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Trace element partitioning between silicate melts: thermodynamics from atomistic simulation

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Element partitioning, i.e. the preferred incorporation of certain cations into a given chemical environment rather than into other coexisting phases, plays a fundamental role in processes such as crystallization of silicate magmas or planetary differentiation. The lattice strain model proposed by Blundy and Wood [1] attempts to explain the observed partitioning of trace elements between coexisting minerals and melts entirely in terms of the strain induced in the host crystal lattice by the size misfit of the incorporated cation: the closer the cation's ionic radius to the ideal ionic radius in the host lattice, the more easily it enters the mineral, otherwise it is enriched in the melt. The influence of the melt structure on the partitioning, on the other hand, is neglected by the lattice strain model.

However, experiments by Prowatke and Klemme [2] challenge this view: they show that, for a given silicate crystal structure, the partitioning of many trace element cations depends strongly on the composition of a coexisting silicate melt, in particular on the ratio of the Al to alkali and alkaline earth contents. It was suggested that this ratio influences the framework structure of the melt and hence also the local environment of incorporated ions, which in turn determines the thermodynamics of partitioning. A detailed understanding of atomic-scale structures in melts leading to the observed behavior is still missing.

Atomistic simulation is a valuable tool to investigate the local environment of ions in melts. It provides a direct link between the atomic-scale structure and thermodynamic properties of matter, supports the interpretation of experimental results and allows predictions about systems that are not accessible to experiments. Simulations based on fundamental laws of physics (quantum mechanics) are very accurate but rather demanding in terms of computing time. On the other hand, simulations using classical interaction potentials are computationally much cheaper, but the potentials have to be tested carefully before being used as a predictive tool, in order to assure their transferability to different chemical environments and pressure and temperature conditions.

We developped and assessed a classical interaction potential for the system CaO-Al_2O_3-SiO_2 and the trace elements Y and La. Using this potential, we performed molecular dynamics simulations of different silicate melts containing Y and La in order to explore the local environment of the trace elements as a function of melt composition, revealing a systematic dependence of coordination and bond lengths on melt polymerization. This effect provides a qualitative understanding of the observed partitioning behavior of Y and La.

The computational method of thermodynamic integration allows the calculation of free energies. We applied it to the exchange reaction Y(melt1) + La(melt2) $\rightleftharpoons$ La(melt1) + Y(melt2) and evaluated the associated change in free energy. We were thus able to quantitatively predict the exchange coefficient, i.e. the ratio of partition coefficients $D_{\mathrm{Y}}^{\mathrm{melt1/melt2}}/D_{\mathrm{La}}^{\mathrm{melt1/melt2}}$. Finally, we investigated the systematic dependence of partitioning on model parameters like the ionic radius of the trace element.

References:

[1] Blundy, J., Wood, B. (1994), Prediction of crystal-melt partition coefficients from elastic moduli, Nature 372, 452

[2] Prowatke, S., Klemme, S. (2005), Effect of melt composition on the partitioning of trace elements between titanite and silicate melt, Geochim. Cosmochim. Acta 69, 695