



Oxygen isotope compositions of phosphate from Middle Miocene–Early Pliocene marine vertebrates of Peru

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ABSTRACT

Phosphatic remains of marine vertebrates recovered from five fossil sites of the Pisco Formation ranging from the latest Middle/earliest Late Miocene (Ca 11–13 Ma) to the Early Pliocene (Ca 3.5 Ma) have been analysed for their oxygen isotope compositions ($\delta^{18}\text{O}_p$). Coexisting seals, dolphins, whales, penguins and sharks from each locality have distinct $\delta^{18}\text{O}_p$ values reflecting ecology and physiology differences, ranging from 18.2‰ to 21.4‰ for marine mammals, from 19.5‰ to 21.5‰ for marine birds and from 20.9‰ to 23.1‰ for sharks. Systematic offsets observed between dolphin teeth and bones as well as between dolphin and whale bones indicate that the fractionation equation established by using data from extant cetaceans may not be directly applicable to Miocene cetaceans in order to estimate water $\delta^{18}\text{O}_w$ values. Assuming that polar ice-caps were not totally developed during this time interval, marine palaeotemperatures ranging from 13.0 ± 1.3 °C to 17.2 ± 1.3 °C were estimated. Comparison of our results with those obtained in other World's areas suggests that the oxygen isotope ratios of Pisco vertebrates reflect the influence of both global and local events, such as the setting of the Atacama Desert, the cold Humboldt Current or the global phases of ice-cap growth and decay.

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1. Introduction

Quantitative reconstitutions of temperatures and oxygen isotope compositions of past seawater ($\delta^{18}\text{O}_{sw}$) mainly rely on the oxygen isotope analysis of skeletal phosphate ($\delta^{18}\text{O}_p$) and carbonate ($\delta^{18}\text{O}_c$) secreted by marine organisms. As the oxygen isotope fractionation between these biominerals and water is temperature-dependent, the $\delta^{18}\text{O}_p$ or $\delta^{18}\text{O}_c$ value of aquatic ectothermic organisms (such as marine invertebrates and most fish) both reflect environmental temperature and water composition whereas endothermic organisms (marine mammals) provide $\delta^{18}\text{O}_w$ estimates. Temporal variations in both temperature and $\delta^{18}\text{O}_w$ value of sea or fresh waters can be tracked by analysing the phosphatic tissues of both coexisting marine mammals and fish or reptiles and fish (Barrick et al., 1993; Lécuyer et al., 1996; Barrick et al., 1999) using the fractionation equations established between phosphate and water for cetaceans ($\delta^{18}\text{O}_p = 0.773 \delta^{18}\text{O}_w + 17.8$;

Yoshida and Miyazaki, 1991), fish (T °C = $113.3 - 4.38 (\delta^{18}\text{O}_p - \delta^{18}\text{O}_w)$); Kolodny et al., 1983), turtles ($\delta^{18}\text{O}_w = 1.01 \delta^{18}\text{O}_p - 22.3$; Barrick et al., 1999) or crocodylians ($\delta^{18}\text{O}_w = 0.82 \delta^{18}\text{O}_p - 19.13$; Amiot et al., 2007). It is noteworthy that using cetaceans is not possible for periods older than the Eocene when these marine mammals appeared (Fordyce, 1994).

The Miocene and Pliocene were periods of great changes in the Earth's global climatic regime marked by the development of polar ice-caps and by the progressive global cooling that followed the Middle Miocene Climatic Optimum (see Zachos et al., 2001 for a review). Oxygen isotope compositions of phosphatic remains from coexisting cetaceans and fish have been used as proxies of thermal changes and ice volume fluctuations (Barrick et al., 1992, 1993). Surprising conclusions were drawn from their study of fossil samples recovered from Miocene deposits of the Chesapeake Bay (North America, Atlantic coast). Assuming that the studied samples were not diagenetically altered, Barrick et al. (1992) applied the oxygen isotope fractionation equation established for modern cetaceans (Yoshida and Miyazaki, 1991) to Miocene porpoises and whales. They obtained unrealistically high $\delta^{18}\text{O}_w$ values ranging from +2 to +4.7‰. They also observed a positive correlation between estimated marine temperatures and $\delta^{18}\text{O}_w$ values, meaning that warmer marine conditions prevailed during polar glaciations and conversely cooler temperatures during ice-cap melting. Moreover, the inferred variations in $\delta^{18}\text{O}_w$ values suggest larger volumes of polar ice involved during the Miocene growth

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and decay stage than previously suspected (Haq et al., 1987; Miller et al., 1991). These results raised several questions concerning the meaning of the oxygen isotope compositions recorded in Miocene cetacean bones from Chesapeake Bay. Do they reflect global palaeoenvironmental conditions or local ones (Barrick et al., 1992, 1993)? To which extent is the equation established by Yoshida and Miyazaki (1991) applicable to any fossil cetacean given the excessively high $\delta^{18}\text{O}_w$ values estimated from the $\delta^{18}\text{O}_p$ values of their Miocene counterparts?

The fossil sites of the Pisco Formation (Peru, Pacific coast) have yielded rich and well-preserved marine vertebrate fauna of Miocene and Pliocene ages that include cetaceans (porpoises, whales), pinnipeds (seals), birds (among others, penguins), turtles, crocodiles and sharks. Fossil remains of these animals having various ecologies and physiologies have been analysed for their oxygen isotope contents in order to estimate the variations in marine temperatures and ice volume changes as well as to search for answers to questions raised by the results provided by Barrick et al. (1993)'s study.

