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 Fe$^{2+}$/Fe$^{TOT}$ from 0 to 1, determined previously by Mössbauer spectroscopy, were used to test methods for quantifying Fe$^{2+}$/Fe$^{TOT}$ 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 ±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 Fe$^{2+}$/Fe$^{TOT}$ value of the glass. The resulting average Fe$^{2+}$/Fe$^{TOT}$ 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 Fe$^{2+}$/Fe$^{TOT}$ 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

INTRODUCTION

Mid-ocean ridge basalts (MORB), derived from partial melting of the upper mantle, are central to our understanding of the geochemistry of the mantle and the formation of the oceanic crust (e.g., Langmuir et al. 1992; Asimow et al. 2004; O’Neill and Jenner 2012; Gale et al. 2013). MORB glasses, formed by rapid cooling at the rim of pillow lavas, enable the composition of the melts to be determined (e.g., Jenner and O’Neill 2012), including volatile contents (Kendrick et al. 2013) and oxidation states (Christie et al. 1986; Bézos and Humler 2005; Cottrell and Kelley 2011, 2013; Berry et al. 2018; Zhang et al. 2018; O’Neill et al. 2018). This, in turn, allows the intensive and extensive thermodynamic conditions of the mantle source to be calculated (e.g., Asimow et al. 2004). In particular, the oxidation state of Fe in MORB, expressed as Fe$^{2+}$/Fe$^{TOT}$ with Fe$^{TOT}$ = Fe$^{2+} +$ Fe$^{3+}$, is important because it affects estimates of temperature, mineral assemblages, and the speciation of volatile elements, both during the production of the parental magmas in the mantle and their subsequent low-pressure evolution.

The latest average Fe$^{2+}$/Fe$^{TOT}$ values of natural MORB glasses from global sources have been determined to be 0.10 ± 0.02 (Berry et al. 2018) and 0.14 ± 0.01 (Zhang et al. 2018) by Fe K-edge XANES spectroscopy, and 0.11 ± 0.02 by wet-chemistry (corrected for plagioclase phenocrysts, Bézos and Humler 2005). Wet chemistry is a destructive method that lacks spatial resolution and is unsuitable for inhomogeneous glasses or small samples such as melt inclusions (e.g., see Bézos and Humler 2005). Fe K-edge XANES spectroscopy has excellent precision and micrometer spatial resolution in two dimensions but requires glass standards that are compositionally matched and for which Fe$^{2+}$/Fe$^{TOT}$ has been determined by another technique, such as $^{57}$Fe Mössbauer spectroscopy (e.g., Berry et al. 2008). There are also questions concerning possible photo-oxidation during the analysis of hydrous glasses (e.g., Cottrell et al. 2018). A considerable drawback for routine analysis is that it requires access to a synchrotron light source.

Raman spectroscopy is an alternative technique for determining Fe$^{2+}$/Fe$^{TOT}$ that is often readily accessible, is non-destructive, has micrometer-scale spatial resolution, requires minimal sample preparation, is easy to perform, and spectra can be acquired within minutes. Previous studies have shown how Raman spectroscopy can be used for quantifying the concentration of H$_2$O (Thomas 2000; Zajacz et al. 2005; Behrens et al. 2006; Thomas et al. 2008; Mercier et al. 2009, 2010; Le Losq et al. 2012) and CO$_2$ (Amalberti et al. 2011; Morizet et al. 2013) in glasses, with applications to pumices and melt inclusions (Shea et al. 2014; Métrich et al. 2016). The potential of Raman spectroscopy to determine Fe$^{2+}$/Fe$^{TOT}$ in glasses has been demonstrated previ-