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The post-mortem history of a bone revealed by its trace element signature: The case of a fossil whale rostrum

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ABSTRACT

Studies dedicated to palaeoenvironments and taphonomy have made wide use of rare earth elements (REE) contents of fossil bones as proxies. However, the complex diagenetic history of individual specimens combined with intra-bone REE fractionation and the uncertain timing of REE uptake generally prevents the robust interpretation of REE patterns. In this case study we show that combining REE analysis with, on the one hand, histology and microstructural observations and, on the other hand, additional analyses of other trace elements, allows deciphering at least three distinct trace element uptake stages, as well as one leaching event.

More than 35 trace elements (including the REE) are analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) within compact rostrum bones of the Miocene-Pliocene beaked whale *Globicetus hiberus* from deep-sea deposits and a comparable extant specimen (Blainville's beaked whale *Mesoplodon densirostris*). Comparison of the extinct and the extant bones allows a better quantification of the diagenetic trace element content.

This study highlights the crucial role played by diagenetic minerals such as the Fe-Mn oxyhydroxides in the uptake and release of trace elements (Co, Ni, Ti, V, Zr, Hf and Nb) and REE by bones, in response to changes of the diagenetic fluid redox conditions over time. Such changes of the geochemical environment help constraining the post-mortem history of the bone and its interaction with diagenetic fluids. We conclude that the unique interpretation of geochemical proxies within individual fossil bones requires a thorough investigation of each individual specimen.

1. Introduction

Rare earth elements (REE) distribution in bioapatite has been widely used as a proxy for the study of palaeoenvironments (e.g., Kemp and Trueman, 2003; Patrick et al., 2004; Zigaite et al., 2015) and taphonomy (e.g., Trueman and Benton, 1997; Cook and Trueman, 2009; Suarez et al., 2010; Herwartz et al., 2011, 2013a,b; Kowal-Linka et al., 2014; Kowal-Linka and Jochum, 2015; Chen et al., 2015; McCormack et al., 2015; Keenan and Engel, 2017a), as well as for tracing the origin/provenance of fossil specimens (e.g., Trueman and Tuross, 2002; Patrick et al., 2002; Martin et al., 2005; Trueman et al., 2006; Patrick et al., 2007). While the REE have received much, attention, other trace elements are seldom considered (e.g., Koenig et al., 2009; Suarez et al., 2010; Kohn and Moses, 2013).

Trace element contents in fresh bones are generally low and increase during diagenesis (e.g., Trueman et al., 2006; Koenig et al., 2009; Suarez et al., 2010; Herwartz et al., 2011). From mineralogical and geochemical points of view, a bone can be described as a composite of nanometric crystals of carbonated hydroxylapatite, interwoven with organic matter, mostly collagen fibres (e.g., Trueman and Tuross, 2002 and references therein). Biological molecules such as collagen degrade rapidly post mortem, sometimes even before burial (e.g., Trueman et al., 2004), thus generating a porosity for diagenetic fluids to migrate through the mineralized tissue (Pfretzschner, 2004). Trace elements diffuse through the liquid phase or along grain boundaries and adsorb onto the apatite. Such a diffusion-adsorption mechanism has been favoured by many authors (e.g., Millard and Hedges, 1996; Kohn, 2008; Trueman et al., 2011). In the early phase of the fossilization process, carbonated hydroxylapatite is

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transformed into carbonated fluorapatite by dissolution-reprecipitation (Pasteris and Ding, 2009). Adsorbed trace elements are probably incorporated into the apatite lattice during this process (e.g., Herwartz et al., 2011; Kohn and Moses, 2013). However, diffusion is still required as a main transport mechanism for the elements from the sediment to the reaction/recrystallization front (Herwartz et al., 2011). Bone acts as a pump and scavenges the elements present in the surrounding soil/(marine) sediment (Kohn and Moses, 2013; Chen et al., 2015), inducing differential concentration gradients in the host media (Kohn and Moses, 2013). Recent experiments suggest that volume diffusion is too slow to explain trace elements enrichment in young fossil bones (Kohn and Moses, 2013). Transport limitations in the soil/sediment affect element distributions in fossil bones (Kohn and Moses, 2013). Intra-bone porosity changes dynamically with the degradation of biological tissue, dissolution-reprecipitation of bone apatite and subsequent precipitation of diagenetic minerals.

Investigations into the distribution of intra-bone trace elements have improved the understanding of the underlying physical processes (Millard and Hedges, 1996; Kohn, 2008; Koenig et al., 2009; Suarez et al., 2010; Trueman et al., 2011; Herwartz et al., 2011, 2013a,b; Kohn and Moses, 2013; Kowal-Linka et al., 2014; Kowal-Linka and Jochum, 2015; Chen et al., 2015; McCormack et al., 2015; Zigaite et al., 2015). REE intra-bone fractionation is variable between individual fossil sites, reflecting the local geology and fluid chemistry (e.g., Patrick et al., 2002, 2004; Trueman et al., 2006, 2011; Herwartz et al., 2013b; McCormack et al., 2015). The diagenetic fluid chemistry, however, can vary over the duration of the REE uptake (e.g., Suarez et al., 2010; Herwartz et al., 2011, 2013a,b; Kowal-Linka et al., 2014; Chen et al., 2015; McCormack et al., 2015). REE uptake into the bone is not restricted to early diagenesis, when bone porosity is high, but continues over a prolonged period of time (Kocsis et al., 2010; Herwartz et al., 2011, 2013a,b). Therefore, the robust interpretation of REE patterns and other trace element data requires detailed petrological and geochemical investigations (Suarez et al., 2010).

