



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/243136/>

Version: Accepted Version

Article:

Liao, X., Li, D., Poulton, S.W. et al. (2026) Organic matter controls rare earth element hyper-enrichment in Pacific deep-sea bioapatite. *Geochimica et Cosmochimica Acta*, 427. pp. 102-19. ISSN: 0016-7037

<https://doi.org/10.1016/j.gca.2026.07.003>

This is an author produced version of an article published in *Geochimica et Cosmochimica Acta*, made available via the University of Leeds Research Outputs Policy under the terms of the Creative Commons Attribution License (CC-BY), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

1 Organic matter controls rare earth element hyper-enrichment in
2 Pacific deep-sea bioapatite

3 Xijiao Liao¹, Dengfeng Li^{1, *}, Simon W. Poulton², John R. Reinfelder³, David Chew⁴, Yu
4 Fu¹, Yongjia Liang⁵, Zhengkun Li⁵, Jinzhou Peng¹, Xiaoming Sun^{1, 5}

5 ¹*School of Marine Sciences, Guangdong Provincial Key Laboratory of Marine Resources and*
6 *Coastal Engineering, Sun Yat-sen University, Southern Laboratory of Ocean Science and*
7 *Engineering (Zhuhai), Zhuhai, Guangdong 519082, China*

8 ²*School of Earth, Environment and Sustainability, University of Leeds, Leeds, LS2 9JT, UK*

9 ³*Department of Environmental Sciences, Rutgers University, New Brunswick, NJ 08901, USA*

10 ⁴*Department of Geology, School of Natural Sciences, Trinity College Dublin, Dublin 2, Ireland*

11 ⁵*School of Earth Sciences and Engineering, Sun Yat-sen University, Zhuhai 519082, China*

12
13 * Corresponding author: lidf3@mail.sysu.edu.cn
14

Abstract

Bioapatite is a predominant sink for rare earth elements (REE) in global deep-sea sediments, where the REE accumulate either via organic matter remineralization or Fe-Mn (oxyhydr)oxide dissolution. While the sequestration of REE into bioapatite has been extensively documented, the mechanistic pathways governing REE transfer from these carrier phases to bioapatite during diagenesis remain poorly constrained. This limits understanding of REE hyper-enrichment in deep-sea sediments, and impacts the reliability of REE signatures in bioapatite as palaeoceanographic tracers. In this study, we elucidate the mechanisms of REE hyper-enrichment from marine porewaters into bioapatite in the presence of Fe-Mn (oxyhydr)oxides and organic matter, using a combination of adsorption experiments integrated with micro-X-ray absorption fine structure (μ -XAFS), X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) analyses. Results demonstrate that bioapatite can rapidly adsorb REE from a simulated porewater environment (equilibrium time < 1 h) via the formation of stable inner-sphere complexes. XANES and EXAFS evidence further reveals that these complexes are strongly coordinated by PO_4^{3-} groups, as exemplified by Y^{3+} with well-defined coordination shells: Y-O (2.37 Å), Y-P₁ (3.50 Å), and Y-P₂ (3.71 Å), which maintains long-term REE retention in bioapatite. Furthermore, we show that organic matter regulates REE cycling through coupled direct and indirect pathways: (1) enhancing short-term REE adsorption onto bioapatite through complexation with C=O and O-H bonds, accounting for 79–94% of initial REE uptake; and (2) indirectly promoting long-term REE sequestration by driving the reductive dissolution of Fe-Mn (oxyhydr)oxides, which enhances the REE supply to porewaters for subsequent adsorption by bioapatite. We therefore propose that organic matter plays a central role in controlling REE hyper-enrichment by coupling REE sources (organic matter and Fe-Mn (oxyhydr)oxides) with long-term

38 retention in bioapatite during early diagenesis. This explains the spatial variability in REE
39 enrichment observed across Pacific sediments, and establishes a refined framework for evaluating
40 the early diagenetic alteration of REE signatures.

41

42 *Keywords:* Rare earth elements; Marine bioapatite; Organic matter; Fe-Mn (oxyhydr)oxides; REE
43 enrichment mechanisms

44

1. Introduction

The demand for rare earth elements (REE) has increased over recent years, as they are required for high-technology development and the green energy transition (Elderfield and Greaves, 1982; Haxel et al., 2002). To meet this growing demand, various potential REE sources are being explored. Traditionally, research on REE resources has focused on terrestrial deposits, such as carbonate-hosted (Anenburg et al., 2021; Yuan et al., 2024) and ion-adsorption deposits (Borst et al., 2020). In recent years, however, attention has gradually expanded beyond continental settings to marine environments. For example, continental shelves have been identified as potential REE resources (Pourret and Tuduri, 2017). In addition, deep-sea REE-rich muds ($\Sigma\text{REE} > 400$ ppm; Kato et al., 2011) have attracted increasing attention (Kashiwabara et al., 2018; Ohta et al., 2021). Within deep-sea REE-rich muds, Ca-phosphates (e.g., bioapatite-rich fossils and authigenic carbonate fluorapatite, CFA; Ren et al., 2022; Liao et al., 2025) and Fe-Mn (oxyhydr)oxides (e.g., micronodules; Kato et al., 2011) have been identified as the dominant carriers of REE (Fig. 1). Leaching experiments have shown that Ca-phosphates can account for approximately 70–90% of the total REE content of deep-sea muds, with bioapatite concentrations potentially reaching tens of thousands of ppm (Kim et al., 2022). However, fresh bioapatite is extremely REE-poor (< 3 ppm; Labs-Hochstein and MacFadden, 2006) compared to fossil bioapatite (up to 30,000 ppm; Bi et al., 2021) in the deep-sea sediment record. This stark contrast between fresh and fossil bioapatite highlights the potential role of diagenetic processes in controlling REE uptake.

Geochemical evidence suggests that the early diagenetic uptake of REE into bioapatite results from transfer of REE from carrier phases, in particular Fe-Mn (oxyhydr)oxides and organic matter (Deng et al., 2022). These mechanisms are generally conceptualized as a progression from initial surface adsorption to deeper structural integration, such as lattice incorporation (Liao et al.,

2019). Despite these advances, no study has directly examined how Fe-Mn (oxyhydr)oxides and organic matter regulate REE uptake into bioapatite at the molecular scale.

The high REE content in bioapatite is mainly attributed to contributions from porewater (Toyoda and Tokonami, 1990), whereby high REE-enriched porewaters favour formation of REE-rich bioapatite due to progressive diagenetic uptake of porewater REE (Bright et al., 2009). This process is controlled by the availability of REE in porewaters, which mainly relies on the amount of REE release from parental phases (Haley et al., 2004; Deng et al., 2017, 2022). In the shallow subsurface, while the high REE contents of porewaters are mainly sourced from the reduction of Fe-Mn (oxyhydr)oxides (De Baar et al., 1988) or the oxidation of organic matter (Freslon et al., 2014), or both (Haley et al., 2004; Deng et al., 2022). When bulk samples are considered, the REE content of bioapatite exceeds that expected to accumulate by adsorption alone (Chen et al., 2015; Ijiri et al., 2018). Furthermore, given the characteristically low organic matter content in deep-sea sediments, the degradation of organic matter would appear insufficient to sustain the high REE porewater contents required for such enrichment (Haley et al., 2004). Consequently, direct experimental and microscopic evidence is required to elucidate how these phases drive REE hyper-enrichment.

Observations on skeletal material (e.g., fish teeth and bones) reveal that REE uptake into bioapatite is often associated with the degradation of internal organic matter within bioapatite tissues during early diagenesis (Tütken et al., 2008). Notably, bioapatite in deep-sea sediments typically exhibits low total organic carbon contents alongside exceptionally high REE concentrations (Dubinin and Rims kaya-Korsakova, 2011; Yu et al., 2021), while continental margin bioapatite and phosphorites have higher total organic carbon contents but yield significantly lower REE levels (Lécuyer et al., 2004). These observations suggest a significant

correlation between organic matter removal and REE enrichment. However, it remains unclear whether organic matter degradation plays a role in facilitating REE enrichment.

In this study, we provide a new mechanistic perspective on REE hyper-enrichment in Pacific Ocean sediments by explicitly linking porewaters, organic matter, and Fe-Mn (oxyhydr)oxides dissolution to long-term REE retention in bioapatite. To achieve this, we integrate adsorption experiments with micro-scale characterization approaches (μ -XAFS, XANES and EXAFS).

2. Methods

2.1 Samples and materials

The teeth of *Lophius piscatorius* (monkfish) were obtained as frozen specimens from a commercial seafood market in Lianyungang, China. The large teeth of these deep-sea fish provide sufficient homogeneous material for precise sampling, with negligible initial REE content and serve as a suitable analogue for primary bioapatite prior to diagenetic modification. In addition, natural marine bioapatite (NAP) was obtained from deep-sea sediment collected from cruise DY-41 of the Chinese R/V *Hai Yang Liu Hao* in the western North Pacific Ocean (159°46'E, 17°23'N), at a water depth of 5652 m (Fig. 1A). The REE concentration in this NAP sample ranges from 2,500 to 33,000 ppm (averaging ~11,000 ppm; D. Li et al., 2023), which is suitable for XAFS analysis. Goethite and vernadite were selected as representative Fe-Mn (oxyhydr)oxides endmembers, representing contrasting Fe- and Mn-dominated adsorption behaviors that control REE scavenging and release (Liao et al., 2022).

Fresh bioapatite samples were obtained by soaking fresh *Lophius piscatorius* teeth in deionized water for 1 day. The samples were transferred into centrifuge tubes and freeze-dried

using a vacuum freeze-dryer (LGJ-50F) at -50°C under vacuum conditions ($<10\text{ Pa}$) for 24 h. The centrifuge tubes were sealed with perforated Parafilm to prevent contamination during drying. The dried samples were then ground to 200 mesh in a ball mill. These powders are rich in organic matter (sample AP-1). To remove this organic matter, a portion of the powder was treated with 30% hydrogen peroxide (H_2O_2) solution at 4°C , subsequently washed with alcohol and deionized water, and lyophilized (sample AP-2; Hyeong and Capuano, 2000; Jackson, 2005). The powder samples were then characterized by scanning electron microscope-energy-dispersive X-ray spectroscopy (SEM-EDS; Fig. 2) and X-ray diffraction analyses (XRD; Fig. S1), while total carbon (TC) contents were measured by isotope ratio mass spectrometry (IRSM, MAT 253 Plus). The apatite samples AP-1, AP-2 and HAP (hydroxyapatite from Macklin; Fig. S1) were then employed for the adsorption experiments and further analyses.

Goethite (Fig. S1) was obtained from Sigma-Aldrich. Vernadite (Fig. S1) was synthesized via the oxidation of MnCl_2 with KMnO_4 in an alkaline environment (Li et al., 2024), whereby a mixed solution of KMnO_4 and NaOH was reacted with MnCl_2 , stirred for 12 h and then left to stand for 4 h. The synthesized vernadite was subsequently separated by suction filtration and was purified via washing with 1 M NaCl and deionized water, followed by freeze-drying and grinding for further use.

For microanalysis, representative bioapatite (AP-1 and NAP) was mounted in resin and ground using a series of silicon carbide papers (from 200 to 20,000 grit) to expose the axial cross-sections. This procedure yielded a planar geometry, effectively removing the surface relief for subsequent measurements.

2.2 Adsorption experiments

Adsorption experiments followed established methods (Schmitt et al., 2023; Liang et al., 2024). The background electrolyte was 0.5 M NaNO₃ to simulate the ionic strength of marine porewaters, consistent with protocols for REE uptake in marine Fe oxide and phosphate systems (Ohta and Kawabe, 2000; Liang et al., 2024). NaNO₃ was chosen because NO₃⁻ is weakly coordinating, minimizing solution-phase REE complexation and thereby isolating uptake driven by bioapatite (Millero, 1992). A stock solution of REE was prepared by using 0.5 M NaNO₃ to dilute a multi-element standard solution of REE (1000 ppm of each REE in 5% HNO₃) from Aladdin Biochemical Technology Co., Ltd.

The adsorption experiments were carried out in 50 mL Corning centrifuge tubes at room temperature (25°C), as follows: 1) 45 mL of 0.5 M NaNO₃ was added to a centrifuge tube; 2) 1.4 mM of NaHCO₃ was added to one centrifuge tube to replicate the carbonate concentration of marine porewaters (Ohta and Kawabe, 2000), while a second centrifuge tube had no NaHCO₃ added; 3) a stock solution of REE was added to obtain 15 ppb (each REE), which was selected to provide ample signal for ICP-MS measurement and provide similar concentrations to REE-enriched porewaters, and to ensure chemical undersaturation; 4) to avoid localized over-saturation and subsequent REE-hydroxide formation, REE were introduced into a slightly acidic electrolyte (Ohta and Kawabe, 2000) before adjusting the pH to 7.1 (using < 30 µL of 0.05 M NaOH or 0.05 M HNO₃). This target pH prevents both bioapatite dissolution and REE precipitation, with the final volume fixed at 50 mL; 5) the prepared solutions were left overnight, prior to the adsorption experiments being performed. The above steps were performed in an ultra-clean laboratory (ambient air) and an anaerobic glove box (Ar: 98%; H₂: 2%) to isolate the influence of atmospheric CO₂. By comparing the results from these two settings, we can distinguish between surface

adsorption and CO₂-induced carbonate precipitation. This methodology ensures that the observed REE sequestration is driven primarily by adsorption rather than mineral precipitation.

Before kinetic studies, the effect of pH on REE adsorption was investigated (pH 1.71–7.28; ambient atmosphere). 5 mg of bioapatite was added to 50 mL of 15 ppb REE solution (equivalent to a mass/volume ratio of 0.1 mg/mL). Subsequently, kinetic experiments were conducted using the same mass/volume ratio for AP-1 and AP-2. All kinetic experiments were performed in duplicate to ensure the reproducibility of data. The mixture was constantly shaken to ensure complete contact. Reaction solutions (with bioapatite powder added) were incubated on a shaking table for 1 h, and filtered water samples were collected at 0, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 40, 50 and 60 mins. To isolate the influence of pH on adsorption kinetics, the pH of the suspension was strictly monitored and maintained at 7.1 via the addition of small volumes of dilute HNO₃ or NaOH. This regulation ensured a stable thermodynamic environment and constant proton concentration throughout the adsorption process.

Water samples were filtered using a MillexGP 0.22 µm filter and a sterile syringe. The filtrate was subsequently diluted 60–110 times with 2% HNO₃ and was analyzed on an Agilent ICP-MS 7700 (inductively coupled plasma mass spectrometer) equipped with an Agilent ASX-500 auto-sampler. Procedural blanks, certified reference standards and laboratory duplicates were processed alongside the samples. REE recovery ranged from 88% to 102%, with the relative standard deviation consistently below 5%. Despite dilution, the final concentrations remained significantly above instrumental detection limits (0.0001–0.0105 ppb), ensuring high signal-to-noise ratios. The adsorption ratio was calculated from the total amount of REE adsorbed by the sample and the REE concentration of the initial solution, as follows:

$$\text{Adsorption ratio(\%)} = \frac{\text{amount of REE adsorbed}}{\text{amount of REE initial}} \times 100$$

Based on the REE concentrations in each phase, the partition coefficient, K_d , between the solid and liquid phase was calculated as follows (Koeppenkastrop and De Carlo, 1992):

$$K_d = \frac{\text{conc. REE solid phase (ppb)}}{\text{conc. REE liquid phase (ppb)}}$$

2.3 Desorption experiments

Some solid residues were recovered after the adsorption experiments (detailed in section 2.2) and were used for REE desorption experiments. A two-step desorption experiment was carried out on these REE-adsorbed samples. First, 10.0 mM of sodium acetate ($\text{CH}_3\text{COONH}_4$) solution was added followed by 2.0 mM of disodium ethylenediamine tetraacetate (EDTA-2Na) solution, to sequentially extract adsorbed REE from the samples. In general, $\text{CH}_3\text{COONH}_4$ leaches ions fixed on the samples via surface exchange, while the EDTA-2Na ligand exhibits strong chelation and is commonly used to remove adsorbed metal ions from various materials (Xu et al., 2016; Qin et al., 2021). The residual phase after EDTA-2Na extraction might be related to the REE transitioning from being easily leachable to a more stable binding state (Li et al., 2024). While this bulk approach does not distinguish between surface adsorption and lattice substitution, it serves as a proxy for the stability of the REE binding modes. The percent desorption was calculated as:

$$\text{Desorption ratio(\%)} = \frac{\text{amount of REE desorbed}}{\text{amount of REE sorbed}} \times 100$$

2.4 Migration and leaching experiments

To prepare the REE-adsorbed mineral phases, REE were adsorbed onto goethite and vernadite (~30 mg in 500 mL of ~100 ppb REE solution) under the same conditions as the batch adsorption experiments (pH 7.1 and IS = 0.5 M NaNO_3). These mixtures (mass/volume ratio $\approx$

0.06 g/L) were shaken for 24 h to ensure adsorption equilibrium, as goethite and vernadite reach steady state within 24 h and 10 h, respectively (Liang et al., 2024; Ohta and Kawabe, 2001). REE adsorption from the supernatant was then quantified via ICP-MS (average REE adsorption ratio: > 99% for vernadite and ~ 48% for goethite), where the REE-adsorbed solids were separated from the final suspension with a membrane filter (0.22 μ m), then rinsed with deionized water and freeze-dried for subsequent migration experiments.

