

Oxygen isotope fractionation between apatite-bound carbonate and water determined from controlled experiments with synthetic apatites precipitated at 10–37 °C

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Abstract

The oxygen isotope fractionation between the structural carbonate of inorganically precipitated hydroxyapatite (HAP) and water was determined in the range 10–37 °C. Values of $1000 \ln \alpha(\text{CO}_3^{2-}\text{-H}_2\text{O})$ are linearly correlated with inverse temperature (K) according to the following equation: $1000 \ln \alpha(\text{CO}_3^{2-}\text{-H}_2\text{O}) = 25.19 (\pm 0.53) \cdot T^{-1} - 56.47 (\pm 1.81)$ ($R^2 = 0.998$). This fractionation equation has a slightly steeper slope than those already established between calcite and water (O'Neil et al., 1969; Kim and O'Neil, 1997) even though measured fractionations are of comparable amplitude in the temperature range of these experimental studies. It is consequently observed that the oxygen isotope fractionation between apatite carbonate and phosphate increases from about 7.5‰ up to 9.1‰ with decreasing temperature from 37 °C to 10 °C. A compilation of $\delta^{18}\text{O}$ values of both phosphate and carbonate from modern mammal teeth and bones confirms that both variables are linearly correlated, despite a significant scattering up to 3.5‰, with a slope close to 1 and an intercept corresponding to a $1000 \ln \alpha(\text{CO}_3^{2-}\text{-PO}_4^{3-})$ value of 8.1‰. This apparent fractionation factor is slightly higher or close to the fractionation factor expected to be in the range 7–8‰ at the body temperature of mammals.

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1. INTRODUCTION

Stable isotope compositions of biogenic apatites are now widely used to reconstruct terrestrial and marine environments. Since the pioneering studies of Longinelli (1965,

1966), Longinelli and Nuti (1968, 1973) and Kolodny et al. (1983), several oxygen isotope fractionation equations between apatite phosphate and water have been established (e.g. Longinelli, 1984; Luz and Kolodny, 1985; Kohn, 1996; Lécuyer et al., 1996; Amiot et al., 2007) to quantify marine and air temperatures over the Phanerozoic (Kolodny and Luz, 1991; Fricke et al., 1998; Vennemann and Hegner, 1998; Joachimski and Buggisch, 2002; Pucéat et al., 2003; Daux et al., 2005; Kocsis et al., 2007; Trotter et al., 2008). Minor amounts of carbonate (3–6 wt%) occur natu-

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rally in substitution of phosphate in the crystal lattice of apatites (LeGeros, 1981; Okazaki et al., 1982; Schuffert et al., 1990; LeGeros et al., 1996). Decreasing amounts of structural carbonate are correlated with increasing apatite crystallinity, thus improving the stability of apatite crystals by reducing its solubility (Shemesh, 1990; Kohn et al., 1999). These carbonate contents have been used as indicators of bone or enamel diagenesis (Shemesh, 1990; Bryant et al., 1994). In the apatite of living vertebrates, oxygen from phosphate and carbonate exchanges isotopes with body water, and co-existing $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_p$ values are linearly correlated (Bryant et al., 1996; Iacumin et al., 1996). This property was used as a test for identifying diagenetic alteration in fossil teeth and bones (Iacumin et al., 1996; Tütken et al., 2006). Because different rates of oxygen isotope exchange in the phosphate–water and carbonate–water systems are expected in the case of inorganic or microbially mediated interactions, the $\delta^{18}\text{O}$ values of altered fossils should deviate from equilibrium values (Zazzo et al., 2004). For samples which escaped diagenetic alteration, both carbon and oxygen isotope ratios of carbonate from apatites constitute valuable proxies of the diet, ecology and environments of many terrestrial vertebrates since the Mesozoic (e.g. Wright and Schwarcz, 1998; Kohn and Cerling, 2002; Smith et al., 2002; Zazzo et al., 2002; Jim et al., 2004; Hoppe, 2006). The record of seasonal temperature variations has been proposed on the basis of measured sinusoidal-like isotopic time series obtained from the intra-tooth sampling of hypsodont vertebrates (e.g. Fernanez and MacFadden, 2000; Gadbury et al., 2000; Bocherens et al., 2001; Balasse, 2002; Stanton Thomas and Carlson, 2004; Arppe and Karhu, 2006). However, the quantification of temperatures is still lacking in the absence of any experimental determination of the oxygen isotope fractionation between hydroxyapatite (HAP) carbonate and water. Such an isotopic fractionation equation would be very useful for understanding the meaning of $\delta^{18}\text{O}$ values of apatite carbonate that are now commonly measured along those of apatite phosphate in the same tooth or bone samples (Zazzo et al., 2002; Lécuyer et al., 2003; Stanton Thomas and Carlson, 2004; Tütken et al., 2004). Oxygen isotope ratios of phosphate and carbonate are roughly linearly correlated (Bryant et al., 1996; Iacumin et al., 1996; Zazzo et al., 2004). However, the isotopic difference between carbonate and phosphate recorded in terrestrial mammals samples is not a constant ($\Delta^{18}\text{O}_{(\text{CO}_3^{2-}-\text{PO}_4^{3-})}$ differences range from about 8‰ to 11‰) despite near constant body temperatures ($T = 37 \pm 2$ °C). Therefore, we propose to determine the oxygen isotope fractionation between the carbonate ions of inorganically precipitated HAP and water in the range (10 °C $< T < 37$ °C) of Earth's surface and terrestrial vertebrate body temperatures.

