Nanoscale mineral/contaminant redox reaction processes: impact on oxyanion contaminant fate in oscillating anoxic environments

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Oscillating oxic/anoxic conditions induces processes at mineral-fluid interfaces affecting the speciation and fate of redox active elements. Such fluctuations occur in natural environments (at watershed and delta water table or in lake water chemocline) and in engineered systems (in oil refinery drainage water peatbogs or nuclear waste repository). In presence of aqueous sulfide or ferrous iron ions, Se, Sb, Pu and Re undergo heterogeneous reductive precipitation. At the nanosecond scale, selenate adsorption onto the net pyrite surface is shown by ab-initio computations to proceed via the formation of a chemical bond between the oxyanion oxygen atom and a surface Fe atom, weakening the other Se-O bonds and reducing Se atom oxidation state. At hour-to-day scale, mobile Se(VI), Se(IV), Sb(V), Pu(V) and Re(VII) oxyanions are shown by strictly anoxic wet chemistry experiments, XAFS and Mossbauer spectroscopy [1] to be reduced, in presence of nanosized particles (iron sulfides (mackinawite or pyrite) [2], oxides (magnetite) [3] [4] [5] or clays [6]) and aqueous iron (II) or S(II), to solids (Se(0), Sb2O3, PuO2, ReO2, ReS2 or Re(0)) or to highly specific Sb(III) [7] and Pu(III) [8] sorption complexes. STEM-HAADF microscopy demonstrates the formation of Se(0) trigonal gray selenium nanowires after co-adsorption of selenate and ferrous iron ions on 10 nm nanomagnetic [4], a reaction which results from a complex, kinetically controlled interplay of intermediate reduced surface complexes and transport of these reduced species to the tip of the nanowires. These processes in far-from-equilibrium conditions are of prime importance in the safety assessment of petroleum industry and geological repositories, as well as in the bioavailability to crop or human beings.