

Online Resource 3: Supplementary Methods

Vapor Bubble CO₂ Concentrations: Raman Spectroscopy

Raman measurements of CO₂ vapor density were made on melt inclusion vapor bubbles using a WITEC alpha300 Raman microscope at the University of California, Berkeley. Spectra were collected using a 532.046 nm green laser, a spectral center of 1325 cm⁻¹, and a grating density of 1800 grooves nm⁻¹.

Detection limits for CO₂ depend on the size of the bubble, the laser power, and the depth of the bubble below the surface. Routine protocols in the Berkeley lab can quantify CO₂ densities down to 0.01-0.02 g cm⁻³ using 10 mW of laser power. Higher laser powers make lower densities detectable, but can cause issues for quantification (see DeVitre et al., 2023). Initial acquisitions were thus made using 10 mW, but failed to detect a CO₂ diad in any of the measured bubbles. Only two bubbles showed very faint diads at 20 mW.

For the two bubbles with a hint of a diad at 20mW (Fig. OR3.1), spectra were acquired with a 45 s acquisition time with 3 accumulations. Each acquisition was repeated three times. Peaks were fitted with a pseudovoigt curve using DiadFit (Wieser and DeVitre, 2023). Instrument drift in the measured splitting (distance between the two peaks) was corrected using repeated acquisitions of neon lines throughout the analytical session following the method of Lamadrid et al. (2017) for the 1117-1447 line. Corrected splitting was converted into CO₂ density using the relationship developed by DeVitre and Wieser (2024) for this specific instrument and set of analytical conditions, using a gas calibration cell adapted from DeVitre et al. (2021). The resulting densities are within error of ~0 g cm⁻³, and the splitting was below the lowest value recorded using the gas calibration cell (indicating the CO₂ density is <<0.01 g cm⁻³). No secondary phases such as carbonates were observed during Raman acquisitions.

Volatile Concentrations: Secondary Ion Mass Spectrometry (SIMS)

Glass H₂O and CO₂ concentrations (mass fractions) were measured by SIMS on a Cameca IMS 7f-GEO at California Institute of Technology, Pasadena, USA. A 10 kV Cs⁺ primary ion beam of ~6-7 nA (~15 µm in diameter) was used to sputter the samples and produce secondary ions. The samples were first pre-sputtered with the Cs beam rastering 8 × 8 µm. Then the rastering size was reduced to 5 × 5 µm for data collection. A field aperture of 100 µm in diameter was used to enable only the ions from the central 8 µm of the craters to be transmitted for detection. Possible edge effect was further eliminated with a 63% (in area) electronic gating. Secondary ions (¹²C⁻, ¹⁶OH⁻, ¹⁸O⁻, and ³⁰Si⁻) of -9 keV were collected with an electron multiplier (EM) in the peak-jumping mode. Each measurement consisted of a 120 s pre-sputtering, followed by automated secondary beam alignment, peak centering, and 20 cycles of data collection. The counting time of each mass was 1 s per cycle. The energy bandwidth for the secondary ions was set at ~45 eV. Sample charging compensation was provided by a normal-incidence electron gun (NEG) at -9 kV. A mass resolving power (MRP) of ~5000 was used to remove any significant interferences to the masses of interest (e.g., ¹⁷O⁻ from the ¹⁶OH⁻ peak). Data were corrected for EM background and deadtime.

Volatile concentrations in measured samples were calculated using calibration curves (Figs. OR3.1, OR3.2) derived from glass reference materials, based on the linear relationship:

$$C_{\text{volatile}} = m * \frac{X}{30\text{Si}^-} * C_{\text{Si}} \quad [\text{Equation 1}]$$

where C_{volatile} is the concentration of the volatile component in µg g⁻¹, $X/^{30}\text{Si}^-$ is counts per second for corresponding secondary ion (¹²C⁻ for CO₂ and ^{17.003}OH⁻ for H₂O) relative to the counts per second for ³⁰Si⁻ (see Online Resource 5 for raw SIMS counts data), C_{Si} is the concentration of Si in the glass in µg g⁻¹, and m is the calibration slope. Calibrations for basaltic glasses are based on the WOK5-4 and WOK16-2 basaltic glasses of Newman et al. (2000), and an additional suite of basaltic glasses from

Hughes (2019) (Table OR3.1, Fig. OR3.2). For silicic glasses, calibrations are based on the ATHO-G (Jochum et al., 2006), M3N and M6N (Devine et al., 1995; Waelkens et al., 2021), and mc84-bb-4b-r (Newman et al., 1988) rhyolitic glasses (Table OR3.2, Fig. OR3.3). Calibration curves were derived by weighted least squares regression, calculating weights based on the absolute uncertainty in the $X/^{30}\text{Si}$ ratio for each measurement and the relative uncertainties of volatile concentrations in each reference material. Where no uncertainty was provided for reference values, a $\pm 10\%$ relative uncertainty was assumed for volatile elements and a ± 0.5 wt% absolute uncertainty was assumed for SiO_2 . The curves were forced through the origin (i.e., no intercept term was included). Uncertainties in volatile concentrations for each sample measurement were then calculated by propagating the uncertainties in the calibration slopes (95% confidence intervals), measured $X/^{30}\text{Si}$ ratios (2 S.D.) and glass Si concentrations measured by EPMA (2 S.D.) through Equation 1. For samples where the Si content was not independently measured (e.g., small melt inclusions where insufficient material was left after SIMS to get a reliable EPMA measurement), the mean ± 2 S.D. Si content of all inclusions measured from the corresponding sample was used.

