Journal of Archaeological Science 38 (2011) 3234–3243

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Differentiation of archaeological ivory and bone materials by micro-PIXE/PIGE with emphasis on two Upper Palaeolithic key sites: Abri Pataud and Isturitz, France

K. Müller*, I. Reiche

LC2RMF UMR 171 CNRS, Palais du Louvre – Porte des Lions, 14 quai F. Mitterrand, 75001 Paris, France

ARTICLE INFO

Article history:
Received 17 December 2010
Received in revised form
18 June 2011
Accepted 26 June 2011

Keywords:
Bone
Antler
Ivory
Identification
PIXE/PIGE
Non-destructive micro chemical analysis

ABSTRACT

The exact identification of the raw material used for ancient bone objects is the basis to understand the manner in which humans in ancient times chose the medium for the manufacture of objects. The material identification is not trivial in the case of highly modified surfaces – worked by man or degraded by diagenesis. Even if bone materials are morphologically quite different, they show in general a very similar chemical composition. Nevertheless, slight differences can be observed in their chemical composition on minor and trace level. These variations may be used as a marker of their exact nature, when other means such as morphological observations are limited. A large data base was built up by analysing different modern and archaeological osseous materials in order to define chemical markers for the identification of the raw materials used to manufacture objects.

Micro-Proton Induced X-ray and Gamma-ray Emission (micro-PIXE/PIGE) was chosen to analyse the different bone materials as a non-invasive method is generally required for the study of ancient worked osseous objects. These analyses were performed at the particle accelerator AGLAE installed at the laboratory of the C2RMF, Paris.

This paper presents the results obtained on about 150 objects made of different bone materials dating from the Palaeolithic to today and coming from various archaeological sites, mainly in France. Some chemical markers seem to be characteristic, such as the magnesium to calcium ratio for well preserved ivory on one hand and the fluorine content versus strontium to calcium ratio for bones of marine mammals on the other hand. The limits of this approach and the different parameters to consider for an identification of ancient bone and ivory material based on this method are particularly discussed in the case of Palaeolithic material from Abri Pataud and Isturitz, France.

1. Introduction

Bone materials play an important role in archaeology, being exploited by man to manufacture tools and other objects since Palaeolithic times (Choyke and Bartosiewicz, 2001; Luik et al., 2005; Gates St-Pierre and Walker, 2007; Legrand-Pineau et al., 2010). Bone objects are witnesses of human occupation, cognitive capabilities, collective identities, but also individual expressions and technical know-how (Villa and d'Errico, 2001; Pétillon, 2008). Scientific investigation of these objects contributes therefore to our understanding of ancient societies. However, as raw materials used for object manufacture, osseous tissues do not form a homogeneous group. Antler, land-mammal bone, sea-mammal bone, mammoth ivory – to name but a few – are all different in terms of economic availability, technical workability and reactions to use and wear. Furthermore, as products of animal origin, they are inevitably linked to the way human groups culturally perceived the animal world in general, and specific species in particular. Therefore, especially for prehistoric periods, determining the nature and characteristics of the used raw material is one of the key questions for archaeological and anthropological interpretation. It is the basis to understand habits of raw material exploitation, whether technical, economic or symbolic. In many cases ivory, bone or antler can easily be identified visually by macro- and microscopic observations based on specific morphological characteristics. However, this is not always possible on artifacts that are fully worked, small and/or fragmentary. Raw materials can also get mixed up in case of diagenetically altered bone materials.

* Corresponding author.
E-mail address: katharina.mueller@culture.gouv.fr (K. Müller).

0305-4403/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jas.2011.06.029

1.1. Composition and structure of bone materials

Bone materials are hierarchical composites consisting of a mineral (~55–65 wt %) and an organic phase (~25–35 wt %) and about 10 wt % water. The mineral phase can be described as carbonated hydroxyapatite particles imbedded in the organic matrix, basically collagen type I with lesser amounts of other non-collagenous proteins. The proportion of the mineral and the organic phase varies marginally between the different kinds of bone materials comprising bone, antler and ivory as well as teeth and tendon. This study will only deal with ivory, bone and antler.

Ivory is generally associated with the dentine part of proboscidian tusks. But strictly speaking, ivory is a generic term, which describes the material obtained from predominantly exo-skeletal incisor teeth or tusk of several animal species: elephant, mammoth, walrus, hippopotamus, pig (bush, boar, and warthog), sperm whale, killer whale and narwhal. Since ancient times ivory has been highly prized as a medium for the manufacture of artefacts and art works. The main part of an ivory tusk, the dentine, lies between pulp cavity and the outmost layer at the periphery, called cementum. As all bone materials ivory has a strongly hierarchical structure (Su and Cui, 1999; Locke, 2008). At the molecular (fibril) level the hierarchical structure of ivory is very similar to bone and antler. At higher structure levels ivory differs from the other bone materials. In ivory the collagen fibril bundles are organised to radial around the pulp cavity in the centre of the tusk distributed layers (layer thickness 0.3–0.4 mm) interweaved forming a network. At microscale the characteristic feature of ivory are regular microtubular pores with a diameter of about 2 μm (Reiche et al., 2011). The microstructure of compact bone and antler is characterized by histological units called osteons (100–200 μm in diameter). Osteons are composed of circularly-distributed layers (lamellae) of collagen fibril bundles (layer thickness ~2–3 μm) around the Haversian channels (containing blood vessels) (Currey, 2002; Wagermeier et al., 2006).