2. EXPERIMENTAL PROTOCOL AND ANALYTICAL TECHNIQUES

2.1. Precipitation of inorganic hydroxyapatites

In this study, carbonate-bearing hydroxyapatite was synthesized by adapting the protocol given by Balter and

Lécuyer (2004). A first aqueous solution (“PC”) was prepared by adding 0.5 ml of KNaCO_3 (10^{-1} M) to 500 ml of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (10^{-2} M), pH was then adjusted to 7.4 by adding 0.3% HNO_3 . A second solution was made by adding NaOH (10^{-1} M) to 500 ml of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (10^{-2} M) until a pH of 7.4 was reached (solution “CA”). Aqueous solutions were held at constant temperatures of 10 °C, 15 °C, 20 °C, 25 °C, 30 °C and 37 °C, respectively, for 48 h to ensure oxygen isotope equilibrium in the carbonate–water system for the “PC” solutions according to kinetic data determined by Zeebe and Wolf-Gladrow (2001). Equal volumes of “PC” and “CA” solutions were mixed at a given temperature. Concentrations of Ca^{2+} and PO_4^{3-} in the resulting solution are the same order of magnitude as in blood plasma ($[\text{Ca}^{2+}] = 2.5$ mM and $[\text{PO}_4^{3-}] = 1$ mM) and seawater ($[\text{Ca}^{2+}] = 10$ mM), but P in seawater typically has a concentration of 1 μM (Broecker and Peng, 1982; Kaim and Schewderski, 1994) compared to our solutions having a $[\text{PO}_4^{3-}]$ of 5.3×10^{-3} M. According to Balter and Lécuyer (2004), at least 96 h of maturation of the solid phase is required to obtain well-crystallized HAP crystals in the temperature range of this study. During the maturation of the solid phase, the Erlenmeyer flasks, covered with watch glasses to prevent evaporation of the solution, were gently shaken at regular intervals in order to avoid extensive sedimentation as well as the development of a concentration gradient in the solution. At the end of the experiment, the solid phase was separated from the supernatant by centrifugation, washed with distilled water and dried at room temperature whereas the aqueous solutions were filtered through a 0.22 μm filter and sealed in a glass tube.

2.2. Scanning Electron Microscopy and Infrared Spectroscopy

HAP samples were mounted on the conductive support (i.e., aluminium stub) with double-sided conductive carbon tape. An ultra-thin coating (ca 20 nm) of gold was then deposited on the samples by low vacuum sputter coating prior to imaging with a Jeol JSM 6400 SEM (University of Geneva, Geneva, Switzerland). Transmission IR spectra were recorded using a Perkin-Elmer GX II FTIR spectrometer. Disks containing 1 mg of sample in 150 mg of KBr were employed. The spectra were collected after 40 accumulations with a spectral resolution of 0.4 cm^{-1} in the 400–4000 cm^{-1} range.

2.3. Oxygen isotope analysis of HAP-bound carbonate

Oxygen isotope ratios were determined by using a MultiPrep™ automated preparation system coupled to a dual-inlet Elementar™ Isoprime™ isotope ratio mass spectrometer (IRMS). For each sample, an aliquot of about 1200 μg of carbonate-bearing HAP was reacted with anhydrous supersaturated phosphoric acid at 90 °C for 90 min. An acid fractionation factor value of 1.0080 was used to calculate the oxygen isotope composition of carbonate, the same as that used for calcite reacted with anhydrous phosphoric acid at 90 °C (Swart et al., 1991), which is also the value

recommended by Passey et al. (2007) for F-poor apatite (modern tooth enamel). Isotopic compositions are reported in the delta notation in ‰ relative to V-SMOW. All sample measurements were adjusted to the international reference NIST NBS19 according to the method developed by Werner and Brand (2001). Reproducibility of oxygen isotope measurement was $\pm 0.1\text{‰}$ (1σ).

