

Combination of high-resolution mapping with infrared spectroscopy and electron microprobe to study incorporation and retention of H in metamorphic garnet

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Metamorphic garnet is typically formed by dehydration reactions during prograde metamorphism. Although garnet is an anhydrous mineral, it can incorporate small amounts of H₂O in the form of OH groups. During the metamorphic history of a mineral, the pressure, temperature and the reactive bulk composition change. This leads to compositional zoning in garnet. These zoning offer opportunity to investigate the compositional control of OH incorporation (by coupled substitutions) and OH retentivity with respect to diffusive modification during the metamorphic history.

In order to harvest this information, a combined mapping protocol and a suite of routines have been developed in order to superimpose maps obtained with the electron microprobe (EPMA) and high-resolution infrared spectroscopy (FPA-FTIR). The distributions of minor and major elements (EPMA) are compared in 2D with the OH content (FTIR) at the scale of 6 μm. Statistic correlation between OH absorption bands and garnet composition based on 10'000's of analyses can then be achieved.

This method has been used to investigate the Ti-OH relationship in metamorphic Ti-bearing garnets (grossular & andradite). A molar 1/1 correlation has been found between Ti and H in both garnets. This correlation suggests a coupled substitution in the form of a Ti₂H₂ point defect. This means that for a given OH quantity, twice the amount of Si-vacancy are needed in comparison to a hydrogarnet substitution [O₄H₄], which might influence rheology of the host garnet. The compensation of Ti⁴⁺ extra charges with H⁺ has strong influence on the Fe²⁺/Fe³⁺ calculation. On another hand, the preservation of H₂O-zoning at the 50 μm scale in rocks that reached 550 °C enables to compute a minimal diffusional loss during the metamorphic history, showing that the Ti₂H₂ substitution is more retentive than other H defects.

The strategy presented in this study opens new perspectives for the investigation of NAMs and especially concerning the effect of major and trace elements on the mechanism of OH incorporation. This includes the investigation of coupled substitutions, documentation of hydration events and the discrimination between OH zoning related to growth zoning and diffusion.