Synchrotron Infrared Absorbance Measurements of Hydrogen in $MgSiO_3$ Perovskite

Charles Meade,* John A. Reffner, Eiji Ito

Micro-infrared spectroscopic measurements on single crystals of $MgSiO_3$ perovskite document two pleochroic hydroxyl absorbance peaks at 3483 and 3423 centimeter^{-1}. These measurements were obtained with the use of a synchrotron infrared source for spectroscopy. These data are consistent with a trace hydrogen content of 700 ± 170 hydrogen atoms per 10^6 silicon atoms in the nominally anhydrous $MgSiO_3$ perovskite. When integrated over the volume of the lower mantle, this concentration is comparable to 12 percent of the mass of hydrogen in the Earth's hydrosphere.

There has been broad interest in assessing the hydrogen content of the Earth's mantle and core because of its important implications for mineral transport properties (*1*), melt formation processes (*2*), and the evolution of the atmosphere and oceans (*3*). In this effort, recent observations of structurally bound hydrogen within a wide range of nominally anhydrous silicates and oxides at concentrations of 10 to 1000 parts per million (ppm) of H_2O have been particularly important (*4–9*). These results imply that large amounts of hydrogen could be stored within the Earth at mineral defect sites without the requirement of new high-pressure hydrous phases or changes in the major element chemistry of the mantle (*10*). Analyses of such trace hydrogen in xenoliths and basaltic glasses have demonstrated that the uppermost mantle contains 100 to 200 ppm of H_2O by weight (*4*, *11*). Though this is a small concentration, it represents ~6% of the mass of the hydrogen in the hydrosphere when integrated to a depth of 400 km.

Earlier studies have used spectroscopic methods to describe the occurrence of defect hydrogen in upper mantle and transition zone silicates. The hydrogen content of the Earth is critically dependent on the concentration in the lower mantle, however, because this region constitutes the largest fraction of the planet on a volume basis. For this reason, we have carried out similar measurements on silicate perovskite ($MgSiO_3$), the predominant phase of the lower mantle. In the past, such experiments have been hindered by the difficulty of making quantitative infrared absorbance measurements on the characteristically small crystals of perovskite (<50 μm in the largest dimension) (*12*). We used recent developments in the instrumentation for micro-infrared spectroscopy to address this problem (*13*).

We examined single crystals of perovskite grown directly from an H_2O-rich melt of $MgSiO_3$ composition at a pressure of 27 GPa and a temperature of 1830°C (*14*). This is the standard synthesis technique for making large single crystals of silicate perovskite, and it provides ideal conditions for investigating defect hydrogen in the nominally anhydrous crystal structure. In the synthesis of perovskite, H_2O plays two important roles: it lowers the melting temperature of $MgSiO_3$ to an easily accessible range for the multi-anvil press and it serves as a flux to facilitate the growth of perovskite with a large grain size. On average, the crystals in this study are ~40 μm in their largest dimension, although the optically transparent region through the samples is typically much smaller (<25 μm). Turbid regions can contain large numbers of fluid inclusions that affect the measurements. Extensive characterization of samples grown with these methods show that their structure, elasticity, and vibrational properties are identical to those of polycrystalline perovskite formed under anhydrous conditions (both in the diamond cell and in the multi-anvil press) (*15*). Microprobe analyses of these samples show that their nominal composition is $MgSiO_3$, though they contain impurities at the level of 100 to 1000 ppm (*16*).

Because of their size and low absorbance near 3 μm, single crystals of perovskite test the capabilities of conventional infrared microscopy for characterizing structurally bound hydrogen. We have been able to obtain absorption spectra only by imaging entire crystals in unpolarized light from a thermal emission source (*17*) (Fig. 1). Such data suggest that there is an absorption peak near 3450 cm^{-1}; however, it is difficult to resolve this peak from the predominant underlying broad absorption peak that we attribute to fluid H_2O (*18*). The presence of fluid H_2O (presumably from inclusions) indicates that the crystals were grown under H_2O-saturated conditions and that these samples probably represent an upper bound for the hydrogen content of silicate perovskite synthesized at this pressure and temperature and with this particular composition. These data are suggestive of structurally bound hydroxyl; however, they also show that quantitative studies of hydrogen in perovskite are not possible with the limited spatial resolution and signal that one can obtain from a black-body thermal emission source in laboratory-based infrared spectroscopy.