At the elemental level, the apatite nanocrystals are non-stoichiometric and exhibit a variety of substitutions (e.g. H_2O, CO_3^{2-}, F^-, Cl^-, Mg^{2+}, Na^+, Sr^{2+}...) and vacancies for all bone materials. The degree of substitution may vary between different bone materials being also highly sensitive to the environmental in vivo conditions.

During burial, bone materials undergo various diagenetic alterations depending on the burial conditions (hydrology, temperature, geochemistry, biological factors, and mechanical pressure) and time. Changes happen to osseous materials during burial are above all the uptake of groundwater solutes, dissolution of soluble components, breakdown and leaching of collagen, crystallinity increase and alterations caused by micro-organisms. Numerous researches have been carried out aiming at a better understanding of the diagenetic and taphonomic alteration of bone during burial time depending on the respective environmental conditions (e.g. Weiner and Bar-Yosef, 1990; Hedges et al., 1995; Reiche et al., 1999, 2001, 2003; Collins et al., 2002; Trueman et al., 2004, 2008; Nielsen-Marsh et al., 2007; Fernández-Jalvo et al., 2010). Relatively few studies focused on ivory diagenesis. Chemical and structural changes in dentine of elephant and mammoth tusks as well as tooth due to diagenetic processes were studied by chemical, structural and morphological analyses (Godfrey et al., 2002; Wang et al., 2007; Edwards et al., 2005). Alterations in archaeological antler have been studied by Chadefaux et al. (2008).

1.2. Identification studies on ivory and other bone materials

Normally, no identification problems arise when large sections of tusks, antlers or bones are available. For smaller objects the specific discrimination of the materials relies on the experiences of archaeologists or archaeozoologists and is often difficult in the case of carved objects where characteristic features of the raw material may be lost. Thus, depending on the respective problem and the conservation state of the objects it could be necessary to apply further analytical methods to obtain the wished information.

Ivory, bone and antler can be distinguished based on their micro-morphology by optical and electron microscopy, if the preparation of cross, thin or ultrathin sections is possible. An identification guide for ivory and its substitutes was published by Espinoza and Mann, 1991. The authors describe characteristic morphological properties like Schreger pattern, 'annual rings', ring of cementum and secondary dentine for ivories originating from different species and compare them with common ivory substitutes, including bone, leading to an unambiguous determination by means of several analytical methods (optical and UV microscopy, FT-IR). The Schreger pattern as an important morphometric feature can also serve for the differentiation between modern elephant and mammoth ivory (Espinoza and Mann, 1993; Trapani and Fischer, 2003). However, the Schreger angles depend on their location within the tusk (Singh et al., 2006; Abelova, 2008) and this method cannot be applied to small objects.

The identification of ivory species on artefacts plays an important role in wildlife protection law enforcement (CITES) in order to trace poaching and illegal trading. Therefore, several studies have been focused on the establishment of non-destructive identification methods that were applied mainly on modern samples. Fourier-transform (FT) Raman spectroscopy was applied to analyze ivories originating from different animal species and objects made of ivory or ivory substitutes in order to distinguish between them (Edwards and Farwell, 1995; Edwards et al., 1997). For the differentiation between modern bone materials and different ivory species chemometrics analysis were used (Brody et al., 2001; Shimoyama et al., 2004). However, this identification method was faced with significant difficulties in case of degraded archaeological artefacts (Edwards et al., 2005, 2006).

Furthermore, sampling-requiring methods were applied to identify ivory species and/or origin by means of DNA analysis (Lee et al., 2009) or chemical analysis using different analytical techniques and method combinations. Raubenheimer et al. (1998) used Atomic Absorption Spectroscopy, Induced Coupled Plasma (ICP) – Optical Emission Spectroscopy as well as amino acid analysis and Singh et al. (2006) employed X-ray fluorescence analyses, ICP-Mass Spectrometry (MS) and ICP-Atomic Emission Spectroscopy. Matrix-assisted Laser Desorption/Ionization (MALDI) -MS investigations were aimed at the identification of bone species (Buckley et al., 2010). A few studies deal with the differentiation between bone and antler using electron microscopy (Paral et al., 2007; Chadefaux et al., 2008). Reiche et al. (2011) studied micro-morphological features by means of non-destructive micro computed tomography (micro-CT) in order to distinguish between ivory, bone and antler.

As already mentioned, the different kinds of bone material are chemically very similar. Slight differences can be detected in several minor and trace element amounts as well as in the proportion of organic material and the constitution of collagen molecules. Christensen (1999) established that a significant enhanced magnesium value (about 5% MgO) is a characteristic chemical feature for ivory (values for bone and antler lied below the limit of detection of the applied method).

However, most of the cited identification methods have been conducted on modern samples and/or have been shown to be limited when the objects are small, altered or when sampling is not possible. This study was focused on the evaluation of a non-destructive distinction method for ivory, bone and antler based on the chemical composition of the mineral part, which generally lasts longer than the organic fraction in the archaeological context.