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Effect of iron and nanolites on Raman spectra of volcanic glasses: A reassessment of existing strategies to estimate the water content

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ABSTRACT

The effect of iron content and iron nanolites on Raman spectra of hydrous geologically-relevant glasses is presented. Current procedures to estimate the water content using Raman spectra were tested to explore potential effects of iron content, its oxidation state, and nanolites on models' reliability. A chemical interval spanning from basalt to rhyolite, including alkali- and iron-rich compositions, with water content up to 5.6 wt% was investigated using two spectrometers. When considering nanolite-free samples, the area of the band at 3550 cm^{-1} linearly correlates with the sample water content regardless of chemical composition. Using this approach, data were reproduced with a root-mean-square error (RMSE) of ~0.15 wt%. Depending on the sample chemistry, water content, and acquisition conditions the laser-induced sample oxidation led to underestimating the water content up to ~90% with a long acquisition time (26 min). Normalising the water band region to the silicate band region minimises such a limitation. The area ratio between these bands linearly correlates with the water content and the use of different baseline procedures does not remove the dependence of such a correlation by the iron content and its oxidation state. With this procedure, data were reproduced with a RMSE of ~0.16 wt%. For both approaches, the presence of iron nanolites may result in underestimating the water content.

1. Introduction

Water is the most abundant volatile species dissolved in natural melts and greatly affects, even at low concentration, a variety of thermodynamic and physical properties, from phase equilibria, to reaction kinetics, element diffusivities, electrical conductivity, heat capacity, and partial melting (Behrens and Zhang, 2009; Giordano et al., 2015; Lange and Carmichael, 1990; Poe et al., 2012; Scaillet and Macdonald, 2001; Stebbins et al., 1995). Moreover, bulk properties such as viscosity and density of the melt can vary by several orders of magnitude depending on the dissolved water content (Bouhifd et al., 2015; Dingwell et al., 1996; Lange and Carmichael, 1990; Whittington et al., 2000). Such properties control the entirety of magmatic and volcanic processes occurring from the melt generation, magma rise, decompression and, ultimately, the fate and style of volcanic eruptions.

Volcanic glasses, from glass shards to melt inclusions trapped in crystals, represent the products of most of volcanic eruptions. Analytical studies of water distribution in natural glasses are crucial for understanding the plethora of physical and chemical processes, and their feedbacks, occurring before, during, and after the eruption (Bachmann et al., 2009; Berry et al., 2008; Blundy and Cashman, 2005; Dingwell, 2006; Hartley et al., 2014; Kennedy et al., 2005; Métrich et al., 2010). Moreover, investigations of run products from solubility, diffusion, decompression, crystallisation, and bubble nucleation experiments help to constrain the timescale of physical and chemical processes in hydrous systems (Blundy and Cashman, 2005; Fanara et al., 2015; Gardner et al., 2000; Gonnermann and Gardner, 2013; Hammer et al., 2000; Le Gall and Pichavant, 2016; Martel and Iacono-Marziano, 2015; Shishkina et al., 2010).

Raman spectroscopy is a non-destructive technique used to chemically discriminate glasses, study and estimate the oxygen fugacity and volatile content (e.g., Di Genova et al., 2016a, 2016b; Di Muro et al., 2006a, 2009; Le Losq et al., 2012; Morizet et al., 2013; Thomas, 2000). The minor sample preparation and high-spatial resolution of few μm^2 represent the main advantages of using Raman spectroscopy over other standard techniques typically used for water content determination

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Table 1
Dry composition (wt%) of the starting materials. The associated errors are reported in Section 2.3 of this work and in the mentioned studies.

Sample	KR[a]	HO[a]	ETN[b]	FR[c]	AMS[b]	PS-GM[b]	472AD[d]	79AD[d]	V_1631_W[e]	RH[f]
Composition	Fe$^+$ basalt	Dacite	Trachy-basalt	Latite	Trachyte	Fe$^+$ rhyolite	Fe$^+$ phonolite	Fe$^-$ phonolite	Tephri-phonolite	Fe$^-$ rhyolite
H_2O[g]	TGA	TGA	KFT + NIR	KFT + NIR	KFT + NIR	KFT + NIR	KFT	KFT	NIR	TGA
SiO_2	50.24	66.17	48.06	56.55	57.72	69.21	51.36	56.09	53.52	78.87
TiO_2	1.99	0.77	1.67	0.81	0.39	0.5	0.48	0.19	0.6	0.10
Al_2O_3	13.55	15.96	16.72	17.92	18.4	9.18	21.63	22.02	19.84	12.52
$FeO_{tot.}$	14.08	5.02	9.92	6.59	4.51	7.94	4.54	2.26	4.8	1.55
MnO	0.25	0.12	0.24	0.17	0.1	0.32	–	–	0.14	0.04
MgO	5.86	1.70	5.46	2.36	1.46	0.08	0.74	0.18	1.76	0.04
CaO	10.09	4.65	10.03	5.52	4.23	0.6	5.90	2.8	6.76	0.84
Na_2O	2.46	3.70	3.68	4.55	3.72	6.52	5.92	6.22	4.66	1.01
K_2O	0.32	2.23	1.83	4.53	7.9	4.35	9.42	10.25	7.91	5.28
P_2O_5	0.55	0.01	0.48	0.01	0.19	0.04	–	–	–	0.02

[a] This study.
[b] Di Genova et al. (2014a).
[c] Di Genova et al. (2014b).
[d] Scaillet and Pichavant (2004).
[e] Romano et al. (2003).
[f] Di Genova et al. (in press).
[g] The dissolved water content in glass was determined by thermogravimetric (TGA), Karl–Fischer titration (KFT), and near-infrared spectroscopy (NIR) analyses.

