



Preservation assessment of Miocene–Pliocene tooth enamel from Tugen Hills (Kenyan Rift Valley) through FTIR, chemical and stable-isotope analyses

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ABSTRACT

We investigated fossil tooth enamel of mammals and crocodiles from two Mio-Pliocene East-African formations (Lukeino and Mabaget Fms) using infrared spectroscopy and chemical and stable-isotope analyses. Infrared spectra indicate that the fossil enamel contains biological apatite (bioapatite), without significant secondary carbonate contaminations. Several empirical infrared indexes were used to analyze the crystal–chemical characteristics of enamel. Fossil enamel has less organic matter, water and structural carbonate of apatite than modern enamel with which it was compared. Fossil apatite has a better crystallinity than bioapatite. The calcium/phosphorus mass ratio and the fluorine content of fossil apatite show intermediate values between bioapatite and geological fluorapatite. The samples also display significant crystal–chemical variations, depending on the vertebrate group (mammals vs. reptiles) and the taphonomic context (Lukeino Fm vs. Mabaget Fm). In spite of these changes, no relationship was observed between the chemical contents (carbonate and fluorine) and the stable-isotope ratios of carbonate ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in fossil enamel. Preservation of the palaeoenvironmental signals is strongly supported by the fact that the stable-isotope composition of the three investigated fossil mammalian taxa (deinotheres, equids and hippos) is consistent with their ecological features. For instance, typical C_3 - and C_4 -plant isotope compositions are reflected in the deinotheres and equids, respectively, and amphibious hippos display lower $\delta^{18}\text{O}$ values than terrestrial herbivores, as expected.

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1. Introduction

Biological apatite (or bioapatite) is the mineral fraction of vertebrate skeleton (bones, teeth, fish scales) and corresponds to carbonate–hydroxylapatite. During biomineralization, the stable-isotope composition of carbonate and phosphate ions records the environmental features of the vertebrates. Thus carbon and oxygen isotope ratios can provide information on the composition of the diet consumed by organisms (DeNiro and Epstein, 1978; Krueger and Sullivan, 1984; Lee-Thorp et al., 1989; Ambrose and Norr, 1993; Tieszen and Fagre, 1993; Cerling and Harris, 1999; Passey et al., 2005) and, also, on the climatic conditions which prevail in the environments (Longinelli, 1984; Fricke et al., 1998; Kohn and Cerling, 2002; Levin et al., 2006). These properties are widely

used to reconstruct terrestrial palaeoenvironments during Mesozoic (i.e. Amiot et al., 2004; Botha et al., 2005; Tütken et al., 2007) and Cenozoic times (i.e. Morgan et al., 1994; Cerling et al., 1997; Kingston and Harrison, 2007; Ségalen and Lee-Thorp, 2009).

Bioapatite shows a great chemical variability due to the tolerance of the crystal structure (LeGeros, 1981; Skinner, 2005). For enamel bioapatite, an empirical formula has been proposed (Elliot, 2002): $[\text{Ca}_{8.86} \text{Na}_{0.29} \text{Mg}_{0.09} \text{K}_{0.01}] [(\text{PO}_4)_{5.31} (\text{CO}_3)_{0.41} (\text{HPO}_4)_{0.28}] [(\text{OH})_{0.70} \text{Cl}_{0.08} (\text{CO}_3)_{0.05}]$. The Ca site, called also the Z-site, usually incorporates other alkaline-earth (e.g. Mg, Ba, Sr), alkaline (e.g. Na, K) and transition cations (Fe, Mn, Zn) in minor or trace amounts. The B-site corresponds to the P tetrahedral site in which this element occurs as PO_4 (c.a. 95%) and as HPO_4 (c.a. 5%). The A-site mostly contains hydroxyls but can incorporate halides (e.g. Cl, F) and molecular water. Moreover CO_3 occur both in the B- (85–90%) and A- (10–15%) sites (Eanes, 1979; LeGeros, 1981; LeGeros and LeGeros, 1984; Michel et al., 1995; Elliot, 2002; Skinner, 2005).

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Table 1

Description of the FTIR spectrum of bioapatite (LeGeros, 1991; Michel et al., 1995; Sponheimer and Lee-Thorp, 1999a; Trueman et al., 2008).

Approximate positions of apparent bands (cm ⁻¹)	Approximate positions of decomposed bands (cm ⁻¹)	Chemical groups	Location of chemical groups	Chemical bonds and Vibrational modes
dome between 2400 and 3800	3570	Hydroxyl (OH)	A-site of apatite	O–H Stretching
	between 3300 and 3430 (two bands at least)	Water (H ₂ O)	Adsorbed on apatite surface and A-site of apatite	O–H Stretching ν_1 and ν_3
1650	between 1660 and 1670	Amide (CO–NH)	Organic matrix	C=O Stretching ν_1
	between 1620 and 1640	Water (H ₂ O)	Adsorbed on apatite surface and A-site of apatite?	O–H Bending ν_2
1545	1545	Carbonate (CO ₃)	A-site of apatite	C–O Stretching ν_3
1450	1500	Carbonate (CO ₃)	<i>not determined</i>	C–O Stretching ν_3
	1470	Carbonate (CO ₃)	B-site of apatite and adsorbed on apatite surface?	C–O Stretching ν_3
	1450	Carbonate (CO ₃)	A-site of apatite and adsorbed on apatite surface?	C–O Stretching ν_3
1415	1415	Carbonate (CO ₃)	B-site of apatite	C–O Stretching ν_3
1090	1090	Phosphate (PO ₄)	B-site of apatite	P–O Stretching ν_3
1040	1040	Phosphate (PO ₄)	B-site of apatite	P–O Stretching ν_3
960	960	Phosphate (PO ₄)	B-site of apatite	P–O Stretching ν_1
880	880	Carbonate (CO ₃)	A-site of apatite	C–O Bending ν_2
875	875	Carbonate (CO ₃)	B-site of apatite	C–O Bending ν_2
		Hydrogenophosphate? (HPO ₄)	B-site of apatite	P–O Stretching ν_3
	865	Carbonate (CO ₃)	<i>not determined</i>	C–O Bending ν_2
605	630	Hydroxyl (OH)	A-site of apatite	O–H Bending
	605	Phosphate (PO ₄)	B-site of apatite	P–O Bending ν_4
565	575	Phosphate (PO ₄)	B-site of apatite	P–O Bending ν_4
	565	Phosphate (PO ₄)	B-site of apatite	P–O Bending ν_4
470	470	Phosphate (PO ₄)	B-site of apatite	P–O Bending ν_2

