



## SCIENTIFIC COMMENT

## Oxygen isotope partitioning between phosphate and carbonate in mammalian apatite

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**Abstract**—The oxygen isotope compositions of phosphate and structural carbonate in mammalian enamel and bone apatite are linked to that of body water at constant body temperature near 37°C, but the isotope systematics of oxygen in structural carbonate are not well understood. Using coupled measurements of the oxygen isotope composition of structural carbonate and phosphate from horse tooth enamel, the apparent oxygen isotope fractionation factor between structural carbonate and body water is estimated to be  $1.0263 \pm 0.0014$ . These estimates provide a quantitative basis for using the oxygen isotope composition of structural carbonate in mammalian biogenic apatite for ecological, climatological, and physiological reconstruction.

## 1. INTRODUCTION

The oxygen isotope composition of phosphate in mammalian biogenic apatite is linked to that of the body water from which the apatite precipitates at constant body temperature (Longinelli, 1984; Luz et al., 1984). In turn, the isotopic composition of body water reflects that of oxygen inputs to the body, which are sensitive to climate (Luz et al., 1984; Tatner, 1988; Ayliffe and Chivas, 1990; Bryant and Froelich, 1995). Biogenic apatite [generalized as  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{CO}_3)_2$ ] also contains oxygen in structural carbonate. Variation in the isotopic composition of structural carbonate is also interpreted as a climatic signal (Land et al., 1980; Koch et al., 1989, 1995; Quade et al., 1992). While it is generally assumed that the oxygen isotope composition of structural carbonate in mammalian apatite is also linked to that of the body water, this assumption is not well tested. Analysis of the  $\delta^{18}\text{O}$  of structural carbonate is easier, less expensive, and more precise than current methods of  $\delta^{18}\text{O}$  analysis of phosphate. Furthermore,  $\delta^{18}\text{O}$  of structural carbonate is determined concurrently with  $\delta^{13}\text{C}$ , which also yields ecological and dietary information. Hence, it is important to understand the oxygen isotope systematics of structural carbonate in mammalian apatite.

The oxygen isotope composition of phosphate ( $\delta^{18}\text{O}_p$ ) and structural carbonate ( $\delta^{18}\text{O}_{sc}$ ) in mammalian biogenic apatite should be linked to that of body water because of the presence in blood of enzymes that catalyze oxygen isotope exchange between phosphate and body water (ATPases; Fallner and Elgavish, 1984), and carbon dioxide, bicarbonate, and body water (carbonic anhydrase; Silverman, 1982). However, the oxygen isotope fractionation factor between structural carbonate in apatite and water is not known. Furthermore, the  $\delta^{18}\text{O}$  of carbonates is normally determined by phosphoric acid dissolution. The  $\delta^{18}\text{O}$  of  $\text{CO}_2$  gas liberated

by phosphoric acid dissolution of carbonate, relative to the  $\delta^{18}\text{O}$  of the solid carbonate, varies among minerals (Friedman and O'Neil, 1977). The acid fractionation factor for structural carbonate in apatite is also unknown and cannot be determined by standard methods (e.g., fluorination to release  $\text{O}_2$ ) because apatite contains numerous oxygen-bearing moieties.

One way to quantify the oxygen isotope systematics of structural carbonate in biogenic apatite is to compare  $\delta^{18}\text{O}_{sc}$  to  $\delta^{18}\text{O}_p$ . The oxygen isotope fractionation factor between phosphate and body water in mammals is well known (Luz and Kolodny, 1985). Because mammals have a constant body temperature near 37°C, the  $\delta^{18}\text{O}$  of body water at the site of mineralization can be determined from  $\delta^{18}\text{O}_p$ , which provides a method for calculating a fractionation factor between  $\delta^{18}\text{O}_{sc}$  and body water.

