Supplementary Material

Time-dependent ratio flank method protocol

1. Set analytical conditions: 15 kV accelerating voltage, 10 nA beam current and focussed beam. Focus z.

2. Assign spectrometers: TAPs (e.g., TAP, LTAP, TAPH) on F$K\alpha$, PETs on K$K\alpha$, and LIFs on Fe$K\alpha$.

3. Change conditions: 10 μm beam diameter (may need 50 nA beam current for peaking MgF$_2$).

4. Peak-up spectrometers and set PHA windows: F$K\alpha$ on MgF$_2$, K$K\alpha$ on sanidine, and Fe$K\alpha$ on basaltic glass.

5. Calculate current Fe$L\alpha_f$ and Fe$L\beta_f$ positions using spectrometer positions from F$K\alpha$ peak positions.

6. New spectrometer set-up: change TAPs to Fe$L\alpha_f$ and Fe$L\beta_f$.

7. If using Probe for EPMA software: select MAN backgrounds, collect standards (e.g., on sanidine, basaltic glass, NaCl and MgO) otherwise software will not let you export the data.

   a) If using Probe for EPMA software use Time-Dependent Intensity option: each measurement is 120 s with 24 intervals.

   b) Otherwise: each measurement 5 s. Either add 24 measurements on the same point or add a line scan of 24 points where the start and end position are the same.

8. Collect unknowns and standards (e.g., ten analyses per sample).

9. Average data for each sample.

10. Process data – R code available in Supplementary Material.

11. Produce calibration curve and calculate Fe^{2+}/Fe$_T$ for unknowns.

Experimental glass synthesis: ETNA glasses

Starting powders were made of a mechanical mixture of albite, anorthite, sanidine, fayalite, wollastonite, SiO_2, MnO, MgO, TiO_2, Fe_2O_3, $Ca_3(PO_4)_2$, and $CaCO_3$, by grinding in an agate mortar. Approximately 50 mg of starting powder was loaded into 3 (diameter) by ~15 (length) mm Au_{80}-Pd_{20} capsules, except ETNA24 where ~500 mg was loaded into a 5 (diameter) by ~30 (length) mm Au_{75}-Pd_{25} capsule, and welded shut. Capsules were immersed in water at 50 ^{o} C then put in an ~100 ^{o} C oven for 10 minutes to check for leaks. Glasses were synthesised (6 capsules at a time, except ETNA24) in an internally-heated pressure vessel (IHPV) for ~18 hours at 1250 ^{o} C and 1, 3, 5 or 7 kbar (see Table 1 for details) using Ar gas as the pressurising medium at the Institut für Mineralogie, Leibniz Universität Hannover, Germany. Experiments were run under intrinsic oxygen fugacity conditions. The sample holder is equipped with four S-type thermocouples: two are used to control the furnace temperature and two are used to record the sample temperature. Temperature varied by < 5 ^{o} C during experiments. Pressure variations during the experiment were limited to ±0.02 kbar. Samples were quenched using a rapid-quench device at ~150 $°C·s^{-1}$ (Berndt et al., 2002).

Table 1 Synthesis pressure of experimental samples.

Pressure (kbar)	Sample numbers
1	12, 13, 14, 15, 16, 17
3	1, 2, 3, 6, 7, 11
5	24, 25, 26, 27, 28, 29, 30
7	4, 5, 8, 9, 10

Analytical techniques

Electron Probe Micro-Analysis (EPMA). Major and minor element chemistry of ETNA and AR glasses were measured using the JEOL JXA 8530F Hyperprobe at the School of Earth Sciences, University of Bristol, UK. Glass chips were mounted in epoxy, ground to a ~1 μm polish then carbon coated (~15 nm thickness). Analytical conditions were: 15 kV accelerating

voltage, 10 nA beam current, and 10 μm beam diameter. For quantification, H was included as an element by difference and O was calculated from stoichiometry, with all Fe as FeO. Further analytical details are specified in Table 2 for ETNA glasses and Table 3 for AR glasses.

Table 2 Analytical details for EPMA of ETNA glasses.

	Spectrometer - Crystal				
	1 – TAP	2 – TAP	3 – PETH	4 – LIFH	5 - PETL
1	Si (BCR-2)	Na (BCR-2)	Ca (BCR-2)	Fe (BCR-2)	K (Sanidine)
2	Al (BCR-2)	Mg (BCR-2)	Ti (TiO$_2$)	Mn (Mn metal)	P (Durango apatite)

Notes: elements were peaked on their standard (given in brackets) and BCR-2 is the USGS basaltic glass standard Columbia River Basalt. Peak counting times were 10 s and high and low background counting times were 5 s each. For each sample, 36 analyses on fresh areas of glass were averaged.

Table 3 Analytical details for EPMA of AR glasses.

	Spectrometer – Crystal				
	1 – PETJ	2 – TAP	3 – TAPH	4 – PETH	5 – LIFL
1	Ca (Wollastonite, BCR-2)	Si (BCR-2)	Na (Albite, BCR-2)	K (Sanidine)	Fe (Andradite, BCR-2)
2	Ti (TiO$_2$)	Al (BCR-2)	Mg (SJIO, BCR-2)	P (Durango apatite)	Mn (Mn metal)
3	Cl (NaCl)			S (VG2, Barite)	

Notes: Glass and mineral standards were used for peaking (first item in brackets) and calibration counts (second item in brackets if different), and BCR-2 is the USGS basaltic glass standard Columbia River Basalt, SJIO is St John's Island Olivine, and VG2 is a Smithsonian Microbeam glass standard. Peak counting times were 60 s except K which was 120 s. Mean Atomic Number (MAN) backgrounds were used. The first element on each spectrometer had Time-Dependent Intensity (TDI) data collected to extrapolate to time zero in case of element migration. For each sample, three analyses on fresh areas of glass were averaged.

