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Element Partitioning: The Role of Melt Structure and Composition

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Element Partitioning - the Role of Melt Structure and Composition

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Experimental methods

Although the piston cylinder is minimized and reduced to 13 pieces, it hosts a standard salt-pyrex-graphite- crushable MgO 14 mm O.D. assemblage with a furnace of 36 mm length, 8 mm O.D. and 6 mm I.D., thus resulting in standard piston cylinder temperature gradients of 5-10 ^{o}C (at 1100-1250 ^{o}C) over the capsule length. Temperature is measured by a B-type PtRh-thermocouple and controlled by a standard Eurotherm control unit to nominally within ±1 ^{o}C. Up to 400 A current are transmitted through a 40-ring slip water cooled ring stack sitting at the lower and of the hollow rotation axis. Cooling water to the piston cylinder is provided through the center of the lower slip ring stack and through tubing sitting exactly in the axis, it flows radially through the piston cylinder pressure vessel and is finally centrifuged outwards, where the water spray is collected by a conical ring running around the rotation table. Oil pressure in the hydraulic ram is measured and monitored on-board by a standard pressure transducer mounted vertically in the axis and connected to the hydraulic ram (which in turn is integrated into the piston cylinders base plate) by a NovaSuisse 4000 bar capillary. Pressure cannot be changed during centrifuging but only statically through a standard hand pump. The pressure and temperature mV readings are converted on-board to a 4-20 mA signal, resulting in a perfectly smooth and rotation speed independent control signal. The latter signals is transmitted through a 16 channel slip ring stack at the upper end of the rotation axis. The essential safety parameter is centrifuge vibration which is kept to less than 0.8 mm/s at 1800 rpm (equivalent to ca. 1000 *g*) by balancing the table to better than 10 gram. Nevertheless, the centrifuge does not have a breaking system and it takes about 25 minutes to cast down from 1800 rpm. As an additional safety, oil pressure, temperature, cooling water flow, furnace resistance, and heating power are computer monitored and any significant deviation after the startup phase of the experiment would result in immediate shutdown of the centrifuge and heating.

When chemically equilibrating the experiments at static conditions, current is directly provided to the piston cylinder without using the lower slip ring stack.

For our purposes, i.e. to correlate the behavior of trace elements with the melt structure, it is essential that only ferrous iron is present because ferric iron is a network-former and an unknown Fe^{2+}/Fe^{3+} would preclude calculation of melt polymerization from atomic proportions. Thus, our experimental setup was designed to assure that all Fe is present as ferrous iron. The starting material contained all Fe in the ferrous state as synthetic fayalite. Experiments were initially run in AuPd capsules pre-equilibrated with the starting material, surrounded by BN, crystallizing minor wuestite at the capsule rims defining oxygen fugacities below magnetite-wuestite and above wuestite-iron. Later experiments run in Mo-capsules crystallized $FeMo_2O_5$ at the capsule rims, indicating a fugacity near MoO_2-Mo, which is about IW+1.5 at the experimental temperatures.

Analytical methods

The elemental analyses were carried out using laser ablation inductively coupled plasma mass spectrometry. Therefore, a 193 nm ArF Excimer laser (GeoLas M, Lambda Physik, Göttingen, Germany) was coupled to an ELAN 6100 DRC ICP-MS (Perkin Elmer, Norwalk, USA). The laser was operated at 17 J cm^{-2} using repetition rates between 5 and10 Hz and crater sizes between 10 and 40 μm. The laser aerosol produced in a standard cell (21 cm^3) was transported using helium as carrier gas into the ICP. The ICP-MS was operated under standard conditions (*S1*). NIST 610 was used as external reference material and Fe was used as internal standard. The background was acquired for 30 s followed by 30-60 s signal acquisition depending on the crater diameter used for the analysis. The data reduction and concentration calculation is based on the protocol described by Longerich et al. (*S2*).

