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Véronique Michel, Philippe Ildefonse, Guillaume Morin. Assessment of archaeological bone and dentine preservation from Lazaret Cave (Middle Pleistocene) in France. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 1996, 126, pp.109-119. hal-04562819v2

HAL Id: hal-04562819

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Submitted on 3 May 2024

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**Assessment of archaeological bone and dentine preservation from Lazaret Cave
(Middle Pleistocene) in France**

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Received 19 July 1995; revision 30 October 1995; accepted 1 July 1996

Abstract

Chemical and structural changes in bones and dentine from *Cervus elaphus* jaws during fossilization were studied by chemical analysis, infrared spectroscopy (IR) and X-ray diffraction (XRD). Data were used to discuss the modifications of bones and dentine from the Lazaret prehistoric cave (Nice, France) which is an important archeologic site of Middle Pleistocene age. Fossil bones and dentine mainly consisted of hydroxy-carbonate apatite as the primary phase and of calcite as a secondary phase. Carbonation, fluorination and recrystallization processes are shown as more important in bone and dentine than in tooth enamel. A good correlation was found between the *a* cell parameter of apatite and its CO₃ and fluorine contents in the bones studied. Fluorine enrichment seems to be related to the permeability of the upper sedimentary levels. Lazaret fossil bones and dentine are less stable than enamels and their use for dating has to be taken with caution.

Keywords: bone; dentine; fossilization; Middle Pleistocene; Lazaret; X-ray diffraction; IR spectrometry; apatite

1. Introduction

Remains of many mammals as well as of eight hominids and numerous stone tools were found in the Lazaret Cave (Lumley, 1976; Valensi, 1994). In order to date with a good accuracy the archaeological levels of the Lazaret Cave (Michel, 1995), we attempted to evaluate the history of bones and enamels that were discovered. After burial, chemical and structural changes in bone and tooth can provide information on palaeoenvironmental and taphonomic conditions. For instance, the ESR and U-Th dating of bones and teeth is controlled by the degree of their preservation and to the uranium uptake (Grun and Schwarcz, 1987). It is important to choose the best conserved sample on which to apply these dating techniques. The mineral stability and the history of uptake of some elements remain uncertain. The main question arises in the choice of appropriate methods. For bones and teeth which mainly consist of hydroxy-carbonate apatite, chemical analysis, infrared spectroscopy and X-ray diffraction are most helpful. Some Lazaret enamels have already been analyzed (Michel et al., 1995) and they have been found to be well preserved considering their Pleistocene age. The aim of this paper is to characterize the chemical evolution and the crystallographic changes of fossil bones and dentine (Lazaret Cave) during fossilization.

2. Materials and methods

2.1. Material studied

Modern and fossil bones together with two fossil dentine originating from adult *Cervus elaphus* were analysed. Fossil bones consist of twelve mandibles and two tibias and were collected from the Middle Pleistocene levels of Lazaret Cave (Nice, France). Fossil samples have been distinguished according to their stratigraphic position in the deposit (Table 1). Samples were taken from mandibular compact bones and dentine from the M 3 or M2 molar crown (Fig. 1). Archaeological and modern bones were cleaned and stripped of the upper periostic layers with a dentist's drill and reduced to powder at a size < 50 µm for chemical analyses and at a size < 20 µm for X-ray diffraction in an agate mortar.

2.2. Methods

2.2.1. Chemical analysis

Ca, P, Na, Mg and Si contents were determined by XR fluorescence spectrometry (+ 0.01 wt.%) on ashed bones in a muffle furnace at 500°C for 16 h. F contents were measured by fluorine specific ion electrode (\pm 20 ppm), and the CO₃ contents (\pm 0.01 wt%) were determined by a coulometric titration of the CO₂ released from an acidified aqueous solution of the powdered samples. These chemical analyses were done at the X-Ray laboratory in Canada. The CO₃ contents were measured on unashed samples before and after dissolution of CaCO₃ in a triammonium citrate solution (pH=8.1, 0.5 M) (Silverman et al., 1952) in order to determine the total amount of CO₃, the CaCO₃ content and the CO₃ apatitic content.

2.2.2. X-ray diffraction and Rietveld analysis

Bone samples were ground at size < 20 µm and mixed with an internal standard NaF (10 wt.%). X-ray powder data were collected on an automated Siemens D501 diffractometer, equipped with a graphite monochromator and operating in a step scan mode using Cu K α radiation. X-ray data were collected between 2 θ 25 and 140° with a 0.04° 2 θ step and counting 40 s per step. Rietveld refinements were done with the XND code (Berar, 1990; Michel et al., 1995). Since X-ray diffraction patterns of bones had very broad reflections, only cell parameters and reflection profiles were refined. OH-apatite (Sudarsanan and Young, 1969) was used as the starting model and atomic positions, site occupancies and thermal parameters were fixed.

