Microanalysis of H2O and CO2 in silicate melt using laser Raman spectroscopy

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Introduction

Water and carbon dioxide are the major volatile components in the crust and mantle. Development of microanalytical techniques of these volatiles has made it possible to investigate mechanisms of igneous and volcanic processes. FTIR has been used as a fundamental tool for this purpose, but its spatial resolution is too large (≈30 μm) to analyse small melt inclusions and micro-scale volatile distribution within a high-pressure experimental sample. In this study, we developed a new technique for volatile analysis in silicate glasses with ≈1 μm spatial resolution using laser Raman spectroscopy.

Experimental and analytical procedure

Standard glasses were synthesized by using a piston-cylinder apparatus in M. Nakamura’s laboratory. Basaltic glass powder was loaded into a platinum-sleeved nickel capsule together with oxalic acid and run at 1473 K and 0.5-1.2 GPa. After quench, the H2O and CO2 (dissolved as CO32−) contents of the glasses were measured by using FTIR. The same glasses were then analysed with a Thermofisher DXR laser-Raman spectrometer. Wave length, power and diameter of the laser beam were 532 nm, 10 mw and 0.7 μm, respectively. We normalized the Raman spectra by the intensity of a peak at 500 cm⁻¹ (T-O-T bond) and subtracted the spectrum of the volatile-free glass. The intensities of peaks at 3550 cm⁻¹ (H2O) and 1080 cm⁻¹ (CO32−) in the resulting spectra were compared with the H2O and CO2 contents determined by FTIR spectroscopy.

Results

The H2O and CO2 contents were determined to be 0.7-2.1 wt% and 0.05-0.82 wt%, respectively. Raman spectroscopy showed that the intensities of peaks at 3550 and 1080 cm⁻¹ increased with increasing H2O and CO2 contents, respectively. We fitted a linear equation to the data and obtained H2O (wt%) = (3.58±0.14)×I3550 and CO2(wt%) = (4.61±0.21)×I1080.

Application

We applied this technique to volatile analysis of an experimentally-produced bubble-bearing basaltic glass. In the experiment, basaltic melt was first equilibrated with H2O-CO2 mixture fluid at 1473 K and 1 GPa, and then decompressed to 0.5 GPa and kept for 10 minutes. After quench, the H2O and CO2 contents around bubbles were measured along the radial direction at 2-μm intervals for a total of 50 μm. The CO2 contents decreased on moving towards the bubble, indicating that CO2 was diffusing into the bubble. Fitting the diffusion equation to this profile, we estimated the diffusivity of CO2 to be 1.2×10⁻¹² m²/s. This value is consistent with that reported by Zhang et al. (2007). In contrast to CO2, H2O showed a flat profile, suggesting that H2O was already equilibrated with the fluid in the bubble. This is because the diffusivity of H2O is one order of magnitude greater than that of CO2. Such a diffusive fractionation was observed also in rhyolitic melt (Yoshimura and Nakamura, 2010).

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