Isotopic Alteration of Mammalian Tooth Enamel

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ABSTRACT   Mammalian tooth enamel carbonates from a Pliocene site at Allia Bay in northern Kenya show variable carbon and oxygen isotopic alteration. Sample screening by cathodoluminescence, prior to isotopic analysis, identified areas of extensive chemical alteration and others that were minimally altered. The luminescent patterns were used to guide sampling for the isotope study. Carbon stable isotope ratios of the apatite carbonate from luminescent enamel exteriors differ from the ratios in the enamel interiors and the magnitude of difference varies widely. The interior of the enamel usually retains the carbon isotope ratios expected based on faunal identification, but in a minority of cases, all of the enamel appears to be altered isotopically. Among fauna with an apparent mixed feeding signal, it is particularly difficult to determine whether the $\delta^{13}C$ value is due to an actual mixed feeding strategy during life or to alteration toward sediment values. Palaeoecological reconstructions based on the $\delta^{13}C$ values of enamel carbonate in browsing fauna would be affected, in many cases, since differences of 1‰ are significant for such reconstructions. Even so, careful selection of unaltered enamel sections should avoid this problem. Palaeodiet reconstruction would be less affected except in those cases where the alteration approaches 5‰. In such cases, a mixed feeding strategy would be the erroneous interpretation of the data. Oxygen isotope ratios in the enamel carbonates show no pattern and the retention of biogenic values is unlikely. For this reason, palaeotemperature reconstructions, based on the $\delta^{18}O$ values of the enamel carbonate, would not be possible at this site. Copyright © 2003 John Wiley & Sons, Ltd.

Key words: Pliocene fossils; diagenesis; carbon isotopes; oxygen isotopes

Introduction

The mineral compositions of vertebrate teeth and bones from fossil sites are commonly used as indicators of palaeoclimate, palaeodiet, and palaeoecology (e.g., Brink & Lee Thorp, 1992); but in bone, multiple processes can alter the original composition. Alteration occurs by precipitation of authigenic carbonate (Michel *et al.*, 1996), phosphate (Blake *et al.*, 1998), or other minerals (Kohn *et al.*, 1999), exchange reactions in the original carbonate (Wang & Cerling, 1994) or

phosphate (Blake *et al.*, 1998), and uptake or loss of various trace elements (Lambert *et al.*, 1991). Fluorine commonly replaces OH^- producing fluorapatite (Bryant *et al.*, 1996b), $CO_3 \cdot F^{3-}$ can replace PO_4^{3-} producing francolite (Schuffert *et al.*, 1990) and, less commonly, CO_3^{2-} can replace OH^- (LeGeros, 1981; Sponheimer & Lee-Thorp, 1999). Recrystallization also occurs producing various phosphate-containing compounds (Newesely, 1989) with trace levels of various cations often replacing calcium at higher concentrations than found in modern bone (Williams *et al.*, 1997). Assessment by X-ray diffraction (XRD) (Shipman *et al.*, 1984; Michel *et al.*, 1996), Fourier transform infra-red spectroscopy (Williams *et al.*, 1997),

chemical composition and isotope ratios (Nelson *et al.*, 1986; Bryant *et al.*, 1996a) often shows evidence of rapid diagenesis (Hedges *et al.*, 1995), depending on the burial environment (Pate *et al.*, 1989). The intensity of alteration can vary from bone to bone, within and between depositional sites (Hedges *et al.*, 1995), and can be distributed heterogeneously within a single bone or crystallite (Wang & Cerling, 1994). Precipitates along cracks or within pores can sometimes be removed in the laboratory (Sillen & Sealy, 1995) but isolation of unaltered bone hydroxylapatite has not always been possible (Nelson *et al.*, 1986; Tuross *et al.*, 1989b; Hoppe, n.d.). These processes can affect both the isotopic and chemical composition of bones (Tuross *et al.*, 1989a).

