Invited research article

Water quantification in silicate glasses by Raman spectroscopy: Correcting for the effects of confocality, density and ferric iron

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ABSTRACT

New series of alumino-silicate glasses spanning a wide range of chemical compositions (basanites, tholeiitic basalts, calcalkaline andesites, peraluminous and peralkaline rhyolites) and with water contents from 0.02 to 6.70 wt% were used for improving the method of quantification of dissolved water with a highly confocal Raman micro-spectrometer. After reconsideration of previously proposed methods for spectra acquisition and post-analysis data treatment, we define the main critical steps that allow minimizing glass matrix effects. First, we carefully assess the variation of Raman band intensities, in both water ($\sim$3000–3800 cm^{-1}) and alumino-silicate vibration ($\sim$200–1250 cm^{-1}) regions with focus depth of the laser beam inside the sample. Our results indicate that in the first 2–10 μm depth, the intensity increase in the alumino-silicate region is twice as high as that in the water region. Optimal focus depths, where the signal of the water band is maximum and the intensity ratio of the water band to alumino-silicate band is minimum, vary with glass composition and confocal performance of the Raman spectrometer. This influences both external and internal calibration slopes. Second, this study recognizes critical parameters related with glass density, presence of ferric iron and dissolved carbonates as mainly responsible for matrix effects on the internal calibration method. (a) We provide a procedure for correcting the effect of glass density on water internal calibration based on the observation that the integrated intensity (i.e. the area) of the alumino-silicate envelope generally drops with the increase of water content and decrease of glass density. (b) In CO_2-bearing glasses, the intensity of the ν_1 Raman vibration of dissolved carbonate at $\sim$1087 cm^{-1} has to be subtracted from the intensity of the alumino-silicate envelope before applying the density correction. (c) Using peak-fitting, the intensity of the 850–1250 cm^{-1} envelope of peralkaline rhyolitic glasses is corrected for the effect of the presence of four-fold coordinated Fe^{3+}, as revealed by the strong Raman scattering of the vibrational mode at $\sim$980 cm^{-1}. Following this procedure, all the studied glasses define a single calibration line in spite of their compositional variability, when using either of the two classical approaches referred to as *external* and *internal* calibration methods. The linear fits of the external and internal calibrations reproduce the whole dataset within 0.13–0.11 wt% (high and standard confocality) and 0.17 wt%, respectively. The accuracy of the external calibration is evaluated based upon comparison with ion-probe measurements of water dissolved in natural glass inclusions: the relative standard deviation is $\sim$4% (1σ) on average, and reaches $\sim$12% (1σ) for water contents of $\sim$0.1 wt%.

1. Introduction

Concentration, speciation and distribution of volatile species dissolved in silicate melts are key factors that control the physico-chemical evolution of magmas from their genesis to their final emplacement and affect the dynamics, style, and intensity of volcanic eruptions (e.g., Carroll and Holloway, 1994; Cashman, 2004; Sanchez-Valle et al., 2015). Volatiles are also important in mantle processes as they control melting and mantle rheology. Crucial information about volatile contents of magmas and behavior of volatiles at depth is usually recorded in small objects, such as phenocryst-hosted melt and fluid inclusions and tiny pockets of glassy matrix (e.g., Andersen and Neumann, 2001; Métrich and Wallace, 2008).

Raman spectroscopy is a useful micro-analytical technique for

identification and quantification of volatiles contained in a variety of materials, which are of interest in volcanological and petrological studies, in particular water (regardless of speciation) dissolved in natural glasses. With respect to the other micro-analytical techniques used for quantification of water in rock samples, such as Fourier transform infrared spectroscopy (FTIR), secondary ion mass spectrometry (SIMS), and elastic recoil detection analysis (ERDA), Raman spectroscopy has several advantages: (i) it requires minimal sample preparation, (ii) it is non-destructive, (iii) it allows rapid analysis with high spatial resolution, which is of utmost importance for characterization of small samples and samples with small-scale heterogeneity, and (iv) it allows analysis of unexposed glass, fluid and solid inclusions contained in transparent minerals and interstitial glass pockets (e.g., Thomas, 2000; Thomas et al., 2006; Chabiron et al., 2004; Zajacz et al., 2005; Di Muro et al., 2006a; Severs et al., 2007; Frezzotti et al., 2012; Morizet et al., 2013; Freitas et al., 2017).

Since the work by Thomas (2000), several studies have shown that accurate quantification of water dissolved in natural glasses can be achieved after proper calibration of Raman spectrometers (Chabiron et al., 2004; Zajacz et al., 2005; Behrens et al., 2006; Di Muro et al., 2006a, 2006b; Thomas et al., 2006; Mercier et al., 2009, 2010; Le Losq et al., 2012; Di Genova et al., 2017). These studies investigated the advantages and limitations of distinct calibration methods. The first method is called "external calibration", as quantification of water in the unknown sample is obtained by comparing the intensity (i.e. the height, hereafter I_{OH}) or the integrated intensity (i.e. the area, hereafter A_{OH}) of the water band located around $3570 \, cm^{-1}$ (Fig. 1b) with water band intensities or integrated intensities of well-characterized standard glasses. The relationship between intensity of the water Raman band and water concentration (hereafter referred to as "calibration curve") determined in previous studies displays a slope that varies as a function of glass type. Dependence of the slope on glass composition is especially apparent when glasses belonging to alkaline and sub-alkaline series are compared (Behrens et al., 2006; Di Muro et al., 2006b; Mercier et al., 2010). According to Mercier et al. (2010), glass reflectance and density, as well as water environment, are the main parameters causing matrix effects on the external calibration. Thus, a set of glass standards spanning a wide range of compositions seems required for accurate quantification of water in natural glass samples.