To overcome such intensity-limited spectroscopic problems, we used the new infrared beamline (U2B) of the National Synchrotron Light Source at Brookhaven National Laboratory (*19*). From the synchrotron, the radiation is highly collimated and polarized, and it is almost three orders

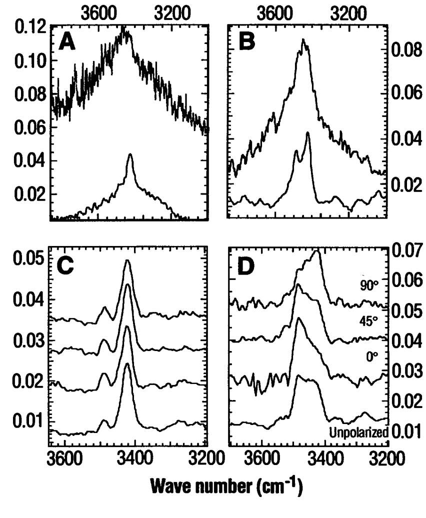

Fig. 1. Micro-infrared absorption measurements on single crystals of $MgSiO_3$ perovskite. (**A** and **B**) Comparison between synchrotron (bottom) and laboratory (top) measurements. We collected laboratory spectra by imaging entire crystals in unpolarized light (50-μm apertures). Synchrotron spectra are from 15-μm apertures through optically transparent regions with polarized radiation. Accounting for the relative aperture sizes, the data are consistent with an increase in the signal of two orders of magnitude from the synchrotron source. Both laboratory spectra show broad band absorption from fluid water. In (B), the fluid component is eliminated by the smaller aperture. In (A), a contribution from water is evident in the synchrotron spectra, indicating that microscopic fluid inclusions are present in this crystal. (**C**) Profile of unpolarized absorption spectra across a single crystal with a 15-μm aperture. (**D**) Comparison between unpolarized and polarized spectra at different orientations. The differences between the unpolarized measurements in (C) and (D) are due to the strong polarization of the synchrotron source (*20*).

C. Meade, Geophysical Laboratory, Center for High Pressure Research, 5251 Broad Branch Road NW, Washington, DC 20015, USA.
J. A. Reffner, Spectra-Tech, Stamford, CT 06906, USA.
E. Ito, Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-Ken 682-02, Japan.

*To whom correspondence should be addressed.

of magnitude brighter than a conventional laboratory source at 3 μm. By coupling an infrared microscope and interferometer to the synchrotron, it has been possible to obtain absorption measurements with a diffraction-limited spatial resolution (*20*).

A comparison of infrared absorption spectra on individual crystals obtained with laboratory and synchrotron infrared microscopes shows several improvements in the data (*21*). First, the signal is significantly increased, even for apertures that are smaller than in the laboratory measurements. Second, because of the enhanced spatial resolution the optically transparent regions of the crystals can be isolated to remove much of the fluid H_2O background that corrupts the laboratory spectra. And finally, we are able to confirm the directional nature of the OH absorption in the crystals through measurements of polarized spectra.

