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

Burcu Ciner · Yang Wang · William Parker

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.

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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

Table 1 Summary results of oxygen isotope analyses of phosphate in bioapatite from modern cetaceans

Species	Common name	Mean $\delta^{18}O_P$ (vs. VSMOW)	±1σ	Number of samples	Number of individuals	Estimated body T (°C)
North Atlantic						
Globicephala macrorhynchus	Short-finned pilot whale	19.9	0.4	37	5	35.5
Kogia breviceps	Pygmy sperm whale	19.6	0.8	35	10	35.5
Physeter macrocephalus	Sperm whale	19.7	0.3	28	2	33.5
Ziphius cavirostris	Cuvier's beaked whale	19.1	0.2	8	4	35.5
Orcinus orca	Killer whale	17.8	1.1	23	1	35.5
East Pacific						
Globicephala macrorhynchus	Short-finned pilot whale	18.9	1.6	5	1	35.5

serial samples from five teeth from five individuals, were obtained for stable isotope analyses of phosphate in bioapatite. In addition, 19 samples were obtained from three densely ossified fossil ear bones (tympanic bullae) representing three whale individuals of Early-/Mid-Miocene and Early Pliocene ages for oxygen isotope analysis of phosphate (Table S4). The fossils were collected on the community open access day on the Lee Creek Mines by the landowner (personal communication with Dr. Zhexi Luo of University of Chicago). The Early Pliocene ear bones were from an unnamed pygmy sperm whale [34] and a cetotheriid mysticete or baleen-bearing whale (*Herpetocetus* sp.) [35]. They were collected from mining spoil piles traceable to the Pliocene Yorktown Formation at the Lee Creek Mines, N. Carolina [34]. The Early-/Mid-Miocene specimen was also a Cetotheriid baleen whale (*Parietobalaena*) collected from the Culvert Formation in Maryland (on an outcrop by the Chesapeake Bay, near the Culvert Marin Museum of Maryland) [36]. These fossil whale ear bones are from the same general area and of the same or similar ages as the cetacean fossils analyzed by Barrick et al. [11]. No permits were required for the described study, which complied with all relevant regulations.

Each ear bone specimen was cleaned by scraping off any dirt and organic matter from its surface with a rotary tool. Samples were then milled from two or more different locations on the cleaned surface (Fig. S1). Similarly, each tooth was cleaned by removing dirt, organic matter, and cementum from one side of the tooth using a rotary tool. A bulk sample was then obtained from the cleaned area by drilling along the length (growth axis) of the tooth, which represents the entire period of tooth formation. Serial samples were also collected from five selected teeth by drilling at different points on the cleaned area along the growth axis (Figs. S1, S2) in order to obtain a record of isotopic variations during the growth of the tooth. Because cetaceans have extremely thin enamel that caps only the upper most part of a tooth and does not extend far down the

tooth (Fig. S2), our tooth samples consist primarily of dentine, which was formed incrementally along the length (growth axis) of a tooth with the oldest growth layer closest to the cusp and the youngest growth layer closest to the pulp cavity or root (Fig. S2). Dentine growth layers in cetacean teeth are accreted at a shallow angle to the growth axis (Fig. S2). Thus, each serial sample may consist of more than one growth layer. As a result of this time-averaging effect associated with our sampling method, serial samples from a tooth provide a "running average" isotopic profile reflecting long-term (>1 year) trends in the isotopic composition of environmental water during the tooth growth. Although short-term seasonal signals may be smoothed out in the isotopic profile due to the sampling effect, these serial samples provide valuable insights into the life history of an individual whale that is consistent with its known behavior and habitat preference as discussed in a later section. The ideal method for obtaining higher time-resolution samples would be to cut the tooth longitudinally, and then use one half for age determination and another half for isotopic sampling of individual growth layers in order to get isotopic composition for each year. Unfortunately, this is not possible with museum specimens that we sampled. For fossil ear bones, each specimen was cut in half, and samples were then drilled at different points along a transect from the edge to the center on the cut surface (Fig. S1).

All of the samples were prepared for isotopic analysis using the Ag_3PO_4 method [37–40]. This method involves extraction of the PO_4^{3-} ions from bioapatite and subsequent precipitation of the extracted ions as solid crystals of Ag_3PO_4 for oxygen isotope analysis. 5–10 milligrams (mg) of sample powder was used for each sample. The sample powder was treated with 5 % sodium hypochlorite overnight to remove organic matter. After rinsing several times with distilled (DI) water, 1 mL 2 mol L^{-1} HF was added to the sample to precipitate CaF_2. The solution was transferred to another tube, and 20 % NH_3OH (~6 drops) was added to bring it to a neutral pH. 800 μL of 2 mol L^{-1}

AgNO$_3$ was added to the solution to precipitate Ag$_3$PO$_4$. The Ag$_3$PO$_4$ precipitates were separated from the solution via centrifugation, washed with DI water several times, and freeze-dried. Then, ~150 micrograms (µg) of Ag$_3$PO$_4$ were weighed into a silver capsule for oxygen isotope analysis. Oxygen isotope ratios were measured on CO using a high-temperature conversion elemental analyzer (TC/EA) connected to a Finnigan MAT Delta Plus XP stable isotope ratio mass spectrometer (IRMS) at the Florida State University. Triplicates of Ag$_3$PO$_4$ from each sample were analyzed to ensure no memory effect and good reproducibility (1σ = ±0.1 or better) and to obtain an average measured value for the sample. Two sets of three different laboratory standards were also analyzed in triplicates in each batch of samples and used to calibrate the results. The results are reported in the standard δ^{18}O notation relative to V-SMOW (Vienna Standard Mean Ocean Water). The analytical precision, based on repeated analysis of laboratory standards over the project period, is ±0.3 ‰ (1σ) or better. A value of 21.7 ‰ for NBS120a, which is the same as NBS120c [39], was used for data normalization.

4 Body temperatures, habitats, and migration of modern cetaceans

Cetaceans are marine mammals commonly known as whales, dolphins, and porpoises. Like other mammals, a cetacean maintains a constant body temperature. Most cetaceans have body temperatures in the range of 35 °C–37 °C [41–43] except the sperm whale which has a lower body temperature of 33.5 °C [44]. Higher temperatures (>37 °C) have been observed in unhealthy individuals [41, 42]. Heat production in marine mammals decreases during diving or submergence, and body temperature could decrease by as much as 2 °C during a long free dive [42]. Compared to other mammal species, whales can remain under water for longer periods of time (from 7 to 120 min depending on species). Below is a brief discussion of habitats and migration behaviors of the modern whales analyzed in this study (Fig. 1).