The second calibration method is known as "internal calibration" because the intensity of the Raman water band is normalized to the intensity of bands located in the silicate region: either in the entire alumino-silicate region between 200 and $1250 \, cm^{-1}$ (Behrens et al., 2006; Le Losq et al., 2012; Di Genova et al., 2017), the band located at high wavenumbers between 850 and $1250 \, cm^{-1}$ (Zajacz et al., 2005; Behrens et al., 2006; Severs et al., 2007; Mercier et al., 2009), or the band at low wavenumbers ranging from 200 to $650 \, cm^{-1}$ (Thomas, 2000; Chabiron et al., 2004; Behrens et al., 2006; Mercier et al., 2009) (Fig. 1a,c). Intensity versus content relationships obtained with an internal calibration procedure are expected to be less affected by instrumental and analytical conditions, such as laser power fluctuations, focusing errors, and differences in confocal volume size, light absorption and reflectance that depend on glass structure and composition. In reality, internal calibrations also depend on glass chemical composition, because both bands in the alumino-silicate region and the average Raman scattering cross section of all the different alumino-silicate structural units (Q^n) depend on glass composition (Frantz and Mysen, 1995).

In order to correct the calibration of water concentration for compositional dependence, some authors have proposed additional normalization procedures taking into account the degree of glass polymerization (Zajacz et al., 2005; Mercier et al., 2010). Le Losq et al. (2012) defined a new protocol for spectra background subtraction that partly eliminates the effects of matrix composition. However, this method tends to overestimate and underestimate the water content of iron-poor and iron-rich samples, respectively (Di Genova et al., 2017). According to Di Genova et al. (2017), the use of different baseline procedures is not sufficient to remove the dependence of the internal calibration procedure on the iron content and oxidation state.

So far, there is no satisfactory methodology that allows quantifying the water content in glasses of variable composition using Raman spectroscopy. In this study, we reconsider previously proposed strategies for spectra acquisition and post-analysis data treatment, with the aim to establish the procedures under which a composition-independent calibration can be obtained when applying both external and internal calibration methods. For this purpose, we have studied glasses spanning a wide range of compositions belonging to both sub-alkaline and alkaline magma series. First, we investigate in detail how confocal performance and focus depth of the laser beam affect the calibration and highlight the importance of considering these parameters. Then, the effects of physico-chemical characteristics of alumino-silicate glasses, in particular those in relation to density and presence of ferric iron, are quantified, and we propose correction strategies to minimize matrix effects on the internal calibration. Finally, we test our method by analyzing natural glass inclusions of variable composition, whose water content was measured using SIMS or FTIR techniques.
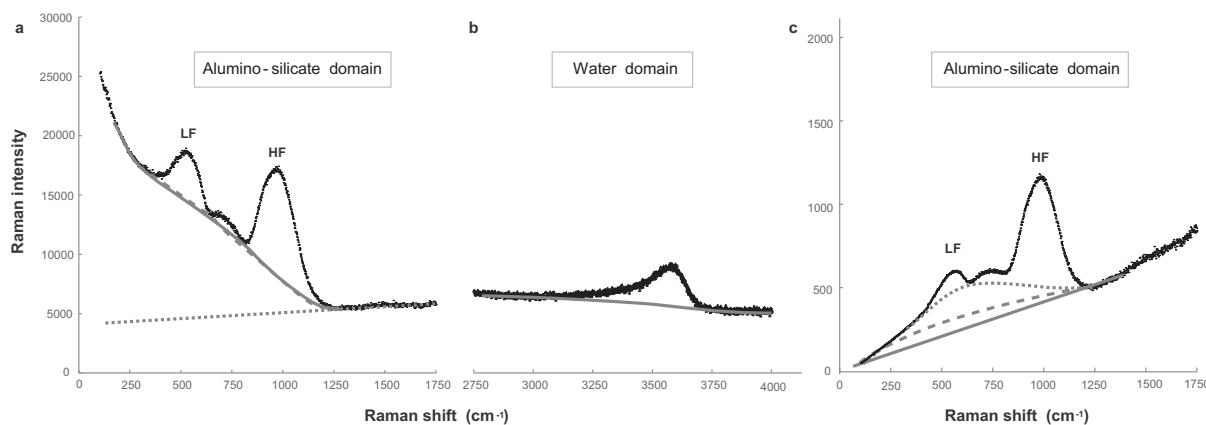

Fig. 1. Procedures for background subtraction used in previous studies. (a–b) Baseline fitting on raw Raman spectra. (a) In the alumino-silicate domain: cubic baseline (Mercier et al., 2009; dashed curve), cubic spline baseline (Behrens et al., 2006; continuous curve), and linear extrapolation method by Zajacz et al. (2005, dotted line); (b) cubic baseline in the water domain. (c) Baseline fitting on Long-corrected spectra in the alumino-silicate domain: cubic baseline (Di Muro et al., 2009; dashed curve) and cubic spline baseline (Behrens et al., 2006; continuous line) anchored at the extremities of the domain, or to a limited number of intermediate minima (Le Losq et al., 2012; dotted curve). LF and HF indicate low-frequency and high-frequency bands.