

Solubility of H₂O in nominally anhydrous mantle minerals using ¹H MAS NMR

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ABSTRACT

The dissolved H₂O concentrations of experimentally produced, Fe-free, nominally anhydrous minerals (NAMs) have been measured using, for the first time, ¹H magic-angle-spinning NMR spectroscopy. At least two types of hydrous species are present in all the samples studied, leading to peaks of different widths: (1) a broad resonance probably due to clustered OH such as that in static H₂O molecules within the structure, clusters of OH or hydrogarnet substitution, and (2) narrower peaks presumably due to nonclustered OH associated with point defects. The solubility of H₂O in clinopyroxene close to the Di-CaTs join is 0.26–0.41 wt% H₂O at 1000–1100 °C and 1.5 GPa. The solubility of H₂O in enstatite and forsterite is 0.087 and 0.18 wt%, respectively, under similar conditions. It is possible that the broad components result from submicroscopic hydrous mineral or glass impurities or static H₂O molecules at grain boundaries; if only the narrow peaks are considered to be due to hydrous species within the structure of the NAM, the solubilities are 0.12–0.24 wt% for the clinopyroxene, 0.024 wt% for enstatite, and 0.056 wt% for forsterite.

INTRODUCTION

The storage and behavior of H₂O in the mantle are central to the H₂O budget of the Earth and the evolution of the atmosphere and oceans. H₂O plays an important role in partial melting, subduction, and convection, and an understanding of H₂O storage in the mantle is essential for interpreting the degassing history of the Earth. It has become widely accepted that nominally anhydrous minerals (NAMs) such as olivine, pyroxene, and garnet can accommodate sufficient dissolved H₂O to account for a large fraction of the H₂O in the mantle (e.g., Bell and Rossman 1992; Kohlstedt et al. 1996). H₂O storage in NAMs has wide-ranging implications for phase equilibria, melting behavior, and physical properties of the mantle, but there is still rather little experimental data on the solubilities of H₂O in mantle phases as a function of pressure, temperature, and composition.

Infrared (IR) spectroscopy has been used widely to study hydrous species dissolved in large single crystals of minerals of natural origin (e.g., Skogby et al. 1990; Libowitzky and Beran 1995). However, infrared spectroscopy has limitations: (1) To obtain quantitative data, extinction coefficients of the bands must be known. This is particularly problematic for NAMs because of difficulties in obtaining independent measurements of H₂O concentrations and the wide variability in the relative intensities of the individual component bands in the spectra; (2) IR spectra often contain a sloping baseline that is difficult to correct; (3) fluid inclusions result in a broad band centered on 3400 cm⁻¹, which can be difficult to subtract from the spectrum; (4) it is even more difficult to make quantitative measurements on powders than on single crystals causing problems for studies of the prod-

ucts of high-*P*, high-*T* syntheses; (5) the pleochroism of IR absorption can be a problem if only crystals too small to orient are available.

Because of perceived problems with sensitivity, ¹H magic-angle-spinning (MAS) NMR has not previously been used to study H₂O in NAMs. However, this technique offers several advantages over infrared spectroscopy: (1) NMR is an intrinsically quantitative technique, and if the measurements are performed correctly the area of the spectrum is directly proportional to the amount of H, independent of the matrix of the sample. (2) The chemical shifts are characteristic of the H environment, and if resolved lines are present, the number of sites and their occupancies can be deduced. These methods have been shown to be applicable to minerals (Yesinowski et al. 1988) and glasses (Kohn et al. 1989). (3) Baselines are not usually a problem, and fluid inclusions give a narrow line such that quantitative correction of the spectra is easy. (4) Because the technique uses powders it is ideally suited to studying experimental products. (5) Proton homonuclear dipolar coupling should be removed completely for samples with dilute H using the MAS speeds currently available (see Fig. 14 of Yesinowski et al. 1988). The exception is cases in which H is clustered, e.g., the hydrogarnet substitution, and indeed the residual width of the MAS line shape can be used to give some information on H clustering. The strength of dipole-dipole coupling can be used to determine the size of H clusters by applying multiple quantum methods (Cho and Rossman 1993) and line shape analysis of dipole-dipole broadened lines can in some cases give a measure of H-H distances (Phillips et al. 1996). The main limitation of the ¹H MAS NMR technique is that it can only be used for

nearly Fe-free samples. It is therefore most useful for studying the systematics of H₂O solubility in Fe-free synthetic mantle minerals rather than natural xenolithic specimens.

