposium 6*, J.-L. Le Mouel, Ed. (International Union of Geodesy and Geophysics, Brussels, in press)].
20. S. Karato, *Phys. Earth Planet. Inter.* **51**, 107 (1988).
21. We thank K. Wright for providing unpublished data on creep in single-crystal $CaTiO_3$, D. L. Kohlstedt for the use of some of his experimental facilities and for reading the earlier version of the manuscript, D. A. Yuen, A. M. Forte, and Y. Wang for stimulating discussions, and Q. Bai and Z. Wang for assistance in the laboratory studies. J. Tullis's constructive criticism was particularly helpful in improving the paper. This research is supported by the National Science Foundation through grant EAR-9005279.

8 October 1991; accepted 3 January 1992

Mechanics of Wind Ripple Stratigraphy

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Stratigraphic patterns preserved under translating surface undulations or ripples in a depositional eolian environment are computed on a grain by grain basis using physically based cellular automata models. The spontaneous appearance, growth, and motion of the simulated ripples correspond in many respects to the behavior of natural ripples. The simulations show that climbing strata can be produced by impact alone; direct action of fluid shear is unnecessary. The model provides a means for evaluating the connection between mechanical processes occurring in the paleoenvironment during deposition and the resulting stratigraphy preserved in the geologic column: vertical compression of small laminae above a planar surface indicates nascent ripple growth; supercritical laminae are associated with unusually intense deposition episodes; and a plane erosion surface separating sets of well-developed laminae is consistent with continued migration of mature ripples during a hiatus in deposition.

LOOSE GRANULAR BEDS OFTEN RESPOND to the presence of a moving fluid by assuming characteristic regular undulations called ripples, megaripples, sandwaves, antidunes, or dunes, depending on their size and genesis (*1, 2*). In a depositional environment, slight variations with time in the mean grading, orientation, packing, or mineral content of the surficial grains may be preserved in the accumulating column of sediment as the individual laminae; collectively these make up the strata observed in clastic sedimentary rocks. Knowledge of the fluid and sediment conditions that can lead to stratigraphic patterns in rocks would make it possible to assess the paleomechanical conditions under which the

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