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Rare earth elements and U uptake by fish remains in seawater: how fast?

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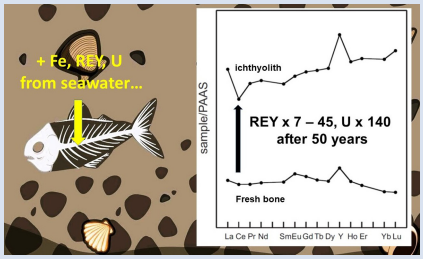
Abstract



During diagenesis, biogenic phosphates are considerably enriched in trace elements, particularly in U and rare earth elements (REEs), which makes them palaeoceanographic proxies for the composition of past seawater. The rate at which this enrichment occurs is unknown. Here, we report on present day ichthyoliths that have spent the last 50 years in contact with seawater and show that their uptake of REEs is largely dominated by quantitative incorporation without fractionation, probably *via* the development of authigenic phases, in particular Fe oxides. Enrichments take place rapidly, for example at a rate of around 1.2 ng/g per year for Nd and 300 ng/g per year for U. Transposed to known fossils displaying the highest REE and U abundances, these results suggest that contact with seawater may have persisted for several thousand years, implying very slow sedimentation rates. Alternatively, post-burial enrichment processes could be much more efficient, which would imply that the signatures shown by these kind of fossils, rich in rare earth elements and yttrium, may largely reflect diagenetic overprinting rather than pristine marine signatures.

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Introduction

Vertebrate fossils, teeth and bones, composed of apatite ($Ca_{10}(PO_4)_6(OH,F,Cl)_2$), have been common in many sedimentary formations since the Devonian period. The chemistry of these fossils is an active field of research since their elemental and isotopic compositions provide access to a wealth of information, including dating, palaeoceanography, reconstruction of the palaeoenvironment, as well as taphonomy, provenance and even diet of the animals (*e.g.*, Staudigel *et al.*, 1985; Tütken *et al.*, 2011; Reynard and Balter, 2014, among many others). These fossils often have high concentrations of uranium and rare earth element (REEs), whereas the teeth or bones of living animals are practically devoid of them (*e.g.*, Arrhenius *et al.*, 1957; Elderfield and Pagett, 1986; Li *et al.*, 2024). It is generally assumed that this post-mortem enrichment takes place quickly when the bones and teeth are at the water/sediment interface and/or during burial. However, the rate of accumulation/absorption of trace elements in biogenic phosphates has never been directly constrained. This can be determined experimentally, but the limited duration of experiments that can reasonably be conducted in a laboratory limits the feasibility of the approach. Alternatively, enrichment rates can be deduced from vertebrate remains left in a constrained environment for a known period of time. Such samples are rare. Here, we report on the chemical compositions of cod remains (*Gadus morhua*) that have been in contact with seawater for precisely half a century and deduce the uptake rates of U and REEs for these materials.

Historical Setting and Sampling

From the 16th century onwards, the coasts of Newfoundland were an extremely important fishing area, and the source of a large proportion of the cod consumed in Europe. In this context, the main activity of Saint Pierre and Miquelon (a French archipelago located south of Newfoundland, Figure S-1) was, throughout this period, the preparation of a colossal quantity of cod for France. This led to overfishing, particularly in the second half of the 20th century. To prevent the disappearance of cod around Newfoundland, the Canadian government imposed a fishing moratorium in 1992, resulting in a suspension of production from that date. The economic activity of Saint Pierre and Miquelon before the moratorium was based on the preparation of cod, with the installation of refrigeration facilities by the Société de Pêche et de Congélation (SPEC) in the port of Saint Pierre. From 1920 until the liquidation of SPEC in 1974, the waste from cod preparation was thrown directly into the port at the foot of the buildings on the quays. The accumulation of cod bones produced a layer of ichthyoliths at 15 m water depth near the SPEC facilities, the thickness of which is unknown (Figure S-2). No other waste from cod was deposited at this site after SPEC ceased operations. In June 2024, samples were taken from the surface of the ichthyolith layer by a scuba diver (Laurent Chauvaud), in the area where the last waste was thrown (46° 47′ 37″ N, 56° 09′ 31″ W). The selected samples were never buried and remained in contact with seawater with a salinity of 32 ‰ for 50 years, at a temperature varying from 0 to 16 °C depending on

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the season (on average 6 °C). Furthermore, a codfish was caught off the coast of Saint Pierre in July 2024, and its bones were collected for comparison with the ichthyoliths.

