

Pathways for abiotic reduction in the FeS/Se(IV) and FeS₂/Se(IV) systems

E. BREYNAERT¹, W. WANGERMEZ¹, D. DOM¹,
A. C. SCHEINOST², T. N. PARAC-VOGT³,
C. E. A. KIRSCHHOCK¹ AND A. MAES¹

¹KULeuven, Center for surface chemistry and catalysis,
kasteelpark arenberg 23 – box 2461, B-3001 Leuven,
Belgium Eric.breynaert@biw.kuleuven.be

²HZDR, Inst. of Resource Ecology, Bautzener Landstrasse
400, 01314 Dresden, Germany

³KULeuven – Department of Chemistry, Celestijnenlaan 200F,
B-3001, Leuven, Belgium

The geochemical behaviour and bio-availability of selenium have an unexpectedly intricate impact on modern society. While selenium is an essential micronutrient for many living organisms, the window between deficiency and toxicity is very narrow (0.04 ppm ; essential; 0.04 – 0.1 ppm beneficial; 3 ppm toxic). Due to its similarity to sulphur, it is commonly encountered in subsurface deposits such as coal and uranium, phosphate and sulphidic transitionmetal ores. The release of selenium to the environment is closely associated with the economic exploitation of such deposits. Because of its significant contribution to long-term radiation exposure, ⁷⁹Se is considered as one of the important isotopes in the inventory of the long-lived radioactive waste produced by nuclear industry.

In view of redox properties and abundant occurrence in reducing soils and sediments, iron sulphides play an important role in the availability of mobile inorganic selenium in the environment.

While previous studies have demonstrated the formation of FeSe and Se⁰ upon reduction of Se(IV) with respectively iron monosulphides and iron disulphides, the mechanistic pathways explaining the different outcome are missing.

Combination of published results in a wide range of relevant systems^[1-5] with new spectroscopic information (XAS and NMR spectroscopy) obtained for specifically synthesized key intermediates allows to rationalise all previous observations. These results allow to outline the different pathways and demonstrate how the intermediary selenium, sulphur and selenosulphur species determine the final outcome of the reactions.

[1] Scheinost *et al* (2008), *ES&T*, **42**, 1984–1989 [2] Breynaert *et al* (2008), *ES&T*, **42**, 3595–3601 [3] Scheinost *et al* (2008), *J. Contam. Hydrol.*, **102**, 228–245 [4] Breynaert *et al* (2010), *ES&T*, **44**, 6649–6655 [5] Kang *et al* (2011), *ES&T*, **45**, 2704–2710