



Rare-earth elements scavenged by fossil bioapatite in metalliferous deep-sea mud: Mineralogical and geochemical evidence from the Central Pacific Ocean

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Metalliferous deep-sea mud in the Pacific Ocean is currently explored as a potential alternative resource for rare earth elements (REE: La–Lu; REY: La–Lu and Y), which are crucial for cutting-edge electronics and green-energy technologies. Although bioapatite (fish-debris) is commonly proposed as the main REY host in deep-sea mud, the metal enrichment mechanism remains undetermined. In order to characterize the REY scavenging scheme, we investigate the mineral phase, REY concentrations, and nano- to micro-scale structures of fish-debris from the Central Pacific deep-sea mud. The fish-debris samples could be divided into two types (type 1: well-preserved fish teeth; type 2: broken fish teeth and bone fragments). Fish-debris in the REY-rich mud is identified by X-ray diffraction (XRD) showing clear peaks of typical hydroxyapatite. In situ laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis reveals that these studied fish-debris samples generally contain high \sum REY concentrations (up to 10,864 ppm). LA-ICP-MS trace element mapping reveals that type 1 fish tooth has a radial distribution of REY and concentrates more REY in the root part than the tip, possibly result from dense enamel inhibits REY absorption from ambient fluids (seawater and/or pore-water). In contrast, type 2 broken fragment contains homogenous high REY across the whole grain. High-resolution transmission electron microscopy (HRTEM) is firstly applied to identify the microstructure of fish-debris from deep-sea mud, and the result reveals that fish tooth dentin is composed of numerous nanoscale biogenetic hydroxyapatite, but no independent REY minerals can be identified. Lattice distortion along the boundary of biogenetic hydroxyapatite nanocrystal is visualized by HRTEM and associated energy-filtered TEM (EFTEM), indicating that either the $REE_{3+} + Si_{4+} = Ca_{2+} + P_{5+}$ (major) substitution scheme and/or $REE_{3+} + Na^{+} = 2Ca_{2+}$ (minor) might constrain the REY exchange and enrichment in fish-debris. This contribution not only highlights the importance of fish teeth histology which constrains the elemental diffusion in fish teeth, but also provides a new understanding of the mechanisms of the uptake of REY into biogenetic apatite in the metalliferous deep-sea mud.