This paper focuses on the REE and other trace element inventory (mostly based on laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analyses of 35 elements) of an extremely thick (85 mm) and compact rostrum bone of the Miocene-Pliocene beaked whale (Cetacea, Odontoceti, Ziphiidae) *Globicetus hiberus* (*G. hiberus* hereafter; Bianucci et al., 2013; Antunes et al., 2015).

The *G. hiberus* specimen offers a good opportunity to investigate the post-mortem trace element uptake in a well-constrained marine environment. Special emphasis is given to (i) the effect of bone macroanatomy (especially tissue compactness) and histology on trace element uptake, (ii) the changes in chemistry (redox conditions) of the diagenetic fluids over time, and (iii) the impact of Fe-Mn oxyhydroxides precipitation/degradation on the trace elements uptake and loss.

In addition, a sample from the rostrum of the extant ziphiid *Mesoplodon densirostris* (*M. densirostris* hereafter) (Blainville's beaked whale) is studied for comparison. The compact and dense bone of this modern beaked whale (de Buffrenil et al., 2000; Li et al., 2013, 2015) is exempt of any kind of alteration.

2. Material and methods

2.1. Studied specimens

The fossil ziphiid specimen studied here (IEO DR26 026) is a partial skull, including the incomplete rostrum and part of the facial area (Fig. 1B–E), of *Globicetus hiberus*. This specimen is presently curated at the Instituto Español de Oceanografía, Gijón, Spain (Bianucci et al., 2013). The fossil (partial skull) has been preserved at ~1500 m depth on the border of the continental platform (Galicia Bank, Spain, 42°27′N, 11°59′W, 20 miles from the coast; Bianucci et al., 2013; Fig. 1A), a fossil-rich area where various extinct ziphiid taxa have been found. A latest Miocene – Early Pliocene age for this fauna has been deduced from the planktonic foraminifera found in cavities of cetacean skulls (Antunes et al., 2015). The fossil was associated with phosphorite pebbles and possibly partly buried under a thin layer of sediments (Bianucci et al., 2013).

The extant ziphiid sample selected for comparison is from an adult male Blainville's beaked whale *Mesoplodon densirostris*, curated at the Muséum National d'Histoire Naturelle, Paris, France (specimen number: MNHN AC. 1922/143; Fig. 1F).

2.2. Histological context of the REE analyses

Several transverse sections were made along the rostrum for a study on bone histology and microstructure (Dumont et al., 2016). A brief summary of this work is provided here. The bone tissue of the rostral hemispherical prominence and medial pad of *G. hiberus* displays extreme compactness (from 98 to 100%, by examination of the porosity), but five pairs of neurovascular canals with diameters up to 5.5 mm cross the bone longitudinally. Constituting the dorsal part of the rostrum, the prominence and medial pad are made of the joined, greatly thickened premaxillae, whereas the maxillae and the vomer form the ventral region. The premaxillary prominence and medial pad consist of parallel-woven osseous tissue (according to the recent terminology proposed by Prondvai et al., 2014) displaying an atypical laminar structure. In its most basal part, the structure of the prominence changes to plexiform or reticular patterns (see Francillon-Vieillot et al., 1990 for descriptive data on bone tissue type classification). Occupied by the maxillae and vomer, the ventralmost region of the rostrum is entirely occupied by large secondary osteons (400–700 µm in diameter), irregular in shape and orientation, forming a dense Haversian tissue. Haversian remodelling did not occur in the more dorsal part of the prominence. In terms of colour, the outermost part of the transverse sections of the rostrum is greyish, while the most internal parts of the bone are white.

For the present work, the transverse section crossing the medial pad of the premaxillae in front of the large spherical premaxillary prominence (slice B in Dumont et al.'s study) was sampled along a vertical axis in the domains of the premaxillae (dorsal), vomer (central), and maxillae (ventrolateral) (Fig. 1B, C). In the sections, the dorsal half of the premaxillae (up to the outer margin of the bone) displays a grey to brown colour, suggesting heavy diagenetic alteration of the bone. This zone (called PAZ from here on) seemingly corresponds topographically to the laminar organization of the bone tissue. The vomer and the maxillae appear orange-brown either in the vicinity of the vascular canals, or around secondary osteons. The vomer is more (dark) greyish near the premaxillae (Figs. 1C, 2A, B). In contrast, most of the maxillae is whitish to translucent (Fig. 1C, 2A, B). Scanning electron microscopy reveals that small amounts of Fe oxides and barite were deposited in the vicinity of openings interpreted as smaller vascular canals (Fig. 1D, E). Apart from these zones and notwithstanding the variegated colour pattern of the bone, the chemistry of the bone is homogeneous for the major elements composing it (2.86–4.45% F, 48.87–50.47% CaO, 33.60–35.11% P_2O_5; microprobe analyses). From a mineralogical point of view, this fossil bone is made of carbonate fluorapatite, taking into account (1) the fact that IR spectroscopy allows determining peaks that are characteristic of the carbonate group (see Appendix 1), and (2) its F contents.

The extant ziphiid specimen selected for comparison in the frame of this study is the rostrum of an adult male Blainville's beaked whale *M. densirostris*. Samples from numerous transverse and longitudinal sections of this specimen were analysed in previous works (e.g., de Buffrenil et al., 2000; Li and Pasteris, 2014). The samples of this histologically and structurally homogeneous specimen originate from a transverse section at about mid-length of the rostrum, in the dorsal domains of the maxillae, premaxillae, and vomer (Fig. 1F). *M. densirostris* is characterized by highly mineralized rostral bones (mineral rate above 86%) made of a dense Haversian tissue, with hypermineralized

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