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Checking collagen preservation in archaeological bone by non-destructive studies (Micro-CT and IBA)

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ABSTRACT

The material to be studied is a piece of human skull discovered (1999) in Pleistocene sediments from the Orsang river (Gujarat state, India). From anatomical view point, this skull is highly composite: modern Homo sapiens characters are associated to undoubtedly more ancient features. Absolute dating by ^{14}C is critical to understand this discovery.

Prior to dating measurements, non-destructive studies have been carried out. Micro-CT reconstruction (X-ray microtomography) and Ion Beam Analysis (IBA) have been undertaken to check the structural preservation of the fossil and the collagen preservation. PIXE elemental map was used to select well-preserved bone area. RBS/EBS and NRA were used for light element quantification, in particular C, N and O contents.

We also demonstrate that the PIXE-RBS/EBS combination is a effective tool for the whole characterization of archaeological and recent bones by analysing in one experiment both mineral and organic fractions. We have shown that the archaeological bone, a fragment of the potentially oldest modern Indian, is enough preserved for radiocarbon dating.

We propose that Elastic Backscattering Spectrometry (EBS) using 3 MeV protons could be a good non destructive alternative to conventional CHN method using Carbon–Hydrogen–Nitrogen analyzer for measuring C and N before ^{14}C dating.

1. Introduction

IBA techniques are commonly used for the characterization of bone. In most cases, these techniques are applied to medical and biological purposes [1–3] or to archaeological and anthropological studies [4–12].

Bone is a composite material formed by an organic fraction (mainly collagen) and an inorganic mineral phase composed of carbonate-hydoxylapatite structure $Ca_{10}(PO_4)_{6-x}(CO3)_xH_{2+x}$. For the past years, trace element analysis of archaeological bone by PIXE and PIGE has tended to focus on the investigation of the mineral fraction for studies of biogenic process (dietary, toxic, pathological) and diagenetic alteration [9–11]. More recently, identification between ancient bone, ivory or antler has been developed on the basis of the Ca, Mg and P contents [12]. RBS has been little employed for the characterisation of bone and only applied in two directions: heavy element contamination such as Pb [13] and light biological matrix analysis [1,14]. A PIXE-RBS comparative study has been undertaken to verify the Ca/P ratio in hydroxyapatite [15]. Finally, NRA has been used to estimate the preservation status of archaeological bone by the analysis of the light elements C, N, O by deuteron induced nuclear reactions [6]. These three elements are very important since they represent the organic fraction, mainly collagen, of the bone tissue. The preservation of this fraction is a necessary condition for applying radiocarbon dating [16–18].

The advantages of IBA are the possibility to analyze both mineral and organic parts of bone by combining PIXE and NRA. However, the use of deuteron is not always possible due to radiation safety regulation and, when possible, it implies an additional measurement. It has been recently demonstrated that the combination of PIXE and RBS/EBS can provide information in two-phase materials (composed of mineral and organic constituents) such as painting [19–21] and biomaterials [1,13,22].

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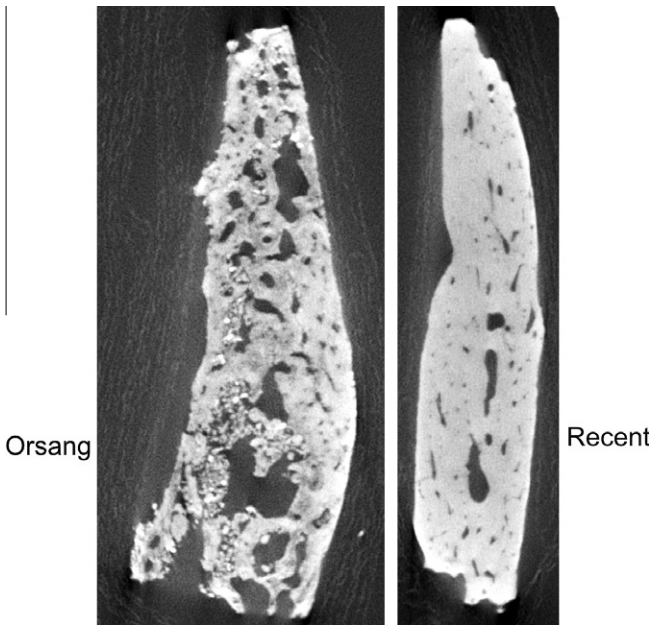

Fig. 1. Comparison of micro-CT reconstruction for the archaeological bone "Orsang" and a modern bone. Both are part of human skull.

In this paper, we propose to combine PIXE and RBS/EBS simultaneously in order to analyse in one experiment both mineral and organic fractions of archaeological bone material. In such a case, PIXE is used to analyze major, minor and trace elements heavier than sodium and proton elastic backscattering spectrometry (EBS) is applied to the determination of light elements, mainly C, N and O. This procedure has been applied to a bone fragment of the potentially oldest modern Indian in order to estimate the organic fraction preservation prior radiocarbon dating. Due to the importance of this human remain, non destructive techniques were required instead of conventional CHN method using Carbon–Hydrogen–Nitrogen analyzer [16]. PIXE and RBS mapping has been also performed to localize the best preserved areas.