## 2. MATERIALS AND METHODS

Samples were obtained from domestic horses (*Equus caballus*) and wild Burchell's zebra (*Equus burchelli*). Samples include enamel from deciduous (juvenile) and permanent teeth that were fully mineralized and erupted through the jaw bone, enamel from unerupted permanent teeth that were not fully mineralized, and jaw bone. Enamel samples were prepared by drilling away the dentin and cement and powdering in an agate mortar and pestle. Powder was drilled from bone fragments. Analyses of each sample were performed on splits of a single homogenized powder. The oxygen isotope composition of phosphate was determined by  $\text{BrF}_5$  fluorination of silver phosphate prepared from apatite by an ion-exchange method (Crowson et al., 1991). Reproducibility was monitored with NIST phosphorite rock standards SRM-120c ( $\delta^{18}\text{O}_p = 21.36 \pm 0.18$ ,  $1\sigma$ ,  $n = 13$ ) and SRM-694 ( $\delta^{18}\text{O}_p = 19.62 \pm 0.18$ ,  $1\sigma$ ,  $n = 20$ ). To determine the oxygen isotope composition of structural carbonate in apatite, organic matter was oxidized by soaking the powder overnight in ~3% sodium hypochlorite solution and rinsing several times with water. Labile (rapidly exchangeable) carbonate phases were removed by soaking overnight in a solution of 1 M acetic acid

buffered with 1 M calcium acetate (pH ~4). The powder was then rinsed several times with water and freeze-dried. Samples (~7 mg) were reacted with >100% phosphoric acid (density ~1.92 g/cm<sup>3</sup>) at 90°C for 10 min (enamel) or 15 minutes (bone) in a VG Isocarb automated common acid bath carbonate device. Liberated CO<sub>2</sub> was cryogenically purified and introduced into a VG Optima stable isotope ratio mass spectrometer for isotopic analysis. As in other studies (e.g., Koch et al., 1995), the acid fractionation factor for structural carbonate was assumed to be the same as for calcite, which for a common acid bath reaction vessel at 90°C is 1.00795 ± 0.00003 (Swart et al., 1991). Reproducibility was monitored with two internal enamel standards, EE (elephant enamel, δ<sup>18</sup>O<sub>SC</sub> = 27.25 ± 0.09, 1σ, n = 5) and F:MM 1219-M2 (domestic horse enamel, δ<sup>18</sup>O<sub>SC</sub> = 22.41 ± 0.08, 1σ, n = 4).

Results are reported in standard delta notation relative to SMOW. The fractionation factor (α) is used to express oxygen isotope fractionation between two substances (Friedman and O'Neil, 1977), where

$$\alpha_{A-B} = \frac{(1000 + \delta_A)}{(1000 + \delta_B)} \quad (1)$$

Uncertainties for regression statistics and fractionation factors calculated from regression statistics (e.g., the phosphate and carbonate paleotemperature equations) are 95% confidence intervals recalculated from the published data.

### 3. RESULTS

Results for forty-two samples of bone, enamel from erupted permanent and deciduous teeth, and the mineral phase of enamel from unerupted permanent teeth (Table 1) demonstrate a strong linear relationship between δ<sup>18</sup>O<sub>SC</sub> and δ<sup>18</sup>O<sub>P</sub> (Fig. 1), with no dependence on delta values (Fig. 2). Structural carbonate is ~8.7‰ more enriched in <sup>18</sup>O than is phosphate. The average apparent fractionation factor between structural carbonate and phosphate (α<sub>SC-P</sub>) is 1.0086 ± 0.0007 (1σ). This result compares well with an α<sub>SC-P</sub> of 1.0089 ± 0.0007 derived by Iacumin et al. (1996) for analyses of seventeen pooled samples of enamel and bone by similar analytical methods. These results are also comparable to an α<sub>SC-P</sub> determined by laser ablation, which yielded an α<sub>SC-P</sub> of 1.0083 ± 0.0014 after correcting for the carbonate-oxygen contribution to the phosphate-oxygen (Sharp and Cerling, 1996; Cerling and Sharp, 1996; T. Cerling, pers. commun., 1996). The mineral phase of unerupted tooth enamel is predominantly apatite but may include nonapatitic enamel precursors such as brushite (CaHPO<sub>4</sub>·2H<sub>2</sub>O) or octacalcium phosphate [Ca<sub>8</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·5H<sub>2</sub>O]. Based on how closely the results for the unerupted teeth compare with those for fully mineralized and erupted teeth (Fig. 1), the nonapatitic phases do not significantly affect the observed fractionation between δ<sup>18</sup>O<sub>SC</sub> and δ<sup>18</sup>O<sub>P</sub>. The measured α<sub>SC-P</sub> in biogenic apatite is very different from that calculated by subtracting the apatite paleotemperature equation from the calcite paleotemperature equation (Shemesh et al., 1988), which at mammalian body temperature (37°C) is 1.0070 ± 0.0008 (Fig. 1). The observed α<sub>SC-P</sub> of 1.0086 corresponds to a precipitation temperature of ~6°C from the combined calcite-apatite paleotemperature equation of Shemesh et al. (1988). Similarly, the measured α<sub>SC-P</sub> in biogenic apatite is also very different from a theoretical paleotemperature equation combining calcite and hydroxylapatite (Zheng, 1996) solved at 37°C, which yields a fractionation factor (1.0071) indistinguishable from the Shemesh et al. (1988) estimate.