2. Geological settings

The Pisco Formation consists of marine Neogene deposits located along the southern coast of Peru, and is known for its abundant marine vertebrate fauna. The Pisco Formation extends about 300 km from the city of Pisco south to Yauca (Fig. 1) and is about 640 m thick (Brand et al., 2003). Its geology and palaeoecology in the Sacaco area were studied by Muizon and DeVries (1985). The age of the sediments is constrained by vertebrate and molluscan biostratigraphies and radioisotopic dating. Samples come from different localities within the Pisco Formation representing different age levels: El Jahuay (ELJ, ca. 9–10 Ma), Late Miocene; Aguada de Lomas (AGL, ca. 7–8 Ma; Muizon and Bellon, 1986; Muizon et al., 2003), Late Miocene; Sacaco Sud (SAS, ca. 5 Ma), Early Pliocene; Sacaco (SAO, ca. 3.5 Ma; Muizon and Bellon, 1981), Early Pliocene. All these localities are in the Sacaco area, Arequipa Department. Northwards, the latest Middle/earliest Late Miocene

locality of Cerro la Bruja, belongs to the Ica Department (ca. 11–13 Ma; Muizon, 1988). Deposits from the Pisco Formation range in age from the Middle Miocene (ca. 14 Ma) to the Late Pliocene (ca. 2 Ma) with a time span of about 12 Ma (Muizon and DeVries, 1985).

3. Sample collection

Phosphatic remains of marine vertebrates (whales, dolphins, seals, penguins, marine sloths, turtles, crocodilians and sharks) recovered from five fossil sites of the Pisco Formation were collected, cleaned and analysed for their oxygen isotope compositions. Except for small teeth for which bulk analyses were performed as well as two aquatic sloth teeth covered with durodentine, enamel was preferentially selected and sampled with a microdrill. Cortical regions of various bones which are the most compact bone parts were selected from penguins, whales, seals and marine sloth skeletal remains. Dense petriotic and tympanic bones of dolphins and whales were also sampled. Number of samples, location and age, the phosphatic tissues analysed and taxonomic identification are reported in Table 1.

4. Analytical techniques

Measurements of oxygen isotope ratios of apatite consist of isolating phosphate ions using acid dissolution and anion-exchange resin, according to a protocol derived from the original method published by Crowson et al. (1991) and slightly modified by Lécuyer et al. (1993). Silver phosphate is quantitatively precipitated in a thermostatic bath set at a temperature of 70 °C. After filtration, washing with double deionised water, and drying at 50 °C, 8 mg of Ag_3PO_4 are mixed with 0.5 mg of pure powder graphite. $^{18}\text{O}/^{16}\text{O}$ ratios are measured by reducing silver phosphates to CO_2 using graphite reagent (O'Neil et al., 1994; Lécuyer et al., 1998). Samples are weighed into tin reaction capsules and loaded into quartz tubes and degassed for 30 min at 80 °C under vacuum. Each sample was heated at 1100 °C for 1 min to promote the redox reaction. The CO_2 produced was directly trapped in liquid nitrogen to avoid any kind of isotopic reaction with quartz at high temperature. CO_2 was then analyzed with a GV Isoprime™ and a GV Prism™ mass spectrometer at the Laboratory UMR CNRS 5125 'PEPS', University Claude Bernard Lyon 1. Isotopic compositions are quoted in the standard δ notation relative to V-SMOW. Silver phosphate precipitated from standard NBS120c (natural Miocene phosphorite from Florida) was repeatedly analyzed ($\delta^{18}\text{O} = 21.70 \pm 0.13\%$; $n = 37$) along with the silver phosphate samples derived from the Miocene and Pliocene vertebrate remains.

5. Results

Oxygen isotope measurements of tooth and bone phosphate are reported in Table 1. The whole $\delta^{18}\text{O}$ dataset ranges from 17.5‰ to 23.1‰. For each of the five localities sampled, mean $\delta^{18}\text{O}_p$ values of teeth and bones for each taxonomic group are plotted against their relative age in Fig. 2. Significant isotopic differences are observed at any given locality between the various groups of vertebrates, with ranges from 18.2‰ to 21.4‰ for marine mammals, 19.5‰ to 21.5‰ for marine birds and 20.9‰ to 23.1‰ for sharks. Relationship between the oxygen isotope composition of teeth and bones is not the same for any taxon. Indeed, teeth have $\delta^{18}\text{O}$ values higher than bones in the case of dolphins and one crocodile and conversely in the case of seals and one whale, and there is no significant isotopic difference between the tooth and bone for the specimen of marine sloth from "Sacaco Sud". Oxygen isotope compositions define distinct trends with time as a function of the considered taxon; only shark and seal teeth have $\delta^{18}\text{O}$ values that clearly increase by about 1‰ from the Miocene to the Pliocene. Oxygen isotope compositions of penguin bones show two maxima during the Late Miocene and the Pliocene. All taxa, including tooth and bone data, show $\delta^{18}\text{O}$ values for the latest Middle/earliest

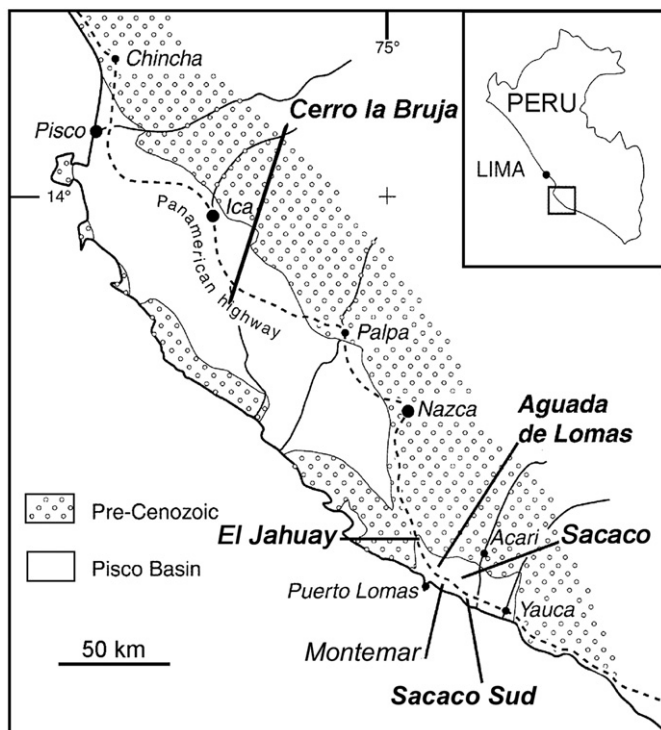


Fig. 1. Map showing the Miocene and Pliocene localities of the Pisco formation, Peru. Localities where samples have been analysed are printed in bold. Modified after McDonald & Muizon (2002: fig.1).

