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Benefits of combined PIXE and AMS with new accelerators

Guy Demortier, Gianluca Quarta and Lucio Calcagnile

CEDAD – University of Salento – Lecce (Italy)

Abstract. Combination of the elemental non destructive analysis of artefacts by IBA multi-elemental techniques (but mostly PIXE) with the AMS measurement of the age of the organic material discovered in the close vicinity of these artefacts (mainly available for recent excavations) gives new tools to archaeologists to improve their diagnostic in the study of the composition of ancient objects and of their workmanship in ancient times by using the same experimental facility for IBA and AMS. For potteries and metallic samples IBA and AMS are to be applied on different samples excavated in the same environment but for organic archaeological samples IBA and AMS techniques could be sequentially used on the same material. Results of these combined techniques on artefacts of various origins recently studied at CEDAD (CEntre of Dating and Diagnostic investigations) are presented. .

Keywords: AMS, PIXE, Archaeology, Gold artifacts, Bones, Obsidians, Egyptian Pyramids

INTRODUCTION

PIXE and associated IBA techniques for the study of archaeological artefacts are now widely used by interdisciplinary teams. These non destructive surface techniques were generally performed with single ended particle accelerators in the late 70's when external beams became available in nuclear physics laboratories involved in applications to archaeological problems. New facilities, especially in Europe, are now available with tandem accelerators using negative incident ions and often equipped with microprobes in- and outside vacuum target ports. These negative ion sources allowing eliminating nitrogen ions from the ^{14}C beams are also used to implement the performances in dating of organic materials by comparison with the time consuming procedure involving the counting of low energy and low intensity β particles. The implementation concerns the lower quantity of necessary material to be consumed as well as the determination of all accessible ages

THE AMS-IBA FACILITY AT CEDAD

The AMS-IBA facility of the University of Salento is based on a 3 MeV Tandetron accelerator (figure 1) manufactured by High Voltage Engeneering Europa. It is equipped with several experimental lines able to perform :

- accelerator mass spectrometry for radiocarbon dating in full operation since 2003 (1),
- in vacuum ion beam analysis by conventional methods (PIXE, PIGE, RBS, NRA),
- external beam (exit foil of kapton or silicon nitride) mainly equipped for elemental analysis of archaeological and environmental samples,
- and recently (since mid-2006) for microprobe analysis with the well known triplet Oxford system.

In addition, beam lines are also available for high energy ion implantation, and simultaneous measurements of the modification of solids irradiated with a high power laser beam. Medical applications are also in progress.

The possibility of performing radiocarbon dating with a high precision (0.2 % on the ^{14}C /^{12}C ratio, and 0.05-0.1% on the ^{13}C /^{12}C ratio) has been demonstrated (2). Radiacarbon age of more than 2000 samples was routinely determined on varied materials (charcoal, wood, animal and human bones, sediments, marine carbonates,...). The required amount of material may be as low as 0.2 mg but is currently around 2 mg and the radiocarbon age determination may vary from present time down to 42000 years before present.

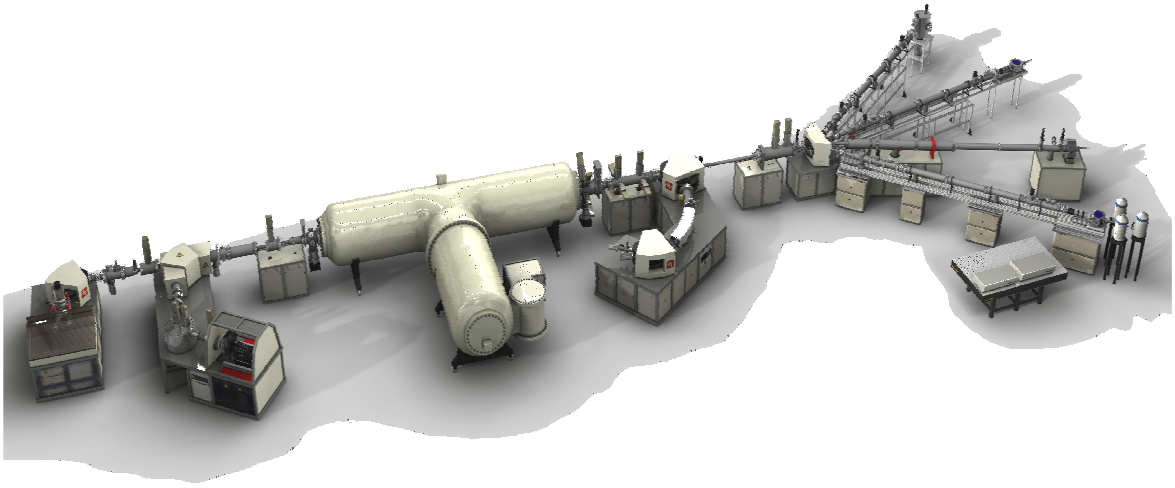

Figure 1. The AMS-IBA facility of CEDAD (Lecce-Italy). From left to right : the light elements ion source for IBA, the heavy elements ion source for AMS, the Tandetron accelerator, the heavy elements magnetic spectrometer and the detector assembly for AMS, the IBA beam lines with, from top to bottom : the internal beam and vacuum chamber, the external beam, the implantation facility, the nuclear microprobe, the high power laser.

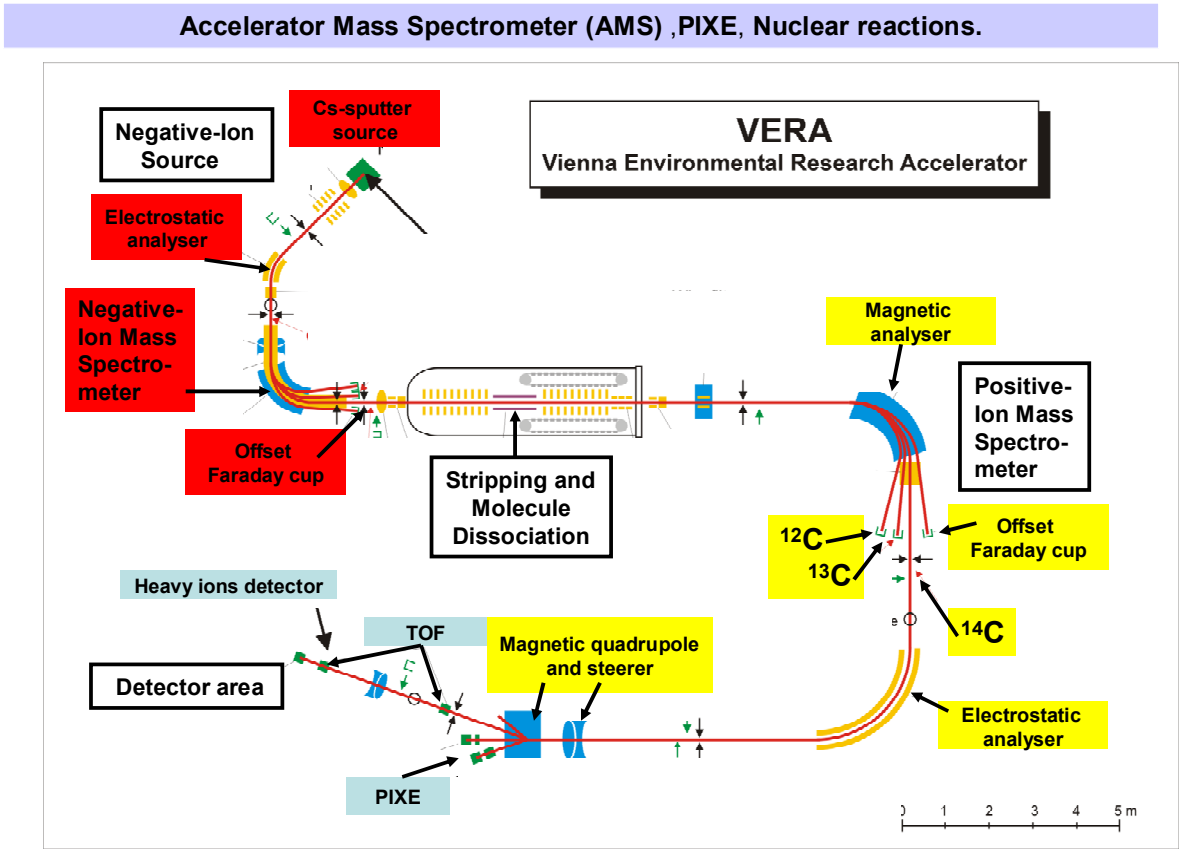

Figure 2 : The AMS-IBA facility of the Institut für Radiumforschung und Kernphysik of the Universität Wien.