Secondary Ion Mass Spectrometry (SIMS). H$_2$O was measured in the ETNA glasses using the Cameca IMS-4f at the School of Geosciences, University of Edinburgh, UK. Glass chips were mounted in epoxy, ground to a ~1 μm finish, remounted in indium then gold coated. The analytical target was pre-sputtered over a 20 μm^2 area for three minutes to reduce surface contamination. Prior to H$_2$O measurements, CO$_2$ was measured in the same raster pit, but those data are not discussed here. For H$_2$O analyses, a O$^-$ beam at 15 kV and 5 nA was used to produce positive ions over a 60 μm imaging field which was reduced to ~20 μm using apertures. During peak centering a rastered 25 μm image field was used. Secondary ions were extracted at 4.5 kV with a 75 kV offset and 40 eV window and a low mass resolution of 400 was used.

Species, masses, count times and wait times are detailed in Table 4 and eight cycles were collected for each measurement, although typically only the last six were used. A working curve of H_2O against $^1H/^{30}Si$ using background-corrected ^1H was constructed using standards containing $0 - 5$ wt% H_2O. Samples were analysed $3 - 5$ times, except for ETNA24 that was analysed 20 times on three separate chips.

Table 4 Details of SIMS analysis.

Species	0.7	^1H	^{23}Na	^{26}Mg	^{30}Si	^{39}K	^{42}Ca	^{47}Ti
Mass	0.7	1.01	22.99	25.98	29.97	28.96	41.96	46.95
Count time (s)	1	4	4	4	2	2	2	2
Wait time (s)	1.5	1	0.2	0.2	0.2	0.2	0.2	0.2

Time-Dependent Ratio Flank Method Calibration Curves. Figure 1 shows the additional calibration curves for sessions $#2 - 4$ using analytical conditions of 15 kV accelerating voltage, 50 nA beam current, and 4 μm beam diameter. Details of the calibration curves are in Table 5.
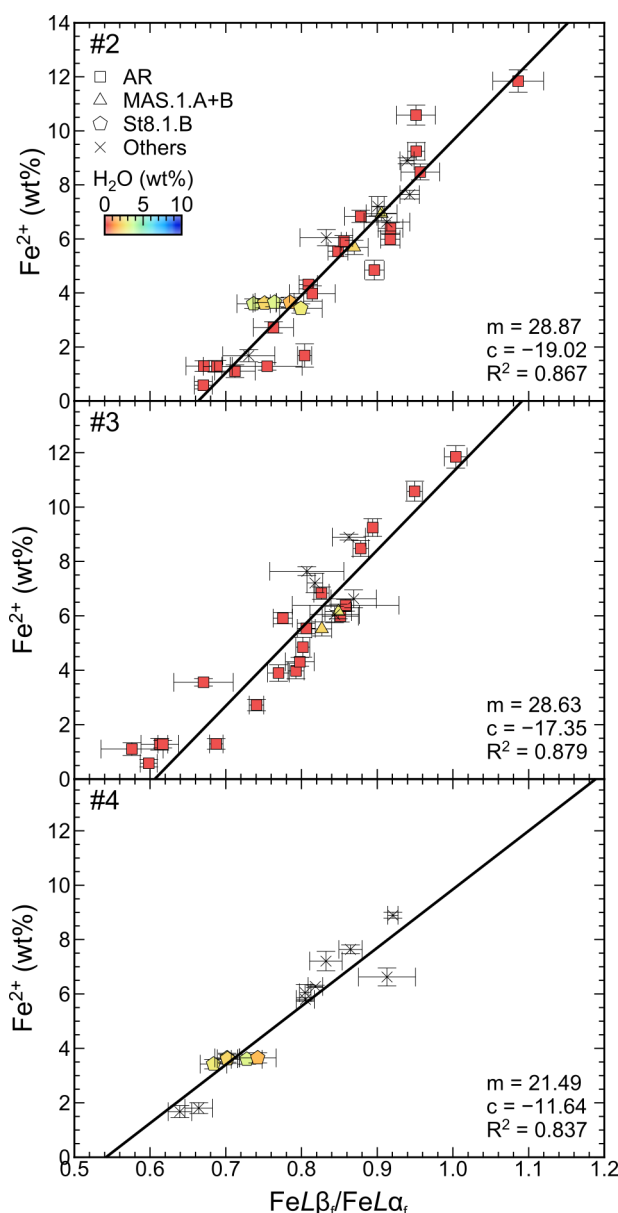
Figure 1 Calibration curves for sessions #2 – 4, with independently constrained Fe^{2+} against corrected $FeL\beta_f/FeL\alpha_f$, where symbol shape indicates average glass composition and colour indicates H_2O. Analytical conditions were: 15 kV accelerating voltage, 50 nA beam current, and 4 μm beam diameter. Session number (#) indicated in the top left corner.

Table 5 Results for weighted linear regression for each session.

#	n	m	c	Adj. R^2	R.S.E. (wt%)
2	32	28.67 ± 2.05	-19.02 ± 1.77	0.87	0.55
3	27	28.63 ± 2.12	-17.35 ± 1.75	0.88	0.50
4	14	21.49 ± 2.72	-11.64 ± 2.16	0.84	0.36

Notes: Data were collected during separate sessions (#) using analytical conditions of a 15 kV accelerating voltage, 50 nA beam current, and 4 μm beam diameter. n is the number of measurements included in the fit. m and c are the slope and intercept respectively for $Fe^{2+} = m \cdot (Fe\ L\beta/L\alpha) + c$. Adj. R^2 is the adjusted R^2. R.S.E. is the residual standard error on estimated Fe^{2+}.