Finally, live thalli of coralline algae (*Lithothamnion sp.*, probably *L. tophiforme*), which are excellent proxies for REEs and Y (REY) chemistry of seawater (Barrat *et al.*, 2024), were also collected from 15 m water depth in June 2024, north east of Saint Pierre (46° 47′ 54″ N, 56° 08′ 54″ W), about 1 km from the ichthyoliths.

Analytical Procedures

The fresh codfish bones, ichthyoliths and coralline algae were dried overnight in an oven at 60 °C. The ichthyoliths were examined under a binocular magnifier and the cleanest were gently brushed with a soft toothbrush to remove any traces of mud. Compared to fresh bones, the surface of ichthyoliths, as well as the interior of the vertebrae, is slightly orange-yellowish due to traces of iron oxides. This coloration decreases toward the interior of the bones. The surfaces of four thick bones were cleaned with a Dremel™ rotary tool equipped with a steel brush, to expose the internal part of the samples. All the brushed samples were then rinsed with deionised water and dried.

The (uncrushed) samples (50–380 mg) were then spiked with Tm (Barrat *et al.*, 1996), and directly dissolved in hot HNO_3 (14 N, 100 °C) for the phosphates or in HCl (2.5 N at room temperature) for the coralline algae ("mother solution"). An aliquot of the mother solution containing the equivalent of 4 mg of sample was evaporated to dryness and taken up with 5 ml HNO_3 (0.4 N) with traces of HF prior to analysis. Elemental abundances were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), with a Thermo Scientific ELEMENT XR™ spectrometer at Pôle Spectrométrie Océan (IUEM, Plouzané), using the same procedure as Barrat *et al.* (2024). As fresh codfish bones have relatively low concentrations of REEs, we used the remaining mother solution and separated the REEs using ion exchange columns filled with DGA resin (Barrat *et al.*, 2020).

Based on duplicates and various reference materials, the inferred reproducibility (RSD) for concentrations and elemental ratios is generally better than 3 % (*e.g.*, Barrat *et al.*, 2012, 2016, 2020, 2024 and references therein). The La and Ce anomalies are calculated using the La/La*, Ce/Ce* ratios, where X* is the extrapolated concentrations for a smooth PAAS-normalised REE pattern and X_{sn} is the concentration of element X normalised to PAAS: $La_{sn}^* = Pr_{sn}^3/Nd_{sn}^2$, $Ce_{sn}^* = Pr_{sn}^2/Nd_{sn}$ (Barrat *et al.*, 2023).

Results and Discussion

Four vertebrae of a fresh codfish and thirty-six ichthyoliths (mainly vertebrae) were analysed (Table S-1). The compositions obtained from the fresh samples vary little for most of the measured elements. Apart from some of them, such as Sr, V, Mn, Fe and Ba, which exceed a few µg/g, the others have low concentrations well below 1 µg/g. For the four samples, the U concentrations are almost constant and vary only between 110 and 120 ng/g. The REY concentrations are quite low, ranging from 2×10^{-5} to $4 \times 10^{-4} \times$ PAAS. However, the patterns are quite variable (Figure 1): two of them show negative Ce anomalies, while the other two do not (Ce/Ce* = 0.84–1.11). These significant variations within a single fish are quite unexpected and are not yet explained. It seems more likely that REY distributions acquired *in vivo* in the bones would reflect

