Modeling Ge/Si weathering signatures using thermodynamic data for synthetic Germanium minerals

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We have developed a new set of synthetic thermodynamic properties for alumino-germanate clays and feldspars to model Ge-Si fractionation during silicate weathering using an adimensional batch reactor and a 1-D reactive transport simulation. Thermodynamic data for Ge-bearing phyllo-germanates was generated using a model for predicting thermodynamic properties of clays[1] to estimate formation enthalpies and entropies to calculate Gibbs free energies. Ge-clays solubility coefficients were calculated using SUPCRT92. Ge-feldspar solubility data were generated from Ge-Si partition coefficients[2]. Germanium substitutes ideally for Si in the tetrahedral site of silicate minerals. During weathering, Ge/Si ratios undergo fractionation as secondary minerals preferentially incorporate Ge.

The numerical experiment consists of a batch reactor starting with an ideal solution between albite and $NaAlGe_3O_8$ with an initial Ge/Si ratio of 1.5 μmol/mol undergoing kinetically controlled dissolution and precipitation as a solid solution between kaolinite and $Al_2Ge_2O_5(OH)_4$. Our results show that Ge/Si_{clay} reaches a maximum value of 4.2 μmol/mol at pH = 5.5 while increasing pH results in lower Ge/Si_{clay} ratios. Ge/Si_{fluid} show great variability at short timescales of 1-10 years, independent from pH. Ge/Si_{fluid} increases to 2.5 μmol/mol due to feldspar dissolution; followed by a rapid decrease to 0.2 μmol/mol as the clay begins to precipitate. As Ge/Si_{clay} increases and stabilizes at 3.9-4.2 μmol/mol, Ge/Si_{fluid} stabilizes at values between 0.5 to 0.6 μmol/mol. At longer timescales of 10^2 to 10^3 years, Ge/Si in the solid increases, reaching ratios $\approx$ 5 to 6 μmol/mol. The Ge-Si fractionation model is implemented in a 1-D reactive transport weathering model and compared to field observations from granitic systems.

[1] Blanc *et al*. (2015), *American Journal of Science* **315**, 734-780.

[2] Capobianco, Navrotsky (1982), *American Mineralogist* **67**, 718-724.