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, $K_{\text{D}_{\text{(i-Mg)}}} = (C_{\text{i}}/C_{\text{m}})^{\text{Oliv}}/(C_{\text{i}}/C_{\text{m}})^{\text{M}}$, is an exponential function of melt NBO/T for $i = \text{Ca}^{2+}$, Mn$^{2+}$, Co$^{2+}$, and Ni$^{2+}$. For $i = \text{Fe}^{2+}$, the relationship is parabolic with maximum $K_{\text{D}_{\text{(i-Mg)}}}$ values at NBO/T near 1. At constant melt NBO/T, $K_{\text{D}_{\text{(i-Mg)}}}$ increases systematically with decreasing cation radius, an effect that is more pronounced the more polymerized the melt. The $K_{\text{D}_{\text{(i-Mg)}}}$ is also a positive and linear function of Na/(Na+Ca) of Al-free melts. This latter effect results from changes in Q$^r$-species abundance governed by Na/(Na+Ca) of the melts. The enthalpy of the exchange equilibrium, $\Delta H_{\text{olivine}|\text{melt}} = \Delta H_{\text{melt}|\text{olivine}}$, derived from the temperature-dependence of $K_{\text{D}_{\text{(i-Mg)}}}$, 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 $K_{\text{D}_{\text{(i-Mg)}}}$ does not, however, follow this trend possibly because the bond distance, $d_{\text{Fe}^{2+}-\text{O}}$, 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$^r$-species, their abundance, and on the Al-distribution between the Q$^r$-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$^r$-species, and the distribution of network-modifying cations among nonbridging in these Q$^r$-species.

Keywords: Element partitioning, spectroscopy, melt structure, Mössbauer

INTRODUCTION

Characterization of mass transfer processes in the Earth is aided by knowledge of the partitioning of geochemically important elements between minerals and magmatic liquids. These partition coefficients are governed by the solution behavior of the elements in coexisting crystals and melts. Here, we will address solution behavior in silicate melts.

Existing experimental data point to significant melt composition dependence of major-, minor-, and trace-element partition coefficients (e.g., Watson 1977; Ryerson and Hess 1978; Mysen and Virgo 1980; Kohn and Schofield 1994; Kushiro and Walter 1994; Libourel 1999; Jaeger and Drake 2000; Kushiro and My-
nen 2002; Toplis and Corgne 2002; Toplis 2004; Schmidt et al. 2006). In fact, even Fe$^{2+}$-Mg partitioning between olivine and melts, which for some time was considered nearly independent of composition with $K_{\text{D}_{\text{(Fe}^{2+}-\text{Mg)}}} = (\text{Fe}^{2+}/\text{Mg})^{\text{olivine}}/(\text{Fe}^{2+}/\text{Mg})^{\text{melt}}$ near 0.3 (Roeder and Emslie 1970), more recently has been found to depend on melt composition with $K_{\text{D}_{\text{(Fe}^{2+}-\text{Mg)}}}$-values ranging between 0.15 and 0.45 (Takahashi 1978; Longhi et al. 1978; Colson et al. 1988; Shi and Libourel 1991; Sack et al. 1987; Toplis et al. 1994; Xiouchakis et al. 2001; Kushiro and Mysen 2002; see also Toplis 2004, for review and discussion of available data). These $K_{\text{D}_{\text{(i-Mg)}}}$-variations, at least in part, reflect melt compositional control on the relative activity of iron and magnesium oxides in silicate melts (e.g., Doyle and Naldrett 1986; Doyle 1989; Gaillard et al. 2001, 2003). The activity coefficient of other transition metals might also vary with melt compositions.

Activity-composition relations that depend on melt composition are related to melt structure. Various structure parameters have been proposed to account for these effects. For example, several empirical relations between mineral/melt partition coefficients and melt NBO/T (nonbridging oxygen, NBO, per tetrahedrally coordinated cations, T) have been suggested (e.g., Mysen and Virgo 1980; Kohn and Schofield 1994; Richter and Drake 1999; Jaeger and Drake 2000; Walter 2001; Toplis and Corgne 2002). It has also been argued, however, that the use of NBO/T of a melt to calibrate mineral/melt element partitioning is of limited utility (O’Neill and Eggins 2002; Bennett et al. 2004) in part because NBO/T of a melt offers only limited insight into important details of structural positions of cations in silicate melts (see Mysen and Richet 2005, chapters 7, 9, 11–13, for review of relevant melt structure data).

Many geochemically important minor and trace elements