Effect of Redox Relations of Iron on Olivine/Melt Partitioning Behavior of Ca, Mg and Transition Metals at Ambient Pressure

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Olivine/melt partitioning of ΣFe, Fe^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} has been determined in the systems CaO-MgO-FeO-Fe_2O_3-SiO_2 (FD) and CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2 (FDA3) as a function of oxygen fugacity (f_{O2}) at 0.1 MPa pressure. Total iron oxide content of the starting materials was ~ 20 wt%. The f_{O2} was used to control the $Fe^{3+}/\Sigma Fe$ (ΣFe: total iron) of the melts. The $Fe^{3+}/\Sigma Fe$ and structural roles of Fe^{2+} and Fe^{3+} were determined with ^{57}Fe resonant absorption Mössbauer spectroscopy. The Mössbauer spectra were deconvoluted using site-distribution modeling. From these data, Fe^{2+} is dominantly a network-modifier, whereas in oxidized melts, Fe^{3+} is primarily a network-former. In reduced melts, Fe^{3+} is also dominantly a network-modifier. In all cases there is a distribution of oxygen coordination numbers. Changes in average melt polymerization, NBO/T, as a function of f_{O2} was estimated from the Mössbauer data (based on average coordination numbers). It varies by ~100% in melts coexisting with olivine in the FDA3 system (NBO/T~0.6-1.2)) and by about 300% in the FD system (NBO/T~1-2.8) between fully oxidized and fully reduced melts.

The partition coefficients of all the elements examined (K_D^i= wt % in olivine/wt % in melt) are systematic functions of f_{O2} and, therefore, NBO/T of the melt. This relationship is not dependent on whether the element undergoes a change in redox ratio. There is a K_D^i-minimum in the FDA3 system at NBO/T-values corresponding to intermediate $Fe^{3+}/\Sigma Fe$ (0.34-0.44). This redox ratio corresponds to NBO/T~1. In the Al-free system, where all melts have NBO/T$\geq$1, FD, all partition coefficients are positively correlated with decreasing $Fe^{3+}/\Sigma Fe$ because this decrease of $Fe^{3+}/\Sigma Fe$ results in melt depolymerization (increasing NBO/T).

Recast as exchange equilibrium coefficients, K_D^{i-Mg} (i= Fe^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}), their activity coefficient ratios relative to Mg in melt, $\gamma_i(m)/\gamma_{Mg}(m)$, were derived with the assumption that this ratio is constant in the olivine in the composition range studied. Tis assumption is consistent with literature data. The $\gamma_i(m)/\gamma_{Mg}(m)$ follows the same trend with f_{O2} (and, therefore, $Fe^{3+}/\Sigma Fe$ and NBO/T of the melt) as the partition coefficients. These trends are explained by consideration of solution behavior governed by Q^n-unit distribution, energetics of nonbridging oxygen, and structural behavior of the divalent cations in the melts (coordination number, complexing with Fe^{3+}, and distortion of the polyhedra).