Chemical leaching can quantitatively assess the specific contribution ratio of different mineral components to the total REE in the sediment. To assess the proportion of REE migrating from Fe-Mn (oxyhydr)oxides to bioapatite, mixed samples were prepared by 5 mg of organic-rich bioapatite with 5 mg of REE-adsorbed vernadite or goethite in 0.5 M NaNO₃ (pH = 7.1). These mixtures were left to react in an anaerobic chamber for 10 days and then freeze-dried. The leaching of REE within bioapatite was as follows (Liao et al., 2022): Mixed samples were shaken with 20 mL of 1 M acetic acid/Na-acetate buffer (pH = 4.5) for 24 h, then centrifuged at 4000 rpm for 10 min. The supernatant was filtered using a 0.22 μ m filter and syringe and then diluted with 2% HNO₃ for REE analysis using an Agilent ICP-MS 7700.

2.5 XRD, SEM and IRSM analyses

XRD analyses were determined on a Rigaku Rapid II X-ray diffraction instrument in the School of Marine Sciences, Sun Yat-sen University (SYSU), at 50 kV and 30 mA with Mo K α radiation, and at a scan rate of 1°/s with a 0.02° step. The obtained images were converted to 2 θ versus intensity patterns using Rigaku's 2DP software. Finally, the PDXL software was used for data processing and mineral identification.

Microscale observations were performed at SYSU with a TESCAN MIRA Field Emission SEM coupled with a Bruker XFlash 6160 energy dispersive spectroscopy (EDS) detector. The

samples (bioapatite before and after the adsorption experiments) were fixed on the sample stages with conductive tapes, then coated with platinum. The analysis beam voltage and current were set as 15 kV and 1 nA, respectively. Images were collected in SE or BSE mode by scanning for 95 s with a resolution of 1024×1109 pixels.

Total carbon contents were measured by IRSM using a MAT 253 Plus at SYSU. A soil standard (Peat) sample with a carbon-certified value of 15.95 wt% was employed as the standard sample.

2.6 FTIR analyses

To obtain REE-adsorbed apatite samples for the Fourier transform infrared spectroscopy analysis (FTIR), experiments were conducted following the batch adsorption procedures described in Section 2.4. To ensure the REE concentration in the solids reached the detection threshold (> 1 wt%), a low mass/volume ratio was employed (0.02 g/L; 10 mg of sorbent in 500 mL of REE solution). Three series of adsorption experiments were conducted for both AP-1 and HAP substrates: one multi-element set (initial concentration of ~ 14 ppb for each REE), and two single-element sets (initial Nd and Y concentration of ~ 200 ppb each) representing LREE and HREE, respectively (Table S1). The REE-adsorbed apatite sample (~ 1 wt%) was then verified by ICP-MS analysis of the supernatant to ensure sufficient REE concentration in the apatite for FTIR characterization.

FTIR analysis was conducted using a Nicolet 6700 spectrometer equipped with a Continuum microscope at the Instrumental Analysis and Research Center at SYSU. For sample preparation, finely ground samples were mixed with KBr at a 1:80 ratio and then pressed into transparent slices. Measurements were recorded in transmission mode over a wavenumber range of 400 to 7500 cm^{-1} , at a resolution of 0.09 cm^{-1} and a signal-to-noise ratio of 5000:1, using a

triglycine sulfate (DTGS) detector. All data were recorded as absorbance spectra. To ensure accuracy, background scans were conducted before each measurement to automatically correct for atmospheric CO₂ and H₂O interference, and baseline corrections were applied using the OMNIC software.

2.7 μ -XRF mapping

The μ -XRF mapping was performed on polished axial cross-sections of the NAP fossil to represent the diagenetic end-state, as short-term experiments cannot capture REE uptake occurring on longer timescales. The mapping of the marine bioapatite was performed at the soft X-ray micro characterization beamline (SXRMB) and the very sensitive elemental and structural probe employing radiation from a synchrotron (VESPERS) at the Canadian Light Source (CLS) synchrotron. The beamline is an undulator beamline with a Si (111) monochromator (monochromator energy: 17111.56 eV), with an energy resolution ($\Delta E/E$) of 10^{-4} at 6215 eV. The fluorescence detector (1-el XMap Vortex) distance to the sample was 20.0 mm, and the sample was spatially scanned by a step size of 2.0 μm (horizontal, H) $\times$ 2.0 μm (vertical, V), using pulse motors. The intensity of the incident X-ray was measured using an ionization chamber filled with N₂. The X-ray was detected at each point with a dwell time of 2.0 s. The measurements were carried out under ambient conditions.

2.8 μ -XAFS measurement

μ -XAFS measurements of the NAP fossil were performed at the CLS under the same experimental conditions as μ -XRF mapping. High REE loading in this sample was required to meet the spectroscopic detection limits. The Nd L₃-edge XANES analyses were performed with Si (111) crystal monochromators at the SXRMB beamline, and the Nd L₃-edge XAFS spectra of

the sample were collected in fluorescent mode at room temperature. The Y K-edge EXAFS analyses were performed at the VESPERS beamline, and the XAFS spectra were collected in fluorescent mode. Negligible changes in the line shape and peak position of Nd L₃-edge XANES spectra and Y K-edge EXAFS spectra were observed between multiple scans taken from the sample. Spectral analysis was carried out with the XAFS analysis software Athena and Artemis (Ravel and Newville, 2005). Athena was used for all the main steps in data processing, including conversion of raw data to $\mu(E)$ spectra, background subtraction, and Fourier transformation. Artemis carried out curve fitting analysis in R space. The number of Y adjacent atoms, the distance between Y and adjacent atoms, and the Debye-Waller factor of marine bioapatite and reference materials were calculated by curve fitting analysis.

2.9 Diffusion-limited mass-balance modelling

To evaluate the physical feasibility of REE hyper-enrichment in bioapatite, a diffusion-limited mass-balance model was developed to integrate the intrinsic adsorption capacity observed in laboratory experiments with the physical flux constraints in sedimentary microenvironments. This modelling explicitly distinguishes between the surface-saturation regime, which characterizes the near-instantaneous adsorption kinetics observed in our batch experiments ($k_2 = 0.0183 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), and the supply-limited regime that governs long-term enrichment on geochemical timescales. Since surface equilibration is reached within approximately 30 mins in laboratory experiments, the supply-limited regime is invoked as appropriate for calculating enrichment durations. This choice accounts for the shift in the rate-limiting step from surface reaction kinetics in batch settings to the physical replenishment of REE via porewater diffusion in natural environments.

The enrichment duration (t) required to reach a target REE inventory (M_{req}) is estimated using a diffusion framework derived from Fick's First Law, where the supply rate is defined by the effective sediment diffusivity (D_{eff}), the total reactive surface area (A_{tot}), and the concentration gradient across a characteristic diffusion length (L). The mass-balance is formulated as (Berner, 1980; Burdige, 2007):

$$t = \frac{M_{\text{req}} L}{D_{\text{eff}} A_{\text{tot}} (C_{\infty} - C_s)}$$

where C_{∞} represents the bulk porewater REE concentration and C_s denotes the concentration at the mineral-water interface. Idealized boundary conditions were adopted, assuming a constant bulk concentration C_{∞} and taking $C_s \approx 0$ to represent the maximum potential concentration gradient. All transport parameters and boundary conditions utilized are detailed in Table S2. This approach ensures that the timescales of long-term REE build-up are explicitly distinguished from short-term adsorption kinetics. Accordingly, this model is intended to provide first-order constraints on enrichment timescales, rather than a full reactive-transport simulation.

3. Results

3.1 Morphology and structure of bioapatite

Leaching experiments confirmed that the surfaces of initial apatite samples (e.g., AP-1, AP-2 and HAP) contained no adsorbed REE (Supplementary Data 1). Analysis by artifacts, LA-ICP-MS further confirmed negligible REE concentrations in the internal matrix of the fresh fish teeth (below detection limits; Supplementary Data 2). These results demonstrate that fresh bioapatite has a very low initial REE abundance. Therefore, both the rapid REE uptake and the high REE concentrations in natural bioapatite fossils are interpreted to originate from external sources.

Compared to the original AP-1 powder, SEM-EDS and XRD analyses of treated AP-2 showed significant enamel damage and exposed porous dentine (Fig. 2), with EDS mapping and total carbon analysis (16.64 wt% in AP-1 vs. 11.70 wt% in AP-2) confirming the partial removal of organic components. Combined with XRD (Fig. S1) and FTIR (Fig. S2) evidence revealing that the mineral framework and lattice-bound carbonate remained stable, the lower total carbon content in AP-2 is interpreted to reflect the partial removal of labile carbon-bearing organic components during H₂O₂ treatment (Crowley and Wheatley, 2014). The absence of a pronounced decrease in the C=O band is attributed to the partial removal of organic components, which is consistent with the high residual carbon content in AP-2. Furthermore, SEM morphological analysis showed the bioapatite is stable after REE adsorption, with no discernible surface recrystallization or secondary precipitation (Fig. S3). This indicates that REE sequestration was primarily governed by surface adsorption rather than mineralogical transformations.

3.2 Adsorption behavior

The adsorption behavior of REE onto bioapatite is characterized by rapid kinetics and strong pH dependence, and is significantly influenced by the presence of organic matter (Fig. 3; Supplementary Data 3).

1) Adsorption kinetics: REE adsorption occurred rapidly, reaching equilibrium within 15–30 mins (Fig. 3). Notably, the presence of organic matter in bioapatite (AP-1) accelerated REE uptake relative samples with organic matter removed (AP-2), even under varying bicarbonate-buffered conditions ($\text{HCO}_3^- = 0\text{--}1.4\text{ mM}$; Figs. S4–S6). Adsorption kinetics were investigated under strictly anaerobic conditions (Revellame et al., 2020), with model selection performed using the corrected Akaike Information Criterion (AICc), where $\Delta\text{AICc} = \text{AICc}_i - \text{AICc}_{\min}$. For AP-1,

the pseudo-second-order (PSO) model provided the most best fit ($\Delta AICc = 0$), significantly outperforming the pseudo-first-order (PFO) model ($\Delta AICc = 32.8$; Fig. 3A and Table S3). The resulting rate constant, k_2 , was $0.0183 \pm 0.0009 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ($R^2 = 0.999$; $n = 2$). By contrast, adsorption kinetics for AP-2 were better described by the PFO model ($\Delta AICc = 0$ vs. PSO $\Delta AICc = 14.8$, Fig. 3B), yielding a k_1 of $0.107 \pm 0.007 \text{ min}^{-1}$ ($R^2 = 0.986$; $n = 2$). These results demonstrate that REE uptake by bioapatite is rapid, with organic matter significantly enhancing adsorption kinetics.

2) Desorption behavior: Desorption experiments were conducted to assess the stability of REE associated with bioapatite. The average extraction efficiencies for individual REE (La–Lu) via $\text{CH}_3\text{COONH}_4$ were minimal ($< 2\%$), whereas 55–74% of total REE were extracted by EDTA-2Na solution (Supplementary Data 4). These contrasting efficiencies indicate a strong and stable association between REE and bioapatite, consistent with those calculated by Visual MINTEQ ver. 3.1 (Supplementary Data 5; Gustafsson, 2018).

3) pH dependence: REE adsorption onto bioapatite exhibited strong pH dependence (Fig. 3C). Under atmospheric conditions, the adsorption ratio increased sharply from $\sim 5\%$ at $\text{pH} < 3$ to a plateau of $\sim 99\%$ at $\text{pH} > 4$ (Supplementary Data 6). In the blank experiments (without samples), a significant decrease in aqueous REE concentrations was observed at $\text{pH} > 4$, accompanied by the formation of a visible white precipitate. This indicates that REE precipitation contributes to apparent removal at elevated pH.

To isolate the adsorption behavior from precipitation effects, further experiments were conducted in a CO_2 -free glove box (Ar: 98%; H_2 : 2%) to simulate porewater conditions ($\text{pH} \sim 7$). Under these CO_2 -free conditions, no REE precipitation was observed even at $\text{pH} 6.8$ to 7.2 , indicating that the solids previously observed in ambient air were REE-carbonates induced by CO_2 .

availability. Consequently, a pH of 7.1 in a CO₂-free environment was selected for subsequent experiments (I $\approx$ 0.5 M; carbonate: 0 mM) to ensure that REE removal was driven solely by adsorption. This setup is consistent with previous studies (Gorman-Lewis et al., 2005; Ramazanov et al., 2025) and effectively maintains ~99% removal efficiency, while interference from REE precipitation or bioapatite dissolution is minimal.

3.3 Migration characteristics of REE adsorbed by Fe-Mn (oxyhydr)oxides to bioapatite

In simulating early diagenetic conditions, REE enrichment in bioapatite demonstrated a strong dependence on organic matter content. First, a significant positive correlation was observed between the organic matter content and final REE concentrations within the bioapatite (Fig. 4A), reflecting a higher capacity to capture REE in organic matter-rich samples. Second, during the 10-day reaction between organic matter-rich bioapatite (initially no adsorbed REE) and REE-adsorbed Fe-Mn (oxyhydr)oxide (Supplementary Data 1), the migration of REE to the bioapatite phase was confirmed via leaching experiments. To isolate the contribution from internal organic matter, the migration data were baseline-corrected using organic matter-free hydroxyapatite control groups (Fig. 4B; Supplementary Data 1). Concurrently, dissolved Mn was detected in the supernatant (Supplementary Data 1), which is consistent with the reductive dissolution of Mn oxides via reaction with organic matter (Ye et al., 2025). This process facilitated the release of REE from the oxides and their subsequent accumulation in bioapatite (Fig. 4B). Notably, the extent of this REE migration was also positively correlated with the organic matter content of bioapatite.

3.4 FTIR analyses of bioapatite before and after adsorption experiments

FTIR spectra of AP-1 and HAP exhibit high consistency before and after adsorption to Nd, Y and total REE (Fig. 5). Both the initial and treated samples display the characteristic bands of the amide vibration region, the organic O-H band, and phosphate (PO₄) vibrations, with highly consistent spectral profiles maintained across all groups (Figs. 5A and C). Compared with the initial samples, the treated samples show only minor fluctuations in band intensities, accompanied by subtle yet systematic peak-position shifts (Figs. 5B and D). Although small, these shifts consistently exceed the instrumental resolution (0.09 cm⁻¹). These systematic shifts, occurring under controlled experimental conditions and using homogeneous starting materials, indicate that the vibrational states of the functional groups were affected by REE adsorption.

3.5 μ -XRF and μ -XAFS analyses of bioapatite

μ -XRF mapping of the NAP fossil reveals that Nd and Y are primarily concentrated within the bioapatite interior (Figs. 6C and D; Fig. S7), confirming REE incorporation into the structure rather than remaining restricted to the surface over geological timescales. Due to the spectral overlap of the Nd L₃-edge with neighboring Ce and Pr, Y was selected as a proxy to enable precise EXAFS coordination analysis of the REE group (particularly HREE), as Y is free from spectral overlaps.

The Nd L₃-edge and Y K-edge XANES spectra of bioapatite are similar to those of the Nd₂O₃ and Y₂O₃ standards (marked by blue dashed lines in Figs. 6E and F), showing that Nd and Y are present as trivalent cations. Further structural details from Y EXAFS radial structural functions (RSFs: phase shift uncorrected) exhibit three distinct coordination shells between 1.0 Å to 4.0 Å (Figs. 6G and H; see parameters in Table 1).

