CHARACTERIZATION OF ARCHAEOLOGICAL BONES FROM CENTRAL SUDAN: PRESERVATION, STRUCTURE AND ISOTOPIC ANALYSIS OF BIO-APATITE

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Abstract

The main aim of this project is to provide and evaluate a methodological approach for bone apatite dating. Crucial for the validation of this approach is to assess the preservation state of bone apatite, in particular if isotopic exchange occurred during burial between the bone and the environment. For this reason the study of diagenetic processes affecting bones is necessary in order to identify preserved and altered portions of bone tissue and secondary phases that can alter the final result. A diagenetic study, performed on a large set of samples coming from Al Khiday archaeological site (Central Sudan), characterised by a well preserved and radiometrically dated archaeological stratigraphic sequence, enables a clearer and more complete comprehension of the processes involved during burial. Further analysis and radiocarbon dating of bone samples will provide results for the discussion and validation of this method.

Introduction:

The archaeological excavation carried out since 2006 at Al Khiday 2 (Khartoum, Sudan), brought to light nearly 180 graves. The stratigraphic sequence revealed that the site was used as a cemetery during at least three distinct phases: a “pre-Mesolithic” phase, which precedes a well-defined and radiometrically dated Mesolithic occupancy of the site (6550-6200 cal BC); a Neolithic phase, dated between 4460 and 4330 cal BC; a Meroitic phase, dated between 20 and 210 cal AD (Salvatori et al. 2011; Zerboni 2011). A fourth burial phase identified during the archaeological excavation is not clearly chronologically defined, however graves belonging to this phase are called “Mesolithic” since this is the most probable attribution, so far. Since this unique archaeological site in Central Sudan revealed a preserved stratigraphic sequence, burial phases are indirectly dated (or chronologically constrained) by the study of associated materials and archaeological features. This context provides a set of samples that suite the purpose of bone direct dating by \(^{14}\text{C}\) dating of the carbonate fraction of bioapatite: information obtained from indirect dating can be useful to evaluate the reliability of results from direct dating.

Define and understand diagenetic changes occurring in archaeological bones is the first essential step to validate direct dating of bioapatite and distinguish altered from preserved bone tissue is mandatory to obtain reliable results. In this sense diagenetic study of bone samples was carried out by analytical methods in order to define changes in bone microstructure from the burial onwards.

Materials and methods:

The initial set of bone samples was enlarged selecting 1 femur and 1 humerus fragment from 30 graves belonging to different burial phases (12 pre-Mesolithic, 6 Neolithic, 6 Meroitic, 6 uncertain – possibly Mesolithic). Compact cortical bone samples were preferred to other types of bone on the base of preliminary analysis that showed a potentially better preservation state. Three molar teeth were also sampled (1 pre-Mesolithic, 1 Neolithic, 1 Meroitic); a modern molar tooth was analysed as reference. On bone samples Scanning Electron Microscopy (SEM) and (to some extent) High Resolution X-ray Computed micro-Tomography (HRXCT) analysis were performed; FT-IR spectroscopy and Raman analysis are in progress at L.A.M.S., Paris. On tooth samples SEM, X-ray computer micro-tomography and EMPA analysis were performed. As regarding SEM and EMPA analysis, samples were embedded in epoxy resin, cut in cross sections and polished. Calcium carbonate concretions from the soil in the surrounding area of the archaeological site were sampled and preliminary \(^{14}\text{C}\) dating was performed.
Results and future plans:

SEM and HRXCT analysis on 60 bone samples validated preliminary results obtained last year, hence a statistical significative dataset enables a more complete comprehension of processes involved in bone diagenesis. Numerous alterations due to diagenetic processes were identified among the samples:

- Microscopical focal destruction (MFD) caused by bacteria: traces left by bacterial colonies (Fig. 1a) consist on bone portions characterised by intense micro-tunnelling, ranging from 0.1 to 2 μm in diameter, surrounded by hypermineralised rim due to dissolution and reprecipitation of hydroxyapatite (Jackes et al., 2001; Jans et al., 2004)

- Microscopical focal destruction (MFD) caused by fungal activity is characterised by microtunnelling (Fig. 1b) up to 8 μm in diameter and by the absence of hypermineralised rims (Fernandez-Jalvo et al., 2010)

- Deposition of manganese dendrites (Fig. 1c) forming dark coatings (nearly 1 mm thick) on the external surface of bones, constituted by mineral phases belonging to the psilomelane group (Potter et al., 1979)

- Deposition of secondary calcite in the bone vascular system (Fig. 1d) and micro-fractures, related to the formation of calcium carbonate concretions in the soil, as a consequence of enhanced evapotranspiration during the aridification phases occurred in the region (the last phase started in Central Sudan at the beginning of the VI millennium BC).

Fig. 1: Backscattered electron image of a) bacterial colonies; b) fungal attack; c) Manganese dendrites in dark coatings; d) Secondary calcite in bone vascular system

Observing textural relationship between those diagenetic features a chronological sequence of diagenetic events since the body deposition was established. MFD caused by bacterial and fungal activity is the first type of alteration affecting bones, presumably after few months/years after burial, and defined an early diagenetic process (Fernandez-Jalvo et al., 2010). The second event is the formation of manganese
dendrites that fill the micro-porosity of bone tissue and partially the micro-tunnelling left by bacterial activity. Subsequently calcite deposition occurs.

