

Supplementary materials – Riker et al.: VOLATILE PARTITIONING IN THE SYSTEM APATITE–SILICATE MELT

EPMA analytical conditions - apatite

Our standard analytical setup for electron probe microanalysis of apatite using the 5-spectrometer Cameca SX-100 electron microprobe at University of Bristol was (peak counting times given for each element; background counting times half as long):

Spectrometer 1 [LPET]:	Cl (120 s)			
Spectrometer 2 [PC1]:	F (120 s)			
Spectrometer 3 [LPET]:	Ca (30 s)	P (30 s)	K (30 s)	Ti (30 s)
Spectrometer 4 [TAP]:	Na (60 s)	Si (30 s)	Al (30 s)	Mg (60 s)
Spectrometer 5 [LLIF]:	Fe (60 s)	Mn (60 s)		

A 15 kV, 10 nA, 10 μm electron beam was used as a pragmatic compromise between the need for accurate analyses and the need to mitigate sample damage (e.g. Stormer et al. 1983; Goldoff et al. 2012; Stock et al. 2015). Na was calibrated on albite; Si and Mg on St John's Island olivine; Cl on NaCl; F on MgF_2 ; P and Ca on Durango apatite; K and Al on sanidine; Mn on Mn metal and Ti and Fe on ilmenite. Oriented secondary standards of Durango (Young et al. 1969) and Wilberforce apatite were analysed before, during and after every run.

EPMA analytical conditions - glass

Our standard analytical setup for electron probe microanalysis of hydrous glass using the 5-spectrometer Cameca SX-100 electron microprobe at University of Bristol was (peak counting times given for each element; background counting times half as long):

Spectrometer 1 [LPET]:	Cl (120 s)			
Spectrometer 2 [PC1, or PC0 for Fe-bearing glasses]:	F (120 s)			
Spectrometer 3 [LPET]:	Ca (30 s)	P (30 s)	K (30 s)	Ti (30 s)
Spectrometer 4 [TAP]:	Na (60 s)	Si (30 s)	Al (30 s)	Mg (30 s)
Spectrometer 5 [LLIF]:	Fe (60 s)	Mn (60 s)		

We used a 15 kV, 2 nA, 15 μm electron beam to mitigate sample damage (e.g. Devine et al. 1995; Humphreys et al. 2006). Na and Si were calibrated on albite; Mg on St John's Island olivine; Cl on NaCl; F on MgF_2 ; P on Durango apatite; Ca on wollastonite; K and Al on sanidine; Mn on Mn metal and Ti and Fe on ilmenite. Secondary standards KN18 (Nielsen & Sigurdsson 1981) and BCR were analysed before, during and after every analytical run, together with Durango apatite and three synthetic, fluorine-bearing basaltic glasses prepared using starting material SH3.

Reference materials used for analysis of volatiles

Reference	Sample	Phase	Used for
Shishkina et al. (2010)	M5, M10, M21, M36, M40, M47, N72	Basalt glass	Glass CO_2
Shishkina et al. (2010)	M5, M36, M40, N72	Basalt glass	Glass H_2O
Mangan & Sisson (2000)	# 51	Rhyolite glass	Glass CO_2 and H_2O
Hauri et al. (2002)	519-4-1	Basalt glass	Glass CO_2 and H_2O
Brooker et al. (1999)	RB480	Basalt glass	Glass CO_2
Mandeville et al. (2002)	Run84	Andesite glass	Glass H_2O
Hunt & Hill (1993)	Lipari	Rhyolite glass	Glass H_2O , F and Cl

Vetere et al. (2014)	AH1, AH2_4, St3_AH2_3, St3_AH1_2	Alkali glass	Glass CO ₂ and H ₂ O
In-house standards	DUR, TNK, LIN, YAT, BAH2, IML5, SIB1, WIL2, JUM, PAN2, MAD2	Apatite	Apatite volatiles
Schettler et al. (2011)	APS-17, APS-26, APS25	Apatite	Apatite volatiles

Volatile-exchange K_D s (mole fraction basis)