Text

S1) Phosphorous and Molybdenum

Phosphorous, a glass former, may play different roles in silicate melts. When network-modifying cations are absent in relative low concentration, P co-polymerizes with the silicate network. In glasses containing abundant network modifiers present (as in our case), P coordinates exclusively with NBOs. The 5+ charge in combination with a 4-fold coordination results in a partial charge of 1.25 of the oxygen next nearest to Mo^{5+} or P^{5+} and according to Pauling's second rule, a second nearest neighbor of charge 4+ and tetrahedral coordination (such as Si) is unfavorable. It is thus likely, that the second nearest oxygens are also NBOs (*24-25*), which explains the strong partitioning of P and Mo into the less polymerized melt. For the latter, it has been shown (*25*) that Si is not a second nearest neighbor in NBO-rich melts.

Major Element Solution Model for the Melt Phase

The formulation here makes use of elementary thermodynamic principles concerning regular solution models and phase equilibria, these are summarized in numerous texts, e.g. (*S3*). We assume the major element chemistry of the melt can be described as a regular solution between a network-modifying component MO_n and a network-forming component $\mathrm{C}_o\mathrm{O}_p$. Accordingly, the thermodynamic activities of these components are

$$a_{\mathrm{MO}_n} = x_{\mathrm{MO}_n} \exp\left(\left(1 - x_{\mathrm{MO}_n}\right)^2 W'_{\mathrm{MO}_n-\mathrm{C}_o\mathrm{O}_p}\right) \tag{1}$$

$$a_{\mathrm{C}_o\mathrm{O}_p} = \left(1 - x_{\mathrm{MO}_n}\right) \exp\left(x^2_{\mathrm{MO}_n} W'_{\mathrm{MO}_n-\mathrm{C}_o\mathrm{O}_p}\right) \tag{2}$$

where x_{MO_n} is the mole fraction of the MO_n component and the non-dimensional parametric group $W'_{\mathrm{MO}_n\text{-}\mathrm{C}_o\mathrm{O}_p} = W_{\mathrm{MO}_n\text{-}\mathrm{C}_o\mathrm{O}_p} / \mathrm{R}T$ characterizes non-ideal interactions in $\mathrm{MO_n}$-$\mathrm{C}_o\mathrm{O}_p$ melts. Writing the dimensionless Gibbs energy ($G/\mathrm{R}T$) of the melt as

$$G' = x_{\mathrm{MO}_n} \ln a_{\mathrm{MO}_n} + \left(1 - x_{\mathrm{MO}_n}\right) \ln a_{\mathrm{C}_o\mathrm{O}_p} \tag{3}$$

and setting the second and third derivatives of G' to zero, yields two equations which can be solved for the critical composition ($x^{\mathrm{crit}}_{\mathrm{MO}_n} = 1/2$) and critical value of the parametric group $W'_{\mathrm{MO}_n-\mathrm{C}_o\mathrm{O}_p}$ ($W'^{\mathrm{crit}}_{\mathrm{MO}_n-\mathrm{C}_o\mathrm{O}_p} = 2$). For $W'_{\mathrm{MO}_n-\mathrm{C}_o\mathrm{O}_p} < W'^{\mathrm{crit}}_{\mathrm{MO}_n-\mathrm{C}_o\mathrm{O}_p}$ the melt phase has a solvus that separates MO_n-poor granitic liquids from MO_n-rich gabbroic liquids. Because of the symmetry of the regular solution model, if $x_{\mathrm{MO}_n}^{\mathrm{granite}}$ is the composition of a melt on the $x_{\mathrm{MO}_n} < 1/2$ limb of the solvus, then this melt may coexist with a melt of composition $1 - x_{\mathrm{MO}_n}^{\mathrm{granite}}$, on the $x_{\mathrm{MO}_n} > 1/2$ limb of the solvus. Equating the activities of either component for these compositions yields the transcendental function

$$\ln\left(\frac{x_{\mathrm{MO}_n}^{\mathrm{granite}}}{1 - x_{\mathrm{MO}_n}^{\mathrm{granite}}}\right) = W'_{\mathrm{MO}_n - \mathrm{C}_o\mathrm{O}_p}\left(2x_{\mathrm{MO}_n}^{\mathrm{granite}} - 1\right) \tag{4}$$

which can be solved numerically for the parametric group $W'_{\mathrm{MO}_n - \mathrm{C}_o\mathrm{O}_p}$ as a function of the experimentally determined values of $x_{\mathrm{MO}_n}^{\mathrm{granite}}$.