Short-finned pilot whales (*Globicephala macrorhynchus*) are a larger member of the dolphin group [45]. They prefer warmer tropical and subtropical waters and are primarily found in moderately deep waters with greater abundance of squids. Their diet is primarily based on squid, but they also eat octopus and fish. They usually dive to >300 m depths and stay up to 15 min. They are known as the "Cheetahs of the Deep" because of their high speed in deep waters. The maximum life span is 46 years in males and 63 years in females [45].

Pygmy sperm whales (*Kogia breviceps*) are found in the tropical to temperate waters of the Atlantic, Pacific, and Indian Oceans [46]. They are thought to prefer deep offshore waters over outer continental shelf and beyond, ranging from 400 to 3,500 m in depth, especially where upwelling of deep water produces local concentrations of food [46–48]. They can dive up to 45 min, but the average duration of dive reported is about 11 min, and their diet is based primarily on cephalopods [49]. Because they are rarely seen in the wild, little is known about their precise range and migration [46, 50].

Sperm whales (*Physeter macrocephalus*) are the largest among toothed whales. They inhabit ice-free marine waters mostly along the edges of continental and island shelves [51]. Sperm whales dive deeper and stay under water for longer periods of time than any other whale except the Cuvier's beaked whale [52]. They usually dive between 300 and 800 m and stay submerged for up to 40 min, but can dive to >2,000 m depths [51, 53]. Their life span is 60–70 years, although some females can reach age 90. They feed mostly on large- and medium-size squids, octopuses, demersal rays, sharks, and fishes [49]. Males and females behave differently when it comes to migration [54]. Only the adult males are known to travel to high latitudes for feeding, while females and their young usually remain in tropical and temperate waters [54].

Cuvier's beaked whales (*Ziphius cavirostris*) have the widest distribution of all the beaked whales and can be found in temperate, subtropical, and tropical waters [44]. They prefer deepwater habitats typically far from shore. They are deep divers and capable of diving to more than 1,000 m (up to ~3,000 m) depth and for more than 60 min [52]. They feed on squid, octopus, and deep-sea fish and possibly crustaceans living near the seafloor [44]. Their life span is at least 40 years and possibly more than 60 years. Their teeth are not functional teeth so they probably capture most of their prey by suction like most or all other beaked whales [44].

Killer whales (*Orcinus orca*) are the most widespread cetaceans in the oceans from polar waters to tropical seas, although they seem to prefer high latitudes and coastal waters [54]. During the summer, most killer whales live near the ice edge where they prey on baleen whales, penguins, and seals. Their migration destination and distance is not well known, and some may stay in high-latitude waters year-round. The life span is 50–60 years for males and 80–90 years for females. Killer whales have a diverse diet ranging from small schooling fish and squid to large baleen and sperm whales [54]. Kusuda et al. [43] monitored the body temperature of a female killer whale over a course of more than a year and found that its body temperature changed cyclically from 35.3 °C to 35.9 °C, with an average of 35.5 °C.
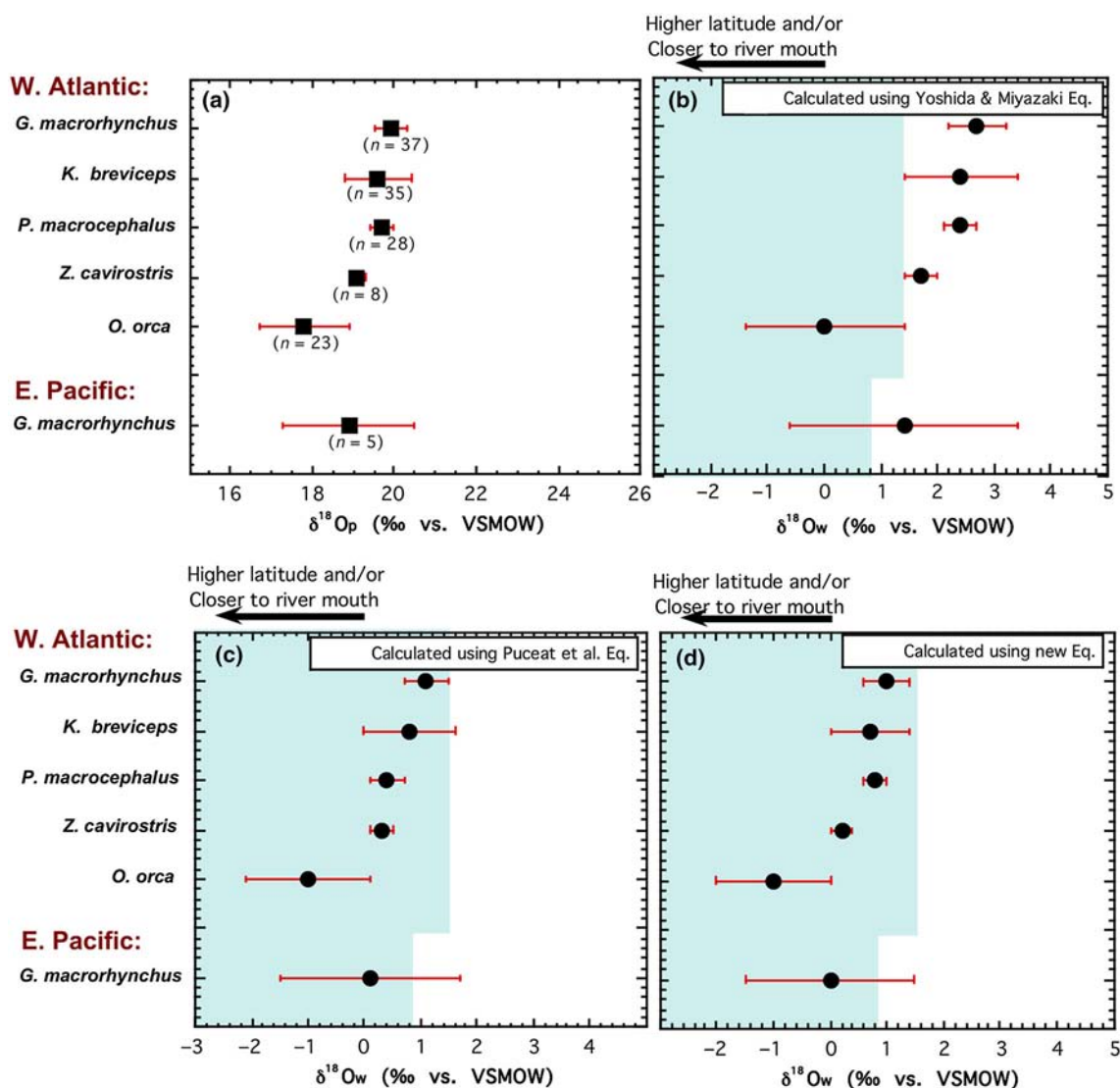
Fig. 1 a Mean $\delta^{18}O_p$ values of modern whales; **b** calculated seawater $\delta^{18}O_w$ values using the empirical equation of Yoshida and Miyazaki [10], **c** calculated seawater $\delta^{18}O_w$ values using the phosphate–water oxygen isotope fractionation equation [58] and body temperatures of 33.5 °C and 35.5 °C for the sperm whale and all other whales, respectively (see Sect. 6 in the text), **d** calculated seawater $\delta^{18}O_w$ values using the new empirical equation. Numbers in brackets in **a** indicate the number of phosphate samples analyzed. Shaded areas are observed $\delta^{18}O_w$ of the present-day western Atlantic and eastern Pacific waters [61]