Table 1

Taxon, location, phosphatic tissue, and oxygen isotope composition of Miocene and Pliocene Pisco vertebrate samples, Peru

Sample	Tissue	Taxon	Common name	Locality	Age (My)	$\delta^{18}\text{O}$ (‰ V-SMOW)
AL	Tooth enamel	<i>Hexanchus</i> sp.	Shark	Sacaco	3.5	23.1
AO	Tooth enamel	<i>Carcharhinus</i> sp.	Shark	Sacaco	3.5	21.5
SAO 69-AW	Femur	<i>Spheniscus urbinai</i>	Penguin	Sacaco	3.5	20.7
SAO 70-AX	Femur	<i>Spheniscus urbinai</i>	Penguin	Sacaco	3.5	20.9
BE	Periotic	<i>Kojia</i> sp.	Sperm whale	Sacaco	3.5	19.7
SAO 32-BF	Periotic	Delphinidae	Dolphin	Sacaco	3.5	18.2
SAO 82-BG	Periotic	Delphinidae	Dolphin	Sacaco	3.5	19.3
BH	Periotic	Delphinidae	Dolphin	Sacaco	3.5	18.6
SAO 13-BI	Humerus	<i>Thalassocnus carolomartini</i>	Aquatic sloth	Sacaco	3.5	21.2
SAO 201-BJ	Metatars MTV	<i>Thalassocnus carolomartini</i>	Aquatic sloth	Sacaco	3.5	20.7
SAO 136-BL	Tooth bulk	Phocidae	Seal	Sacaco	3.5	19.7
BM	Humerus	Phocidae	Seal	Sacaco	3.5	20.4
SAO 11-BN	Periotic	Mysticete	Whale	Sacaco	3.5	20.3
SAO 11-BN	Periotic	Mysticete	Whale	Sacaco	3.5	19.4
BP	Periotic	Mysticete	Whale	Sacaco	3.5	20.1
SAS 1380w-A	Tibiotarsus	<i>Spheniscus urbinai</i>	Penguin	Sacaco Sud	5	20.4
SAS 1036-B	Tibiotarsus	<i>Spheniscus urbinai</i>	Penguin	Sacaco Sud	5	19.8
SAS 1380u-C	Femur	<i>Spheniscus urbinai</i>	Penguin	Sacaco Sud	5	20.5
SAS 305-D	Coracoid	<i>Spheniscus urbinai</i>	Penguin	Sacaco Sud	5	20.2
SAS 126-E	Tibiotarsus	<i>Spheniscus</i> sp.	Penguin	Sacaco Sud	5	20.3
SAS 501-F	Tooth enamel	<i>Piscophoca pacifica</i>	Seal	Sacaco Sud	5	18.7
SAS-G	Tooth enamel	<i>Piscophoca pacifica</i>	Seal	Sacaco Sud	5	18.9
SAS 1610-H	Tooth dentine	<i>Thalassocnus littoralis</i>	Semi-aquatic sloth	Sacaco Sud	5	21.3
SAS-I	Tooth dentine	<i>Thalassocnus littoralis</i>	Semi-aquatic sloth	Sacaco Sud	5	21.6
SAS-J	Tooth enamel	<i>Piscolithax longirostris</i>	Dolphin	Sacaco Sud	5	19.8
SAS-K	Tooth bulk	<i>Piscolithax longirostris</i>	Dolphin	Sacaco Sud	5	19.6
SAS-L	Tympanic	<i>Piscobalaena nana</i>	Whale	Sacaco Sud	5	19.9
SAS-M	Radius	<i>Piscobalaena nana</i>	Whale	Sacaco Sud	5	20.1
SAS-N	Tooth enamel	-	Sperm whale	Sacaco Sud	5	19.6
SAS-O	Tooth enamel	<i>Carcharodon carcharias</i>	Shark	Sacaco Sud	5	21.3
AR	Tooth enamel	<i>Cosmopolitodus</i> sp.	Shark	Sacaco Sud	5	21.6
AS	Tooth enamel	<i>Cosmopolitodus</i> sp.	Shark	Sacaco Sud	5	21.6
SAS-P	Tooth bulk	<i>Indet.</i>	Longirostrine crocodylian	Sacaco Sud	5	21.6
SAS-Q	Osteoderm	<i>Indet.</i>	Longirostrine crocodylian	Sacaco Sud	5	20.2
SAS 50-BQ	Rib	<i>Thalassocnus littoralis</i>	Semi-aquatic sloth	Sacaco Sud	5	21.4
SAS 53-BR	Rib	<i>Thalassocnus littoralis</i>	Semi-aquatic sloth	Sacaco Sud	5	21.7
AGL 145F-AE	Carpometacarp	<i>Spheniscus urbinai</i>	Penguin	Aguada de Lomas	7–8	21.2
AGL PPI 145G-AY	Distal femur	<i>Spheniscus urbinai</i>	Penguin	Aguada de Lomas	7–8	20.4
AGL PPI 145C-AZ	Humerus	<i>Spheniscus urbinai</i>	Penguin	Aguada de Lomas	7–8	21.0
SMNK-AGL-AF	Tooth enamel	<i>Tursiops oligodon</i>	Dolphin	Aguada de Lomas	7–8	19.5
AT	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	Aguada de Lomas	7–8	21.8
AV	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	Aguada de Lomas	7–8	21.7
BS	Tooth enamel	Phocidae	Seal	Aguada de Lomas	7–8	18.9
BT	Tooth enamel	Phocidae	Seal	Aguada de Lomas	7–8	17.5
BU	Tooth enamel	Phocidae	Seal	Aguada de Lomas	7–8	18.9
BV	Periotic	-	Dolphin	Aguada de Lomas	7–8	18.1
BW	Periotic	-	Dolphin	Aguada de Lomas	7–8	18.8
BX	Tympanic	-	Whale	Aguada de Lomas	7–8	19.3
BY	Radius	<i>Piscolithax</i> sp.	Dolphin	Aguada de Lomas	7–8	19.0
AJ	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	El Jahuay	9–10	21.5
AK	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	El Jahuay	9–10	21.6
ELJ PPI 141B-BA	Prox. radius	<i>Spheniscus urbinai</i>	Penguin	El Jahuay	9–10	21.5
ELJ PPI 141C-BB	Carpometacarp	<i>Spheniscus urbinai</i>	Penguin	El Jahuay	9–10	21.4
ELJ PPI 141D-BC	Dist. Femur	<i>Spheniscus urbinai</i>	Penguin	El Jahuay	9–10	20.8
ELJ PPI 142-BD	Tibiotarsus	<i>Spheniscus urbinai</i>	Penguin	El Jahuay	9–10	21.1
BZ	Tooth bulk	-	Dolphin	El Jahuay	9–10	20.4
CA	Periotic	-	Dolphin	El Jahuay	9–10	18.9
CB	Periotic	-	Dolphin	El Jahuay	9–10	18.6
CC	Mandible	-	Whale	El Jahuay	9–10	21.4
CD	Long bone	<i>Piscobalaena</i> sp.	Whale	El Jahuay	9–10	20.6
PPI2-CE	Humerus	Phocidae	Seal	El Jahuay	9–10	20.3
PPI3-CF	Humerus	Phocidae	Seal	El Jahuay	9–10	20.5
CLB PPI-T	Osteoscut	-	Marine turtle	Cerro la Bruja	11–13	21.3
CLB PPI-U	Osteoscut	-	Marine turtle	Cerro la Bruja	11–13	20.7
CLB PPI-V	Tooth bulk	<i>Atocetus iquensis</i>	Dolphin	Cerro la Bruja	11–13	19.5
CLB PPI-W	Tympanic	<i>Atocetus iquensis</i>	Dolphin	Cerro la Bruja	11–13	18.6
CLB PPI-X	Tooth enamel	<i>Megaselachus megalodon</i>	Shark	Cerro la Bruja	11–13	20.9
AG	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	Cerro la Bruja	11–13	21.3
AH	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	Cerro la Bruja	11–13	21.2
AI	Tooth enamel	<i>Cosmopolitodus hastalis</i>	Shark	Cerro la Bruja	11–13	21.0
CLB PPI-Y	Tooth enamel	<i>Monachine n. sp.</i>	Seal	Cerro la Bruja	11–13	18.8
CLB PPI-Z	Tooth enamel	<i>Monachine n. sp.</i>	Seal	Cerro la Bruja	11–13	18.2
CLB PPI 151-AA	Femur	<i>Spheniscus muizoni</i>	Penguin	Cerro la Bruja	11–13	19.5
CLB PPI 147F-AB	Tibiotarsus	<i>Spheniscus muizoni</i>	Penguin	Cerro la Bruja	11–13	20.1
CLB PPI 147e-AC	Femur	<i>Spheniscus muizoni</i>	Penguin	Cerro la Bruja	11–13	19.5