EXPERIMENTAL METHODS

Synthesis of samples

The starting compositions Dicat1, Dicat3, Fo, and En were sintered mixtures of oxides carbonates and occasional gels. The starting material for the Dicat2 experiment was a glass. For the high-pressure experiments, the starting materials were sealed into 0.2 inch OD platinum capsules with 1.1–1.7 wt% distilled water. Typically, 250–300 mg of powder was loaded into each capsule. The samples were placed in a 0.75 inch piston-cylinder apparatus with a talc-pyrex cell and a tapered furnace to minimize temperature gradients along the large capsules used. Experiments were performed by pressurizing nearly to the experimental pressure and then heating while simultaneously pumping to maintain the desired pressure. The samples were synthesized at 1.5 GPa and 1000–1150 °C with run times of 24–70 h. No pressure correction was applied. All samples were heated directly to the experimental temperature, except Dicat1-9, which was heated to 1400 °C for a few minutes, cooled to 1000 °C at 1 °C/min, and held at 1000 °C for 60 h. After being quenched and removed from the platinum capsules, all samples were crushed under deionized water and then dried at 110 °C in glass bottles. The bottles were then sealed while still hot using PTFE tape and stored until needed for NMR analysis.

¹H MAS NMR

All spectra were collected using a Bruker MSL 200 (Inorganic Chemistry Laboratory, University of Oxford) and a homebuilt MAS probe based on a Doty Scientific 5 mm supersonic spinning assembly. This probe has a stator assembly made of silicon nitride, and it has a fairly low H background. Spectra were acquired using 160 or 180 2 μs (π/4) pulses, 20s recycle delay (sufficiently long to avoid saturation), 80 kHz sweep width, and 8–9 kHz MAS. The chemical shifts are reported relative to TMS using water as a secondary shift reference (δ = 4.8 ppm). A synthetic hydrous glass containing 2 wt% H₂O was used as a standard for quantification.

The powdered samples were loaded into an Si₃N₄ rotor in a normal laboratory environment, but care was taken to avoid touching the sample with fingers. Kel-F caps were used. A background spectrum for an empty spinning rotor was always taken under conditions identical to those used for the samples. The free-induction decay (FID) of the background was then subtracted from the FID of the sample plus background before Fourier transformation. Because the H background is very stable, this proved to be an effective way of minimizing the background signal and resulted in very low detection limits for H and the ability to obtain quantitative H₂O concentration measurements at the level of about 50 ppm (by weight; unpub-

lished data, Kohn and Skogby 1996). At this level the signal from the sample is small in comparison with that for the background, and the practical lower limit is controlled by the background subtraction.

RESULTS

XRD and EPMA

Three clinopyroxene samples along the Di-CaTs join, forsterite, and enstatite were studied. All samples were characterized by XRD and electron probe microanalysis (EPMA) as well as ¹H MAS NMR. EPMA indicated that within analytical uncertainty, Fo-10 (forsterite) and En-2 (enstatite) were homogeneous and on composition. No impurity phases could be found by EPMA or XRD. All the Di-CaTs samples contained small concentrations of impurity phases, and the pyroxene samples showed some variation in composition along the Di-CaTs join. Dicat1-9 had the nominal composition Di₈₆CaTs₁₄, but EPMA showed a range of compositions between CaTs₄ and CaTs₂₉, with the mean being CaTs₁₁ and a standard deviation of CaTs₄. The sample contained 2–3% (by volume) grossular as an impurity. Dicat2-1 had the nominal composition Di₇₆CaTs₂₄, a range of composition between CaTs₂₃ and CaTs₂₇, and a mean of CaTs₂₅, and contained 1–2% vesuvianite as an impurity. Dicat3-1 is nominally Di₂₁CaTs₇₉, with an analyzed mean composition of Di₁₈CaTs₈₂ and a range of CaTs contents of 81–85%. Dicat3-1 also contains at most a few percent of gehlenite and spinel.

NMR spectra

Description of spectra. Figure 1 shows the centerbands of the five samples. The most prominent features in the spectra, the very narrow, liquidlike peaks with full-width at half-maximum (FWHM) of about 0.3 ppm, are actually the least important. The 4.8 ppm peak is due to water in fluid inclusions, whereas those at 1.3 and 0.8 ppm are probably due to some sort of organic surface contaminant. A similar narrow peak at 1.5 ppm was also reported by Yesinowski et al. (1988). Although these liquidlike peaks are conspicuous, they account for only a small fraction of the total area of each spectrum and are not relevant to the dissolution of H₂O in NAMs; they are therefore disregarded in the following discussion.