[Fourier transform infrared spectroscopy (FTIR), Karl Fischer titration (KFT), and thermogravimetric analysis (TGA)]. The potential of Raman spectroscopy, together with progress in the performance of spectrometers, now opens future opportunities for producing high-resolution maps of water distribution in volcanic and experimental products necessary to constrain processes involved in volcanic eruptions and their equilibrium versus disequilibrium timescales.

Over the past few decades, several authors have adopted different protocols for the quantification of water content by Raman spectroscopy based on internal and external calibrations (Behrens et al., 2006; Chabiron et al., 2004; Di Muro et al., 2006b; Mercier et al., 2009; Thomas, 2000; Thomas et al., 2008; Zajacz et al., 2005). The external calibration requires a set of standards where the water content is independently determined (Behrens et al., 2006; Thomas et al., 2008; Mercier et al., 2009). Moreover, each spectrometer needs to be calibrated due to the different performance of detectors and instrumental settings (e.g., grating, excitation source, objective, acquisition time, focus depth) which affect the spectra intensity and the band area. Differently, the internal calibration is based on spectra normalisation between the water and silicate regions. This approach is expected to remove most of instrumental effects on Raman spectra. Therefore, so far, the internal calibration has been considered to allow different laboratories to use a common calibration.

In order to provide a single calibration valid over a large compositional interval, Le Losq et al. (2012) embedded the chemical-dependence of Raman spectra into a background procedure which depends on the sample SiO_2 content (more details are provided in the following sections). After background subtraction, their calibration relied on the ratio (HW/LW) between the water (HW, 2700–3900 cm^{-1}) and silicate (LW, 200–1300 cm^{-1}) area bands to estimate the dissolved water content H_2O (wt%) as follows:

$$\frac{H_2O}{(100 - H_2O)} = A\cdot\frac{HW}{LW} \qquad (1)$$

The left member of the equation represents the water/glass proportion and the A coefficient is equal to $7.609 \cdot 10^{-3}$. While A might change with the used spectrometer, the relationship between HW/LW and the water/glass proportion was found to be unique and linear regardless of the sample composition (Le Losq et al., 2012).

However, the starting materials used in their study were mainly iron-free glasses (9 out of 12 glasses). Natural glasses contain iron which is present in both reduced (Fe^{2+}) and oxidised (Fe^{3+}) forms depending on temperature, oxygen fugacity, and chemical composition. The dual behaviour of iron affects the Raman spectra of natural glasses (Di Muro et al., 2009; Di Genova et al., 2016a). Moreover, Di Muro et al. (2006a, 2006b) and Di Genova et al. (in press) found that iron-bearing crystals at the micro- and nanoscale dramatically alter the Raman features of glasses. These particles nucleate and grow during cooling or thermal annealing above the glass transition temperature and have been recently recognised to be pervasive in experimental specimens and natural products (Di Genova et al. in press). Based on these observations, it is evident that any Raman model used to estimate the water content of natural products should consider such effects.

These considerations led us to reassess the relationship between Raman spectra and the water content of volcanic glasses. Here, we investigate a series of hydrous glasses with $FeO_{tot.}$ up to 14.1 wt% characterised by chemical composition spanning from basalt to iron-poor and iron-rich phonolite and rhyolite. We used two Raman instruments to investigate possible effects of diverse instrumental characteristics. This contribution aims to test current strategies and provide reliable procedures to estimate the water content of naturally-occurring glasses by Raman spectrometry.

2. Materials and analytical methods

2.1. Samples from previous studies and starting materials

To explore chemical effects on Raman spectra of glasses, we investigated hydrous samples with variable water content over a wide range of chemical composition. Sample set includes 20 glasses from previous studies and 9 glasses synthesised specifically for this study. In term of silica, iron, and alkali content, the used compositions span almost the entire chemical spectrum of magmas erupted on Earth.

2.2. Samples and starting material from previous studies

The chemical composition of samples synthesised in previous studies is reported in Table 1 and shown in a TAS (total alkali versus silica) diagram in Fig. 1A. The samples include:

- Trachybasalt (ETN, Di Genova et al., 2014a) from Etna (1991–1993 lava flow field in Val Calanna, Italy);
- Latite (FR, Di Genova et al., 2014b) from Fondo Riccio eruption (9.5 ka Campi Flegrei, Italy);