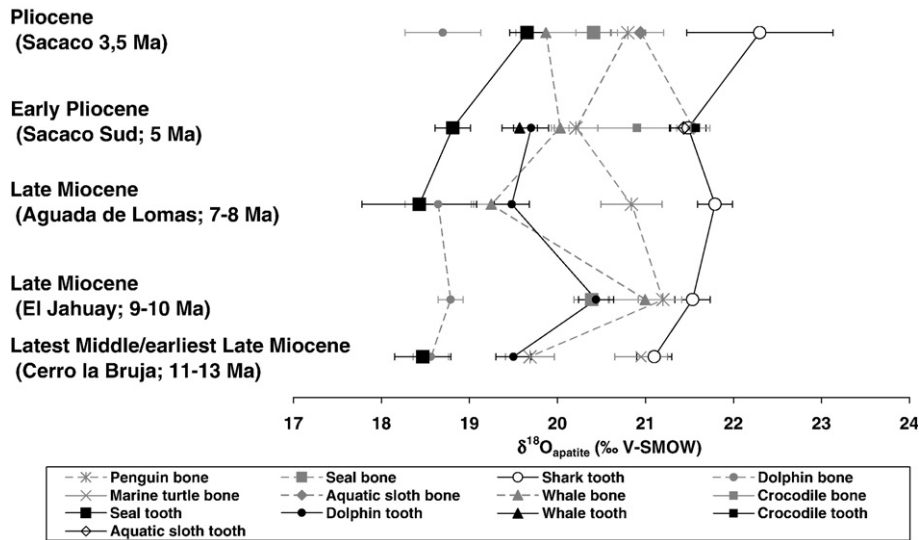


Fig. 2. Mean oxygen isotope compositions of teeth and bones from the various studied vertebrate taxa from Pisco, Peru. Fossil sites are ordered by their relative geological age.

Late Miocene that are lower than for the Late Miocene recorded in “El Jahuay” (time span=9–10 Ma).

6. Discussion

6.1. Pristine oxygen isotope conservation of fossil apatite

Secondary precipitation of apatite and isotopic exchange during microbially-mediated reactions may scramble the primary isotopic signal (Blake et al., 1997; Zazzo et al., 2004). However, apatite crystals that make up tooth enamel are large and densely packed, and isotopic exchange under inorganic conditions has little effect on the oxygen isotope composition of phosphates even at geological time scales (Kolodny et al., 1983; Lécuyer et al., 1999). Although no method is available to demonstrate definitely whether diagenetic processes may have affected oxygen isotope compositions of bulk tooth or bone phosphate, several indicators of preservation of the pristine oxygen isotope compositions of phosphates are given by the present dataset.