In contrast to bone, tooth enamel is generally assumed to be resistant to diagenetic alteration because of its structure (Koch *et al.*, 1997; Lee-Thorp, 2000). The few studies investigating the process conclude that the overall effect is minimal, and that it proceeds as a solid-state process (Sponheimer & Lee-Thorp, 1999; Lee-Thorp, 2000). It is also assumed, although not explicitly stated, that the process affects all fossils within a single site to the same extent. It seems possible, however, that reactions similar to those reported for bone could occur on all enamel surfaces and that such reactions could occur along sequentially exposed cracks or micro-cracks in the enamel. If such surfaces were exposed at different times during weathering and fossilization, as when secondary deposition occurs (e.g., Boaz & Behrensmeyer, 1976; Behrensmeyer & Hill, 1976; Shipman, 1981), different processes or variable extents of the same process could affect individual fossils. Such differential processes or extents could explain why pristine bone chemical and isotopic signals are recovered at times, while at others they are not (see Hoppe, this volume).

In order to extend our understanding of the stability of enamel, we have undertaken a series of studies using several different approaches. All studies focus on a single set of Pliocene mammal teeth collected within the sedimentary basin east of Lake Turkana in northern Kenya and made available through the National Museums of Kenya. Modern teeth during surface survey in 1984 and 1993 in an area of the lake basin just north of the fossil locality, serve as our baseline comparative sample.

The fossil teeth were recovered from a single excavation within locality 261-1 of the Allia Bay fossil site, which lies along the eastern shore of present-day Lake Turkana. At the time of deposition, the site was located beside a perennial river (the fossil Omo) occupying a broad floodplain (Feibel *et al.*, 1991). The bone-bearing bed is a manganese-cemented sandstone lying just beneath the Moiti Tuff. Repeated K/Ar dating indicates that the tuff dates to 3.9 MA and falls within the Lonyumun Member of the Koobi Fora Formation (Leakey *et al.*, 1995). Although the complete fossil collection from the deposit includes an early hominid species *Australopithecus anemensis*, our diagenesis studies have been conducted on material excavated in a different area of exposure (Coffing *et al.*, 1994).

The results of our previous studies suggest that the fossil enamels are altered chemically and that there is differential alteration of individual enamels within the site (Kohn *et al.*, 1999; Reeser *et al.*, unpublished). The results are summarized here because they guided the sampling strategy for the present study, which investigated the effect on oxygen and carbon isotope ratios. The first study used transmission electron microscope imaging, ion microprobe analysis of 8–10 µm-diameter spots and scanning electron microprobe spot analysis ($\approx$1 µm), imaging, and x-ray mapping to compare the elemental composition of four fossil tooth fragments with three modern teeth. In brief, the results show higher levels of various elements (manganese, iron, silica, rare earth elements, uranium, fluorine, and strontium) in the fossil enamels than in the modern teeth (Table 1). The pattern of the data suggested contamination by fine-grained secondary oxyhydroxides, low levels of clay incorporation, and chemical alteration of the original apatite.

The second study applied cold cathode cathodoluminescence and electron microprobe analyses to six modern teeth and 31 Pliocene enamel fragments to investigate the location of the chemical alteration identified by the first study. Cathodoluminescence refers to photon emission in the visible range resulting from excitation of a sample (a mounted thin section in this case) by high-energy electrons. In synthetic

Table 1. Elemental composition varies between cathodoluminescent areas

Number of points analysed	SiO$_2$ (range)	FeO (range)	MnO (range)	Ce2O$_3$ (range)
MODERN				
7*	0.01 (0.00–0.05)	0.01 (0.00–0.03)	0.01 (0.00–0.03)	0.05 (0.00–0.13)
Blue Luminescence				
9†	<0.12	<0.29	<0.28	<0.26
PLIOCENE				
Dark Luminescence				
17†	<0.12	0.33 (4) (<0.29–0.34)	0.33 (4) (<0.28–0.33)	<0.26
Moderate Green Luminescence				
5†	0.24 (5) (0.17–0.35)	1.48 (5) (0.31–3.23)	0.38 (5) (0.38–0.55)	<0.26
Bright (yellow and orange) Luminescence				
25†	0.45 (4) (<0.12–0.72)	1.55 (5) (<0.29–2.58)	0.56 (6) (<0.28–0.63)	0.28 (2) (<0.26–0.28)

Data are reported as parts per hundred; numbers in parentheses next to the data refer to the number of analysed points that contained detectable levels of the particular element (e.g., five points of five analysed points had detectable silica in the Pliocene teeth with moderate green luminescence).
* Data from Kohn *et al.*, (1999).
† Data from Reeser *et al.*, unpublished.

