Magnesium in palaeoenvironmental carbonates

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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 in unclear, we conclude that Mg in aragonitic biominerals is not hosted by macroscopic aragonite.

Selenium retention by iron sulfides

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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 (T₁/₂ > 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 (FeS₆₄) 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 FeS₆₄, 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 FeS₆₄ 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 (FeS₆₄) [2]. First XANES data suggested a partial oxidation of Se, a behavior identical to S when oxidizing FeS₆₄ to FeS₂. [1] Butler & Rickard (2000) GCA 64, 2665–2672. [2] Lingane & Niedrach (1948) JACS 70, 4115–4120.