Measured volatile concentrations in basalt glass secondary reference materials and olivine (used as a blank to assess backgrounds) are reported in Table OR3.3. Measurements of silicic glasses previously characterised by Newman et al. (1988) via Fourier Transform Infrared Spectroscopy (FTIR) are in Table OR3.4. Blanks (analysed near the start of the analytical session, and thus representing a worst case scenario for the background when samples were measured) were $\sim 5 \mu\text{g g}^{-1}$ for CO_2 and negligible for all other volatiles, hence blank subtraction was neglected when calculating volatile concentrations in the samples. Measured values for secondary basaltic glass reference materials are generally in good agreement with reference values (Fig. OR3.4). Our values for the Newman et al. (1988) silicic glasses are in reasonable agreement with their published values (Fig. OR3.5).

Major and Minor Element Concentrations: Electron Probe Microanalysis (EPMA)

Major element compositions of melt inclusions, host minerals and groundmass glasses were measured on a Cameca SX-100 electron microprobe equipped with 5 wavelength dispersive spectrometers at Oregon State University, Corvallis. All analyses were performed using a 15 kV accelerating voltage. Beam currents and diameters, respectively, were 50 nA and 1 μm (olivine), 30 nA and 5 μm (basaltic glass, plagioclase) or 10 nA and 10 μm (silicic glass). Details of the spectrometer crystals used, calibration reference materials, and peak and background count times for each element are in Table OR3.5. Repeat analyses of secondary standard reference materials are in Online Resource 5. For elements with concentrations >1 wt%, estimates of measurement precision (2 S.D.) based on repeat analyses of reference materials are usually better than 5% relative, and biases between average measured values and reference values are almost always $<5\%$ (often $<1\%$) (Table OR3.6).

S Speciation: $\text{K}\alpha$ Peak Shift Measurements by EPMA

Electron microprobe measurements of sulphur speciation ($\text{S}^{6+}/\text{S}^{\text{total}}$) were performed for 6 basaltic and 5 dacitic melt inclusions on the Cameca SX-100 at Oregon State University, following methods similar to Rowe et al. (2007). $\text{SK}\alpha$ wavelength shifts were measured simultaneously on 3 spectrometers (2 with a PET crystal and 1 with an LPET crystal) to check that measurements were reproducible. Anhydrite (theoretical $\text{S}^{6+}/\text{S}^{\text{total}} = 1$) and pyrite (theoretical $\text{S}^{6+}/\text{S}^{\text{total}} = 0$) were measured at the start and end of each analytical session, and troilite was measured between each melt inclusion analysis to correct for instrumental drift. All wavelength scans were performed using a 15 kV accelerating voltage, 30 nA beam current and 5 μm beam diameter. Each scan consisted of between 80 and 100 steps, with each spectrometer moved 5 $\sin \theta$ units between each step. Counting times for each step were 5 s for anhydrite, pyrite and troilite, 30 s for basaltic melt inclusions and 60 s for dacitic melt inclusions. To avoid

oxidation of the samples by the electron beam, the beam was incrementally moved at a rate of 1 $\mu\text{m min}^{-1}$, and beam-damaged areas from prior EPMA spot analyses were avoided.

Each wavelength scan was fitted with a skewed Gaussian curve, which was found to give a better fit (higher R^2) than a standard Gaussian. Peak fitting was performed in Python using the `curve_fit` function from SciPy (<https://docs.scipy.org/doc/scipy/index.html>). The skewed Gaussian has the form:

$$f(x; \alpha, \xi, \omega, \delta) = A \cdot \phi\left(\frac{x-\xi}{\omega}\right) \cdot \Phi\left(\alpha \frac{x-\xi}{\omega}\right) + \delta \quad [\text{Equation 3}]$$

where:

A is a scaling factor for the amplitude, ω is the scale parameter, α is a skewness parameter, ξ is a location parameter, δ is a baseline, $\phi(z)$ is the standard normal probability density function, and $\Phi(z)$ is the standard normal cumulative density function.

Peak positions [$\lambda(\text{SK}\alpha)$] were determined for each fitted curve. Uncertainties in each peak position were then estimated using a bootstrap method implemented in Python. For each curve, the corresponding wavelength scan data were randomly sampled with replacement to generate 1000 bootstrap samples, and a skewed Gaussian was fitted to each. Two standard deviations on the peak positions across the bootstrap samples were then taken as the estimate for the peak position uncertainty. All data and fitted curves are in Online Resource 4, along with details of peak positions and R^2 values for each fit.

