LETTER

MAS NMR spectroscopic study of Mg^{29}SiO$_3$ with the perovskite structure

R. James Kirkpatrick, David Howell, Brian L. Phillips, Xian-Dong Cong

Department of Geology, University of Illinois, Urbana, Illinois 61801, U.S.A.

Eiji Ito

Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken, 682-02, Japan

Alexandra Navrotsky

Department of Geological and Geophysical Sciences, Princeton University, Princeton, New Jersey 08544, U.S.A.

Abstract

A ^{29}Si MAS NMR spectroscopic study of three samples of MgSiO$_3$ perovskite with 95% isotopically enriched ^{29}Si prepared at 24 GPa and 1800 °C shows the following. (1) There is only one ^{29}Si peak, with a chemical shift of -191.7 ppm. (2) This peak is extremely narrow, with a Lorentzian shape and a full-width at half-height of 19–27 Hz (0.19–0.27 ppm). (3) The static peak shows no singularities attributable to chemical shift anisotropy (CSA). The peak breadth is probably substantially influenced by ^{29}Si dipole-dipole interaction. These results demonstrate that MgSiO$_3$ with the perovskite structure is extremely well ordered and that its Si coordination polyhedron is a very symmetrical octahedron. There is no evidence for Mg-Si disorder, for Si on the central site, or for more than one next-nearest-neighbor Si environment. Thus, configurational entropy does not play a role in stabilizing this phase. The presence of small amounts of an amorphous phase in all our samples suggests that the octahedral Fe detected by Jackson et al. (1987) in an Mg$_{0.88}$Fe$_{0.12}$SiO$_3$ perovskite sample may be located in a similar amorphous phase, eliminating the need for charge balancing by eightfold-coordinated Si in perovskite, which we do not detect.

Introduction

Perovskite that is MgSiO$_3$ rich may be the dominant mineral in the earth's lower mantle (Jackson, 1983; Ito et al., 1984), and understanding the structure and behavior of this phase is essential to better understanding the nature and history of this part of the earth. XRD results have shown that MgSiO$_3$ perovskite has a well-ordered structure with Si in octahedral coordination and Mg in distorted 12-fold coordination (Ito and Matsui, 1978; Horiuchi et al., 1987). We present here a ^{29}Si NMR spectroscopic study of a set of three synthetic, 95% ^{29}Si-enriched MgSiO$_3$ perovskite samples that confirms its well-ordered structure and provides additional chemical shift and spin-lattice relaxation data for octahedrally coordinated Si. These results confirm the absence of eightfold-coordinated Si and suggest that the octahedrally coordinated Fe detected by Jackson et al. (1987) may be present in an amorphous phase.

Experimental methods

The perovskite was synthesized at 24 GPa and 1800 °C with a uniaxial split-sphere apparatus using the methods of Ito and Yamada (1981) and Ito et al. (1990). Three samples weighing 8.4, 8.3, and 4.4 mg were made. The samples were approximately cylindrical in shape and extremely dense and hard.

The starting material for this high-pressure synthesis was crystalline MgSiO$_3$ with the pyroxene structure, which crystallized at 1450 °C and 1 atm from a glass of the same composition. This glass was melted at 1600 °C from the appropriate amounts of ^{29}SiO$_2$ (from Oak Ridge National Laboratory) and 99.999% MgO. This glass was not analyzed to save isotopically enriched material, but its composition is probably very close to the nominal composition.

