

Isotope fractionation of antimony during oxidative weathering of stibnite (Sb_2S_3)

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Antimony (Sb) has two stable isotopes with almost equal abundances ($^{121}\text{Sb} = 57.213\%$, $^{123}\text{Sb} = 42.787\%$). Similar to Mo, V, Fe and U, Sb is redox-sensitive, however, with a higher redox potential (Eh value) than the aforementioned elements. It can occur in four formal (-I, 0, +III, +V) oxidation states with commonly +III and +V encountered in nature. Therefore, stable Sb isotope signatures could have great potential as a redox proxy in low-temperature surface studies to reconstruct the weathering conditions of recent and Early-Earth environments. The transport of Sb in the environment (including soils, water and sediment) was reviewed by Herath et al. (2017), however, only scarce experimental data exist, regarding the environmental release of Sb (e.g., Biver et al. 2012) under different Eh conditions. In this study, we experimentally explored the leaching behaviour of stibnite (Sb_2S_3), the most common Sb mineral in nature, and associated isotope fractionation. For this, we performed leaching experiments with an isotopically homogeneous stibnite powder (0.14 g) and three different acids (0.05 M HCl, 0.5 M HNO_3 and 0.1 M oxalic acid) with a volume of 200 ml each. Antimony concentration, isotope composition, pH, and Eh values were determined at selected time steps in a time interval from 30 minutes to 13 days. During the leaching experiments, the pH value of oxalic acid and HCl solutions remained constant at 1.4 and 1.5, respectively, whereas that of HNO_3 rapidly increased from 0.7 to 1.2 and stabilized at 1. The Eh of the HCl solution was adjusted at 570 mV during the first 20 hours, whereas the Eh of HNO_3 and oxalic acid decreased to <630 mV till the end of the experiment. During the first 6 hours, with high Eh (>730 mV) for HNO_3 and oxalic acid, stibnite released almost 1% of Sb (>900 μg), resulting in $\sim 0.1\%$ heavier and $\sim 0.3\%$ lighter $\delta^{123}\text{Sb}$ for oxalic acid and HNO_3 , respectively. In comparison, HCl, without large Eh changes, preferentially mobilized the lighter Sb isotope, resulting in $\delta^{123}\text{Sb} \sim -0.4\%$ compared to the precursor material ($\delta^{123}\text{Sb} = -0.21\%$). In the HCl experiment, equilibrium was achieved after 20h with constant Sb concentration and $\delta^{123}\text{Sb}$. Conversely, progressive leaching with HNO_3 and oxalic acid, accompanied with a Eh drop, resulted in an increase of the Sb content (>2 %) with preferential mobilisation of the heavy Sb isotope. The leachate for the first 20 hours of leaching is marked by <0 saturation indexes relative to Sb oxides, resulting into progressive dissolution of Sb. After a further slight decrease of Eh values (e.g. from 630 mV to down to 565 mV for oxalic acid) at >20 hours, the leachate became alternately over- and undersaturated relative to Sb oxides, resulting in the precipitation of Sb oxides along with additional Sb leaching. In comparison, natural secondary minerals show an isotopic variation of -0.5 to +0.3 ‰ with also preferentially enrichment of light Sb isotope compared to primary minerals (isotopic range: -0.4 to +0.8) that are consistent with our leaching results with weak acids of HNO_3 and HCl, which generates heavy isotopic Sb enriched residues. With this in mind, our first results indicate the potential of Sb isotopes as a new proxy to interpret modern and past weathering and hydrothermal alteration environments.

Biver M, Shotyk W (2012): Stibnite (Sb_2S_3) oxidative dissolution kinetics from pH 1 to 11. – *Geochim Cosmochim Acta* 79, 127-139

Herath I, Vithanage M, Bundschuh J (2017): Antimony as a global dilemma: Geochemistry, mobility, fate and transport. – *Environmental Pollution* 223, 545-559