AMORPHOUS MATERIALS†

Determination of water content in silicate glasses using Raman spectrometry: Implications for the study of explosive volcanism

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ABSTRACT

Raman spectroscopy can measure water concentrations of hydrous silicate glasses with several advantages such as: (1) high-spatial resolution of 1–2 μm; (2) non-destructive character; and (3) easy access, without any specific sample preparation or mounting techniques. The latter reasons render Raman highly suitable for studying natural products, such as volcanic pumice and scoria fragments. Two spectral regions can be distinguished in Raman spectra of hydrated silicate glasses: a low-wavenumber region (15–1500 cm⁻¹), which corresponds to vibrations of the silicate network, and a high-wavenumber region (3100–3750 cm⁻¹), corresponding to the OH stretching vibrations of H₂O molecules and OH groups. Behrens et al. (2006) have published empirical equations relating the area ratio between these two regions and the water content. However, the proposed internal calibrations depend on chemical composition of the glasses. In this paper, we reinvestigated the previous procedures to improve the background subtraction. Our results allow us to present a more general and linear calibration. Water concentrations up to 13 wt% can be measured for a broad range of natural silicate melts, from basalts to rhyolite (40 up to 80 wt% SiO₂), using a single calibration curve with an absolute error of 0.2 wt%.

Keywords: Water, Raman spectroscopy, quantification, glass, melt, volcanic scorias

INTRODUCTION

Water plays a fundamental role in magma dynamics and evolution, from melting processes at mantle or crustal depths up to magma extrusion during volcanic eruptions. In addition to temperature, the melt water content is one of the main parameters that strongly influence the physical properties of magmas, regulating their extraction from the source and their mobility. For instance, the addition of 1 wt% H₂O to an andesitic melt results in a viscosity decrease of more than three orders of magnitude (Richet et al. 1996; Vetere et al. 2006). This behavior reflects major changes in the silicate melt network. Understanding silicate melts’ structural and rheological properties clearly demands an accurate quantification of the water dissolved in it.

Many techniques are available to measure the water content of silicate melts, e.g., weight loss on ignition, hydrogen manometry, Karl-Fischer titration, infrared and Raman spectroscopy, ion microprobe and electron microprobe analysis (e.g., Stolper 1982; Newman et al. 1986; Ihliger et al. 1994; Behrens and Stuke 2003). However, none yet provides a routinely, fairly accurate determination of the water concentration with a high-spatial resolution without the use of standard glasses or without knowing precisely the glass chemical composition. The most accurate methods (e.g., weight loss on ignition or Karl Fischer titration) require bulk samples of significant size and are destructive. Achieving a high-spatial resolution is currently very expensive and time consuming due to sample preparation, calibration, and/or very costly instruments (e.g., ion microprobe).

Raman spectroscopy offers several advantages in the study of natural silicate glasses and melts: (1) a high-spatial resolution of 1–2 μm; (2) the non-destructive nature of this analysis; (3) minimum sample preparation (just a freshly broken sample is needed); and (4) important possibilities for in situ experiments [for high-temperature applications, see Mysen and Frantz (1992); for high-pressure applications see Durben et al. (1993)]. Several studies pointed out the potential of this spectroscopy in determining water concentration in microscopic samples. Certain variations exist on the proposed methodology (e.g., Thomas 2000; Chabiron et al. 2004; Zajac et al. 2005; Behrens et al. 2006; Thomas et al. 2008). Also, the concentration of other volatiles can be measured, like for instance N₂ (Roskosz et al. 2006), SO₂ (Manara et al. 2007; Lenoir et al. 2009), CO₂ and CO (Amalberti et al. in prep.), thus opening new perspectives for multiple volatile determinations in melts and glasses via a single spectroscopic determination.

In Raman spectra, different features can be observed depending on both structure and chemistry of the investigated material.

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