X-ray diffractometry of the 24-GPa samples shows only perovskite, and electron-microprobe analysis yields the composition MgSiO$_3$ within analytical uncertainty. Despite a large electron beam diameter (25 μm) and low beam current, (5 nA), most of the electron microprobe totals are low (averages of 99.39%, 98.08%, and 96.93% for the three samples). These low totals may be due to beam damage or the presence of some H$_2$O that entered the sample during exposure to the atmosphere. The average Si/Mg ratio is unity within experimental error for
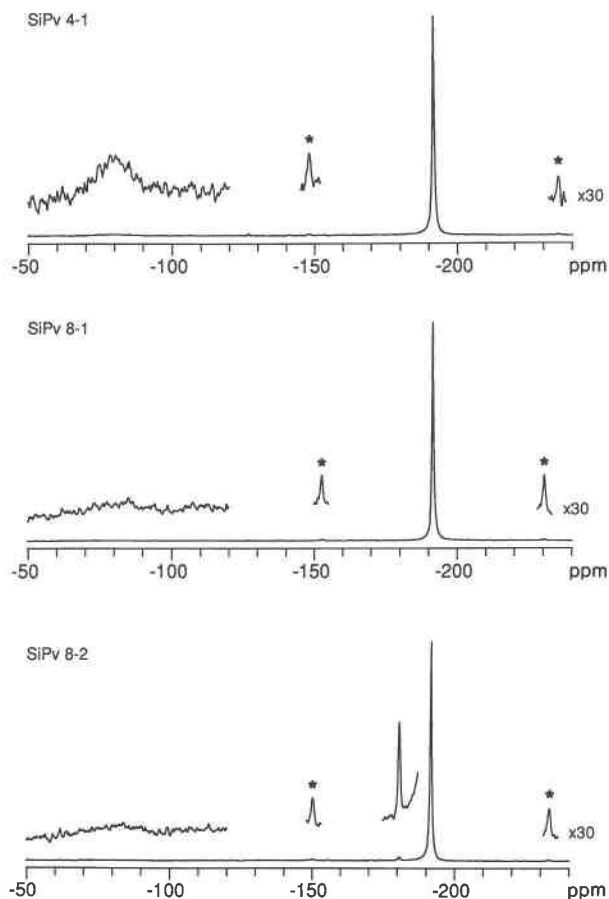
Fig. 1. The ^{29}Si MAS NMR spectra of isotopically enriched MgSiO$_3$ perovskite samples. The large peak at -191.7 ppm is due to octahedrally coordinated Si in perovskite. The broad, low peak near -80 ppm is due to tetrahedrally coordinated Si in an amorphous phase, probably with a composition close to MgSiO$_3$. The small peak at -180.7 ppm for sample 8-2 is probably due to octahedrally coordinated Si in $\sim 1.5\%$ of MgSiO$_3$ with the ilmenite structure in the sample (see Kanzaki and Stebbins, 1991).

TABLE 1. ^{29}Si MAS NMR data for MgSiO$_3$ perovskite samples

Sample name	Chemical shift (ppm)	FWHH (ppm)	T1 relaxation time (s)
8-1	−191.7	0.22	8 ± 1
8-2	−191.7	0.19	ND
4-1	−191.7	0.27	ND

The ^{1}H-^{29}Si proton cross polarization (CPMAS) spectra were measured at 71.49 MHz with the same spectrometer using contact times of 800 μs to 80 ms. No CPMAS signal was detected. Static spectra were measured at 71.49 MHz using similar instrumental conditions and 2000 scans. The ^{29}Si spin-lattice relaxation rates were determined at 71.49 MHz using a saturation-recovery sequence with 10 $\pi/2$ pulses spaced 100 ms apart and a $\pi/2$ observe pulse.

RESULTS AND SPECTRAL INTERPRETATION

The MAS NMR spectra of all the synthetic perovskite samples contain a large, narrow peak at -191.7 ppm and associated spinning sidebands near -150 and -230 ppm (Fig. 1; Table 1). The full-widths at half-height (FWHH) of these peaks with no added line broadening are very narrow (between 19 and 27 Hz, $= 0.19$–0.27 ppm), and all are Lorentzian in shape. The spectra all also contain a broader and smaller peak centered at about -80 ppm with a FWHH of about 10–15 ppm. The relative area of this peak varies from approximately 2 to 6%. In addition, one of the samples contains a very small, narrow peak at -180.7 ppm, which has a relative area of about 1.5% and a FWHH of 38 Hz.

