Stability of selenium-doted pyrite under variable hydrochemical conditions

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Natural pyrite formation is known to be an important sink for different radionuclides. This iron disulfide exists with up to five weight percent in claystones which is taken into account for a repository of high level nuclear waste. If radionuclides would be released into the host rock by contact with groundwater, it is possible to migrate into the biosphere. Due to natural retention mechanisms such migrations could be prevented by sorption or incorporation through minerals or mineral formations in the host rock [1].

The radionuclide ^{79}Se is a fission product of ^{235}U and ^{239}Pu and in case of a release of radionuclides it plays an important role for migration due to the long lifetime and the high mobility of its oxidized species Se^{4+} and Se^{6+} [2,3].

In our experiments, dissolved selenium was incorporated during fast precipitation of pyrite with a selenium content up to 2.4 wt.-% at initial Se^{2-} concentrations of $10^{-3} – 10^{-6}$ M. The heat capacities show hardly any differences of the unoxidized synthesized minerals for both pyrite and Se-doted pyrite. Structural investigations of the Se-doted pyrite with Rietveld refinement show a slightly distorted pyrite structure in which the lattice parameter were enlarged in contrast to pure pyrites with no contaminants. In addition to this evaluation, the results of the measurements of XANES and EXAFS show an incorporation in pyrite of Se^0 which is surrounded by sulfur and iron, supposing not to be a direct substitution of sulfur (S_2^{2-}). In contrast to this, XPS measurements show that the dominant species at the surface is Se^{2-}.

The long-term immobilization of selenium depends on the stability of these Se-doted pyrites. After contact of Se-doted pyrite with oxidized water for several weeks, the reduced Se species tend to higher oxidation states evident by XANES measurements.

[1] Liu et al. (2008) *Radiochim. Acta* **96**, 473-479 [2] Howard III (1977) *Geochim. Cosmochim. Ac.* **41**, 1665-1678 [3] Jörg et al. (2010) *Appl. Radiat. Isotopes* **68**, 2339-2351