

Appendix 4

Extended Methods

A4.1. Measurements of H₂O and CO₂

H₂O and CO₂ contents of doubly polished melt inclusion wafers were measured using a Thermo-Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer at the American Museum of Natural History (AMNH). Concentrations were calculated using the Beer-Lambert law. Thickness was determined using a reflectance technique (Wysoczanski and Tani, 2006), which yields values within 5% of measurements using a desktop micrometer. Total H₂O (i.e., OH⁻ and H₂O) concentration was determined from the peak centered at 3520 cm⁻¹, using an absorption coefficient of 63 L/mol·cm (Dixon 1997). CO₂ concentration (as CO₃²⁻) was calculated by averaging the heights of the carbonate doublet peaks at 1430 and 1515 cm⁻¹ and using a compositionally dependent absorption coefficient (Dixon and Pan, 1995). Backgrounds were interpolated using a cubic spline (Fig. A4.1). This results in a nearly flat background for the 3520 cm⁻¹ peak. The background of the carbonate doublet is curved, and the curvature is sensitive to the choice of data points used for the interpolation. To address uncertainty stemming from this issue, we average the results of three different interpolations for each baseline correction. The absorbance at 3520 cm⁻¹ is difference between the peak height and background. For the carbonate doublet, we fit gaussian functions to peaks centered at 1630, 1430, and 1515 cm⁻¹ (Fig. A4.1). In most cases, three replicate analyses were conducted, and reported values are averages. Reported errors include error in absorption (from replicate analyses, and multiple background interpolations) and thickness.

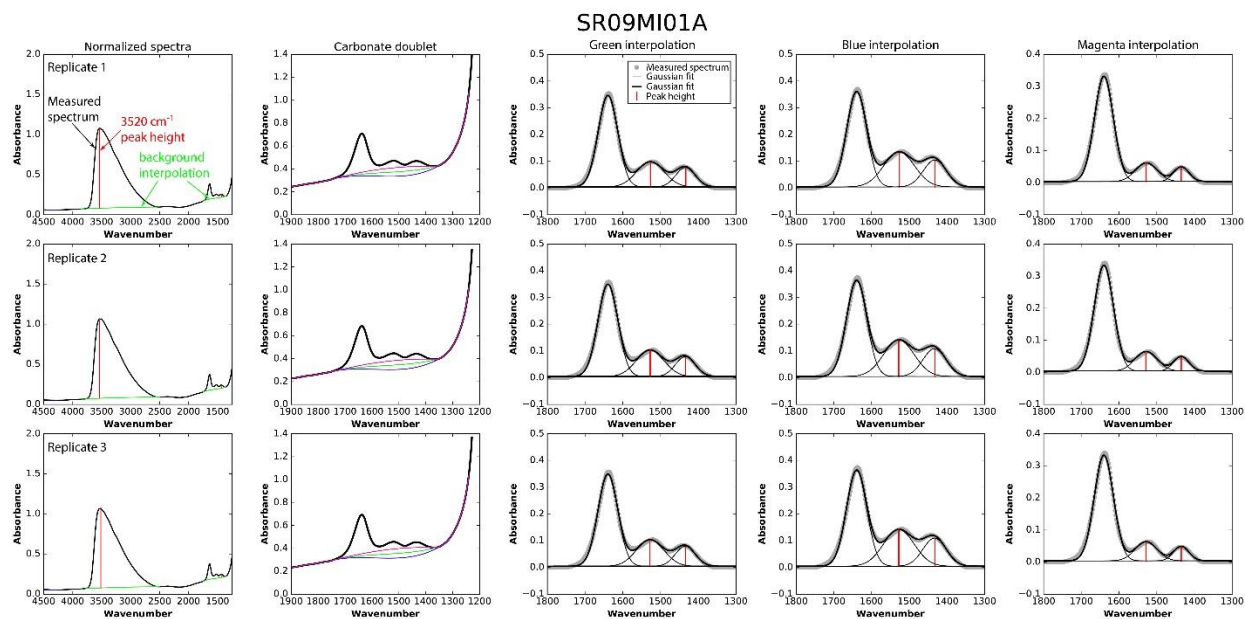


Figure A4.1. Example spectra collected using Fourier transform infrared spectroscopy.

A4.2. Measurements of major elements, sulfur, and chlorine

We performed electron probe microanalysis (EPMA) to determine major element contents of melt inclusions and host olivines and the S and Cl contents of melt inclusions. Measurements were performed at the AMNH using a Cameca SX-100. For melt inclusions, we used a defocused beam (10 μm diameter) with a 15 kV accelerating voltage and currents of 10 nA (Na, Si, Mg, Al, K, Ca, Fe) and 50 nA (P, S, Cl, Ti, Mn). Olivines were analyzed with a focused beam (1 μm diameter) with a 15 kV accelerating voltage and a 20 nA current (Si, Mg, Ca, Fe, Mn). Typically, we performed three replicate analyses and report the average of these analyses and the standard deviation as the 1σ error.

S contents of check standards (892-1 and ND70) measured by EPMA are systematically lower (68% and 71%, respectively) than accepted values. The peak finding routine was performed on barite (sulfate). Because our samples have a mix of sulfate and sulfide, we attribute the offset to incorrect peak positioning during analysis. To address this issue, we have adjusted all S measurements according to the check standard offset of each session. In most cases, the correction factor is ~ 1.4 . Additionally, P analyses were too high by a factor of ~ 2 in one session, which was likely an interference problem. P contents of those samples were adjusted by that factor.

A4.3. References

- Dixon, J.E. and Pan, V., 1995. Determination of the molar absorptivity of dissolved carbonate in basaltic glass, *American Mineralogist*, pp. 1339.
- Wysoczanski, R. and Tani, K., 2006. Spectroscopic FTIR imaging of water species in silicic volcanic glasses and melt inclusions: An example from the Izu-Bonin arc. *Journal of Volcanology and Geothermal Research*, 156(3): 302-314.