

Selenium isotope fractionation during reduction by organic carbon-limestone/zerovalent iron mixtures

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Fractionation of selenium in acid mine drainage (AMD) during reduction by two types of reactive mixtures, i.e., organic carbon-limestone (OC-LS) and organic carbon-zerovalent iron (OC-ZVI), was evaluated through column experiments. Se(VI) (40 mg/L) was spiked into the AMD collected in an abandoned metal mine site in Korea, and reduction of selenium along with other geochemical changes was assessed. The results showed that the isotope ratios of $\delta^{82/76}\text{Se}$ increased as the fraction of Se remaining in aqueous-phase decreased. The maximum δ values in the OC-LS and OC-ZVI columns were $3.16 \pm 0.4\text{‰}$ and $3.41 \pm 0.4\text{‰}$, respectively, as compared to the input solutions of $-0.44 \pm 0.4\text{‰}$ and $-0.22 \pm 0.4\text{‰}$, respectively. By applying the Rayleigh fractionation model, the effective fractionation curve for the OC-LS column was fitted to have $\varepsilon = 1.4\text{‰}$, which is close to the minimum value for the reduction by bacteria [1]. The ε value in the OC-ZVI column was 5.1‰ , which is similar to the value reported for the reduction of selenium by granular zerovalent iron [2]. With other geochemical changes, the results suggest that microbial reduction of selenium occurred in the OC-LS column, while abiotic reduction by ZVI is an important reaction mechanism in addition to the microbial reduction in the OC-ZVI column. X-ray absorption near edge structure (XANES) analysis of the solid phase indicated that selenium was reduced to the forms of SeS_2 and/or $\text{Se}(0)$ in the OC-LS column, while reduction to FeSe , SeS_2 and/or absorption of $\text{Se}(\text{IV})$ occurred in the OC-ZVI column.

[1] Herbel *et al.* (2000) *Geochim. Cosmochim. Acta* **64**, 3701-3709. [2] Shrimpton *et al.* (2015) *Environ. Sci. Technol.* **49**, 11688-11696.