Table 1
Composition measured by PIXE, of a fragment of modern human skull and a fragment of the archaeological human skull discovered in Pleistocene sediments from the Orsang river. Concentrations are in wt % (Na_2O to Fe_2O_3) or in ppm (TiO_2 to PbO).

	Modern bone		Archaeological bone (Orsang)	
	Mean	Standard deviation (1σ)	Mean	Standard deviation (1σ)
In %				
Na_2O – K	2.4	0.3	0.7	0.2
MgO – K	0.7	0.1	1.3	0.4
Al_2O_3 – K	1.6	0.9	2.5	1.7
SiO_2 – K	1.9	2.5	3.8	3.0
P_2O_5 – K	33.0	2.6	33.9	2.3
SO_3 – K	3.5	1.0	0.2	0.1
Cl – K	0.06	0.02	0.04	0.01
K_2O – K	0.47	0.24	<dl	–
CaO – K	55.6	2.2	56.4	3.5
Fe_2O_3 – K	0.6	0.4	0.8	0.5
In ppm				
TiO_2 – K	412	307	682	463
Cr_2O_3– K	424	340	32	16
MnO – K	791	519	887	830
CoO – K	<dl	–	<dl	–
NiO – K	10	7	10	9
CuO – K	68	39	22	22
ZnO – K	825	379	225	126
As_2O_5 – K	30	17	4	4
Br – K	139	30	9	7
Rb_2O – K	<dl	–	<dl	–
SrO – K	337	104	2066	1054
Y_2O_3 – K	<dl	–	<dl	–
ZrO_2 – K	<dl	–	<dl	–
BaO – K	<dl	–	<dl	–
PbO – LA	280	255	12	4

2. Material and experimental conditions

2.1. Archeological and modern samples

The archeological bone fragment is a piece of human skull discovered in 1999 in Pleistocene sediments from the Orsang river (Gujarat state, India) [23]. From anatomical view point, this skull is highly composite: modern *Homo sapiens* characters are associated to undoubtedly more ancient features such as Asiatic sub-species of *Homo erectus*. Thus, regarding anatomy, the Orsang skull may be related to a very ancient human realm known by rare specimens from Chinese and South-East Asian anthropological sites. For comparison, a fragment of the same part of a recent and modern human skull has been analysed. For both samples, no preparation and cleaning procedures were applied in anticipation of the ^{14}C dating.

2.2. Preliminary tests

Prior to dating and chemical composition measurements, non-destructive examination has been carried out in order to check the structural preservation of the fossil. A piece from the orbital bone cavity was made available for investigations on fine-scale

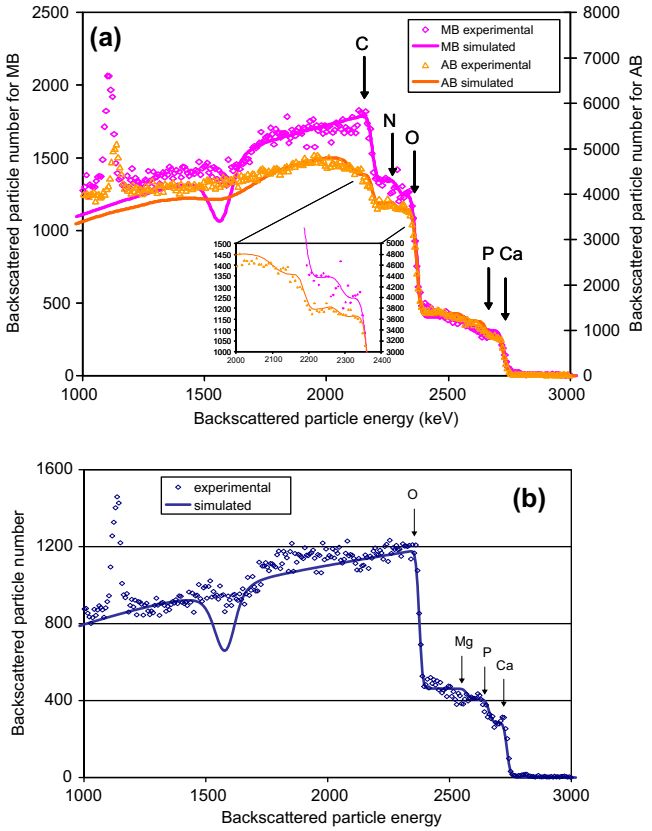

Fig. 2. (a) 3 MeV proton RBS/EBS spectra and SIMNRA simulations for archaeological bone (AB) and modern bone (MB). (b) For comparison, 3 MeV proton RBS/EBS spectrum and SIMNRA simulation for an archaeological bone from "Abri Pataud, Dordogne, France", containing no carbon, from [21], The non simulated peak at 1100 keV corresponds to helium atmosphere around the sample.