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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 ($\delta^{18}O_p$). Coexisting seals, dolphins, whales, penguins and sharks from each locality have distinct $\delta^{18}O_p$ 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 $\delta^{18}O_w$ 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.

1. Introduction

Quantitative reconstitutions of temperatures and oxygen isotope compositions of past seawater ($\delta^{18}O_{sw}$) mainly rely on the oxygen isotope analysis of skeletal phosphate ($\delta^{18}O_p$) and carbonate ($\delta^{18}O_c$) secreted by marine organisms. As the oxygen isotope fractionation between these biominerals and water is temperature-dependent, the $\delta^{18}O_p$ or $\delta^{18}O_c$ 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 $\delta^{18}O_w$ estimates. Temporal variations in both temperature and $\delta^{18}O_w$ 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 ($\delta^{18}O_p = 0.773\ \delta^{18}O_w + 17.8$; Yoshida and Miyazaki, 1991), fish (T °C $= 113.3 - 4.38\ (\delta^{18}O_p - \delta^{18}O_w)$; Kolodny et al., 1983), turtles ($\delta^{18}O_w = 1.01\ \delta^{18}O_p - 22.3$; Barrick et al., 1999) or crocodilians ($\delta^{18}O_w = 0.82\ \delta^{18}O_p - 19.13$; 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 $\delta^{18}O_w$ values ranging from +2 to +4.7‰. They also observed a positive correlation between estimated marine temperatures and $\delta^{18}O_w$ values, meaning that warmer marine conditions prevailed during polar glaciations and conversely cooler temperatures during ice-cap melting. Moreover, the inferred variations in $\delta^{18}O_w$ 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 $\delta^{18}O_w$ values estimated from the $\delta^{18}O_p$ 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).

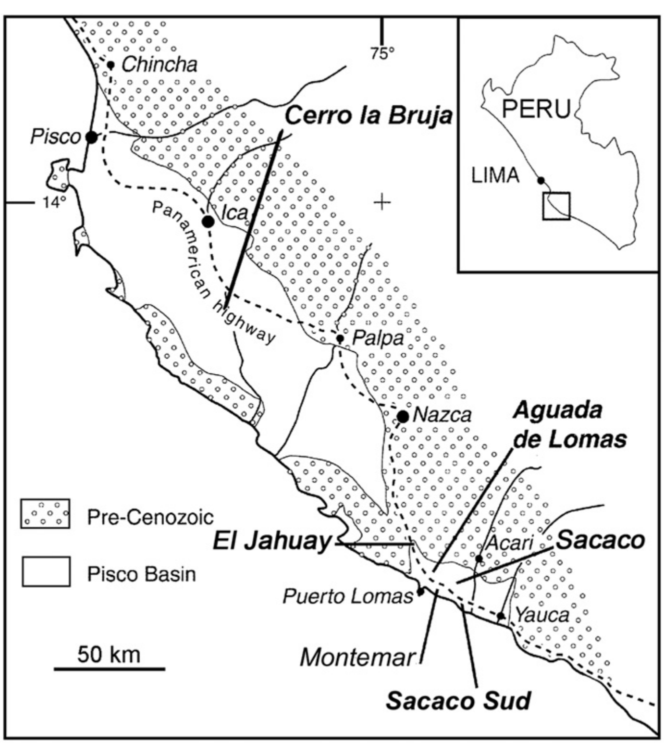

Fig. 1. Map showing the Miocene and Pliocene localities of the Pisco formation, Peru. Localities where samples have been analysed are printed in bold. Modified after McDonald & Muizon (2002: fig.1).

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 periotic 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. $^{18}O/^{16}O$ ratios are measured by reducing silver phosphates to CO_2 using graphite reagent (O'Neil et al., 1994; Lecuyer 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 ($\delta^{18}O = 21.70 \pm 0.13$‰; $n = 37$) 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 $\delta^{18}O$ dataset ranges from 17.5‰ to 23.1‰. For each of the five localities sampled, mean $\delta^{18}O_p$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ values for the latest Middle/earliest