The peak at -191.7 ppm is in the range expected for octahedrally coordinated Si (Smith and Blackwell, 1983; Grimmer et al., 1986; Kanzaki and Stebbins, 1991) and is readily assigned to the octahedral Si of MgSiO$_3$ perovskite. The small, narrow peak at -180.7 ppm is similar to that previously observed for octahedral Si in MgSiO$_3$ ilmenite (Kanzaki and Stebbins, 1991). It is likely that this one sample contains $\sim 1.5\%$ of the ilmenite-structure phase.

The peak near -80 ppm is in the range of tetrahedrally coordinated Si. Its large breadth and the lack of a second phase detectable by XRD suggests that it is due to Si in an amorphous phase. The chemical shift of approximately -80 ppm is consistent with an average polymerization of the silica tetrahedra of about Q^2 (an average of two bridging O atoms per tetrahedron), indicating that the composition is close to MgSiO$_3$. No points with a composition different from this were found by electron microprobe analysis. The relative abundance of this peak is in the 2–6% range. The ^{1}H-^{29}Si CPMAS experiments yielded no signal, indicating either that this amorphous phase is not hydrous or that the protons are in rapid motion. It is most likely that this phase is a residual glass close to MgSiO$_3$ in composition that did not crystallize during the perovskite synthesis or an amorphous phase formed from the perovskite during decompression or

all samples (as expected for the bulk composition), and no other elements were detected.

Most of the ^{29}Si NMR spectra were measured at 99.33 MHz using a home-built spectrometer based on an 11.7-T superconducting magnet (Oxford Instruments, Oxford, U.K.) and a Nicolet (G.E.) model 1280 automation system. The sample probe is a MAS probe from Doty Scientific (Columbia, South Carolina, U.S.A.) with a cylindrical rotor with an outside diameter of 5 mm. MAS frequencies were about 4 kHz. The exciting pulse was 4 μs (45°) and the recycle time was 60 s, sufficient for measurement of quantitative peak intensities. For all experimental conditions the signal could be easily detected with one pulse, but for the MAS spectra between 712 and 982 scans were obtained to provide excellent signal-to-noise ratios. Chemical shifts are reported relative to external TMS. For all spectra the samples were unground pieces packed in NaCl to allow stable spinning.

sample storage. It could contain some H_2O if the H_2O molecules are in rapid motion.

The static spectrum of sample 8-1 (not shown) contains a single peak with a maximum at −192.2 ppm and a FWHH of 13 ppm caused by the perovskite. This peak contains no singularities that can be fitted to determine the chemical shift anisotropy (CSA; see Smith et al., 1983 for an introduction). Simple calculations of the ^{29}Si-^{29}Si dipole interaction indicate that about 8 ppm (600 Hz) of this peak breadth is due to ^{29}Si-^{29}Si dipolar coupling. This interaction is not normally a problem with ^{29}Si MAS NMR spectroscopy, because the natural relative concentration of this isotope is only 4.7%, leading to large average ^{29}Si internuclear distances. At 95% enrichment, however, it can become significant, especially for phases with little CSA.

Attempts to determine the CSA from the sideband intensities (Herzfeld and Berger, 1980) were unsuccessful, because the static peak breadth is so small that only two sidebands occur on either side of the main peak at the lowest possible spinning speed (~1 kHz), insufficient for this type of analysis. The CSA for this site must be small (cf. Smith et al., 1983).

The ^{29}Si spin-lattice relaxation time for sample 8-1 at 79 MHz is 8 ± 1 s. The relaxation is exponential, implying efficient relaxation to paramagnetic impurities by spin diffusion.

There is no evidence in our spectra for Si with a coordination number greater than six. Such Si should have a chemical shift more negative than [6]Si, but to our knowledge such a shift has never been observed.