2.2.3. IR spectrometry

A standard procedure was used for sample preparation (Michel et al., 1995). KBr pellets were prepared by mixing 0.75 mg of sample (ground at size < 5µm) and 300 mg KBr, and the mixture was pressed at 11 ton.cm⁻² to get a 300mg transparent pellet. The IR spectra were recorded in transmittance mode with a Perkin-Elmer 16 FPC-FTIR spectrometer.

3. Results and discussion

3.1. Chemical data

Modern bone and most fossil bones are complex tissues mostly consisting of hydroxyapatite which is dispersed in an organic collagen matrix. Chemical compositions are known to vary considerably with the type of bone, the age of the fossil and the palaeoenvironmental conditions. During fossilization, bones lose most of their organic matter. In order to compare chemical composition data, samples

were heated at a temperature that deleted all organic matter before chemical analysis. Weight losses between room temperature and 940°C for modern bone and fossil bone F268 are presented in Fig. 2. They may be related to the differences in the organic/inorganic ratio of the modern and fossil bones. At a temperature below 200°C, weight losses are mainly due to adsorbed H₂O (LeGeros, 1981). Between 200°C and 500°C, the organic matter is destroyed. The amount of organic matter in fossil bones (some wt.%) is smaller than that in the modern bone studied (~20 wt.%) as usually found. At 300°C, weight losses related to CO₃²⁻ begin (Legros, 1984), and therefore, the CO₃ contents were measured on unashed bones. Chemical compositions of samples studied are reported in Table 1. Weight losses at 500°C were measured and are designed as WL. WL for modern bone (32.6 wt.%) is around three times higher than those in fossil bones (8-12.3 wt.%). This difference is mainly due to a higher organic matter content as yet discussed in Fig. 2. Major changes during fossilization of red deer bones in Lazaret Cave consist of an increase of Ca, CO₃, F and a decrease of P, Na and Mg (Table 1). The increase of Ca in fossil bones is mainly due to the presence of calcium carbonates in the porosity of bones as evidenced by microscopic examinations and XRD data (see below). Calcite precipitated in the porous spaces or Haversian canals and in the post-depositional cracks (Michel, 1995). The apatitic CO₃ contents (CO₃Ap, Table 1) are higher for the five fossil bones analyzed (6.16-7.11 wt.%) than that in the modern bone (4.03 wt.%). Even if organic matter is considered, this difference denotes a carbonation particularly important during fossilization. Since the Ca content decreases and the P content increases during fossilization, the molar Ca/P ratios in fossil bones (1.91-2.17) are always higher than that in the modern value (1.57) and that in stoichiometric apatite (1.67). Increase of the Ca/P ratios together with the increase of CO₃Ap in fossil bones have been related to a carbonate for phosphate substitution at the B-site (Pate et al., 1991). Fluorine determination provides interesting information about geochemical conditions since it depends on the groundwater chemical composition, the circulating water rate and the enclosing sediment permeability (Toots and Parker, 1979). All fossil samples analyzed have a fluorine content higher than 0.30 wt.%, but the oldest L80 bone which contains nearly as little fluorine (0.035 wt.%) as a modern bone (0.04 wt.%). A good correlation was found between the fluorine contents of teeth enamels and bones originating from the same mandibles (Fig. 3). The fluorine content of enamel is 10 times lower than that of the bones. This difference is due to the more porous structure of bone and dentine than that of enamel, as already reported (Parker et al., 1973; Matsu'ura, 1982). Besides, Parker and Toots (1970) suggested that fluorine substitutes for OH⁻ at the A-site in the apatite structure. Fluorine content of Lazaret bones and enamels decreases with increased depth of burial (Table 1). Here, fluorine dating did not yield chronological but geochemical information. Our fluorine data suggest that, in the Lazaret Cave, the upper deposits (clayey gravel) are more permeable than the bottom deposits where the groundwater would stagnate. However, the fluorine dating method has been used with some success for many prehistoric hominid sites from Pliocene and Lower Pleistocene. When the fluorine content of fossil bones was high enough, and if the distribution profile relating to depth of burial was accurate, fluorine dating can be used (Matsu'ura, 1982).