The first coordination sphere (Y-O shell; CN $\approx$ 8) is consistent with characteristic HREE-O coordination (Habenschuss and Spedding, 1979). The Debye-Waller factor (σ^2) reflects the static disorder from inner-sphere complexes, where hydrated Y³⁺ ions share oxygen atoms with the solid surface (Yamaguchi et al., 1988). Crucially, the Y-P₁ and Y-P₂ shell distances correspond to the P=O $\rightarrow$ Y-O-P linkages and other phosphate-associated REE forms. These results confirm that Y primarily binds to the phosphate sites within bioapatite.

4. Discussion

4.1 Two-stage REE sequestration in bioapatite from initial adsorption to stable coordination

The rapid adsorption of REE by bioapatite, starting from REE-free fresh bioapatite (see Section 3.1), provides critical insight into REE enrichment during early diagenesis in marine environments. At initial concentrations of 15 and 100 ppb, the adsorption ratio exceeded 99% within 30 mins (Figs. 3A and B; Fig. 4A). Notably, increasing the initial concentration further reduced the equilibrium time to 15 mins (e.g., AP-2; Fig. 3B and Fig. 4A). These rapid adsorption kinetics are comparable to that of abiotic hydroxyapatite (Gad and Youssef, 2018), possibly due to a similar crystal structure (Fig. S1). Given the stability of the bioapatite structure (Fig. S3) and the absence of significant Ca²⁺ release (Fig. 3C), formation of new adsorption sites and ion competition are unlikely drivers for this kinetic acceleration. Instead, the acceleration may be primarily driven by the enhanced concentration gradient, promoting faster diffusion of REE ions into internal sites. This trend is consistent with heavy metal adsorption (e.g., Patel, 2020). Such rapid REE adsorption from porewater provides a plausible explanation for the enrichment (increasing from < 1 ppm to 3–4 orders of magnitude higher) observed in fossil bioapatite within c–10 kyr after burial (Finlay et al., 2013).

The adsorption of REE by bioapatite is irreversible (i.e., showing no significant desorption) under simulated porewater conditions (pH 7.1; $I \approx 0.5$ M; carbonate 0–1.4 mM). The desorption ratio was negligible ($< 1.1\%$) when leached by $\text{CH}_3\text{COONH}_4$, whereas 55–74% of the adsorbed REE were extracted by EDTA-2Na (Supplementary Data 4). The minimal release in $\text{CH}_3\text{COONH}_4$ indicates that REE retention is not driven by reversible outer-sphere complexation. By contrast, significant leaching by EDTA-2Na suggests that REE are mainly immobilized via inner-sphere complexes, rather than outer-sphere complexes or precipitation (Qin et al., 2021; Liang et al., 2024). This is consistent with adsorption kinetic results (e.g., for AP-1, the PSO model is uniquely supported; Table S3). FTIR spectra further support this, maintaining broadly similar characteristics after REE treatment with subtle and systematic peak shifts in the C=O and PO_4^{3-} bands (Fig. 5; Eischens and Pliskin, 1958; Grunenwald et al., 2014; Marques et al., 2021). HAADF-STEM imaging and EDS mapping were also conducted on the REE-adsorbed AP-1 powder (see Supplementary Information). The REE show a relatively uniform distribution across the bioapatite surface at the nanometer scale (Figs. S8–10) while EDS spectra further confirm the existence of REE. While these observations clarify the initial mechanisms of REE sequestration, the short experimental duration is insufficient to replicate long-term diagenetic processes.

To further understand the final occurrence state of REE over geological timescales, spectroscopic characterization was conducted on natural marine bioapatite as a representative endmember. As expected, XANES spectra of the NAP fossil confirm that Nd and Y are sequestered in their trivalent states (Figs. 6E and F), providing a basis for subsequent EXAFS structural analysis. Building upon this, the EXAFS data characterize the local coordination environment of REE, including a primary Y-O shell at 2.37 Å alongside two distinct Y-P coordination shells at 3.50 Å and 3.71 Å (Figs. 6G and H; Table 1). These structural features align

with those reported for apatite (Kashiwabara et al., 2018), demonstrating that the inner-sphere phosphate complexation represents the predominant retention mechanism for long-term REE retention in bioapatite. Notably, the similarity between the interatomic distance of observed Y-O (2.37 Å) and that of Ca-O (2.29–2.43 Å) suggests the REE structurally ordered in the apatite matrix. This interpretation is also consistent with previous HAADF-STEM observations in fossil bioapatite (Liao et al., 2019). Since substituting divalent Ca^{2+} with trivalent REE^{3+} necessitates charge balance, this incorporation is stabilized by three possible coupled substitutions. Given the sodic nature of the porewater environment, $\text{REE}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Ca}^{2+}$ and $\text{REE}^{3+} + \text{O}^{2-} \leftrightarrow \text{Ca}^{2+} + \text{OH}^-$ (Anenburg et al., 2024) may represent a key pathway, while $\text{REE}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$ (Liao et al., 2019) may also contribute to the REE uptake. Notably, carbonate and silica can balance the charge through a coupled substitution ($\text{SiO}_4^{4-} + \text{CO}_3^{2-} \leftrightarrow 2\text{PO}_4^{3-}$), and their combined presence enhances the substitution of both (Anenburg et al., 2025). The resulting crystal structure defects could then enable the REE enrichment observed in carbonate-rich bioapatite fossils. We thus propose that REE enrichment in bioapatite follows a two-stage process: rapid adsorption dominates the initial REE uptake, while long-term enrichment depends on subsequent structurally stable coordination into the apatite lattice during diagenesis. This transition from surface adsorption to structural incorporation may require mineral recrystallization and dissolution-reprecipitation (Qin et al., 2021; Kral et al., 2022), consistent with evidence that diagenesis modifies the apatite lattice through ionic substitution (Keenan et al., 2015). The extent of this transition is likely controlled by both kinetic (e.g., reaction time and recrystallization extent) and chemical effects (e.g., porewater composition and charge-balance constraints).

4.2 Porewater scarcity as the primary limiting factor for REE enrichment

Although the adsorption mechanism is well constrained, the connection between REE hyper-enrichment and porewater chemistry remains poorly understood. Notably, REE contents in bioapatite covary with porewater REE profiles (Fig. S11), rather than increasing linearly with sediment age. This suggests that enrichment is not a simple cumulative function of time but is instead governed by the available REE pool in porewaters.

To evaluate this dependency, we constructed a mass-balance model (see Method 2.9) following the diffusion-limited framework. We parameterized the model using idealized transport limits (e.g., D_{eff} , φ , θ^2) and assumptions detailed in Table S2, to quantify the enrichment timeframe. The equation decouples long-term REE build-up from the near-instantaneous surface-saturation kinetics ($k_2 = 0.0183 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$), as follows:

$$t = \frac{0.03 \times 0.025}{(4.0 \times 10^{-10}) \times 0.026 \times 0.015} = 4.81 \times 10^9 \text{ s} \approx 1.52 \times 10^2 \text{ year}$$

This calculation indicates that under an idealized supply-limited regime with a constant porewater REE concentration of 15 ppb (our simulated concentration) and instantaneous replenishment, bioapatite could theoretically reach 30,000 ppm in approximately 150 years. While such enrichment is ultimately constrained by charge balance, this model highlights high theoretical supply potential under idealized conditions. However, this timeframe is predicated on an elevated REE supply. In situ deep-sea porewater REE concentrations are typically 10^{-2} to 10^{-1} ppb (Deng et al., 2017, 2022; Yang et al., 2018), three orders of magnitude lower than our experimental conditions. Consequently, the theoretical enrichment period extends by 100 to 1000 times, shifting the system into a steady-state supply-limited regime. Our box model (see Supplementary Information; Fig. S12) indicates that hyper-enrichment requires sustained REE release from reactive phases rather than porewater renewal alone. Thus, additional sources (e.g., organic matter-

mediated and Fe-Mn dissolution; [Haley et al., 2004](#); [Deng et al., 2022](#)) are essential to sustain porewater REE at levels compatible with the observed inventories.

Within this supply-limited box model, sustained low-flux REE supply implies protracted timescales for hyper-enrichment, aligning with fossilization records of 1 kyr to 10 Myr ([Trueman and Tuross, 2002](#)). Such a sluggish supply prevents rapid chemical homogenization, consistent with the low internal diffusion coefficient (c. $70 \text{ mm}^2 \text{ Myr}^{-1}$; [Toyoda and Tokonami, 1990](#)) and the non-uniform distribution observed in our polished axial cross-sections ([Figs. 6A–D and Fig. S7](#)). This framework explains why (bio)apatite in calcite-rich continental margin phosphorites has low average REE concentrations ([Hein et al., 2016](#)), as it will compete with calcite for the limited REE pool. Hence, our results suggest that REE hyper-enrichment is primarily constrained by the availability of REE in porewaters rather than the adsorption capacity of bioapatite itself. This also precludes the possibility that enrichment is achieved solely through high bioapatite abundance ([Ohta et al., 2020](#)). As a result, identifying the geochemical factors that generate and maintain high-REE porewaters is essential for understanding REE hyper-enrichment processes in deep-sea sediments.

4.3 Additional REE adsorption by organic matter

Our work provides direct evidence that organic matter within bioapatite acts as an additional source of high-affinity adsorption sites, significantly accelerating REE capture during the earliest stages of fossilization ([Figs. 3A and B](#)). In the initial reaction stage, the high-organic matter sample (AP-1, TC = 16.6 wt%) exhibited a ~61% higher REE adsorption ratio than the low-organic matter sample (AP-2, TC = 11.7 wt%) within the first 3 mins ($\Delta = 60.8\% \pm 12.9\%$, $n = 2$). This disparity narrowed to 10% after 15 mins as both samples approached a kinetic plateau ($\Delta =$

10.3% $\pm$ 2.4%, n = 2). This trend indicates that a higher abundance of internal organic matter provides an additional pool of accessible sites that dominate the initial uptake flux, though this advantage diminishes as these sites reach saturation (Fig. 2F).

FTIR spectra for the samples before and after REE adsorption are broadly similar, but subtle and systematic peak shifts are observed in the amide vibration region (1230–1640 cm⁻¹), including the C=O stretching band at ~1640 cm⁻¹ (Figs. 5A and B; Kimura-Suda et al., 2009; Scaggion et al., 2024). These minor shifts suggest that the vibrational environments of C=O functional groups were modified following REE adsorption, consistent with REE adsorption by organic matter in aqueous systems (Pavlova et al., 2023). However, substantial band overlap in the bioapatite matrix prevents quantitative separation of carboxyl versus amide group contributions. To isolate abiotic pathways, freeze-dried samples were utilized to suppress biological activity, distinguishing chemical processes from microbially-mediated mechanisms (Kleber et al., 2021). The sustained rapid kinetics under these conditions suggest that abiotic chemical complexation dominates the early adsorption process. Furthermore, internal organic matter contributes 79–94% of initial REE adsorption (Table 2), consistent with findings that organic coatings on fossil fish teeth contain up to 70% of the total REE content (Huck et al., 2016).

Organic matter-REE complex stability may be modulated by carbonate availability and ionic strength, as carbonate complexation can compete with organic matter-bound REE. This effect is directly constrained by our bicarbonate-buffered experiments (HCO₃⁻ = 0–1.4 mM). With ionic strengths similar to porewaters, adsorption ratios are less sensitive to carbonate fluctuations when organic matter is retained, whereas sensitivity increases markedly after organic matter removal (Fig. S4). Reduced sensitivity in samples with organic matter is consistent with strong

REE-organic matter complexation (Pourret et al., 2007). Notably, carbonate ions drive REE fractionation (Figs. S5 and S6), including a bicarbonate-driven lanthanide tetrad effect (Fig. 3D).

To verify this signal, we used the BLambdaR method (Anenburg and Williams, 2022) with Ce and Eu excluded from the fitting process. We observed a consistently positive τ_1 signature (averaging ~ 0.032) across all carbonate-influenced samples, compared to values near zero (averaging ~ 0.004) in the control group (Supplementary Data 7). Although fractionation in the other tetrad groups was statistically insignificant, this systematic contrast suggests a subtle but consistent M-type tetrad trend in the presence of carbonate. Its absence in carbonate-free systems suggests that internal organic matter alone is comparatively non-selective (Fig. 3D). Therefore, the final REE distribution reflects competitive complexation between aqueous carbonate and organic matter, where carbonate modulates selective partitioning and tetrad trends in marine environments.

In our mass-balance box model, enhanced initial uptake by organic matter does not necessarily translate into net accumulation, as bioapatite hyper-enrichment is ultimately constrained by the long-term flux of REE replenishment into porewaters. This coupling between adsorption potential and supply flux explains why the role of organic matter differs across depositional settings. Although REE exhibit a strong covariance with organic matter in deep-sea porewater and leaching experiments (Haley et al., 2004; Freslon et al., 2014; Deng et al., 2022), this relationship is decoupled in shallow-sea environments where REE concentrations in bioapatite and marginal phosphorites remain relatively low despite high organic matter abundance (Felitsyn and Morad, 2002; Hein et al., 2016).

We propose that this discrepancy stems from the opposing roles of internal versus external organic matter sources. While internal organic matter (e.g., within the bioapatite matrix) provides high-affinity sites to facilitate capture, an abundance of external organic matter (e.g., from primary

productivity; PP) in shallow-sea environments transforms it into a competing sink rather than a carrier. Rapid burial in these marginal settings hinders the degradation of external organic matter (Jahnke et al., 1990), effectively locking REE within the sediments and limiting their release to porewaters. Furthermore, similar to its role in apatite, calcite precipitation through ionic substitution (e.g., $\text{REE}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Ca}^{2+}$; Marques Fernandes et al., 2008) further depletes the available pool, acting as a competing sink. This external scavenging results in a depleted porewater flux, representing a significant supply limitation. For example, in shallow sea sediments with high organic matter burial (c. $200 \text{ mmol m}^{-2} \text{ y}^{-1}$), porewater REE concentrations may be one order of magnitude lower than those in the deep-sea (10^{-1} and 10^0 ppb, respectively; Soyol-Erdene and Huh, 2013; Deng et al., 2022).

4.4 Organic matter-mediated Fe-Mn (oxyhydr)oxide dissolution

Our simulation experiments, conducted under strictly anaerobic conditions, demonstrate that REE migration onto bioapatite is coupled with the removal of internal organic matter and the dissolution of Fe-Mn (oxyhydr)oxides. Using a 0.5 M NaNO_3 background electrolyte ($\text{pH} = 7.1$) to ensure physicochemical stability, the absence of carbonate favored the reductive dissolution of Mn(IV) and Fe(III) phases. Net REE migration shows a positive correlation with internal organic matter content within the bioapatite (Fig. 4B). In addition, significant concentrations of dissolved Mn in the post-reaction solutions provided direct evidence for the reductive dissolution of Fe-Mn (oxyhydr)oxide phases (Supplementary Data 1). These findings align with observations from natural samples (Elderfield and Sholkovitz, 1987) and synthetic material studies (Grybos et al., 2007), supporting a coupled role of internal organic matter and Fe-Mn (oxyhydr)oxides in facilitating cross-phase transfer of REE into the diagenetic aqueous pool.

The mechanistic interpretation of this migration is that internal organic matter serves as an electron donor, facilitating the reduction of Fe(III) and Mn(IV) to their dissolved states via electron transfer (Dong et al., 2023; Ye et al., 2025). This process subsequently liberates the adsorbed REE pool into the surrounding porewater. In our box model, this redox-driven release replenishes the porewater pool, sustaining uptake and long-term retention by bioapatite. This coupled cycling between organic matter degradation and Fe-Mn oxide dissolution is corroborated by REE fractionation patterns. Unlike fresh bioapatite, which shows LREE enrichment (Fig. 3D), fossil bioapatite from REE-rich Pacific muds shows HREE enrichment and strongly negative Ce anomalies (Fig. 7A; Kon et al., 2014; Liao et al., 2019). This fractionation mirrors the REE migration from Fe-Mn (oxyhydr)oxide (e.g., vernadite) into bioapatite as illustrated in our schematic model (Fig. 7B). These results show that diagenetic conditions, rather than the initial seawater signal, dominate REE enrichment in bioapatite (Deng et al., 2022).

