Selenium isotope ratios as novel redox proxies to detect the onset of U(VI) reduction in groundwater

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Dissolved oxidized forms of selenium (i.e., Se(VI), Se(IV)) precipitate with uranium (U) after reduction at the redox fronts in groundwater systems, which often gives rise to sandstone-hosted roll-front type economic U deposits. *in situ* recovery (ISR), a commonly used mining technique, extracts U by oxidative dissolution of the roll-front U ore that causes mobilization of Se and U in their oxidized forms. When mining-generated Se-oxyanions encouter the undisturbed reduced environments downgradient of the ISR activity, Se may be immobilized along with U as a natural attenuation process due to similarities in the redox potentials (Eh) for Se-oxyanion and U(VI) reduction. In such groundwater systems, the stable isotopes of Se may be used to detect Se-oxyanion reduction, which is a precursor of U(VI) reduction, and thus indicative of the onset of U(VI) reduction.

We measured Se concentrations and δ^{82}Se of U ore and groundwater collected from 18 wells located upgradient, within and downgradient of a roll-front U deposit, from both previously mined and unmined parts of an ISR site at Rosita, TX, USA. The Se-oxyanion concentration in Rosita groundwater decreases along the hydraulic gradient to below the detection limit in most of the downgradient wells, where reducing environment is inferred from geochemical and isotopic parameters (e.g., Eh, δ^{238}U). The U ore is depleted in ^{82}Se (δ^{82}Se = -0.40‰ to -1.54‰). In contrast, Se(VI) in Rosita groundwater shows various degrees of ^{82}Se enrichment with δ^{82}Se up to 6.14‰. The elevated δ^{82}Se of Se(VI) in Rosita groundwater suggests Se(VI) reduction in the aquifer. The increasing trend of δ^{82}Se accompanied by a decrease in Se(VI) in groundwater roughly corresponds to a Rayleigh distillation model with an isotopic fractiontion (as ε, where $\varepsilon = 1000*(\alpha-1)$; $\alpha = (^{82}\text{Se}/^{76}\text{Se})_{\text{Product}}/(^{82}\text{Se}/^{76}\text{Se})_{\text{Reactant}}$) of 1.3‰. In the unmined part of the site, the progressive increase in δ^{82}Se in grondwater suggests that the aquifer is approaching U(VI) reducing conditions along the hydraulic gradient. These results demonstrate that Se isotope ratios may be used as effective sensors to detect Se(VI) and possibly U(VI) reduction in groundwater systems.