DISCUSSION AND CONCLUSIONS

The results of our NMR study are consistent with and confirm previous structural interpretations based on powder and single crystal X-ray diffraction (Ito and Matsui, 1978; Horiuchi et al., 1987). The single peak for [6]Si confirms the presence of only one kind of Si site in both the average and real local structure. The very small CSA indicates that the Si octahedron is extremely regular, consistent with the range of Si-O bond distances of only 0.1783 to 0.1801 nm determined by Horiuchi et al. (1987). The narrow widths of the peak indicate that the phase is extremely well ordered. The minimum observed FWHH of 0.19 ppm is even less than the value of 0.40 ppm observed for stishovite by Grimmer et al. (1986) and substantially less than the values they observed for [6]Si in most organic silicates and phosphosilicates.

The observed perovskite chemical shift of −191.7 ppm is almost identical to that of stishovite (−191.1 ppm; Smith and Blackwell, 1983; Grimmer et al., 1986). Stishovite has the rutile structure, in which each O atom is coordinated by three octahedrally coordinated Si atoms, and each SiO_6 octahedron shares two edges with other octahedra. In perovskite, on the other hand, the Si octahedra share only corners, and each O atom is coordinated by two Si atoms and four Mg atoms. Thus, although the

structures are different, the net (isotropic) shielding at Si is very similar. Kanzaki and Stebbins (1991) have investigated structural correlations for octahedral ^{29}Si chemical shifts in considerable detail.

The presence of small amounts (2–6%) of an amorphous phase in all of our samples suggests that the octahedrally coordinated Fe detected by Fe X-ray absorption spectroscopy (Jackson et al., 1987) could be in an amorphous phase in their $Mg_{0.88}Fe_{0.12}SiO_3$ perovskite sample, although their sample was synthesized in a diamond cell by a different route. If Fe is in octahedral coordination in such perovskite and if the perovskite is stoichiometric, Si might have a higher coordination, presumably eightfold, as suggested by Jackson et al. (1987). Spectroscopic methods with short correlation lengths such as NMR and X-ray absorption are much more sensitive to the presence of amorphous phases than XRD or optical techniques. For instance, we cannot detect glass in our samples by either of the latter methods. The use of ^{29}Si NMR spectroscopy of ^{29}Si-enriched samples of Fe-containing perovskite might lead to detection of Si in coordinations other than octahedral, but the presence of Fe normally causes degradation of the signal in NMR spectra.

Our NMR data suggest strongly the presence of only one highly symmetrical Si environment in MgSiO₃ perovskite, and thus imply that Mg-Si disordering of greater than about 1–2% in stoichiometric MgSiO₃ perovskite appears unlikely. This observation refers to a sample quenched from a fairly high temperature, 1800 °C, and samples prepared at lower temperatures would be expected to be ordered to an equal or greater extent. Although these conclusions cannot necessarily be extrapolated to Fe-bearing perovskite or to those with significant deviations from the Mg/Si = 1 stoichiometry, the present data suggest that configurational entropy arising from Mg^{2+}-Si^{4+} disorder is not thermodynamically significant. This is in accord with previous X-ray crystallographic studies (Ito and Matsui, 1978; Horiuchi et al., 1987) and with the recent calorimetric determination of the enthalpy of transition by Ito et al. (1990). The relatively high entropy of MgSiO₃ perovskite and the negative P-T slope of perovskite-forming reactions (Ito et al., 1990; Fei et al. 1990) can be explained satisfactorily by lattice vibrations and the anharmonicity implied by a relatively large thermal expansion, without invoking any cation disorder.

We note that this sample was prepared under conditions similar to those of the sample studied by Ito et al. (1990) in a drop-solution calorimetric determination of its enthalpy of formation. Our conclusions regarding a stoichiometric Mg/Si ratio and the absence of disorder probably apply to the sample used by Ito et al. as well. The sample used for calorimetry also contained some (<5%) material with an index of refraction lower than that of perovskite, but no second phase was detected by XRD. If 5% glass of composition MgSiO₃ was present in that sample, analogous to the glass inferred in this work, the enthalpy of the pyroxene-perovskite transition at 298 K could be corrected as follows.

