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Compositional dependence of alkali diffusivity in silicate melts: Mixed alkali effect and pseudo-alkali effect

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Abstract

Compositional dependence of alkali diffusivities in silicate melts is modeled by explicitly considering mixed alkali and "pseudo-alkali" effects. The well-known mixed alkali effect describes that the presence of light alkalis (Li, Na) retards diffusion of heavy alkalis (K, Rb, Cs) and vice versa, which can be attributed to stronger interaction between dissimilar alkalis and reduction of favorable sites for the alkali in question. Due to the same reasons, Ca, which has similar ionic radius as Li and Na but carries more charge and greater field strength, also impedes the migration of light alkalis. In this regard Ca behaves as a "pseudo-alkali," and I refer to the influence caused by Ca on Li and Na diffusion as the "pseudo-alkali effect," which belongs to the category of mixed cation effects in glass literature. Pseudo-alkali effect is expected to exist also between other size-matching divalent cations and alkali cations, such as Ba blocking K diffusion. Mixed alkali and pseudo-alkali effects are manifested mainly by an increase in the activation energy for diffusion. Sodium diffusivities for melt compositions ranging between albite, orthoclase, and anorthite reveal that the amplitude of the pseudo-alkali effect is much larger than that of the mixed alkali effect. Furthermore, the activation energy increases more rapidly as more Ca substitutes for Na, but the mixed alkali effect approaches saturation as K substitutes for sodium. A general model based on mixed alkali effect and pseudo-alkali effect, together with a special treatment relating Cs diffusion to melt polymerization, successfully characterizes existing experimental data on alkali diffusion in silicate melts. Enthalpies of mixing between end-member melts (e.g., Ab-Or melts and Ab-An melts) inferred from the model agree well with previous experimental investigations.

Keywords: Alkali diffusivity, silicate melts, mixed alkali effect, pseudo-alkali effect