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PIXE Analysis of trace elements in Middle age human and animal bones

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Abstract. A set of human bones recovered in the two deserted Middle Age villages of Apigliano and Quattro Macine in Southern Italy were analyzed by PIXE and PIGE at CEDAD, University of Salento, Lecce, Italy. Some of the samples were also submitted to 14C-AMS dating in order to absolutely date the samples. The analyses allowed to obtain information about the bone preservation status and to identify differences in trace element composition between the two studied sites.

Keywords: PIXE, PIGE, Human Bones

INTRODUCTION

Human bone sample recovered during archaeological excavations in two desert Middle Age villages were submitted to PIXE-PIGE analyses at CEDAD in order to obtain information about major, minor and trace elements composition of the bone mineral phase. In fact several studies have shown the potentialities of IBA methods in these kind of studies [1-3]. Aim of the analyses was to study the degree of preservation of the bone mineral phase and to relate it to diagenetic processes associated with the burial environment. Some of the bone samples were also submitted to ^{14}C-AMS dating in order to obtain an absolute age for the samples.

SAMPLE SELECTION AND ARCHAEOLOGICAL CONTEXT

Bone samples were obtained from two archaeological excavations carried out in two Middle Ages villages in Apigliano (Martano) and Quattro Macine (Giuggianello) in the province of Lecce, Southern Italy. The two sites are only 15 km far and, from the archaeological point of view, they can be considered contemporary between them. Nevertheless, archeological evidences suggest that the two sites had quite different economies with Quattro Macine having a richest and more complex economical life. Furthermore, despites the relative small distance between the two sites and the fact that they are almost contemporary, the preservation status of bone samples from the two sites seems to be completely different. In particular previous investigations performed on hosteological materials found in Apigliano demonstrated a high degree of diagenesis of the both the collagen and the mineral phase fractions [4]. For the present study five human bone samples were selected from Apigliano and five from Quattro Macine, from different burial contexts. Of the five samples obtained from Apigliano three were obtained from individuals buried at direct contact with soil while the other two and all the samples from Quattro Macine were obtained from "open space" graves. Soil samples were also recovered from the two sites in order to identify possible compositional differences between the two sites.

RADIOCARBON DATING RESULTS

Three of the samples from the Quattro Macine archaeological excavation were submitted to AMS-^{14}C dating at CEDAD in order to obtain an absolute chronological reference for the whole site. Unfortunately the bad preservation status of the collagen of the Apigliano osteological samples did not allow to obtain ^{14}C measurements for this site. The results of the radiocarbon analyses performed on extracted bone collagen are summarized in Figure 1: all the samples can be dated to the period between 1300 and 1450 AD.

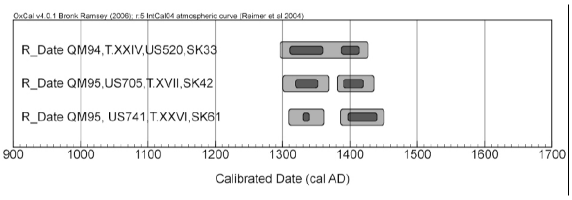

FIGURE 1. Radiocarbon dating results

PIXE-PIXE EXPERIMENTAL SET-UP

The bone samples were irradiated by using 3.7 MeV protons extracted in air through a 8 μm Kapton foil and impinging perpendicularly at the sample surface. In order to attenuate the contribution of low energy x-rays (in particularly K_α and K_β lines at 3.7 and 4.0 keV of calcium, the main component of the bone mineral phase) a 65 μm Al filter was placed in front of the 80160 Si(Li) detector (active area 80 mm^2) placed at 45° relative to the proton beam. Gamma rays were detected with the GC6022 Ge detector . Charge integration was obtained by collecting the 1014 keV gamma line emitted from a 100 μm thick Al wire crossing the beam at the exit of the Kapton extraction window. Reproducible irradiation conditions were obtained by using the luminescence induced by protons as reference for samples position adjustment. PIXE spectra analysis was performed by using the GUPIX code. In Figure 2 typical PIXE and PIGE spectra are shown. Eight elements were determined by PIXE: Ca, Mn, Fe, Cu, Zn, Pb, Br and Sr. The F content was calculated through the $^{19}F(p,p'\gamma)\ ^{19}F$ nuclear reaction emitting gamma rays at 110 and 197 keV, Na through the reaction $^{23}Na(p,p'\ \gamma)^{23}Na$ emitting at 440 keV and P through the gamma emission at 1266 keV.

In order to remove macroscopic soil contamination, the sample surface was cleaned by mechanically removing the uppermost layer and by washing with deionized water.

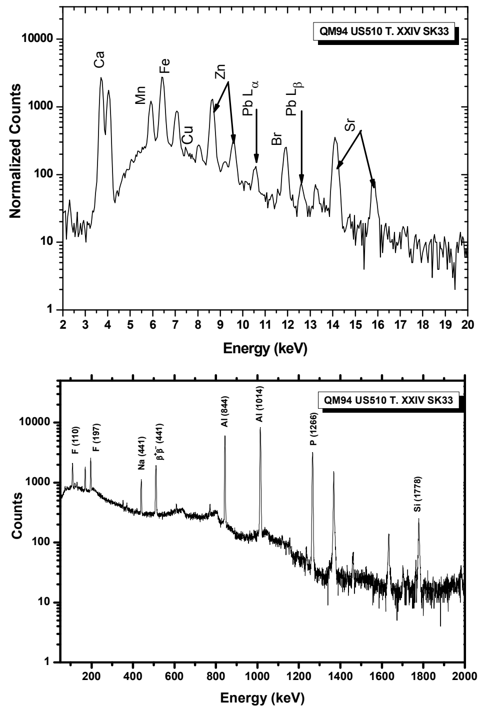

FIGURE 2. PIXE and PIGE spectra obtained for one of the samples (E_p=3.7 MeV)

RESULTS

Figure 3 shows the relationship between Ca and P: a strong positive correlation is present (r=0.8). This is consistent with what found by others and is due to the fact that Ca and P are the main components of the bone apatite ($Ca_5(PO_4)_3OH$) [5].

