Structural incorporation of selenium in pyrite, mackinawite and amorphous iron sulfide

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The Se-79 isotope is one of the long-term potentially harmful radionuclides due to its high mobility and long lifetime ($T_{1/2}$ = 3.77·10^5 yr). Pyrite is considered as one important host phase for radionuclides in high level nuclear waste disposal sites. Therefore, our investigations focus on the amount, type of bonding and distribution of Se-species in pyrite but also in its precursor phases mackinawite and amorphous FeS as solid solution phase for acidic and anoxic conditions predicted for a nuclear waste repository.

The preparation of Se-doted Fe-sulfide grains were accomplished under argon atmosphere in a glove box from solutions with different constant acidic pH-and Eh-levels, containing Se-concentrations (–II) between 10^{-3} – 10^{-6} M.

Results via XRD, XRF and SEM analysis reveal a synthesis of pure spheroidal pyrite grains with a mean diameter of 1-2 μm and Se contents up to 2 mol-%. Furthermore, there is an efficient uptake of selenium by all iron sulphides with values between 90%-99.5% of the provided solute concentration. First XAFS measurements indicate a reduced valence state of Se (-II) or probably a covalent bonding of Se (-I) of the structural substitution of sulfide by selenide.

Bedrock matters

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Three separate hillslope field experiments conducted in coastal California and Oregon (on mélange, sandstone and argillite) during a 20 year period demonstrate that near-surface fractured (and weathered) bedrock strongly influences hydrologic, geomorphic, geochemical, and ecological processes. Nearly all the precipitation travels to channel through a shallow dynamic groundwater in the fracture bedrock. Local elevated pressure gradients in this zone leads to exfiltration back to the soil mantle, leading to saturation overland flow on gentle slopes, and to shallow landsliding on steeper ones. Slow drainage of the groundwater from this zone sustains baseflow in the dry season while residual rock moisture may provide vegetation resilience to droughts. Elsewhere observations suggest rock moisture in weathered granites is also crucial to vegetation in regions with seasonal strong dry periods The near surface fracturing appears to arise from a combination of topographic-induced stresses, from wetting and drying (of the argillite), possibly from gradual creep (in the mélange), and chemical and physical reactions (granite). Data are generally lacking on distribution of this fractured (and weathered) zone beneath landscapes. Available profiles on convex hillslopes bordered by active channel incision show this zone to be thickest at the divide and to systematically thin towards the channel. It is suggested that convex profile of the bottom of this weathered zone corresponds approximately to the top of bedrock that remains saturated. Drainage of the hillslope induced by progressive channel incision should cause this lower boundary to correspondingly drop. Many have specifically proposed that deep weathering and supergene enrichment results from progressive decent of a oxidation front (top of the water table). Prediction of the descent the 'bottom' of the conductive reactive zone and of the co-evolution of the conductivity field above this front will be essential to linking quantitatively the development of this zone to hydrologic, geomorphic and ecological processes.