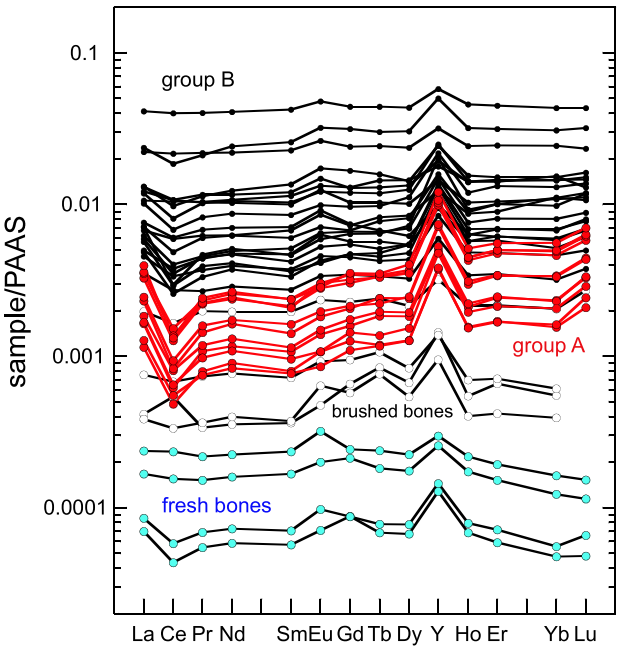

Figure 1 REE + Y patterns normalised to Post-Archean Australian Shale (PAAS; Pourmand *et al.*, 2012; Barrat *et al.*, 2020) for fish bones from Saint Pierre.

the nutrients absorbed by the fish rather than the characteristics of the seawater.

Ichthyoliths show much higher and more variable concentrations as illustrated by U (8.8–24.2 µg/g, average 15.7 µg/g) and REEs (*e.g.*, La = 0.05–1.83 µg/g). The PAAS-normalised REY patterns are also highly variable, and two types of samples can be identified (Figure 1). The samples with the lowest REY levels (Group A) show patterns with the characteristics of seawater, *i.e.* positive anomalies in Y (Y/Ho = 59–65), in La (La/La* = 1.72–2.09), and negative anomalies in Ce (Ce/Ce* = 0.61–0.81). For the other samples with higher REY levels (Group B), these anomalies fade with increasing concentrations (Y/Ho = 32–54, La/La* = 1.03–1.83, Ce/Ce* = 0.77–1.09). They are also correlated and suggest a binary mixture between the Group A samples and a second end member (Figure 2). The variations in the abundances of the other elements (for example, Th, Ga *vs.* Rb, Figure 2) confirm this interpretation: these trends connect the Group A samples to crustal compositions. Traces of detrital or clayey material trapped in the asperities and cavities of the samples, account for the ranges shown by the Group B ichthyoliths. Thus, the chemical heterogeneity recorded by this group should not be ascribed to putative enrichments or fractionations of elements absorbed from seawater nor porewater. The amounts of sedimentary material needed to explain the variations are very small. For the sake of exercise, we use the composition of the upper continental crust given by Rudnick and Gao (2014), and we calculate that the addition of less than 5 wt. % of sedimentary materials is enough to account for the spread of Group B samples. Because detrital particles or clays contain less U than Group A ichthyoliths, the addition of such low amount of these materials has no impact on the concentrations for this element. Unfortunately, this is not the case for REY and most of the other elements, such as alkali elements, Mn, Nb, Th, among others. For this reason, we will limit our discussion to Group A ichthyoliths, and the four samples cleaned with the steel brush.

Group A ichthyoliths are significantly poorer in alkali elements (Rb and Cs) than fresh fish bones (fresh bones contain