3.2. IR data

IR spectra of modern and fossil bones, dentine and enamels are presented in Fig. 4. They have the same characteristic bands as the IR spectra of apatites containing CO₂⁻ at both the A- and B-sites (Bonel, 1972) and of modern human enamel (Holcomb and Young, 1980; Elliott et al., 1985). Details of the assignment and position of the PO₄⁻ and CO₂⁻ IR bands were done in a previous paper (Michel et al., 1995). The IR absorption bands associated with CO₂⁻ in calcite is also presented for

comparison (top spectrum, calcite originating from the E stalagmitic flowstone at Lazaret Cave) (Fig. 4). A preferential carbonation at the apatitic A-site or B-site is difficult to demonstrate by IR spectroscopy when the bone is a mixture of hydroxy carbonate apatite and calcite. The IR bands of calcite at 1415 and 872 cm^{-1} (Nelson and Featherstone, 1982) occur at the same position as the bands of the carbonated apatite which is characteristic of the enamel samples (Fig. 4) and was identified in an earlier study (Michel et al., 1995).

Besides, the IR spectra for modern and fossil samples yield H₂O and OH bands. Fossil samples have lost most of their organic matter and as a consequence contain less adsorbed (3430 cm^{-1} and 1650 cm^{-1} bands) and structural H₂O (3330 cm^{-1} band) (Holcomb and Young, 1980) than modern samples (Fig. 4). The absorption band situated at 1480-1470 cm^{-1} was also attributed to organic matter (Legros, 1984) and it decreases clearly for fossils (Fig. 4). A "crystallinity index" for apatite was measured from the ν_4 PO₄ bands in the 480-780 cm^{-1} range according to Rey et al. (1990) and was designed as PO₄RF resolution factor (Fig. 5, Table 2). PO₄RF values for modern bone and dentine (0.38 and 0.36, respectively) are lower than the PO₄RF for fossil bones and dentine (0.38-0.47 and 0.41-0.43, respectively). Besides, these PO₄RF are lower than those found in modern and Lazaret fossil enamels (0.53-0.54) (Table 2).

3.3. XRD data XRD powder patterns of modern bone, two fossil bones and a fossil enamel are presented in Fig. 6. The hkl diffraction lines of apatite are indexed in the enamel spectrum. XRD powder patterns of modern and fossil bones mainly differ by an increasing broadening of diffraction lines of modern bone. Calcite is also evidenced in fossil bone E1353. The derived calcite/apatite ratios and the refined cell parameters from Rietveld analysis are reported in Table 3 for all samples studied. Calcite was not detected in modern and fossil F268 bones by XRD. Besides, selective dissolution experiments by triammonium citrate give 0.97 and 2.66 wt.% of CO₃ for modern and F268 bone, respectively (Table 1). These data imply that during the selective dissolution, another phase than calcite was dissolved. Amorphous calcium phosphate is a possible candidate for this source of soluble CO₃ (LeGeros et al., 1973; LeGeros, 1981). The presence of CaO in ashed bones has been associated with either the presence of calcite or CO₃-bearing apatite when apatite originally contained more than 5 wt.% (LeGeros, 1981). In ashed modern and F268 bones, CaO was evidenced during the calcination procedure (Fig. 7A:h, B:h). The CaO content is higher in F268 bone than that in modern one since their CO₃A p are 6.03 and 4.08 wt.%, respectively. During calcination, above 700°C, the apatite crystallinity increases significantly for both fossil and modern bones (Fig. 7) as early reported (Shipman et al., 1984).

3.3.1. Hydroxy-carbonate apatite The refined a and c cell parameters of apatite for all bones studied are respectively lower (9.3750 < a < 6.8938 Å) (Table 3) than for OHAp (9.424 and 6.879 Å, Sudarsanan and Young, 1969) and for enamels (9.4410 < a < 9.4468 Å; 6.8861 < c < 6.8887 Å; Michel et al., 1995). There is a correlation between the decrease of a, the increase of c and the increasing CO₃Ap content (Fig. 8A). This behavior can be related to the increasing CO₂- content at the B-site as demonstrated by both IR and Rietveld refinements of fossil enamels (Michel et al., 1995). Besides, in fossil bones from Lazaret Cave, the decrease of a cell parameter is correlated to an increase of the fluorine contents (Fig. 8B). This suggests that F⁻ ions replace OH⁻ ions in the apatite structure. Comparison of the XRD peak width of fossil bones and of the modern bone gives information on crystallinity changes (Fig. 6). A clear distinction between the modern and archaeological bone patterns is revealed and this has already been detected for Holocene bones (Schoeninger et al., 1989; Tuross et al., 1989; Pate et al., 1991). Line profile analysis was done by using Voigt function which allows to deconvolute the strain and the size broadening contributions (Howard and Preston, 1989). Integral breadth of the Lorentzian function, W₁, is related

to mean coherent domain size and integral breadth of the Gaussian function, W_g , is due to structural disorder. For bones with broad diffraction lines, isotropic functions were used as no MCD shape anisotropy was observed in well crystallized enamels (Michel et al., 1995). Derived mean coherent domain sizes, by using the Scherrer formula, range from 138 Å in modern bone to 203 Å in fossil bones (Table 3). These values are significantly lower than the MCD sizes in Lazaret enamels (around 500 Å) (Michel et al., 1995). Refined W_g value is higher for the modern bone (1.92) than those for fossil bones (0.98-1.26) which are nevertheless high in comparison to the W_g values for Lazaret enamels (0.48-0.60) (Michel et al., 1995). Such high structural disorder together with small MCD sizes for bones could be related to the non-stoichiometric composition of the apatite like-mineral found in bones (Montel et al., 1981; Glimcher et al., 1981).