2.4. Oxygen isotope analysis of water

Oxygen isotope measurements of water from HAP synthesis experiments were also performed by using a Multi-Prep™ automated preparation system coupled to a dual-inlet Elementar™ Isoprime™ isotope ratio mass spectrometer. The method used was the water–carbon dioxide equilibration technique (Cohn and Urey, 1938). Aliquots of 200 μl of water were automatically reacted at 40 °C with

CO_2 . Reproducibility of oxygen isotope measurements was $\pm 0.05\text{‰}$. Oxygen isotope ratios are reported relative to V-SMOW in ‰ δ units after scaling the raw data to the “true” isotopic ratios of SMOW, SLAP and GISP international standards.

3. RESULTS

3.1. Mineralogy of the chemical precipitates

IR-spectroscopy (Fig. 1) spectra show that the mineral phases that were precipitated in the temperature range 10–37 °C are well-crystallized HAP. According to previous IR-spectroscopy studies of apatite (e.g. Pucéat et al., 2004), the three intense absorbance peaks of the phosphate group occur at 1035, 603 and 565 cm^{-1} (Fig. 1A) whereas the three peaks representing the B-type carbonate substitution

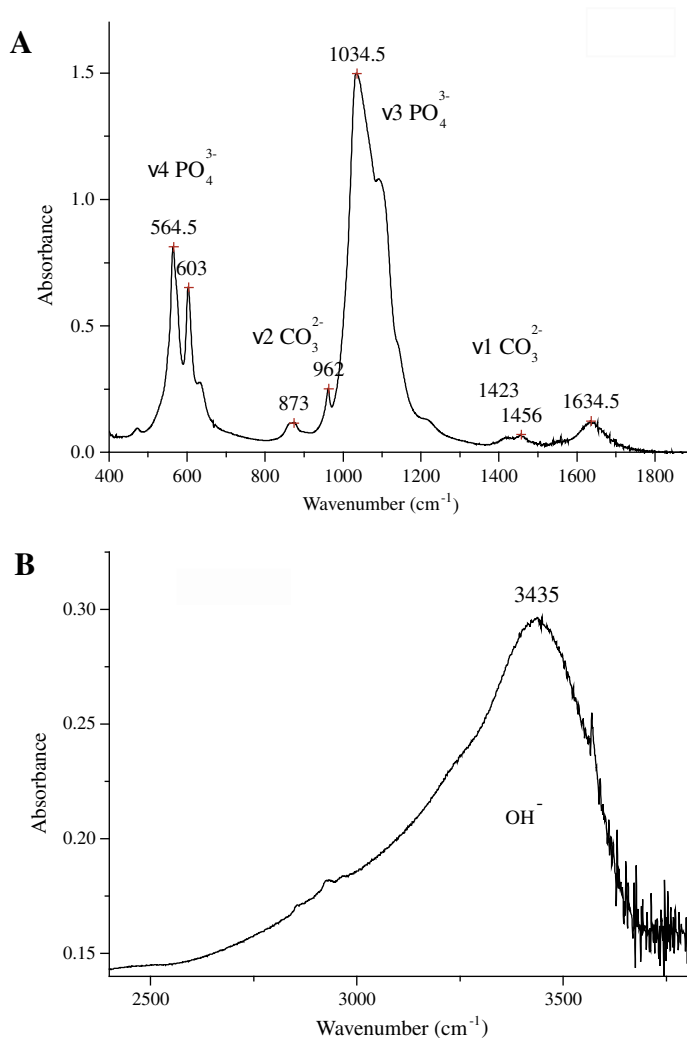


Fig. 1. Infrared spectrum of a carbonate-bearing hydroxyapatite precipitated at a temperature of 37 °C. (A) Three intense peaks of the phosphate group occur at 1035, 603 and 565 cm^{-1} . Three small peaks are observed at 1456, 1423 (stretching modes) and 873 cm^{-1} (deformational modes) and correspond to the B-type carbonate substitution with the replacement of PO_4^{3-} by CO_3^{2-} along with the substitution of Ca^{2+} by Na^+ and K^+ to preserve the crystal electroneutrality. (B) The large peaks observed at 3435 cm^{-1} are attributed to the OH^- groups.

are observed at 1456, 1423 (stretching modes) and 873 cm^{-1} (deformational modes). The peaks observed at 3435 cm^{-1} can be attributed to the OH^- groups (Fig. 1B). Scanning Electron Microscope (SEM) photomicrographs show that HAP precipitates form subhedral to euhedral hexagonal crystals with a tabular habit (5–10 μm in size) co-existing with smaller (<1 μm) poorly crystallized HAP (Fig. 2). Carbonate-bearing HAP is the only solid phase that was identified during these experiments. It is noteworthy that below

10 °C, brushite was precipitated instead of HAP as was previously observed by Balter and Lécuyer (2004). The amount of structural carbonate has been roughly estimated by measuring the CO_2 pressure generated from the carbonate reactions with phosphoric acid using the calibrated transducer readings from the dual inlet of the IRMS. Carbonate content ranges from 0.05 to 0.23 ± 0.05 wt% (Table 1).