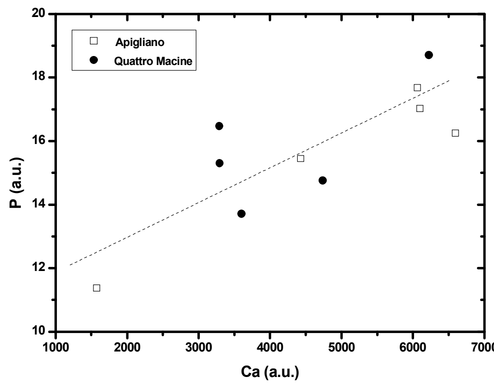

FIGURE 3. Ca-P positive correlation (r=0.8)

On the other hand negative correlations are found between Fe-Ca (r=-0.8) and Mn-Ca (r=-0.5) (Figure 4). This negative correlation can be explained as the consequence of diagenetic processes with the Fe and

Mn ions which are incorporated in the apatite structure by ion exchanges with the Ca ions [5,6].

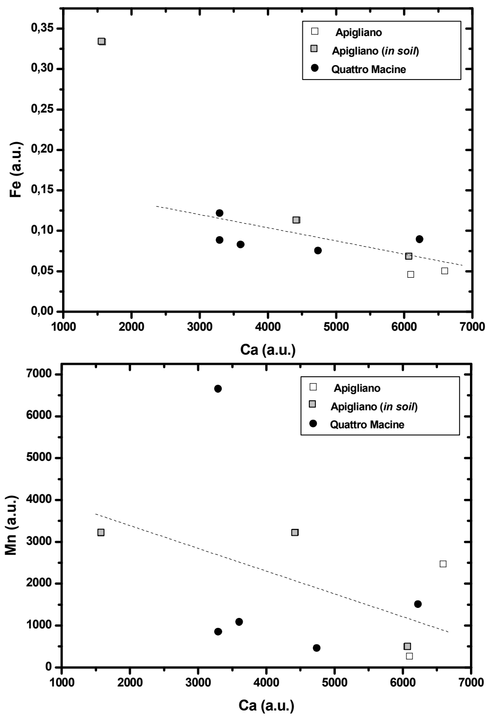

FIGURE 4. Fe-Ca and Mn-Ca correlations (the lines are only to guide the eyes).

It can be seen from Figures 3 and 4 that the samples from the two sites show similar dependencies and that no immediate relationship exists between the burial environment and the Fe or Mn content (open grave or at direct contact with soil). On the other hand, the burial conditions seem to significantly influence the F content (Figure 5). In particular, the bones recovered at direct contact with the soil show higher F concentrations.

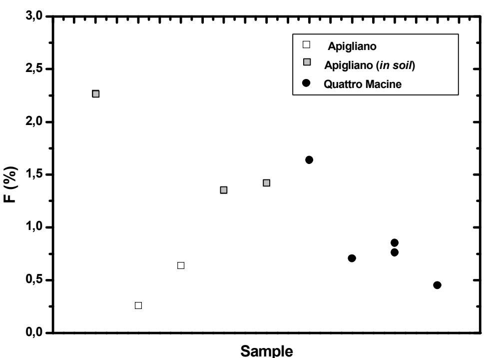

FIGURE 5. F concentration as obtained by PIGE.

In fact it is known that fluoride ions replace hydroxide ions in the apatite structure because of exchanges with the soil surrounding bones [7]. Our measurements show that these exchange depends on the burial conditions being more favorite by the direct contact of the bone with the soil.

When comparing the bones recovered from the two sites the most important difference is found in the Pb content (Figure 6). In fact the bones from Quattro Macine exhibit Pb concentrations significantly higher (> 50 ppm) than those found for Apigliano. A first explanation for this could be in the Pb content of the soils in the two sites. However the PIXE measurements performed on soil samples from the two sites showed comparable Pb concentration in the two soils: 94 and 97 ppm for Quattro Macine and Apigliano, respectively. Further measurements with a nuclear microprobe will probably allow to elucidate if this difference in the Pb concentration is due to a different uptake mechanisms from the environment or to the exposure to Pb during the life.

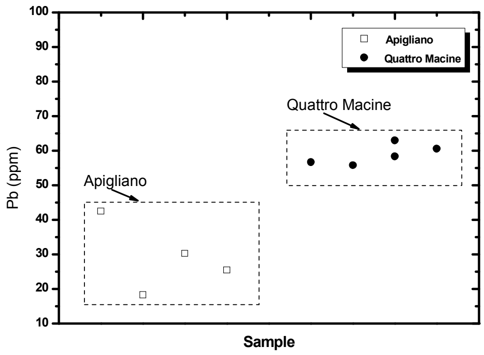

FIGURE 6. Pb concentration.

CONCLUSIONS

A set of human bones from two deserted Middle age villages in Southern Italy were submitted to PIXE-PIGE compositional analyses. A negative statistical correlation was found between Mn, Fe and Ca indicating the occurrence of diagenetic processes. Difference were found in the F content depending on the burial conditions.

Relevant differences were also found in the PB concentration between the two sites.

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