

Testing a potential mantle geohygrometer; the effect of dissolved water on the intracrystalline partitioning of Al in orthopyroxene

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Abstract

The presence of water in the Earth's mantle has wide ranging implications and a detailed picture of the spatial and temporal distribution of water in the mantle is needed to be able to understand fundamental global-scale processes. However the interpretation of measured water concentrations in nominally anhydrous minerals (NAMs) from xenoliths or magmatic phenocrysts is complicated by fast diffusion of H and hence the probability of hydration or dehydration during ascent. Rauch and Keppeler [1]M. Rauch, H. Keppeler, Water solubility in orthopyroxene, *Contrib. Mineral. Petrol.* 143 (2002) 525–536 have proposed that the partitioning of Al between octahedral and tetrahedral sites in orthopyroxene has the potential to be used as a more reliable mantle geohygrometer than direct measurements of water concentrations in xenolith minerals. In the present study, we have tested the theoretical basis for this geohygrometer by experimentally producing aluminous orthopyroxene samples and measuring the intracrystalline partitioning of Al using very high-field ²⁷Al magic angle spinning nuclear magnetic resonance. In both dry and hydrous orthopyroxene, aluminium is shown to be incorporated by a Tschermak's substitution (one tetrahedral and one octahedral Al), thus the incorporation mechanism of Al in orthopyroxene is not a valid basis for a geohygrometer. However, the effect of OH on the local environment of Al has been observed, and quantification of all the different types of Al in the hydrous samples suggests that OH is incorporated by protonation of O21 and O22 sites. The results suggest that NMR studies on nuclei other than ¹H offer new possibilities for studying the interaction of water with mantle minerals.

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1. Introduction

In recent years it has become widely acknowledged that water can play a crucial role in modifying the physical properties and behaviour of the Earth's mantle [2–8]. In particular the realisation that significant concentrations of water can be dissolved in nominally

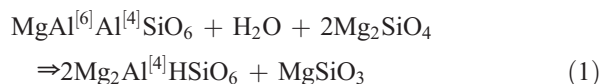
anhydrous minerals (NAMs) such as olivine, pyroxene and garnet has led to numerous measurements of water concentrations in natural mantle materials (e.g., [3,9,10]) and experimental studies of the solubility limits of water in NAMs (e.g., [11–14]). Diffusion studies have shown that H is very mobile in NAMs [3], therefore measurements of the water concentrations of minerals in xenoliths or magmatic phenocrysts are difficult to interpret, because of the potential for hydration or dehydration during ascent. These problems could be avoided if a suitable proxy structural or chem-

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ical signature for dissolved water concentration could be found; if this proxy had sufficiently slow re-equilibration kinetics it could be used as a geohygrometer to determine the original water concentration of xenoliths or phenocrysts.

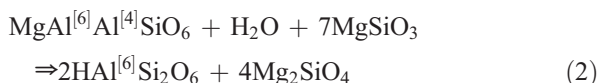
One nominally anhydrous phase which has now been studied a number of times by different groups is orthopyroxene [1,15–18]. These studies have shown that the water solubility depends on pressure, temperature, the concentration of additional components, such as Al, Cr and V and possibly the silica activity. However, in detail, there are disagreements between the different studies concerning the quantification of water solubility, the mechanisms of water dissolution and the quantitative effects of the presence of additional chemical components. Some of the disagreements can be attributed to the methods used to quantify infrared spectra since different groups use different extinction coefficients and background subtractions. Unreported differences in chemical environments may also play a role.

One crucially important factor determining the solubility of water in natural orthopyroxenes is likely to be the concentration of aluminium. Mantle orthopyroxene contains aluminium and other trivalent cations, therefore coupled substitutions such as $\text{Al}^{3+} + \text{H}^+$ substituting for 2Mg^{2+} are to be expected and experimental studies so far have shown a strong correlation between Al and OH concentrations in Al-doped enstatite [1,15,16]. The magnitude of the effect is not clear however, as the effect of Al on the solubility of H reported by Rauch and Keppler [1] is several times larger than in the other studies. The experimental pressures and temperatures in all three studies are quite similar, so the reason for this discrepancy is puzzling. Rauch and Keppler [1] suggested that the coupled substitution could be expressed by the equilibrium

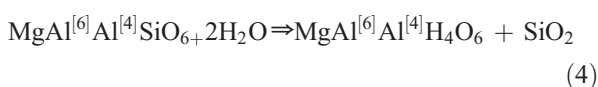
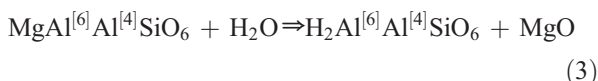


where $\text{MgAl}^{[6]}\text{Al}^{[4]}\text{SiO}_6$ is an orthopyroxene component with Al in Tschermak substitution and $\text{Mg}_2\text{Al}^{[4]}\text{HSiO}_6$ is an orthopyroxene component with tetrahedral Al only, charge balanced by H. They proposed that the intracrystalline partitioning of Al between octahedral and tetrahedral sites could therefore, in principle at least, be used as a geohygrometer for orthopyroxene, even when water is lost from a xenolithic or phenocrystic orthopyroxene during ascent and depressurisation.

However there are alternative possibilities for H and Al incorporation, such as the reaction



suggested by [15], where $\text{MgAl}^{[6]}\text{Al}^{[4]}\text{SiO}_6$ is again an orthopyroxene component with Al in Tschermak substitution and $\text{HAl}^{[6]}\text{Si}_2\text{O}_6$ is an orthopyroxene component with octahedral Al only, charge balanced by H. Finally the H could be incorporated without any change in the ratio of octahedral:tetrahedral aluminium, via reactions such as



These reactions are analogous to the protonation of Mg or Si vacancies in Al-free orthopyroxene, but could potentially be enhanced by the presence of Al, and therefore explain the increase in water solubility as a function of increasing Al concentration.

The aim of the present study is therefore to synthesise both dry and hydrous aluminous enstatite and to study the intracrystalline Al partitioning using ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR). ^{27}Al MAS NMR has been shown to be an excellent atomic scale probe of the environment of aluminium, readily distinguishing AlO_4 , AlO_5 and AlO_6 local environments [19–21]. The different local coordinations can be readily identified through their different chemical shifts. Nuclei like aluminium, which have a nuclear spin $>1/2$, also experience a nuclear electric quadrupole interaction arising from the interaction between the electric quadrupole moment of the nucleus (eQ) and the electric field gradient at the nucleus (eq). This interaction is usually characterised by the quadrupole coupling constant ($\chi_Q = e^2Qq/h$) and asymmetry parameter (η) [19,22]. The results will be used to test the theoretical basis for an Al-based geohygrometer for aluminous orthopyroxene.

2. Experimental methods

2.1. Sample synthesis

The samples were prepared from glass starting materials. The glass was made by finely grinding mixtures of MgO , SiO_2 and Al_2O_3 , melting these mixtures at

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