Cerium anomalies provide additional insight into oxide-mediated REE cycling, because Ce can be oxidized to Ce(IV) and preferentially scavenged by oxide phases. Positive Ce anomalies in organic-rich particulate material may persist even during remineralization, if oxygen remains sufficient to stabilize the oxidized Ce-oxide (Haley et al., 2004), whereas Fe-Mn (oxyhydr)oxides during redox-driven mineral transformations can generate positive Ce anomalies in solid phases (Manceau et al., 2022). In our experiments, positive Ce anomalies were initially observed in bioapatite with organic matter (Fig. 3D), indicating that organic matter contributes to the preservation of this signal under simulated porewater conditions. However, after subsequent interaction with REE-adsorbed Mn oxides, the bioapatite developed negative Ce anomalies, whereas the residual Mn oxides retained positive Ce anomalies (Fig. 7B). These results are consistent with early diagenetic processes where Mn reduction and organic matter degradation

may partially remobilize Ce and modify bioapatite signatures (Freslon et al., 2014; Wang et al., 2025). As a result, Ce anomalies in bioapatite (Zhang et al., 2026) likely reflect signals from coupled Fe-Mn oxide and organic matter processes, and should therefore be interpreted with caution when used as paleoredox indicators.

4.5 Implications for REE hyper-enrichment in deep-sea sediments

The spatial variation of REE enrichment in marine environments is fundamentally governed by coupling between REE sources (Fe-Mn (oxyhydr)oxide and organic matter), the primary sink (phosphorus (P), including bioapatite and CFA), and the diagenetic driver (organic matter degradation). While REE sequestration occurs globally, continental shelves exhibit diluted REE signals compared to deep-sea sediments, reflecting distinct sedimentation regimes and diagenetic conditions. Integrating our experimental results with REE spatial distribution data, we evaluate these variations of REE enrichment through three scenarios based on the diagnostic triad of P, organic matter, and Fe-Mn:

1) Low to moderate enrichment under restricted coupled cycling. On continental margins such as the Peru shelf, intense upwelling and high PP result in elevated phosphate and organic matter (Piper et al., 1988), but the absence of the dissolution-precipitation cycle of Fe-Mn (oxyhydr)oxides restricts the REE supply. Rapid burial of coastal organic matter further hinders coupled cycling, maintaining enrichments at < 500 ppm (Fig. 8A). This suppressed partitioning is shown by negligible Ce anomalies ($Ce/Ce^* \approx 1$) and near-flat PAAS-normalized REE patterns ($(La/Yb)_N \approx 1$), confirming REE decoupling from seawater or porewater fluxes. Crucially, these signatures reflect the absence of efficient REE scavenging by Fe-Mn (oxyhydr)oxides where seawater REE contributions are negligible (Piper et al., 1988). Low and unstable REE/P ratios (0–

1.2×10⁻³) further indicate an unfilled P-sink highly sensitive to minor porewater variations. Similarly, in seamount settings, REE enrichment remains below 2000 ppm (Fig. 8B; Peng et al., 2024) due to limited organic matter inhibiting reductive dissolution of Fe-Mn phases. The lack of a strong diagenetic influence is supported by the observation that CFA within Fe-Mn crusts does not undergo significant diagenesis (Peng et al., 2024). Consequently, although REE/P ratios increase to ~7.81×10⁻³, the Ce/Ce* values (~0.5) primarily reflect passive inheritance of background signatures, rather than diagenetic amplification.

2) Moderate enrichment under sink-limited sequestration. In regions such as the Clarion-Clipperton Fracture Zone (CCFZ), abundant Fe-Mn (oxyhydr)oxides coupled with a moderate particulate organic carbon flux (Baker and Beaudoin, 2013) promote REE mobilization and benthic transfer (Kim et al., 2022; Xiang et al., 2024). However, low phosphorus availability (< 2.0 wt%, compared to up to 13.1 wt% in the western Pacific Ocean; Fig. S13; Tanaka et al., 2020) acts as a critical bottleneck for stable REE sequestration within apatite. Consequently, despite efficient diagenetic processing, REE enrichment remains restricted to an average content of less than 1000 ppm (Fig. 8C). This decoupling is characterized by a high capture efficiency per unit of phosphate, but insufficient sink abundance. Diagnostic proxies, including significant negative Ce anomalies (Ce/Ce* = 0.3–0.6) and pronounced MREE enrichment (ΣREE > 400 ppm; Kim et al., 2022), indicate that bioapatite effectively scavenges REE from porewaters. This high partitioning efficiency is manifested by exceptionally elevated REE/P ratios (range from 200×10⁻³ to over 1000×10⁻³; Kim et al., 2022; Xiang et al., 2024), signifying an efficient diagenetic pump that drives high REE loading in each phosphate grain. However, the total REE concentration is restricted by the scarcity of phosphate, highlighting that a deficient P-sink fundamentally limits hyper-enrichment in these settings.

3) Hyper-enrichment through synergistic interaction among the three components (REE sources, a primary bioapatite / CFA sink and a diagenetic driver). In the western North Pacific, enhanced eolian dust input and nutrient-rich currents promote both organic matter supply and Fe-Mn (oxyhydr)oxide formation (Ohta et al., 2016; Tanaka et al., 2020; Liao et al., 2024). Combined with relatively slow sedimentation rates (Iijima et al., 2016), vigorous coupled cycling is sustained and drives REE hyper-enrichment to levels up to ~7000 ppm (Fig. 8D; Tanaka et al., 2020). This scenario can be detected by geochemical proxies reflecting profound diagenetic amplification. Pronounced negative Ce anomalies ($Ce/Ce^* = 0.1\text{--}0.2$) and significant HREE enrichment ($(La/Yb)_N < 0.5$) indicate robust coupling between the REE budget and porewater fluxes, driven by repetitive redox cycling of Fe-Mn carriers (Iijima et al., 2016; Tanaka et al., 2020). This efficiency is demonstrated by stabilized and high REE/P ratios (averages $\sim 80 \times 10^{-3}$) in high REE layers. Unlike the coupled cycling-limited or sink-limited scenarios, these sediments represent a balanced optimization where a large P-sink is efficiently utilized by a high-flux diagenetic pump. The sequestration potential of the apatite is fully realized in this scenario, establishing the essential prerequisites for REE hyper-enrichment in the deep-sea.

Combining our experimental evidence with spatial patterns identified across the Pacific, we propose a REE hyper-enrichment model for deep-sea sediments with a slow deposition rate, which occurs via the following mechanisms during early diagenesis: 1) organic matter degradation (internal and external) encourages the dissolution of Fe-Mn (oxyhydr)oxides in reducing environments, releasing substantial REE into porewater during this initiation phase (Figs. 9A and B); 2) Continuous deposition and degradation of organic matter enhances the reduction-reprecipitation cycles of Fe-Mn (oxyhydr)oxides, and this coupled cycling mechanism further increases REE availability (Fig. 9B); 3) Under a steady-state supply-limited regime, the release

flux of REE from these coupled sources (organic matter degradation and Fe-Mn reduction) governs the overall enrichment rate. This slow replenishment explains the protracted timescales (1 kyr to 10 Myr) required to reconcile near-instantaneous surface adsorption with long-term hyper-enrichment (Fig. 9C); 4) Bioapatite acts as the long-term REE reservoir/carrier, where REE steadily accumulate through chemical complexation, thereby achieving the observed hyper-enrichment during early diagenesis (Fig. 9D).

These processes are likely modulated by large-scale climate variability, as the formation of bioapatite, organic matter and Fe-Mn (oxyhydr)oxides is controlled by climate-driven variables, such as ocean currents and dust input. Among these, upwelling can substantially enhance marine PP, increasing organic matter deposition and potentially boosting fish biomass. However, the link between climate change and fish production remains debated. Some studies suggest that topographically induced upwelling during the late Eocene cooling event caused fish proliferation and subsequently REE enrichment (Ohta et al., 2020), while others argue that such effects were minimal, with pelagic fish production remaining largely stable during the Eocene–Oligocene transition (Sibert et al., 2020). Meanwhile, observations from regions like the Indian Ocean (DSDP Site 223) over the past ~20 million years indicate a negative correlation between marine organic carbon burial and REE enrichment (Yasukawa et al., 2016; Z. Li et al., 2023). This pattern may reflect a complex balance between organic matter degradation and sedimentary redox conditions: lower carbon burial rates imply greater remineralization, which intensifies the reductive dissolution of Fe-Mn (oxyhydr)oxides and promotes REE release. Consequently, enhanced organic matter and its degradation, by driving the formation of redox boundaries, may represent an important factor in REE hyper-enrichment, although the extent and significance of this relationship requires further investigation.

709

710 **5. Conclusions**

711 This study provides molecular-scale insights into REE enrichment mechanisms in marine
712 bioapatite by combining adsorption experiments with comprehensive characterization techniques
713 (e.g., XRF and XAFS). We demonstrate REE hyper-enrichment is driven by coupled cycling
714 between organic matter degradation and Fe-Mn (oxyhydr)oxide dissolution during early
715 diagenesis. Unlike purely inorganic adsorption, internal organic matter within bioapatite facilitates
716 rapid REE adsorption from simulated porewaters via the formation of stable inner-sphere
717 complexes. Simultaneously, organic matter degradation promotes the reductive dissolution of Fe-
718 Mn (oxyhydr)oxides, releasing additional REE into porewater. This adsorption in bioapatite is
719 irreversible and remains far from saturation, allowing for sustained and repeated adsorption that
720 contributes to the observed hyper-enrichment in natural settings. Our findings highlight that
721 coupled cycling of organic matter degradation with Fe-Mn (oxyhydr)oxide dissolution controls the
722 efficiency and extent of REE enrichment, thereby providing new understanding on the cycling and
723 burial of REE in deep-sea sediments.

724 Beyond sedimentary environments, these findings have implications for REE recycling
725 during subduction. By constraining how REE and Ce anomalies are retained and modified in
726 bioapatite, this study helps constrain how REE are involved in deep Earth cycling. REE-rich
727 sedimentary components can contribute to mantle REE enrichment during subduction ([Zhu et al.,
728 2024](#)). Our results align with the view that the stable sequestration of REE into apatite likely limits
729 REE mineralization in carbonatites and magmas ([Li et al., 2025](#); [Qiu et al., 2025](#)). The strong
730 retention of REE within the apatite lattice may help explain why the negative Ce anomalies
731 characteristic of REE-rich marine sediments are not always recycled into mantle-derived

carbonatite deposits (Anenburg and Liu, 2024). While these findings provide new perspectives on the ultimate origin of REE in carbonatites, further research is required to bridge the gap between initial sedimentary enrichment and deep magmatic-hydrothermal enrichment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (42422306 and 42272066) (D.F.L.), (92262304) (X.M.S.), the MNR Key Laboratory for Exploration Theory & Technology of Critical Mineral Resources (202403), and Fundamental Research Funds for the Central Universities (23lgbj024) (D.F.L.). DC acknowledges support from Research Ireland under Grant Number 13/RC/2092_P2 (iCrag, the Research Ireland Centre in Applied Geosciences). We thank Dr. Yuzhou Feng for support with XRF and XAFS analyses, and writing suggestions from Huacheng Xu and Junyue Wang. This manuscript was significantly improved by the constructive reviews of Dr M. Anenburg, an anonymous reviewer and associate editor Prof. M. Davranche.

Appendix A. Supplementary material

Supplementary material to this article mainly includes research data and detailed descriptions of the box model.

Data Availability

756 The authors declare that all data supporting the findings of this study are available within
757 the paper and its supplementary files. Data are available through Mendeley Data at:
758 [\[http://dx.doi.org/ 10.17632/9kdv8yp5mh.2\]](http://dx.doi.org/10.17632/9kdv8yp5mh.2).

References

- Anenburg M., Broom-Fendley S. and Chen W. (2021) Formation of Rare Earth Deposits in Carbonatites. *Elements* **17**, 327–332.
- Anenburg M. and Williams M. J. (2022) Quantifying the Tetrad Effect, Shape Components, and Ce–Eu–Gd Anomalies in Rare Earth Element Patterns. *Math Geosci* **54**, 47–70.
- Anenburg M. and Liu Y. (2024) A Global Marine Sediment Compilation and a Cerium Anomaly Perspective on Metasomatized Mantle Sources for REE-Mineralized Carbonatites. *JGR Solid Earth* **129**, e2023JB028546.
- Anenburg M., Panikorovskii T. L., Jennings E. S., Shendrik R. Yu., Antonov A. A. and Gavrilenko V. (2024) An Apatite-Group Praseodymium Carbonate Fluoroxylbritholite: Hydrothermal Synthesis, Crystal Structure, and Implications for Natural and Synthetic Britholites. *Inorg. Chem.* **63**, 11788–11801.
- Anenburg M., Chen J., Gardiner M. G., De Hoog J. C. M., Humphreys M. C. S., Missen O. P., Mills S. J. and Pašić B. (2025) Silica substituted carbonate apatite: synthesis and analytical challenges. *J. Mater. Chem. B* **13**, 9968–9981.
- Baker E. and Beaudoin Y. (Eds.) (2013). *Deep Sea Minerals: Manganese Nodules, a physical, biological, environmental, and technical review*. Vol. 1B, Secretariat of the Pacific Community, Suva, Fiji.
- Berner R. A. (1980) Diagenetic Physical and Biological Processes. In *Early Diagenesis: A Theoretical Approach*. Princeton University Press, Princeton, pp. 15–56.
- Bi D., Shi X., Huang M., Yu M., Zhou T., Zhang Y., Zhu A., Shi M. and Fang X. (2021) Geochemical and mineralogical characteristics of deep-sea sediments from the western North Pacific Ocean: Constraints on the enrichment processes of rare earth elements. *Ore Geology Reviews* **138**, 104318.
- Borst A. M., Smith M. P., Finch A. A., Estrade G., Villanova-de-Benavent C., Nason P., Marquis E., Horsburgh N. J., Goodenough K. M., Xu C., Kynický J. and Geraki K. (2020) Adsorption of rare earth elements in regolith-hosted clay deposits. *Nat Commun* **11**, 4386.
- Bright C. A., Cruse A. M., Lyons T. W., MacLeod K. G., Glascock M. D. and Ethington R. L. (2009) Seawater rare-earth element patterns preserved in apatite of Pennsylvanian conodonts? *Geochimica et Cosmochimica Acta* **73**, 1609–1624.
- Burdige D. J., (2007) *Geochemistry of Marine Sediments*. Princeton University Press, NJ.
- Chen J., Algeo T. J., Zhao L., Chen Z.-Q., Cao L., Zhang L. and Li Y. (2015) Diagenetic uptake of rare earth elements by bioapatite, with an example from Lower Triassic conodonts of South China. *Earth-Science Reviews* **149**, 181–202.
- Couturier J., Lallemand C., Levard C., Chaurrand P., Rose J. and Collin B. (2022) Y K edge XAS transmission and XAS fluorescence of Yttrium components at 20K. [Dataset/Spectral Data]. SSHADE/FAME (OSUG Data Center).

795 Crowley B. E. and Wheatley P. V. (2014) To bleach or not to bleach? Comparing treatment methods for
796 isolating biogenic carbonate. *Chemical Geology* **381**, 234–242.

797 De Baar H. J. W., German C. R., Elderfield H. and Van Gaans P. (1988) Rare earth element distributions
798 in anoxic waters of the Cariaco Trench. *Geochimica et Cosmochimica Acta* **52**, 1203–1219.

799 Deng Y., Guo Q., Liu Congqiang, He G., Cao J., Liao J., Liu Chenhui, Wang H., Zhou J., Liu Y., Wang
800 F., Zhao B., Wei R., Zhu J. and Qiu H. (2022) Early diagenetic control on the enrichment and
801 fractionation of rare earth elements in deep-sea sediments. *Sci. Adv.* **8**, eabn5466.

802 Deng Y., Ren J., Guo Q., Cao J., Wang H. and Liu C. (2017) Rare earth element geochemistry
803 characteristics of seawater and porewater from deep sea in western Pacific. *Sci Rep* **7**, 16539.

804 Dong H., Zeng Q., Sheng Y., Chen C., Yu G. and Kappler A. (2023) Coupled iron cycling and organic
805 matter transformation across redox interfaces. *Nat Rev Earth Environ* **4**, 659–673.

806 Dubinin A. V. and Rinskaya-Korsakova M. N. (2011) Geochemistry of rare earth elements in bottom
807 sediments of the Brazil Basin, Atlantic Ocean. *Lithol Miner Resour* **46**, 1–16.

808 Eischens R. P. and Pliskin W. A. (1958) The Infrared Spectra of Adsorbed Molecules. In *Advances in*
809 *Catalysis* Elsevier. pp. 1–56.