$\text{SK}\alpha$ wavelength shifts were calculated relative to troilite, using the average $\lambda(\text{SK}\alpha)$ values of the bracketing troilite measurements:

$$\Delta(\text{SK}\alpha)_{\text{sample}} = \lambda(\text{SK}\alpha)_{\text{troilite}} - \lambda(\text{SK}\alpha)_{\text{sample}} \quad [\text{Equation 4}]$$

Sulphur speciation was then calculated relative to the peak shift of anhydrite:

$$S^{6+}/S^{\text{total}} = \Delta(\text{SK}\alpha)_{\text{sample}} / \Delta(\text{SK}\alpha)_{\text{anhydrite}} \quad [\text{Equation 5}]$$

Uncertainties in measured peak positions were propagated through equations 4 and 5 to give an uncertainty estimate for each calculated S^{6+}/S^{total} value.

Independent S^{6+}/S^{total} measurements of each sample from the three spectrometers almost always overlap within uncertainty (all measurements are in Online Resource 4). Weighted means of these three independent measurements are thus reported as our preferred S^{6+}/S^{total} values. In the single case where all three measurements did not overlap within uncertainty (melt inclusion TAN1213-45-3-G-a), we take the middle value and its corresponding uncertainty as our preferred estimate.

Trace Element Concentrations: Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Glass trace element concentrations (mass fractions) of melt inclusions and matrix glasses were analysed by LA-ICP-MS at Victoria University of Wellington (New Zealand) using a Resonetics RESolution S155-SE laser ablation system equipped with an ATL ArF Excimer laser (wavelength 193 nm), coupled to an Agilent 7900 ICP-MS. Mass spectrometer tuning to optimise signal sensitivity and stability was performed by rastering a 50 μm -diameter circular laser beam across the NIST 612 reference material at a scan rate of 5 $\mu\text{m s}^{-1}$, with a 10 Hz pulse frequency. Tuning parameters were adjusted to ensure that element oxide production (estimated from the measured ThO^+/Th^+ ratio) was <1% and that fractionation across the mass range (estimated from the measured $^{238}\text{U}/^{232}\text{Th}$ ratio) was minimal. The laser energy was set at 5 mJ with 25% transmittance, for an energy density of $\sim 4.0 \text{ J cm}^{-2}$.

Olivine-hosted melt inclusions and basaltic matrix glasses were ablated using a 40 μm diameter circular spot. Due to their smaller size, a 35 μm spot was used for the plagioclase-hosted inclusions and silicic matrix glasses. The washout time between measurements was 90 s. Data were processed with Iolite 4 (<https://iolite.xyz/>) using NIST612 as the calibration standard, with ^{43}Ca as an internal standard for basaltic glasses and ^{29}Si as an internal standard for silicic glasses.

The isotopes measured for basaltic glasses were: Si^{29} , Sc^{45} , Ti^{47} , V^{51} , Cr^{53} , Co^{59} , Ni^{60} , Cu^{63} , Zn^{66} , As^{75} , Rb^{85} , Sr^{88} , Y^{89} , Zr^{90} , Nb^{93} , Mo^{98} , Sn^{118} , Ba^{138} , La^{139} , Ce^{140} , Nd^{146} , Sm^{147} , Eu^{153} , Gd^{157} , Ho^{165} , Er^{166} , Yb^{172} , Lu^{175} , Ta^{181} , Pb^{208} , Th^{232} , U^{238} .

Isotopes measured for silicic glasses were: Li^7 , Na^{23} , Mg^{25} , Ca^{43} , Sc^{45} , Ti^{47} , V^{51} , Mn^{55} , Co^{59} , Ni^{60} , Cu^{63} , Zn^{66} , Ga^{71} , Rb^{85} , Sr^{88} , Y^{89} , Zr^{90} , Nb^{93} , Mo^{98} , Cs^{133} , Ba^{138} , La^{139} , Ce^{140} , Pr^{141} , Nd^{146} , Sm^{147} , Eu^{151} , Gd^{157} , Tb^{159} , Dy^{163} , Ho^{165} , Er^{166} , Tm^{169} , Yb^{172} , Lu^{175} , Hf^{178} , Ta^{181} , W^{182} , Pb^{208} , Th^{232} , U^{238} .

All reference material and repeat sample measurements are in Online Resource 5. Measurement precision (2 S.D.) on repeat measurements of the USGS BHVO-2G and BCR-2G basaltic glass reference materials using a 40 μm spot are usually better than 5-10% relative and always better than 15% relative. Mean measured values for both BHVO-2G and BCR-2G generally show absolute biases of <10% (commonly <5%) and almost always <15% relative to accepted values: exceptions are Zn (<37%) and Sn (<22%). Measurement precision (2 S.D.) on repeat measurements of the ATHO-G, StHs6_80-G and T1-G intermediate to silicic glass reference materials using a 35 μm spot are usually better than 15% relative (commonly better than 5-10% relative) for most elements, and always better than 20% relative (excluding Cs in ATHO-G and Gd in StHs6_80-G: both better than 22% relative). Mean measured values for these three reference materials generally show absolute biases of <10% (commonly <5%) and almost always <20% relative to accepted values: exceptions are Sc in ATHO-G (48%), Mo in ATHO-G and T1-G (28% and 56%, respectively) and W in StHs6_80-G and T1-G (22% and 29%, respectively).