There are significant differences in the shapes of the resonances for the clinopyroxene samples. The peak for Dicat1-9 is fairly symmetrical, with a FWHM of 1.6 ppm, whereas that for Dicat2-1 has a FWHM of 1.7 ppm and is slightly asymmetric. The resonance for Dicat3-1 is much broader, with a FWHM of 3.0 ppm, and is asymmetric; there appears to be a shoulder on the main peak at about 7–8 ppm. The peak shapes of the centerbands for all three clinopyroxene samples suggest that there may be a broad component to the resonances. The forsterite spectrum Fo-10 consists of a fairly broad resonance centered on 4.3 ppm with some small, narrow features at 6.9 and possibly 5.5 ppm. The peak at 1 ppm is within the range assigned to the two organic surface-con-

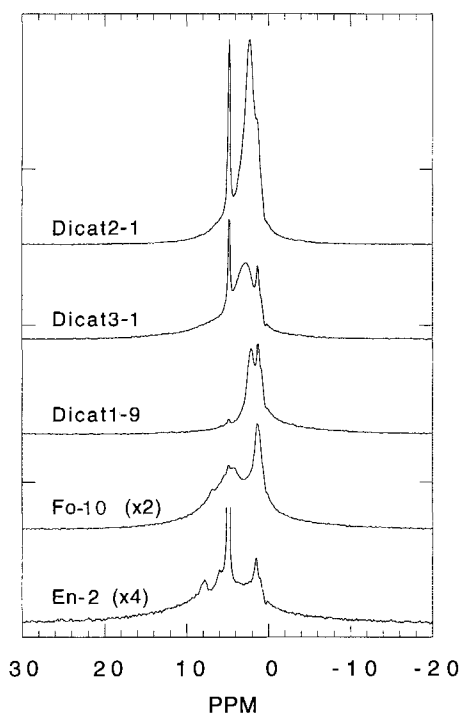


FIGURE 1. Centerbands of the ¹H MAS NMR spectra of NAMs. The spectra are all on the same intensity scale except Fo-10 and En-2, which are multiplied by factors of 2 and 4, respectively, to aid comparison of peak positions and widths. Note that the peak for fluid inclusions in En-2 was truncated.

taminant peaks, but it does seem to be anomalously intense and slightly broader than that in the other samples. Therefore, it is possible that this peak has some component from structural OH within the olivine. The spectrum for enstatite En-2 consists of several narrow peaks superimposed on a broad resonance. Resolved peaks at 7.9 and 5.9 ppm suggest a moderately strong hydrogen bonded OH within the enstatite structure, with O-H...O distances of 2.79 and 2.87 Å, respectively (on the basis of the compilation of data in Eckert et al. 1988).

Additional information can be obtained from examination of the spinning sidebands. As an example, in Figure 2 the spinning sidebands for Dicat2-1 are shown on an expanded intensity scale. It is evident that the sidebands have two components, a broad peak with FWHM of 11–12 ppm and a narrow peak with FWHM of 1.8 ppm. The components are more easily resolved in the sidebands than in the centerbands because the broad peak is relatively much larger and because the liquidlike peaks are absent. For the other samples the width of the broad resonance varies from 12–20 ppm. By measuring the positions of the broad and narrow components in the sidebands, the center of the spinning sideband envelopes for each of the peaks can be estimated. In the case of Dicat2-1, the narrow component is centered on 2.3 ppm and the broad component is centered on about 4 ppm. In addition, the apparent position of the equivalent centerband

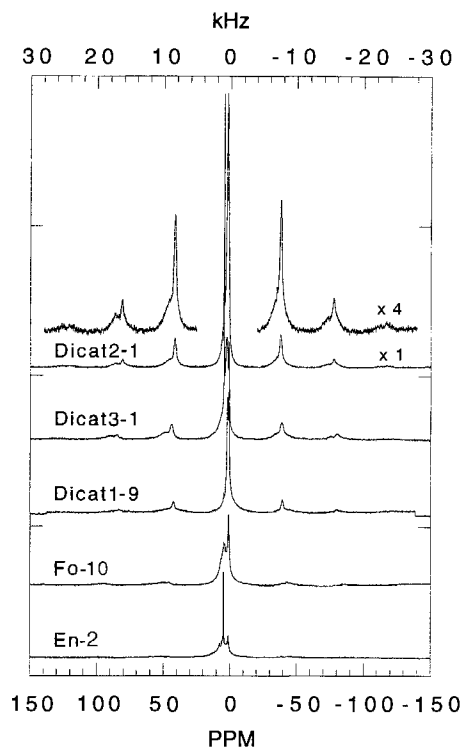


FIGURE 2. The ¹H MAS NMR spectra of three clinopyroxene samples, forsterite, and enstatite. All spectra are on the same scale, i.e., the total areas of the spectra are proportional to the H₂O concentrations, except where indicated. Vertical expansion of the sidebands for Dicat2-1 shown at the top of the figure illustrates how two components can be resolved more easily in the sidebands than in the centerband.

of the broad component becomes more positive for the higher order sidebands. This implies that the broad peak has contributions from more than one species, and that these species have distinct chemical shifts and static line widths. The broad sidebands in all five samples display this behavior.

