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EFFECT OF SILICATE-MELT STRUCTURE ON MINERAL-MELT PARTITION

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Qualitative and semi-quantitative information on the nature and availability of cation coordination sites in a silicate magma may be obtained from the measured partition coefficients, $k = [M]_{cryst}/[M]_{melt}$, of elements between the host magma and coexisting crystal phases of known structure. Partitioning behavior at constant temperature, pressure, and composition is determined by site availability, ionic radii, and bonding parameters which, in the case of the transition-element ions, include crystal-field effects.

Transition-element ions that show a smooth variation in ionic radius (VI coordination) with change in crystal-field octahedral-site-preference-energy (OSPE) often define linear plots in ln k versus OSPE graphs (Henderson & Dale 1969) and smooth curves in ln k versus ionic-radius diagrams (Jensen 1973). Such ions include Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}. Ions of similar radii, but with very different OSPE values, show departures from these plots as illustrated by the partitioning behavior of Sc^{3+}, V^{3+}, Cr^{3+}, and Fe^{3+} between clinopyroxene and host magma. These patterns of behavior indicate that a large proportion of some ions, including Cr^{3+}, is accommodated in the magma in energetically unfavorable sites, most probably of fourfold coordination.

Changes in element partition and associated changes in temperature with change in melt composition reveal contrasting trends for different sizes of ions. For example, the partition coefficient for Cr^{3+} between pyroxene and host magma rises more than twentyfold as the proportion of network-forming cations (Si, Al, P) increases in the melt in passing from basic to peralkaline systems. However, the partition coefficient for Sr^{2+} between plagioclase feldspar and melt shows only a fourfold increase over the same range in melt composition. This increase in the strontium partition coefficient is far less than would be expected for the associated change in temperature of crystallization over the compositional range, as indicated by the experimental work of Sun *et al.* (1974). The inference is drawn that crystallizing magmas of acidic composition contain sufficient numbers of large sites (coordination number >6) to accommodate a significant proportion of the large cations, but that in passing from basic to acid melts there is a decline in the availability of sixfold coordination sites for the accommodation of chromium ions.

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