First-principle partitioning and disequilibrium of chromium in garnet – clinopyroxene assemblage

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Using partition coefficients is extremely useful to model melting processes and fluid-rock interactions. However, partition coefficients values remain scarce in regard of their sensitivity to mineral composition and to the variability of mineral composition. In addition, the inferred equilibrium between phases is not necessarily reached, even in high-grade metamorphic conditions associated to melting. Disequilibrium may dramatically hamper the effective mobility of species and lead to element distribution far from the predicted values.

This contribution aims at estimating partition coefficients for chromium (Cr) between garnet and clinopyroxene, and testing them in natural rocks of various metamorphic grades. As a poorly mobile trivalent element, Cr is chosen as a proxy to rare earth elements.

Theoretical partition coefficients for Cr between garnet and clinopyroxene are calculated \textit{ab initio} from structures where Cr\(^{3+}\) is modelled as a defect in Al\(^{3+}\) sites using CRYSTAL17 (Dovesi et al., 2014) and the thermodynamic description of Dubacq and Plunder (2018). Results are compared to electron microprobe measurements in mineral assemblages containing tens to thousands of ppm of Cr, where element mapping brings much information.

Results of \textit{ab initio} computations highlight the role of crystal-chemistry over the strain field around point defects, controlling the dynamics of the Cr\(^{3+}\) = Al\(^{3+}\) exchange between clinopyroxene and garnet. As expected, the partitioning of Cr between garnet and clinopyroxene depends strongly on the grossular and pyrope content: Cr incorporates grossular preferentially to jadeite, but jadeite incorporates Cr preferentially to pyrope.

Comparison between predicted and measured partition coefficients allowed to estimate the deviation from equilibrium. Disequilibrium is evidenced even for samples metamorphosed around 850°C, as shown by the distribution of Cr-rich and Cr-depleted domains. Disequilibrium is attributed to slow diffusivity of Cr in fluid and at grain boundaries during crystal growth, leading to interface-coupled dissolution-precipitation.