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Water quantification in olivine and wadsleyite by Raman spectroscopy and study of errors and uncertainties

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Abstract

The study of nominally anhydrous minerals with vibrational spectroscopy, despite its sensitivity, tends to produce large uncertainties (in absorbance or intensity) if the observed dispersion of the values arising from the anisotropy of interaction with light in non-cubic minerals is not assessed. In this study, we focused on Raman spectroscopy, which allows the measurement of crystals down to a few micrometers in size in backscattered geometry, and with any water content, down to 200 ppm by weight of water. Using synthetic hydrous single-crystals of olivine and wadsleyite, we demonstrate that under ideal conditions of measurement and sampling, the data dispersion reaches ±30% of the average (at 1σ) for olivine and ±32% for wadsleyite, mostly because of their natural anisotropy. As this anisotropy is linked to physical properties of the mineral, it should not be completely considered as an error without treatment. By simulating a large number of measurements with a 3D model of the OH/Si spectral intensity ratio for olivine and wadsleyite as a function of orientation, we observe that although dispersion increases when increasing the number of measured points in the sample, analytical error decreases, and the contribution of anisotropy to this error decreases. With a sufficient number of points (five to ten, depending on the measurement method), the greatest contribution to the error on the measured intensities is related to the instrument's biases and reaches 12 to 15% in ideal cases, indicating that laser and power drift corrections have to be carefully performed. We finally applied this knowledge on error sources (to translate data dispersion into analytical error) on olivine and wadsleyite standards with known water contents to build calibration lines for each mineral to convert the intensity ratio of the water bands over the structural bands (OH/Si) to water content. The conversion factors from OH/Si to parts per million by weight of water (H_2O) are 93 108 ± 24 005 for olivine, 250 868 ± 53 827 for iron-bearing wadsleyite, and 57 862 ± 12 487 for iron-free wadsleyite, showing the strong effect of iron on the spectral intensities.

Keywords: Wadsleyite, olivine, nominally anhydrous minerals, Raman spectroscopy, water quantification