Measurement precision (2 S.D.) on repeat measurements of individual basaltic melt inclusions (where the size of the inclusion allowed for multiple spots) or matrix glass shards with a 40 μm spot is commonly better than 5 to 10% relative, and always better than 20% relative except for Cr (usually better than 10%, stretching to 30% relative in one case), Sn (< 51% relative), and Ta (<44% relative). Measurement precision (2 S.D.) on repeat measurements of silicic matrix glass shards with a 35 μm spot is commonly better than 5 to 10% relative, and always better than 20% relative except for W (better than 26%), Mg (better than 30%) and Ni (>100%).

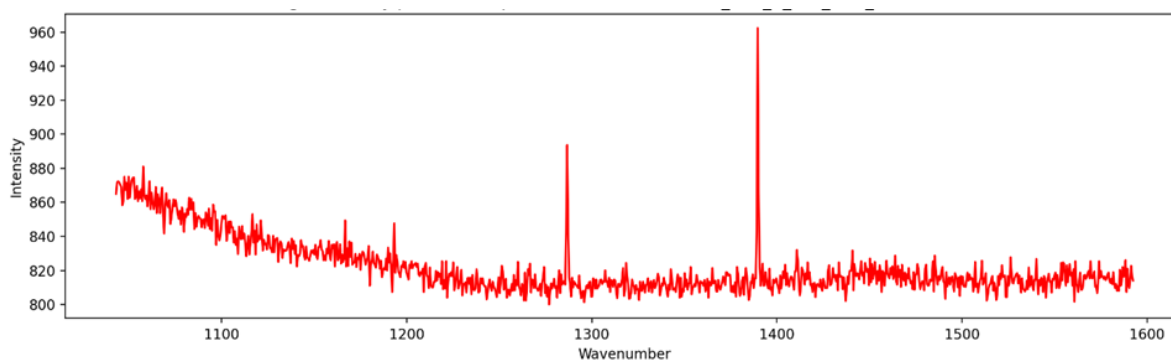


Figure OR3.1. Extremely weak CO₂ diad in Raman spectrum collected at 20 mW power from a vapor bubble in a plagioclase-hosted melt inclusion (inclusion SO253-081-12B-A-a).

Reference Material	SiO ₂ (wt%)	H ₂ O (wt%)	CO ₂ (μg g ⁻¹)
WOK5-4	51 [1]	1.6 ± 0.10 [2]	64 ± 12 [2]
WOK16-2	50.3 [1]	0.64 ± 0.02 [2]	184 ± 12 [2]
ETNA01	48.88 ± 0.22 [3]	2.53 ± 0.12 [3]	745 ± 80 [3]
ETNA04	49.10 ± 0.24 [3]	2.32 ± 0.12 [3]	2862 ± 94 [3]
ETNA28	47.81 ± 0.24 [3]	3.91 ± 0.12 [3]	1787 ± 82 [3]

Table OR3.1. Accepted compositions of basaltic glass reference materials used for SIMS H₂O and CO₂ measurement calibrations. Uncertainties are 2 S.D. [1] Accepted Caltech value. [2] Newman et al. (2000). [3] Hughes (2019).

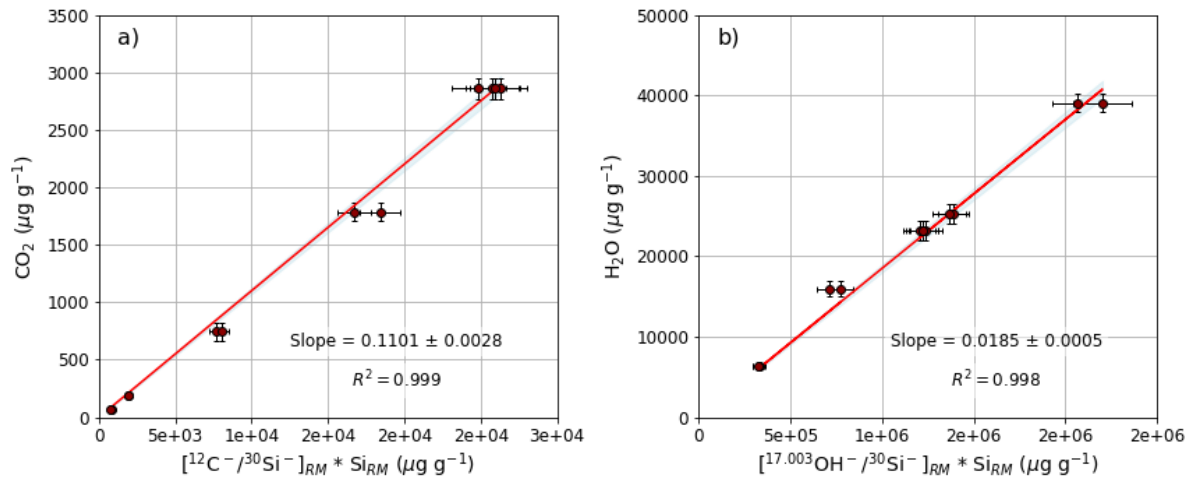


Figure OR3.2. SIMS calibration curves for volatile concentration measurements in basaltic glasses, derived from measurements of reference materials (Table OR3.1). Uncertainties on the slopes are 95% confidence limits, plotted as light blue envelopes around the best fit lines. Error bars show 2 S.D. uncertainties. RM = Reference material.