5 Results

The results of oxygen isotope analyses of phosphate ($\delta^{18}O_p$) in bioapatite from modern whales are summarized in Table 1. All the specimens analyzed in this study were collected along the coasts of Florida and Georgia, except one short-finned pilot whale (UF18769) which was from the coast of southern California. The $\delta^{18}O_p$ values of bioapatite from the studied whales range from 15.5 ‰ to 21.3 ‰, averaging 19.6 ‰ ± 0.8 ‰ ($n = 136$) (Table S1).

Most of the modern species examined display relatively narrow ranges of oxygen isotopic variation except the short-finned pilot whale (UF18769) from the southern California coast and the killer whale (UF1507) from Florida (Fig. 1a; Tables S1 & S2). Serial samples from five individual teeth from selected species display intra-tooth $\delta^{18}O$ variations ranging from 0.5 ‰ to 2.8 ‰ (Figs. 2–4). The largest intra-tooth $\delta^{18}O$ variation is observed in the killer whale (*O. orca*) (Fig. 2a). The $\delta^{18}O_p$ values of bioapatite samples from two Pliocene ear bones are (19.7 ‰ ± 0.6 ‰) ($n = 8$), similar to the mean $\delta^{18}O_p$ of modern samples, whereas the $\delta^{18}O_p$ values of samples from a Miocene whale yielded a lower mean $\delta^{18}O_p$ value of (18.7 ‰ ± 0.3 ‰) ($n = 10$) (Table S3).
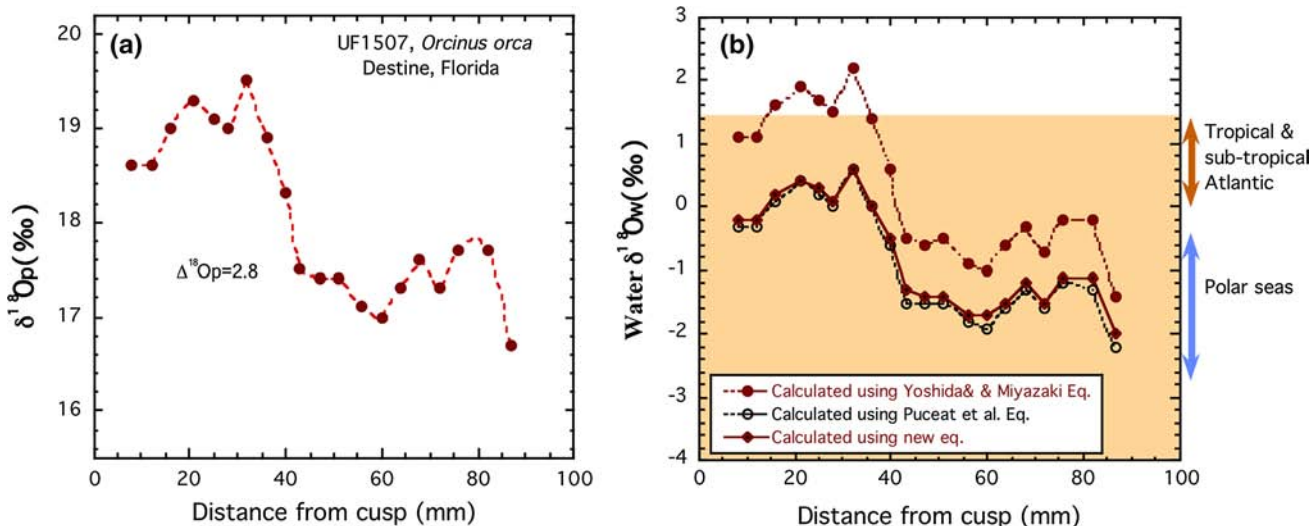
Fig. 2 **a** Intra-tooth $\delta^{18}O_p$ variations in a modern killer whale, **b** calculated seawater $\delta^{18}O_w$ values using empirical equations (i.e., Yoshida and Miyazaki equation and the new equation established in this study) and the phosphate–water oxygen isotope fractionation equation [58] assuming a body temperature of 35.5 °C (see Sect. 6 in the text). The serial sample closest to the cusp represents the earliest years of growth, and samples farther away from the cusp represent progressively later years of growth

6 Discussion

6.1 $\delta^{18}O_p$ and $\delta^{18}O_w$ relationship

Oxygen isotopes in biogenic phosphate have been investigated since 1960s [1–4, 8, 55–58]. These studies have shown that $\delta^{18}O_p$ values of bioapatite are a valuable environmental proxy because bioapatite appears to form in isotopic equilibrium with body water. The phosphate–water oxygen isotope equilibrium fractionation equation [4, 59] was recently revised by Puceat et al. [58]. The revised equation takes into account the differences in analytical methods used to determine the isotopic composition of phosphate-bound oxygen and is expressed as follows [58]:

$$T(°C) = 118.7 - 4.22\,[(\delta^{18}O_p + (22.6 - \delta^{18}O_{NBS120c})) - \delta^{18}O_w], \tag{2}$$

where T is the temperature at which phosphate is formed, $\delta^{18}O_w$ is the $\delta^{18}O$ of water from which phosphate is precipitated, and $\delta^{18}O_{NBS120c}$ is the $\delta^{18}O$ of the phosphate standard NBS120c used to normalize the data. Currently, oxygen isotope measurements of phosphate are standardized using a $\delta^{18}O$ value of either 21.7 ‰ [60] or 22.6 ‰ for NBS120c in different laboratories [40]. Eq. (2) allows the water isotopic composition ($\delta^{18}O_w$) to be calculated from the oxygen isotopic composition of phosphate ($\delta^{18}O_p$) if the temperature is known.

Since whales maintain constant body temperatures and the water in their food has the same oxygen isotopic composition as the environmental water, their bioapatite

$\delta^{18}O_p$ values are expected to reflect the $\delta^{18}O_w$ values of their environmental water [10, 14]. Yoshida and Miyazaki [10] established an empirical relationship between cetacean $\delta^{18}O_p$ and environmental water $\delta^{18}O_w$ as defined by Eq. (1). As the body temperatures of most whales, especially ancient whales, are not known, Eq. (1) offers a useful tool that permits the $\delta^{18}O_w$ values of seawater to be calculated from the cetacean $\delta^{18}O_p$ values alone without having to measure or make assumptions about their body temperatures.