Table 1. Oxygen isotope results (vs. SMOW) for phosphate and structural carbonate of modern horse tooth enamel and bone. Abbreviations: uppercase letters, upper teeth; lowercase letters, lower teeth; dP, deciduous premolar; P, premolar; M, molar.

Tooth Position	Phosphate δ <sup>18</sup> O	Carbonate δ <sup>18</sup> O
AMNH-M 27744, <i>Equus burchelli</i> , Athi River Plains, Kenya		
P2	20.76	29.92
P3	20.39	29.53
P4	21.00	30.00
M1	20.35	29.71
M2	19.85	29.26
M3	21.28	29.84
Bone #1	18.52	27.07
Bone #2	18.76	26.87
PK-93-W1, <i>Equus burchelli</i> , Amboseli Park, Kenya		
P2	23.07	32.45
P3	23.69	32.12
P4	23.20	32.19
M1	24.88	33.06
M2	23.00	32.08
M3	22.87	32.50
Bone	22.91	31.89
F:MM 1218, <i>Equus caballus</i> , Shannon County, South Dakota		
P2	10.56	19.57
P3	10.76	19.06
P4	10.67	20.06
M1	12.24	20.07
M2	10.39	19.90
M3	10.25	19.89
p2	9.99	19.29
p3	10.14	19.17
p4	9.28	17.83
m1	12.46	19.91
m2	12.09	20.21
m3	10.70	18.61
Bone	13.51	21.83
F:MM 1219, <i>Equus caballus</i> , Brown County, Nebraska		
dP2	15.49	24.47
dP3	13.39	22.55
dP4	15.31	24.16
P2 (Unerupted)	13.27	21.45
P3 (Unerupted)	14.76	22.66
P4 (Unerupted)	14.03	21.86
M1	14.34	23.16
M2	13.49	22.34
M3 (Unerupted)	16.82	24.31
Bone	15.02	22.13
AMNH-M 14131, <i>Equus caballus</i> , Schoharie County, New York		
M2	19.83	28.60
AMNH-M 165057, <i>Equus burchelli</i> , Etosha Pan, Namibia		
M2	21.80	30.48
AMNH-M 42753, <i>Equus burchelli</i> , Cape Province, South Africa		
P4	17.01	25.99
AMNH-M 83453, <i>Equus burchelli</i> , Mababe Flats, Botswana		
M2	25.41	34.54

### 4. DISCUSSION AND CONCLUSIONS

The relationship between the δ<sup>18</sup>O of body water and the δ<sup>18</sup>O of CO<sub>2</sub> gas liberated by phosphoric acid dissolution of apatite is a function of two fractionation factors. The first is between the structural carbonate and body water (α<sub>SC-BW</sub>), essentially a "paleotemperature equation" for structural carbonate in apatite. This is not expected to be the same as equations for organically or inorganically precipitated carbonate minerals. In humans there is typically 2–3% carbonate occupying two structural positions in enamel apatite (Brudevold and Söremark, 1967). Approximately 11% of the carbonate occupies the hydroxyl position (the A site), while the balance occupies the phosphate position (the B