From the synchrotron measurements, we consistently observed two moderately pleochroic absorption peaks in the single crystals of perovskite at 3483 and 3423 cm^{-1}. In two crystals, we have also observed a peak at 3690 cm^{-1}. Infrared absorption spectra measured at different spots across a single crystal show that the relative and absolute intensities in the spectra are relatively constant; this result implies that hydrogen is uniformly distributed throughout (Fig. 1). As the polarization of the beam is rotated, the relative intensities of the absorption peaks at 3483 and 3423 cm^{-1} change; however, the integrated absorbance of these two is constant within 15%. Also, the integrated absorbances from the polarized and unpolarized measurements are similar (Fig. 1D). A comparison between the integrated absorbance of the two peaks and the crystal thickness shows a systematic trend, which indicates that the absorption in this region is associated with structurally bound hydroxyl in the perovskite crystal structure and that it is not associated with hydrogen adsorbed on surfaces. On the basis of the Beer-Lambert law (*22*) and Paterson's molar absorption coefficients for hydrogen in silicates at a similar wavelength (*23*), the data in Fig. 2 are consistent with a concentration of 700 ± 170 H atoms per 10^6 Si atoms (*24*).

The frequency of the absorption peak indicates that there is weak hydrogen bonding in the perovskite crystals and that the proton is positioned between two oxygen atoms that are spaced $\sim$2.75 Å apart (*25*). The splitting of the frequency between the two peaks is consistent with a variation of 0.1 Å in the total hydrogen bond length (O···O distance). This bond distance is considerably longer than the near-neighbor oxygen atom distances along the octahedral edge in the $MgSiO_3$ perovskite structure ($\sim$2.55 Å). It is comparable, however, to second near-neighbor distances between oxygen atoms on adjacent octahedrons that are tilted toward each other in the 001, 110, and $\bar{1}$10 planes (Fig. 3). Notably, the magnitude and variation in this oxygen spacing (two O···O distances at 2.71 and 2.81 Å) are in excellent agreement with the position and splitting of the observed hydroxyl absorption peaks. If hydrogen atoms were randomly distributed on all of these O···O pairs in the perovskite structure, the integrated absorbance of the hydroxyl peaks would appear isotropic for measurements along different orientations and polarizations (*26*).

The formation of these hydrogen bonds could be associated with a number of defect reactions in $MgSiO_3$ perovskite, including the formation of MgO Schottky pairs (*27*) and the substitution of trivalent ions (for example, Al^{3+} and Fe^{3+}) for silicon. The chemical composition of our samples suggests that the latter may be the most prevalent mechanism in these crystals. In the Earth, we expect that the incorporation of hydrogen in perovskite is critically influenced by nonstoichiometry, the oxidation state of iron, and the ambient temperature and pressure. Notably, the hydrogen concentrations of natural olivines and pyroxenes from the upper mantle vary by almost four orders of magnitude, depending on the concentration of impurities (*4, 8*). In the lower mantle, the effects of substitutional iron and aluminum and significantly higher temperatures compared to those of our synthesis conditions (and measurements) should increase the defect population in perovskite relative to our samples and hence increase the maximum possible concentrations of structurally bound hydrogen.

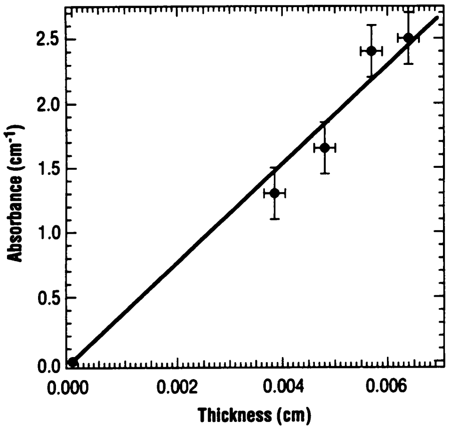

Fig. 2. Integrated absorbance for crystals with different thicknesses. Absorbance values are the average of polarized and unpolarized measurements made with the synchrotron source. The fit to the data is constrained to pass through the origin.