During fossilization, several mechanisms can affect the mineralogical and crystal–chemical composition of vertebrate skeletal tissues: the decay of the organic matrix, the dehydration, the recrystallization of bioapatite with a loss of original elements (e.g. structural carbonates) and with an ab-/ad-sorption of exogenous elements (e.g. fluorine, rare earth elements, uranium), and the precipitation of secondary minerals (e.g. calcite, Fe–Mn–Ba oxyhydroxides) (Person et al., 1995; Michel et al., 1996; Millard and Hedges, 1996; Kohn et al., 1999; Reynard et al., 1999; Schoeninger et al., 2003a; Passey et al., 2007; Ségalen et al., 2008). Moreover enamel is regarded as being more chemically resistant to diagenesis than bone and dentine (Wang and Cerling, 1994; Kohn et al., 1999; Zazzo et al., 2004; Pasteris and Ding, 2009) because enamel has a low porosity (causing less secondary contaminations potentially) and a low solubility of apatite (due to its low structural CO₃ content and high crystallinity) (LeGeros, 1981).

Table 2

Description of the FTIR indexes of bioapatite. The letters “B”, “V” and “AV” mean the height of the bands, the valleys and the “above-valley”, respectively (see the measure of the “above-valley” in Rey et al., 1990 or Michel et al., 1996). Numbers in parenthesis represent the approximate positions of the apparent bands.

Indexes	Formulas	References
PCI (Phosphate Crystallinity Index) other names: Cl _{IR} (Crystallinity Index _{InfraRed}) IRSF (InfraRed Splitting Factor)	$\frac{B(605)+B(565)}{V(590)}$	Sponheimer and Lee-Thorp, 1999a Shemesh, 1990 Weiner and Bar-Yosef, 1990 Rey et al., 1990
PO ₄ RF (PO ₄ Resolution Factor)	$\frac{AV(590)}{AV(590)+V(590)}$	Rey et al., 1990
BPI (B-carbonate on Phosphate Index)	$\frac{B(1415)}{B(605)}$	LeGeros, 1991
API (A-carbonate on Phosphate Index)	$\frac{B(1545)}{B(605)}$	Sponheimer and Lee-Thorp, 1999a
CO ₃ /PO ₄ index	$\frac{B(1450)+B(1415)}{B(605)+B(565)}$	Pucéat et al., 2004
WAMPI (Water–AMide on Phosphate Index)	$\frac{B(1650)}{B(605)}$	this study

In this study, we firstly compare crystal–chemical characteristics of the tooth enamel between modern and fossil mammals and crocodiles, using infrared spectroscopy and elementary analyses. Next, we check the potential influence of chemical modifications on the stable-isotope composition of carbonate in the fossil apatite. Lastly, we assess the ecological consistency of the isotopic values of the three fossil mammalian groups.

2. Material

The studied material consists of 21 modern teeth (20 mammals and one crocodile) and 62 fossil teeth (57 mammals and 5 crocodiles). Modern mammalian teeth belong to bovines, camelids and suids and come from Africa (Kenya, Mauritania, Namibia, Uganda) and Europe (French Pyrenees). Modern crocodilian tooth originates from India. Fossil mammalian teeth belong to several ungulate taxa (equids, hippos, proboscideans, rhinos, ruminants and suids), coming from the Tugen Hills in the Kenyan Rift Valley. They were collected in Mio-Pliocene hominid-bearing deposits (Senut et al., 2001; Pickford and Senut, 2001; Pickford et al., 2004) within the Lukeino Formation (20 mammals and 5 crocodiles) and the Mabaget Formation (37 mammals). These two formations are dated to 6.2–5.7 Ma (Lukeino Fm: Sawada et al., 2002) and to 5.3–4.3 Ma (Mabaget Fm: Pickford et al., 1983; Deino et al., 2002). The sedimentary context is fluvio-lacustrine and exposed to a volcanic activity (Pickford, 1974).

3. Methods

Enamel powder was obtained with a rotary drill equipped with a diamond-tipped burr. After cleaning its surface, enamel was collected by abrading powder from the upper occlusal surface to the enamel-dentine junction at the base of the crown. This ensured that samples cover several months or years of biomineralization.

For the infrared analysis, 2–3 mg of enamel powder and 300 mg of potassium bromide (KBr) were mixed, by using an agate mortar and

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