In order to assess the reliability of using the $\delta^{18}O_p$ values of cetacean bioapatite as a proxy for $\delta^{18}O_w$ of seawater, we first calculated the $\delta^{18}O_w$ of seawater from the measured $\delta^{18}O_p$ values of bioapatite from modern whales in two different ways: (1) using Eq. (1)—the empirical equation established by Yoshida and Miyazaki [10]; and (2) using Eq. (2)—the phosphate–water isotope fractionation equation [58], assuming that body temperatures are 33.5 °C for the sperm whale [44] and 35.5 °C for all the other whales [41–43].

The $\delta^{18}O_w$ values derived from the $\delta^{18}O_p$ values of our modern whale samples (with the exception of the killer whale) using Eq. (1) are mostly higher than the observed $\delta^{18}O_w$ values of modern Atlantic and Pacific Ocean waters (Figs. 1b, 2b, 3b, 4a–c). The $\delta^{18}O_w$ values of body water calculated using Eq. (2) and body temperatures, on the other hand, are generally consistent with the seawater $\delta^{18}O_w$ values of these whales' habitats (Figs. 1c, 2b, 3b, 4a–c). Thus, comparisons of calculated and observed seawater $\delta^{18}O_w$ values show that reliable seawater $\delta^{18}O_w$
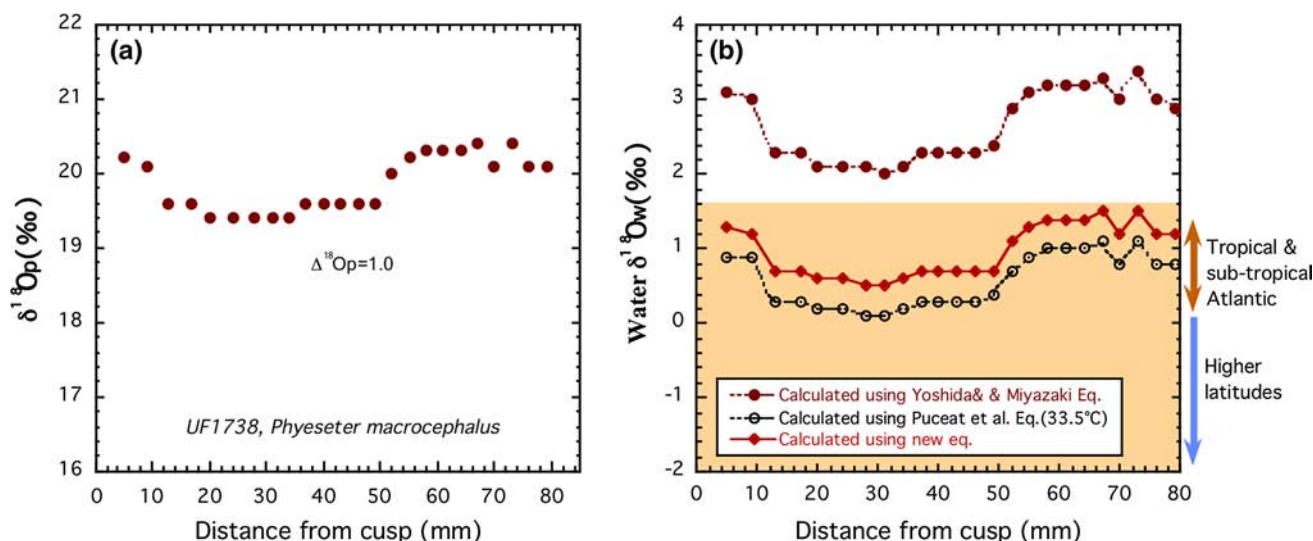
Fig. 3 **a** Intra-tooth $\delta^{18}O_p$ variations in a sperm whale, **b** calculated seawater $\delta^{18}O_w$ values using empirical equations (i.e., Yoshida and Miyazaki equation and the new equation in this study) and the phosphate–water oxygen isotope fractionation equation [58] assuming a body temperature of 33.5 °C (see Sect. 6 in the text). The serial sample closest to the cusp represents the earliest years of growth and samples farther away from the cusp represent progressively later years of growth

values can be derived from cetacean $\delta^{18}O_p$ values using the phosphate–water oxygen isotope fractionation equation, provided that the body temperature of the whale is known. However, the empirical equation of Yoshida and Miyazaki [10], which is based on limited data, is not applicable to modern whales in the Atlantic Ocean and the east Pacific Ocean, yielding unreasonably high seawater $\delta^{18}O_w$ values (Figs. 1b, 2b, 3b, 4a–c).

Using a greatly expanded global modern cetacean $\delta^{18}O_p$ dataset (Tables S2, S4) that includes the new data from this study and previously published $\delta^{18}O_p$ data [10], in conjunction with seawater $\delta^{18}O_w$ data [Fig. S3, 61], we re-evaluated the relationship between $\delta^{18}O_w$ and $\delta^{18}O_p$ (Fig. 5) and derived the following regression equation:

$$\delta^{18}O_w = 0.95317\,(\pm 0.03293)\delta^{18}O_p - 17.971\,(\pm 0.605),$$
$$r = 0.97253. \tag{3}$$

The intercept of the above equation has a standard error of 0.605 and is significantly different from zero (the null hypothesis) with a p value of $<2.0 \times 10^{-16}$. The slope (0.953) has a standard error of 0.033 and is also significantly different from zero ($p < 2.0 \times 10^{-16}$). It is important to note that only bulk sample $\delta^{18}O_p$ data were used in the regression analysis (Fig. 5). For a specimen that was serial-sampled, a bulk $\delta^{18}O_p$ value for the specimen was calculated by averaging the $\delta^{18}O_p$ values of all serial samples from that specimen. Our regression analysis did not include $\delta^{18}O_p$ data from migrants (i.e., the short-finned pilot whale UF18769 from the east Pacific and the killer whale UF1507) as indicated by their relatively large isotopic variability ($1\sigma > 1$ ‰) (Table 1). This is because a migrant that traveled through geographically

distinct habitats with different $\delta^{18}O_w$ values would have recorded the $\delta^{18}O_w$ variability of its environmental water in phosphate mineralized at different times during the growth of its teeth and bones, resulting in large isotopic variations in samples collected from different parts of a tooth or from different hard tissues (such as enamel, dentine, and bulla bone). Consequently, the average $\delta^{18}O_p$ value for a migrant may not reflect the $\delta^{18}O_w$ of a specific habitat or the habitat in which it was last found. The $\delta^{18}O_p$ data of Barrick et al. [11] were also excluded in the regression analysis because of possible methodological differences in sample processing and analyses as discussed below.