810 Elderfield H. and Greaves M. J. (1982) The rare earth elements in seawater. *Nature* **296**, 214–219.

811 Elderfield H. and Sholkovitz E. R. (1987) Rare earth elements in the pore waters of reducing nearshore
812 sediments. *Earth and Planetary Science Letters* **82**, 280–288.

813 Felitsyn S. and Morad S. (2002) REE patterns in latest Neoproterozoic–early Cambrian phosphate
814 concretions and associated organic matter. *Chemical Geology* **187**, 257–265.

815 Finlay A. J., Drewicz A. E., Terry D. O., Grandstaff D. E. and Ash R. D. (2013) Suitability of Bioapatite
816 as Backfill Material for Nuclear Waste Isolation. *MRS Proc.* **1518**, 191–196.

817 Freslon N., Bayon G., Toucanne S., Bermell S., Bollinger C., Chéron S., Etoubleau J., Germain Y.,
818 Khripounoff A., Ponzevera E. and Rouget M.-L. (2014) Rare earth elements and neodymium
819 isotopes in sedimentary organic matter. *Geochimica et Cosmochimica Acta* **140**, 177–198.

820 Gad H. M. H. and Youssef M. A. (2018) Sorption behavior of Eu(III) from an aqueous solution onto
821 modified hydroxyapatite: kinetics, modeling and thermodynamics. *Environmental Technology* **39**,
822 2583–2596.

823 Gorman-Lewis D., Elias P. E. and Fein J. B. (2005) Adsorption of Aqueous Uranyl Complexes onto
824 *Bacillus subtilis* Cells. *Environ. Sci. Technol.* **39**, 4906–4912.

825 Grunenwald A., Keyser C., Sautereau A. M., Crubézy E., Ludes B. and Drouet C. (2014) Revisiting
826 carbonate quantification in apatite (bio)minerals: a validated FTIR methodology. *Journal of*
827 *Archaeological Science* **49**, 134–141.

828 Grybos M., Davranche M., Gruau G. and Petitjean P. (2007) Is trace metal release in wetland soils
829 controlled by organic matter mobility or Fe-oxyhydroxides reduction? *Journal of Colloid and*
830 *Interface Science* **314**, 490–501.

831 Gustafsson J. P. (2018) Visual MINTEQ, Version 3.1; Department of Land and Water Resources
832 Engineering. KTH: (Royal Institute of Technology), Stockholm. <https://vminteq.com/download/>.

833 Habenschuss A. and Spedding F. H. (1979) The coordination (hydration) of rare earth ions in aqueous
834 chloride solutions from x-ray diffraction. II. LaCl₃, PrCl₃, and NdCl₃a). *The Journal of Chemical*
835 *Physics* **70**, 3758–3763.

836 Haley B. A., Klinkhammer G. P. and McManus J. (2004) Rare earth elements in pore waters of marine
837 sediments. *Geochimica et Cosmochimica Acta* **68**, 1265–1279.

838 Haxel G. B., Hedrick J. B. and Orris G. J. (2002) *Rare Earth Elements—Critical Resources for High*
839 *Technology*., US Geological Survey.

840 Hein J., Koschinsky A., Mikesell M., Mizell K., Glenn C. and Wood R. (2016) Marine Phosphorites as
841 Potential Resources for Heavy Rare Earth Elements and Yttrium. *Minerals* **6**, 88.

842 Huck C. E., Van De Flierdt T., Jiménez-Espejo F. J., Bohaty S. M., Röhl U. and Hammond S. J. (2016)
843 Robustness of fossil fish teeth for seawater neodymium isotope reconstructions under variable
844 redox conditions in an ancient shallow marine setting. *Geochem Geophys Geosyst* **17**, 679–698.

845 Hyeong K. and Capuano R. M. (2000) The effect of organic matter and the H₂O₂ organic-matter-removal
846 method on the δ D of smectite-rich samples. *Geochimica et Cosmochimica Acta* **64**, 3829–3837.

847 Iijima K., Yasukawa K., Fujinaga K., Nakamura K., Machida S., Takaya Y., Ohta J., Haraguchi S.,
848 Nishio Y., Usui Y., Nozaki T., Yamazaki T., Ichiyama Y., Ijiri A., Inagaki F., Machiyama H.,
849 Suzuki K., Kato Y., and KR13-02 Cruise Members (2016) Discovery of extremely REY-rich mud
850 in the western North Pacific Ocean. *Geochem. J.* **50**, 557–573.

851 Ijiri A., Okamura K., Ohta J., Nishio Y., Hamada Y., Iijima K. and Inagaki F. (2018) Uptake of porewater
852 phosphate by REY-rich mud in the western North Pacific Ocean. *Geochem. J.* **52**, 373–378.

853 Jackson M. L. (2005) Soil Chemical Analysis: Advanced Course. Parallel Press, University of Wisconsin-
854 Madison Libraries, Madison, Wis.

855 Jahnke R. A., Reimers Clare. E. and Craven D. B. (1990) Intensification of recycling of organic matter at
856 the sea floor near ocean margins. *Nature* **348**, 50–54.

857 Kashiwabara T., Toda R., Nakamura K., Yasukawa K., Fujinaga K., Kubo S., Nozaki T., Takahashi Y.,
858 Suzuki K. and Kato Y. (2018) Synchrotron X-ray spectroscopic perspective on the formation
859 mechanism of REY-rich muds in the Pacific Ocean. *Geochimica et Cosmochimica Acta* **240**,
860 274–292.

861 Kato Y., Fujinaga K., Nakamura K., Takaya Y., Kitamura K., Ohta J., Toda R., Nakashima T. and
862 Iwamori H. (2011) Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth
863 elements. *Nature Geosci* **4**, 535–539.

864 Keenan S. W., Engel A. S., Roy A. and Lisa Bovenkamp-Langlois G. (2015) Evaluating the
865 consequences of diagenesis and fossilization on bioapatite lattice structure and composition.
866 *Chemical Geology* **413**, 18–27.

- 867 Kim M. G., Hyeong K. and Yoo C. M. (2022) Distribution of Rare Earth Elements and Yttrium in
868 Sediments From the Clarion-Clipperton Fracture Zone, Northeastern Pacific Ocean. *Geochem*
869 *Geophys Geosyst* **23**, e2022GC010454.
- 870 Kimura-Suda H., Kajiwaru M., Matsumoto N., Murayama H. and Yamato H. (2009) Characterization of
871 Apatite and Collagen in Bone with FTIR Imaging. *Molecular Crystals and Liquid Crystals* **505**,
872 64/[302]-69/[307].
- 873 Kleber M., Bourg I. C., Coward E. K., Hansel C. M., Myneni S. C. B. and Nunan N. (2021) Dynamic
874 interactions at the mineral–organic matter interface. *Nat Rev Earth Environ* **2**, 402–421.
- 875 Koeppenkastrup D. and De Carlo E. H. (1992) Sorption of rare-earth elements from seawater onto
876 synthetic mineral particles: An experimental approach. *Chemical Geology* **95**, 251–263.
- 877 Kon Y., Hoshino M., Sanematsu K., Morita S., Tsunematsu M., Okamoto N., Yano N., Tanaka M. and
878 Takagi T. (2014) Geochemical Characteristics of Apatite in Heavy REE -rich Deep-Sea Mud
879 from Minami-Torishima Area, Southeastern Japan. *Resource Geology* **64**, 47–57.
- 880 Kral A. G., Lagos M., Guagliardo P., Tütken T. and Geisler T. (2022) Rapid alteration of cortical bone in
881 fresh- and seawater solutions visualized and quantified from the millimeter down to the atomic
882 scale. *Chemical Geology* **609**, 121060.
- 883 Labs-Hochstein J. and MacFadden B. J. (2006) Quantification of diagenesis in Cenozoic sharks:
884 Elemental and mineralogical changes. *Geochimica et Cosmochimica Acta* **70**, 4921–4932.
- 885 Lécuyer C., Reynard B. and Grandjean P. (2004) Rare earth element evolution of Phanerozoic seawater
886 recorded in biogenic apatites. *Chemical Geology* **204**, 63–102.
- 887 Li D., Peng J., Chew D., Liang Y., Hollings P., Fu Y., Dong Y. and Sun X. (2023) Dating rare earth
888 element enrichment in deep-sea sediments using U-Pb geochronology of bioapatite. *Geology* **51**,
889 428–433.
- 890 Li X.-H., Xie M.-C., Yang K.-F., Li K., Han C.-M., She H.-D., Liang G.-Z., Li X.-C. and Fan H.-R.
891 (2025) Calcium-O-Sr-Nd isotope evidence for the origin of REE-bearing carbonatite from
892 metasomatized lithospheric mantle without recycled carbonate. *Contrib Mineral Petrol* **180**, 46.
- 893 Li Z., Sun X., Li D., Huang F. and Liang Y. (2024) Isomorphic substitution behavior of Pt on synthetic
894 vernadite (δ -MnO₂): A model reaction to elucidate the mechanism of Pt enrichment in marine
895 ferromanganese crust. *Chemical Geology* **652**, 122027.
- 896 Li Z., Zhang Y. G., Torres M. and Mills B. J. W. (2023) Neogene burial of organic carbon in the global
897 ocean. *Nature* **613**, 90–95.
- 898 Liang Y., Sun X., Li D., Peacock C. L. and Fu Y. (2024) Effects of phosphate on REY adsorption by
899 goethite: Insights into REY enrichment and release in marine iron oxyhydroxides during early
900 diagenesis. *Chemical Geology* **649**, 121966.
- 901 Liao J., Chen J., Sun X., Deng Y., Wang Y., Wang D., Hong G., Klose L. and Koschinsky A. (2024)
902 Controlling Factors on REY Enrichments in Basins From the Pacific Ocean: Early Diagenesis
903 and Local Constraints. *Geochem Geophys Geosyst* **25**, e2023GC011111.

- 904 Liao J., Chen J., Sun X., Wu Z., Deng Y., Shi X., Wang Y., Chen Y. and Koschinsky A. (2022)
905 Quantifying the controlling mineral phases of rare-earth elements in deep-sea pelagic sediments.
906 *Chemical Geology* **595**, 120792.
- 907 Liao J., Sun X., Li D., Sa R., Lu Y., Lin Z., Xu L., Zhan R., Pan Y. and Xu H. (2019) New insights into
908 nanostructure and geochemistry of bioapatite in REE-rich deep-sea sediments: LA-ICP-MS,
909 TEM, and Z-contrast imaging studies. *Chemical Geology* **512**, 58–68.
- 910 Liao J., Wang D., Sun X., Hong G., Deng Y., Yao W., Manceau A. and Koschinsky A. (2025) Carbonate
911 fluorapatite pellets in pelagic sediments: Implications for REY enrichment and Nd isotopic
912 signatures in abyssal environments. *Earth and Planetary Science Letters* **671**, 119658.
- 913 Manceau A., Paul S. A. L., Simionovici A., Magnin V., Balvay M., Findling N., Rovezzi M., Muller S.,
914 Garbe-Schönberg D. and Koschinsky A. (2022) Fossil Bioapatites with Extremely High
915 Concentrations of Rare Earth Elements and Yttrium from Deep-Sea Pelagic Sediments. *ACS*
916 *Earth Space Chem.* **6**, 2093–2103.
- 917 Marques Fernandes M., Schmidt M., Stumpf T., Walther C., Bosbach D., Klenze R. and Fanghänel Th.
918 (2008) Site-selective time-resolved laser fluorescence spectroscopy of Eu³⁺ in calcite. *Journal of*
919 *Colloid and Interface Science* **321**, 323–331.
- 920 Marques M. P. M., Gonçalves D., Mamede A. P., Coutinho T., Cunha E., Kockelmann W., Parker S. F.
921 and Batista De Carvalho L. A. E. (2021) Profiling of human burned bones: oxidising versus
922 reducing conditions. *Sci Rep* **11**, 1361.
- 923 Millero F. J. (1992) Stability constants for the formation of rare earth-inorganic complexes as a function
924 of ionic strength. *Geochimica et Cosmochimica Acta* **56**, 3123–3132.
- 925 Ohta A. and Kawabe I. (2000) Rare earth element partitioning between Fe oxyhydroxide precipitates and
926 aqueous NaCl solutions doped with NaHCO₃: Determinations of rare earth element complexation
927 constants with carbonate ions. *Geochem. J.* **34**, 439–454.
- 928 Ohta A. and Kawabe I. (2001) REE(III) adsorption onto Mn dioxide (δ -MnO₂) and Fe oxyhydroxide:
929 Ce(III) oxidation by δ -MnO₂. *Geochimica et Cosmochimica Acta* **65**, 695–703.
- 930 Ohta J., Yasukawa K., Machida S., Fujinaga K., Nakamura K., Takaya Y., Iijima K., Suzuki K. and Kato
931 Y. (2016) Geological factors responsible for REY-rich mud in the western North Pacific Ocean:
932 Implications from mineralogy and grain size distributions. *GEOCHEMICAL JOURNAL* **50**, 591–
933 603.
- 934 Ohta J., Yasukawa K., Nakamura K., Fujinaga K., Iijima K. and Kato Y. (2021) Geological features and
935 resource potential of deep-sea mud highly enriched in rare-earth elements in the Central Pacific
936 Basin and the Penrhyn Basin. *Ore Geology Reviews* **139**, 104440.
- 937 Ohta J., Yasukawa K., Nozaki T., Takaya Y., Mimura K., Fujinaga K., Nakamura K., Usui Y., Kimura J.-
938 I., Chang Q. and Kato Y. (2020) Fish proliferation and rare-earth deposition by topographically
939 induced upwelling at the late Eocene cooling event. *Sci Rep* **10**, 9896.
- 940 Patel H. (2020) Batch and continuous fixed bed adsorption of heavy metals removal using activated
941 charcoal from neem (*Azadirachta indica*) leaf powder. *Sci Rep* **10**, 16895.

942 Pavlova L. M., Shumilova L. P., Radomskaya V. I., Sorokin A. P., Ivanov V. V., Noskova L. P. and
 943 Leusova N. Yu. (2023) Sorption of Rare Earth Elements by Organic Matter from Aqueous
 944 Solutions according to Experimental Data. *Dokl. Earth Sc.* **512**, 946–952.

945 Peng J., Li D., Poulton S. W., O’Sullivan G. J., Chew D., Fu Y. and Sun X. (2024) Episodic
 946 intensification of marine phosphorus burial over the last 80 million years. *Nat Commun* **15**, 7446.

947 Piper D. Z., Baedeker P. A., Crock J. G., Burnett W. C. and Loebner B. J. (1988) Rare earth elements in
 948 the phosphatic-enriched sediment of the Peru shelf. *Marine Geology* **80**, 269–285.

949 Pourret O., Davranche M., Gruau G. and Dia A. (2007) Rare earth elements complexation with humic
 950 acid. *Chemical Geology* **243**, 128–141.

951 Pourret O. and Tuduri J. (2017) Continental shelves as potential resource of rare earth elements. *Sci Rep*
 952 **7**, 5857.

953 Qin H.-B., Yang S., Tanaka M., Sanematsu K., Arcilla C. and Takahashi Y. (2021) Scandium
 954 immobilization by goethite: Surface adsorption versus structural incorporation. *Geochimica et*
 955 *Cosmochimica Acta* **294**, 255–272.

956 Qiu K.-F., Long Z.-Y., Romer R. L., Halama R., Williams-Jones A. E., Yu H.-C., Li S.-S., Wu M.-Q. and
 957 Deng J. (2025) The mantle source of REE-rich alkaline silicate magmas can be enriched by
 958 continent-derived sediment subduction. *Nat Commun* **16**, 11191.

959 Ramazanov E., Sharma N., Flynn E. D., Stagg O., Catalano J. G. and Giammar D. E. (2025) Adsorption
 960 of REEs to Kaolinite via Ion Exchange and Surface Complexation as a Function of Water
 961 Chemistry. *ACS Earth Space Chem.* **9**, 1430–1442.

962 Ravel B. and Newville M. (2005) *ATHENA*, *ARTEMIS*, *HEPHAESTUS*: data analysis for X-ray
 963 absorption spectroscopy using *IFEFFIT*. *J Synchrotron Rad* **12**, 537–541.

964 Ren J., Jiang X., He G., Wang F., Yang T., Luo S., Deng Y., Zhou J., Deng X., Yao H. and Yu H. (2022)
 965 Enrichment and sources of REY in phosphate fractions: Constraints from the leaching of REY-
 966 rich deep-sea sediments. *Geochimica et Cosmochimica Acta* **335**, 155–168.