and geological apatites, manganese and silica-containing minerals activate a yellow luminescence (Mariano, 1988; Barbarand & Pagel, 2001), rare earth elements activate various colours (pink, violet, red, etc.) when they substitute for calcium (Mitchell *et al.*, 1997) and a light blue colour results from defects in the apatite lattice, caesium replacement of calcium and/or low levels of carbonate substitution (Barbarand & Pagel, 2001; Gotze *et al.*, 2001). Dark areas in geological apatites associate with the presence of iron and of manganese in the oxide form (Roeder *et al.*, 1987; Filippelli & Delaney, 1993).

All of the modern teeth showed a light blue colour, whereas the Pliocene enamels had areas that were dark or were coloured yellow, green, and/or orange. The blue colour in the modern teeth associates with low levels of caesium (Table 1) and previously reported apatite defects and carbonate substitution (LeGeros, 1981). The Pliocene enamel fragments clustered loosely into three groups that appear altered in different ways. The largest group (n = 25) had enamel interiors that were dark (no colour), although a majority of them (n = 17) had very bright, yellow luminescent zones at the margins of the thin sections. A smaller, second group (n = 5) had moderate, but uneven, intensity of greenish

luminescence throughout the enamels; one of them had a bright, yellow luminescent zone at its outer margin. The last enamel fragment (the single member of group three) was bright orange-yellow throughout the enamel thin section.

In general, the coloured areas appear to have elemental compositions that are different from the dark areas (see Table 1). Only a small number of points analysed in the dark areas (four of 17 points analysed) have detectable iron and manganese, the concentrations in these points are very low and none of the points has detectable silica. The presence of manganese in the dark areas supports the first study's suggestion of contamination by fine-grained secondary oxyhydroxides since manganese in the oxide configuration does not luminesce (Roeder *et al.*, 1987; Filippelli & Delaney, 1993). In contrast, iron and manganese was detected in all points analysed in the moderate green sections (five of five points analysed) and the concentrations were much higher than in the dark areas of the first group.

The bright yellow zones along the edges of the enamel sections and the single section that was bright orange-yellow differ from both the dark and the green areas. Manganese replacement of calcium in the apatite lattice, at levels

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below the detection limit of the second study, and incorporation of silica-bearing minerals are most commonly correlated with orange and yellow luminescence (Mariano, 1988; Mason & Mariano, 1990; Gotze *et al.*, 2001). This suggests variable manganese replacement of calcium in these enamels as well as incorporation of silica-bearing minerals. The possibility deserves further exploration since the points with detectable silica and manganese (five and six of 25 points analysed) in these bright yellow and orange zones have higher concentrations than occur in the green areas. Overall, the data suggest minimal alteration in the dark zones of the first and largest group but more extensive elemental substitution and apatite alteration in the bright yellow zones and in the orange-yellow and moderate green areas of the remaining sections.

This alteration was not apparent in the visual appearances of these fragments or in some other commonly used indicators of alteration. Bright, dark or moderate luminescence occurred in fragments that looked solid brown or black, mottled brown or black, or chalky, milky or yellow (Table 2). All the fossil samples had slightly elevated calcium to phosphate ratios (CaO to P_2O_5 values reported in Kohn *et al.*, 1999; Reeser *et al.*, unpublished) compared with modern samples (1.32–1.42 in the Pliocene enamels versus 1.26–1.28 in the modern enamels), although the significance is uncertain. When analysed by XRD, however, all samples in the group with the dark interiors were hydroxylapatite whereas the samples in the other groups with either moderate green or orange-yellow luminescence were either fluorapatite or had peaks shifted toward fluorapatite (Reeser *et al.*, unpublished). The yellow zones on the edges of the thin sections were too small for separate analysis by XRD but it is likely that these zones are also altered in the direction of fluorapatite.

