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Partitioning of calcium, magnesium, and transition metals between olivine and melt governed by the structure of the silicate melt at ambient pressure

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ABSTRACT

Olivine/melt partitioning of the transition metal cations, Fe^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}, together with Mg^{2+} and Ca^{2+}, has been examined experimentally as a function of melt composition at ambient pressure. Melt structure was inferred from bulk-chemical composition, existing structural data, and ^{57}Fe resonant absorption Mössbauer spectroscopy. Under isothermal conditions, $K_{D(i\text{-}Mg)}^{olivine/melt} = (C_i/C_{Mg})^{olivine}/(C_i/C_{Mg})^{melt}$, is an exponential function of melt NBO/T for i = Ca^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}. For i = Fe^{2+}, the relationship is parabolic with maximum $K_{D(Fe^{2+}\text{-}Mg)}^{olivine/melt}$-values at NBO/T near 1. At constant melt NBO/T, $K_{D(i\text{-}Mg)}^{olivine/melt}$ increases systematically with decreasing cation radius, an effect that is more pronounced the more polymerized the melt. The $K_{D(i\text{-}Mg)}^{olivine/melt}$ is also a positive and linear function of Na/(Na + Ca) of Al-free melts. This latter effect results from changes in Q^n-species abundance governed by Na/(Na + Ca) of the melts. The enthalpy of the exchange equilibrium, $i^{olivine} + Mg^{melt} = i^{melt} + Mg^{olivine}$, derived from the temperature-dependence of $K_{D(i\text{-}Mg)}^{olivine/melt}$, is also a positive function of the ionic radius of the cation. The relationship of enthalpy to melt polymerization also depends on cation radius. The $K_{D(Fe^{2+}\text{-}Mg)}^{olivine/melt}$ does not, however, follow this trend possibly because the bond distance, $d_{Fe^{2+}\text{-}O}$, in the melts depends on melt composition.

The cations examined in this study are network-modifiers in silicate melts at ambient pressure. The solution behavior of network-modifying cations in melts is governed by the extent of steric hindrance near nonbridging oxygen, which in turn affects the energetics of metal-nonbridging oxygen bonds. Those structure effects, in turn, are related to the type of Q^n-species, their abundance, and on the Al-distribution between the Q^n-species. It is suggested, therefore, that the observed variations of mineral/melt partition coefficients with melt composition can be understood by considering bulk polymerization (NBO/T), the distribution of Al^{3+} among coexisting Q^n-species, and the distribution of network-modifying cations among nonbridging in these Q^n-species.

Keywords: Element partitioning, spectroscopy, melt structure, Mössbauer