

Online Resource 7: Crystallisation and Second Boiling Models

Fractional Crystallisation Model

Least squares mass balance calculations were performed to determine the fractionating assemblage required to produce the most evolved Brothers matrix glass (sample J2-1041-6-R1-Glass1) from the least evolved Brothers melt inclusion (sample SO253-081-12B-N-a) via pure fractional crystallisation of the observed minerals. Calculations were performed with the Geobalance spreadsheet of Li et al. (2020), using average Brothers dacite-hosted mineral major element compositions (Table OR7.1) from Georgatou et al. (2024, for apatite) and Brandl et al. (2023, for all other minerals). Results suggest that 23.4% crystallisation of an assemblage comprising 70.0% plagioclase, 8.8% clinopyroxene, 11.4% orthopyroxene, 5.7% titanomagnetite, 2.3% ilmenite and 1.9% apatite can produce the observed matrix glass composition with a low sum of squares error (SSE; Table OR7.2).

Second Boiling Model for Cl and Cu

Isobaric, crystallisation-driven exsolution of a Cl-bearing aqueous fluid (i.e., second boiling) was modelled by linking our fractional crystallisation mass balance model for silicic Brothers melts with the fluid-melt Cl partition coefficient model of Tattitch et al. (2021). Calculations were performed by fixing the melt H₂O contents to a saturation limit appropriate for the modelled pressure (based on VolFe calculations for the average Brothers silicic melt inclusion saturated with a pure H₂O fluid phase: 3.1 wt% for 50 MPa, 4.4 wt% for 100 MPa and 5.4 wt% for 150 MPa). Changes in H₂O solubility with differentiation are minor over the compositional range considered, so are neglected here for simplicity. Calculations were performed in 1% crystallisation increments, subtracting the mass of the crystallising cumulate from the melt, then adjusting the mass of H₂O in the remaining melt to yield the required saturation concentration; any additional H₂O at each step was then partitioned into a fluid phase. The fluid-melt Cl partition coefficient model of Tattitch et al. (2021: their equation 1) was then applied to solve for the evolving melt Cl contents and the salinity of the exsolved fluid (calculated as wt% NaCl equivalent) along the crystallisation pathway, applying mass balance to conserve the total Cl content of the system. Calculations were solved with an iterative scheme in Excel to account for the interdependence of $D_{\text{Cl}}^{\text{fluid-melt}}$, fluid salinity, and Cl contents of the evolving melt. Finally, Cu partitioning into the exsolving fluid was modelled by applying the salinity-dependent partitioning model of Tattitch et al. (2021: their equation 14). The mole fraction of H₂S in the fluid was set to 0.01, based on VolFe model calculations (see Online Resource 9). Calculations are detailed in an Excel spreadsheet within this Online Resource.

Phases	Reference	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO* (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	P ₂ O ₅ (wt%)	Total (wt%)
Plagioclase (An50)	Brandl et al. (2023)	55.40	0.04	28.62	0.56	0.00	0.06	9.74	5.38	0.20	0.00	100.00
Clinopyroxene (En42Fs18Wo40)	Brandl et al. (2023)	51.61	0.49	1.92	10.83	0.37	14.82	19.64	0.32	0.00	0.00	100.00
Orthopyroxene (En60.5Fs37Wo3.5)	Brandl et al. (2023)	52.09	0.20	0.52	22.88	0.92	21.57	1.78	0.02	0.03	0.00	100.00
Titanomagnetite	Brandl et al. (2023)	0.10	12.56	2.91	80.68	0.62	3.13	0.00	0.00	0.00	0.00	100.00
Ilmenite	Brandl et al. (2023)	0.60	43.93	0.36	51.82	0.77	2.51	0.00	0.00	0.00	0.00	100.00
Apatite	Georgatou et al. (2024)	1.80	0.00	0.00	1.05	0.12	0.60	53.79	0.00	0.00	42.64	100.00
Parent melt (SO253-081-12B-N-a)	This study	67.75	0.97	14.57	4.76	0.13	1.21	3.48	4.59	2.28	0.26	100.00
Daughter melt (J2-1041-6-R1-Glass1)	This study	73.44	0.73	12.85	3.28	0.11	0.34	1.57	4.46	3.10	0.11	100.00

Table OR7.1. Mineral and melt major element concentrations used in least squares fractionation calculations.

Phases	Proportion (wt% total system)						Proportion (wt% in cumulate)					
Plagioclase (An50)	16.4						70.0					
Clinopyroxene (En42Fs18Wo40)	2.1						8.8					
Orthopyroxene (En60.5Fs37Wo3.5)	2.7						11.4					
Titanomagnetite	1.3						5.7					
Ilmenite	0.5						2.3					
Apatite	0.4						1.9					
Daughter melt (J2-1041-6-R1-Glass1)	76.6						-					
Sum	100						100					

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SSE
Residual	-0.044	-0.012	-0.054	-0.027	0.005	0.001	-0.011	0.282	-0.128	-0.011	0.102

Table OR7.2. Results of least squares mass balance calculations for generation of the most evolved matrix glass from the least evolved silicic Brothers melt inclusion via pure fractional crystallisation.

References

- Brandl PA, Portnyagin M, Zeppenfeld H, Tepley FJI, de Ronde CEJ, Timm C, Hauff F, Garbe-Schönberg D, Bousquet R (2023) The origin of magmas and metals at the submarine Brothers volcano, Kermadec arc, New Zealand. *Econ Geol* 118:1577-1604
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