This interpretation is supported by the fluorine (F) distribution pattern and the carbon dioxide (CO_2) concentrations in Pliocene samples (Table 3). Although all the fossil teeth show elevated levels of carbon dioxide and fluorine compared with modern samples, these levels were higher in the bright yellow zones and in all analysed points in the moderate green and

Table 2. Surface appearance uncorrelated with colour

Number of thin sections	Surface*	Cathodoluminescent colour on edge
MODERN		
2	1 (cracking)	Blue
1	2 (outer layers flaking)	Blue
2	4 (large & small splinters)	Blue
1	5 (falling apart)	Blue
PLIOCENE		
8	Solid brown or black	Bright
1	Mottled black or brown	Bright
10	Chalky, milky, or yellow	Bright
2	Solid brown or black	Moderate
1	Mottled black or brown	Moderate
1	Chalky, milky, or yellow	Moderate
1	Solid brown or black	Dark
3	Mottled black or brown	Dark
4	Chalky, milky, or yellow	Dark

* Modern data were scored by weathering stages as described in Behrensmeyer, (1978).

the orange-yellow thin sections. The concentration patterns suggest that substitution begins at surfaces and moves inward as demonstrated previously in bone (Williams & Potts, 1988) and as expected from solid-state processes (Lee-Thorp, 2000). The present study investigates the possibility that the exteriors of these fragments have different isotope ratios than the interior of the sections as would be expected if such alteration affected the carbonate portion of the apatite as well as fluorine replacement of OH^-.

Table 3. Elevated CO_2 and F in Pliocene enamel

Number of points analysed	CO_2	F	Total
MODERN			
7*	—	0.10	90.55
Blue Luminescence			
9[†]	2.12	0.31 (1)	92.42
PLIOCENE			
Dark Luminescence			
17[†]	2.57	0.25 (15)	92.53
Bright Yellow Luminescence			
20[†]	—	1.77 (20)	92.22
Moderate Green Luminescence			
7[†]	2.59	2.45 (7)	92.21
Bright Orange-yellow Luminescence			
3[†]	3.81	3.32 (3)	97.06
Undetermined Luminescence			
9*	—	0.45	90.80

* Data from Kohn *et al.*, (1999).
[†] Data from Reeser *et al.*, unpublished.

Materials and methods

Five fragments from the first group of Pliocene enamel fragments had relatively thick bright yellow zones along the outer edges of their otherwise dark thin sections. These zones were thick enough that we removed and analysed the bright zones and the dark interiors as separate samples. An additional three fragments had the same cathodoluminescence appearance along the edge as the interior of the thin section. One of these was dark throughout, the second had moderate, green luminescence throughout and the third was the bright orange-yellow section. We removed approximately 0.5 mm from the exteriors of each of these samples and compared the stable isotope data with samples taken from each fragment's interior. Finally, an additional 18 fragments were sampled by taking approximately 0.5 mm from each fragment's exterior and analysing it separately from enamel taken from the fragment's interior.

Following Koch (Koch *et al.*, 1997) and Lee-Thorp (Lee-Thorp & van der Merwe, 1987), samples were cleaned of matrix, enamel was separated from dentine and cementum using a hand-held dremel drill and small samples were removed for analysis. Samples were reduced in a Spex mill and pretreated with sodium hypochlorite (bleach) and acetic acid. Carbon dioxide was produced by hydrolysis in 100% phosphoric acid at 25 °C (see McCrea, 1950) and collected cryogenically. Some of the samples were analysed on a Finnegan MAT 251; others were analysed on a VG 602E Micromass isotope ratio mass spectrometer. Data are reported in the standard delta (δ) notation relative to the PeeDee Belemnite standard. Precision based on standard replicates is 0.1‰ δ^{13}C and δ^{18}O. Duplicates (n = 8 pairs) analysed with different mass spectrometers showed differences that ranged between 0 and 0.6‰ in δ^{13}C and 0.2 to 1‰ in δ^{18}O.

