Visualizing Technetium Incorporation within Iron Oxides through Mineral Transformation

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Technetium (^{99}Tc) is a fission product with a long half-life and high mobility in oxidizing subsurface environments that raises many environmental concerns. Since reduced Tc(IV) is barely soluble relative to mobile pertechnetate species ($Tc(VII)O_4^-$), immobilization of radionuclide ^{99}Tc has been synonymous with reduction, often by ferrous iron. Incorporation of Tc(IV) into iron oxide mineral structures is proposed for ^{99}Tc sequestration and to protect Tc(IV) from reoxidation. In this study, ^{99}Tc incorporation into magnetite with or without Ni-doping through mineral tansformation using $Fe(OH)_2(s)$ as precursor was explored. The Tc(IV)-doped magnetite was obtained through simulaneous Tc(VII) reduction and Tc(IV) incorporation by Tc(VII) exposure to $Fe(OH)_2(s)$ during oxidation and mineral transformation. The oxidative transformation kinetics from $Fe(OH)_2(s)$ to magnetite in aqueous solution were observed using *in situ* μ-X-ray diffraction. The ^{99}Tc speciation, incorporation mechanisms, and distribution within the produced iron minerals is revealed with clear visual evidence using extensive solid chracterization methods including FIB/STEM-EDS, EELS, and XAFS. The results show that nearly 100% ^{99}Tc was removed from the solutions, and the immobilized Tc(IV) is heterogeneously incorporated into different iron oxide/hydroxide phases as Tc(IV)-incorporated magnetite and/or $TcO_2{\cdot}2H_2O(s)$ via different incorporation mechanisms. In addition, with Ni-doping, metallic ^{99}Tc was found in spheroidal, Ni-rich and metallic nanoparticles exhibiting a core/shell microstructure. This work shows how FIB/STEM-EDS may be used to visualize dopants in mineral systems, and the results indicate that ^{99}Tc incorporation within iron oxide minerals through mineral transfomation processes could be an effective pathway for ^{99}Tc remediation.