Quantitative hydrogen analysis in minerals based on a semi-empirical approach

P. Kristiansson1, 2, M. Borysiuk1, H. Skogby2, L. Ros1, N. Abdel1, M. Elfman3, E.J.C. Nilsson1 and J. Pallon1

1 Division of Nuclear Physics, Department of Physics, Lund University, Lund, Sweden
2 Swedish Museum of Natural History, Department of Mineralogy, Stockholm, Sweden

Introduction and model

Hydrogen normally occurs as hydroxyl ions related to defects at specific crystallographic sites in the structures, and is normally characterised by infrared spectroscopy (FTIR). For quantification purposes the FTIR technique has proven to be less precise since calibrations against independent methods are needed. Hydrogen analysis by the NMF technique can solve many of the problems, due to the low detection limit, high lateral resolution, insignificant matrix effects and possibility to discriminate surface-adsorbed water.

In this work we present the last step towards a quantitative technique for hydrogen measurement based on a set of mineral standards and pre-sample charge normalization. We will present characterization of the calibration standard and give examples from analysis of minerals with known hydrogen concentration.

In earlier work it has been noted that a large portion of the energy distribution has an exponential behaviour and this has been the basis for the idea parameterization of the inner part of the energy spectra.

\[ N(E) = N_0 \cdot e^{-E/k} \]

Hence, the concentration is

\[ R_{\text{concentration}} = \frac{N_{\text{sample}}(E)}{N_{\text{standard}}(E)} = \frac{N_{\text{sample}} \cdot e^{-E/k}}{N_{\text{standard}} \cdot e^{-E/k}} = \frac{N_{\text{sample}}}{N_{\text{standard}}} \]

Calibration samples

**Muscovite**
- Easy to prepare, natural
- Strongly bound hydroxyl ions
- Ternal stability
- Stoichiometry: 4.2% H2O

**Zoisite**
- Verified concentration by continuous flow mass spectroscopy
- Stoichiometry: 2.01% H2O

Measured elemental concentration of the in muscovite sample measured with an electron microprobe. The concentrations marked with an * are calculated from stoichiometry.

Depth profiles with DSSSD
- 10 µm muscovite sample and zoisite sample
- Zoisite sample much thicker
- Lower concentration in zoisite than in the muscovite but more than expected
- exponential lines to guide the eye.

Summary
- A semi-quantitative set-up for hydrogen bulk analysis and profiling has been suggested.
- Combination of the pre-sample charge measurement and a mineral-based standard.
- Model needs improvement, thickness dependent.
- Muscovite concentration not verified.

Improvement of system
- The DSSSD acquisition needs an upgrade.

Selected references

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