Results

The δ^{13}C values of the samples from the bright yellow zones (closed symbols in Figure 1; each symbol represents an individual enamel fragment) of the exteriors of the five, otherwise dark, enamel
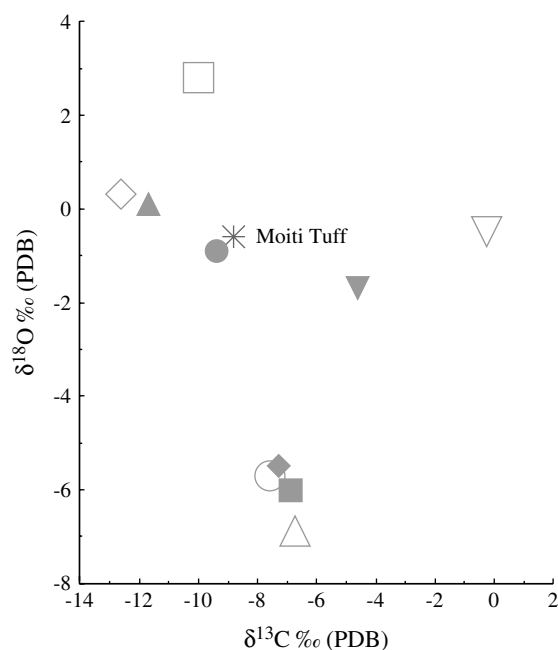

Figure 1. Analyses of carbonate from tooth enamel apatite of fauna recovered from a single excavation at the Pliocene site of Allia Bay in northern Kenya. The solid symbols refer to samples taken from the exterior of fossil fragments while the open versions of the same symbols are from the interior of the same fragment. All five fragments had bright yellow zones along the exterior of the enamel surfaces when viewed by cathodoluminescence. This colour indicates manganese replacement of calcium in the apatite lattice and uptake of silica-bearing minerals (see text for further discussion). The samples from these yellow zones have δ^{13}C and δ^{18}O values that differ from samples taken from the enamel interior although there is no correlation with the average value for soil carbonates from the capping Moiti Tuff (Cerling *et al.*, 1988).

fragments differ from the interior zones (open symbols in Figure 1) of the same fragment. The δ^{13}C value for the sediments surrounding the fossil enamel fragments is unknown as yet, and comparing the exterior enamel samples with the average δ^{13}C values of the capping Moiti Tuff (Cerling *et al.*, 1988) shows no clear pattern. Two of the samples have exterior enamel δ^{13}C values that are closer to the Moiti Tuff values than is true for the sample taken from the fragment's interior, but the other three do not. The three samples that have the same luminescence on the edges of their thin sections as in the interiors also show no pattern with respect to the Moiti Tuff. The dark fragment has a δ^{13}C value on the exterior that is closer to the value in the Moiti Tuff than is the interior. In contrast, the green and the

bright orange-yellow fragments show little to no difference in $\delta^{13}C$ values between the interior of the fragment and the exterior of the fragment. The $\delta^{18}O$ values show no pattern, whatsoever, although most of the apatite carbonate samples have values that are lower than those in the Moiti Tuff.

When all 26 of the enamel fragment $\delta^{13}C$ values are considered relative to the animal's presumed feeding strategy (based on the $\delta^{13}C$ values of the interior enamel), a pattern emerges (Table 4). All of the browsing fauna have exterior enamel that is enriched in ^{13}C relative to their interior enamel. In contrast, all of the grazing fauna, with the exception of two bovid samples, have exterior enamels that are depleted in ^{13}C relative to their interior enamels. The mixed feeders show the same pattern as the grazing fauna. As with the smaller set of eight fragments discussed above, the $\delta^{18}O$ values of the enamel carbonates show no pattern.

Discussion and conclusions

Several issues arise when considering the data presented above. First, the difference between the surface and interior of the enamel demonstrates that there has been alteration of the carbon isotope ratios during fossilization. The zones, apparent under cathodoluminescence, are reflective of elemental changes in the apatite composition; but they also appear to indicate changes in the carbonate fraction. This pattern of difference suggests that the surface of the enamels is altered in the direction of sediments that surrounded the enamel during fossilization as suggested previously (Lee-Thorp, 2000). The magnitude of the change, however, is much larger in some cases than previously recognized and it varies between fragments. Some of the fragments show a difference of greater than 2‰ between the exterior enamel and the interior of the same fragment. In two of 26 cases, the difference is 5‰ although most of the samples show differences that are on the order of 1‰. Second, the lack of pattern relative to the Moiti Tuff data suggests that at least some of the sediments responsible for the enamel alteration have $\delta^{13}C$ values that differ from the Moiti Tuff. Third, in a minority