6.2 Reconstruction of seawater $\delta^{18}O_w$ from $\delta^{18}O_p$ of modern and fossil whales

Eq. (3) differs significantly from the Yoshida and Miyazaki [10] equation in both intercept and slope at 99.99 % confidence level (Fig. 5). Application of this new empirical equation to the $\delta^{18}O_p$ data from our modern bulk and serial samples yielded $\delta^{18}O_w$ values that are consistent with the observed seawater $\delta^{18}O_w$ values of these whales' known habitats and are also very similar to those calculated using the oxygen isotope fractionation equation and body temperature (Figs. 1–4).

A previous study [11] showed that the Yoshida and Miyazaki [10] equation yielded unreasonably high seawater $\delta^{18}O_w$ values ranging from 2 ‰ to 5 ‰ for the Miocene and Pliocene oceans. The $\delta^{18}O_p$ values of our fossil ear bone samples range from 18.3 ‰ to 20.7 ‰, averaging 19.2 ± 0.7 ($n = 19$). Using the Yoshida and Miyazaki [10]
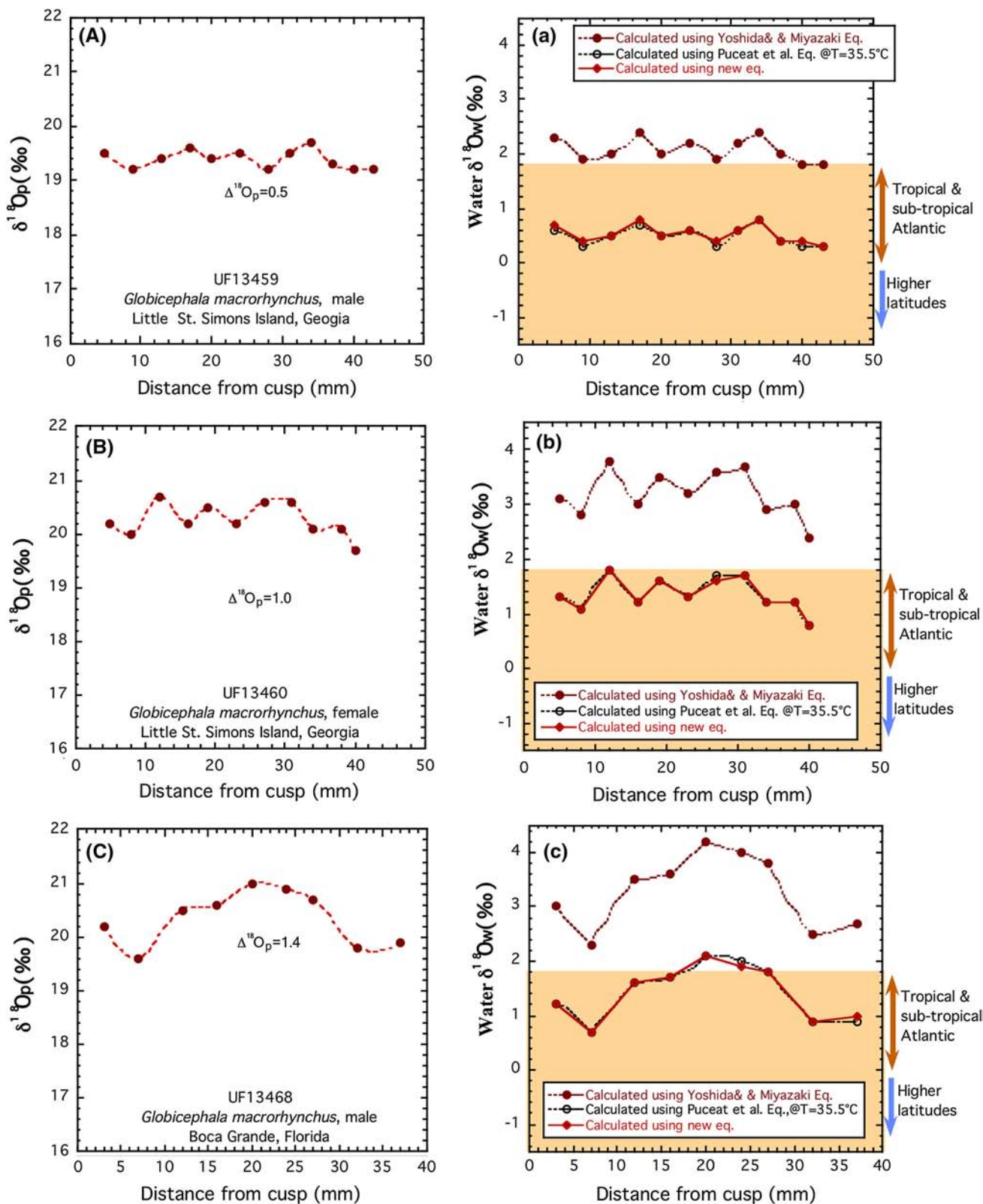
Fig. 4 **A–C** Intra-tooth $\delta^{18}O_p$ variations in three short-finned pilot whales and **a–c** corresponding seawater $\delta^{18}O_w$ values calculated using empirical equations (i.e., Yoshida and Miyazaki equation and the new equation in this study) and the phosphate–water oxygen isotope fractionation equation [58] assuming a body temperature of 35.5 °C (see Sect. 6 in the text)
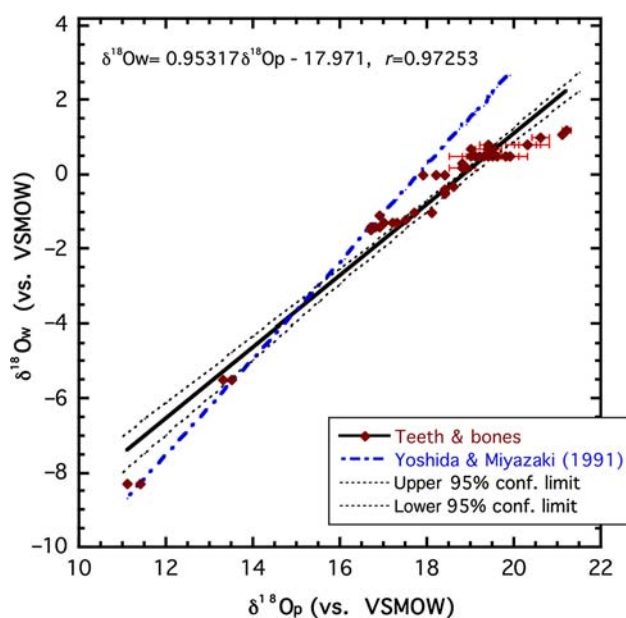
Fig. 5 Relationship between $\delta^{18}O$ of water ($\delta^{18}O_w$) and $\delta^{18}O_p$ values of bio-apatite from modern cetaceans, including new data produced in this study and data from the literature [10]. Each datum point represents an individual specimen. Error bar represents one standard deviation from the mean of multiple samples from the same specimen. Error envelope represents 95 % confidence limits for the mean response on the independent variable $\delta^{18}O_p$

