



Water incorporation in spinel: modelling hydrogen storage in the transition zone

Geoffrey Bromiley (1), Fabrizio Nestola (2), Simon A.T. Redfern (3), and Ming Zhang (3)

(1) School of GeoScience/CSEC, University of Edinburgh, UK(geoffrey.bromiley@ed.ac.uk), (3) Dept. Earth Sciences, University of Cambridge, Cambridge, UK, (2) Dipartimento di Geoscienze, Università Padova, Italy

Under conditions of the lower part of Earth's mantle transition zone, $(\text{Mg,Fe})_2\text{SiO}_4$ adopts a spinel type structure as the mineral ringwoodite. This structure, although nominally anhydrous, has the capacity to incorporate significant amounts of water (up to several weight percent) in the form of structurally-incorporated OH groups. This has led to the suggestion that a significant volume of water could be incorporated in Earth's mantle transition zone, and even that this reservoir might be connected to water present on the surface of the Earth. Characterising the cause and effects of hydrogen incorporation in ringwoodite remains difficult due to the high-pressure/temperature conditions under which it is stable.

In order to characterise mechanisms for H incorporation in spinel-type structures we have investigated H incorporation in natural and synthetic MgAl_2O_4 spinel in a series of high-pressure/temperature annealing experiments. In contrast to most other nominally anhydrous minerals, natural spinel appears to be completely anhydrous. On the other hand, non-stoichiometric Al-rich synthetic (defect) spinel can accommodate several hundred ppm water in the form of structurally-incorporated hydrogen. Infrared (IR) spectra of hydrated defect spinel contain one main O-H stretching band at 3343-3352 cm^{-1} and a doublet consisting of two distinct O-H bands at 3505-3517 cm^{-1} and 3557-3566 cm^{-1} . IR spectra and structural refinements based on single-crystal X-ray data are consistent with hydrogen incorporation in defect spinel onto both octahedral and tetrahedral O-O edges. Fine structure of O-H bands in IR spectra can be explained by partial coupling of interstitial hydrogen with cation vacancies, or by the effects of Mg-Al disorder on the tetrahedral site. The concentration of cation vacancies in defect spinel is a major control on hydrogen affinity. The commercial availability of large single crystals of defect spinel coupled with high water solubility and similarities in water incorporation mechanisms between hydrous defect spinel and hydrous ringwoodite (Mg_2SiO_4) suggests that synthetic defect spinel may be a useful low-pressure analogue material for investigating the causes and consequences of water incorporation in the lower part of Earth's mantle transition zone.