Experiment	$\log K_D^{\text{OH-F}}$	$\log K_D^{\text{OH-Cl}}$	$\log K_D^{\text{Cl-F}}$	XOH _m	XF _m	XCl _m
BA6	-1.070			0.041	0.016	
BA9	-1.032			0.168	0.028	
BA10	-1.228			0.088	0.02	
BA11	-1.026			0.062	0.031	
BA12	-1.074	-0.766	-0.148	0.054	0.018	0.015
BA14	-1.183	-0.468	0.627	0.171	0.017	0.015
BM13	-1.546			0.081	0.017	
BM14	-1.584	-0.716	-0.391	0.078	0.017	0.025
BM16	-1.604	-0.684	-0.276	0.085	0.019	0.025

References

- Brooker, R.A., Kohn, S.C., Holloway, J.R., McMillan, P.F., and Carroll, M.R. (1999). Solubility, speciation and dissolution mechanisms for CO₂ in melts on the NaAlO₂-SiO₂ join. *Geochimica et Cosmochimica Acta*, 63, 3549-3565
- Devine, J.D., Gardner, J.E., Brack, H.P., Layne, G.D., and Rutherford, M.J. (1995) Comparison of microanalytical methods for estimating H₂O contents of silicic volcanic glasses. *American Mineralogist*, 80, 319-328
- Goldoff, B., Webster, J.D., and Harlov, D.E. (2012) Characterization of fluor-chlorapatites by electron probe microanalysis with a focus on time-dependent intensity variation of halogens. *American Mineralogist*, 97, 1103-1115
- Hauri, E., Wang, J., Dixon, J.E., King, P.L., Mandeville, C., and Newman, S. (2002) SIMS analysis of volatile in silicate glasses 1. Calibration, matrix effects and comparisons with FTIR. *Chemical Geology*, 183, 99-114
- Humphreys, M.C.S., Kearns, S.L., and Blundy, J.D. (2006) SIMS investigation of electron-beam damage to hydrous, rhyolitic glasses: Implications for melt inclusion analysis. *American Mineralogist*, 91, 667-679
- Hunt, J.B., and Hill, P.G. (1993) Tephra geochemistry: a discussion of some persistent analytical problems. *The Holocene*, 3, 271-278
- Mandeville, C.W., Webster, J.D., Rutherford, M.J., Taylor, B.E., Timbal, A., and Faure, K. (2002) Determination of molar absorptivities for infrared absorption bands of H₂O in andesitic glasses. *American Mineralogist*, 87, 813-821
- Mangan, M., and Sisson, T. (2000) Delayed, disequilibrium degassing in rhyolite magma: decompression experiments and implications for explosive volcanism. *Earth and Planetary Science Letters*, 183, 441-455
- Nielsen, C.H., and Sigurdsson, H. (1981) Quantitative methods for electron microprobe analysis of sodium in natural and synthetic glasses. *American Mineralogist*, 66, 547-552

- Schettler, G., Gottschalk, M., and Harlov, D.E. (2011) A new semi-micro wet chemical method for apatite analysis and its application to the crystal chemistry of fluorapatite-chlorapatite solid solutions. *American Mineralogist*, 96, 138-152
- Stock, M.J., Humphreys, M.C.S., Smith, V.C., Johnson, R.D., Pyle, D.M., and EIMF (2015) New constraints on electron-beam induced halogen migration in apatite. *American Mineralogist*, 100, 281-293
- Stormer, J.C., Pierson, M.L., and Tacker, R.C. (1993) Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis. *American Mineralogist*, 78, 641-648
- Vetere, F., Holtz, F., Behrens, H., Botcharnikov, R.E., and Fanara, S (2014) The effect of alkalis and polymerization on the solubility of H₂O and CO₂ in alkali-rich silicate melts. *Contributions to Mineralogy and Petrology*, 167, 1014
- Young, E.J., Myers, A.T., Munson, E.L., and Conklin, N.M. (1969) Mineralogy and geochemistry of fluorapatite from the Cerro de Mercado, Durango, Mexico. USGS Professional Paper 650D, 84-93