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Probing atomic scale transformation of fossil dental enamel using Fourier transform infrared and nuclear magnetic resonance spectroscopy: A case study from the Tugen Hills (Rift Gregory, Kenya)[☆]

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ABSTRACT

A series of fossil tooth enamel samples was investigated by Fourier transform infrared (FTIR) spectroscopy, ¹³C and ¹⁹F magic-angle spinning nuclear magnetic resonance (MAS NMR) and scanning electron microscopy (SEM). Tooth remains were collected in Mio-Pliocene deposits of the Tugen Hills in Kenya. Significant transformations were observed in fossil enamel as a function of increasing fluorine content (up to 2.8 wt.%). FTIR spectroscopy revealed a shift of the ν_1 PO₄ stretching band to higher frequency. The ν_2 CO₃ vibrational band showed a decrease in the intensity of the primary B-type carbonate signal, which was replaced by a specific band at 864 cm⁻¹. This last band was ascribed to a specific carbonate environment in which the carbonate group is closely associated to a fluoride ion. The occurrence of this carbonate defect was consistently attested by the observation of two different fluoride signals in the ¹⁹F NMR spectra. One main signal, at ~-100 ppm, is related to structural F ions in the apatite channel and the other, at -88 ppm, corresponds to the composite defect. These spectroscopic observations can be understood as resulting from the mixture of two phases: biogenic hydroxylapatite (bioapatite) and secondary fluorapatite. SEM observations of the most altered sample confirmed the extensive replacement of the bioapatite by fluorapatite, resulting from the dissolution of the primary bioapatite followed by the precipitation of carbonate-fluorapatite. The ν_2 CO₃ IR bands can be efficiently used to monitor the extent of this type of bioapatite transformation during fossilization.

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1. Introduction

The main component of bones and teeth is carbonate-hydroxylapatite. Its stable isotope composition records a combination of environmental parameters and biological processes and fossil samples can yield important information on paleoenvironmental conditions. Of particular interest is the isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of carbonate groups occurring in the apatite structure as it provides information on terrestrial paleoenvironments and dietary preference of vertebrates [1]. For example, it has helped elucidate issues as diverse as dinosaur thermoregulation [2–5], mammals' paleoecology [6,7], topographic uplift [8] and the demise of Norse

colonies in Greenland [9,10]. Over the last 20 years, stable isotope analyses of tooth enamel carbonate of fossil herbivorous mammals have also proved useful for exploring African Neogene environments [11–15].

A fundamental difficulty in using the carbonate isotopic composition of fossil vertebrate remains lies in its potential modification related to the diagenesis of bioapatite during the fossilization. This difficulty is partly circumvented by selecting the enamel part of fossil teeth. Compared with bone or dentine, enamel mostly displays large (tens of nanometers wide and thick, and up to hundreds of nanometers long) apatite crystals [1,16,17], low porosity and low organic matter content. It is thus expected to be more resistant to post-mortem alteration (e.g. Refs. [18,19]). The extent of post-mortem alteration can be assessed using a number of “crystallinity” parameters obtained from vibrational spectroscopy [20–23] or X-ray diffraction measurements [24]. Depending on the technique used, these parameters reflect changes in the local or long-

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range order of the crystal structure and/or in the size and shape of apatite particles. It is also possible to assess the modification of carbonate concentration by comparing modern and fossil samples. Previous studies have reported gains [18] or moderate losses [25] of carbonate, depending on the geochemical parameters of the fossilization environment. A peculiarity of carbonate incorporation in apatite structure stems from the various substitution mechanisms potentially involved [26–28]. Carbonate groups can indeed substitute for phosphate groups (B-type) or for OH groups in the structural channels (A-type), and both types coexist in biological apatite. The speciation of carbonate groups in fossil apatite could thus be used as a sensitive tracer of alteration.

This work is a case study investigating the relations between the modifications of the carbonate speciation and the structural transformations of the primary biological material in a series of fossil enamel samples. The samples come from the Rift Gregory (Kenya) and are representative of the series whose carbon and oxygen isotopic compositions have been previously used by researchers [25,29] for throwing light on the environmental context of the earliest Kenyan hominids.

2. Sample description and methods

The fossil material consists of five tooth enamel samples of large herbivorous mammals. The latter are distributed among four families: deinotheres (specimen D1), elephantids (A1), hippopotamids (H7, H12) and rhinocerotids (R1). Fossil teeth were collected in the Lukeino Formation (Late Miocene, 6.1–5.7 Ma) and the Mabaget Formation (Early Pliocene, 5.3–4.5 Ma) [30]. The deposits are located at the foot of the Tugen Hills in the Kenyan Rift Valley, where the remains of early hominids, including *Orrorin tugenensis*, have been found [31]. To provide comparative data, an enamel sample of a modern camelid (specimen T1) from Mauritania was also analyzed. A previously investigated [32,33] carbonate-fluorapatite sample (francolite) from the Taiba phosphate deposit (Senegal) was also used as a reference sample. Calcium, fluorine and phosphorus concentration of the samples are reported in Table 1.

For Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopic measurements, the enamel powder was obtained using the approach described in Roche et al. [25]. Pellets for FTIR measurements were obtained by pressing a mixture of ~1.0 mg of gently ground sample diluted in 300 mg of dried KBr. Transmission IR spectra were recorded between 400 and 4000 cm^{-1} , with a resolution of 1 cm^{-1} , using a Nicolet 7600 FTIR spectrometer. The infrared splitting factor IRSF is calculated as: $\text{IRSF} = (A_{605} + A_{565})/A_{590}$, where A_x is the measured absorbance at wavenumber x [21,22]. Detailed analysis of the $\nu_1 \text{PO}_4$ band and the $\nu_2 \text{CO}_3$ band is performed after subtraction of a baseline [34] due to the strong $\nu_3 \text{PO}_4$ band.

Single-pulse ^{13}C magic-angle spinning (MAS) experiments were performed on an Avance 300 Bruker spectrometer (7.0 T) operating at a Larmor frequency ν_L of 75.51 MHz using a 7 mm double resonance MAS probe head and a spinning frequency of the rotor of 5 kHz. Chemical shifts were referenced to TMS. Single-pulse ^{19}F

Table 1
Source and chemical composition^a of apatite samples.

Sample	Type	Locality	Ca (wt.%)	P (wt.%)	F (ppm)
Francolite	Sedimentary CO_3 -fluorapatite	Taiba, Senegal	36.8	16.9	33,000
R1	Fossil enamel Rhinocerotidae	Mabaget Fm, Kenya	38.0	17.5	28,600
H12	Fossil enamel Hippopotamidae	Lukeino Fm, Kenya	33.9	15.2	17,600
D1	Fossil enamel Deinotheriidae	Mabaget Fm, Kenya	35.6	17.4	16,300
A1	Fossil enamel Elephantidae	Lukeino Fm, Kenya	34.4	16.2	5900
H7	Fossil enamel Hippopotamidae	Mabaget Fm, Kenya	35.0	16.8	5000
T1	Modern enamel Camelidae	Mauritania	35.0	17.8	80

^a Chemical compositions taken from Refs. [25,33]. Analytical precision is ~5% based on repeated measurements of the samples.

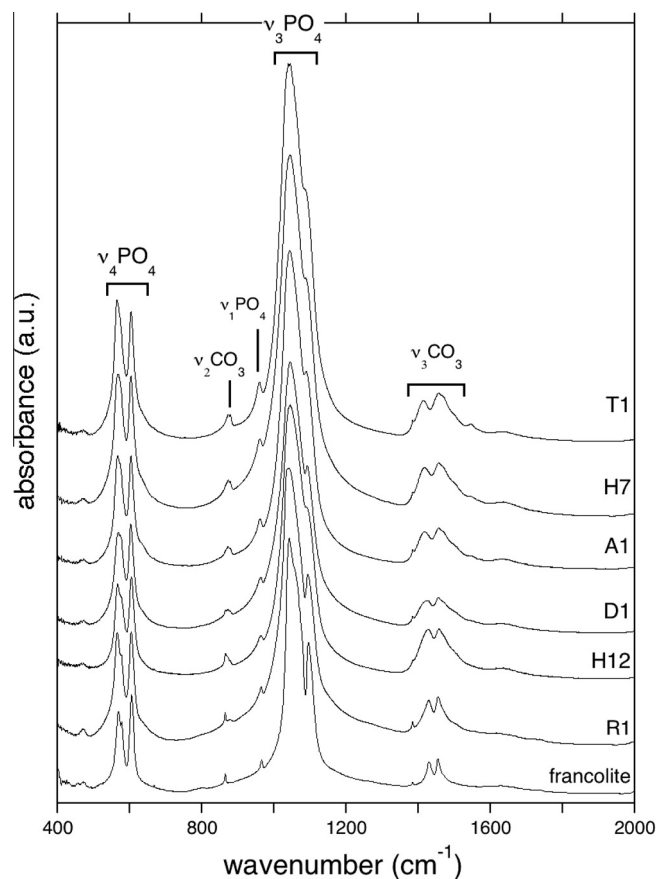


Fig. 1. Powder transmission infrared spectrum of apatite samples. The fluorine content of the samples increases from top (modern enamel sample) to bottom (francolite). The absorption bands correspond to specific vibrational modes of phosphate or carbonate groups.

Table 2
Crystallinity and chemical indices [25] and parameters obtained from infrared spectra.

Sample	API	BPI	IRSF	$\nu_1 \text{PO}_4$ FWHM (cm^{-1})	$\nu_1 \text{PO}_4$ ω (cm^{-1})
Francolite	0.07	0.31	7.2	6.2	965.6
R1	0.05	0.34	5.1	12.1	964.0
H12	0.12	0.48	4.6	14	962.4
D1	0.05	0.21	4.2	17	961.3
A1	0.11	0.30	4.4	14.3	961.0
H7	0.08	0.24	4.0	14.8	959.7
T1	0.14	0.34	4.3	14.2	959.7

MAS NMR experiments were performed on an Avance 850 Bruker spectrometer (19.9 T) operating at a Larmor frequency ν_L of 800.07 MHz using a 2.5 mm double resonance MAS probe-head and a spinning frequency of the rotor of 30 kHz.

Scanning electron microscope (SEM) observations were performed using a Zeiss Supra 55 field emission SEM operating in

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