equation, these $\delta^{18}O_p$ values yielded estimated seawater $\delta^{18}O_w$ values of (2.4 ‰ ± 0.8 ‰) for the Early Pliocene and (1.2 ‰ ± 0.5 ‰) for the Early-/Middle Miocene (Table S3), which are ∼1 ‰–3 ‰ higher than those derived from paired measurements of Mg/Ca ratios and benthic foraminiferal $\delta^{18}O$ values [62]. However, using the new empirical Eq. (3), these same samples from the western Atlantic region yielded seawater $\delta^{18}O_w$ values of (0.5 ‰ ± 0.5 ‰) for the modern, (0.8 ‰ ± 0.6 ‰) for the Early Pliocene, and (−0.1 ‰ ± 0.3 ‰) for the Early/Middle Miocene ocean (Fig. 6; Tables S2, S3), which are very reasonable given our understanding of the long-term trend in global climate and isotopic balance between the ice and the ocean [7].

Applying the new empirical equation to previously published modern and fossil cetacean $\delta^{18}O_p$ data, we estimated the $\delta^{18}O_w$ values of both modern and ancient ocean waters (Fig. 6a). The estimated $\delta^{18}O_w$ values are 1 ‰–2 ‰ lower than those derived from the Yoshida and Miyazaki [10] equation (Tables S3, S4). The seawater $\delta^{18}O$ values for the Pliocene and Miocene oceans estimated from cetacean tooth/bone $\delta^{18}O_p$ values using the new empirical equation are generally within the $\delta^{18}O$ range of modern seawater (Fig. 6a) and also in broad agreement with the seawater $\delta^{18}O_w$ record derived from paired measurements of benthic foraminiferal $\delta^{18}O$ values and Mg/Ca ratios [62], except those derived from fossil bone-$\delta^{18}O_p$ data of Barrick et al.

[11]. This difference reflects a consistent offset between the $\delta^{18}O_p$ values of cetacean fossils reported in Barrick et al. [11] and the $\delta^{18}O_p$ values of similar aged fossil samples analyzed in this study and in Amiot et al. [63]. Our fossil whale samples yielded $\delta^{18}O_p$ values of (19.2 ‰ ± 0.7 ‰) ($n = 19$), and the fossils analyzed by Amiot et al. [63] have an average $\delta^{18}O_p$ value of (19.5 ‰ ± 0.8 ‰) ($n = 24$). In comparison, the fossils analyzed by Barrick et al. [11] have $\delta^{18}O_p$ values of (20.7 ‰ ± 0.7 ‰) ($n = 45$), which is 1 ‰–2 ‰ higher than the $\delta^{18}O_p$ values of our samples of similar age from the same region and also higher than the $\delta^{18}O_p$ values reported in Amiot et al. [63]. This isotopic difference may be in part due to the differences in sample preparation and analysis methods.

As shown in Fig. 6, the estimated seawater $\delta^{18}O$ values, excluding those derived from $\delta^{18}O_p$ data reported in Barrick et al. [11], display a long-term trend that is consistent with the global cooling trend during the Late Cenozoic [7]. Because polar ice caps and mountain glaciers are highly depleted in the heavy oxygen isotope ^{18}O, the oceans became enriched in ^{18}O (i.e., higher $\delta^{18}O_w$ values) as the volume of continental ice increased due to climate cooling in the Late Cenozoic (Fig. 6). Despite the large uncertainties in the age estimates of the fossil whales, these initial data show that application of the new empirical Eq. (3) to bioapatite-$\delta^{18}O_p$ values of fossil cetaceans yielded reasonable estimates of the oxygen isotopic composition of ancient seawater (Fig. 6).

The above analyses of available cetacean $\delta^{18}O_p$ data show that the $\delta^{18}O_w$ of seawater can be reliably estimated from the $\delta^{18}O_p$ of phosphate-bound oxygen in cetacean teeth and bones using either Eq. (2), provided that the body temperature is known, or Eq. (3). For whales whose body temperatures are unknown, the new empirical equation provides a useful tool for reconstructing the $\delta^{18}O_w$ values of their environmental waters.

