

## Structural incorporation of selenium in iron sulfides

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One of the key issues regarding the disposal of high-level nuclear waste in deep geological formations is related to the long term safety of a waste repository. Different performance assessment calculations for such repositories show a domination of  $^{79}\text{Se}$  radionuclide with regard to the total exposure to the biosphere in the period of  $10^4$ - $10^6$  years after disposal. Selenium is often associated with sulfides such as pyrite, a frequent minor constituent of host rocks and bentonite backfills considered for radioactive waste disposal. In this study, we investigated the incorporation of Se(-II) and Se(+IV) into pyrite.

The syntheses occurred via direct precipitation in batch and as coatings on natural pyrite in mixed flow reactor (MFR) experiments under anoxic conditions for Se-concentrations in the solutions up to  $10^{-3}$  molL $^{-1}$ . Furthermore, a high temperature synthesis by chemical vapor transport enabled the synthesis of Se-doped pyrite for single-crystals with a size up to 1 cm.

The mineralogical analyses by SEM and XRD reveal the syntheses of pure phases. Neither achavalite (FeSe), nor ferroselite (FeSe $_2$ ) were detected. The average of Se-uptake in 34 samples in batch experiments has been 98% and in MFR syntheses 99.5%, indicating a high potential for the retention of selenium by pyrite.

XAFS investigations have been performed at synchrotron light facility ANKA, Karlsruhe. These analyses and additional XPS measurements point out a reduced valence state of Se by initially dissolved Se(-II) and Se(IV) coprecipitated in pyrite and mackinawite. Curve progression and k-edge values [1,2] for selenide doped mackinawite ( $E_0$ : 12655.3 eV) in batch experiments imply a valence state of Se(-II) and for selenide doped pyrite ( $E_0$ : 12656.9 eV  $\pm$  0.3) in batch experiments a valence state of Se(-I), while the k-edge value of Se(0) as reference is higher ( $E_0$ : 12658.0 eV).

XAFS analysis on the coatings from MFR-syntheses, performed under slightly supersaturated conditions, indicate a coprecipitation of Se(-II) and Se(IV) predominantly as Se(0). With regard to batch experiments, these results indicate a substitution of sulfur with selenide just for high supersaturated solutions. In selenide doped mackinawite via direct precipitation in batch experiments occurred a substitution of S with Se in an achavalite-type compound. As well, S is substituted by Se in selenide doped pyrite, ending in a FeSSe compound which could be best described by a slightly distorted pyrite structure.

[1] Charlet *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, 5731–5749. [2] Scheinost *et al.* (2008) *J. of Contam. Hydr.* **102**, 228-245.

## Geochemical expression of buried iron-oxide Copper Gold mineralisation within physical and chemical interfaces of the deep cover at the Hillside Prospect, South Australia

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Iron-Oxide Copper Gold (IOCG) mineralisation is an economically important mineral system in Australia, and includes the enormous Olympic Dam resource. Relative to its economic significance, however, little is known about the regolith geochemical expression of IOCG mineralisation, and therefore geochemistry has been under-utilised within the exploration for further deeply (10s-100s metres) buried deposits. This study shows that the weathered and transported cover overlying buried mineralisation can host systematic geochemical expressions of buried IOCG mineralisation.

The Hillside Prospect is 100 km northwest of Adelaide within the southern end of the IOCG prospective, eastern Gawler Craton. Mineralisation here is associated with N-S trending structures of the Pine Point Fault Zone.

Surface (soil) geochemistry results have shown locally elevated Cu-Au concentrations overlying buried mineralisation. The processes and associations with the underlying mineralisation and parts of the 10s-100s m deep cover in between the mineralisation and the soil are poorly constrained. Coastal cliffs in the area expose buried mineralisation at 10s of metres depth and the overlying saprolite, palaeodrainage, marine and aeolian sediments. Multi-element geochemical characterisation of these profiles shows variations in the chemical parameters associated with physical interfaces (e.g. unconformities and sediment lithologies) and chemical interfaces (e.g. palaeo- and contemporary redox boundaries, watertables) that provide strong expression and contrast within the cover for settings laterally proximal or distal to mineralisation. Many of the chemical interfaces are associated with supergene halos that are organised into locally enriched and differentiated U, Au and Cu zones flanking mineralisation. Whilst redox conditions and secondary iron oxide hosts provide important constraints on this geochemical expression, the secondary carbonate minerals and deep-rooted plant biogeochemical processes are also important.