$$\Delta H \text{ (observed)} = 0.95\ \Delta H(\text{Px} \rightarrow \text{Pv})$$

$$+\ 0.05\ \Delta H(\text{Px} \rightarrow \text{Gl})$$

$$110.5 = 0.95\ \Delta H(\text{Px} \rightarrow \text{Pv}) + 0.05(84.2)$$

where 110.5 kJ/mol is the observed enthalpy difference in dry solution between MgSiO$_3$ enstatite (Px) and the perovskite sample (Pv) (Ito et al., 1990) and 84.2 kJ/mol is the enthalpy difference between MgSiO$_3$ glass (Gl) and MgSiO$_3$ enstatite (Hervig et al., 1985). This correction gives $\Delta H(\text{Px} \rightarrow \text{Pv}) = 111.9$ kJ/mol, a correction of 1.5 kJ/mol, well within the uncertainties estimated by Ito et al., (1990). Thus, none of the conclusions in that paper needs to be changed.

REFERENCES CITED

Fei, Y., Saxena, S.K., and Navrotsky, A. (1990) Internally consistent thermodynamic data and equilibrium phase relations for compounds in the system MgO-SiO$_2$ at high pressure and high temperature. Journal of Geophysical Research, 95, 6915–6928.

Grimmer, A.R., von Lampe, F., and Magi, M. (1986) Solid-state high-resolution ^{29}Si MAS NMR of silicates with sixfold coordinated silicon. Chemical Physics Letters, 132, 549–553.

Hervig, R.L., Scott, D., and Navrotsky, A. (1985). Thermochemistry of glasses along joins of pyroxene stoichiometry in the system Ca$_2$Si$_2$O$_6$-Mg$_2$Si$_2$O$_6$-Al$_4$O$_6$, Geochimica et Cosmochimica Acta, 49, 1497–1501.

Herzfeld, J., and Berger, A.E. (1980) Sideband intensities in NMR spectra of samples spinning at the magic angle. Journal of Chemical Physics, 73, 6021–6030.

Horiuchi, H., Ito, E., and Weidner, D.J. (1987) Perovskite-type MgSiO$_3$: Single-crystal X-ray diffraction study. American Mineralogist, 72, 357–360.

Ito, E., and Matsui, Y. (1978) Synthesis and crystal-chemical characterization of MgSiO$_3$ perovskite. Earth and Planetary Science Letters, 38, 443–450.

Ito, E., and Yamada, H. (1981) Stability relations of silicate spinels, ilmenites, and perovskite. In S. Akimoto and M.H. Manghnani, Eds., High-pressure research in geophysics, p. 405–419. D. Reidel, Dordrecht, the Netherlands.

Ito, E., Takahashi, E., and Matsui, Y. (1984) The mineralogy and chemistry of the lower mantle: An implication of the ultrahigh-pressure phase relations in the system MgO-FeO-SiO$_2$. Earth and Planetary Science Letters, 67, 238–240.

Ito, E., Akaogi, M., Topor, L., and Navrotsky, A. (1990) Negative P-T slopes for reactions forming MgSiO$_3$ perovskite in the mantle from calorimetry. Science, 249, 1275–1278.

Jackson, I. (1983) Some geophysical constraints on the chemical composition of the Earth's lower mantle. Earth and Planetary Science Letters, 62, 91–103.

Jackson, W.E., Knittle, E., Brown, G.E., and Jeanloz, R. (1987) Partitioning of Fe within high-pressure silicate perovskite: Evidence for unusual geochemistry in the lower mantle. Geophysical Research Letters, 14, 224–227.

Kanzaki, M., and Stebbins, J.F. (1991) Local structure and chemical shifts for six-coordinated silicon in high pressure mantle phases. Science, 251, 294–298.

Smith, J.V., and Blackwell, C.S. (1983) Nuclear magnetic resonance of silica polymorphs. Nature, 303, 223–225.

Smith, K.A., Kirkpatrick, R.J., Oldfield, E., and Henderson, D.M. (1983) High-resolution silicon-29 nuclear magnetic resonance spectroscopic study of rock-forming silicates. American Mineralogist, 68, 1206–1215.