

Online Resource 4

Contributions to Mineralogy and Petrology

Temporal evolution of a post-caldera, mildly peralkaline magmatic system: Furnas volcano, São Miguel, Azores

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Whole rock analyses

For WD-XRF analyses, samples were cleaned using distilled water and weathered surfaces were removed, before crushing using a jaw-crusher and an agate mill. Fused glass discs for major element analysis were prepared using 0.7 g of rock powder mixed with 3.5 g of lithium metaborate. Trace element concentrations were determined using PVC bound pressed powder pellets. Loss on ignition (LOI) was reported as weight difference after ignition at 1,000 °C for two hours. Data quality was evaluated by repeated analyses of the following standards: WS-E, OUG94, GSP-2, W2a, and AC-E. The mean deviation from the accepted standard values was < 10 % and reproducibility was < 3 % for major elements and < 10 % for trace elements.

Samples analysed via ICP-MS at the Open University, U.K., were prepared using a standard HF-HNO₃ digestion procedure (e.g. Eggins et al. 1997). The instrument was calibrated using up to six international standards (BCR1, BIR1, AC, RGM1, BHVO1-2, AGV1), using recommended element concentrations. Instrumental drift was monitored by and corrected using an internal standard solution containing Be, In, Rh, Tm, Re and Bi, which was introduced on-line during analysis. Residual drift in individual elements was corrected externally using replicate determinations of a representative sample after every 10 unknowns. Samples analysed via ICP-AES and ICP-MS at Bureau Veritas Mineral Laboratories, Canada, were cleaned to remove altered surfaces, and crushed in an agate mill prior to drying at 60 °C, mixing with a LiBO₂/Li₂B₄O₇ flux and dilute nitric digestion. LOI was reported as weight difference after ignition for two hours at 1,000 °C. Standard analyses indicate accuracy of < 5 % for major elements and < 7 % for trace elements, whilst reproducibility was < 1 %

For samples analysed by XRF at Keele University, U.K., a minimum of five clasts were analysed for each eruptive unit. Clasts were analysed individually where possible. Samples had any visibly weathered surfaces removed prior to soaking in distilled water for at least 24 hours and crushing in an agate mill. Elemental determinations were performed on PVC bound pressed powder pellets, using 8 g of rock powder. Reproducibility was found to

be in the order of 0.5 % for Zr, and < 2.5 % for Nb and Sr. The data were calibrated with a calibration curve comprising up to 34 igneous standards, and up to 23 secondary standards comprising various igneous rocks from Furnas, and also from nearby Terceira Island, which indicate average accuracies of ≤ 6 % for Rb, Zr, and Nb, and 11 % for Sr. Repeat analyses indicate precision of < 1 % for Zr, Nb, and Sr, and < 2 % for Rb.

Electron microprobe analyses

For mineral phases, peak counting times per element were 10 to 30 seconds using a 10- μm defocused beam, an acceleration voltage of 20 kV and a beam current of 20–27 nA. Major elements in glass (both groundmass glass and melt inclusions) were analysed using peak count times between 10 and 30 seconds, and 90 to 120 seconds, respectively. To minimize Na-loss, the acceleration voltage and beam current were reduced to 15 kV and 15 nA, respectively, whilst the beam diameter was, where possible, increased to 20 μm . Furthermore, Na was always analysed first, with a peak count time of 10 seconds. The following natural minerals and synthetic materials (denoted as formulae) were used as primary calibration standards: albite, sanidine, anorthite, wollastonite, TiO_2 , rhodonite, haematite, olivine, apatite, NaCl, ZnS, Al_2O_3 , celsian, SrTiO_3 , Cr_2O_3 , NiO, MgO, V, gahnite, and celestine. Volcanic glass standards (VG-2, KN-18 and KE-12) were routinely analysed as secondary standards (Online Resource 5). Repeat analyses of secondary standards indicate accuracy of < 4 %, and reproducibility of < 3 % (mean standard deviation).