Body temperature differences between ectotherms and endotherms as well as differences in ecology between coexisting animals result in different $\delta^{18}\text{O}$ values of apatite phosphate (e.g. Kohn, 1996; Fricke et al., 1998; Amiot et al., 2006). Diagenetic processes are expected to modify and homogenise $\delta^{18}\text{O}_p$ values of all vertebrate phosphatic remains during isotopic exchange between apatite and local groundwaters through processes of dissolution–recrystallization (see Lécuyer et al. 2003). Mio-Pliocene vertebrates from the Pisco Formation have $\delta^{18}\text{O}_p$ values ordered by their physiology (body temperature, metabolism rates) and ecology (diet, living environment) at any sampling locality. Indeed, sharks and aquatic reptiles (turtles and crocodylians) have the highest $\delta^{18}\text{O}_p$ values due to their body temperature which depends on that prevailing in the water mass where they live whereas marine mammals maintain a constant body temperature around 37 °C, having therefore lower $\delta^{18}\text{O}_p$ values. Penguins have higher $\delta^{18}\text{O}_p$ values than marine mammals most likely because of avian metabolism known to be somewhat higher than the mammal one. It is also noteworthy that oxygen isotope differences between cetacean bones and shark teeth are similar to those obtained from Miocene cetacean and shark remains from the Chesapeake Bay (Barrick et al., 1992). A slight difference pointed out by Barrick and colleagues between the $\delta^{18}\text{O}_p$ values of whales and porpoises is also observed in the present dataset with $\delta^{18}\text{O}_p$ values of whales that are more positive than dolphins. From these observations, primary physiological or ecological oxygen isotopic record of vertebrate

phosphate is assumed to be preserved in marine vertebrate teeth and most likely in bones for which, however, care is required for further interpretations because bones have been shown to be potentially highly sensitive to diagenetic processes (see Kolodny et al. (1996) and references herein).

6.2. Meaning of the oxygen isotope composition of phosphate from Pisco vertebrates

6.2.1. Dolphins

Based on previous works (Yoshida and Miyazaki, 1991; Barrick et al., 1992, 1993; Lécuyer et al., 1996), $\delta^{18}\text{O}_p$ values of aquatic endotherms are expected to track water $\delta^{18}\text{O}_w$ values. Thus offsets in $\delta^{18}\text{O}_p$ values between seals, cetaceans and penguins should remain constant at any locality, but significant differences are observed. A first source of variations might be due to differences between bone and tooth isotopic records. Dolphin teeth have a $\delta^{18}\text{O}_p$ value systematically more positive (about 1.1 to 1.7‰) than bones (Fig. 2). As mammals, young dolphins breast-feed during the first 12 to 18 months of their life and have ingested mother milk that is ^{18}O -enriched compared to environmental water (Wright and Schwarcz, 1998). Dolphins have only one generation of teeth that grow a little bit each year until they reach their adult size. It is thus expected that the oxygen isotope compositions of teeth mineralized during this period could be influenced by the mother milk unlike bones which are constantly remodeled during the animal's life using newly ingested oxygen. However, only slight differences of about 0.1‰ or 0.2‰ between $\delta^{18}\text{O}_p$ values of teeth and bones of present-day dolphins (*Stenella* and *Delphinus*) were observed by Barrick et al. (1992), indicating that a ‘milk signature’ cannot explain the observed isotopic offsets. Another possible source of variations proposed by Barrick et al. (1992) is local heterothermy that dolphins may experience between their body core and their thin rostral region. In cold waters, dolphin rostrum and teeth may have a lower temperature than the main body thus leading to higher $\delta^{18}\text{O}_p$ values. Keeping in mind that bone diagenesis can be responsible for these differences, further investigations should be performed on modern dolphins to allow a better understanding of the origin of these offsets.

6.2.2. Seals vs. dolphins

It is noteworthy that in the sites of Cerro la Bruja, Aguada de Lomas and Sacaco Sud, seal and dolphin teeth have a constant $\delta^{18}\text{O}_p$ value offset of $1.0 \pm 0.1\%$ (Fig. 2). This suggests that both of them have most

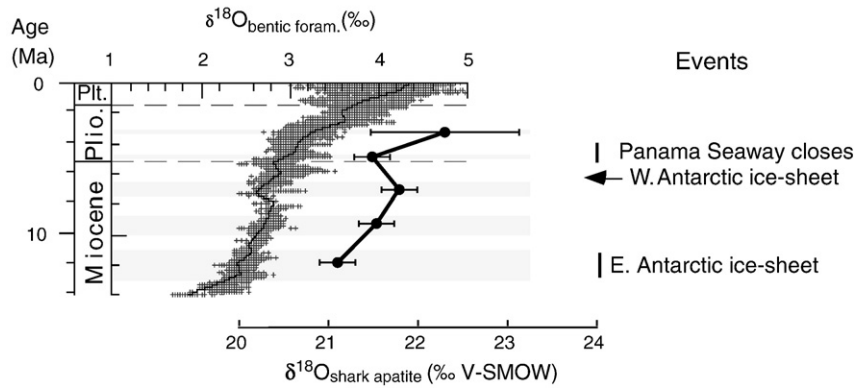


Fig. 3. Comparison between the $\delta^{18}\text{O}_p$ curve of sharks (bold black) and the synthetic curve of $\delta^{18}\text{O}_e$ values of benthic foraminifera (Zachos et al., 2001). Shaded horizontal areas represent the uncertainties associated with the geological ages of the Pisco localities.

likely recorded the same environmental signal, the offset being caused by differences in physiology. Indeed, contrary to dolphins, seals have a daily sun-basking activity on land, which allow them spending less metabolic energy for keeping their body at 37 °C. From a study carried out on modern cetaceans and seals, it has been observed that the metabolic rates of marine mammals resting on the water surface are higher than those of mammals resting in air (Williams et al., 2001). If seals of the Pisco Formation shared a similar basking behaviour, this may contribute to explain their lower $\delta^{18}\text{O}_p$ values.

6.2.3. Whales vs. dolphins

Large cetacean (whales and sperm whales) from Pisco localities have $\delta^{18}\text{O}_p$ values higher than dolphins and porpoises. Such differences have already been observed for Miocene cetaceans (Barrick et al., 1992) but not for modern species (Yoshida and Miyazaki, 1991). Several hypotheses have been proposed to account for these isotopic offsets such as differences in body temperatures between fossil whales and porpoises or differences in $\delta^{18}\text{O}$ values of body fluids (Barrick et al., 1992). The systematic isotopic offset between whales and dolphins points out a major problem concerning the applicability of the oxygen isotope fractionation equation between any cetacean phosphate and water (Yoshida and Miyazaki, 1991) to fossil cetaceans. Yoshida and Miyazaki (1991) did not find any relationship between body size and oxygen isotope fractionation, a goal difficult to reach when taking into account the uncertainty associated with the $\delta^{18}\text{O}_{sw}$ value of seawater where cetaceans live. Moreover, in the computed equation of Yoshida and Miyazaki, whales are only represented by one species *Balaenoptera acutorostrata* with four $\delta^{18}\text{O}_p$ values ranging from 17.5‰ to 18.4‰, all having the same $\delta^{18}\text{O}_w$ value. If recalculated without using whale values, the new regression does not significantly differ from the original one ($\delta^{18}\text{O}_p = 0.763 \delta^{18}\text{O}_w + 17.7$ instead of $\delta^{18}\text{O}_p = 0.773 \delta^{18}\text{O}_w + 17.8$). From these considerations, the direct applicability of the fractionation equation of Yoshida and Miyazaki (1991) seems to be restricted to dolphins. For further use of the $\delta^{18}\text{O}_p$ value of cetaceans to estimate past seawaters' $\delta^{18}\text{O}_w$ values, separate calibrations are needed for whales, and more modern dolphin teeth have to be measured for comparison with bone values.

