# IR Absorption Coefficients for the Quantification of Water in Hydrous Ringwoodite

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Raman spectroscopy, combined with the 'Comparator technique' has been developed to determine water contents ranging from a few wt ppm to wt% in glasses and nominally anhydrous minerals including garnets, olivine, and $SiO_2$ polymorphs (Thomas et al. 2009). The routine is one promising example of quantification tools to determine mineral specific molar absorption coefficients ($\varepsilon$) for IR spectroscopy. Mineral specific absorption coefficients are required because general IR calibrations do not necessarily apply to minerals with water incorporated as hydroxyl point defects.

Here we utilize the 'Comparator technique' to provide $\varepsilon$-values for a set of synthetic Fe-free ($Fo_{100}$) and Fe-bearing ($Fo_{90}$, $Fo_{87}$, $Fo_{83}$, $Fo_{60}$) ringwoodites, as well as for $\gamma$-$Mg_2GeO_4$. Ringwoodite is considered one of the major phases of the Earth's lower transition zone (520-660 km depth) and the knowledge of its absolute water storage capacity is essential for modeling the Earth's deep water cycle. Samples were synthesized at variable P-T conditions in a multi-anvil press and cover a range of OH contents. Single-crystals were characterized using X-ray diffraction and IR spectroscopy. Mineral specific IR absorption coefficients were calculated from independently determined water contents from Raman spectroscopy. Unpolarized IR spectra of Mg-ringwoodite show broad absorption features in the OH region with band maxima at $\sim$2350, 2538, 3130, 3172, 3598 and 3688 $cm^{-1}$. In the spectra of Fe-bearing ringwoodite and $\gamma$-$Mg_2GeO_4$ the maxima of the main OH band are shifted to 3244 $cm^{-1}$ ($Fo_{60}$) and 3207 $cm^{-1}$, respectively. For Mg-ringwoodite with the mean wavenumber (area-weighted average of the peak position) of 3170 $cm^{-1}$ an $\varepsilon$-value of 191500 $\pm$ 38300 L $cm^{-2}$/ $mol_{H2O}$ was determined. For the ringwoodites with $Fo_{90}$, $Fo_{87}$ and $Fo_{83}$ composition and the mean wavenumbers of 3229 $cm^{-1}$, 3252 $cm^{-1}$ and 3163 $cm^{-1}$ values of 123600 $\pm$ 24700 L $cm^{-2}$/ $mol_{H2O}$, 176300 $\pm$ 52900 L $cm^{-2}$/ $mol_{H2O}$ and 155000 $\pm$ 46500 L $cm^{-2}$/ $mol_{H2O}$ were computed.

Our value for pure Mg-ringwoodite is in very good agreement with the value according to Libowitzky & Rossman (1997) and the absorption coefficient proposed by Balan et al. (2008), but is higher than the extrapolated value from Koch-Müller & Rhede (2010). However, in case of the sample with $Fo_{60}$ composition water content and $\varepsilon$-value determined here are in excellent agreement with those calculated by Koch-Müller & Rhede (2010).

Here, we will further discuss general IR calibrations and the dependence of $\varepsilon$ on structure, composition and frequency for the $(Mg,Fe)_2SiO_4$ polymorphs in the mantle. We agree with the findings of Koch-Müller & Rhede (2010), which report that using the calibrations according to Paterson (1982) and Libowitzky & Rossman (1997) leads to a water content underestimation in case of Fe-rich (Fay-$Fo_{60}$) samples. At this point this cannot be generalized for Mg-rich ringwoodite.

References

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