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Oxygen isotopic variations in modern cetacean teeth and bones: implications for ecological, paleoecological, and paleoclimatic studies

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Abstract The oxygen isotope ratios ($\delta^{18}O$) preserved in marine sediments have been widely used to reconstruct past ocean temperatures. However, there remain significant uncertainties associated with this method, owing to assumptions about the $\delta^{18}O$ of ancient seawater which affects the temperature inferred from sediment $\delta^{18}O$ records. In this study, oxygen isotope compositions of phosphate in teeth and bones from five different modern cetacean species, including sperm whale, pygmy sperm whale, short-finned pilot whale, killer whale, and Cuvier's beaked whale, and three fossil whales were determined. The data were used to assess whether the oxygen isotope ratios of biogenic phosphate ($\delta^{18}O_p$) from cetaceans are a reliable proxy for the oxygen isotopic composition of ocean water ($\delta^{18}O_w$). The $\delta^{18}O_p$ values of modern cetaceans range from 15.5 ‰ to 21.3 ‰, averaging (19.6 ‰ ± 0.8 ‰) ($n = 136$). Using a greatly expanded global cetacean $\delta^{18}O_p$ dataset, the following regression equation is derived for cetaceans: $\delta^{18}O_w = 0.95317\ (\pm 0.03293)\ \delta^{18}O_p - 17.971\ (\pm 0.605)$, $r = 0.97253$. The new equation, when applied to fossil teeth and bones, yielded reasonable estimates of ancient seawater $\delta^{18}O_w$ values. Intra-tooth isotopic variations were observed within individual teeth. Among the selected species, the killer whale (*O. orca*) has the lowest $\delta^{18}O_p$ values and the largest intra-tooth $\delta^{18}O_p$ variation, reflecting its habitat preference and migratory behavior. The results show that oxygen isotope analysis of phosphate in cetacean teeth and dense ear bones provides a useful tool for reconstructing the oxygen isotopic composition of seawater and for examining environmental preferences (including migratory behavior) of both modern and ancient whales.

Keywords Oxygen isotopes · Phosphate · Cetacean · Whales · Teeth · Bones

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1 Introduction

Reconstruction of the oxygen isotopic compositions of ancient ocean waters through time is important for understanding the evolution of Earth's ocean and climate system. Oxygen isotope ratios of minerals that grow in seawater are related to both temperature and the oxygen isotopic composition of seawater. In previous studies, oxygen isotopic compositions of biogenic phosphates ($\delta^{18}O_p$) and other oxygen-containing minerals have been used to reconstruct the temperatures of ancient oceans [1–9]. These paleotemperature calculations require an assumption about the oxygen isotopic composition of ancient seawater. Based on oxygen isotope analysis of 23 biogenic phosphate samples from modern dolphins, porpoises, and whales, Yoshida and Miyazaki [10] show that there is a strong correlation between oxygen isotopic ratios of biogenic phosphate ($\delta^{18}O_p$) in cetaceans and their environmental water ($\delta^{18}O_w$) as defined by the following regression equation:

$$\delta^{18}O_p = 0.773\delta^{18}O_w + 17.8, \left(r^2 = 0.978\right). \quad (1)$$

However, application of the above equation to Miocene whales from Chesapeake Bay yielded unrealistically high $\delta^{18}O$ values of seawater ranging from +2 ‰ to +5 ‰ and unreasonable relationships between estimated ocean temperatures and seawater–$\delta^{18}O$ values [11].

In this study, we analyzed the oxygen isotope ratios of phosphate in teeth and bones from five different species of modern cetaceans. In addition, bone phosphate samples from three fossil whales from the Mio-Pliocene formations along the west coast of the Atlantic Ocean were analyzed. These data were used, in conjunction with data from the literature, to examine how the oxygen isotopic composition of biogenic phosphate from a diverse group of modern whales reflects the oxygen isotopic composition of modern seawater, and to assess whether the oxygen isotopic composition of phosphate in whale teeth and bones could serve as a reliable proxy for the oxygen isotopic composition of ocean water. The data were also used to examine how the oxygen isotopic variations within individual teeth reflect the migratory behaviors of these individuals.