6.2.4. Aquatic sloths

A few $\delta^{18}\text{O}_p$ values of bones and teeth from two species of the sloths *Thalassocnus* were obtained. These vertebrates were unusual xenarthran mammals having phylogenetic affinities with other Nothrother ground sloths (Muizon and Mc Donald, 1995; Mc Donald and Muizon, 2002; Muizon et al., 2004b). The most striking feature is their progressive anatomical adaptations to semi-aquatic or aquatic habits (Muizon and Mc Donald, 1995) and to feed on marine plants (Muizon et al., 2004a). Interestingly, these sloths have high $\delta^{18}\text{O}_p$ values about 1‰ to 3‰ more positive than other coexisting aquatic

mammals. Despite their marine foraging environments, these high values can suggest that marine sloth kept some physiological characteristics of land mammals with ^{18}O -enriched body fluids due to elevated metabolic activity, evaporation and sweat. However, given that no terrestrial vertebrates have been discovered so far in these localities, it is also likely that differences in $\delta^{18}\text{O}_p$ values between these sloths and other marine mammals reflect differences in physiology. Indeed, at least two species of modern ground sloth (*Choelophus didactylus* and *Choelophus hoffmanni*) have incomplete homeothermy with body temperatures lower than 34.4 °C for *C. didactylus* (Bush and Gilroy, 1979) and varying within a day between 33.4 °C and 36.2 °C for *C. hoffmanni* (Goffart, 1971). According to the phosphate-water temperature scale (Longinelli and Nuti, 1973), a 4 °C difference in temperature (between a sloth at 33 °C and another mammal at 37 °C) should result in a 1‰ offset in the $\delta^{18}\text{O}_p$ value. If Pisco marine sloths also possessed low and fluctuating body temperatures, then the differences in $\delta^{18}\text{O}_p$ values observed between *Thalassocnus* and other marine mammals may at least partly reflect differences in body temperatures.

6.2.5. Sharks

Stable isotope and trace element contents of shark teeth are commonly used for palaeoenvironmental studies (e. g. Kolodny and Raab, 1988; Lécuyer et al., 1993, 1996; Pucéat et al., 2003; Scher and Martin, 2006). However, significant variations in $\delta^{18}\text{O}_p$ values have been observed between various species of present-day sharks living in the same region, most likely as a consequence of different living habitats, and also between teeth from the same individual (Venne-mann et al., 2001). Most of the shark teeth available for this study were sampled from species belonging to the great white shark lineage (*Carcharodon carcharias*, *Megaselachus megalodon* (Cappetta, 2006) and *Cosmopolitodus hastalis*). These sharks are ubiquitous large predators that can forage over long distances and large ranges of water depths, i.e. their teeth $\delta^{18}\text{O}_p$ values may reflect marine environments well distinct from those where Pisco vertebrates lived. Mean $\delta^{18}\text{O}_p$ values of shark teeth from the five Pisco localities are at variance with the global trend (Fig. 3) provided by the temporal synthetic curve of benthic foraminifera $\delta^{18}\text{O}$ values which are considered to reflect global temperatures and continental ice volume (Zachos et al., 2001).

6.2.6. Crocodylians and turtles

Reptile remains are very scarce in the Pisco formation, and only two scute fragments of marine turtles from the locality of Cerro la Bruja, one tooth and one osteoderm fragment of a longirostrine crocodylian from the locality of Sacaco Sud were available for oxygen isotope analysis. Although being ectotherm animals, thus having fluctuating body temperatures as a function of environmental ones, they synthesise bone or tooth phosphate under relatively narrow temperature ranges (Barrick et al., 1999; Amiot et al., 2007). Using

empirical linear fractionation equations established between their phosphate and environmental waters, a mean living water $\delta^{18}\text{O}_w$ value of $-1.1 \pm 0.3\text{‰}$ is inferred from the $\delta^{18}\text{O}_p$ values of marine turtles from Cerro la Bruja, and $-1.4 \pm 1\text{‰}$ from the crocodilian tooth from Sacaco Sud. Whereas the value of -1.1‰ for Middle Miocene seawaters at Cerro la Bruja recorded by marine turtles is expected considering the absence of polar ice-caps, the origin (brackish or pure marine) of the water value estimated from the crocodilian tooth is questionable. Indeed, very little is known about Pisco crocodilians. One crocodilian species *Piscogavialis jugaliperforatus* (Kraus, 1998) recovered from the locality of Montemar (Pisco Formation; ca. 6 Ma to 4.5 Ma) has been described and attributed to the family Gavialidae. The living environment of these gharials is still unclear. Their occurrence in marine deposits of Peru, Chile and Venezuela (Kraus, 1998; Sánchez-Villagra et al., 2001; Brochu and Rincon, 2004; Walsh and Suárez, 2005) suggests that they were marine animals but it cannot be excluded that they lived in brackish waters or estuarine environments.