Trace Element Model for the Melt Phase

To evaluate the trace element partitioning in the context of the major element regular solution model we assume non-ideality arises only through pair-wise interactions of the trace element oxide BO$_m$ and the network-forming component C$_o$O$_p$. In the trace element limit, the major component concentrations are independent of the trace components such that $x_{\mathrm{C}_o\mathrm{O}_p} \approx 1 - x_{\mathrm{MO}_n}$. The thermodynamic activity coefficient of the trace element is thus

$$\gamma_{\mathrm{BO}_m} = \exp\left(\left(1 - x_{\mathrm{MO}_n}\right)W'_{\mathrm{BO}_m - \mathrm{C}_o\mathrm{O}_p} + x_{\mathrm{MO}_n}\left(1 - x_{\mathrm{MO}_n}\right)W'_{\mathrm{MO}_n - \mathrm{C}_o\mathrm{O}_p}\right) \tag{5}$$

and x_{BO_m} is the mole fraction of the BO$_m$ component. Equating the activity of the trace element oxide ($a_{\mathrm{BO}_m} = x_{\mathrm{BO}_m}\gamma_{\mathrm{BO}_m}$) in coexisting MO$_n$-poor and MO$_n$-rich melts compositions yields, after rearrangement, the molar trace element partition coefficient

$$Q_{\mathrm{BO}_m}^{\mathrm{gabbro/granite}} = \exp\left[\left(1-2x_{\mathrm{MO}_n}^{\mathrm{granite}}\right)W'_{\mathrm{BO}_m\text{-}\mathrm{C}_o\mathrm{O}_p}\right] \tag{6}$$

or, making use of the critical condition $W'^{\mathrm{crit}}_{\mathrm{BO}_m-\mathrm{C}_o\mathrm{O}_p} = 2$,

$$Q_{\mathrm{BO}_m}^{\mathrm{gabbro/granite}} = \exp\left[\frac{2\left(1-2x_{\mathrm{MO}_n}^{\mathrm{granite}}\right)}{T'_{\mathrm{BO}_m-\mathrm{C}_o\mathrm{O}_p}}\right] \tag{7}$$

where $T'_{\mathrm{BO}_m-\mathrm{C}_o\mathrm{O}_p}$ is the homologous temperature measured relative to the critical temperature of the BO_m-$\mathrm{C}_o\mathrm{O}_p$ binary solvus. Eq. 7 expresses the trace element distribution coefficient as a function of the major element composition, and the homologous temperature defined relative to the critical temperature of the BO_m-$\mathrm{C}_o\mathrm{O}_p$ solvus. As such critical temperatures are unknown they are in practice the sole fitting parameters for the model.

Effect of Melt composition on Crystal-Melt Distribution Coefficients

The effect of melt composition on trace element crystal-melt distribution coefficients predicted by the lattice strain model (*5,7*) can be assessed by considering a generalized exchange reaction

$$\mathrm{BO}_m + \text{M-crystal} = \frac{m}{n}\,\mathrm{MO}_n + \text{B-crystal} \tag{8}$$

where M-crystal and B-crystal represent the pure major and trace element limiting compositions of the crystalline solution, chosen so that formula unit of pure B-crystal contains 1 mole of B, and BO_m and MO_n are components of the melt. We adopt a thermodynamic reference state in which the Gibbs energy of the pure melt components are zero at the pressure and temperature of interest, and a Henry's law reference state for the pure B-crystal phase such that as $x_{\text{B-crystal}} \to 0$, $a_{\text{B-crystal}} \to x_{\text{B-crystal}}$. Following the argumentation of (*7*), the reference state Gibbs energy change of reaction 8 is then approximated as the strain energy, ΔG_{strain}, that arises as a result of replacing the M-atoms in M-crystal with B-atoms. Thus, for a dilute solution of B-crystal, the equilibrium condition for reaction 8 is