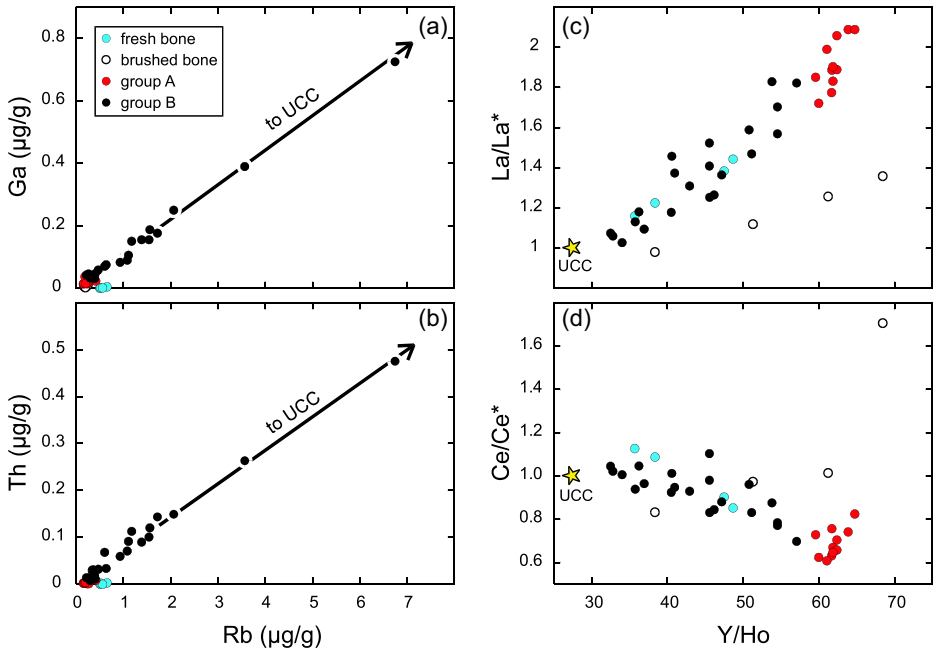

Figure 2 **(a)** Ga, **(b)** Th, *vs*. Rb, and **(c)** La/La*, **(d)** Ce/Ce* *vs*. Y/Ho plots for fish bones from Saint Pierre. The Upper Crust Composition (UCC) is shown for comparison (Rudnick and Gao, 2014).

about 0.5 µg/g Rb and about 0.02 µg/g Cs and Group A samples always less (*e.g.*, Rb = 0.16–0.41 µg/g, Table S-1). These differences could be attributed to organic matter still present in fresh bones or, more likely, could also be a consequence of apatite diagenesis. More significant are the notable enrichments in Fe in the ichthyoliths, which are correlated with the enrichments in U, Sr and REY (Figure 3). These variations are related to the development of authigenic phases during diagenesis, in particular Fe oxides (Kohn, 2008; Decrée *et al.*, 2018). The four strongly brushed samples show trace element abundances transitional between fresh bone and Group A ichthyoliths. Thus, the effects of diagenesis, although detectable in these samples, are more limited in the centre of the larger ichthyoliths.

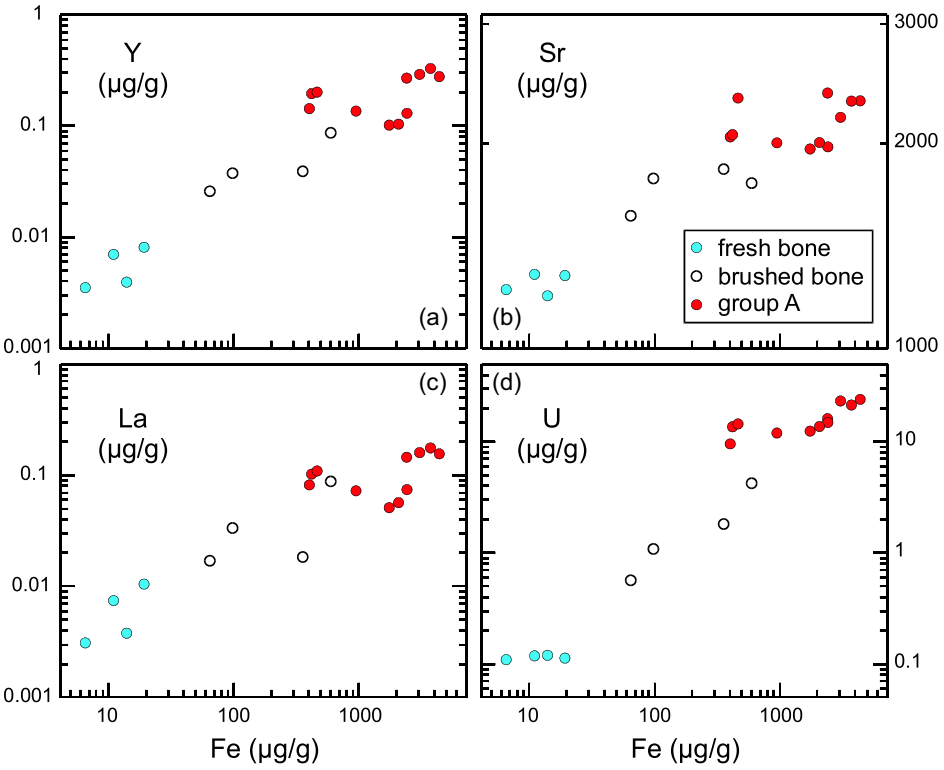

Figure 3 **(a)** Y, **(b)** Sr, **(c)** La, and **(d)** U *vs*. Fe plots for fish bones from Saint Pierre.

