Archaeological objects as a record of sediment redox conditions in the past

I. Reiche
M. Menu
L. Quattropani

Laboratoire de Recherche des Musées de France, CNRS-UMR 171, 6 rue des Pyramides, F-75041 Paris Cedex 01, France

H. Bocherens

Laboratoire Biogéochimie Isotopique, UPMC-CNRS-INRA, UMR 162, UPMC, Case 120, 4 place Jussieu, F-75252 Paris Cedex 05, France

L. Charlet

Groupe de Géochimie de l'Environnement, L.G.I.T., CNRS-UMR C5559, Université de Grenoble I (UJF), B.P. 53, F-38041 Grenoble Cedex 9, France

Archaeological bones buried in sediments are often the unique witnesses of ancient civilisations. In this context, they give evidence of human occupation, climatic and surrounding conditions. As they are submitted to alteration processes such as erosion, dissolution or, more frequently, a modification of their composition, they register every event or change of the surrounding. For the archaeologist it is important to understand these alteration processes, in order to know if the quantity of bones found in a site is representative of its past human or animal population, or if a site without any bones was nonetheless occupied by men. Furthermore, bone remains are often used for ^{14}C dating and for the study of the ancient dietaries or palaeoclimates, studies relying on the initial chemical composition of the bones, and for which the contaminations or the alterations in the burial environment can distort the results. So the burial conditions (pH, oxic or anoxic environment, mechanical pressure, biological factors and particle transport dependent on the grain size, pore volume and dissolution conditions) influence the conservation degree of bones found in archaeological sites which can be very variable. That is why aquatic geochemistry studies on the archaeological objects are very important in order to understand their chemical alteration processes induced by the environment. At the other hand the archaeological artefacts which recorded the various sediment redox conditions in the past are the result of in situ geochemical experiments.

Presentation of the site

The archaeological site of Bercy, an ancient channel of the Seine river in the eastern part of Paris, is chosen as an example to show bone preservation differences depending on the sediment redox conditions. The studied bones found in a layer of the site are about 6000 years old and come either from the river bank (oxic surroundings) or directly from the Seine palaeochannel (anoxic environment). The layer is rich in stone artefacts, flints, pottery fragments, wood piles and bones from domestic and hunted animals. The sedimentary environment in the channel consists of dark clay and of a lot of organic remains. The emerged zone consists of light sands. Bones from the emerged zone (river bank) are in general white and are characterised by a complete

TABLE 1. Average trace elemental concentrations in the bone samples from the immersed and from the emerged area in comparison to the mean concentrations of two fresh bones in ppm

Element	Bone (immersed zone) (ppm)	Bone (emerged zone) (ppm)	Fresh bones (ppm)
F	15000/1000	8100	1500
Na	4000	2100	8200
Mg	1800	1100	7900
Al	0	3200	0
Si	0	25800	0
S	9300	5200	1600
Cl	190	170	700
Mn	1100	400	0
Fe	14500	1400	0
Cu	0	30	0
Zn	120	220	120
Sr	1700	1200	250

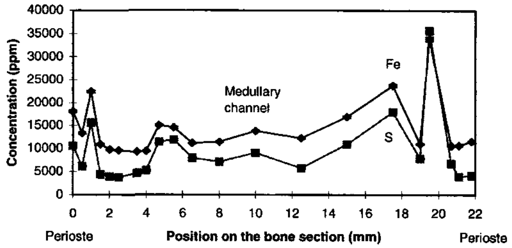

FIG. 1. Concentration profiles of Fe and S in the immersed bone sample of Bercy, measured by PIXE on a polished transverse bone section from one outside via the centre to the other bone periphery. The statistical error lies between 1.3% for iron and 1.7% for sulphur. The energy of the proton beam on the target is about 2.8 MeV (diameter ~150 μm). That represents an integrate deposited charge of 0.23 μC. The acquisition time is ~400 s for each point. Detector resolution of the low energy detector is 150 eV (S) and that of the high detector 180 eV (Fe).

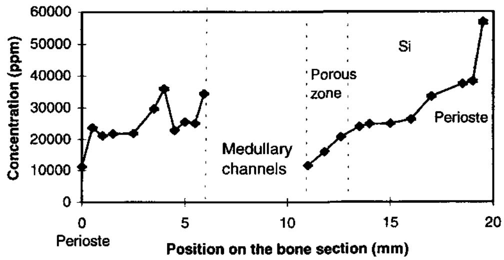

FIG. 2. Concentration profile of Si in the emerged bone, measured by PIXE on a polished transverse bone section at the same analytical conditions as the other profile. The relative statistical error is about 1%.

loss of their histological structure and by traces of microbial activity. The total nitrogen content (0.7% N) is very low, i.e. that represents a low amount of preserved collagen. Bones from the immersed zone are in contrast brown. Their bone collagen is well preserved and they present a nearly intact histological structure. The nitrogen content (about 3.5% N) is high in the central part, close to that of fresh bone (4.5–5% N). Some bone artefacts in the immersed area, especially from the bottom of the channel, show surface desquamation. Nearly no nitrogen (0.2% N in the studied sample) remains in the outer parts of these bones. Microbial activity and a darker colour is also observed in the peripheries of these bones (Bocherens *et al.*, 1997).

Methods of Analyis

We carry out Proton Induced X-ray Emission (PIXE) and Proton Induced Gamma-ray Emission (PIGME) Analysis with an external beam accelerator facility (AGLAE) at the Research Laboratory of the French Museums (Calligaro *et al.*, 1996) on transverse archaeological bone sections to provide elemental distribution in the bones and discuss the results in comparison to the burial environment. The combination of these two methods enables us to determine in a sensible, multi-elemental and non-destructive way the elements (like the major elements P and Ca for bones) and the contaminants such as F, Al, Si, S, Cl, Mn, Fe, Cu, Zn, Br, Sr or Ba with generally a limit of detection between 5 and 30 ppm depending on the element. The polished bone transverse sections are placed perpendicularly in front of the external beam (diameter 150 μm) with an proton energy of 2.8 MeV on the target (Calligaro *et al.*, 1998). Concentration profiles are measured by shifting the sample, with a stepping motor, in front of the proton beam.

Results and discussion

We present typical diffusion profiles of some elements into the measured samples and try to correlate these results with the sediment conditions. Among others, the contaminations particularly observed in the immersed zone are iron and sulphur. High concentrations of aluminium and silicon are found for the sample of the emerged area. Lower concentrations of light elements like sodium, magnesium or chlorine are observed in both bones in comparison to the composition of fresh bones. Table 1 present the main contaminants of the bones measured by PIXE/PIGME (Quattropani *et al.*).

The concentration profiles of iron and sulphur is given in Fig. 1 for the sample of the immersed area. There is an evident correlation between the iron and sulphur contents in the bone, which is due to the presence of an iron sulphide inclusions (pyrite, FeS_2) and of iron and sulphur substitutions in the bone apatite confirmed by a scanning electron microscope energy dispersive X-ray analysis. Bacteria are known to introduce sulphides into archaeological objects in anoxic sediment conditions (Pradell *et al.*, 1996).

The profile of silicon content in the bone from the emerged zone, an element which is not found in the bone sample from the immersed zone nor in the fresh bone, is represented in Fig. 2. Silicon seems to be present in the bone structure as a silicate which can replace a part of the bone phosphates (Johnsson, 1997) due to their an analogous structure.