4. Conclusion During fossilization, the Lazaret bones and dentine have suffered more important chemical and structural changes than enamels (Michel et al., 1995). The modern and fossil bones and dentine calcified tissues have a high reactive surface area and therefore interactions with the hydrologic and sedimentary environments were significant. Calcite precipitates in the porous structure of the bones (Pate and Hutton, 1988), particularly as a consequence of bacterial and fungal processes (Baud, 1986; Boquet et al., 1973). As for enamels, the apatite-like component is carbonated but at a higher level for bones and dentine. Both substituted F at the A-site and CO₃ at the B-site lead to a decrease of the *a* cell parameter. The fluorination rate has been related to permeability of the surrounding sediments rather than to the age of the samples studied. Both XRD powder patterns and IR spectra show an important recrystallization of the apatitic component after burial. Recrystallization of apatite and precipitation of calcite were catalysed by losses of the organic matter and by the karstic environment of Lazaret Cave. Nevertheless, because of the non stoichiometry of their apatite-like component, both fossil bones and dentine are poorly crystallized in comparison to enamels. Substituted CO₃ is known to increase the solubility of apatites while incorporation of fluorine increases their crystallinity (Sillen and LeGeros, 1991). For bones and dentine, there is not a real correlation between the fluorine content and the crystallinity since fossil bone L80 contains as little F as the modern one. Other processes would control the crystallinity and order/disorder in calcified tissues. Since bones and dentine experienced significant changes during fossilization and are not stable through time, dating interpretations, taphonomic and palaeodiet analyses have to be carefully conducted when studying archaeological bone.

Acknowledgements

Authors are indebted to Dr. J.-D. Vigne and Professor H. de Lumley for supplying the modern red deer mandible and the fossil *Cervus elaphus* mandibles respectively. Authors would like to thank Dr F. Fröhlich for the help in the IR and XRD acquisitions. This paper benefited of thoughtful review comments of Y. Nathan and S. Deganelo. This study has been supported by IGP/1452 (Ph.I.).

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Table 1
Stratigraphic position and chemical composition of fossil red deer bones and dentine, and modern red deer bone

Sample ^a	Z	WL	*Samples are ashed before analysis							Natural samples		
			Ca	P	N ^a	Mg	Si	Ca/P	F	Total CO ₃	CO ₃ (s) ^d	CO ₃ Ap ^d
modern bone	-	32.6	35.3	17.4	0.55	0.61	0.01	1.57	0.040	5.05	0.97	4.08
E5 bone	-224	12.3	38.2	15.4	0.24	0.25	0.44	1.92	-	9.49	2.38	7.11
E565 bone	-265	9.9	39.7	15.5	0.19	0.21	0.17	1.98	1.200	9.35	-	-
F41 bone	-283	10.2	40.6	15.1	0.21	0.22	0.78	2.08	1.170	12.53	-	-
E1061 bone	-287	101	40.2	14.6	0.12	0.25	0.28	2.13	1.040	12.68	-	-
E1060 bone	-287.5	10.9	40.5	15.2	0.17	0.35	0.47	2.06	1.160	10.04	-	-
E1334 bone	-317	9.6	39.6	15.2	0.38	0.24	0.21	2.01	0.794	9.80	-	-
E1334 dentine	-317	9.6	39.8	16.4	0.26	0.19	0.05	1.87	-	-	-	-
E1353 bone	-317.5	8.0	41.2	15.3	0.20	0.25	0.03	2.08	0.600	10.81	4.33	6.48
F72 bone	-362	11.1	40.7	14.5	0.11	0.22	0.45	2.17	0.728	10.40	3.29	7.11
F268 bone ^b	-367	8.0	40.4	16.2	0.18	0.21	0.12	1.92	0.714	8.69	2.66	6.03
L18 bone	-435	10.0	40.2	14.8	0.21	0.23	0.86	2.10	0.574	10.99	-	-
L23 bone	-435	9.9	39.0	15.8	0.21	0.26	0.51	1.91	0.349	10.04	-	-
F4607 bone ^b	-525	8.1	39.7	16.5	0.30	0.24	<0.01	1.87	-	9.86	3.70	6.16
L82 bone	-630	8.5	39.2	16.4	0.33	0.31	<0.01	1.85	-	-	-	-
L80 bone	-660	8.3	38.7	15.7	0.13	0.29	<0.01	1.91	0.035	9.94	-	-
L80 dentine	-660	-	-	-	-	-	-	-	-	9.90	4.45	5.45

^aThe stratigraphic reference plane (Z=0 cm) corresponds to +28.63 m above sea level. The excavated area is indicated as E= fouille entrée; F= fouille centre; L=: Locus.