6.3 Intra-tooth $\delta^{18}O_p$ variations and migratory behaviors

Mammalian teeth are valuable archives of changes in diet and environmental water during the time period of tooth growth. As a tooth grows, enamel and dentine are formed incrementally along the growth axis of a tooth. Cetaceans' teeth, unlike terrestrial mammalian teeth, are made mostly of dentine, with a very thin enamel cap that does not extend far down the tooth (Fig. S2). Dentine growth layers in cetacean teeth are thought to be annual layers, and the age of a cetacean is commonly estimated by counting dentine layers [64]. As cetacean teeth grow incrementally, changes in habitats and differences in migration behaviors among cetacean species should be reflected in their intra-tooth isotopic records [14].
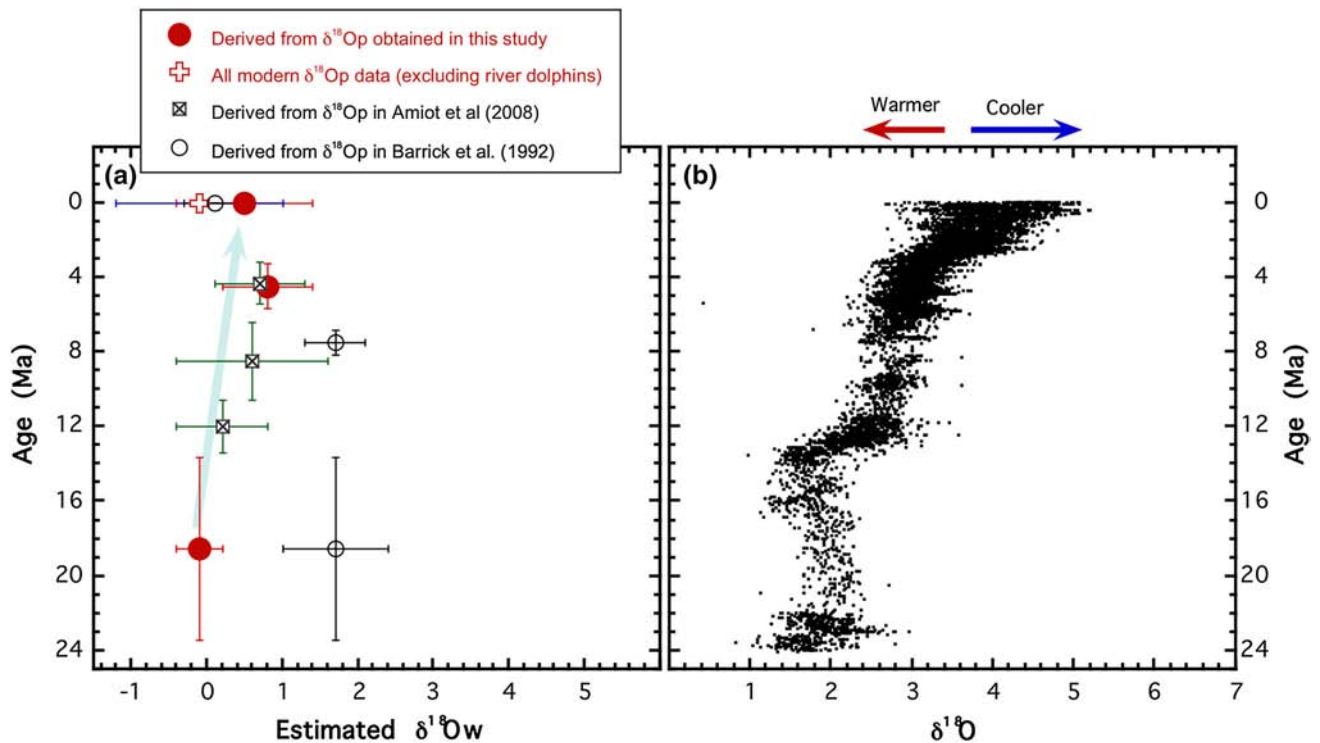
Fig. 6 Temporal variations in **a** seawater $\delta^{18}O_w$ values derived from the $\delta^{18}O_P$ values of cetacean bioapatite using the new empirical equation, **b** the marine foraminiferal $\delta^{18}O$ record [7]. $\delta^{18}O_P$ data include data obtained in this study and those reported in the literature [11, 63]. The estimated seawater $\delta^{18}O_w$ values, excluding those derived from the $\delta^{18}O_P$ data in Barrick et al. [11], display a long-term trend consistent with the global cooling trend during the Late Cenozoic [7]

Surface ocean water has slightly higher $\delta^{18}O_w$ values (>0 ‰) in regions affected by intense evaporation, while coastal areas receiving ^{18}O-depleted freshwater runoff may have lower $\delta^{18}O_w$ values (<0 ‰) (Fig. S3). Seawater in high latitudes or polar regions also has lower $\delta^{18}O_w$ values (<0 ‰) resulting from the input of precipitation or melt-water runoff that is highly depleted in ^{18}O (Fig. S3). Thus, individuals that migrate would be expected to display intra-tooth $\delta^{18}O_p$ variations within their teeth as the oxygen isotopic composition of seawater may change among different marine environments (Fig. S3). Also, some cetaceans may prefer to stay offshore while others inhabit nearshore environments. Species that prefer near shore environments may have lower $\delta^{18}O_p$ values than their offshore counterparts [33], due to inputs of ^{18}O-depleted freshwater into coastal waters. Different species may display different characteristics of migration patterns and habitat preferences [65, 66]. These behavioral differences may be examined by studying their intra-tooth isotopic patterns. Stable C and N isotope analyses of collagen extracted from dentine growth layers in cetacean teeth have been shown to provide valuable information about ontogenetic shifts in diets of killer whales in northeast Pacific Ocean [13]. As discussed in a previous section, collagen is poorly preserved in fossils, whereas phosphate-bound oxygen is very resistant to diagenetic alteration and tends to preserve its original isotopic

signature [4, 67–69]. Below we demonstrate that precise serial oxygen isotopic measurements of phosphate-bound oxygen from individual teeth can be a potentially powerful tool for examining environmental preferences over the duration of tooth growth for both modern and fossil cetaceans. Such data can be used further to infer migration of whales between habitats with different oxygen isotopic signatures over the lifetime of a whale.

Serial samples were collected from five teeth from five individual whales, including a killer whale, a sperm whale, and three short-finned pilot whales, for measurements of $\delta^{18}O_p$ values (Figs. 2–4, Table S1). As discussed in the previous section, seawater $\delta^{18}O_w$ can be reliably reconstructed from the $\delta^{18}O_p$ of cetacean bioapatite using either Eq. (2) if body temperature is known or Eq. (3). The serial $\delta^{18}O_p$ data from the killer whale (O. orca) range from 16.7 ‰ to 19.5 ‰ (Fig. 2a), with an average of (18.0 ‰ ± 0.9 ‰) ($n = 20$). These $\delta^{18}O_p$ values are significantly lower than those of the other whales analyzed (t test, $t = 11.366$, $d.f. = 74$, M.D. $= 1.8$, $p < 0.0001$). The intra-tooth $\delta^{18}O_p$ variation (2.8 ‰) observed in this killer whale is the highest among all the species examined. The high intra-tooth $\delta^{18}O_p$ variability suggests that it might be a "transient" or an "offshore" killer whale, and migrated great distances between low and high latitudes. The seawater $\delta^{18}O_w$ values estimated from the serial $\delta^{18}O_p$

data using Eq. (3) are $(-1.0 ‰ \pm 1.0 ‰)$ $(n = 20)$, ranging from about 0.6 ‰ to -2.0 ‰ (Fig. 2b). Because the tip (~ 5 mm) of the tooth is broken, the oldest growth layers representing the earliest part of its life history are missing (Fig. S1b, S1d). The reconstructed $\delta^{18}O_w$ values suggest that this killer whale lived in temperate waters in mid latitudes during the earlier years of its life and then migrated to polar waters characterized by lower $\delta^{18}O$ values (Fig. 2b, Fig. S3). Both the tooth and ear bone samples from this killer whale have the lowest $\delta^{18}O$ values of all species examined in this study, indicating that this individual (UF1507) spent most of its lifetime in high-latitude environments where seawater has lower $\delta^{18}O$ values due to inputs of ^{18}O-depleted precipitation and meltwater (Fig. 2b, Fig. S3). Since bones continuously remodel during an animal's lifetime using newly ingested oxygen [63], the $\delta^{18}O_p$ value of the outermost layer of an ear bone should reflect the $\delta^{18}O_w$ value of the environmental water of the animal's most recent residence. Ear bone samples belonging to the same individual (UF1507) have an average $\delta^{18}O_p$ of $(16.1 ‰ \pm 0.1 ‰)$ $(n = 3)$. Applying Eq. (3), these $\delta^{18}O_p$ values yielded a seawater $\delta^{18}O_w$ value of $(-2.7 ‰ \pm 0.4 ‰)$, which is close to the $\delta^{18}O_w$ calculated from the serial sample representing the latest period of the whale's life (Fig. 2b). However, if the ear bone (tympanic bullae) was fully mineralized within first year after birth and was not remodeled like other skeletal bone as suggested by some studies [30, 70], the negative seawater $\delta^{18}O_w$ values derived from the ear bone $\delta^{18}O_p$ values would indicate that this individual was born in coastal water in high latitudes (Fig. S3). It then spent most of its early years in temperate waters at mid latitudes and later years in polar waters at high latitudes (Fig. 2b).