Thermobarometric models

To minimize the error introduced by mineral-liquid disequilibrium, the $K_{\text{d}_{\text{Ab-Or}}}$ equilibrium test proposed by Mollo et al. (2015) was applied, allowing a single suitable liquid composition to be selected for each case. Input pressure values were set at 100 MPa, and it was observed that a variation of 100 MPa led to a change in temperature of only 0.1 $^{\circ}\text{C}$, suggesting that the thermometer is not significantly influenced by pressure variations. The standard error of estimate (SEE) associated with the thermometer is ± 23 $^{\circ}\text{C}$. The average temperature

estimate derived from alkali feldspar-melt thermometry was used as a primary input for feldspar-melt hygrometry, alongside feldspar and potential equilibrium liquid compositions. The SEE associated with these results is ± 0.53 wt. %.

Geochemical modelling

Mass balance and trace element modelling

Least squares mass balance calculations after Bryan et al. (1969) were performed using the IgPet software package. The modelling was performed in two steps: 1) fractionation from basalt to the least evolved trachyte (LET), and 2) LET to the most evolved trachyte (MET). For a parental basalt composition, a young basaltic lava located ~ 6 km south west of Furnas village (sample 98SM33 of Elliott et al. 2007) was selected due to its low Zr content and high magnesium number (294 ppm and 64, respectively). For the LET and MET compositions, the UFG sample with the lowest and highest Zr contents were chosen (SM7-1 and SM1-2, respectively). Model results were considered acceptable if $\sum r^2 = < 1$ (e.g. White et al. 2009). To produce models involving evolution from basalt to trachyte, mineral chemical data for plagioclase, clinopyroxene, olivine, biotite and magnetite were taken from analyses from Sete Cidades (Beier et al. 2006). Declining P_2O_5 concentration indicates apatite fractionation; therefore a stoichiometric $Ca_5(PO_4)_3(OH)_2$ composition was also included. For evolution within the trachytes, mineral compositions derived from the UFG were used.

Trace element modelling was undertaken using the Rayleigh fractionation law and batch melting equations. Sample 98SM33 of Elliott et al. (2007) was applied to represent mantle-derived parental basalt, or partially melted gabbroic crust. Trace element Rayleigh fractionation models were performed in two steps, each using the predicted fractionating assemblages from mass balance model steps 1 and 2, respectively. Based upon the Zr content of the UFG rocks, the change in fractionating mineral assemblage from step 1 to 2 was placed at 650 ppm Zr, which corresponds to 60 % fractionation from basalt. Batch melting models were calculated assuming the following mineral proportions: plagioclase (50

%), clinopyroxene (30 %), olivine (15 %), Ti-magnetite (5 %). Bulk distribution coefficients for Rayleigh fractionation models were calculated based on the fractionating assemblages predicted from the two steps of mass balance modelling. Batch melting models were performed using the same partition coefficients as those of the first Rayleigh fractionation step. Partition coefficient values were taken from literature values found in the GERM KD database (Nielsen 2006). For the batch melting models and step 1 of the Rayleigh fractionation models, partition coefficients were selected primarily from alkali basalts, whilst those of the second Rayleigh fractionation step were taken primarily from peralkaline trachytes and rhyolites. Where a range of partition coefficients were available, averages were applied. A partition coefficient for Ta was used for $KD_{Nb}^{Biotite}$ and $KD_{Nb}^{Ti-magnetite}$ due to lack of available literature data.

Thermodynamic modelling

Magmatic differentiation processes were modelled thermodynamically using the MELTS algorithms (Ghiorso and Sack 1995; Asimow and Ghiorso 1998; Gualda et al. 2012), which use an experimentally derived database of solid-liquid phases at specific temperature, pressure and fO_2 to calibrate models of thermodynamic phase stability. The Rhyolite-MELTS calibration (Gualda et al. 2012) was used to calculate 100 fractional crystallisation models over five starting water contents (0.5, 1.0, 1.5, 2.0, and 4 wt. %), four isobaric pressures (50, 150, 300, and 500 MPa) and redox conditions ranging from FMQ +2 to FMQ -2. An additional 50 models were generated for polybaric conditions, assuming a pressure change from 500 to 150 MPa at varying points during magma evolution. Due to the capability of differentiation trends in peralkaline magmas to decrease the SiO_2 content of residual liquids (e.g. Scaillet and Macdonald 2001), the MgO content and calculated peralkalinity index were used as primary differentiation indices. Sample 98SM33 of Elliott et al. (2007) was used as a starting melt composition.

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