3.2. Oxygen isotope fractionation between HAP-bound carbonate and water

Carbonate-bearing HAP was precipitated in waters with $\delta^{18}\text{O}$ ranging from -10.46‰ to -6.89‰ V-SMOW (Table 1). Experiments were performed in a restricted range of low temperatures from 10 °C to 37 °C, therefore resulting values of $1000 \ln \alpha(\text{CO}_3^{2-}\text{-H}_2\text{O})$ were reported as a function of the inverse of the temperature (K) according to the recommendation given by O'Neil (1986). Both variables are linearly correlated according to the following equation (Fig. 3):

$$1000 \ln \alpha(\text{CO}_3^{2-}\text{-H}_2\text{O}) = 25.19 (\pm 0.53) \cdot T^{-1} - 56.47 (\pm 1.81) \quad (R^2 = 0.998) \quad (1)$$

This fractionation equation has a slightly steeper slope than those already established between calcite and water (O'Neil et al., 1969; Kim and O'Neil, 1997) even though measured fractionations are comparable within analytical uncertainties in the temperature range 20–37 °C (Fig. 4). Blake et al. (1997), Lécuyer et al. (1999) and O'Neil et al. (2003) have shown that oxygen isotope exchange between dissolved phosphate and water is extremely slow. Indeed, according to the temperature dependence of the rate constant ' k ' as determined by Lécuyer et al. (1999), the fraction of exchanged oxygen isotopes between phosphate and water is negligible for reaction times of 96 h and temperatures ranging from 10 °C to 37 °C. Consequently, comparison of oxygen isotope fractionation between HAP-bound carbonate and water with that of phosphate–water can only be made with oxygen isotope fractionation equations that were established empirically with apatites of biogenic origin. It is then observed that the oxygen isotope fractionation between apatite carbonate and phosphate (Kolodny et al., 1983) increases from about 7.5‰ up to 9.1‰ with the temperature decreasing from 37 °C to 10 °C (Fig. 5).

4. DISCUSSION

4.1. Did HAP-bound carbonate reach isotopic equilibrium during precipitation?

Podlesak et al. (2008) performed diet-controlled experiments on woodrats and measured oxygen isotopic fractionations between enamel carbonate and body water in the range 24.4–29.4‰. These values bracket the fractionation value determined during our experiments performed at 37 °C. Oxygen isotope fractionations that were measured between HAP carbonate and water are also close to those determined between calcite and water (O'Neil et al., 1969;