A similar European facility with the same Tandetron is in the way of full operation in the new laboratory of Pier Andrea Mando at the University of Florence. After a long and outstanding use of 3 MeV Pelletron accelerator for numerous applications in AMS (not only ^{14}C, but also ^{10}Be, ^{26}Al, ^{182}Hf, ^{236}U and ^{244}Pu) an ion beam lines has been installed for IBA at the Institut für Radiumforschung und Kerphysik of the Universität Wien (3). The general set up is given in figure 2. The group of Walter Kutschera uses the same ion source and the same switching magnet in the high energy part of the assembly for AMS and for IBA. They have then also the possibility to use both technologies to study environment problems without searching for complementary methods outside their own laboratory. They have indeed perform AMS (for^{14}C) and LAMMA microprobe (for Li, Na, Al, Mg, Si, K, Ca) to investigate combusted particles in ice and snow having undergone long-range transport to arrive in the Arctic (4). A general presentation of AMS capabilities with small accelerators may be found in reference (5). Up to now very few examples of combined use of AMS and IBA methods have been published. Other IBA-AMS facilities have been also installed at the University of Seville, at the University of Madrid, at ANSTO in Sidney. Other groups involved in archaeometry in Debrecen and Paris would have in the near future separeted facilities for AMS and IBA.

In the next part of this short presentation we will refer to a selection of recent problems treated at CEDAD : gold discs and bones excavated in two different sites of Puglia (South of Italy) . We will conclude with partially solved questions related to :

(1) samples from the pyramids of Giza which have been analysed by PIGE and PIXE and
(2) obsidian tools found in a recent excavation in Turkey for which the date of burial has been already determined by AMS and preliminary results of Si map using the PIXE-microprobe.

SELECTED EXAMPLES FROM CEDAD

A set of gold discs have been found in the Archaeological site of Roca Vecchia which is located on the Adriatic coast of the Salento peninsula in Apulia, South Italy. Excavations are performed in this region since 1987 by the Department of Cultural Heritage of our University. They have brought to light testimonies of the use of this site for a wide time range from the Bronze Age to the Middle Age. Numerous ^{14}C dating measurements have been made on organic material discovered at different levels in the site and particularly four short living samples (pollen of Vicia Faba Minor) archaeologically associated with the gold discs. The four radiocarbon dates are 2964 BP, 2930 BP, 2929 BP and 2923 BP with an accuracy of 40 to 55 years (BP is conventionally taken from the year 1950). When converted in calendar dates (using absolute dates from dendrochronology), it could be said that the time of burial of the gold discs is situated between 1230 and 1040 BC (6). PIXE analysis (with an external 3 MeV proton beam) of these discs gives concentrations ranging from 79.6 to 83.1 % for gold 14.7 to 18.2 % for silver, the balance being the copper content. These data would mean that the artefacts have been manufactured in natural electrum The observed difference in the basic content of gold and silver is much higher than the experimental statistical accuracy (less than 1%) but cannot be explained by some depth non-homogeneity this question has been solved by using Au-L/Au-K lines by collecting data in a Si-Li and a LEGe detectors simultaneously used for the analysis. These ratios were the same than those of a certified homogeneous reference material containing 75% Au, 15% Ag and 10% Cu.