6.2.7. Penguins

Bone remains of Miocene and Pliocene penguins *Spheniscus urbinai* (Stucchi, 2002) and *Spheniscus muizoni* (Göhlich, 2007) have higher $\delta^{18}\text{O}_p$ values than bones or teeth of coexisting marine endotherms (cetaceans and seals) probably reflecting differences in metabolic activities. Indeed, birds and especially marine birds tend to have activity metabolic rates greater than mammals, leading to higher $\delta^{18}\text{O}_p$ values (see Kohn, 1996; Nagy et al., 1999 and references therein). Interestingly, penguin $\delta^{18}\text{O}_p$ values roughly vary the same way than shark teeth values. Although diets and drinking behaviours of these two penguin species are not known, most of the oxygen constituting their phosphatic tissues likely comes from seawater, directly from drinking water, or indirectly from eaten marine ectothermic organisms (krill, fish or cephalopods), themselves reflecting seawater conditions ($\delta^{18}\text{O}_{sw}$ value and temperature variations).

6.3. Reconstruction of seawater temperatures and $\delta^{18}\text{O}_{sw}$ values

Given the significant differences in $\delta^{18}\text{O}_p$ values observed between whales and dolphins and between dolphin teeth and bones, it is not possible to calculate ocean $\delta^{18}\text{O}_w$ values by simply applying the phosphate-water fractionation equation established for cetaceans (Yoshida and Miyazaki, 1991) to any Pisco whale or dolphin remains. Only relative variations in sea $\delta^{18}\text{O}_w$ values through time may be calculated using dolphin values from the Pisco Formation, considering that the above isotopic calibration almost exclusively relies on dolphin bone $\delta^{18}\text{O}_p$ values. For this purpose, $\delta^{18}\text{O}_p$ values of dolphin teeth (Fig. 2) have been selected because tooth enamel is the most resistant biomineral in terms of isotopic preservation. Given the near constant offset of $1.0 \pm 0.1\text{‰}$ measured between seals and dolphins, suggesting that they have both recorded similar variations in sea $\delta^{18}\text{O}_w$ values, a hypothetical dolphin tooth $\delta^{18}\text{O}_p$ value of 20.7‰ has been estimated using seal tooth $\delta^{18}\text{O}_p$ value from the Sacaco site (as no dolphin tooth

Table 2
Variations in seawater $\delta^{18}\text{O}_w$ values and marine temperatures calculated using $\delta^{18}\text{O}_p$ values of dolphins, seals, and shark tooth enamels and marine turtle scutes

	$\delta^{18}\text{O}_w$ (‰ V-SMOW)	$D\delta^{18}\text{O}_w$ (‰ V-SMOW)	SD	T °C	SD
Sacaco – Sacaco Sud	+0.7	-0.2	0.3	14.8	1.3
Sacaco Sud – Aguada de Lomas	+0.2	-0.9	0.3	15.2	1.3
Aguada de Lomas – El Jahuay	-0.7	-1.1	0.3	13.0	1.3
El Jahuay – Cerro la Bruja	+0.7	-0.4	0.3	17.2	1.3
Cerro la Bruja		-1.1 ^a	0.3 ^a	16.1	1.3

Variations in $\delta^{18}\text{O}_w$ values were estimated using the slope of the Yoshida and Miyazaki (1991) equation, and palaeotemperatures were calculated using the equation of Kolodny et al. (1983).

^a Value calculated using $\delta^{18}\text{O}_p$ values of marine turtles.

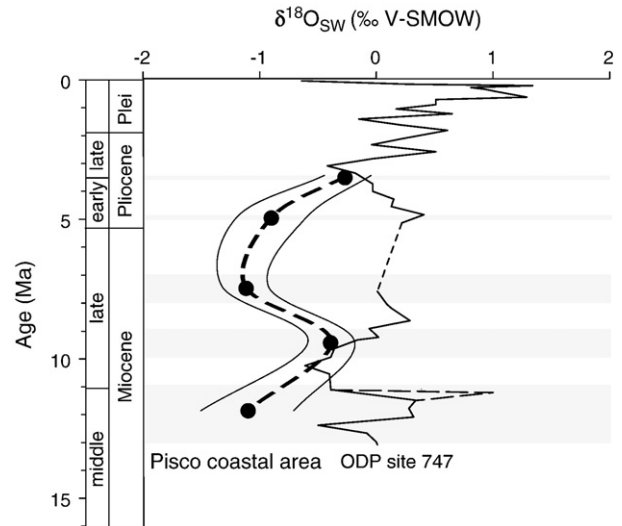


Fig. 4. Comparison between two seawater $\delta^{18}\text{O}_w$ curves obtained from the $\delta^{18}\text{O}_p$ values (bold black) of dolphins, seals and marine turtles (this study) and by using paired Mg/Ca and $\delta^{18}\text{O}_c$ values (black) of benthic foraminifera (Billups and Schrag, 2002). The $\delta^{18}\text{O}_{sw}$ value of -1.1‰ was estimated for the oldest site (Cerro la Bruja) using $\delta^{18}\text{O}_p$ values of marine turtles. Shaded areas represent the uncertainties associated with the geological ages of the Pisco localities.

was available). The difference in oxygen isotope compositions calculated between two sites is multiplied by the slope (0.773) of the fractionation equation of Yoshida and Miyazaki (1991) (Table 2). By using $-1.1 \pm 0.3\text{‰}$ (calculated from the $\delta^{18}\text{O}_p$ values of marine turtles) as the seawater $\delta^{18}\text{O}_w$ value at Cerro la Bruja, then absolute values are tentatively estimated for each site (Table 2). These computed isotopic values as well as shark tooth $\delta^{18}\text{O}_p$ values of the same sites are inserted into the oxygen isotope fractionation equation established between fish phosphate and water (Kolodny et al., 1983) to retrieve Sea Surface Temperature (SST) (Table 2; Fig. 4). The overall range is about 1‰ in ocean $\delta^{18}\text{O}_w$ values and about 5 °C in SST.