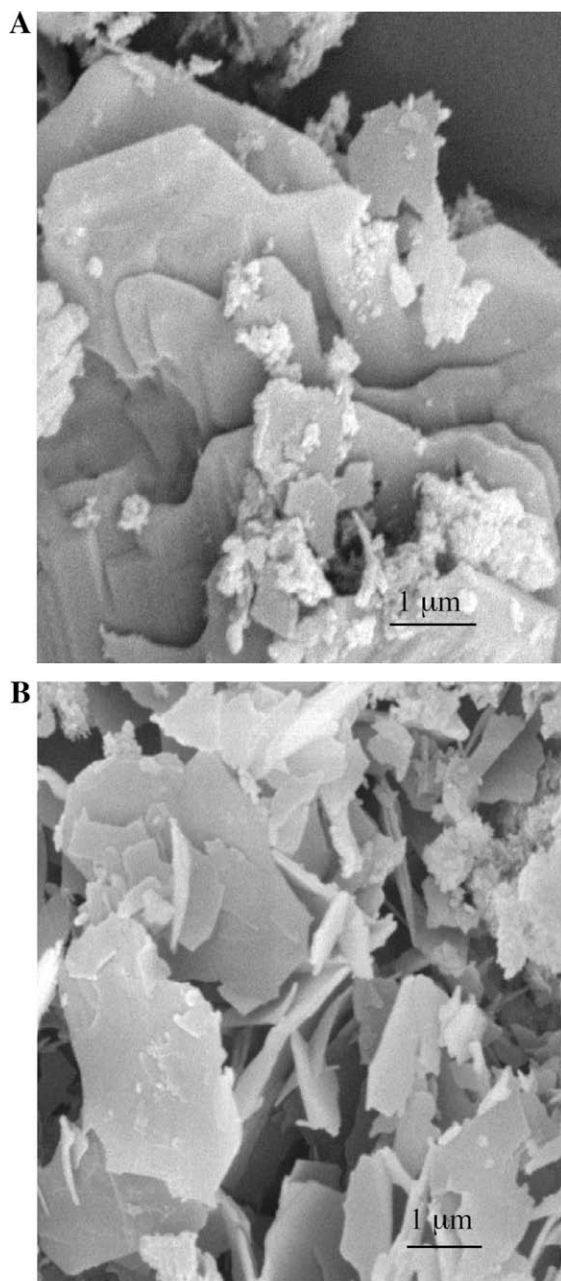


Fig. 2. Photomicrograph by Scanning Electron Microscopy of inorganically precipitated crystals of carbonate-bearing hydroxyapatite. (A) HAP crystals precipitated at 10 °C (magnification of 9000 \times). (B) HAP crystals precipitated at 37 °C (magnification of 5000 \times).

Table 1

Oxygen isotope compositions of carbonate ions in hydroxyapatites that were inorganically precipitated in waters of known isotopic compositions in the range 10–37 °C. Samples correspond to HAP precipitates obtained from distinct aqueous solutions, each HAP sample has been duplicated or triplicated (n) for the $\delta^{18}\text{O}$ analysis of apatite carbonate.

| Sample | n | CO_3^{2-} (wt%) | $\delta^{18}\text{O}$ (CO_3^{2-}) (‰ V-SMOW) | $\delta^{18}\text{O}$ (H_2O) (‰ V-SMOW) | $1000 \ln \alpha$ | T (°C) |
|---------|-----|--------------------------|---|---|-------------------|----------|
| HAP10-1 | 2 | 0.1 | 22.57 | −10.09 | 32.46 | 10 |
| HAP10-2 | 2 | 0.12 | 22.92 | −10.09 | 32.80 | 10 |
| HAP10-3 | 2 | 0.15 | 22.79 | −10.09 | 32.68 | 10 |
| HAP15-1 | 3 | 0.11 | 21.23 | −10.07 | 31.13 | 15 |
| HAP15-2 | 3 | 0.21 | 21.03 | −10.04 | 30.90 | 15 |
| HAP20-1 | 3 | 0.05 | 19.99 | −9.96 | 29.80 | 20 |
| HAP20-2 | 3 | 0.06 | 19.37 | −9.94 | 29.17 | 20 |
| HAP25-1 | 3 | 0.21 | 17.50 | −10.46 | 27.86 | 25 |
| HAP30-1 | 3 | 0.19 | 17.33 | −9.81 | 27.04 | 30 |
| HAP30-2 | 3 | 0.17 | 16.85 | −9.77 | 26.53 | 30 |
| HAP37-1 | 2 | 0.23 | 16.02 | −9.30 | 25.24 | 37 |
| HAP37-2 | 2 | 0.18 | 17.74 | −6.89 | 24.50 | 37 |

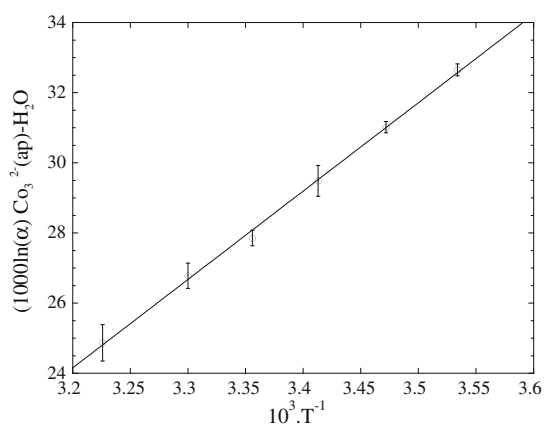


Fig. 3. Oxygen isotope fractionation equation between inorganic hydroxyapatite carbonate and water in the range 10–37 °C. $1000 \ln \alpha(\text{CO}_3^{2-}-\text{H}_2\text{O}) = 25.19 (\pm 0.53) \cdot T^{-1} - 56.47 (\pm 1.81)$ with $R^2 = 0.998$.

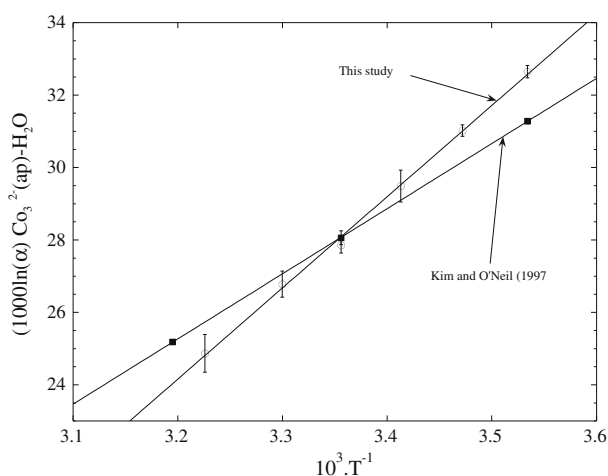


Fig. 4. Oxygen isotope fractionation equation between inorganic hydroxyapatite carbonate and water compared to the inorganic calcite–water equation (Kim and O'Neil, 1997).

