Quantification of Hydrogen Traces in Nominally Anhydrous Minerals ◇

S.M. Thomas [a], A. Bergmaier [b], P. Reichart [b], G. Dollinger [b], and M. Koch–Müller [a]
[a] GeoForschungsZentrum Potsdam, Sektion 4.1, Telegrafenberg, 14473 Potsdam
[b] Universität der Bundeswehr München, Dept. für Luft- und Raumfahrttechnik 2, 85577 Neubiberg

Experimental studies have shown that major earth's crust and mantle constituents, that by their formulae do not contain any hydrogen, are able to dissolve traces of hydrogen in form of hydroxyl groups (expressed as wt ppm H_2O: 1 to 8000). Hydrogen is incorporated in the structures of these so-called nominally anhydrous minerals (NAMs) as point defect. Even these low water contents in minerals are able to constitute the majority of earth's water and thus, on a global scale, the water dissolved in the upper mantle may exceed the amount of water in the hydrosphere. The presence of water in the earth has enormous effects on geodynamical processes, because it changes the physical mineral properties such as electrical conductivity and deformation strength. To understand those effects and their influence on crust and mantle processes, it is crucial to know the influence of varying water contents on mineral properties as well as maximum solubility, incorporation mechanisms and liable parameters. At the GeoForschungsZentrum Potsdam we are able to synthesize NAMs with varying water contents and investigate the hydrogen incorporation. Essential part and aim of this project is to quantify the trace amounts of water and finally the introduction of a new mineral specific infrared calibration for the quartz and the olivine system to facilitate a future routinely hydrogen quantification.

A high-throughput method to determine trace amounts of hydrogen in minerals is the Fourier–transform infrared spectroscopy (FTIR). This technique allows characterizing hydrogen bond geometry, spatial OH–dipol orientation and finally the necessary information about proton localization. However, for quantification of FTIR a calibration using reference samples is essential. Several now commonly used calibrations have been developed [1,2] on the basis of hydrous minerals and glasses,but recent studies showed that these calibrations are not applicable to NAMs. Thus, there is need for an appropriate mineral specific calibration for each NAM by means of an independent absolute method. Another method to detect hydrogen traces is the secondary ion mass spectrometry. Still, the secondary ion yields vary greatly according to the chemical environment and the sputtering conditions and a well characterized reference sample is required as with FTIR. Additionally, due to possible matrix effects this reference sample should be of the same structure and composition.

To overcome these quantifications problems, ion beam analysis methods with high energetic ions are suitable methods as they allow direct quantification without influence of structure or composition. Only proton–proton–(pp) scattering [3] has sufficient sensitivity to quantify the hydrogen content of NAMs and we are using this method at the Munich accelerator lab in order to get homogeneous, well characterized reference material for FTIR and SIMS studies. To provide a series of reference material with varying water concentrations we selected various natural samples. Natural samples are likely to have large scale heterogeneity of the hydrogen content as demonstrated in Fig. 1.

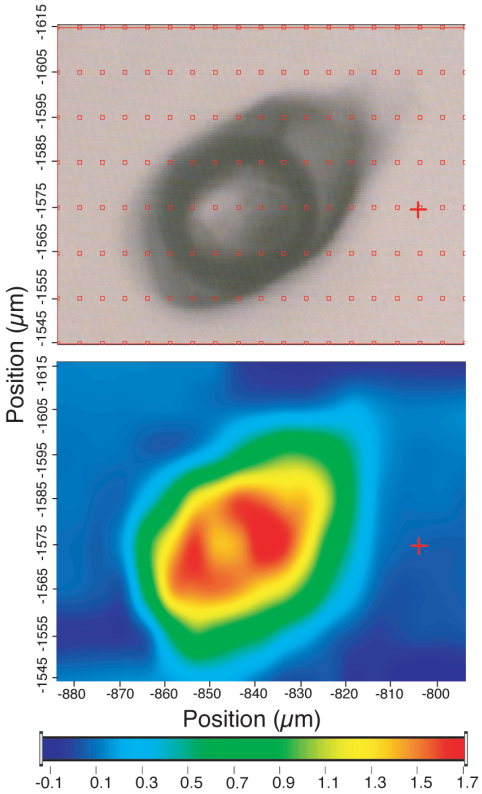

Fig. 1: Measuring points (upper) and resulting chemical map (lower) of the OH–distribution in a quartz sample (measured sample area: 50×90 μm) recorded using synchrotron infrared spectroscopy with a local resolution of 15×15 μm. The chemigram resembles the integrated spectral intensity of the measured spectral region ($3700 - 3000$ cm^{-1}) for each sample point. The final area map (step size 5×10 μm) reveals an inclusion and therewith the heterogeneity of the sample. Since our study requires homogeneous material, such substances are removed from the list of reference samples.

The lower images shows a map of the OH–distribution recorded with Synchrotron IR–microspectroscopy. This allows us to choose a set of homogeneous samples for the study. First samples have been investigated with broad-beam pp–scattering and the hydrogen content could be quantified with a detection limit around 2 ppm(at) [4]. Future studies are planned at the microprobe SNAKE. The microscopic spatial resolution will allow us to investigate synthetic samples (which usually have dimensions of only few 100 μm) and avoid wrong quantifications due to microscopic inclusions as shown in Fig. 1.

References

[1] E. Libowitzky, G.R. Rossman, Am. Mineralogist **82** (1997) 1111
[2] M.S. Paterson, Bulletin de minéralogie **105** (1982) 20
[3] P. Reichart *et al.*, Science **306** (2004) 1537
[4] P. Reichart *et al.*, Annual report 2006

◇ corresponding author: Sylvia-Monique Thomas, smthomas@gfz-potsdam.de