2 Oxygen isotopes in calcified tissues

Mammalian calcified tissues such as enamel, dentine, and bone are all mineral/organic composites [12]. The mineral component in these calcified tissues is primarily in the form of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)—often referred to as bioapatite, while the organic component is mostly collagen. Bioapatite also contains a small amount of "structural" carbonate as carbonate ion substituting for phosphate and hydroxyl ions. Although carbon and nitrogen isotope analyses of collagen extracted from bones and teeth have been widely used to study the diets of modern and historic humans and animals including modern marine mammals [13, 14], the method is not useful for fossils because collagen is poorly preserved in pre-Holocene skeletal remains [15, 16]. Bioapatite, on the other hand, is often well preserved for much longer time in the geologic record [4].

Bioapatite is thought to precipitate in isotopic equilibrium with an animal's body water, and consequently, its oxygen isotopic composition should be determined by both precipitation temperature and oxygen isotopic composition of body water [4]. Because mammals typically maintain a constant body temperature that is not affected by fluctuations in environmental temperature, the oxygen isotope composition of bioapatite is directly related to the oxygen isotopic composition of body water, and the latter is controlled by a number of variables including the $\delta^{18}O$ of environmental water ingested by the animal (through food and/or drink) and physiological processes [17, 18]. Empirical data show that $\delta^{18}O$ of bioapatite from mammals is strongly correlated with the $\delta^{18}O$ of environmental water, although the relationship may differ for different animals due to differences in physiology and diet/drinking behavior [10, 19–24]. As such, oxygen isotope analysis of either the phosphate or "structural" carbonate component of bioapatite has been used to obtain valuable information about paleoenvironment [9, 25–28].

In paleoenvironmental studies, enamel is often the preferred material because the extremely low porosity of enamel makes its isotopic composition less susceptible to diagenetic alteration than dentine and bone [29]. The susceptibility of calcified tissues to isotopic alteration by diagenetic fluid increases with increasing porosity from enamel to dentine and bone [29]. Because bone is in general very porous, it has normally been considered unsuitable or less suitable for paleoenvironmental studies using its isotope ratios, especially the oxygen isotope ratios of "structural" carbonate which is readily altered by diagenesis [29]. The tympanic bullae and petrosals of cetaceans, however, are densely ossified ear bones [30]. These dense ear bones have a greater potential than other bones to preserve the original isotopic signatures. Because "structural" carbonate is much more susceptible than phosphate to isotopic exchange with fluids during diagenesis [31, 32], we focus our study on oxygen isotope ratios of phosphate-bound (PO_4^{3-}) oxygen ($\delta^{18}O_p$) rather than "structural" carbonate-bound (CO_3^{2-}) oxygen ($\delta^{18}O_c$) in bioapatite in cetacean teeth and ear bones.

3 Sample materials and methods

In this study, we selected and sampled 47 dense ear bones (tympanic bullae) and 13 teeth from 23 individual cetaceans from the collection of modern cetacean specimens at the Florida Museum of Natural History in Gainesville (Florida) for oxygen isotope analyses (Table 1 & Tables S1–S3). These individuals represent five different species of cetaceans belonging to the suborder Odontoceti (toothed whales), including *Physeter macrocephalus* (sperm whale), *Globicephala macrorhynchus* (short-finned pilot whale), *Ziphius cavirostris* (Cuvier's beaked whale), *Orcinus orca* (killer whale), and *Kogia breviceps* (pygmy sperm whale). A minimum of five different individuals from each species whenever possible were sampled for this study to ensure that the samples are representative of the population [22, 33]. A total of 136 samples, including 76