Kim and O'Neil, 1997) for temperatures between 20 °C and 37 °C (isotopic differences do not exceed 0.5‰). However, the steeper slope observed for the fractionation equation between HAP carbonate and water is rather surprising (Fig. 3) when considering that equations determined for calcite, aragonite and HAP phosphate have similar slopes (O'Neil et al., 1969; Kolodny et al., 1983; Grossman and Ku, 1986). It must be also kept in mind that oxygen isotope fractionation between HAP-bound carbonate and water can be distinct from the fractionation between calcite and water considering the differences in chemistry and crystal lattice between the two minerals. However, we must question whether or not our experimental data reflect the oxygen isotope composition of natural carbonate-bearing HAP, taking into account that the amount of carbonate in experimental HAP is much lower than that of most biogenic apatites. Indeed, Koch et al. (1997) and Zazzo et al. (2004) reported CO_3^{2-} amounts ranging from 3.4 to 4.0 wt% for untreated enamel and enamel treated with acetic acid or sodium hypochlorite solutions. Experimental HAP crystals precipitated in this study contain only 0.05–0.23 wt% of CO_3^{2-} , which is

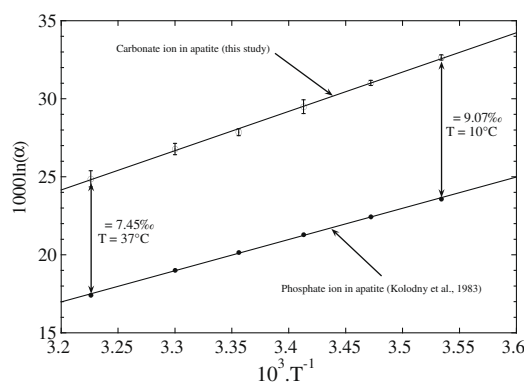


Fig. 5. Oxygen isotope fractionation equation between inorganic hydroxyapatite carbonate and water compared to the biogenic phosphate–water equation (Kolodny et al., 1983).

most likely the result of a high degree of crystallization in the absence of organic matrix. It has been documented that collagen-rich biogenic apatites such as bone and dentine have a poor crystallinity and a high carbonate content (LeGeros et al., 1967; Daculsi et al., 1997), thus at least partly explaining this difference in chemical composition. As observed in the case of divalent carbonates by Kim and O'Neil (1997), highly concentrated solutions or high rates of precipitation can generate 'non-equilibrium' minerals that are characterized by larger fractionation factors by as much as 2–3‰ associated with a poorer reproducibility. Similarly, Liang and Blake (2006, 2007) observed that apatite precipitates may be enriched in $P^{16}O_4$ relative to residual dissolved phosphate. Consequently, fractionation equations have a steeper slope than those attributed to 'equilibrium minerals'. However, several observations argue in favour of HAP precipitated near oxygen isotope equilibrium with the aqueous solution, which are (1) most crystals are well-crystallized as shown by XRD and IR-spectroscopy data, (2) the low solubility of HAP precludes the use of highly concentrated aqueous solutions, (3) fractionation values are independent of the water $\delta^{18}O$ at 37 °C (Table 1). Oxygen isotope equilibrium between precipitated HAP carbonate and water cannot be demonstrated, however, these first experimental data suggest that measured fractionations are close to those established between calcite and water in the range of temperature of most living ectothermic and endothermic animals.

4.2. Oxygen isotope compositions of carbonate and phosphate in biogenic apatites

The dependence on temperature of the oxygen isotope fractionation between biogenic phosphate and water has been empirically determined several times and according to the Longinelli and Nuti (1973), Kolodny et al. (1983) and Lécuyer et al. (1996); $1000 \ln \alpha(PO_4^{3-}-H_2O)$ equals $17.4 \pm 0.5\text{‰}$ at 37 °C. Consequently, when using the fractionation equations experimentally determined for calcite by O'Neil et al. (1969) and Kim and O'Neil (1997), the oxygen isotope fractionation factor between carbonate (approximated by that of calcite–water) and phosphate in apatite from vertebrate bones and teeth lies between 7‰ and 8‰ over the studied range of temperatures (10–37 °C) because the slopes of these curves are close to each other. This estimate is in agreement with the result of calculations made by Bryant et al. (1996) who combined fractionation equations proposed by both Shemesh et al. (1988) and Zheng (1996) and which were based on measurements of natural samples and theoretical calculations, respectively. Measured oxygen isotope fractionation between HAP-bound carbonate (this study) and phosphate (Kolodny et al., 1983) is close to 7.5 at 37 °C (Fig. 5) and is in agreement with previous estimates presented above. However, an increasing oxygen isotope fractionation with decreasing temperature remains to be confirmed (Fig. 5).

