V33C-0253 - Depleted Ge/Si groundwater ratios and a thermodynamic model for equilibrium fractionation in natural systems.

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Abstract

Ge/Si ratios are a useful tracer of weathering of silicate rocks. During incongruent weathering Ge is preferentially incorporated into secondary clays, leaving a Ge-depleted fluid. Here, we have estimated the equilibrium fractionation coefficient of germanium in kaolinite, from new Ge-Si data at the Kings River Experimental Watershed (KREW). Ge/Si ratios in Providence Creek are below 0.1 μmol/mol, lower than typical river values, suggesting that Ge is completely fractionated into secondary minerals. Based on this dataset, we develop a solid-solution model between the Si and Ge kaolinite end-members—Si Al O (OH) and Ge Al O (OH) —to estimate the equilibrium fractionation factor of Ge. From this fractionation factor, we further determine the solubility constant and Gibbs formation energy of Ge-kaolinite . We show that the values are consistent within uncertainty with a parametric model for clays and calorimetric data on Ge-substituted phyllosilicates. The new parameters can be incorporated in reaction path and reactive transport codes to model Ge-Si fractionation. We tested the calculated thermodynamic properties of Ge-kaolinite in a batch-reactor model of plagioclase dissolution and kaolinite precipitation. We show that reaction affinity controls the fractionation extent of Ge/Si ratios through kaolinite precipitation rates, pH, and W/R ratios. The modeling results reconcile global Ge/Si riverine ratios with the more depleted values measured at KREW. We interpret the depleted Ge/Si ratios to reflect long fluid residence times. While the actual length of this equilibrium timescale remains to be determined by better constraints on kaolinite field precipitation rates, our Ge/Si equilibrium fractionation model brings together observations from natural systems and thermodynamics to understand global silicate weathering processes.

1 Perez-Fodich, A. & Derry, L. A. A model for germanium-silicon equilibrium fractionation in kaolinite. Submitted to Earth and Planetary Science Letters.