

Trace element partitioning dependence on melt structure: A first-principles simulation study

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Knowledge of trace element partition coefficients is crucial, e.g. for our understanding of global element cycles. Although a great number of experimental studies on mineral-melt partitioning have been performed in the past, the influence of melt structure on the partitioning coefficient has at most been considered empirically. One of the major challenges is the lack of reliable structure models for typical melts at the relevant P/T conditions. First-principles molecular dynamics simulations are predictive and provide a unique approach to structure and thermodynamic properties of both minerals and melts. In this study, we explore a molecular scale simulation approach to investigate the influence of melt structure and predict partitioning by means of atomistic computer simulations only. We use first principles molecular dynamics to investigate several geochemically important trace elements (e.g. Y, Sc, Zr). To predict the free energy change of the exchange reaction when an element X is distributed between the two phases, the method of thermodynamic integration is employed. Here we use an alchemical transmutation by which the identity (here expressed by its pseudopotential parameters) of a major element (e.g. Al) is gradually changed from 100% Al to 100% X. However, depending on the site on which the partitioning takes place, it is often necessary to perform coupled substitutions to maintain charge balance e.g. $Y^{3+} + Al^{3+} \rightarrow Ca^{2+} + Si^{4+}$. We choose two different melt pairs for our starting compositions. A granitic and basaltic melt (low and high NBO/T) as well as two titanite melts with varying alkali contents. After the melt pairs are equilibrated at 3000 K and ambient pressure, we perform the thermodynamic integration and compare the free energy of the exchange reaction. We will discuss the potential of the method in terms of quantitative predictions and compare our results to experimental findings. We will also discuss the effect of coupled substitutions and how to ensure to reach geochemical equilibrium during these types of simulations. Potentially, this new tool may allow us to make predictions for almost any composition and condition available to computer simulations, e.g. fluid–mineral element distribution in subduction zones and their P/T dependence.