

## 1.1.24

### Is hydrogen loss via iron oxidation an important mechanism in nominally anhydrous minerals?

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The quantification of OH bound in nominally anhydrous minerals (NAM) is a key issue for estimating OH content and its repartition in the upper mantle. However, OH values obtained from xenolithic minerals may not be representative of the actual OH content of the upper mantle, since hydrogen may be lost during the xenoliths' ascent. The relatively fast redox reaction ( $\text{Fe}^{2+} + \text{OH}^- = \text{Fe}^{3+} + \text{O}^{2-} + \frac{1}{2} \text{H}_2$ ) is believed to be largely responsible for this partial OH loss. In the present study, both  $\text{OH}^-$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  were measured in grossular and diopside single crystals to evaluate the significance of this dehydrogenation-oxidation reaction in NAM.

Infrared and Mössbauer spectra were taken during stepwise dehydration (at 1 atm and 600 to 900°C) of a natural grossular single crystal. The results indicate that, initially, the OH decrease is correlated with a decrease in  $\text{Fe}^{2+}$ , but not in a 1:1 ratio as would be the case if the dehydration occurred only through iron oxidation. In a second step, the dehydration proceeds without further oxidation of iron, indicating that another dehydration mechanism must be responsible for the final OH loss.

Synthetic diopsides with well-suited iron contents and no initial OH were treated stepwise in  $\text{H}_2$  at 700°C and 1 atm. Owing to the small crystal size, the iron oxidation state was analyzed by optical spectroscopy (using the  $\text{Fe}^{2+}$  band at  $9650\text{-}9700\text{ cm}^{-1}$ ) rather than Mössbauer spectroscopy. Infrared and optical spectroscopy results show that hydrogen incorporation by diopside is accompanied by an increase in the amount of  $\text{Fe}^{2+}$  in the octahedral site. However, the amount of  $\text{Fe}^{2+}$  produced appears to be higher than the amount of hydrogen incorporated. This excess reduction must therefore be charged-balanced by a mechanism other than hydrogen diffusion.

Hydrogenation-dehydrogenation via reduction-oxidation of iron is occurring in the grossular and diopsides studied. The divergence of  $\text{OH}:\text{Fe}^{2+}$  from 1:1, however, indicates that other competing reactions must occur during the dehydration/hydration of these NAM. The redox reaction may nevertheless be the most efficient process for removing OH from ascending mantle xenoliths owing to its fast kinetics.

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### Micro-analysis of hydrogen in minerals by use of a proton beamline technique

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With the increased interest in the occurrence of light elements in geological materials the need for accurate micro-analytical methods applicable to such elements has become evident. An important element in this respect is hydrogen, which has been shown to occur as a trace element in many nominally anhydrous minerals. Specifically, the presence of hydrogen in several of the major minerals in the Earth's mantle has received attention, due to the possibility that these phases provide a significant hydrogen reservoir. Development of both spectroscopic (FTIR) and analytical techniques (NRA, SIMS) has improved the knowledge on hydrogen abundances in minerals, but a precise micro-analysis method is strongly needed.

The possibility to measure hydrogen in thin mineral samples by elastic proton-proton scattering has been investigated by use of a proton beamline facility at Lund Institute of Technology. A special annular surface-barrier detector composed of two insulated halves, which are read out simultaneously, is used to detect recoiled and scattered protons in coincidence. Conditions on the difference in time and energy of the detected particles make it possible to distinguish true hydrogen events from false or random ones. Homogenous Mylar foils with known hydrogen content are used as reference. The method has been tested with a 2.8 MeV proton beam on samples of hydrous minerals with relatively high hydrogen contents, and on nominally anhydrous minerals with hydrogen concentrations in the range 100-1000 ppm  $\text{H}_2\text{O}$ . The results appear promising, and demonstrate that it is possible to distinguish intrinsic hydrogen from water molecules adsorbed on the sample surfaces. The spatial resolution of the method is in the  $\mu\text{m}$  (or sub- $\mu\text{m}$ ) range, and the analytical detection limit is estimated to 10 ppm  $\text{H}_2\text{O}$ .