Reference Material	SiO ₂ (wt%)	H ₂ O (wt%)	CO ₂ (μg g ⁻¹)
M3N	71.38 ± 0.66 [1]	2.94 ± 0.16 [2]	89 ± 20 [3]
M6N	69.47 ± 0.96 [1]	5.11 ± 0.38 [2]	170 ± 20 [4]
ATHO-G	75.60 ± 1.40 [5]	0.014 [5]	3.7 [5]
mc84-bb-4b-r	76.45 ± 1.46 [6]	0.921 ± 0.014 [6]	10 [6]

Table OR3.2. Accepted compositions of silicic glass reference materials used for SIMS calibration. Uncertainties are 2 S.D. [1] Devine et al. (1995). [2] Karl Fischer titration by Hank Westrich, pers. comm. to John Stix (1989). [3] Repeat FTIR measurements by Clara Waelkens, pers. comm. (2024). [4] Waelkens et al. (2021). [5] Jochum et al. (2006). [6] Newman et al. (1988).

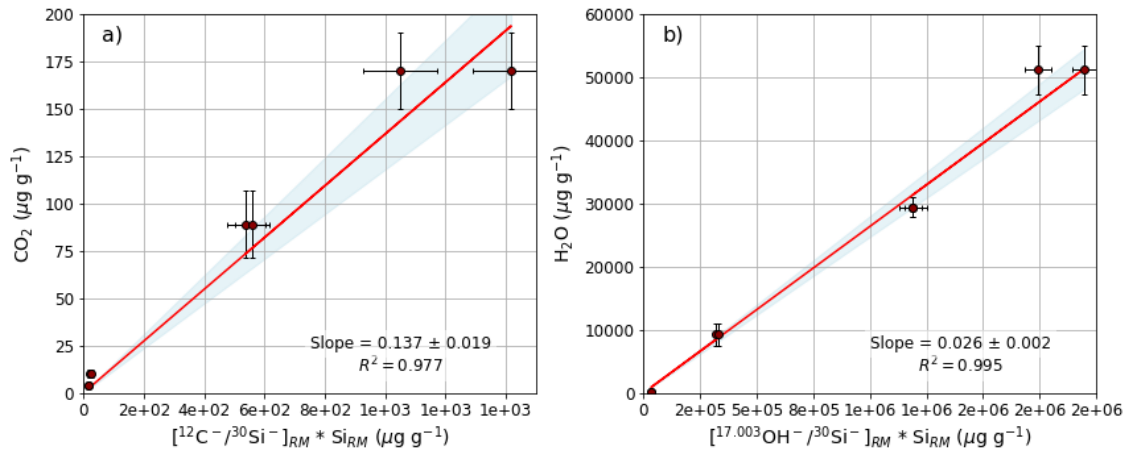


Figure OR3.3. SIMS calibration curves for volatile concentration measurements in silicic glasses, derived from measurements of reference materials (Table OR3.2). Uncertainties on the slopes are 95% confidence limits, plotted as light blue envelopes around the best fit lines. Error bars show 2 S.D. uncertainties. RM = Reference material.

Reference Material	CO ₂ Accepted (μg g ⁻¹)	CO ₂ Measured (μg g ⁻¹)	H ₂ O Accepted (wt%)	H ₂ O Measured (wt%)
GL-07 D48-4g	104 ± 6 [1]	119 ± 12	1.26 ± 0.11 [1]	1.29 ± 0.09
GL-07 D48-4g	104 ± 6 [1]	107 ± 14	1.26 ± 0.11 [1]	1.09 ± 0.13
ETNA16	51 ± 38 [1]	51 ± 11	3.40 ± 0.12 [1]	3.68 ± 0.24
ETNA16	51 ± 38 [1]	40 ± 5	3.40 ± 0.12 [1]	3.04 ± 0.28
ETNA8	2321 ± 48 [2]	1993 ± 212	6.25 ± 0.12 [2]	4.81 ± 0.39
ETNA8	2321 ± 48 [2]	1994 ± 222	6.25 ± 0.12 [2]	5.35 ± 0.46
ETNA24	1764 ± 200 [2]	1977 ± 182	2.86 ± 0.12 [2]	2.89 ± 0.20
ETNA24	1764 ± 200 [2]	1952 ± 255	2.86 ± 0.12 [2]	2.35 ± 0.27
ETNA33	2015 ± 62 [2]	2137 ± 230	1.04 ± 0.12 [2]	1.34 ± 0.13
ETNA33	2015 ± 62 [2]	1783 ± 190	1.04 ± 0.12 [2]	1.05 ± 0.10
P1326-2	327 ± 34 [3]	424 ± 54	0.27 ± 0.05 [3]	0.29 ± 0.03
P1326-2	327 ± 34 [3]	430 ± 56	0.27 ± 0.05 [3]	0.24 ± 0.02
ND70-Degassed	Blank [3]	3 ± 1	Blank [3]	0.02 ± 0.00
ND70-Natural	145 ± 106 [4]	142 ± 17	1.00 ± 0.34 [4]	1.16 ± 0.13
ND70-Natural	145 ± 106 [4]	153 ± 19	1.00 ± 0.34 [4]	1.32 ± 0.16
Olivine (Blank)	Blank	5 ± 1	Blank	0.00 ± 0.00