^bTibia.

^cin a muffle furnace at 500°C for 16 h. WL are the weigh losses upon heating at 500°C, 16 h (±0.1 wt.%). Ca, P, Na, Mg, Si are determined by XR fluorescence spectrometry (±0.01 wt.%); F is analyzed by fluorine specific ion electrode (±0.002 wt. %); the total amount of CO₃ is determined on the unashed sample, by coulometry (±0.01 wt.%); Ca/P are calculated molar ratios.

^dThe apatitic carbonate content (CO₃Ap) is determined by coulometry after dissolution of CO_{3(s)} in a triammonium citrate solution (Silverman et al., 1952) and with the total amount of CO₃.

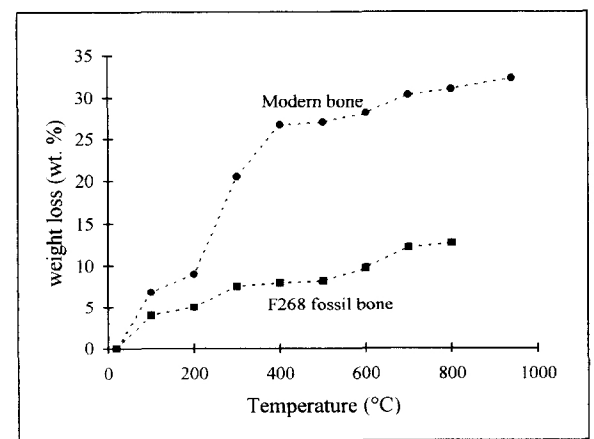
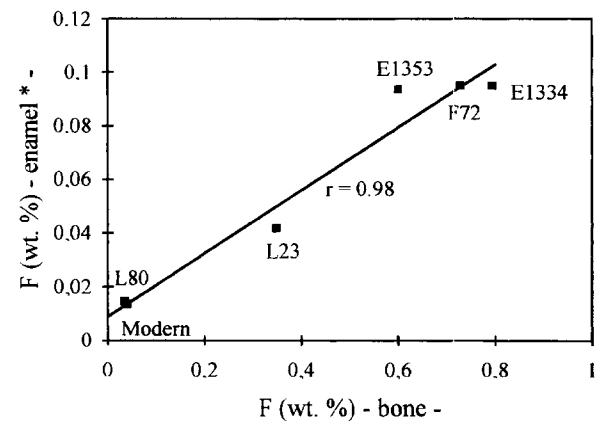


Fig. 2. Weight losses during calcination (in a muffle furnace, at T for 1 hour) of fossil (square) and modern (circle) bones of red deer.



* Michel et al. (1995).

Fig. 3. Comparison of fluorine contents for modern and fossil bones and enamels from red deer mandibles. Bones contain about 10 times more fluorine than enamel.

