Water Stored as OH in Orthopyroxene and Olivine in Peridotites from the Upper Earth Mantle: Combining Infrared Spectroscopy and Proton–Proton–Scattering ◇

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Orthopyroxene and olivine are regarded as the most important hosts of water in the Earth's upper mantle. In these nominally water-free minerals, colloquially 'water' or hydrogen respectively is stored as OH defects [1] in the crystal structure. Single crystals of orthopyroxene in spinel peridotites from the Mid-Atlantic ridge, sampled in the course of the Ocean Drilling Program (ODP Legs 153 and 209), was analysed by Fourier–transformed infrared (FTIR) microspectroscopy using polarized IR–radiation and a MCT–detector. Detectable amounts of OH were found in samples of ODP Leg 153 with concentrations of about $120 - 200$ μg/g OH ($150 - 250$ at-ppm H). The OH concentration in olivine is below the detection limit of about 10 μg/g (12.5 at-ppm H).

A better detection limit could be achieved by thicker single crystal slices. However, the microphotograph of a thin section of spinel peridotite (Fig. 1) clearly shows that preparation of gem-quality single crystals for precise IR measurements is difficult.

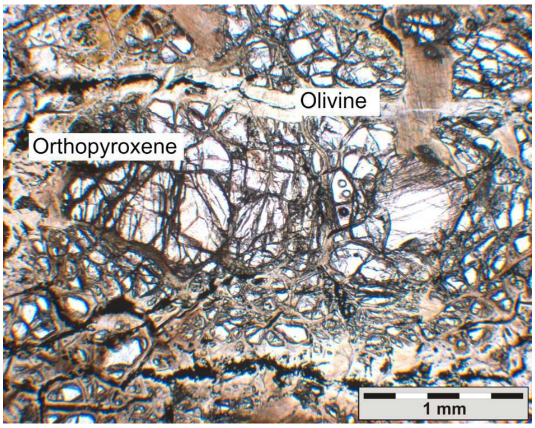

Fig. 1: Microphotograph of a thin section (25-30 μm) of spinel peridotite.

In the second step, we intended to quantify the OH content in olivine and to get more detailed information about the radial OH distribution inside the olivine and orthopyroxene crystals, e.g. to study diffusion processes that give us information on the geological history of rocks.

Although, with IR–spectroscopy one can distinguish between different OH bonds in the structure, significant higher sensitivity (< 1 μg/g OH) and spatial resolution (< 1 μm) is required, particularly in small crystals. Hence, we intended to apply the proton–proton–scattering method at the microprobe SNAKE [2]. The proton–scattering method does not need reference material for calibration and gives the total amount of H–atoms with surface and subsurface hydrogen clearly separated from the bulk content. With IR spectroscopy different H–bonds appear as bands at different wavenumbers. The IR diagram in Fig. 2 shows exemplarily a band with two pleochroitic main peaks, indicating OH stretching vibrations caused by OH defects only [3]. Due to the bands of the IR diagram the concentration of OH and H respectively was calculated using the calibration from Bell et al. [3]. Other types of H–bonds are below the detection limit or absent.

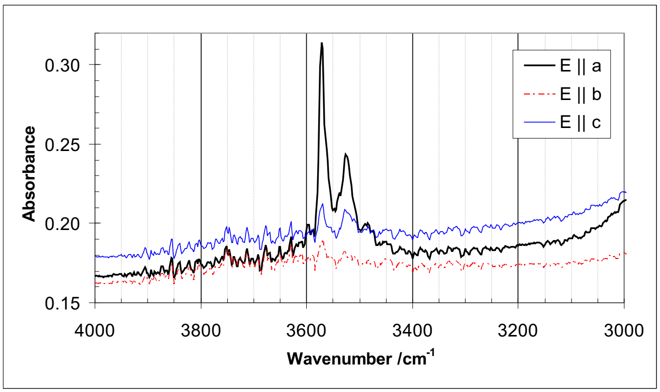

Fig. 2: Diagram of IR measurements with polarized IR radiation of an olivine from Nigeria in the region of OH fundamentals showing the absorbance with the E-vector parallel to the three crystallographic axis a, b, and c. The strongest bands appear when $E \parallel a$, indicating the orientation of the OH bond along the a-axis.

Primarily, the proton scattering method was applied without the microscopic system [4] on samples of gem-quality olivines – simplified formula $(Mg_{0.9}Fe_{0.1})_2SiO_4$ – from different geographic locations. Table 1 shows the results for two olivines compared to the FTIR analysis.

Sample	H-Content [at-ppm]	
	FTIR	Proton-Scattering[a]
Nigeria	17.6	11.6 ± 2.6
Pakistan	83	99 ± 21

Table 1: H-contents in olivine (IR and proton-scattering data). [a]Mean value of two measurements, different sample locations.

The uncertainty for quantification with FTIR is hard to calculate due to local fluctuations in sample mineral and reference materials used for calibration, but is estimated here to be $15 - 20\,\%$ in total. Furthermore we note that for the Nigeria olivine the result is close to the detection limit of the IR spectroscopy system. Therefore, for this first test experiment we conclude that the two analytical methods are in good agreement.

References

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