Table OR3.3. Measurements of secondary basaltic glass reference materials by SIMS. [1] Simons et al. (2002). [2] Hughes (2019). [3] Helo et al. (2011). [4] Moussallam et al. (2024).

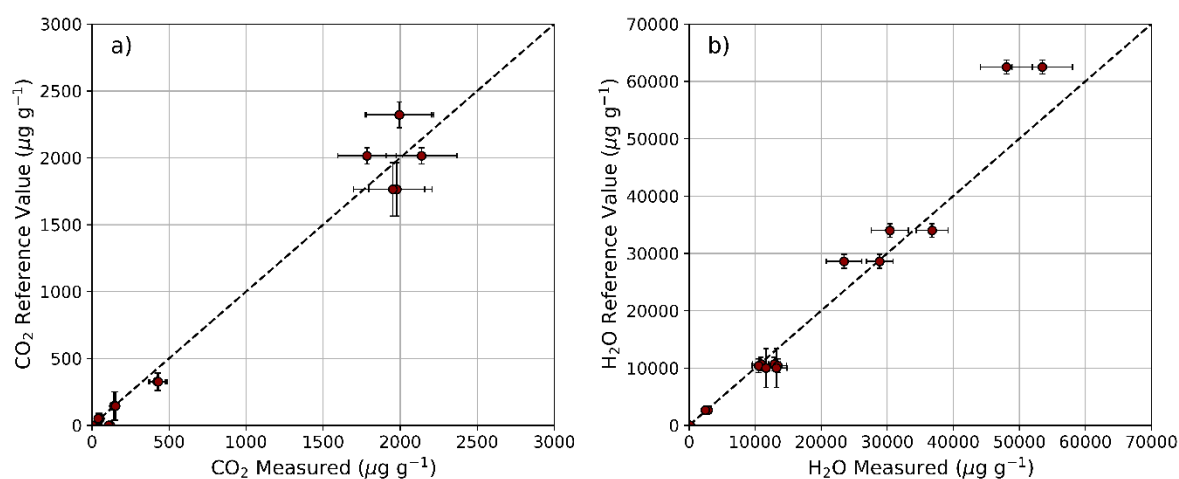


Figure OR3.4. Reference versus measured values for volatile concentrations of basaltic glass secondary reference materials measured by SIMS. Error bars show 2 S.D. uncertainties in reference values, or $\pm 20\%$ relative if no uncertainty in the reference value was specified (see Table OR3.3). Dashed lines show 1:1 correspondence.

Reference Material	CO ₂ Accepted (μg g ⁻¹)	CO ₂ Measured (μg g ⁻¹)	H ₂ O Accepted (wt%)	H ₂ O Measured (wt%)
mc84-bb-4b-b	29 [1]	16 ± 3	2.64 [1]	2.66 ± 0.21
mc84-bb-4b-b	29 [1]	15 ± 3	2.64 [1]	2.84 ± 0.23
mc84-df	7 [1]	5 ± 5	0.70 ± 0.01 [1]	1.17 ± 0.15
mc84-df	7 [1]	5 ± 1	0.70 ± 0.01 [1]	1.14 ± 0.15
mc84-df	7 [1]	6 ± 1	0.70 ± 0.01 [1]	1.19 ± 0.08
Up-NW-CouleeDome	2 [1]	3 ± 1	0.29 ± 0.01 [1]	0.53 ± 0.04
Up-NW-CouleeDome	2 [1]	3 ± 1	0.29 ± 0.01 [1]	0.54 ± 0.04
PanumDome	1 [1]	3 ± 1	0.12 ± 0.01 [1]	0.26 ± 0.02
PanumDome	1 [1]	3 ± 1	0.12 ± 0.01 [1]	0.25 ± 0.02
Olivine (Blank)	Blank	7 ± 2	Blank	0.01 ± 0.00

Table OR3.4. Measurements of secondary silicic glasses by SIMS. [1] Newman et al. (1988).