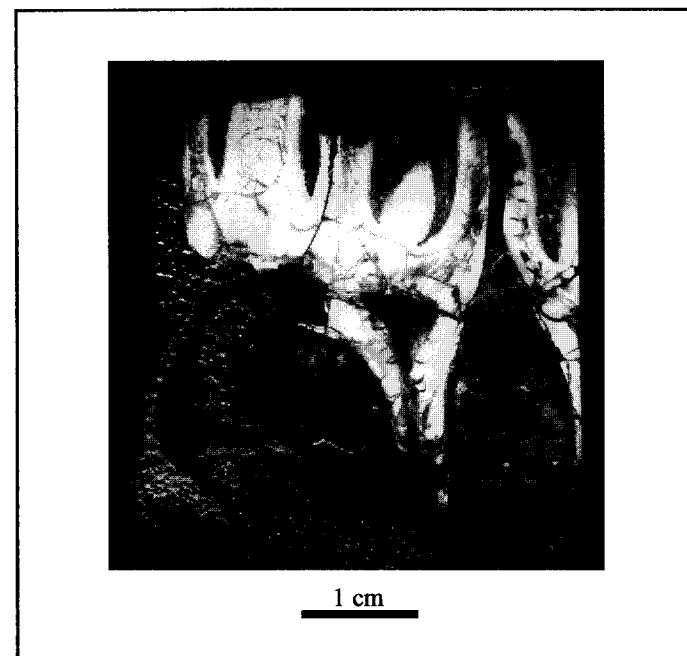
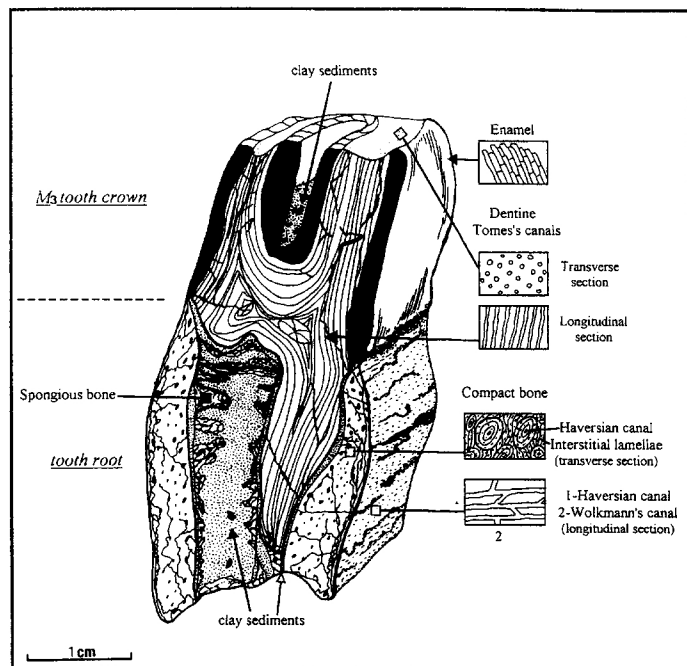
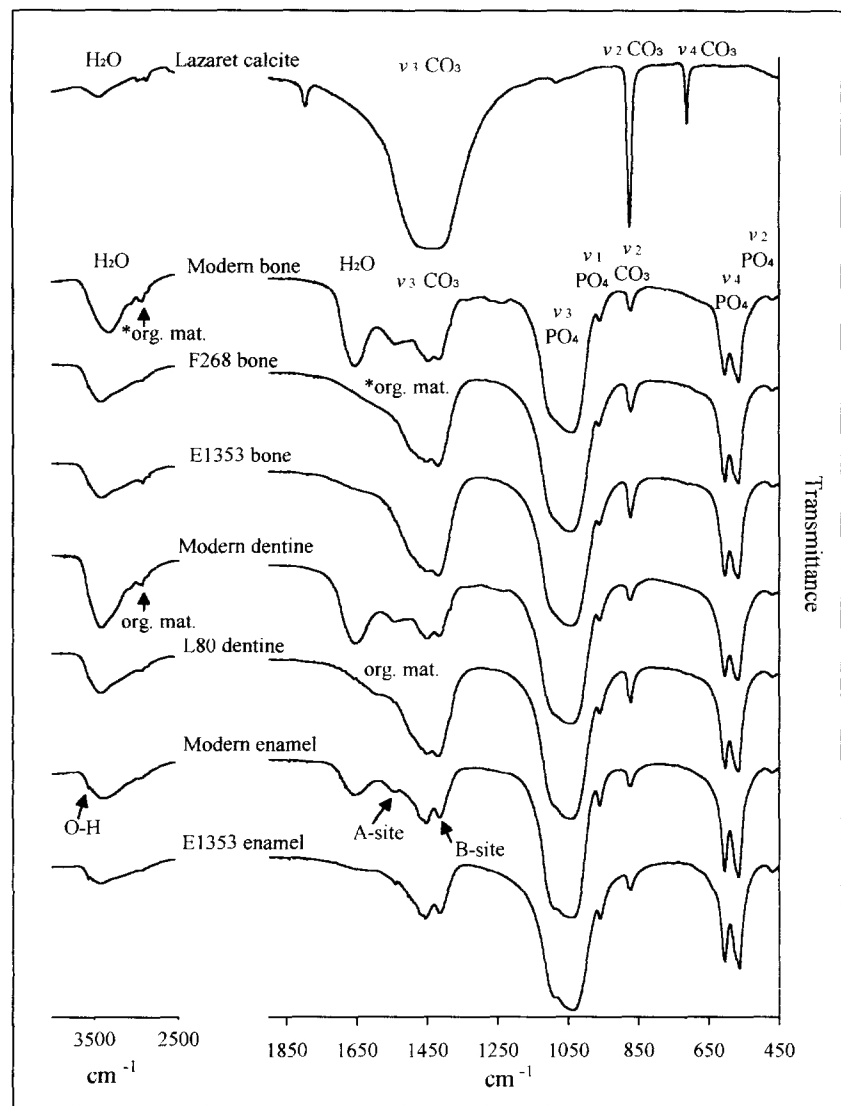


Fig. 1. Section of a fossil *Cervus elaphus* mandibular M₃ molar from Lazaret cave.