967 Revellame E. D., Fortela D. L., Sharp W., Hernandez R. and Zappi M. E. (2020) Adsorption kinetic
 968 modeling using pseudo-first order and pseudo-second order rate laws: A review. *Cleaner*
 969 *Engineering and Technology* **1**, 100032.

970 Scaggion C., Marinato M., Dal Sasso G., Nodari L., Saupe T., Aneli S., Pagani L., Scheib C. L., Rigo M.
 971 and Artioli G. (2024) A fresh perspective on infrared spectroscopy as a prescreening method for
 972 molecular and stable isotopes analyses on ancient human bones. *Sci Rep* **14**, 1028.

973 Schmitt A. D., Gangloff S., Brazier J. M., Nuvoli N. and Tertre E. (2023) Calcium isotope fractionation
 974 associated with adsorption and desorption on/from δ -MnO₂. *Geochimica et Cosmochimica Acta*
 975 **354**, 109–122.

976 Sibert E. C., Zill M. E., Frigyk E. T. and Norris R. D. (2020) No state change in pelagic fish production
 977 and biodiversity during the Eocene–Oligocene transition. *Nat. Geosci.* **13**, 238–242.

978 Soyol-Erdene T.-O. and Huh Y. (2013) Rare earth element cycling in the pore waters of the Bering Sea
979 Slope (IODP Exp. 323). *Chemical Geology* **358**, 75–89.

980 Tanaka E., Nakamura K., Yasukawa K., Mimura K., Fujinaga K., Iijima K., Nozaki T. and Kato Y.
981 (2020) Chemostratigraphy of deep-sea sediments in the western North Pacific Ocean:
982 Implications for genesis of mud highly enriched in rare-earth elements and yttrium. *Ore Geology*
983 *Reviews* **119**, 103392.

984 Taylor S. G. and Bradley C. E. (1985) Optimal Ordering Strategies for Announced Price Increases.
985 *Operations Research* **33**, 312–325.

986 Toyoda K. and Tokonami M. (1990) Diffusion of rare-earth elements in fish teeth from deep-sea
987 sediments. *Nature* **345**, 607–609.

988 Trueman C. N. and Tuross N. (2002) Trace Elements in Recent and Fossil Bone Apatite. *Reviews in*
989 *Mineralogy and Geochemistry* **48**, 489–521.

990 Tütken T., Vennemann T. W. and Pfretzschner H.-U. (2008) Early diagenesis of bone and tooth apatite in
991 fluvial and marine settings: Constraints from combined oxygen isotope, nitrogen and REE
992 analysis. *Palaeogeography, Palaeoclimatology, Palaeoecology* **266**, 254–268.

993 Wang R., Fu Y., Tang Y., Li D., Sun X. and He G. (2025) Cerium behavior during the transformation of
994 birnessite to todorokite: Implications for the origin of Ce anomalies in hydro-diagenetic
995 ferromanganese nodules. *Geological Society of America Bulletin* **137**, 3221–3232.

996 Xiang B., Dong Y., Han X., Li X., Wang Y., Zhang W. and Chu F. (2024) Enrichment of Smectite in the
997 REY-Rich Mud of the Clarion-Clipperton Fracture Zone in the Eastern Pacific and Its Geological
998 Significance. *Geochem Geophys Geosyst* **25**, e2023GC011283.

999 Xu L., Zheng T., Yang S., Zhang L., Wang J., Liu W., Chen L., Diwu J., Chai Z. and Wang S. (2016)
1000 Uptake Mechanisms of Eu(III) on Hydroxyapatite: A Potential Permeable Reactive Barrier
1001 Backfill Material for Trapping Trivalent Minor Actinides. *Environ. Sci. Technol.* **50**, 3852–3859.

1002 Yamaguchi T., Nomura M., Wakita H. and Ohtaki H. (1988) An extended x-ray absorption fine structure
1003 study of aqueous rare earth perchlorate solutions in liquid and glassy states. *The Journal of*
1004 *Chemical Physics* **89**, 5153–5159.

1005 Yang J., Kim J.-H., Torres M. E. and Haley B. (2018) Data report: dissolved rare earth elements (REEs)
1006 in the pore fluids of Sites U1378, U1380, U1381, and U1414 drilled during IODP Expeditions
1007 334 and 344. In (ed. R. N. Harris Sakaguchi, A. ., Petronotis, K. ., and the Expedition 344
1008 Scientists). Integrated Ocean Drilling Program, College Station, TX.

1009 Yasukawa K., Nakamura K., Fujinaga K., Iwamori H. and Kato Y. (2016) Tracking the spatiotemporal
1010 variations of statistically independent components involving enrichment of rare-earth elements in
1011 deep-sea sediments. *Sci Rep* **6**, 29603.

1012 Ye H., Hu Z., Yin R., Boyko T. D., Liu Y., Li Yanzhang, Li C., Lu A. and Li Yan (2025) Electron
1013 transfer at birnessite/organic compound interfaces: mechanism, regulation, and two-stage kinetic
1014 discrepancy in structural rearrangement and decomposition. *Geochimica et Cosmochimica Acta*
1015 **388**, 253–267.

1016 Yu M., Shi X., Huang M., Liu J., Yan Q., Yang G., Li C., Yang B., Zhou T., Bi D., Wang H. and Bai Y.
1017 (2021) The transfer of rare earth elements during early diagenesis in REY-rich sediments: An
1018 example from the Central Indian Ocean Basin. *Ore Geology Reviews* **136**, 104269.

1019 Yuan X., Yang Z., Mayanovic R. A. and Hou Z. (2024) Experimental evidence reveals the mobilization
1020 and mineralization processes of rare earth elements in carbonatites. *Sci. Adv.* **10**, eadm9118.

1021 Zhu X., Liu Y. and Hou Z. (2024) Massive rare earth element storage in sub-continental lithospheric
1022 mantle initiated by diapirism, not by melting. *Geology* **52**, 105–109.

1023 Zhang G., Bai J., Zhao M., Wang P., Zhu Y., Cao J., Wu H., Xu R., He G., Wei G. and Deng Y. (2026)
1024 Cerium isotopic compositions of deep-sea sediments: implications for geochemical behavior of
1025 rare earth elements in the pelagic seafloor. *Geochimica et Cosmochimica Acta* **412**, 186–198.

1026

Figure 1. Location of studied bioapatite sample in the western North Pacific Ocean and regional geochemical conditions associated with REE enrichment. (A) REE abundance is denoted by brown/yellow circles scaled to the highest reported REE concentration. Published data for the western North Pacific Ocean, the Clarion-Clipperton Fracture Zone (CCFZ), and the Peru shelf are sourced from Iijima et al. (2016) and Tanaka et al. (2020), from Kim et al. (2022) and Xiang et al. (2024), and from Piper et al. (1988), respectively. Map created using open source software Generic Mapping Tools (GMT; available at: <http://gmt.soest.hawaii.edu>). **(B–C)** Correlation of Σ REE with Fe-Mn and P_2O_5 contents in sediment cores from the western Pacific Ocean (**B**: PC05; Tanaka et al., 2020) and the CCFZ (**C**: GC03; Xiang et al., 2024).

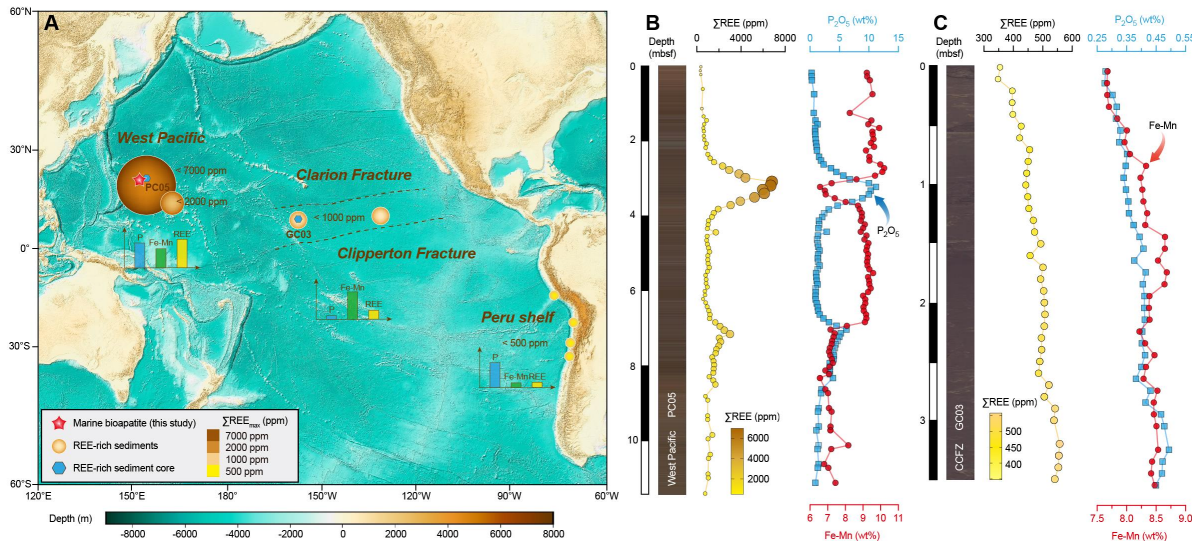


Figure 2. SEM-EDS analyses of bioapatite samples. (A) SEM images of a complete deep-sea tooth of *Lophius piscatorius* (AP-1) reveal well-preserved enamel from tip to root, with cracks on the surface. By contrast, SEM images of bioapatite after hydrogen peroxide infiltration to remove organic matter (AP-2) show significant removal of enamel, with extensive loss of the enamel structure exposing the underlying dentine. (B) The intact enamel exhibits surface cracks and irregular undulations. (C) The remnants of fractured enamel display breakage patterns that follow the orientation of pre-existing cracks and undulations, resulting in a blocky morphology. (D) The exposed dentine showed a parallel arrangement, and the internal structure is relatively porous. (E) The longitudinal profile of the tooth of *Lophius piscatorius* illustrates a cavity structure at the center; most of the gray area is dentine, and the outermost thin layer structure is tooth enamel (not significant in this image). (F) organic matter is distributed within and on the surface of the dentine. (G) SEM images of AP-1 display complete organic components, with EDS showing the high carbon contents (H). (I) The organic matter in AP-2 was destroyed by hydrogen peroxide, with its structure damaged or disappeared. (J) EDS results showing damaged organic matter (high carbon content), with the mapped area on (I) denoted by a white box.

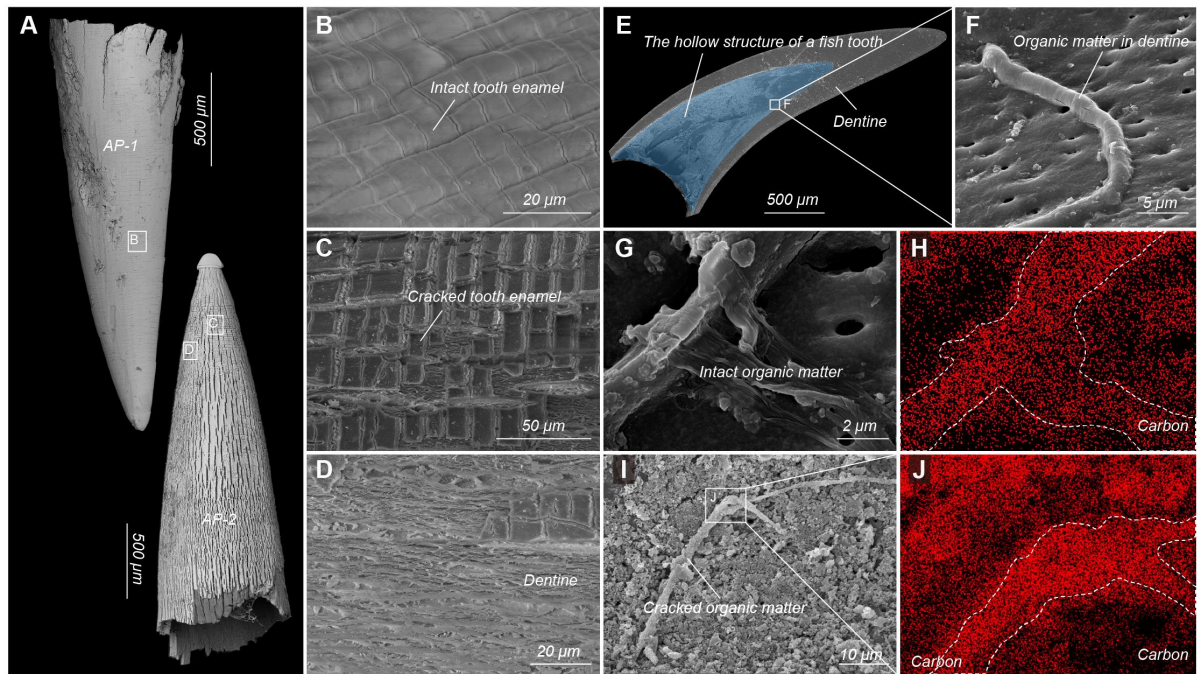


Figure 3. Adsorption characteristics of fresh bioapatite samples. Kinetic data and the corresponding model fit for adsorption of REE on bioapatite without (**A**) and with (**B**) organic matter removal at $\text{pH} = 7.1$, with an REE concentration of 15 ppb in the initial fluid. (**C**) Effects of pH on REE adsorption to bioapatite. The REE adsorption represents the adsorption ratio of REE at different pH values. The REE precipitation represents the precipitation ratio of REE at different pH values. The Ca concentration represents the change in Ca content caused by the dissolution of bioapatite at varying pH values. (**D**) The logarithm of the partition coefficient (K_d) of REE between the solid phase and the liquid phase plotted vs. increasing atomic number within the lanthanide series (AP-1: bioapatite without organic matter removal, AP-2: bioapatite with organic matter removal, $T = 298 \text{ K}$, $M_{\text{sample}} = 5 \text{ mg}$, $C_{\text{REE}} = 15 \text{ ppb}$, $\text{IS} = 0.5 \text{ M NaNO}_3$).