A compilation of $\delta^{18}O$ values of both phosphate and carbonate (Fig. 6) from teeth and bones (Bryant et al., 1996; Iacumin et al., 1996; Zazzo et al., 2004) from modern mammals—which regulate body temperature close to

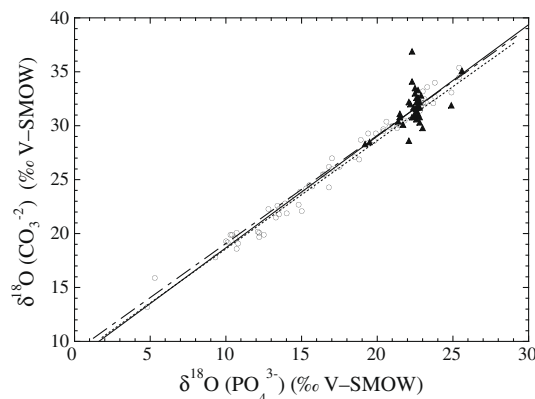


Fig. 6. $\delta^{18}O$ of apatite carbonate reported against $\delta^{18}O$ of apatite phosphate from teeth and bones of modern terrestrial mammals (open circles) and fish (filled triangles) that were compiled from Bryant et al. (1996), Iacumin et al. (1996), Shahack-Gross et al. (1999), Vennemann et al. (2001), Zazzo et al. (2004) and Martin et al. (2008). The intercept value of the regression line for modern mammals is an indicator of the $1000 \ln \alpha(CO_3^{2-}-PO_4^{3-})$ value recorded in these biogenic apatites for a temperature close to 37 °C. $\delta^{18}O(CO_3^{2-}) = 1.035(\pm 0.017) \cdot \delta^{18}O(PO_4^{3-}) + 8.33$ (± 0.30) with $R^2 = 0.983$. Dashed line: $1000 \ln \alpha(CO_3^{2-}-PO_4^{3-})$ by combining calcite and phosphate fractionation equations from Kim and O'Neil (1997) and Kolodny et al. (1983). Dotted line: $1000 \ln \alpha(CO_3^{2-}-PO_4^{3-})$ by combining fractionation equations from this study and the phosphate equation from Kolodny et al. (1983).

37 °C—confirms that both variables are linearly correlated with a slope close to 1 (1.03 ± 0.02) and an intercept of 8.3‰ that corresponds to a $1000 \ln \alpha(CO_3^{2-}-PO_4^{3-})$ value of 8.1‰. This fractionation factor is slightly higher or close to the fractionation factor expected to be in the range 7–8‰. It is noteworthy that the observed apparent oxygen isotope fractionation between carbonate and phosphate in apatite is more scattered in fish than in mammals (Fig. 6) as reported by Vennemann et al. (2001). These authors consider that the mean $\Delta_{\text{carbonate-phosphate}}$ value of 9.1‰ associated with a large standard deviation of 1.5‰ ($n = 44$) could reflect temperature of carbonate formation either higher or lower than that of phosphate, most of the analyzed fish having evolved in waters for which the temperature was in the range 12–23 °C (Vennemann et al., 2001).

Several mechanisms may be involved to explain the slight difference of oxygen isotope composition between carbonates from mammal apatite and inorganic HAP relative to the composition of the co-existing biogenic phosphate. Bryant et al. (1996) proposed that a difference in mineral stoichiometry could partly account for the observed relative slight ^{18}O -enrichment of carbonate in mammal apatite. Acid fractionation factors are indeed sensitive to mineral composition as reported by Friedman and O'Neil (1977). However, chemical compositions and crystallinity of HAP from mammal tooth or bone and from our low-temperature precipitates are close enough to exclude a significant influence on oxygen isotope fractionation factors. A second explanation could be a diachronism in the closure of oxygen isotope exchange between the carbonate–

