

# Redox reactivity of selenium (VI) in the presence of Fe (II) and S(-II) bearing mineral phases under the conditions of Callovo-Oxfordian pore water

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<sup>79</sup>Se with a half-life of  $3.27 \times 10^5$  y [1] is presently considered as a key mobile radionuclide for the disposal of spent fuel and high-level waste [2]. The solubility of selenium (Se) is largely controlled by its oxidation state, and hence depends on the redox conditions present in soils, sediments, bedrock and aquifers. The -II, -I, and 0 oxidation states are commonly predominant in “reducing” anoxic environments, while the +IV and +VI states predominate in more “oxidizing” environments [2]. The interactions with Fe(II) and S(-II)-bearing redox active solids mediate the oxido-reduction kinetics of Se oxyanions, playing an important role in the control of Se speciation [3]. Regarding Se(VI), it was found to be metastable (far from thermodynamic equilibrium) and potentially selenium could coexist in different oxidation states in the Callovo-Oxfordian pore waters [4]. The reduction of Se(VI) by magnetite, much slower than for Se(IV), include different steps (adsorption, reduction to Se(IV), and further reduction to less soluble Se phases: Se<sup>0</sup>(s), FeSe<sub>2</sub>(s), FeSe(s)), each of them imposing a kinetic barrier for the whole reduction process. At present it is not clear whether the Se(VI) initial adsorption or its reduction to Se(IV) are concomitant or not, and extra work needs to be done in this direction to establish the reduction pathway. Furthermore, little is known about the potential competition with ubiquitous ions in porewater such as carbonate or sulfate and especially about their capability to limit the contact of selenate molecules with the Fe(II)-bearing solids, and thus to inhibit the electron transfer.

The redox reactions Se(VI) with magnetite and pyrite under neutral pH conditions will be deciphered at both macroscopic and molecular levels by combining batch sorption studies and advanced spectroscopic techniques (XAS, XPS). In addition, the influence of sulfate ions will be investigated.

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