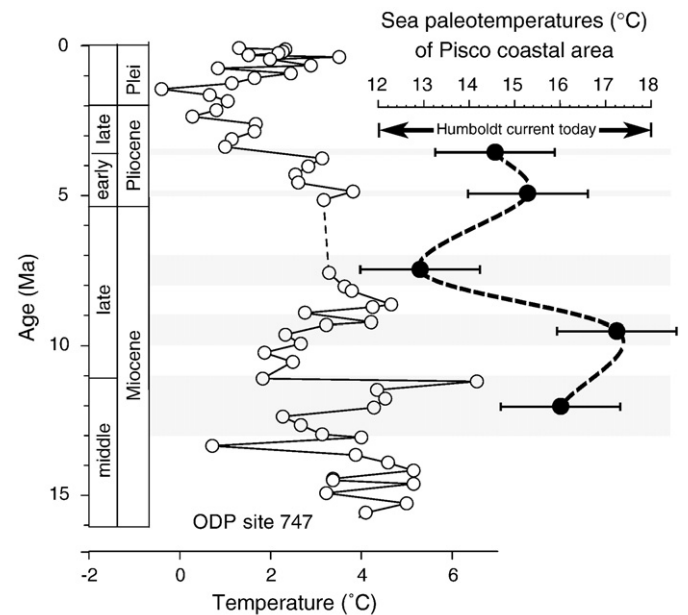


Fig. 5. Comparison between two seawater temperature curves, the first one obtained from the $\delta^{18}\text{O}_p$ values (bold black) of dolphins, seals, turtles and sharks (this study), and the second one by using paired Mg/Ca and $\delta^{18}\text{O}_c$ values (black) of benthic foraminifera (Billups and Schrag, 2002). Shaded areas represent the uncertainties associated with the geological ages of the Pisco localities.

Marine palaeotemperatures estimated from shark tooth $\delta^{18}\text{O}_p$ values ranged from 13.0 ± 1.3 °C to 17.2 ± 1.3 °C (Table 2; Fig. 5). These temperatures match those observed today off the coasts of Peru. The Humboldt Current brings deep, cold (between 12 °C and 18 °C) and nutrient-rich Antarctic waters to the surface. This current originates from the Antarctic Circumpolar Current (ACC) and moves northwards along the Peruvian coasts. According to a Late Eocene age for the complete establishment of the circum-Antarctic pathway allowed by the opening of the Drake Passage and Tasmanian Gateway (see Scher and Martin, 2006), the Humboldt Current might have been already active during the Miocene, a hypothesis supported by the relatively low palaeotemperatures estimated from shark teeth $\delta^{18}\text{O}_p$ values.

The $\delta^{18}\text{O}_{sw}$ curve obtained from Pisco vertebrates is compared to the one calculated on the basis of Mg/Ca and $\delta^{18}\text{O}_c$ values of benthic foraminifera recovered from the Ocean Drilling Program (ODP) Leg 120 Site 747 (Billups and Schrag, 2002). This Core was drilled in the Kerguelen Plateau in the Indian Ocean sector of the Southern Ocean at a water depth of 1695 m. Combined measurements of Mg/Ca and $\delta^{18}\text{O}_c$ of benthic foraminifera allow the calculation of both marine $\delta^{18}\text{O}_{sw}$ values and palaeotemperatures. The estimated evolution of $\delta^{18}\text{O}_{sw}$ values in the Pisco area roughly follows the isotopic record at site 747 except between 5 Ma and 3.5 Ma when the $\delta^{18}\text{O}_{sw}$ value of seawater off Peru increased, a pattern in contradiction with the global isotopic decreasing trend (Fig. 4). This period is marked by the closure of the Panama Isthmus as well as by the main stage of aridification of the Atacama Desert (Hartley and Chong, 2002). Consequently, high evaporation rates of sea surface waters may have been recorded by the relative high $\delta^{18}\text{O}_p$ values of Pisco aquatic mammal phosphatic remains.

A counterintuitive relationship is observed between estimated temperatures and $\delta^{18}\text{O}_{sw}$ values of marine waters, as warmer temperatures correspond to episodes of glaciations and cooler temperatures to ice-cap decay. This correlation has also been observed in the Miocene (Barrick et al., 1992, 1993) and Pleistocene (Ruddiman and Mc Intyre, 1979; Ruddiman and Mc Intyre, 1984) sediments of the Atlantic Ocean. Warmer temperatures may have increased seawater evaporation at low latitudes and created a poleward transport of moisture as well as extensive precipitations and storage of ice at the poles, the so called “snow gun” effect (Johnson and Mc Clure, 1976; Sergin, 1980; Ruddiman and Mc Intyre, 1984).

Therefore, estimated variations in palaeotemperature and $\delta^{18}\text{O}_{sw}$ values of seawater for the Miocene and Pliocene Pacific coastal sea of Peru suggest that both local and global environmental factors have been recorded in the $\delta^{18}\text{O}_p$ values of coexisting aquatic vertebrates recovered from the Pisco Formation.

7. Conclusion

The study of the oxygen isotope compositions of marine vertebrates from Miocene and Pliocene localities of the Pisco formation leads to the following conclusions:

- Coexisting marine mammals, reptiles, birds and fish have different $\delta^{18}\text{O}_p$ values as a result of different ecologies and physiologies. Fish and reptiles tend to have higher $\delta^{18}\text{O}_p$ values than mammals and birds due to their lower body temperature, and birds have higher $\delta^{18}\text{O}_p$ values than marine mammals due to their higher metabolic rates. Body mass may also lead to differences in oxygen isotope compositions between coexisting mammals. In this study, seals tend to have lower $\delta^{18}\text{O}_p$ values than dolphins, themselves lower than those of whales.
- Significant oxygen isotope offsets are observed between dolphin teeth and bones and between dolphin and whale bones, indicating that the phosphate-water fractionation equation established for living cetaceans is not directly applicable to their fossil counterparts in order to retrieve the oxygen isotope composition of seawater.

- Relatively low marine temperatures (between 13.0 ± 1.3 °C and 17.2 ± 1.3 °C) were inferred from shark teeth $\delta^{18}\text{O}_p$ values which are in agreement with the existence of a cold, nutrient-rich Humboldt Current already active during the Miocene and Pliocene.
- Variations in $\delta^{18}\text{O}_w$ values and marine palaeotemperatures recorded by Pisco vertebrates are influenced by both global and local climatic and oceanographic factors.
- Warmer temperatures recorded in both Calvert (Barrick et al., 1992, 1993) and Pisco formations correspond to periods of glacial episodes in polar areas. This relationship suggests that a global rising of marine temperatures at low and mid latitudes may increase moisture transport toward the poles, thus contributing to the development of ice-caps during the Miocene.

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