ANALYTICAL METHODS

Fourier transform infrared (FTIR) spectroscopy

Total dissolved H$_2$O in melt inclusions was measured using the peak heights of the ~5200 cm$^{-1}$ (molecular water) and ~4500 cm$^{-1}$ (OH- groups) absorption bands. In cases where the two peaks heights could not clearly be measured due to the slope and irregularity of the background, the band located at ~3500 cm$^{-1}$ (total water) was used. Because the molar absorption coefficients for water species in rhyolite glasses vary with total water content (Silver et al., 1990), the Beer’s law algorithm of Zhang et al. (1997) was used to calculate total H$_2$O contents. An iterative procedure was used when obtaining total water contents from the band located at ~3550 cm$^{-1}$ due to the effect of water on glass density. Dissolved CO$_2$ was measured using an absorption coefficient of 1214 cm$^{-1}$/mol (Behrens et al., 2004) and the intensity of the band at 2350 cm$^{-1}$ (molecular CO$_2$; Blank et al., 1993).

When possible, we measured melt inclusion thickness using two techniques. The first technique was performed prior to analysis using a digital micrometer ($\pm$ 2 µm). Initially, we measured the glass slide to get an average glass thickness, which we then subtracted from the average thickness of the glass slide plus the melt inclusion wafer (averages based on 3-5 replicate measurements). The second technique was conducted during FTIR analysis, using interference fringes in the IR reflectance spectra (Wysoczanski & Tani, 2006). Results from the two techniques show good agreement ($R^2$ = 0.89; Fig. B.1).
**Electron microprobe (EMP)**

For all electron microprobe analyses of major elements, primary calibration standards and secondary standards are from Jarosewich *et al.* (1980). For all oxides, our analyses on secondary standards were within 1σ of the accepted value. We used the following Oregon State University (OSU) primary standards when analyzing major elements in melt inclusions using the CAMECA SX-100 EMP: RHYO for Si, Al, and Na; BASL for Ti, Ca and Mg; FLAP for P and F; KSPR for K; PYMN for Mn; FO83 for Fe; TUGT for Cl; CHAL for S. We ran RHYO as a secondary standard.

We used the following Smithsonian, National Museum of National History (NMNH) primary standards when analyzing major elements in melt inclusions using the JEOL-8900 EMP: Kakanui hornblende (USNM 143965) for Al, Mg, Fe, and Ca; Kakanui anorthoclase (USNM 133868) for Si and Na, microcline (USNM 143966) for K; manganite (USNM 157872) for Mn; ilmenite (USNM 96189) for Ti; and scapolite (R6600-1) for Cl. We ran VG568 as a secondary standard. Detection limits or chlorine, sulfur and fluorine were 160, 156 and 1330 ppm, respectively. Typically three spots were analyzed within each inclusion, and an average composition was calculated. Replicate standard analyses showed little variability (<1% for SiO₂ and Al₂O₃; <5% for K₂O, CaO, MnO, FeO, Na₂O, MgO, and TiO₂).

To correct for the effects of alkali migration during EMP analyses run at OSU and the Smithsonian Institution, NMNH (Lowenstern, 1995; Nielsen & Sigurdsson, 1981), we always analyzed Na and K as the first element acquired on each spectrometer to utilize the 0-time intercept function associated with the Cameca and JEOL software (Probe for EPMA), respectively. The 0-time intercept function, or the “Time Dependent Intensity
(TDI) Correction”, as it is referred to in Probe for EPMA, measures the count rate versus time and extrapolates back to time zero to get the correct Na counts. The extrapolation correction is quantitative and based on a self-calibration curve that is acquired during each run; the correction uses the actual elapsed time for all 0-time intercept calculations (see detailed description of software correction in Kremser, 2011). We acknowledge the issue of alkali migration when analyzing hydrous, high-silica rhyolite glasses, and therefore, we do not put significant emphasis on the Na contents in melt inclusions and rather, discuss melt variations in the context of trace element concentrations.

**Secondary ion mass spectrometry (SIMS)**

Ion microprobe analyses of trace elements in melt inclusions were performed using a Cameca IMS 6f instrument at Arizona State University. Only those ions with $75 \pm 20$ eV excess kinetic energy were allowed into the mass spectrometer (conventional energy filtering for effective elimination of molecular ion interferences was also performed; Ihinger *et al.*, 1994). The secondary ion signals were normalized to $^{30}$Si$^{4+}$ and the ion ratios were calibrated to NIST 610 and 612 glasses for 14 trace elements (Li, B, Ti, Rb, Sr, Y, Zr, Nb, Ba, Ce, Nd, Sm, Th, U) and with a suite of synthetic hydrous rhyolite glasses for hydrogen (Ihinger *et al.*, 1994).

**Laser ablation ICP-MS analyses**

Additional trace elements were analyzed in melt inclusions using a NewWave DUV 193 ArF Excimer laser ablation system connected to a VG PQ ExCell quadrupole ICP-MS at OSU. Ablation was performed using He as a carrier gas (0.8 L/min). Individual analyses
on melt inclusions were run at a pulse frequency of 4 Hz, using a 50µm spot with a firing
time of 45 s, following the procedure outlined in Kent *et al.* (2004). Trace element
abundances were calculated relative to the GSE-1G synthetic basalt (Jochum *et al.*, 2005)
calibration standard and ATHO-G rhyolite standard. ²⁹Si was used as an internal standard
in addition to average SiO₂ contents measured previously by the electron microprobe.
Uncertainties are shown as 1σ error bars in the plots in Figure 6.

**FIGURE CAPTIONS**

Figure B.1: Comparison of melt inclusion thickness measurements using a micrometer
and the FTIR reflection spectra.

Figure B.2: Comparison between Ti (ppm) in melt inclusions analyzed by LA-ICPMS
and SIMS versus Ti (ppm) by EPM. Line represents 1:1 line, and the equations of
regression lines are shown for each dataset.

Figure B.3: Comparison between Li, B, Rb, Sr, Ba, and Th (ppm) in melt inclusions
analyzed by LA-ICPMS and SIMS. Line represents 1:1 line.

Figure B.4: Comparison between wt.% H₂O derived from SIMS and FTIR on quartz-
hosted melt inclusions in the Tara fallout and ignimbrite pumice.

Figure B.5: H₂O (wt.%) analyzed by FTIR versus the size of melt inclusion longest axis
diameter (µm).
REFERENCES


Figure B.1

\[ y = 0.9625x - 5.9589 \]
\[ R^2 = 0.89336 \]
Quartz hosted MIs analyzed by LA-ICPMS for Ti

LA-ICPMS Ti = 0.83(EMP Ti) + 116.11

R² = 0.71

Quartz hosted MIs analyzed by SIMS for Ti

SIMS Ti = 0.61(EMP Ti) + 77.27

R² = 0.71

Figure B.2
Figure B.3
Figure B.4

SIMS $H_2O$ (wt.%) vs. FTIR $H_2O$ (wt.%)

Quartz hosted MIs from the fallout and ignimbrite pumice
Figure B.5

Longest Axis Diameter (μm)

H₂O (wt.%)