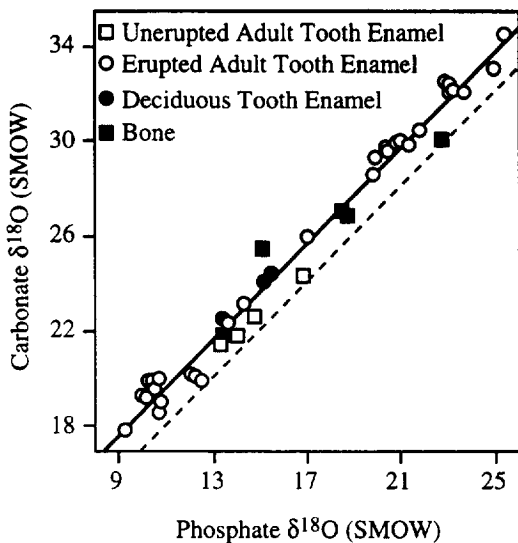


FIG. 1. Comparison of oxygen isotope composition of phosphate ( $\delta^{18}\text{O}_p$ ) and structural carbonate ( $\delta^{18}\text{O}_{sc}$ ) from horse tooth enamel and bone apatite. The solid line is the linear regression through all of the data points:  $\delta^{18}\text{O}_{sc}(\pm 1.3) = 1.02(\pm 0.04)\delta^{18}\text{O}_p + 8.3(\pm 0.7)$ , 95% confidence intervals,  $r^2 = 0.986$ . Residuals are plotted in Fig. 2. The average apparent fractionation factor ( $\alpha_{sc-p}$ ) is  $1.0086 \pm 0.0007$ . The dashed line is the relationship obtained from a combined calcite-apatite paleotemperature equation (Shemesh et al., 1988) and from a combined calcite-hydroxyapatite paleotemperature equation (Zheng, 1996), solved at  $37^\circ\text{C}$  (the result is identical for both combined equations). The measured  $\delta^{18}\text{O}_{sc}$  is  $\sim 1.6\text{‰}$  more enriched in  $^{18}\text{O}$  relative to  $\delta^{18}\text{O}_p$  than calculated by the combined calcite-apatite paleotemperature equations.

site) of hydroxylapatite (Elliott et al., 1985). The content and distribution of carbonate between the A and B sites may vary within and between species. Structural carbonate concentrations as high as  $\sim 5\%$  have been reported for certain species (Rey et al., 1991; Rink and Schwarcz, 1995), but systematic variation in either carbonate content or distribution between the A and B sites is not known. However, it is unlikely that the distribution of carbonate will significantly affect  $\alpha_{sc-BW}$ . For example, if the  $\delta^{18}\text{O}$  of carbonate in the A and B sites is  $5\text{‰}$  different, then the distribution of carbonate would have to vary by 20% to affect  $\delta^{18}\text{O}_{sc}$  by  $0.1\text{‰}$ . Thus, the distribution and oxygen isotope composition of carbonate between the A and B sites would have to vary considerably to affect  $\delta^{18}\text{O}_{sc}$ .

The second fractionation factor is between structural carbonate and  $\text{CO}_2$  liberated by phosphoric acid dissolution of apatite, an "acid fractionation factor." The  $\delta^{18}\text{O}$  of  $\text{CO}_2$  liberated by phosphoric acid dissolution of calcite can vary by  $0.1\text{--}0.4\text{‰}$  due to the reaction method used (Swart et al., 1991). Similarly, the  $\delta^{18}\text{O}$  of  $\text{CO}_2$  gas liberated from different carbonate minerals with the same carbonate- $\delta^{18}\text{O}$  value can vary by  $\sim 1.4\text{‰}$  due to mineralogical effects (Friedman and O'Neil, 1977). Neither the "paleotemperature equation" nor the "acid fractionation factor" for structural carbonate are known independently. Cumulatively, however, these two factors likely explain the offset between the observed relationship of  $\delta^{18}\text{O}_p$  and  $\delta^{18}\text{O}_{sc}$  versus that calculated by subtracting the apatite paleotemperature equation from

the calcite paleotemperature equation (Fig. 1). It is unlikely that the offset is due to mechanisms of phosphate incorporation, because  $\delta^{18}\text{O}_p$  is measured by fluorination (100% oxygen yield, hence no acid fractionation factor), and because analyses of  $\delta^{18}\text{O}_p$  of fish and mammal apatite and of phosphorite rocks conform well to a single paleotemperature equation for phosphate-oxygen in apatite (Longinelli and Nuti, 1973; Kolodny et al., 1983; Luz and Kolodny, 1985; Shemesh et al., 1988).