Table 4. Enamel altered in direction of sediments

Sample	$\delta^{13}C$ interior	$\Delta^{13}C$ ext-int	$\Delta^{18}O$ ext-int
BROWSERS			
Deinotherium			
4857a	−14.7‰	+2.1	−0.7
4858a	−13.1‰	+0.1	−2.8
Giraffe			
4859b	−13.4‰	+0.6	−0.1
4860a	−14.9‰	+2.7	−0.1
†4859a	−15.2‰	+1.6	+2.0
Hippo			
*4890a	−12.6‰	+5.3	−5.8
*4891e	−10.0‰	+0.9	−3.2
Suids			
4884a	−12.9‰	+0.1	−1.3
Bovids			
4869a	−10.7‰	+0.6	−1.8
GRAZERS			
Equids			
4853a	−3.4‰	−0.8	−0.6
Elephants			
4901a	−3.6‰	−1.0	−1.0
4905a	−3.0‰	−2.1	−4.4
4892d	−3.5‰	−0.3	+0.7
4895a	−3.5‰	−0.2	+0.9
4899a	−1.5‰	−2.1	+3.1
Suids			
4883a	−1.2‰	−0.2	+0.1
*4888a	−0.2‰	−4.4	−1.2
Bovids			
4867a	−0.2‰	+1.3	−0.6
4874a	−0.7‰	+0.2	−0.8
MIXED FEEDERS			
Elephants			
4908a	−6.8	−0.3	+0.4
†4901c	−4.8	−0.7	−0.3
Hippos			
*4891d	−6.7	−5.0	+7.0
†4894a	−6.9	−0.8	+3.1
Suids			
*4879a	−7.4	−2.0	+3.0
4889a	−5.5	−1.3	+1.3
Bovids			
4865c	−6.8	−0.3	−1.9

* Fragments with bright yellow luminescent zones along the exterior of the enamel.
† Fragments lacking luminescent zones along the exterior of the enamel.

of cases the alteration is great enough to misinterpret the animal's feeding strategy. In two cases, the $\delta^{13}C$ values from the exterior of the enamel indicate a mixed feeding strategy while the interior enamel carbonate indicates a browser for one (hippo, 4890a) and a grazer for the other

(suid, 4888a). Fourth, more commonly the alteration would affect interpretation of the ecology in which the animals' lived. The browsing fauna from the Turkana Basin have lower $\delta^{13}C$ values in their enamel interiors than in the enamel exteriors. As such, the values from the enamel interiors suggest that the animals fed in regions that were more closed (i.e., forested) than would be apparent based on data from the enamel exteriors. In modern fauna a difference of 1‰ in $\delta^{13}C$ values of arboreal primates separates those feeding in closed habitats versus ones feeding in open, seasonally dry habitats (Schoeninger *et al.*, 1997, 1998). Fifth, and no less important, the variation within the sample set supports our previous interpretation that the enamels are differentially altered (Reeser *et al.*, unpublished). It is not possible to determine whether the same process has affected all portions of these fragments although solid-state processes seem the most likely explanation (Lee-Thorp, 2000). If this is the case, it appears that the process has occurred to a greater extent in some fragments than in others. This, in turn, suggests that the surfaces have been exposed for a longer period. The two bovid samples, which have enamel exterior $\delta^{13}C$ values more positive than their interior values, hint that there may be another process or another altering sediment that has affected some of the samples within this single excavation. In any case, all fragments cannot be treated in the same manner in order to eliminate diagenetic effects. Within single fossil sites, each sample must be treated independently and evaluated independently.

The majority of fragments, however, retain what appear to be biogenic $\delta^{13}C$ values in the enamel interiors. Within this sample set, removal of 0.5 mm of enamel exterior succeeded in producing samples where the animal's feeding strategy was clear in most cases. Questions still remain concerning some of the mixed feeders where the luminescence pattern indicates alteration. In these cases, the exterior enamel was identical to the interior but it is not possible to establish whether the mixed feeding signal reflects the true feeding strategy of the animal during life or whether it is the result of alteration in the direction of sediment $\delta^{13}C$ values.

The results overall suggest that application of screening methods like cathodoluminescence will, for many fossil sites, identify samples that are appropriate for palaeodiet and palaeoecological reconstruction. It appears less likely that the $\delta^{18}O$ values carbonate fraction of enamel apatite will be useful for palaeotemperature reconstructions as part of a palaeoclimate reconstruction.

Acknowledgements

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