

Determination of the oxidation state of iron in Mid-Ocean Ridge basalt glasses by Raman spectroscopy

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ABSTRACT

A series of synthetic Mid-Ocean Ridge Basalt (MORB) glasses with $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ from 0 to 1, determined previously by Mössbauer spectroscopy, were used to test methods for quantifying $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ by Raman spectroscopy. Six numerical data reduction methods were investigated, based on conventional approaches as well as supervised and unsupervised machine learning algorithms. For the set of MORB glass standards, with fixed composition, the precision of all methods was $\leq \pm 0.04$ (1 St.dev.). However, Raman spectra recorded for 42 natural MORB glasses from a wide range of locations revealed a strong correlation between the spectra and composition, despite the latter varying only over a relatively limited range, such that the methods calibrated using the glass standards are not directly applicable to the natural samples. This compositional effect can be corrected by using a compositional term that links spectral variations to the $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ value of the glass. The resulting average $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ determined by Raman spectroscopy was 0.090 ± 0.067 ($n = 42$). This value agrees with the latest Fe *K*-edge XANES and wet-chemistry estimates of 0.10 ± 0.02 . The larger uncertainty of the Raman determination reflects the sensitivity of Raman spectroscopy to small changes in the glass structure. While this sensitivity is detrimental for high precision $\text{Fe}^{3+}/\text{Fe}^{\text{TOT}}$ determinations, it allows the major element composition of natural MORB glasses to be determined within 1 mol% through the use of an artificial neural network. This suggests that Raman spectrometers may be used to determine the composition of samples in situ at difficult to access locations that are incompatible with X-ray spectrometry (e.g., mid-ocean ridges).

Keywords: Mid-ocean ridge basalt, glass, Raman spectroscopy, iron, oxidation state, redox, machine learning