A new in-situ method to quantify water in rutile from eclogites

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Rutile is a common accessory mineral occurring in most lithologies throughout eclogite facies conditions and is frequently used for a variety of applications such as U-Pb age determinations and Zr-in-rutile thermometry. As several studies show, Rutile has an affinity to substitute pentavalent (e.g. Nb^{5+}, Ta^{5+}) and trivalent (e.g. Fe^{3+}, Al^{3+}, Cr^{3+}) cations for Ti^{4+}, with a possibility of charge balance between tri- and pentavalent cations. Additionally, rutile can incorporate high amounts of H^+ up to several 1000 µg/g H_2O. Infrared (IR) absorption of water in rutile is highly anisotropic (*e.g.*, Soffer, 1961). Thus, water measurements by Fourier Transform (FT) IR spectroscopy so far were mainly performed on oriented grains or resulted in high uncertainties when performed on un-oriented grains with statistical approaches to calculate water contents. We present a new method to quantify water in rutile in randomly oriented grains without high uncertainties. Polarized FTIR measurements, with polarization along the crystallographic a-axis leads to the same maximum absorbance spectra (within the instrument error) as measurements on oriented samples cut perpendicular to the crystallographic c-axis. This new method allows the in-situ analysis of Rutile grains in double polished thick sections and thus preserves the textural context. Consequently, it is possible to distinguish different growth phases with the potential of different water activities, i.e., rutile as inclusions in garnet from matrix rutile.

As H^+ incorporation into rutile is linked to the substitution of trivalent cations, it is possible to identify several different trace element-dependent OH-bond positions in FTIR spectra. Several studies on experimentally doped rutile have been able to establish those positions, but very limited work has been done to verify those for natural rutile. We performed FTIR and LA-ICP-MS measurements on a variety of samples to identify trace element-related OH-peak positions. Here we present evidence for several OH-peak positions related to di- and trivalent cations and their inter-sample shifts as deduced by peak deconvolution methods on IR absorption spectra. The main trace element dependent OH-peak positions can be related to Ti^{3+}, Fe^{3+} and Al^{3+}, with OH-bands related to V^{3+} or Mg^{2+} being less common. In natural eclogitic rutile, one specific trace element dependent OH-peak position can vary in a wavenumber range of up to 6 cm^{-1}. Ti^{3+}- and Fe^{3+}-related OH-bonds were found in samples from Alpe Arami (AA), Capoli (CP), Dora Maira (DM), Pfulwe (PF) and Saualpe (SA) in a range of 3278–3282 cm^{-1} and 3293–3297 cm^{-1}, respectively. Al^{3+}-related OH-bonds, at positions between 3322–3327 cm^{-1} were measured in samples from AA and DM. In the DM whiteschist an additional Mg^{2+}-related OH-peak at 3348 cm^{-1} was visible and in a sample from CP an additional V^{3+}-related OH-peaks at 3391 cm^{-1}. Total calculated H_2O contents vary broadly. UHP samples from DM show very low H_2O contents (70–315 µg/g). The average calculated H_2O content in most studied eclogitic rutile from the afore mentioned localities is in a range of 800–1200 µg/g H_2O. Unusually, high H_2O contents were observed in samples from SA (2180 µg/g), PF (4130 µg/g) and Syros (6500 µg/g).

Soffer, B.H., 1961. Studies of the Optical and Infrared Absorption Spectra of Rutile Single Crystals. *Journal of Chemical Physics* 35, 940-945.