Table 1 Selected trace element abundances for fish bones from Saint Pierre, and calculated average accumulation rates.

	fresh bones			group A ichthyoliths			average rate
	average n = 4	minimum	maximum	average n = 11	minimum	maximum	
unit	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g/yr
Fe	12600	6530	19200	1996000	402100	4359000	39670
Sr	1246000	1195000	1286000	2148000	1968000	2380000	18049
Y	5.66	3.51	8.16	199	102	330	3.87
La	6.23	3.12	10.55	108	51.1	177	2.04
Ce	10.85	3.85	20.73	83.0	42.6	134	1.44
Pr	1.25	0.557	2.21	15.69	7.62	24.52	0.29
Nd	4.82	2.18	8.40	63.49	31.12	99.27	1.17
Sm	0.912	0.392	1.62	10.47	5.28	16.38	0.19
Eu	0.209	0.0862	0.389	2.36	1.04	3.68	0.043
Gd	0.955	0.530	1.47	13.49	6.61	21.32	0.25
Tb	0.126	0.061	0.213	2.09	1.04	3.12	0.039
Dy	0.725	0.357	1.20	13.33	6.72	21.43	0.25
Ho	0.142	0.072	0.229	3.24	1.61	5.40	0.062
Er	0.366	0.182	0.595	10.50	5.16	17.08	0.20
Yb	0.29	0.14	0.49	10.05	4.67	16.85	0.20
Lu	0.042	0.021	0.067	1.92	0.92	3.08	0.038
U	116	110	120	16050	9620	24240	319

To date, REY have not been determined in the coastal waters of the Saint Pierre and Miquelon Archipelago or Newfoundland. In the absence of such data, we analysed live coralline algae thalli, which concentrate these elements and whose REY patterns have the same shape as seawater (Barrat *et al.*, 2024). The REY patterns of Group A ichthyoliths and these algae are similar (Figure S-4). This match strongly suggests that REY uptake by ichthyoliths is largely dominated by quantitative incorporation without fractionation. An adsorption mechanism controlled by surface crystal-chemical properties, or a substitution mechanism controlled by bulk crystal-chemical properties, would have generated patterns very different to those of seawater (Koeppenkastrop and De Carlo, 1992; Reynard *et al.*, 1999). The minor differences observed between the patterns of the ichthyoliths and algae should not be overemphasised. The light deviations for Ce or Y anomalies could be explained by either local variations of seawater composition at the interface with sediments, or differences in the incorporation processes of these two types of materials (carbonates and phosphates).

The uptake rates of U and REY in cod bones can be easily deduced from the average compositions of Group A ichthyoliths and of the bones of freshly caught cod (Table 1). Assuming these rates have remained constant over the last 50 years, it can be calculated that the concentrations of U and Nd are increasing on average by 319 ng · g^{-1} · yr^{-1} and 1.2 ng · g^{-1} · yr^{-1}, respectively. These accumulation rates are indicative and representative of the fish bones on the North Atlantic seabed. For other cases, they must be considered as orders of magnitude, because they are certainly dependent on the structure (*e.g.*, crystallinity, porosity) of biogenic phosphates: for example, the dentin and enamel of the same fossil shark tooth display very different REE concentrations even though they fossilised under the same conditions and with the same fluids (*e.g.*, Picard *et al.*, 2002). These rates also depend greatly on the surface exposed to seawater, and therefore on the shape and size of the ichthyoliths. Furthermore, they cannot be applied to biogenic phosphates whose REY patterns indicate different U or REY uptake processes than the present ichthyoliths (*e.g.*, with bell-shape patterns like many Paleozoic phosphatic fossils), or different sources of REYs (*e.g.*, seawater and porewaters).

The results obtained here have important implications for the use of biogenic phosphates as palaeoceanographic proxies for the composition of past seawater. First, our observations confirm that fish remains rapidly accumulate REY and U on the seafloor surface before being buried in sediments. Within a few decades, their biological signatures are erased by those of seawater, and their REY patterns become virtually parallel to that of seawater, with the same anomalies in La, Ce and Y. However, a few decades spent on the surface of sediments cannot account for the high abundances observed in certain fossils. For example, some ichthyoliths found in Moroccan phosphates can have very high concentrations of REEs and U (with more than 80 ppm Nd, 900 ppm U and seawater-like REE patterns, *e.g.*, Balter *et al.*, 2011). Several thousand years at the water/sediment interface would be required to achieve such concentrations, which would only be possible with extremely low sedimentation rates. Alternatively, this could suggest that REY and U enrichments would be much greater after burial than at the water/sediment interface, making the preservation of the original marine signature illusory (*e.g.*, Toyoda and Tokonami, 1990).

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2544.

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