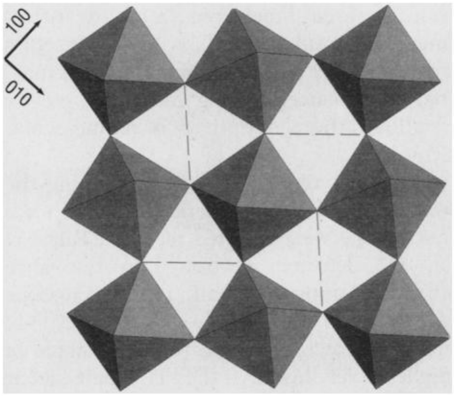

Fig. 3. Polyhedral representation of SiO_6 octahedrons in the 001 plane of the perovskite structure. The dashed lines show possible sites for hydrogen bonds that are consistent with the frequency of the hydroxyl absorption peaks. There is an orthogonal distribution of similar sites in the 110 and $\bar{1}$10 planes.

The hydrogen content of these perovskite crystals is comparable to the concentrations that have been documented in natural olivines and laboratory-synthesized SiO_2 stishovite (*7*). The results are also similar to the lower bound of observations for pyroxenes (*4, 8*) and to the minimum of the range of concentrations that have been reported for β-Mg_2SiO_4 (500 to 65,000 H atoms per 10^6 Si atoms) (*6, 9*). If one integrates the hydrogen content of these perovskite crystals over the mass of the lower mantle, it would represent $\sim$12% of the hydrogen in the hydrosphere and approximately twice the mass of hydrogen that is estimated to be in the upper mantle (0 to 400 km in depth) (*4, 11*). Our results demonstrate that trace hydrogen in perovskite could represent a significant reservoir of hydrogen in the Earth. Future studies to determine the maximum hydrogen concentrations in perovskites synthesized over a range of compositions are needed for assessing the relative importance of hydrous and nominally anhydrous minerals as repositories of the Earth's hydrogen (*28*). If the hydrogen content of perovskite is as variable as that of low-pressure silicates, the hydrogen content of lower mantle perovskite could exceed that of the hydrosphere.

REFERENCES AND NOTES

1. S. Karato, *Nature* **347**, 272 (1990); S. Mackwell and D. L. Kohlstedt, *J. Geophys. Res.* **95**, 5079 (1990).
2. A. E. Ringwood, *Composition and Petrology of the Earth's Mantle* (McGraw-Hill, New York, 1975).
3. H. D. Holland, *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, Princeton, NJ, 1984); J. S. Lewis and R. G. Prinn, *Planets and Their Atmospheres: Origin and Evolution* (Academic Press, Orlando, FL, 1984).
4. D. R. Bell and G. R. Rossman, *Science* **255**, 1391 (1992).
5. J. Smyth, *Am. Mineral.* **72**, 1051 (1987).
6. P. F. McMillan, M. Akaogi, R. Sato, B. Poe, J. Foley, *ibid.* **76**, 354 (1991).
7. A. R. Pawley, P. F. McMillan, J. R. Holloway, *Science* **261**, 1024 (1993).