H₂O concentrations. The ¹H MAS NMR spectra for all five samples are shown in Figure 2. The data are presented on the same intensity scale but with offset baselines. The spectra were integrated, and the total areas of center and sidebands were corrected to remove the areas of fluid inclusion and organic impurity peaks. The values for total H₂O concentration, in parts per million (by weight) H₂O, are 2615, 4100, and 3380 ppm for Dicat1-9, Dicat2-1, and Dicat3-1, respectively, 870 ppm for En-2, and 1790 ppm for Fo-10. These concentrations are believed to be accurate to within 10%. Potential sources of error include uncertainties in the H₂O concentration of the standard, tuning of the NMR circuit, baseline correction, and correction for H in the fluid inclusions and organic impurities. By using the FWHM of the broad peak, measured for the sidebands, it was possible to estimate the size of the broad component of the centerband. The H₂O concentration corresponding to the area of the broad com-

ponents in both center and sidebands could then be subtracted from the total dissolved H₂O concentrations derived above. This gave a value for the H₂O concentration resulting from the narrow components alone. These values are 1160, 2430, 1380, 240, and 560 ppm for Dicat1-9, Dicat2-1, Dicat3-1, En-2, and Fo-10, respectively, and are subject to larger errors, perhaps $\pm 20\%$. Note that the vesuvianite impurity in Dicat2-1 would account for only ~ 400 ppm of the H₂O in the sample, and that the impurities in the other samples are likely to be even less significant.

DISCUSSION

One of the main observations made in this study is the presence of two types of hydrous species in all samples, one giving broad resonances and one giving narrower resonances. The probable explanation for the difference in widths is that the narrow peaks are due to protons in OH groups experiencing only weak dipolar coupling to other ¹H nuclei (or ²⁷Al for the clinopyroxene), whereas the broad peaks are due to protons in clusters of OH molecules experiencing stronger homonuclear dipolar broadening. It is also possible that the peak broadening is due to dynamic effects, but this is not considered likely. There are several possible ways that clusters may be incorporated into a silicate structure, including hydrogarnet substitution, other point defects involving associated OH groups, and dislocations or planar defects with hydrous species concentrated along them. An alternative possibility is that the broad component is not due to hydrous species incorporated within the NAM but instead is due to submicroscopic hydrous mineral or glass impurities (perhaps originating during the quench) or static H₂O molecules present at grain boundaries. The latter possibilities would require studies using additional techniques such as TEM.

The solubilities of H₂O in the Di-CaTs pyroxene samples are higher than any previous determination for clinopyroxene but are not unexpected for these aluminous pyroxene samples. However, it is surprising that the solubility of H₂O in forsterite is higher than in enstatite under very similar conditions. The solubility of 1790 ppm (28,000 H/10⁶ Si) in forsterite at 1150 °C and 1.5 GPa also seems very high in comparison with other recent experimental determinations (Bai and Kohlstedt 1993; Kohlstedt et al. 1996). Even if the broad component in the NMR spectra is dismissed as nonstructural, the 560 ppm in narrow components is still unexpectedly high. There are several possible reasons for this discrepancy: (1) Fo-10 is pure forsterite, in comparison with Fo₉₁ in Bai and Kohlstedt (1993) and Kohlstedt et al. (1996); (2) the forsterite studied here was unbuffered with respect to a_{SiO_2} , f_{H_2} , f_{O_2} , or $f_{\text{H}_2\text{O}}$; (3) Bai and Kohlstedt (1993) and Kohlstedt et al. (1996) used pieces of natural olivine in their experiments, whereas Fo-10 is synthetic and may have a high defect concentration because of the high tem-

perature of annealing of the oxide mix or because of rapid recrystallization during the run; (4) there may be serious shortcomings in the analysis of H dissolved in olivine by one of the two techniques. The difference in the Fe concentration of the samples seems unlikely to be the source of the discrepancy because it is thought that Fe could play an important role in stabilizing hydrous defects. Furthermore, Ginsburg and Kohlstedt (1995) suggested that there is only a weak dependence of H₂O solubility on Fe concentration between Fo₈₃ and Fo₉₀. On the other hand, the differences in the activity of silica, the fugacities of H, O, and H₂O, and the thermal and growth history of the samples could have profound effects on the defect chemistry of forsterite and hence on the H₂O solubility. A further possibility is that current interpretations of the infrared spectra of olivine lead to underestimates of the OH concentration.

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