

**The Competing Effects of Sulfide Saturation versus Degassing on the Behavior of the Chalcophile Elements during the differentiation of hydrous melts**

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## Introduction

The supplementary Information provides detailed information documenting sample localities (Table S1) and analytical techniques used to undertake major, trace and volatile element analyses of glass samples from the Valu Fa Ridge. All analyses were undertaken at the Australian National University, (Research School of Earth Sciences), The Carnegie Institution of Washington (Department of Terrestrial Magnetism) and The Smithsonian Institution. Major, trace and volatile element data are presented in Tables S2. Previous major element analyses for samples from the Valu Fa Ridge are compiled in Tables S3 and S4. Further details regarding replicate analyses of reference materials and materials used for interference corrections are given in Tables S5 and S6, respectively.

### Text S1: Analytical Techniques

Locations, sample descriptions and previous analyses of major element abundances [Goddard, 2007; Mikkelsen, 2005] of samples recovered during the 2003 Tonga-Eastern Lau Vents Expedition (TELVE, SS02/03) of Australia's Marine National Facility RV Southern Surveyor are given in Supplementary Tables 1, 3 and 4. Further voyage information can be found at:

<http://www.marine.csiro.au/nationalfacility/voyagedocs/2003/0203s.htm>

Volatile element contents (S, Cl, F, P, H<sub>2</sub>O and CO<sub>2</sub>; Supplementary Table 2) were measured using secondary ion mass spectrometry (SIMS) following the techniques described in Hauri et al. [2002]. Volcanic glasses were mounted in epoxy and major element compositions were measured using JEOL JXA-8900 automated five-spectrometer wavelength dispersive electron microprobe analysis (EMPA) at the Smithsonian Institution, operated at 15 keV accelerating potential and 20 nA beam current. The beam was rastered over a 12 µm by 10 µm area, with counting times ranging from 20–30 seconds. Data was reduced using the phi-rho-Z routine in Probe for EPMA. Ten elements were analyzed, and their detection limits (in wt%) are given in parentheses: Al (0.02), Ca (0.02), Mg (0.01), Si (0.02), Ti (0.02), Na (0.03), Fe (0.05), K (0.01), P (0.01), and Mn (0.03). The volcanic glass USNM 113498 VG-A99 was used as a standard for all elements except Mn (manganite) and P (fluor-apatite). Each volcanic glass was analyzed three times and averaged to give the presented compositions (Supplementary Table 2).

Trace element abundances were first measured at the Research School of Earth Sciences (RSES), Australian National University (ANU), using laser ablation inductively coupled plasma source mass spectrometry; LA-ICP-MS) following the techniques described in previous studies [Jenner and O'Neill, 2012a; b; Jenner et al., 2009]. Epoxy mounts were subsequently polished and LA-ICP-MS (Photon Machines laser coupled to a Thermo iCAP-Q ICP-MS) analyses were repeated twice at the Department of Terrestrial Magnetism (DTM), Carnegie Institution of Washington (CIW) to ensure reproducibility of data and to permit identification of accidental analysis of microphenocrysts during ablation. Analyses were undertaken using a repetition rate of 14 Htz, an ablation diameter of 238 µm and with elements divided into two analytical routines (element division given in Supplementary Table 5) to maximize counting times on each element. <sup>29</sup>Si, <sup>43</sup>Ca, <sup>49</sup>Ti, <sup>140</sup>Ce, <sup>147</sup>Sm, <sup>157</sup>Gd, were included in both routines to ensure reproducibility of analyses prior to compilation of data from both routines). NIST SRM 612 [values given in Jenner and O'Neill, 2012b] was used for external calibration and <sup>29</sup>Si was used for internal calibration of data. Data for replicate analyses of BCR-2G, analyzed during the same

analytical session as samples from the VFR at both DTM and RSES (RSES data previously compiled, presented and discussed in Jenner and O'Neill, 2012) are presented in Supplementary Table 5. The relative standard deviation (RSD) for average values from both analytical sessions undertaken at DTM are typically  $\leq 3\%$  for both analytical routines. Average analyses of BCR-2G undertaken at DTM are typically within 5% of the PV presented in Jenner and O'Neill [2012b]. However, the content of Ag in the chip of BCR-2G analyzed at DTM (0.751 ppm Ag) was found to be considerably higher than the chip analyzed at the RSES (0.152 ppm Ag). The PV for Ag in BCR-2G of 0.5 ppm given on GeoReM [Jochum et al., 2005] is notably intermediate between both values, demonstrating variability in Ag contents in BCR-2G, potentially inherited during manufacturing. Trace element abundances of each of the VFR glasses analyzed during each of the three analytical routines were averaged to give the final reported compositions (Supplementary Table 2). A preliminary dataset including a subset of the 'ANU' dataset was presented in [Kendrick et al., 2014] and is superseded by the data presented here.

Backarc basin glasses from the VFR have a large range Cl contents up to 3171 ppm (Supplementary Table 2), which are considerable higher than MORB at  $\sim 300$  ppm [Jenner and O'Neill, 2012a], indicating the additional need for  $^{37}\text{Cl}^{40}\text{Ar}$  interference corrections during analysis of Se abundances. Hence, whole rock analyses of Se contents of four glass samples from the North West Lau Spreading Centre [samples previously described in Jenner et al., 2012] were undertaken following the techniques described previous studies [König et al., 2014; König et al., 2012]. Analyses confirmed a systematic offset between LA-ICP-MS hydride generation ICP-MS data (Supplementary Table 6) for samples with high chlorine contents, demonstrating the need for a  $^{37}\text{Cl}^{40}\text{Ar}$  interference correction [in addition to those discussed in Jenner et al., 2009] during analysis of highly evolved backarc basin glasses. For example, comparison of the offset in contents of Se in Eastern Manus Backarc Basin glasses with  $>3$  wt.% MgO are negligible, however, the offset becomes significant for the more evolved Cl-rich, Se-poor glasses (i.e., following sulfide saturation). Consequently, glasses from the Northwest Lau Spreading Centre were analyzed during each analytical session and were used to calculate and make corrections for  $^{37}\text{Cl}^{40}\text{Ar}$  interferences to both analyses of VFR and EMBB analyses.

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