$$\Delta G_{\text{strain}} = -\mathrm{R}T \ln\left(\frac{x_{\text{B-crystal}} a_{\mathrm{MO}_n}^{m/n}}{a_{\text{M-crystal}} a_{\mathrm{BO}_m}} \right) \tag{9}$$

or, rearranging Eq.9 to obtain an expression for the trace element distribution coefficient between the crystalline solution and melt ($x_{\text{B-crystal}} \big/ x_{\mathrm{BO}_m}$)

$$Q_{\mathrm{BO}_m}^{\text{crystal/melt}} = a_{\text{M-crystal}} \frac{\gamma_{\mathrm{BO}_m}}{a_{\mathrm{MO}_n}^{m/n}} \exp\left(-\frac{\Delta G_{\text{strain}}}{\mathrm{R}T} \right) \tag{10}$$

where ΔG_{strain} is derived from the lattice strain model (*5,7*). The second factor in Eq.10 is the correction to the lattice strain model due to melt chemistry and is expressed in terms of major element chemistry from Eqs.1 and 5 as

$$\frac{\gamma_{\mathrm{BO}_m}}{a_{\mathrm{MO}_n}^{m/n}} = \exp\left[\left(1 - x_{\mathrm{MO}_n}\right) \left(W'_{\mathrm{BO}_m\text{-}\mathrm{C}_o\mathrm{O}_p} - W'_{\mathrm{MO}_n\text{-}\mathrm{C}_o\mathrm{O}_p} \left(\left(1 - x_{\mathrm{MO}_n}\right) \frac{m}{n} + x_{\mathrm{MO}_n} \right) \right) \right] \Big/ x_{\mathrm{MO}_n}^{m/n} \tag{11}$$

where $W'_{\mathrm{MO}_n\text{-}\mathrm{C}_o\mathrm{O}_p}$ and $W'_{\mathrm{BO}_m\text{-}\mathrm{C}_o\mathrm{O}_p}$ are functions of the experimental observables $x_{\mathrm{MO}_n}^{\text{granite}}$ (equation 4) and $Q_{\mathrm{BO}_m}^{\text{gabbro/granite}}$ (Eq. 6).