water and phosphate–water systems with a diet-dependent body water of varying $\delta^{18}\text{O}$ value. However such a diachronism seems unlikely because of the large residence time of water in the studied mammals (Nagy and Peterson, 1988) which precludes short-time variations in the $\delta^{18}\text{O}$ of body water. Moreover, such a process should be responsible for a scattering of data but without modifying the mean value of $1000 \ln \alpha(\text{CO}_3^{2-}-\text{PO}_4^{3-})$. Scattering of data in Fig. 6 is high relative to the possible cumulative analytical uncertainties associated with the measurement of $\delta^{18}\text{O}$ values in both carbonate and phosphate components. Indeed, $1000 \ln \alpha(\text{CO}_3^{2-}-\text{PO}_4^{3-})$ values range from 7‰ to 10.5‰, independently of the methods used to analyze oxygen isotope compositions of apatite phosphate and carbonate. Such a data scattering could result from HAP carbonate precipitation out of isotopic equilibrium with body water. Precipitation of biogenic carbonate out of oxygen isotope equilibrium with ambient water (the so-called “vital effect”) has been for example widely documented in brachiopods (Auclair et al., 2003), corals (Swart, 1983; McConnaughey, 1989a,b) and foraminifera (Zeebe, 1999). These isotopic disequilibria can result from high growth rates of the skeleton, varying amounts of metabolic CO_2 available during crystallization and variations in the extracellular pH at the site of mineralization.

Mineralization of bone and enamel from extracellular fluids is promoted by specialized cells (osteoblasts for bones, ameloblasts for enamel). Osteoblasts and ameloblasts are requisite for the synthesis of bone and enamel extracellular matrix production and of mineralized tissues (Robinson et al., 1979; Arnett, 2003). Bone extracellular matrix is composed of nearly 90% collagen (Lian, 2006), while non-collagen proteins comprise enamel extracellular matrix. Mineral accounts for up to 70% of bone weight and 95% of enamel. Since no predictable difference of $1000 \ln \alpha(\text{CO}_3^{2-}-\text{PO}_4^{3-})$ is observed between bone and enamel samples, it is unlikely that the composition of extracellular matrix or bonds between HAP and extracellular matrix will significantly affect the $\delta^{18}\text{O}$ value of HAP-bound carbonate. Regulation of pH and ionic conditions is essential to normal enamel growth and mineralization. The pH of extracellular fluid varies at different stages of the amelogenesis between 5.8 and 7.4 (Aoba and Moreno, 1987; Sasaki et al., 1991). Little is known about bone interstitial fluid composition, however, large pH variations of the extracellular fluid around neutral to acidic values are likely during bone turn-over. Bone mineralization occurs at pH around 7.1–7.4, however, acidification by osteoclasts is required for bone resorption (Fallon, 1984; Arnett and Spowage, 1996). These pH variations could be responsible for the 0–1‰ difference between the oxygen isotope composition of carbonate from inorganic apatite and carbonate from biogenic apatite formed under identical conditions.

5. CONCLUSIONS

Our experimental study demonstrates the temperature dependence of the oxygen isotope fractionation between HAP-bound carbonate and water, in contrast with previous studies in which no significant temperature dependence was

reported. This result suggests the existence of a carbonate–phosphate temperature proxy in ectotherms or endotherms. Values of $1000 \ln \alpha(\text{CO}_3^{2-}-\text{PO}_4^{3-})$ at 37 °C are estimated to be in the range 7–8‰ by combining experimental fractionation equations for calcite–water and HAP-bound carbonate–water with empirical fractionations based on phosphate in biogenic apatites. This value is close to but slightly lower than the value of 8.1‰ deduced from a compilation of data obtained from modern mammals. This data set also shows a significant scattering independent of the analytical methods that were used. These isotopic differences could result either from out-of-equilibrium oxygen isotope fractionation or changes in pH of the extracellular fluid, both processes operating during the incorporation of the minor amounts of carbonate ions in the crystal lattice of the apatite. Despite the sensitive dependence on temperature of the isotopic fractionation between the carbonate component of biogenic apatite and water, the oxygen isotope composition of phosphate remains the most robust proxy of temperatures or water compositions considering the better knowledge of fractionation equations that were determined for aquatic ectotherms and terrestrial mammals.

However, the carbon isotope composition of the carbonate component of apatites is very useful for discussing diet and ecology of past vertebrates while oxygen isotope compositions may help to identify a diagenetic alteration as already shown by Iacumin et al. (1996) and Zazzo et al. (2004). A better understanding of the mechanisms that are responsible for the observed variations in the apparent fractionation factor between carbonate and phosphate could improve the interpretations of data obtained in the fossil record, especially if this isotopic fractionation is sensitive to changes in an animal’s physiology such as growth rate or any metabolic perturbation. Future research should allow evaluating whether oxygen fractionation between synthetic HAP-bound carbonate and water differs or not from the fractionation between biogenic HAP-bound carbonate and water.

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