8. H. Skogby, D. R. Bell, G. R. Rossman, *Am. Mineral.* **75**, 764 (1990).
9. T. E. Young, H. W. Green, A. M. Hofmeister, D. Walker, *Phys. Chem. Miner.* **19**, 409 (1993).
10. A number of high-pressure hydrous silicate phases have been identified. In general, their compositions (for example, their Mg/Si ratio) are not compatible with bulk mantle chemistry [L. W. Finger and C. T. Prewitt, *Geophys. Res. Lett.* **16**, 1395 (1989)].
11. J. E. Dixon, E. M. Stolper, J. R. Delaney, *Earth Planet. Sci. Lett.* **90**, 87 (1988).
12. Spectroscopic studies of defect hydrogen require single-crystal samples to distinguish between hydrogen bound in the crystal structure and that adsorbed on grain boundaries. The intensity of the hydroxyl absorption peaks from these crystals is several orders of magnitude lower than the mid-infrared normal modes that have been documented for (Mg,Fe)SiO_3 perovskite [Q. Williams, R. Jeanloz, P. McMillan, *J. Geophys. Res.* **92**, 8116 (1987)].
13. M. Hanfland, R. J. Hemley, H. K. Mao, G. P. Williams, *Phys. Rev. Lett.* **69**, 1129 (1992).
14. E. Ito and D. J. Weidner, *Geophys. Res. Lett.* **13**, 464 (1986). The end member composition used in this study is the most amenable for the growth of large single crystals.
15. R. J. Hemley and R. E. Cohen, *Annu. Rev. Earth Planet. Sci.* **20**, 553 (1992). Similar single crystals of silicate perovskite have been extensively documented through x-ray diffraction studies [H. Horiuchi, E. Ito, D. Weidner, *Am. Mineral.* **72**, 357 (1987); Y. Kudoh, C. T. Prewitt, L. W. Finger, A. Daravskikh, E. Ito, *Geophys. Res. Lett.* **17**, 1481 (1990)].
16. Microprobe analysis for a single crystal from the same synthesis run has been published [Y. Kudoh, E. Ito, H. Takeda, *Phys. Chem. Miner.* **14**, 350 (1987)]. The most abundant impurities (by weight) are Al_2O_3 (0.33%), P_2O_5 (0.15%), and V_2O_3 (0.12%).
17. The laboratory measurements were carried out at the Smithsonian Institution with a Spectra-Tech IR Plan microscope coupled to a Mattson Cygnus interferometer with a liquid nitrogen–cooled MCT detector. The measurements were made with 2 and 4 cm^{-1} resolution. These and the synchrotron measurements were performed on unoriented single crystals mounted in a nitrogen-purged atmosphere on diamond or BaF_2 substrates. The background spectra were collected from regions adjacent to the crystal.
18. In these samples, the bending mode of the H_2O molecule is observed at 1634 cm^{-1}.
19. G. P. Williams, *Rev. Sci. Instrum.* **63**, 1535 (1992).
20. The synchrotron measurements were carried out with a Spectra Tech IRμs microscope and interferometer with a resolution of 4 cm^{-1}. For many materials, the spatial resolution of this system is limited only by the wavelength of the absorption measurement (*13*). Because of the strong characteristic polarization of synchrotron radiation, the unpolarized measurements from this microscope are actually ~50% polarized.
21. Accounting for differences in the crystal sizes, the signal-to-noise ratio of our laboratory measurements is comparable to that of recent spectroscopic studies of defect hydrogen in samples of SiO_2 stishovite that were synthesized at high pressures (*7*). Notably, the infrared absorbance of the hydroxyl peaks in perovskite is 0.5 to 0.1 of that in stishovite.
22. The Beer-Lambert law can be expressed as $A = \epsilon cl$, where A is integrated absorbance, c is the molar concentration of hydrogen, l is the path length through the sample, and ϵ is the molar absorption coefficient for hydrogen.
23. M. Paterson, *Bull. Mineral.* **105**, 20 (1982).
24. The error in this estimate is predominantly influenced by the uncertainty in the molar absorption coefficient for hydrogen (ϵ) (*4*). For this purpose, we have used a value of 40,000 ± 10,000 cm^{-2} per mole of H per liter (*23*). By comparison, direct ion probe measurements of deuterium contents in samples of this size and concentration are typically uncertain to ±50% (*7*).
25. A. Novak, *Struct. Bonding* **18**, 177 (1974).
26. By comparison, spectroscopic (*7*) and neutron diffraction studies [R. J. Swope and J. Smyth, *Eos* **73**, 651 (1992)] suggest that hydrogen bonding in stishovite occurs along one of the SiO_6 octahedral edges.
27. A. Wall and G. D. Price, in *Perovskite*, A. Navrotsky and D. J. Weidner, Eds. (American Geophysical Union, Washington, DC, 1989), pp. 45–53; D. M. Smyth, *ibid.*, pp. 99–103.
28. Comparisons between equation-of-state measurements on hydrous minerals and seismic density models suggest that the lower mantle could contain up to 2% H_2O by weight [T. S. Duffy, T. J. Ahrens, M. A. Lange, *J. Geophys. Res.* **96**, 14319 (1991); J. A. Tyburczy, T. S. Duffy, T. J. Ahrens, M. A. Lange, *ibid.*, p. 18011].