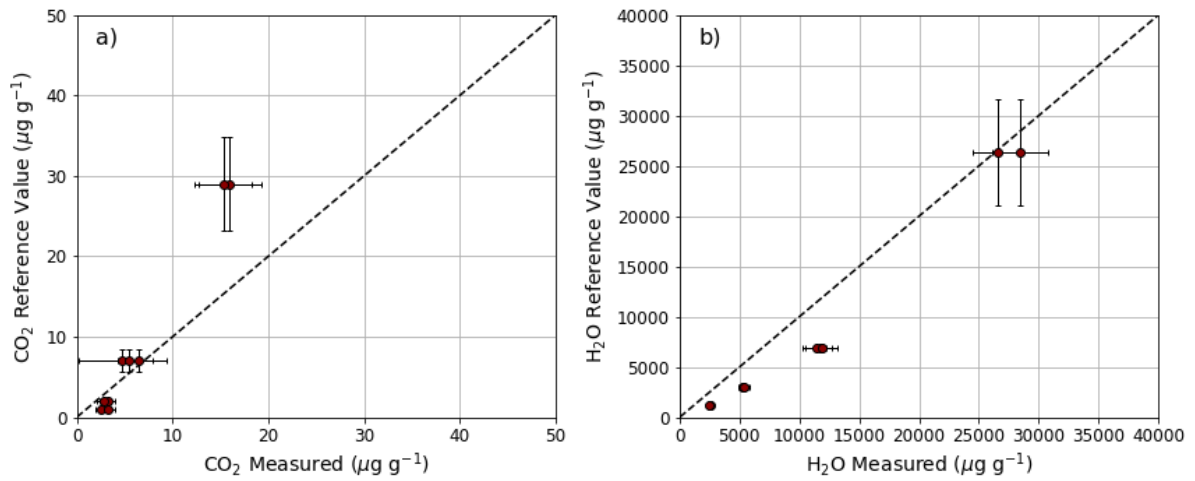


Figure OR3.5. Published versus measured values for volatile concentrations of silicic glasses characterised by Newman et al. (1988). Error bars show 2 S.D. uncertainties in reference values, or $\pm 20\%$ relative if no uncertainty in the reference value was specified (see Table OR3.4). Dashed lines show a 1:1 correspondence.

Basaltic Glass							Silicic Glass						
Element	Spectrometer	Crystal	Calibration Reference Material	Peak Counting Time (s)	Background Counting Time (s)		Element	Spectrometer	Crystal	Calibration Reference Material	Peak Counting Time (s)	Background Counting Time (s)	
Na	2	LTAP	LABR	20	10		Si	1	TAP	RHYO	10	5	
Mg	2	LTAP	BASL	10	5		Al	1	TAP	RHYO	20	10	
Ti	3	LPET	BASL	20	10		Na	2	LTAP	LABR	20	10	
Cl	3	LPET	TUGT	30	15		Mg	2	LTAP	BASL	30	15	
K	5	PET	KSPR	20	10		Ti	3	LPET	BASL	20	10	
Ca	5	PET	LABR	20	10		Cl	3	LPET	TUGT	20	10	
Mn	4	LIF	PYMN	30	15		S	3	LPET	CHAL	30	15	
Fe	4	LIF	BASL	20	10		K	5	PET	KSPR	30	15	
Si	1	TAP	BASL	10	5		Ca	5	PET	LABR	20	10	
Al	1	TAP	BASL	10	5		Fe	4	LIF	BASL	30	15	
S	3	LPET	CHAL	30	15		Mn	4	LIF	PYMN	30	15	
S	5	PET	CHAL	30	15		P	3	LPET	FLAP	20	10	
P	3	LPET	FLAP	20	10		S	5	PET	CHAL	30	15	
P	5	PET	FLAP	20	10		P	5	PET	FLAP	20	10	

Plagioclase							Olivine						
Element	Spectrometer	Crystal	Calibration Reference Material	Peak Counting Time (s)	Background Counting Time (s)		Element	Spectrometer	Crystal	Calibration Reference Material	Peak Counting Time (s)	Background Counting Time (s)	
Na	2	LTAP	LABR	10	5		Si	1	TAP	FO83	20	10	
Si	1	TAP	LABR	10	5		Al	1	TAP	LABR	60	30	
Al	1	TAP	LABR	10	5		Mg	2	LTAP	FO83	10	5	
K	3	LPET	KSPR	20	10		Na	2	LTAP	KANO	30	15	
Ca	5	PET	LABR	10	5		Cr	3	LPET	GROM	60	30	
Mg	2	LTAP	BASL	30	15		Ti	3	LPET	BASL	60	30	
Fe	4	LIF	BASL	30	15		Ni	4	LIF	NiSi	60	30	
Ti	3	LPET	BASL	20	10		Fe	4	LIF	FO83	20	10	
Ti	5	PET	BASL	20	10		Mn	4	LIF	PYMN	30	15	
							Ca	5	PET	KAUG	60	30	

Table OR3.5. Details of EPMA procedures, including spectrometer crystals used, calibration reference materials, and peak counting times for each element. LABR = Plagioclase (NMNH 115900); BASL = VG-A99 basaltic glass (NMNH 113498/1), (NMNH 143966); PYMN = Pyroxmangite (ETH Zurich); CHAL = Chalcopyrite (Astimex); FLAP = Durango fluorapatite (NMNH 72854); FO83 = Springwater olivine (NMNH 2566); KANO = Anorthoclase (NMNH 122142); NiSi = Ni₂Si (Astimex); KAUG = Kalscheurite (NMNH 122142).

