Isotopic fractionation of antimony (Sb) during sorption of Sb(III) and Sb(V) to goethite and illite

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The geochemistry of Sb has gained attention due to the toxicity of the metalloid and perceived similarity to arsenic as a group 15 element with +3 and +5 oxdiation states [1]. Sb(V) forms generally more soluble oxyanions, while Sb(III) can precipitate in various oxide and sulfide phases. Laboratory experiments of microbial and abiotic reduction and oxidation of Sb by a variety of microorganisms and reactants point to the potential for active redox cycling between Sb(III) and Sb(V) in low-temperture environments [e.g. 2, 3]. However, both species adsorb strongly to iron oxyhydroxides and clays, a process that exerts significant influence on Sb mobility [1].

The ratio of Sb stable isotopes, ^{123}Sb/^{121}Sb, has the potential to be a tracer of Sb geochemical reactions in modern or ancient environments. Here, we present an in-depth study of isotopic fractionation of Sb(III) and Sb(V) during sorption to goethite and illite. Batch reactors containing Sb(V) and goethite in a synthetic groundwater matrix at pH 6 and 8 were sampled over a week to examine the influence of kinetics on the isotopic fractionation during adsorption. Within the first 10 minutes, 60% and 40% of Sb(V) adsorbed to goethite at pH 6 and 8, respectively. A 0.45‰ decrease in the dissolved δ^{123}Sb occured in the first 3 hours of adsorption followed by a increase to isotopic equilibrium, $\Delta_{\text{solid-liq}} \sim -0.50‰$, after 4.5 days. Published EXAFS spectra of octahedral $Sb(OH)_6$- adsorption on goethite are interpreted to be a mixture of edge-sharing inner sphere and outer sphere surface complexes at this range of pH [1]. The changes in $\Delta_{\text{solid-liq}}$ over the course of sampling must be the result of competing kinetic and equilibrium isotope effects, which could be due to transformation from outer-sphere to inner sphere complexes. Experiments with illite as the sorbent and both Sb(III) or Sb(V) at pH 7 show a similar enrichement of the heavier isotope in the adsorbed pool within the first 24 hours, followed by an increase in the dissolved δ^{123}Sb relative to the initial liquid. Future work will examine the isotopic effect of sorption and subsequent oxidation of Sb(III) on goethite. [1] Scheinost et al. (2006) *GCA* [2] Kulp et al. (2014) *Env. Sci Tech.* [3] Leuz et al. (2006) *Env. Sci Tech.*