

Selenide retention by mackinawite: A multi-edge XAS approach

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The fission product ⁷⁹Se ($T_{1/2} > 10^6$ a) is of concern for the safe disposal of High Level nuclear Wastes (HLW). The chemistry of selenium resembles that of sulfur, and the Se solubility is controlled by its oxidation state. Ubiquitous in nature, iron sulfides are believed to control the *in situ* redox potential of most rock formations envisaged for the disposal of HLW. Under HLW repository relevant (reducing) conditions, Se may occur in low oxidation states. Robust structural data for selenide (Se(-II)) binding to mackinawite were obtained by collecting multi-edge XAS data.

Disordered mackinawite (FeS_{am}) was precipitated in the presence of Se(-II) (SeMack). XAS data were collected at the S, Fe and Se K-edge for SeMack, at the S and Fe K-edge for pure FeS_{am} and at the Fe and Se K-edge for FeSe. For each sample, the data were fit at all edges simultaneously. The (compelling) formation of a FeSe-like phase in SeMack is ruled out from the absence of detected neighboring Se atom in the Se first shell. In contrast, the detection of Fe neighbors at ~2.38 Å and higher distances S backscatterers strongly points to Se located in a FeS-like environment. Separately, selenide ions were contacted with pre-existing FeS_{am} in suspension (Se/FeS). Analysis of the Fe and Se K-edge XAS data reveals the presence of different crystal-chemical environments. The detection of Se neighbors in the Se first coordination sphere points to the presence of Se(0). The (compelling) presence of selenium in a FeSe-like environment is ruled out by the absence of higher distance Se backscatterer. In contrast, part of retained Se may be located in an environment close to that of SeMack. The presence of Se in a reduced form (0, -II) in SeMack and Se/FeS will ensure a low mobility in the near field of HLW disposal sites.

This multi-edge XAS approach places high confidence in the molecular scale process understanding of selenide binding to mackinawite.

Osmium, carbon and trace element investigations into archaeological material

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We present initial results from two studies investigating how the utilisation of Osmium (Os) and Carbon (C) isotope analysis as well as trace element geochemistry can be used to provide information on the source and manufacture of archaeological artifacts.

The first study comprises Os and C isotope analysis of drillings from an iron cannon from the pinnacle Swann recovered off the Isle of Mull (Scotland). Os isotope analysis of the cannon provides a radiogenic ¹⁸⁷Os/¹⁸⁸Os ratio (0.825 ± 0.032) which has not been reset during casting. Therefore the ¹⁸⁷Os/¹⁸⁸Os ratio may be applied to identify the source of the ore. Furthermore the $\delta^{13}\text{C}$ ratio of the cannon (-30.3 ‰) is similar to charcoal and may reflect the use of charcoal as a reducing agent in the manufacturing of the cannon.

The second study (incorporating trace element and Os isotopic analysis of source clay, fired source clay and Roman ceramic building material (CBM)) was undertaken to test how trace elements can be utilised to identify the centres of manufacture of tile. Aliquots of raw clay and fired clay as well as CBM samples from York (U.K.) and Carpow (Fife, U.K.) roman fortresses are geochemically indistinguishable, yet are distinct from the published literature. Therefore we believe that trace element geochemistry can be used to identify the centre of construction of CBM and so further understand trade networks within the roman world. Re-Os isotopic analysis of the CBM samples to further aid protolith identification is ongoing. Initial results show that the CBM contains Re and Os abundances similar to average upper continental crust, however, the ¹⁸⁷Os/¹⁸⁸Os ratio is very radiogenic (4.8 ± 0.8) and so may be useful in geochemically isolating CBM manufactured from different sources.

These studies demonstrate how combining isotopic and trace element analysis can further our understanding of the source and manufacture of a wide range of archaeological material.