

## High-resolution X-ray spectroscopy identifies cerium clusters in deep-sea sediments

- Cerium in deep-sea sediments occurs within phosphate-rich amorphous coatings on fossil bioapatite rather than within the crystals.
- Cryogenic, high-energy-resolution micro-X-ray absorption spectroscopy at beamline ID24-DCM was used to determine the oxidation state and local structure of cerium.
- The results clarify how rare earth elements accumulate in deep-sea muds and provide guidance for future, lower-impact extraction strategies.

### The challenge

Rare-earth elements and yttrium (REY) are essential to modern technologies, yet little is known about how they concentrate at the Earth's surface. Marine sediments hold vast reserves, and REY are several million times more enriched in deep-sea mud than in seawater. Understanding their chemical forms is important both fundamentally and practically, as any recovery depends on atomic-scale structure.

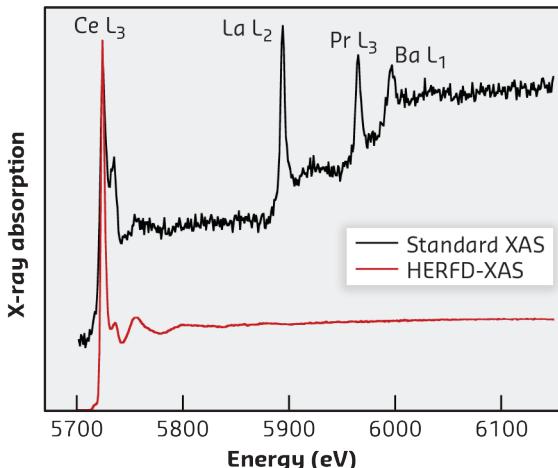
The sedimentary component hosting REY consists of biogenic/authigenic fluorapatite (FAp). When fish die, bones and teeth accumulate on the seafloor; over hundreds of thousands to millions of years, biogenic FAp can adsorb REY from seawater and pore fluids during diagenesis. A long-accepted view is that REY become incorporated into the bioapatite crystal lattice by solid-state diffusion. This study examined whether cerium (Ce) follows that pathway or occurs in another form. Ce is particularly informative because it exists as both Ce(III) and Ce(IV) and uniquely forms a simple phosphate mineral on land (monazite,  $\text{CePO}_4$ ). Because Ce shifts valence with redox conditions, locating its host phase also helps constrain where oxidation and reduction occur during early diagenesis – information that feeds into both geochemical interpretation and practical extraction strategies.

**Fig. 1:** Ce  $\text{L}_3$ -edge X-ray absorption spectrum of bioapatite measured using a silicon-drift detector (standard XAS) and a five-crystal spectrometer (HERFD-XAS).

### The experiment

Fossil bones and teeth were hand-picked at 1.94 and 4.70 metres below the seafloor from a Clarion-Clipperton Fracture Zone core (16GC). Grain sizes were 50–200  $\mu\text{m}$  and contained  $2203 \pm 545 \text{ mg Ce/kg}$  (16GC-194) and  $2081 \pm 414 \text{ mg Ce/kg}$  (16GC-470). Scanning Transmission Electron Microscopy – High-Angle Annular Dark-Field (STEM-HAADF) with elemental mapping revealed FAp nanocrystals embedded in an amorphous matrix rich in phosphorus (P) and silicon (Si) but low in calcium (Ca).