A. Longitudinal section: sample was embedded

in an acrylic resin under vacuum. B. Transverse section.



* absorption bands due to organic matter.

Fig. 4. Infrared spectra of the E Lazaret stalagmitic flowstone (calcite), modern and fossil red deer bones, enamels and dentine (F268 is tibia, E1353 and L80 are mandibles from Lazaret cave).

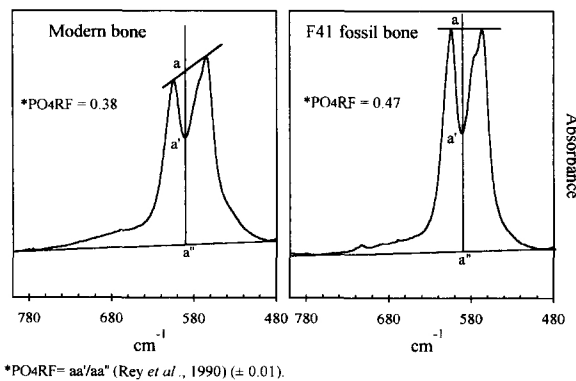


Fig. 5. Determination of the PO_4RF resolution factors for modern and F41 fossil red deer bones from the $\nu_4 \text{PO}_4$ IR bands.

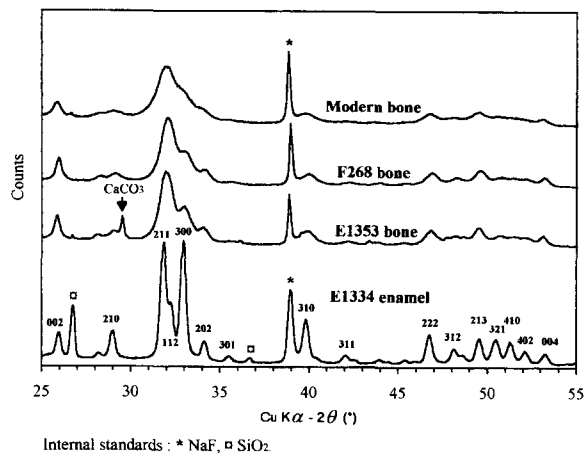


Fig. 6. X-ray powder diffraction patterns for modern red deer bone, fossil bones (E1353 and F268) and fossil enamel (E1334).

Table 3
Rietveld refinement data of the XRD powder diffraction patterns for the fossil bones from Lazaret Cave and the modern bone

Sample	Apatite (space group $\text{P6}_3/\text{m}$)				
	a	c	Wg	MCD	Calc./Ap.
Modern	9.4091	6.8892	1.92	138	–
E565	9.3750	6.8919	0.99	203	0.05
F41	9.3828	6.8923	1.02	197	0.17
E1061	9.3830	6.8925	1.00	183	0.17
E1060	9.3880	6.8916	1.03	190	0.08
E1334	9.3896	6.8929	1.08	186	0.05
E1353	9.3937	6.8938	1.03	189	0.11
F72	9.3923	6.8933	0.96	189	0.09
F268	9.4033	6.8897	1.26	183	–
L18	9.3942	6.8932	0.98	183	0.07
L23	9.3970	6.8926	0.99	193	0.07
L80	9.4073	6.8891	0.99	191	0.15

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For our samples, precision is $\pm 0.0003 \text{ \AA}$ for cell parameters (a and c).

Wg = integral breath ($A_{2\theta}$ at $0^\circ 2\theta$) of the Gaussian function.
MCD = mean coherent domain (\AA) calculated from the integral breath of the Lorentzian function.

Calc./Ap. = derived calcite/apatite ratio.

Table 2
Cristallinity index of the modern and Lazaret fossil bones, dentine and enamels determined by the measurement of the resolution factor PO_4RF ($\nu_4 \text{PO}_4$ IR band) bone dentine enamel

Sample	Z depth (cm)	Bone	Dentine	Enamel
Modern	–	0.38	0.36	0.54
E565	–265	0.44	–	–
F41	–283	0.47	–	–
E1061	–287	0.45	–	–
E1060	–287.5	0.44	–	–
E1334	–317	0.38	–	0.53
E1353	–317.5	0.39	–	0.53
F72	–362	0.45	0.43	0.53
F268	–367	0.40	–	–
L18	–435	0.44	–	–
L23	–435	0.40	–	0.54
L80	–660	0.43	0.41	0.53