Analysing bone samples belonging to different burial phases, a diachronic variation of diagenetic changes have been observed. Dark coatings due to manganese dendrites were observed in pre-Mesolithic and Mesolithic samples, alteration due to bacterial activity and calcite precipitation were detected in pre-Mesolithic, Mesolithic and Neolithic samples while these features are completely absent in Meroitic samples. Alteration due to fungal activity was detected in all samples. These differences are related to different environmental conditions encountered by buried bones from the early Holocene onwards.

Further analysis on manganese dendrites are needed to better define the mineral phases and the environmental conditions of formation.

Results obtained from teeth show a complete accordance to those obtained from bone samples. Types and distribution of diagenetic features identified in bones are present also in tooth samples, noteworthy enamel seems to be better preserved than dentine. This outcome was proved also by preliminary EMPA analysis, performed on enamel and dentine: comparison of Ca/P ratio measurements between archaeological and modern samples shows a greater variability for dentin than for enamel (Fig.2).

As for calcium carbonate concretions, preliminary ^14C dating were performed on 4 samples and results rages between 6500-5500 cal. BC for 3 samples and 17500-16900 cal BC for 1 sample; further investigations have been planned to better understand the formation of calcium carbonate concretions and other radiometric determinations will be available.

Ongoing analysis by FT-IR and Raman spectroscopy (Laboratoire d’Archéologie Moléculaire et Structurale CNRS – UPMC and Département de Préhistoire du Muséum National D’Histoire Naturelle UMR – CNRS, Paris) aims to quantify the secondary calcite in the samples, and to identify and quantify the carbonate content in the hydroxyapatite crystal lattice (B type substitution of CO$_3^{2-}$ for PO$_4^{3-}$) in order to assess the extent of bone apatite diagenetic modifications and the possible uptake of exogenous carbonate from the environment in the crystal lattice. Further information on diagenetic changes will be obtained by FTIR-ATR and micro-XRD mapping on bone cross sections (Lebon et al. 2011).

Chemical treatments will be applied to bone samples in order to remove secondary calcite; treated samples will be analysed by FT-IR spectroscopy and XRPD to assess the reliability of the treatments. A representative set of samples will be select for $^{14}$C and results will be discussed and tested in order to assess whether isotope exchange occurred between bone carbonate and inorganic carbonate present in the soil, hence to validate radiocarbon dates previously obtained on bioapatite (Zazzo et al. 2011).

Once tested the good preservation of bioapatite, isotopic analysis for $^{87}$Sr/$^{86}$Sr ratio will be performed with the aim to gain information about the provenance and mobility of individuals during their lifetime.

![Fig.2: Ca/P ratio on enamel and dentin for Pre-Mesolithic, Neolithic, Meroitic and Modern teeth by EMPA analysis.](image-url)
References


SUMMARY OF ACTIVITY IN THIS YEAR

Courses:

C. WHIGHAM: “Academic Speaking 2”, Centro Linguistico di Ateneo, Università degli Studi di Padova.


M.C. DALCONI: “Corso teorico-pratico sull’analisi dati in diffrazione di raggi X da polveri con il metodo Rietveld, Dipartimento di Geoscienze, Università degli Studi di Padova.

1st Joint SIMP-AIC international school “Crystallography beyond diffraction” 2nd edition, 4-8 September 2013, University of Camerino, Camerino, Italy.

Communications:

DAL SASSO G., MARITAN L., ARTIOLI G., Study of bone diagenesis on the human remains at 16-D-4 site, 1st Meeting of the Centro Studi Sudanesi e Sub-Sahariani – An integrated scientific approach to Central Sudan prehistory: the Al Khiday case, 18 June 2013, Milano, Italy.

DAL SASSO G., MARITAN L., ARTIOLI G., ZERBONI A., Preliminary study on calcium carbonate concretions at 16-D-4 site, 1st Meeting of the Centro Studi Sudanesi e Sub-Sahariani – An integrated scientific approach to Central Sudan prehistory: the Al Khiday case, 18 June 2013, Milano, Italy.

MARITAN L., DAL SASSO G., MAZZOLI C., ARTIOLI G., Variability in the pottery production from the Mesolithic to the Neolithic at Al Khiday, 1st Meeting of the Centro Studi Sudanesi e Sub-Sahariani – An integrated scientific approach to Central Sudan prehistory: the Al Khiday case, 18 June 2013, Milano, Italy.

DAL SASSO G., MARITAN L., ARTIOLI G., USAI D., Assessing bone diagenesis diachronic variation at Al Khiday (Khartoum, Sudan) from the early Holocene to the II century A.D., 7th International Bone Diagenesis Meeting, 22-25 October 2013, Lyon, France.

Posters:

DAL SASSO G., MARITAN L., SALVATORI S., USAI D., Preliminary petrographic analysis on a pottery sample from El Treis, Central Sudan, 12th European Meeting on Ancient Ceramics, 19-21 September 2013, Padova, Italy.

Publications:


Internship: