

## Microanalysis of H<sub>2</sub>O and CO<sub>2</sub> 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 ( $\sim 30 \mu\text{m}$ ) 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 H<sub>2</sub>O and CO<sub>2</sub> (dissolved as CO<sub>3</sub><sup>2-</sup>) 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<sup>-1</sup> (T-O-T bond) and subtracted the spectrum of the volatile-free glass. The intensities of peaks at 3550 cm<sup>-1</sup> (H<sub>2</sub>O) and 1080 cm<sup>-1</sup> (CO<sub>3</sub><sup>2-</sup>) in the resulting spectra were compared with the H<sub>2</sub>O and CO<sub>2</sub> contents determined by FTIR spectroscopy.

### <Results>

The H<sub>2</sub>O and CO<sub>2</sub> 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<sup>-1</sup> increased with increasing H<sub>2</sub>O and CO<sub>2</sub> contents, respectively. We fitted a linear equation to the data and obtained H<sub>2</sub>O (wt%) =  $(3.58 \pm 0.14) \times I_{3550}$  and CO<sub>2</sub> (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 H<sub>2</sub>O-CO<sub>2</sub> mixture fluid at 1473 K and 1 GPa, and then decompressed to 0.5 GPa and kept for 10 minutes. After quench, the H<sub>2</sub>O and CO<sub>2</sub> contents around bubbles were measured along the radial direction at 2- $\mu\text{m}$  intervals for a total of 50  $\mu\text{m}$ . The CO<sub>2</sub> contents decreased on moving towards the bubble, indicating that CO<sub>2</sub> was diffusing into the bubble. Fitting the diffusion equation to this profile, we estimated the diffusivity of CO<sub>2</sub> 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 CO<sub>2</sub>, H<sub>2</sub>O showed a flat profile, suggesting that H<sub>2</sub>O was already equilibrated with the fluid in the bubble. This is because the diffusivity of H<sub>2</sub>O is one order of magnitude greater than that of CO<sub>2</sub>. Such a diffusive fractionation was observed also in rhyolitic melt (Yoshimura and Nakamura, 2010).

Keywords: CO<sub>2</sub>, H<sub>2</sub>O, glass, Raman