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

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Abstract

Direct dating human bones is a challenging task, especially when collagen is poorly preserved. Moreover, diagenetic processes may heavily affect the reliability of results. The purpose of this project is to provide a methodological approach to distinguish between altered and preserved bio-apatite, in order to isolate unaltered bio-apatite and obtain reliable results in isotopic analysis and radiocarbon dating. Validation of this approach is the second important step of this work: numerous samples are available, covering a wide period of time and coming from a nearly unique archaeological context in Central Sudan, with a preserved and dated archaeological stratigraphy. Preliminary analysis was performed on a limited number of samples and results reveal the complexity of diagenesis in this environment. Further analysis on a larger sample will provide a more complete and clear comprehension of this process.

Introduction:

Bone samples come from the archaeological site 16-D-4 at Al Khiday (Khartoum, Sudan), located along the western bank of the White Nile, 25 km south of Omdurman. Archaeological excavations are in progress, at the moment nearly 170 graves have been found, belonging to three different phases, covering a span time of approximately 10000 years: Mesolithic evidences (VII millennium B.C.) of site occupancy constitute the ante quem limit for the Pre-Mesolithic phase, the Neolithic phase dates to the V millennium B.C. and the Meroitic phase to the I century B.C.-II century A.D. (Salvatori et al. 2011; Zerboni 2011)

Due to the poor preservation of bone tissue and the complete loss of collagen attempts of direct dating the graves, so far, failed. Moreover, the deposition of secondary phases, mostly carbonates, during the burial complicate the achievement of a reliable result in $^{14}$C dating. Deposition of calcium carbonates on bones is associated to the formation of caliche, a process related to climatic changes in North Africa, in particular desertification, occurring in Central Sudan from the beginning of the VI millennium B.C. The main aims of this project are the study of diagenetic processes, in relation to the paleoenvironmental conditions and climatic changes, and their effects on bone tissue; the study of carbonated hydroxyapatite of bone and secondary phases, isolation of bio-apatite and $^{14}$C dating (type-B $CO_3^{2-}$ ions substituting for $PO_4^{3-}$ in carbonated hydroxyapatite) (Zazzo et al. 2011); $^{87}$Sr/$^{86}$Sr ratios measurement in bio-apatite in order to obtain information on provenance and mobility of population (Padoan et al. 2011).

Materials and methods:

A surface collection of human and animal bones differently altered by diagenetic processes is available; this was partially used at the beginning of the year to test different sample preparation methods for SEM analysis. Rib and vertebra fragments coming from a Pre-Mesolithic grave (G153) and two Neolithic graves (G120, G128) were also analysed by scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD) for a preliminary study of the bone samples. After that three graves have been selected, one Pre-Mesolithic (G69), one Neolithic (G103) and one Meroitic (G159) and for each skeleton were sampled a fragment of skull, rib and femur in order to study different types of bone tissue (trabecular and compact). On this samples SEM, XRPD and High-Resolution X-ray Computed Tomography (HRXCT) analysis were performed.

Modern samples of animal bone tissue and ivory are used as reference for non-altered bone and enamel for HRXCT analysis. A modern sample of human bone is also available as reference. Samples of caliche were collected, prepared in thin sections, and analysed by SEM and optical cathodoluminescence microscopy (OM-CL), in order to characterize and possibly date the carbonate deposits in detail.
Results and future plans:
XRPD was performed on samples G69, G103 and G159 without any pre-treatment; carbonated hydroxyapatite is present in all samples as main phase, calcite and quartz (desert sand) is present in samples G69 and G103.
SEM and HRXCT analysis on the samples G69, G103 and G159 show different alterations of bone tissue due to diagenetic processes. In the Pre-Mesolithic and mostly in the Neolithic samples there is a considerable alteration due to bacterial activity: numerous colonies are visible (Fig.1), constituted by a cluster of bacterial cavities (0.5-1 μm in diameter) surrounded by a bright rim (Jackes et al. 2001). The characterization of this rim needs further analysis, at the moment no differences in the chemical composition with respect to the unaltered bone are observed. Bacterial destruction of bone tissue usually occurs during the decomposition of the body within few years after burial; the presence of bacterial colonies widespread among the skeleton may suggest a humid burial environment.
Precipitation of calcite mainly affects Pre-Mesolithic samples and to lesser extent also Neolithic samples: calcite covers the external surface of bones and permeates almost all the Haversian canals and vascular channels and micro fractures of the bone structure (Fig.1). Analysis of caliche thin sections by OM-CL and SEM reveal several generations of calcite suggesting that caliche formation is not a single event but a long-term process. Four fragments of calcium carbonate were sampled for 14C dating in order to verify this hypothesis.
In two Neolithic samples (G120, G128) pyrolusite, detected by SEM analysis and confirmed by micro-Raman spectroscopy, permeate the micro-porosity of bone tissue before calcite precipitation, suggesting the presence of circulating water in the soil.
Concerning hydroxyapatite, SEM analysis on Pre-Mesolithic, Neolithic and Meroitic samples shows dark and bright areas among the bone structure; most of the dark areas are located near the external surface, around Haversian canals and fractures. SEM-EDS analysis does not show any chemical difference between the two zones; a hypothesis is a demineralization process occurring in the darker areas but further analysis is needed. In Meroitic samples evidences of bacterial activity and precipitation of calcium carbonate are completely absent (Fig.2).
As expected compact bone (mainly femur) is less altered than trabecular bone (rib).
All the features identified by SEM analysis are well detectable by HRXCT analysis, moreover the volume analysis is a helpful tool to deepen the comprehension of structures identified in section by SEM investigation.
Subsequent steps that will follow these preliminary results are:
- Analysis on modern samples of human bones as reference for the archaeological ones.
- SEM, XRPD and HRXCT analysis on tooth enamel coming from the graves G69, G103 and G159, which is assumed to be less affected by diagenetic processes than bone tissue;
- Enlarge the number of samples of compact bone for Pre-Mesolithic, Neolithic and Meroitic graves in order to obtain statistically significative results and deepen the comprehension of diagenetic processes;
- IR and micro-Raman analysis on bacterial colonies and inhomogeneous areas of hydroxyapatite.
- Application of chemical treatment with buffer solutions to bone samples in order to separate the carbonated hydroxyapatite and proceed with characterization and radiocarbon dating.
References


SUMMARY LAST YEAR'S ACTIVITY

Courses:
E. CALANDRUCCIO: “Corso di inglese parlato”, Università degli Studi di Padova.

School and congresses:
39th INTERNATIONAL SYMPOSIUM ON ARCHAEOLOGY, 28 May – 1 June 2012, Leuven, Belgium.

Posters:
DAL SASSO, G., MARITAN, L., SALVATORI, S., MAZZOLI, C., ARTIOLI, G., Quantification of microstructural features through image analysis in the Mesolithic and Neolithic pottery from Al Khiday (Khartoum, Sudan), 10th EMAS Regional Workshop, 2012, Padova, IT.
MARITAN, L., DAL SASSO, G., SALVATORI, S., MAZZOLI, C., ARTIOLI, G., Mesolithic and Neolithic pottery production at Al Khiday sites (Khartoum, Sudan), 39th International Symposium on Archaeometry, 2012, Leuven, BE.

Teaching activities:
Co-supervisor of the Bachelor degree thesis: “Analisi della porosità in materiali ceramici attraverso un approccio integrato di analisi d’immagine e indagine statistica” (Chiara Minto).
Teaching assistant: “Ceramic Petrology” at Khartoum University within the International Cooperation Project between Università degli Studi di Padova and Khartoum University; 9 November – 3 December 2012.