Because (1) mammalian body temperature is constant near  $37^\circ\text{C}$ , (2) the oxygen isotope fractionation factor for apatite-phosphate relative to body water is well known in mammals, and (3) there is a strong linear correlation between  $\delta^{18}\text{O}_p$  and  $\delta^{18}\text{O}_{sc}$  (Fig. 1), an apparent fractionation factor can be calculated that relates  $\delta^{18}\text{O}_{sc}$  to  $\delta^{18}\text{O}$  of body water. The fractionation factor is termed "apparent" because it is based on the assumption that the acid fractionation factor for structural carbonate is the same as for calcite. First the measured  $\delta^{18}\text{O}_p$  is used to calculate the  $\delta^{18}\text{O}$  of body water from which the apatite precipitated, assuming a constant mammalian body temperature of  $37^\circ\text{C}$  and an oxygen isotope fractionation factor between phosphate and body water of  $1.0176 \pm 0.0005$  (recalculated from Luz and Kolodny, 1985). Although several equations have been proposed for phosphate-oxygen isotope fractionation between apatite and water (Longinelli and Nuti, 1973; Kolodny et al., 1983; Karhu and Epstein, 1986; Shemesh et al., 1988; Kastner et al., 1990; Zheng, 1996), the value of  $1.0176 \pm 0.0005$  was measured directly with mammalian apatite and thus is likely accurate. The apparent fractionation factor between structural carbonate and body water is then calculated from the measured  $\delta^{18}\text{O}_{sc}$  and estimated  $\delta^{18}\text{O}$  of body water. The resulting estimate of the oxygen isotope fractionation factor between  $\delta^{18}\text{O}_{sc}$  and  $\delta^{18}\text{O}$  of body water at  $37^\circ\text{C}$  is  $1.0263 \pm 0.0014$ .

The  $\delta^{18}\text{O}$  values of structural carbonate and phosphate in mammalian apatite are coupled to the  $\delta^{18}\text{O}$  of body water.

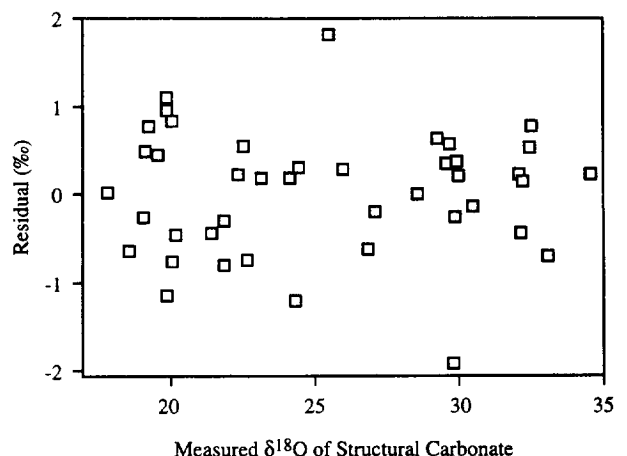


FIG. 2. Residuals of the linear regression shown in Fig. 1 plotted as a function of the measured  $\delta^{18}\text{O}$  of structural carbonate. The residual is the difference of the measured minus the predicted  $\delta^{18}\text{O}$  values, where the predicted value is the estimate from the regression in Fig. 1.

The  $\delta^{18}\text{O}$  of structural carbonate, therefore, can be used to reconstruct variation in the  $\delta^{18}\text{O}$  of body water integrated over the interval of enamel mineralization. The apparent fractionation factor relating  $\delta^{18}\text{O}_{\text{SC}}$  to  $\delta^{18}\text{O}_{\text{P}}$  is estimated as  $1.0086 \pm 0.0007$ , and that relating  $\delta^{18}\text{O}_{\text{SC}}$  to  $\delta^{18}\text{O}$  of body water is estimated as  $1.0263 \pm 0.0014$ . These estimates should be valid if the acid fractionation factor for calcite is used to calculate  $\delta^{18}\text{O}_{\text{SC}}$  from the  $\delta^{18}\text{O}$  of  $\text{CO}_2$  liberated by phosphoric acid dissolution in a common acid bath system.

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