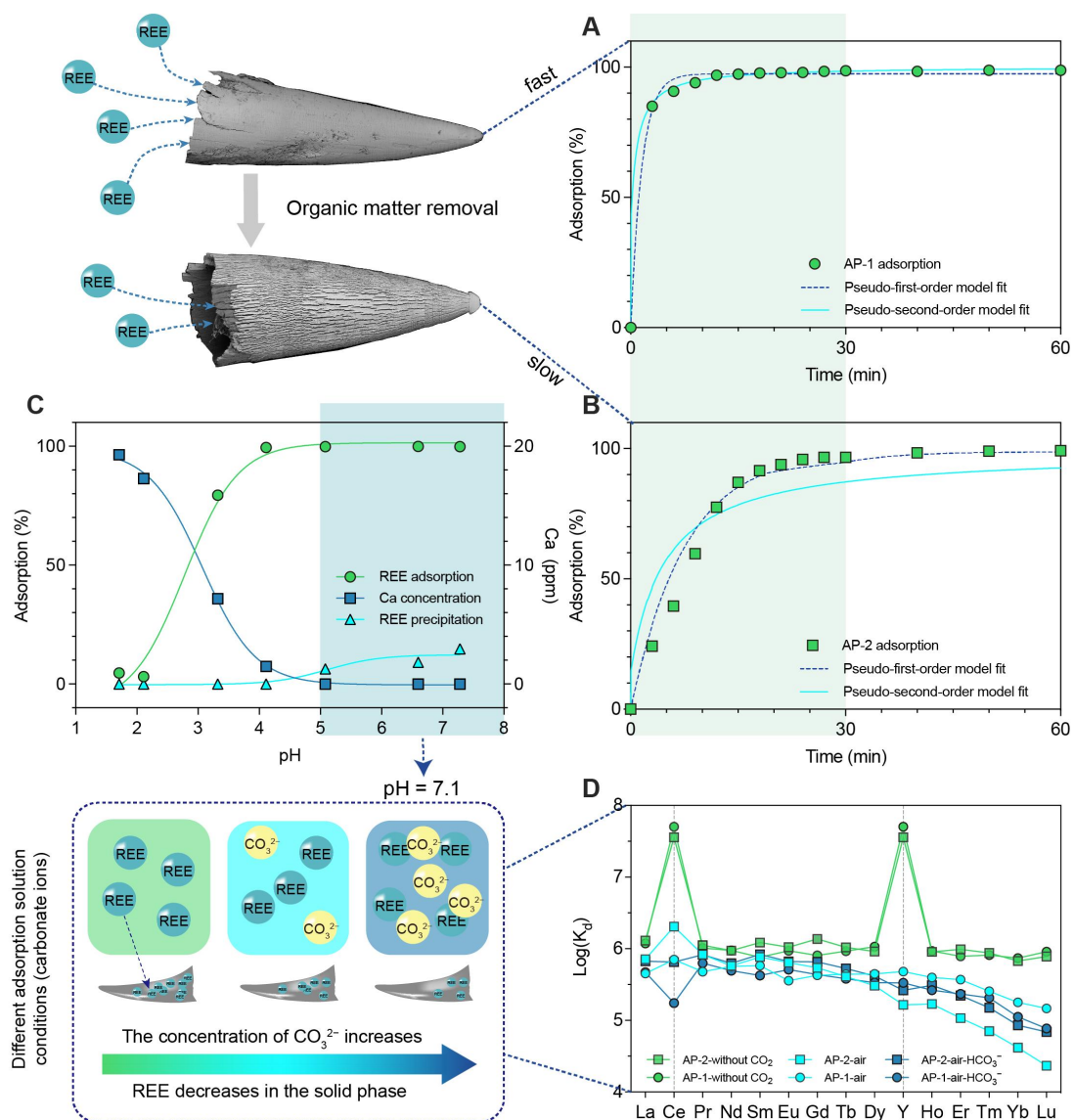
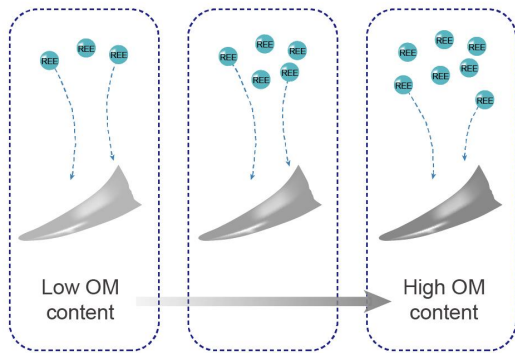
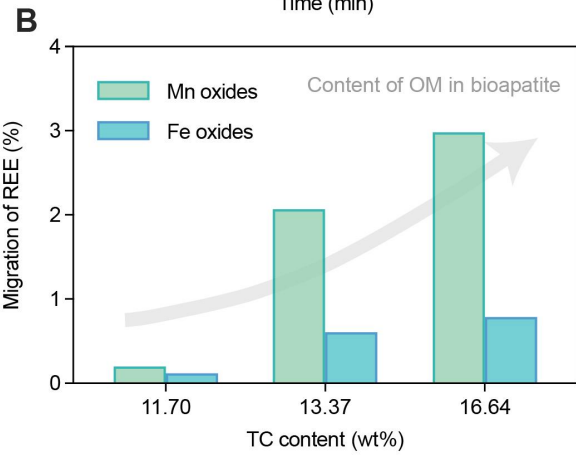
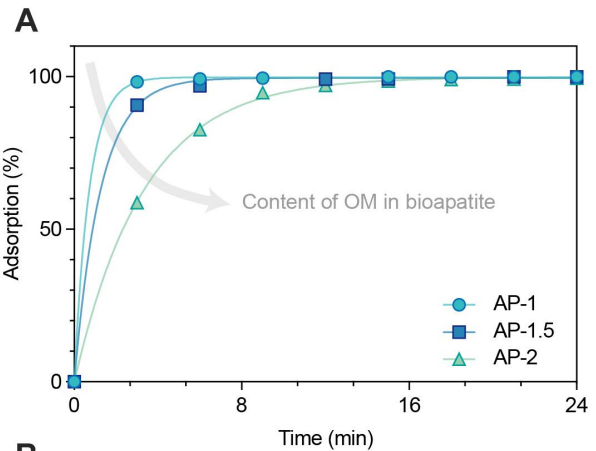
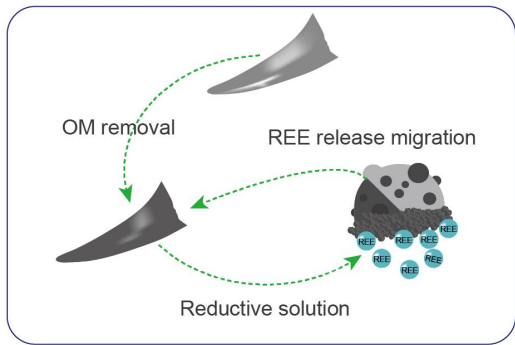


Figure 4. The adsorption ratio for REE in bioapatite with varying organic matter content and the migration ratio of REE from Fe-Mn (oxyhydr)oxides to bioapatite controlled by organic matter removal. (A) The higher the content of organic matter in bioapatite, the more REE enrichment occurs. **(B)** Effect of organic matter content on REE migration efficiency. Relative REE migration (%) is defined as the mass of REE recovered in the bioapatite phase relative to the initial REE content hosted by Fe-Mn (oxyhydr)oxides, calculated as: $\text{Migration (\%)} = (M_{\text{bioapatite}}/M_{\text{initial_oxide}}) \times 100$. Final migration ratios were baseline-corrected for the abiotic adsorption of organic matter-free hydroxyapatite. Higher organic matter promotes more extensive oxide dissolution, thereby driving a higher proportion of REE to migrate into the bioapatite (T = 298 K, pH = 7.1, $M_{\text{sample}} = 5 \text{ mg}$, $C_{\text{REE}} = 100 \text{ ppb}$, IS = 0.5 M NaNO₃; organic matter content of bioapatite: AP-1 (TC = 16.64 wt%) > AP-1.5 (TC = 13.37 wt%) > AP-2 (TC = 11.70 wt%)).



OM presence: it is beneficial to the enrichment of REE
 OM removal: REE released by it and dissolved Fe-Mn oxides



1076 **Figure 5. FTIR analysis of the adsorbents before and after adsorption.** (A) FTIR of the
1077 bioapatite (without organic matter removal) before and after Nd, Y, and total REE adsorption. (B)
1078 Post-REE adsorption shifts in characteristic peaks of the bioapatite FTIR spectra. (C) FTIR of the
1079 hydroxyapatite (HAP) before and after REE adsorption. (D) Post-REE adsorption shifts in
1080 characteristic FTIR peaks of HAP samples. All experimental parameters and sample
1081 identifications are consistent with those detailed in [Table S1](#). Source data are provided as a data
1082 file.

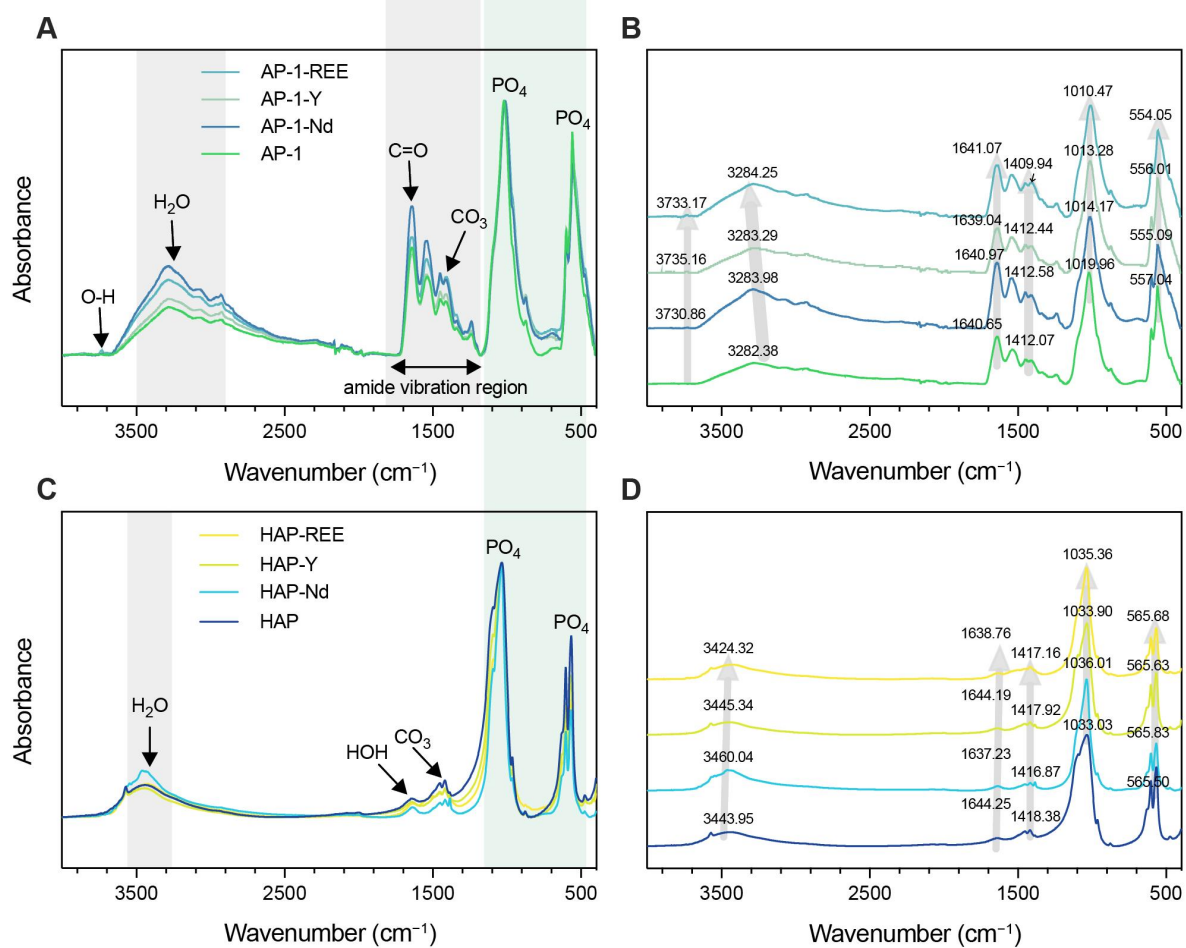
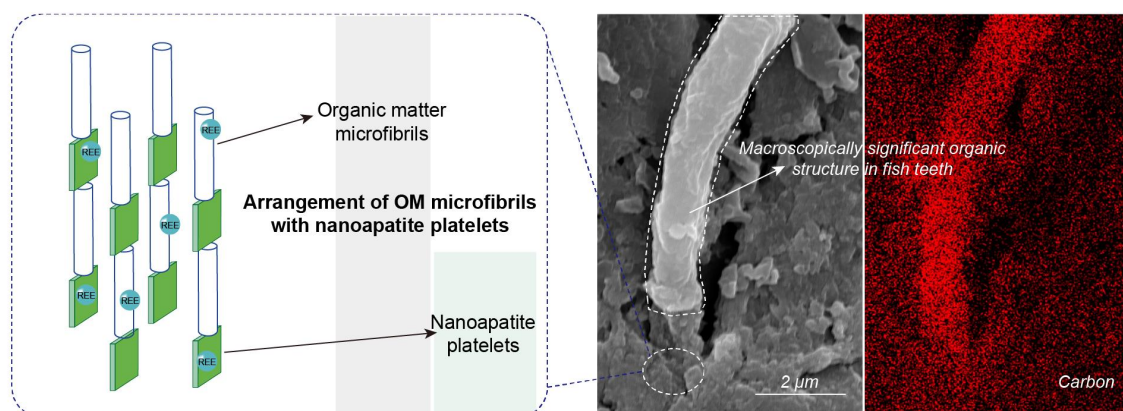


Figure 6. Results of μ -XRF mapping, and Nd L₃-edge and Y K-edge XAFS analyses for bioapatite. (A) SEM images of a bioapatite thin section show that the tip of the fish tooth is well-preserved, and conducive to REE enrichment and storage. (B) The μ -XRF mapping of bioapatite shows that the distribution of P, Y and Nd is homogeneous in the tip, and the concentrations of Nd (C) and Y (D) in the fish tooth are relatively low. (E) The Nd L₃-edge XANES results of bioapatite and standard material (Nd₂O₃). (F) The Y K-edge XANES results of bioapatite and the standard materials (the relevant Y standard reference material is from Couturier et al. (2022)). Data are available at: <https://www.sshade.eu>. (G) k^3 -weighted X-ray absorption extended fine structure (EXAFS) data for the Y K-edge in the marine bioapatite sample and selected standards, showing EXAFS oscillations as a function of wavenumber k ($\text{\AA}^{-1}$). Experimental data are shown in solid lines, and the calculated spectra are shown as dashed lines by a curve-fitting analysis in the Artemis software. (H) Corresponding phase-shifted Fourier transform (radial distribution) functions derived from the EXAFS data. Each peak represents a shell of atoms surrounding the central Y atom at a certain radial distance R ($\text{\AA}$), with the height of the peak corresponding to the number and type of atoms (Table 1), and the position of the peaks corresponding to their average distance to the central Y atom. Source data are provided as a data file.

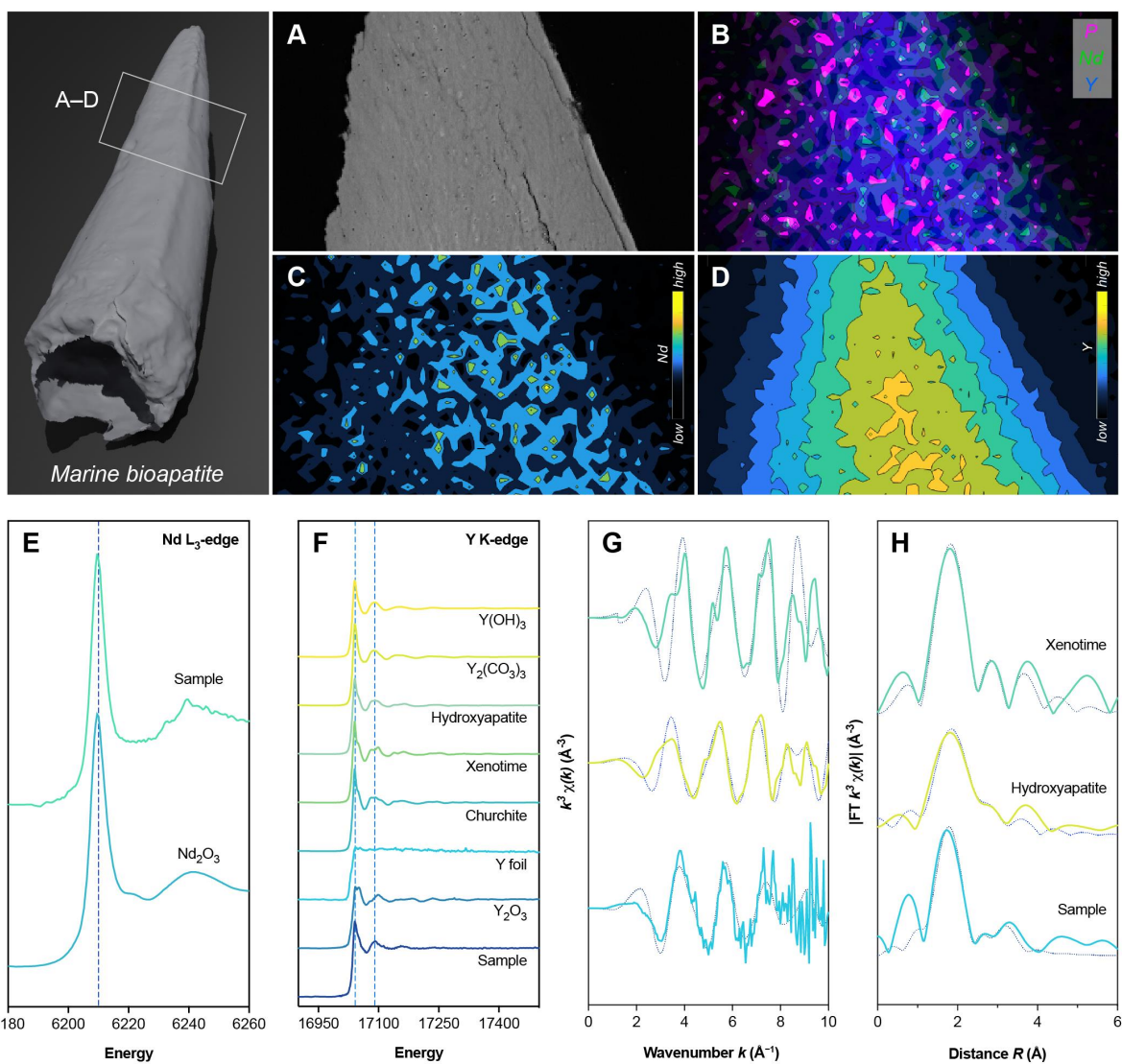


Figure 7. Post-Archean Australian shale (PAAS; Taylor and Bradley, 1985)-normalized REE patterns of different bioapatite samples, and REE enrichment patterns during mobilization from Fe-Mn (oxyhydr)oxides to bioapatite. (A) PAAS-normalized REE patterns for bioapatite in REE-rich mud from the western Pacific Ocean (high/low REE bioapatite; Kon et al., 2014), the central North Pacific Ocean (middle REE bioapatite; Liao et al., 2019), the skeleton of living marine vertebrates (fresh bioapatite; Labs-Hochstein and MacFadden, 2006). **(B)** A HREE enrichment pattern and a significant Ce negative anomaly are seen as a result of REE migration from Fe-Mn (oxyhydr)oxides (e.g., vernadite) into bioapatite. The colored lines show the REE enrichment pattern in bioapatite, while the gray lines show REE remaining in the Fe-Mn phase.