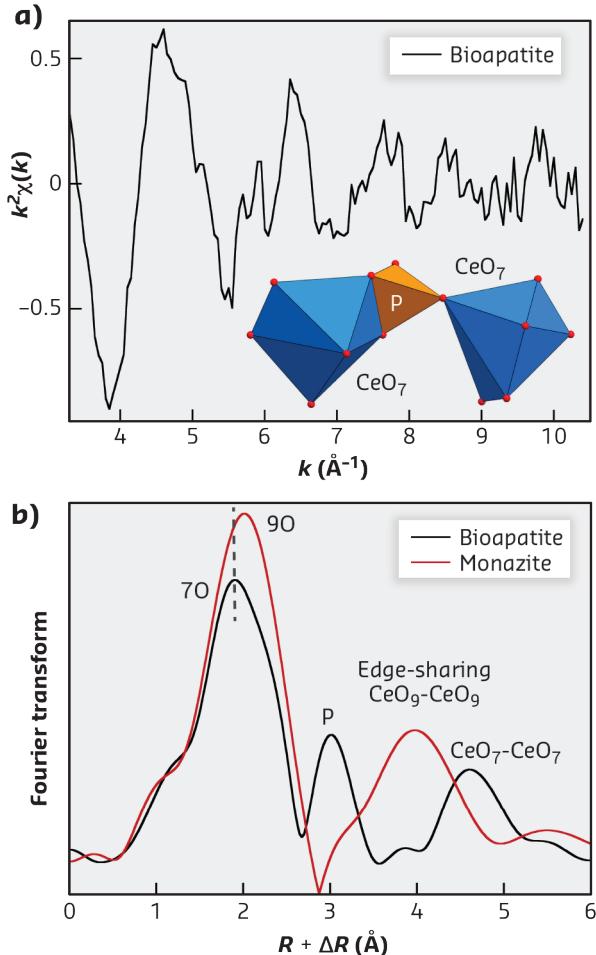
Three issues complicate Ce X-ray absorption spectroscopy (XAS): overlapping absorption edges from other REY (Figure 1), micron-scale heterogeneity, and beam-induced oxidation of Ce(III) to Ce(IV). To address these challenges, bulk and micro-X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected at 2.7 K using a wavelength-dispersive spectrometer in the high energy-resolution fluorescence-detected (HERFD) mode at beamline ID24-DCM. Cryogenic temperatures limited beam damage, while HERFD – which detects fluorescence through a narrow energy window – sharpened spectral features and helped resolve overlapping signals, enabling site-specific speciation in fragile, heterogeneous grains (Figure 2).



In broad terms, XANES identified oxidation state and coordination environment, while EXAFS provided interatomic distances of immediate neighbours; together they defined how Ce is bound.

Two distinct Ce species were identified. The dominant form was multinuclear Ce(III)-phosphate clustered within an amorphous layer coating the FAp nanocrystals; a minor fraction occurred as  $\text{CeO}_2$  precipitates. The local structure of Ce in these clusters differed from monazite and other known Ce-phosphates: spectroscopy indicated approximately seven-fold coordination ( $\text{CeO}_7$ ) with  $\text{PO}_4$  groups linking the polyhedra, whereas monazite had nine-fold coordination ( $\text{CeO}_9$ ) with edge-sharing polyhedra. Computational simulations supported clustering as energetically favourable. **Figure 2b** contrasts the radial structure functions of bioapatite-associated Ce and monazite, illustrating the coordination changes of Ce, consistent with the amorphous surface layer observed by electron microscopy.

These observations indicate a surface-coating mechanism: phosphate-rich pore waters deposit an amorphous layer on bioapatite surfaces, which then accumulates Ce as clusters; diffusion into the lattice is not observed. This has consequences for both geochemical budgets and practical recovery. The effectiveness of simple acid leaching for extracting REY from such sediments suggests that an amorphous host may be significant, as crystalline FAp is relatively resistant to dissolution [1]. Selective leaching protocols could therefore target the coating while leaving the crystal core largely intact, potentially reducing reagent use and limiting co-dissolution of Ca and P from the FAp lattice. The element-specific approach now possible at ID24-DCM can test whether other REY behave in the same way across different marine sediment types, helping to refine models of REY cycling and informing future, lower-impact recovery routes.



**Fig. 2:** a) Ce  $\text{L}_3$ -edge EXAFS spectrum of bioapatite. b) Radial structure functions of bioapatite and monazite ( $\text{CePO}_4$ ). Inset: polyhedral representation of the local structure of Ce in bioapatite.

This research was financed through the ERC grant DEEP-SEE (101052913).

#### PRINCIPAL PUBLICATION

Cerium occurs as cerium-phosphate clusters around bioapatite nanocrystals in deep-sea sediments, A. Manceau et al., *Commun. Earth Environ.* **6**, 466 (2025); <https://doi.org/10.1038/s43247-025-02439-2>

#### REFERENCES

[1] Y. Kato et al. *Nat. Geosci.* **4**, 535 (2011).