NMNH 113498-1 Basaltic Glass (n = 44)													
	Na ₂ O	MgO	TiO ₂	Cl	K ₂ O	CaO	MnO	FeO*	SiO ₂	Al ₂ O ₃	SO ₂	P ₂ O ₅	Total
Mean (wt%)	2.57	5.12	4.07	0.02	0.82	9.17	0.19	13.33	51.09	12.54	0.03	0.44	99.39
2 SD (abs, wt%)	0.14	0.08	0.05	0.01	0.03	0.11	0.05	0.32	0.54	0.19	0.01	0.03	0.69
2 RSD (%)	5.48	1.53	1.23	33.88	4.01	1.25	25.40	2.42	1.05	1.55	53.52	8.01	0.70
Reference (wt%)	2.66	5.08	4.06		0.82	9.30	0.15	13.30	50.94	12.49		0.38	
Measured/Reference	0.97	1.01	1.00		1.00	0.99	1.25	1.00	1.00	1.00		1.15	
% Bias	-3.3	0.7	0.3		0.0	-1.3	25.2	0.2	0.3	0.4		15.0	

NMNH 72854 Rhyolite Glass (n = 51)													
	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	TiO ₂	Cl	SO ₃	K ₂ O	CaO	FeO*	MnO	P ₂ O ₅	Total
Mean (wt%)	76.93	12.17	3.58	0.03	0.08	0.10	0.00	4.98	0.43	1.15	0.02	0.00	99.50
2 SD (abs, wt%)	0.77	0.26	0.45	0.02	0.03	0.02	0.03	0.20	0.05	0.18	0.06	0.03	1.02
2 RSD (%)	1.00	2.17	12.50	52.78	34.21	25.26	-9843	4.08	11.36	15.41	285	-1640	1.02
Reference (wt%)	76.71	12.06	3.75	<0.10	0.12	0.13		4.89	0.50	1.23	0.03	<0.01	
Measured/Reference	1.00	1.01	0.96		0.69	0.75		1.02	0.87	0.94	0.73		
% Bias	0.3	0.9	-4.5		-31.0	-24.7		1.9	-13.5	-6.2	-26.5		

USNM 2566 Springwater Olivine (n = 36)													
	SiO ₂	MnO	FeO*	NiO	MgO	Cr ₂ O ₃	CaO	Al ₂ O ₃	TiO ₂	Na ₂ O	Total	Fo	Fa
Mean (wt% or mol%)	39.17	0.32	16.60	0.01	43.75	0.03	0.01	0.01	0.00	0.00	99.90	82.45	17.55
2 SD (abs, wt% or mol%)	0.51	0.04	0.27	0.02	0.43	0.01	0.01	0.02	0.01	0.01	0.74	0.30	0.30
2 RSD (%)	1.29	12.58	1.60	422	0.98	15.64	75	241	6321	-1727	0.74	0.37	1.73
Reference (wt% or mol%)	38.95	0.3	16.62		43.58	0.02					82.38	17.62	
Measured/Reference	1.01	1.06	1.00		1.00	1.65					1.00	1.00	
% Bias	0.6	5.5	-0.1		0.4	65.3					0.1	-0.4	

NMNH 115900 Plagioclase (n = 34)													
	Na ₂ O	SiO ₂	Al ₂ O ₃	K ₂ O	CaO	MgO	FeO*	TiO ₂	Total	An	Ab	Or	
Mean (wt% or mol%)	3.48	51.10	30.96	0.12	13.60	0.13	0.46	0.04	99.90	67.87	31.44	0.69	
2 SD (abs, wt% or mol%)	0.21	0.89	0.43	0.02	0.20	0.01	0.05	0.01	0.99	1.36	1.32	0.13	
2 RSD (%)	6.09	1.75	1.38	19.20	1.44	8.13	11.50	28.78	0.99	2.00	4.21	18.76	
Reference (wt% or mol%)	3.45	51.25	30.91	0.18	13.64	0.14	0.46	0.05		67.87	31.06	1.07	
Measured/Reference	1.01	1.00	1.00	0.65	1.00	0.95	0.99	0.84		1.00	1.01	0.65	
% Bias	1.0	-0.3	0.2	-35.3	-0.3	-5.0	-0.8	-15.9		0.0	1.2	-35.2	

Table OR3.6. Summary of secondary reference material analyses by EPMA (see Online Resource 5 for individual analyses). Reference values are Smithsonian preferred values (<https://naturalhistory.si.edu/research/mineral-sciences/collections-overview/reference->

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