Table: S1) Element concentrations in coexisting melts

	Z10			Z18a			Coordination*
	gabbro	granite	$D^{gabbro/granite}$	gabbro	granite	$D^{gabbro/granite}$	
	[ppm]	[ppm]		[ppm]	[ppm]		
Cs	2.25±0.42	18.8±0.9	0.12±0.02	32.5±0.9	104±3	0.31±0.01	8 (*S4*)
Rb	66.5±8.0	379±9.9	0.18±0.02	166±3.3	451±16	0.37±0.01	8 (*S4*)
K	6890±1450	30700±1950	0.22±0.05	11290±670	24200±2300	0.47±0.05	8 (*S4*)
Na	745±89	1330±744	0.56±0.32	151±7.2	233±14	0.65±0.12	6 (*S4*)
Li	3.64±0.85	2.52±0.65	1.44±0.50	157±9.4	144±10	1.09±0.10	4 (*S4*)
Ba	649±69	330±30.9	1.97±0.28	309±13	213±11	1.45±0.10	8 (*S4*)
Sr	153±17	46.9±5.2	3.26±0.51	321±9.3	175±6	1.83±0.02	8 (*S4*)
Ca	2440±278	677±130	3.60±0.80	1136±75	603±32	1.88±0.16	6 (*S4*)
Mg	1410±183	295±42	4.78±0.92	231±12	122±13	1.89±0.06	5,**6** (*S4*)
Fe	399500±10400	89400±5200	4.47±0.28	349800±6200	177200±8500	1.97±0.10	4,**5,6** (*12,24*)
Mn	1460±183	287±28	5.09±0.81	1173±39	599±31	1.96±0.03	6 (*S5*)
Co	8.7±1.0	2.02±0.35	4.31±0.90	69.2±2.8	37.4±3.4	1.85±0.18	**4**,6 (*S6*)
Zn	10.6±1.4	4.64±1.62	2.28±0.85	---	---	---	4 (*18*)
Cr	84.2±9.6	24±12	3.5±1.8	180±3	86±14	2.09±0.34	6 (*S7*)
V	10.2±0.97	1.79±0.41	5.7±1.4	197±9.7	78±11	2.53±0.38	6 (*S8*)
Sc	1640±188	266±37	6.2±1.1	241±7.2	107±5.7	2.25±0.14	**6**,7 (*S9*)
Y	2040±234	220±34	9.3±1.8	296±12	105±4.7	2.83±0.17	6,**7** (*S10*)
La	1940±212	196±31	9.9±1.9	234±9.7	80.1±4.7	2.93±0.02	**6,7**,8 (*S11*)
Ce	11.1±1.4	1.15±0.23	9.7±2.2	---	---	---	
Nd	13.8±0.4	1.17±0.35	11.8±3.5	---	---	---	
Sm	1930±223	189±31	10.2±2.1	210.0±9.3	70.0±3.6	3.00±0.20	
Eu	13.9±2.1	1.57±0.33	8.9±2.2	846±35	383±15	2.21±0.13	
Gd	8.2±1.2	1.00±0.34	8.2±3.0	849±43	282±15	3.01±0.22	
Dy	5.04±0.54	0.64±0.12	7.9±1.7	965±40	328±20	2.94±0.22	
Er	2.76±0.46	0.30±0.08	9.2±2.8	968±46	329±17	2.94±0.21	
Yb	4.80±0.43	0.48±0.09	10.0±2.0	---	---	---	
Lu	1850±210	212±36	8.7±1.8	264±12	94.1±5.4	2.80±0.21	
Ti	6360±281	1344±161	4.7±0.6	868±34	406±25	2.14±0.16	5 (*18*)
Zr	7912±872	1989±261	3.98±0.68	221±9.1	112.8±3.5	1.96±0.10	6 (*18*)
Hf	8250±901	2489±269	3.31±0.51	198±9.6	111.0±3.5	1.79±0.10	as Zr
Th	1415±157	171±25	8.3±1.5	314±13	121±5.8	2.60±0.16	6 (*S12*)
U	1570±154	179±21	8.8±1.3	321±11	135±11	2.38±0.21	6 (*S13*)
Mo	3260±285	492±48	6.63±0.87	1221±35	563±44	2.17±0.18	4 (*18*)
Nb	8360±629	1171±152	7.1±1.0	1115±58	406±31	2.75±0.25	6 (*S14,S15*)
Ta	8140±653	1519±176	5.36±0.76	874±38	354±18	2.47±0.17	6 (*S15*)
P	7720±1040	916±122	8.4±1.6	407±19	182±29	2.24±0.37	4 (*S4*)
Sn	---	---	---	170±7	139±13	1.22±0.12	3 (*S16*)
Pb	1.37±0.11	4.2±3.0	0.33±0.23	449±16	296±20	1.52±0.12	3 (*S17*)
As	10.6±2.8	123±67	0.086±0.052	1.8±0.5	6.6±2.4	0.27±0.12	4 or less
Sb	1.2±0.12	3.4±1.2	0.35±0.12	8.2±0.3	8.9±2.4	0.92±0.25	4 or less
Bi	---	---	---	22.4±0.9	22.9±1.3	0.98±0.07	4 or less
Ga	15.0±1.4	9.22±1.34	1.63±0.28	167±6.6	168±8.1	0.99±0.06	4 (*S4,S15*)
Al	18890±930	42300±1500	0.447±0.027	18500±1300	30800±2300	0.60±0.06	4 (*S4*)
Ge	24.4±3.2	304±144	0.080±0.039	9.7±0.6	10.0±1.8	0.97±0.18	4 (*S4*)
Si	172800±4200	337000±8300	0.513±0.018	226000±4600	312200±6100	0.72±0.02	4 (*S4*)

*Coordination numbers are variable in different glass compositions and concentrations, here we selected the most suited one for (a) low concentrations, and (b) melts with abundant NOB's.

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