Se isotopic fractionation as a result of oxidation of Se-bearing minerals

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Selenium (Se) is a micronutrient, but also toxic at moderate concentrations to humans and animals (EPA MCL: 50 µg/L) [1]. Oxidation of insoluble reduced Se, like Se(0) and Se(-II)-bearing minerals, leads to the formation of soluble Se(IV) and Se(VI) oxyanions, both of which can be attenuated in natural systems through adsorption or reduction. As a result of both of these reactions, Se stable isotopes fractionate and are used to monitor remediation efforts of Se-contaminated waters [2, 3, 4]. Oxidation of reduced Se has been thought to produce negligible isotopic fractionation. However, complex incongruent dissolution of a Se-bearing mineral could result in persistant isotopic fractionation.

We present experiments that examine Se isotope effects associated with oxidation of ferroselite ($FeSe_2$), berzelianite (Cu_2Se), and Se-rich arsenopyrite (FeAsS) with H_2O_2. Continuously-stirred batch reactors containing each mineral and synthetic groundwater were amended with 0.4 mM H_2O_2 or 1 mM H_2O_2. Se concentrations for all conditions reached steady state by 72 hrs. Oxidation of berzelianite with 0.4 mM H_2O_2 results in $\delta^{82}Se/^{76}Se$ of dissolved Se(VI) that is 3‰ heavier than dissolved Se(IV), which increases from 1‰ lighter to 0.5‰ heavier than the unreacted mineral. Oxidation of berzelianite with 1 mM H_2O_2 shows a similar trend initially, but the Se(VI) fraction returns to unfractionated values by the end of the experiment. These results indicate that in addition to isotopic fractionation during initial oxidative dissolution, kinetic isotopic fractionation during oxidation of Se(IV) results in isotopically heavy Se(VI) for the less oxic condition. For the ferroselite oxidation dissolved Se(IV) and Se(VI) become immediately isotopically heavy under both conditions due to re-reduction by iron sulfide. In the less oxic condition, Se(IV) evolves to be 3‰ lighter than Se(VI) at the end of the experiment due to isotopic fractionation during the oxidation of Se(IV). Thus, the oxidative dissolution of Se(-II)-bearing minerals produces isotopically heavy Se on short timescales, and should be considered when using Se isotopes to examine modern or ancienct Se biogeochemical cycling. [1] EPA (2019) Natl. Prim. Drinking Water Reg., [2] Herbel et al. (2000) *GCA,* [3] Basu et al. (2016) *ES&T* [4] Xu et al. (2020) *GCA*