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Melt structural control on mineral/melt element partitioning

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Relationships between mineral/silicate melt partition coefficients and melt structure have been examined by combining Ca and Mn olivine/melt partitioning data with available melt structure information. These 2 cations were chosen to extract relationship between ionic radius, Q^n-speciation in the melt and mineral/melt exchange equilibria.

Compositions were chosen so that melts with olivine on their liquidii range in degree of polymerization, NBO/T, from ~0.5 to ~2.5 under near isothermal conditions (1350˚-1400˚C). This melt NBO/T range is such that it covers that encountered in most natural magmatic liquids. Furthermore, the NBO/T-range is such that a broad range in concentration of Q^n-species in the melt will be encountered.

Olivine/melt Ca-Mn exchange coefficients, as a function of melt NBO/T have a parabolic shape with a minimum value at NBO/T near 1. The olivine/melt partitioning data are modeled in terms of structural units (Q^n-species) in the melt. The NBO/T-value corresponding to the minimum Ca-Mn exchange coefficients is near that where the abundance ratio of Q^n-species, X_{Q3}/X_{Q2}, has its largest value. Therefore, the activity coefficient ratio in the melt, $\square_{Ca2+}^{(melt)}/\square_{Mn2+}^{(melt)}$, attains a minimum where the abundance ratio of X_{Q3}/X_{Q2} is at maximum. It is inferred from this relationship that Ca^{2+} in the melts is dominantly bonded to nonbridging oxygen (Ca-NBO) in Q^3-species, whereas Mn^{2+} is bonded to nonbridging oxygen (Mn-NBO) in less polymerized Q^n-species such as Q^2. We further suggest that analogous relations hold for any cation pair whose ionization potential differs significantly.

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Partitioning of chlorine and fluorine in the system apatite—silicate melt—aqueous fluid

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The partitioning behavior of Cl among apatite, mafic silicate melt, and aqueous fluid and of F between apatite and melt have been determined in experiments conducted at 1066-1150°C and 199-205 MPa. The value of $D_{Cl}^{apatite/melt}$ (wt. fraction of Cl in apatite/Cl in melt) ≈ 0.8 for silicate melt containing less than about 3.8 wt. % Cl. At higher melt Cl contents, a small increase in melt Cl concentration is accompanied by a relatively large increase in apatite Cl concentration, forcing $D_{Cl}^{apatite/melt}$ to increase as well. Melt containing less than 3.8% Cl coexists with water-rich vapor; that containing more Cl coexists with saline fluid, the salinity of which increases rapidly with small increases in melt Cl content, analogous to the dependency of apatite composition on melt Cl content. This behavior is due to the fact that the solubility of Cl in silicate melt depends strongly on the composition of the melt, particularly its Mg, Ca, Fe, and Si contents. Once the melt becomes “saturated” in Cl, additional Cl must be accommodated by coexisting fluid, apatite, or other phases rather than the melt itself. Because Cl solubility depends on composition, the Cl concentration that must be reached before $D_{Cl}^{apatite/melt}$ and $D_{Cl}^{fluid/melt}$ start increasing also depends on composition.

The experiments reveal that $D_F^{apatite/melt} \approx 3.4$. In contrast to Cl, the concentration of F in silicate melt is only weakly dependent on composition (mainly on melt Ca contents), so $D_F^{apatite/melt}$ is constant for a wide range of composition.

Cl-rich apatite has been found in large layered mafic intrusions, notably in portions of the Bushveld and Stillwater Complexes, including in their platinum-group-element-rich layers. The experimental data demonstrate that the fluids present in the waning stages of the solidification of these bodies were highly saline. They further affirm that the apatite with high (Cl/F) ratios in layered intrusions formed by the combined processes of extreme fractional crystallization of interstitial melt in the cooling crystal pile and separation of saline fluid from that melt and its accumulation elsewhere, presumably due to compaction.