

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 aluminogermanate 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 $\text{NaAlGe}_3\text{O}_8$ with an initial Ge/Si ratio of $1.5 \mu\text{mol/mol}$ undergoing kinetically controlled dissolution and precipitation as a solid solution between kaolinite and $\text{Al}_2\text{Ge}_2\text{O}_5(\text{OH})_4$. Our results show that $\text{Ge/Si}_{\text{clay}}$ reaches a maximum value of $4.2 \mu\text{mol/mol}$ at $\text{pH} = 5.5$ while increasing pH results in lower $\text{Ge/Si}_{\text{clay}}$ ratios. $\text{Ge/Si}_{\text{fluid}}$ show great variability at short timescales of 1-10 years, independent from pH. $\text{Ge/Si}_{\text{fluid}}$ increases to $2.5 \mu\text{mol/mol}$ due to feldspar dissolution; followed by a rapid decrease to $0.2 \mu\text{mol/mol}$ as the clay begins to precipitate. As $\text{Ge/Si}_{\text{clay}}$ increases and stabilizes at $3.9\text{-}4.2 \mu\text{mol/mol}$, $\text{Ge/Si}_{\text{fluid}}$ stabilizes at values between 0.5 to $0.6 \mu\text{mol/mol}$. At longer timescales of 10^2 to 10^3 years, Ge/Si in the solid increases, reaching ratios ≈ 5 to $6 \mu\text{mol/mol}$. 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.