

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

YOSHIMURA, Shumpei^{1*}; KAGASHIMA, Shin-ichi¹; NAKASHIMA, Kazuo¹

¹Department of Earth and Environmental Sciences, Yamagata University

<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 ($\sim 30 \mu\text{m}$) 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 $\sim 1 \mu\text{m}$ 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 $0.7 \mu\text{m}$, 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 $\text{H}_2\text{O (wt\%)} = (3.58 \pm 0.14) \times I_{3550}$ and $\text{CO}_2(\text{wt\%}) = (4.61 \pm 0.21) \times I_{1080}$.

<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 $2\text{-}\mu\text{m}$ intervals for a total of $50 \mu\text{m}$. 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 $1.2 \times 10^{-12} \text{ m}^2/\text{s}$. 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).

Keywords: CO₂, H₂O, glass, Raman