

^1H MAS NMR studies of water solubilities and dissolution mechanisms in olivine, clinopyroxene and orthopyroxene

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The physical and chemical properties of the Earth's mantle control the most important large scale processes which have dominated the evolution of the Earth, including plate tectonics, formation of the crust, and degassing. Small amounts of water can have a disproportionately large effect on the properties of the mantle, so knowledge of the concentration and distribution of water in the mantle is crucial for understanding the behaviour of the Earth. Nominally anhydrous minerals (NAMs), such as olivine, pyroxene and garnet, can accommodate sufficient dissolved water to account for the 100–500 ppm H_2O thought to be present in the mantle (Bell and Rossman, 1992) but few quantitative solubility data are currently available because of experimental and analytical difficulties. Infrared spectroscopy (IR) is the technique which has been most widely used to measure the water concentrations in NAMs, but it requires the extinction coefficients (the constants which relate the size of an IR peak to the concentration of dissolved hydroxyl) to be known. In the absence of experimental determinations of extinction coefficients an empirical correlation between vibrational frequency and extinction coefficient must be applied. Furthermore, there can be difficulties in subtracting the correct baseline in IR spectra; it is difficult to correct for the presence of fluid inclusions; and other vibrations not related to dissolved water can appear in the OH stretching region. An alternative technique, ^1H magic angle spinning nuclear magnetic resonance (MAS NMR) which is element specific and easier to perform in a quantitative manner has recently been developed (Kohn, 1996), and the work to be presented here is aimed at applying this technique to determine the solubility and dissolution mechanisms of water in NAMs.

^1H MAS NMR of nominally anhydrous minerals

^1H MAS NMR spectra for a olivine, clinopyroxene and orthopyroxene show that at least two types of hydrous species are present, leading to peaks of different widths: i) a broad resonance probably due to

clustered OH such as that in static water molecules within the structure, clusters of hydroxyl or hydrogarnet substitution, and ii) narrower peaks presumably due to non-clustered OH associated with point defects. The resolution between the peaks is not as good in ^1H MAS NMR as in IR, but is enhanced at 8.45 T compared with 4.7 T. This does not affect the application of ^1H NMR to determination of solubilities, but does suggest that studies of dissolution mechanisms should be performed at the highest available magnetic fields.

Solubility of water in olivine

Forsterite samples have been equilibrated with water at pressures of 1.0–3.0 GPa and temperatures of 1050°C to 1400°C. Most starting materials were powders, but a few single crystal forsterite samples (provided by Prof. S. Karato) were also used. The activity of silica was buffered by adding a small amount of enstatite to the starting material. The role of minor elements was studied by using both pure starting materials and starting materials containing small concentrations of other elements such as Al, P or Na.

^1H MAS NMR data imply that the solubility of water in olivine may be higher than previous measurements such as those of Kohlstedt *et al.* (1996) have suggested. However, the experimental and analytical considerations are complex, with the form of the starting material (single crystals vs powders), composition (natural vs iron-free synthetic), oxygen fugacity and analytical methods all potentially affecting the results obtained. Progress towards resolving these difficulties and separating experimental and analytical problems will be reviewed.

Partitioning of water between NAMs and silicate melts

A quantitative description of the role of water in the mantle requires the partition coefficients between the

various NAMs to be known. At present these are very poorly constrained. Preliminary ^1H MAS NMR data suggest that $D > 1$ in contrast to the previously published estimate of 0.2 (Hirth and Kohlstedt, 1996). Further experiments to determine partition coefficients are in progress. The experimental strategy is to equilibrate a series of mixtures of two nominally anhydrous minerals at a fixed set of pressure and temperature conditions, then plot the total water concentration of the mixtures (determined by NMR) as a function of mole fraction of each component. The partition coefficient can then be determined by mass balance.

The water partition coefficients between NAMs and silicate melts are also required if the behaviour of the mantle during partial melting is to be quantitatively understood. At present the three published values of D vary by over two orders of magnitude with values of 0.0004 (Hirth and Kohlstedt, 1996), 0.02 (Kurosawa *et al.*, 1997) and 0.1 (Sweeney *et al.*,

1997). Experimental strategies to resolve this problem will be discussed. Improved values for D will allow the water concentrations of MORBs to be used to calculate the concentration of water in their source regions and provide another constraint on the water concentration of the mantle.

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