Serial samples from a sperm whale (*P. macrocephalus*) tooth (UF1738) have $\delta^{18}O_p$ values ranging from 20.4 ‰ to 19.4 ‰ (Fig. 3a, Fig. S2), with a mean of $(19.9 ‰ \pm 0.4 ‰)$ $(n = 24)$, significantly higher than that of the killer whale (Student's t test, $t = 8.65$, $d.f. = 24$, M.D. = 1.8, $p < 0.0001$). Corresponding seawater $\delta^{18}O_w$ values estimated using Eq. (3) range from 0.5 ‰ to 1.5 ‰ (Fig. 3b), averaging $(1.0 ‰ \pm 0.4 ‰)$ $(n = 24)$. These reconstructed seawater $\delta^{18}O_w$ values are typical of mid-latitude waters in the Atlantic Ocean (Fig. 3b, Fig. S3). Unfortunately, the gender of this specimen was unidentified. Given the relatively high estimated $\delta^{18}O_w$ values and the relatively low intra-tooth $\delta^{18}O$ variation (1.0 ‰), this tooth (UF1738) may belong to a female as female sperm whales are in general less likely to travel great distances to high latitudes [54]. The serial $\delta^{18}O$ data (Fig. 3b) also show that this individual was born in the subtropical water and mostly inhabited subtropical waters of the Atlantic Ocean (Fig. 3b, Fig. S3), which is consistent with the known preferred habitats (i.e., ice-free, offshore marine

waters) of sperm whales [51]. Ear bone samples belonging to another individual (UF9972) yielded $\delta^{18}O_p$ values ranging from 19.4 ‰ to 19.6 ‰, with an average of $(19.5 ‰ \pm 0.1 ‰)$ $(n = 4)$. The $\delta^{18}O_w$ values derived from the ear bone $\delta^{18}O_p$ values using Eq. (3) range from 0.5 ‰ to 0.7 ‰, averaging $(0.6 ‰ \pm 0.1 ‰)$ $(n = 4)$, which is also consistent with the $\delta^{18}O_w$ of subtropical waters in the mid-Atlantic Ocean (Fig. S3).

Serial samples from three short-finned pilot whales (*G. macrorhynchus*) yielded similar $\delta^{18}O_p$ values (Fig. 4A–C) averaging $(20.0 ‰ \pm 0.5 ‰)$ $(n = 32)$, which is very similar to that of the sperm whale (Fig. 3a) but significantly higher (Student's t test, $t = 9.67$, $d.f. = 50$, M.D. = 1.9, $p < 0.0001$) than the mean $\delta^{18}O_p$ value of the killer whale (Fig. 2a). Short-finned pilot whales (*G. macrorhynchus*) are known to mostly prefer tropical and temperate waters [45, 71]. The seawater $\delta^{18}O_w$ values calculated from the serial $\delta^{18}O_p$ data from the three teeth using eq. (3) are $(1.1 ‰ \pm 0.5 ‰)$ $(n = 32)$. Ear bone samples from one individual (UF13468) display $\delta^{18}O_p$ values of $(19.6 ‰ \pm 0.2 ‰)$ $(n = 3)$. Applying Eq. (3), these ear bone $\delta^{18}O_p$ values yielded seawater $\delta^{18}O_w$ values of $(0.7 ‰ \pm 0.2 ‰)$ $(n = 3)$, similar to the average $\delta^{18}O_w$ value estimated from the $\delta^{18}O_p$ values of the teeth. The average $\delta^{18}O_w$ value derived from $\delta^{18}O_p$ data from *G. macrorhynchus* from the Florida coastal waters, including all data from teeth and ear bone samples, is $(1.0 ‰ \pm 0.4 ‰)$ $(n = 37)$ (Table 1). These reconstructed seawater $\delta^{18}O_w$ values indicate that these short-finned pilot whales inhibited mid-latitude region of the Atlantic Ocean (Fig. S3), which is consistent with their known preferred habitats [45, 71]. Unlike the killer whale (Fig. 2), the serial data from these short-finned pilot whales show small intra-tooth $\delta^{18}O_p$ variations and relatively high $\delta^{18}O_w$ values (Fig. 4), indicating that they did not migrate long distances to polar sea regions.

7 Conclusions

Oxygen isotope analyses of biogenic phosphate from a diverse group of modern whales show that the oxygen isotope ratios of phosphate in bioapatite ($\delta^{18}O_P$) from cetaceans can be used as a reliable proxy for the oxygen isotopic composition of environmental water ($\delta^{18}O_w$). Using a significantly expanded modern cetacean $\delta^{18}O_p$ dataset that includes new data produced in this study and data from the literature, the following $\delta^{18}O_w$–$\delta^{18}O_p$ regression equation is derived for cetaceans:

$$\delta^{18}O_w = 0.95317 (\pm 0.03293)\delta^{18}O_p - 17.971 (\pm 0.605),$$
$$r = 0.97253.$$

Although the $\delta^{18}O_w$ of seawater can be reliably estimated from the $\delta^{18}O_P$ of cetacean teeth and bones using the

phosphate–water oxygen isotope fractionation equation if the body temperature is known, the new empirical equation provides a valuable tool for reliably reconstructing seawater $\delta^{18}O_w$ values from the $\delta^{18}O_P$ values of cetaceans whose body temperatures are unknown. The new $\delta^{18}O_p$—$\delta^{18}O_w$ equation, when applied to Mio-Pliocene cetacean fossils, yielded reasonable estimates of ancient seawater $\delta^{18}O$ values. Intra-tooth oxygen isotopic variations within a whale tooth record changes in the isotopic composition of environmental water during the time of tooth growth, providing insights into the life history or migratory behavior of the whale. The results from this study demonstrated the potential of using oxygen isotopes in the phosphate component of cetacean teeth/bones to examine the migratory behaviors and environmental preferences of both modern and ancient whales and to track past changes in ocean water oxygen isotopic composition.

Conflict of interest The authors declare that they have no conflicts of interest.

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