29. We thank M. Baker for help with the laboratory infrared measurements, and G. Williams, R. J. Hemley, and L. Carr for providing beam time to set up an infrared microscope at the National Synchrotron Light Source. We are grateful to D. Bell, R. Cohen, T. Duffy, L. Finger, R. Hazen, R. J. Hemley, R. Jeanloz, and C. T. Prewitt for discussions and comments. Supported by the NSF Center for High Pressure Research.

23 February 1994; accepted 2 May 1994

Force Detection of Nuclear Magnetic Resonance

D. Rugar,* O. Züger, S. Hoen, C. S. Yannoni,* H.-M. Vieth,†
R. D. Kendrick

Micromechanical sensing of magnetic force was used to detect nuclear magnetic resonance with exceptional sensitivity and spatial resolution. With a 900 angstrom thick silicon nitride cantilever capable of detecting subfemtonewton forces, a single shot sensitivity of 1.6 × 10^{13} protons was achieved for an ammonium nitrate sample mounted on the cantilever. A nearby millimeter-size iron particle produced a 600 tesla per meter magnetic field gradient, resulting in a spatial resolution of 2.6 micrometers in one dimension. These results suggest that magnetic force sensing is a viable approach for enhancing the sensitivity and spatial resolution of nuclear magnetic resonance microimaging.

It was recently proposed by Sidles and co-workers (*1–3*) that nuclear magnetic resonance imaging with single spin sensitivity and atomic resolution might be achievable with ultrasensitive force detection techniques. In one possible implementation, a microfabricated cantilever operating at low temperature would detect the weak magnetic force acting between a small ferromagnetic particle and the precessing nuclear spins in the sample. The envisioned "magnetic resonance force microscope" would have elemental identification capability and be able to determine nuclear positions with subangstrom spatial resolution in three dimensions. Such an instrument, if it could be built, would represent a revolutionary advance for the field of magnetic resonance imaging and would greatly facilitate the determination of molecular structures.

The first experiments demonstrating the basic principles of magnetic resonance force microscopy were reported recently. Rugar *et al.* (*4*) detected electron spin resonance (ESR) by using an atomic force microscope cantilever to measure an oscillatory 10^{-14}-N magnetic force acting on a 30-ng sample of diphenylpicrylhydrazyl (DPPH). Subsequent imaging experiments by Züger and Rugar (*5*) showed that spatial maps of the magnetic force could be used to reconstruct the electron spin density of the sample with micrometer spatial resolution.

Here, we report the use of micromechanical force sensing techniques to detect nuclear magnetic resonance (NMR). Compared to the previous ESR work, NMR force detection is considerably more challenging because the magnetic moments of common nuclei are at least 650 times smaller than the moment of the electron. Furthermore, nuclei have much longer spin-lattice relaxation times, necessitating a different approach for manipulating the spin magnetization. We have overcome these obstacles by (i) fabricating ultrathin cantilevers that improve our force detection sensitivity to 5 × 10^{-16} N; (ii) operating the force detection apparatus in a high magnetic field (2.35 T) to enhance the nuclear polarization; and (iii) implementing a magnetization modulation technique based on cyclic adiabatic inversion (*6*). These innovations, in combination with the 600-T/m field gradient generated by a millimeter-size iron particle, resulted in a single shot NMR sensitivity of 1.6 × 10^{13} protons and a spatial resolution of 2.6 μm.

The force detection apparatus (Fig. 1) fit within the room-temperature bore of a superconducting magnet and was operated in a <10^{-3}-torr vacuum to avoid air damping of the cantilever. The sample consisted of 12 ng of ammonium nitrate, which was glued onto a custom-fabricated silicon ni-

---

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120, USA.

*To whom correspondence should be addressed.
†Present address: Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin, Germany.