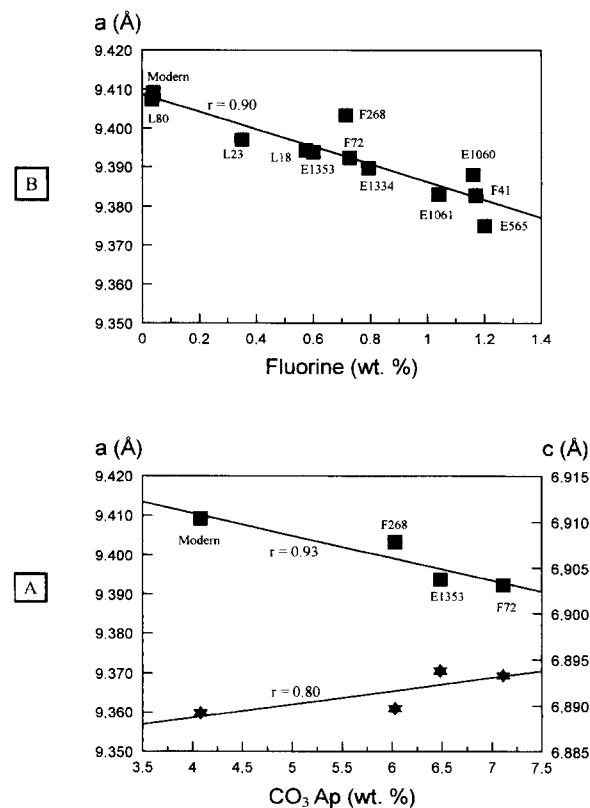
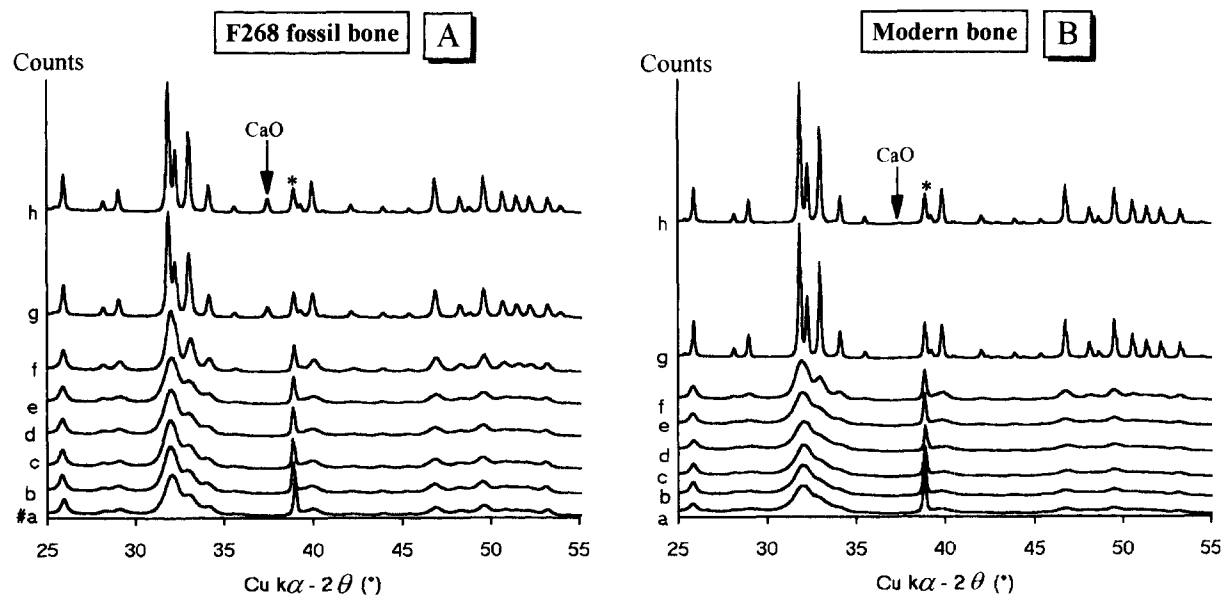


Fig. 8. Changes in unit-cell dimensions a (square) and c (star) (\AA) with (A) the fluorine content and (B) CO_3 apatitic content (wt. %) for the modern and the fossil red deer bones.



#a = unashed, b = 200°C , c = 300°C , d = 400°C , e = 500°C , f = 600°C , g = 700°C , h = 800°C (heating time in a muffle furnace = 1 h); * internal standard : NaF.

Fig. 7. X-ray powder diffraction patterns of the (A) F268 fossil bone and of the (B) modern bone as a function of temperature. For both, crystal size increases with increasing temperature.