

Magnesium in palaeoenvironmental carbonates

ADRIAN A. FINCH^{1*}, NICOLA ALLISON¹,
LAURA FOSTER^{1,2}, LINDSAY WILSON³
AND ED HATHORNE⁴

¹School of Geography & Geosciences, University of St Andrews, KY16 9AL, UK

²Department of Earth Sciences, University of Bristol, Queen's Road, Bristol BS8 1RJ, UK

³Institute for Geology, University of Tromsø Dramsveien 201 N-9037 Tromsø, Norway

⁴DIFM-GEOMAR, Leibniz Institute of Marine Sciences, University of Kiel, D-24148 Kiel, Germany

We compare the Mg K-edge X-ray Absorption Near Edge Structure (Mg K-XANES) of a range of standards and biominerals to determine Mg structural state. Our samples include planktonic foraminifera and tufa (calcite), and corals, speleothem, bivalves and sclerosponges (aragonite). Biogenic calcites have XANES similar to inorganic calcite, with the exception of *Globigerina bulloides*, which has the XANES of aragonite. No biogenic aragonite studied gives XANES consistent with aragonite as a host. The XANES most closely match the Mg-bearing organic standard. The XANES of organics is structureless because Mg is surrounded by elements with poor electron scattering and little long-range order. Similar XANES would also be produced by nanoparticulate material in which long-range electron resonances are absent. This is the structure of amorphous calcium carbonate (ACC), which has short-range order and particle sizes of ~50 nm. Although the exact nature of the host is unclear, we conclude that Mg in aragonitic biominerals is not hosted by macroscopic aragonite.

Selenium retention by iron sulfides

N. FINCK^{1,3*}, K. DARDENNE¹ AND D. BOSBACH^{2,3}

¹Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), Campus Nord, P.O. Box 3640, D-76021 Karlsruhe (Germany)

(*correspondence: nicolas.finck@kit.edu)

(kathy.dardenne@kit.edu)

²Institute for Energy Research 6 (IEF-6), Forschungszentrum Jülich, D- 52425 Jülich (Germany)

(d.bosbach@fz-juelich.de)

³Helmholtz Virtual Institute "Advanced Solid-Aqueous RadioGeochemistry" (Germany)

Ubiquitous in nature, iron sulfides (FeS and FeS₂) are believed to control the *in situ* redox potential (reducing conditions) of most rock formations envisaged for the disposal of HLW. Pyrite (FeS₂), the most stable authigenic iron (II) sulfide phase in the environment, can be formed via several pathways, with FeS often being the initial precipitate [1]. Both substrates are scavenger of trace elements from solution in anoxic environments. ⁷⁹Se (T_{1/2} > 10⁵ yrs) is one of the elements of concern for the safe storage of High Level nuclear Wastes (HLW). The chemistry of selenium resembles that of sulfur, and occurs at low oxidation states under reducing conditions. The retention of selenide by adsorption on and by coprecipitation with iron sulfides were investigated in this work.

Amorphous mackinawite (FeS_{am}) was precipitated in the presence of selenide [2]. Information on the Se oxidation state (XANES) and crystal-chemical environment (EXAFS) were obtained from X-ray absorption spectroscopy (XAS). Upon coprecipitation with FeS_{am}, XANES data pointed to the presence of a reduced Se species associated with the bulk solid. Analysis of the EXAFS data suggested the presence of successive Fe and S shells, typical of mackinawite. The results were consistent with Se incorporation in the bulk solid. In contrast, XANES data suggested a partial oxidation of Se (-II) upon contact with FeS_{am} in suspension. The Se near-range environment by surface reaction also differed from the coprecipitation experiment (EXAFS). Specifically, lower number of neighboring atoms and a distant Se shell (d (Se-Se) ~ 3.6 Å) were detected. The results pointed to an oxidative retention involved in the surface reaction.

Preliminary tests were also conducted to prepare Se-doped pyrite from the doped precursor phase (FeS_{am}) [2]. First XANES data suggested a partial oxidation of Se, a behavior identical to S when oxidizing Fe^{II}S_{am} to FeS₂.

[1] Butler & Rickard (2000) *GCA* **64**, 2665–2672. [2] Lingane & Niedrach (1948) *JACS* **70**, 4115–4120.