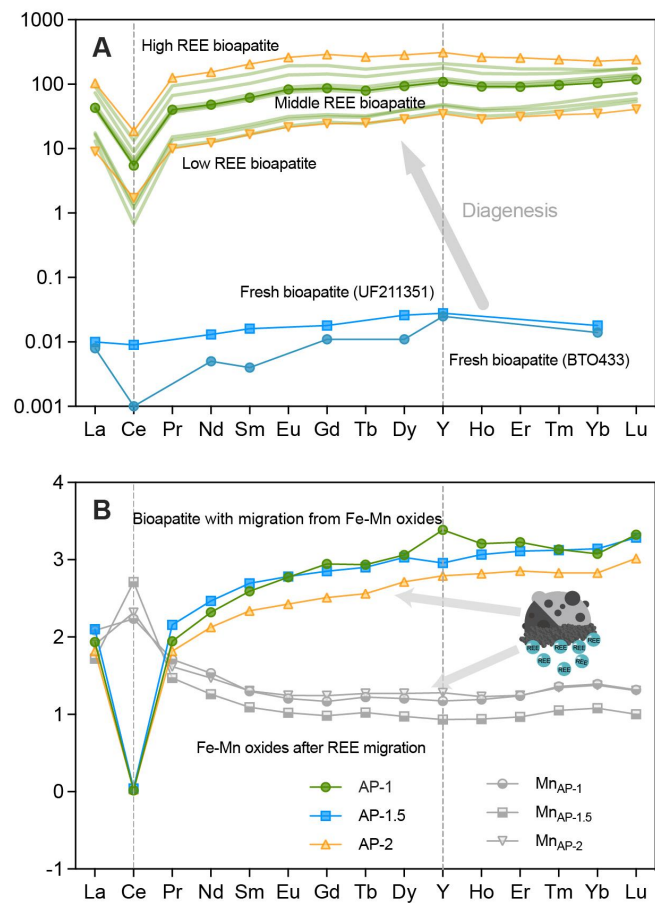
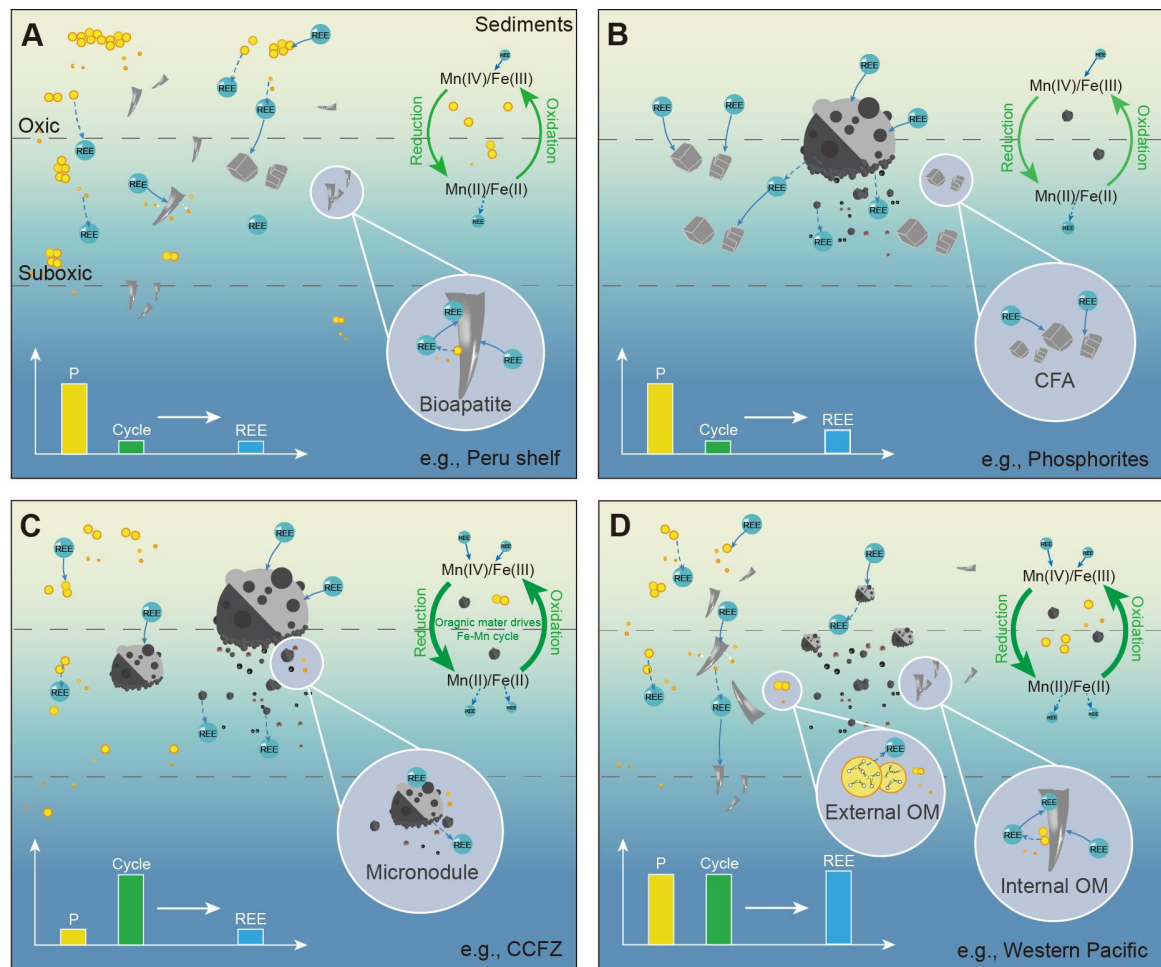
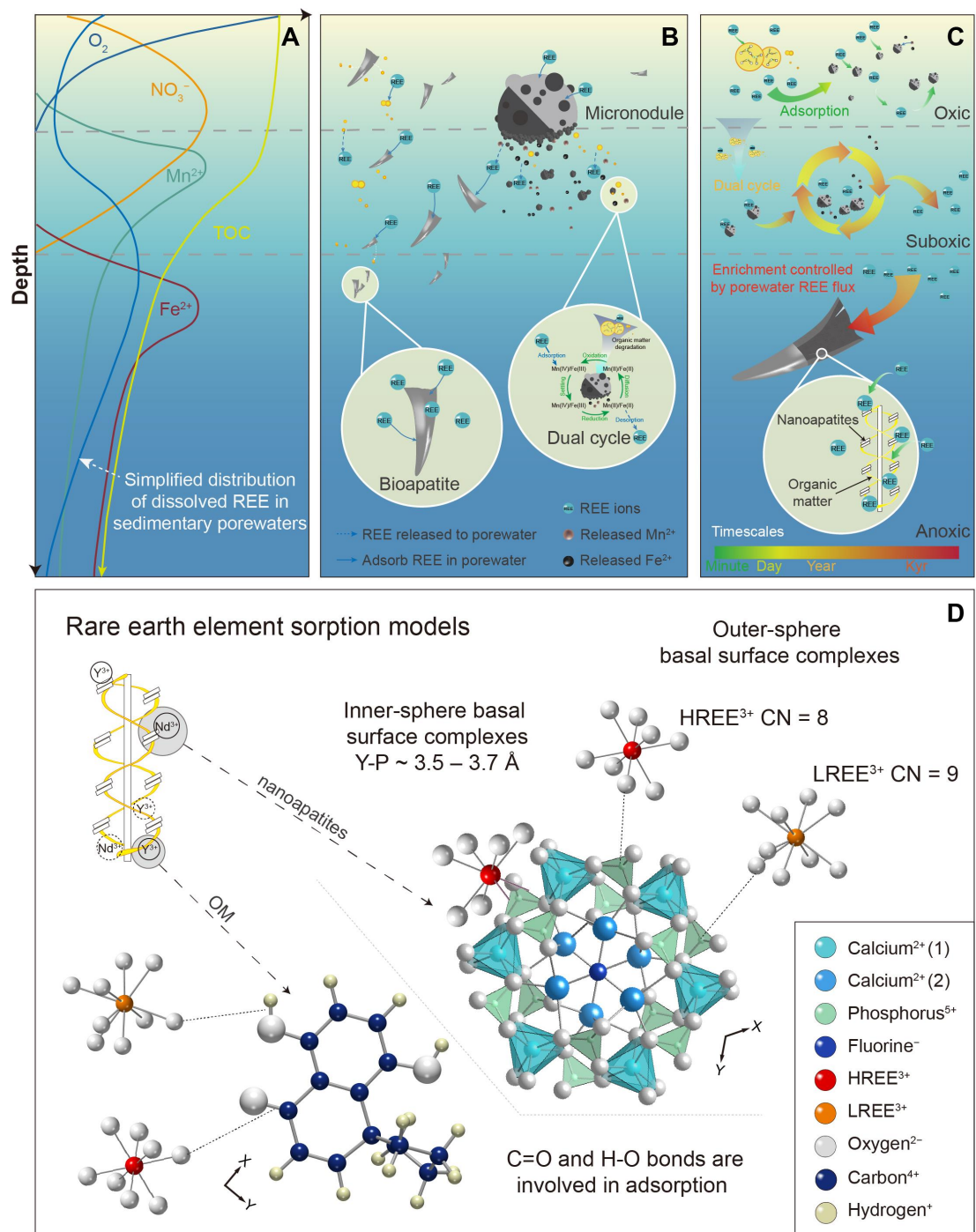


Figure 8. Synergistic effects of organic matter, phosphorus (P), and Fe-Mn (oxyhydr)oxides on REE enrichment under different environmental conditions. (A) In the absence of Fe-Mn (oxyhydr)oxide dissolution to supply REE, REE enrichment is limited even though abundant organic matter and P are present. **(B)** In the absence of organic matter, the interaction between Fe-Mn (oxyhydr)oxides and organic matter leads to weak adsorption and release of REE, thereby causing limited REE enrichment. **(C)** In the absence of P, REE enrichment is low even with abundant organic matter and Fe-Mn (oxyhydr)oxides present. **(D)** When organic matter, P and Fe-Mn interact together (particularly under slow deposition rates), REE hyper-enrichment occurs.



● Released Mn^{2+} ● Released Fe^{2+} ● REE ions ● REE released to porewaters → Adsorb REE in porewaters

Figure 9. Schematic enrichment model for REE in deep-sea sediments during early diagenesis. (A) Marine porewater geochemical profiles indicate variability in Fe, Mn and REE contents during diagenetic removal of marine organic matter (TOC). (B) Geochemical behavior of REE in marine sediments. In the oxic zone, REE are released into porewaters through the aerobic removal of organic matter. In the suboxic zone, REE are further released into porewaters via a coupled cycle (organic matter removal and micronodule dissolution). Meanwhile, REE released into porewaters gradually migrate to bioapatite to give hyper-enrichment. (C) Conceptual model of the coupled-source REE enrichment mechanism. REE are sustained by a supply-limited regime involving organic matter degradation and Fe-Mn oxides reduction. Flux arrows illustrate the migration of REE from these reactive phases toward adsorption sites in bioapatite. The timescale bar highlights the contrast between instantaneous surface adsorption (minutes) and the protracted, long-term sequestration (1 kyr to 10 Myr) necessitated by the slow replenishment of porewater REE. (D) REE adsorption model in bioapatite: internal organic matter participated in REE adsorption mainly through C=O and H-O bonds, and apatite adsorbed REE by forming an inner or outer complex with REE. This study shows that bioapatite mainly enriched REE by inner-sphere complexation.



1136

1137

1140 Table 1. Structural parameters of Y adsorbed on various minerals, obtained by curve-fitting* analysis of EXAFS spectra.

Samples and standard	Shell	CN	R (Å)	ΔE_0 (eV)	σ^2 (10^{-3} Å ²)	R factor (%)	n or Ref.
Marine bioapatite	Y-O	7.71±1.68	2.37±0.02	0.17±1.94	9.69±3.80	1.65	n = 11
	Y-P ₁	3.54±1.89	3.50±0.08				
	Y-P ₂	4.44±2.14	3.71±0.07				
Hydroxyapatite	Y-O	7.05±3.30	2.42±0.04	-7.87±5.71	5.55±5.57	3.94	†
	Y-P ₁	4.22±3.51	3.44±0.05				
	Y-P ₂	3.28±3.36	3.70±0.06				
Xenotime	Y-O	7.26±3.55	2.41±0.04	5.61±4.58	1.46±6.66	1.99	†
	Y-P	4.03±3.10	3.37±0.06				
	Y-O-P-O	5.38±3.91	3.90±0.09				

1141 * S_0^2 was fixed as 1.0. Data ranges of bioapatite: $3.0 \leq k \leq 8.5 \text{ \AA}^{-1}$, $1.0 \leq R \leq 4.0 \text{ \AA}$. The number of variable parameters is 8, out of a
1142 total of 10.3 independent data points. Data ranges of hydroxyapatite: $4.0 \leq k \leq 8.4 \text{ \AA}^{-1}$, $1.0 \leq R \leq 5.0 \text{ \AA}$. The number of variable
1143 parameters is 8, out of a total of 11.0 independent data points. Data ranges of xenotime: $4.0 \leq k \leq 8.0 \text{ \AA}^{-1}$, $1.0 \leq R \leq 4.7 \text{ \AA}$. The number
1144 of variable parameters is 8, out of a total of 9.3 independent data points.

1145 † EXAFS fits based on crystal structures from [Couturier et al. \(2022\)](#). CN is the coordination number (# of atoms nearest to Y). R is the
1146 interatomic distance between the ligand and Y. The Debye-Waller factor (σ^2) is the mean square displacement about the half path length
1147 of the path. The R-factor is a goodness of fit parameter; a perfect fit has an R-factor of 0.

1148 Note: Structural parameters of bioapatite are obtained by curve-fitting analysis (the distance of Y-O is from the crystal structure of Y_2O_3 ;
1149 the distances of Y-P₁ and Y-P₂ are from the crystal structure of apatite).

1150

1151

1152 **Table 2. The contribution ratio^{*} of organic matter and apatite to REE adsorption in bioapatite at the early adsorption stage.**

Time (min)	AP-1 (TC = 16.6 wt%)				AP-2 (TC = 11.7 wt%)			
	Adsorption in bioapatite		Contribution ratio		Adsorption in bioapatite		Contribution ratio	
	Σ REE	Eu (III)	organic matter	apatite	Σ REE	Eu (III)	organic matter	apatite
3	85.0 %	85.4 %	93.5%	6.5%	24.2 %	27.0 %	79.5 %	20.5 %
6	90.7 %	90.9 %	93.9%	6.1%	39.5 %	43.3 %	87.2 %	12.8 %
9	94.0 %	93.9 %	94.1%	5.9%	59.7 %	62.8 %	91.2 %	8.8 %
15	97.3 %	97.1 %	94.3%	5.7%	87.0 %	88.2 %	93.7 %	6.3 %

1153 ^{*} The contribution ratio was calculated by referring to bioapatite adsorption kinetics and total carbon (TC) content. Based on the
1154 experimental results and the fitting of the adsorption kinetics of Eu (III) by apatite of bone powder ([Gad and Youssef, 2018](#)) for
1155 subsequent calculations.