

H in garnet: Implications for upper mantle H₂O storage capacity

ANTHONY C WITHERS AND MARC M HIRSCHMANN

Dept of Earth Sciences, University of Minnesota, MN, USA

The maximum amount of H₂O that can be stored in mantle minerals without saturation to stabilise a fluid or melt (the H₂O storage capacity) varies as a function of pressure, temperature and peridotite phase assemblage. The systematics of H₂O storage capacity in olivine and pyroxene are relatively well established. The H₂O storage capacity of nominally anhydrous garnet, on the other hand, is poorly understood. Measurements of H in pyropes synthesised in hydrothermal experiments at 1000 °C suggest that the hydrogarnet component becomes destabilised at pressures greater than 7 GPa [1], suggesting that under conditions approaching those of the transition zone, where garnet makes up an appreciable proportion of the mantle, garnet does not contribute significantly to the mantle H₂O storage capacity. Annealing of natural pyrope under similar conditions of P and T, however, suggest that other types of H defect may result in pyrope storage capacities approaching 200 ppm H₂O at 10 GPa [2]. In contrast, H contents in excess of 1000 ppm H₂O were measured in natural, Fe-bearing pyropic garnet that was hydrothermally annealed in the presence of olivine at 1100 °C at pressures up to 9 GPa [3]. If such elevated H₂O storage capacities are applicable to mantle garnet, H₂O fluxed melting of the upper mantle overlying the transition zone would require bulk H₂O concentrations in excess of 600 ppm [4].

We have examined the systematics of H incorporation in pyrope in 24h hydrothermal experiments at 2-8 GPa and 1400 °C. Platinum capsules were loaded with 2 compositional layers such that the upper part of the capsule contained pure pyrope (py) composition and the remainder a mixture of forsterite (fo), enstatite (en) + 5 wt.% Al₂O₃. Buffering of SiO₂ activity by growth of fo and en during experiments was verified by Raman spectroscopy. Grain growth in the py composition layer was facilitated by lack of grain boundary pinning. FTIR spectra of 100-700 μm pyropes from experiments at 4, 6 and 8 GPa all display a characteristic hydrogarnet absorption band. Our preliminary results suggest that H content is close to 235±75 ppm H₂O over this pressure range. At mantle temperatures, it is unlikely that garnet is a major contributor to bulk mantle H₂O storage capacity.

[1] Withers *et al* (1998), *Chem Geol* **147**, 161-171. [2] Lu and Keppler (1997), *Contrib. Mineral. Petrol.* **129**, 35-42. [3] Mookherjee and Karato (2010), *Geophys. Res. Lett.* **37**, L03310. [4] Tenner *et al* (2012), *Contrib Mineral. Petrol.* **163**, 297-316.

Comparison of LDI and ESI to study natural organic matter on the molecular level by FT-ICR mass spectrometry

M. WITT¹

¹Bruker Daltonik GmbH, Bremen, Germany

FT-ICR mass spectrometry of NOM

Fourier Transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS) is a well known method to study natural organic matter (NOM) on the molecular level. Mainly electrospray ionization in negative ion mode is used to detect compounds in this complex mixture. However, also Laser/desorption ionization (LDI) in negative ion mode can be used to study NOM. LDI has been used recently to analyze crude oil by FT-ICR mass spectrometry [1]. LDI has the advantage to be independent of the solvent. Several NOM standards have been analyzed by ESI and LDI for comparison of both ionization techniques. Additionally the effect of collision energy and laser power has been studied.

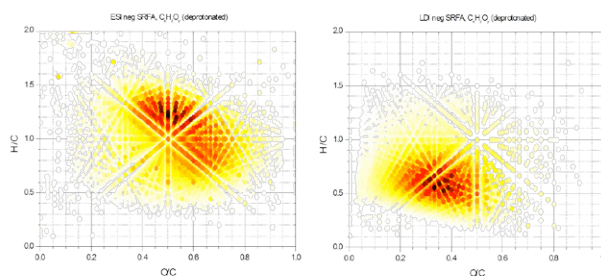


Figure 1: Van Krevelen plots of ESI- and LDI-FT-ICR MS measurement of Suwannee river fulvic acid

Discussion and results

Calculations of the molecular formulas of detected compounds were based on exact mass measurements using ultra-high resolution and high mass accuracy of FT-ICR mass spectrometry. Lower H/C as well as O/C ratios have been observed in LDI than ESI. This effect is shown in the Van Krevelen plots of Suwannee river fulvic acid in Figure 1. Therefore, highly aromatic compounds are ionized using LDI at UV-wavelength of 355 nm.

Collision induced fragmentation results mainly in a loss of CO₂. However, experiments with high laser power results only in a loss of water.

[1] Cho *et al.* (2012) *Anal. Chem.* **84**, 8587-8594.