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Quantitative micro-Raman analysis of volcanic glasses: influence and correction of matrix effects

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Micro-Raman spectroscopy, even though a very promising micro-analytical technique, is still not used to routinely quantify volatile elements dissolved in glasses. Following an original idea of Galeener and Mikkelsen (1981) for the quantification of hydroxyl (OH) in silica glass, several quantitative procedures have been recently proposed for the analysis of water, sulphur and carbon in natural glasses (obsidians, pumices, melt inclusions). The quantification of a single analyte requires the calibration of the correlation between the intensity I (height or area) of the related Raman band, normalized or not to a reference band RB, and the analyte concentration. For the analysis of alumino-silicate glasses, RB corresponds to one of the two main envelopes (LF and HF) related to the vibration of the glass network. Calibrations are linear, provided the increase in the analyte concentration does not dramatically affect RB intensity. Much attention has been paid to identify the most appropriate spectral treatment (spectra reduction; baseline subtraction; etc) to achieve accurate measurement of band intensities. I here show that the accuracy of Raman procedures for volatile quantification critically depends on the capability in predicting and in taking into account the influence of multiple matrix effects, which are often correlated with the average polymerization degree of the glass network. A general model has been developed to predict matrix effects affecting micro-Raman analysis of natural glasses. The specific and critical influence of iron redox state and pressure are discussed. The approach has been extensively validated for the study of melt inclusions and matrices spanning a broad range of compositions and dissolved volatile contents.

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Analytical procedures

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