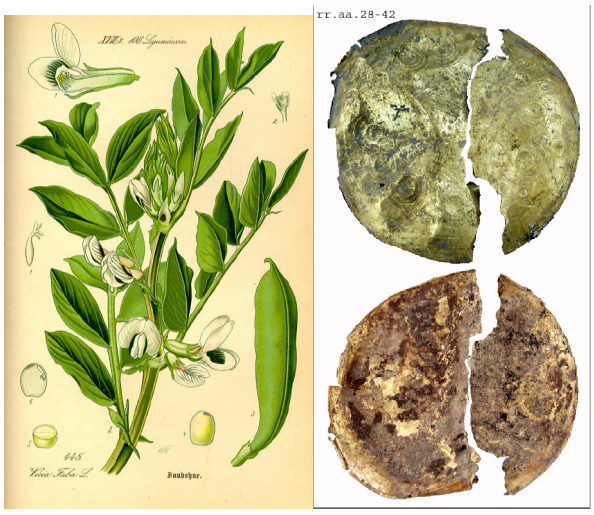

Figure 3. On the left : *Vicia Faba Minor*; on the right: both faces of one of the analysed gold discs of Roca Vecchia.

Bones of seven bodies (3 adults and 4 children) and various objects like flint and obsidian tools, ashes, and a bone fish hook have been excavated during a restoration of a private house in Campignano Salento (South Italy). Radiocarbon age (5665 + 30BP) of the collagen content of the bone (extracted by the Longin method (7) shows that the burial is situated between 4560 and 4440 BC. An interesting feature was that several bones were covered by a red pigment which was analysed by PIXE. In addition to the P, Ca, Mn and Fe signals which are of the same intensity inside and outside of the red region, one observes a large contribution of Hg-L lines in the red region of the bone, the Hg-M lines interfere with the possible K lines of S. K-lines of Ar induced in the air during irradiation in the non-vacuum geometry were used to

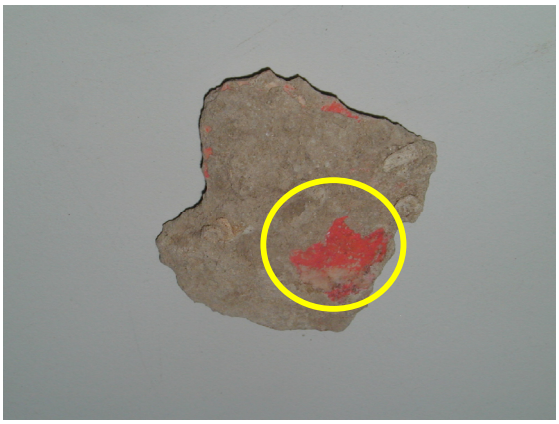

Figure 4. Red region of a bone excavated during the restoration of a private house of Campagnino Salentino.

monitor the measurements. The provisional attribution of the red colour could be the use of a pigment made with cinnabar.

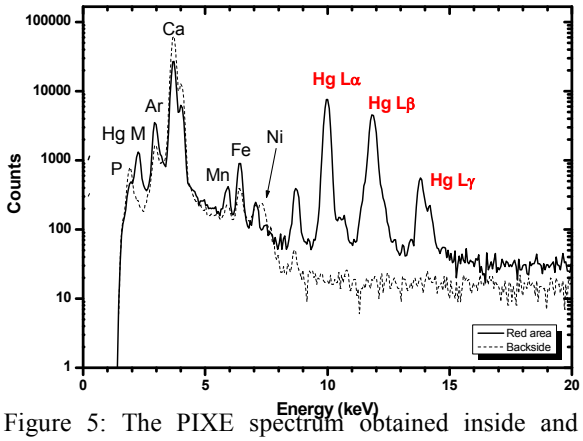

Figure 5: The PIXE spectrum obtained inside and outside of the red region.

FUTURE PROJECTS AT CEDAD

Amongst future projects of the combined use of AMS and IBA, we would like to indicate two projects already studied by one of these complementary methods. The first is the study of the blocks of the Egyptian pyramids of Giza. The second concerns the study of obsidian samples discovered during the long and deep excavation project in Turkey (8).

Pyramid's samples

Small samples of the pyramids of Khufu and Kaphra were studied by one of us (9) since about 15 years at LARN (University of Namur) by PIXE and PIGE using a maximum incident proton energy of 2.5 MeV.

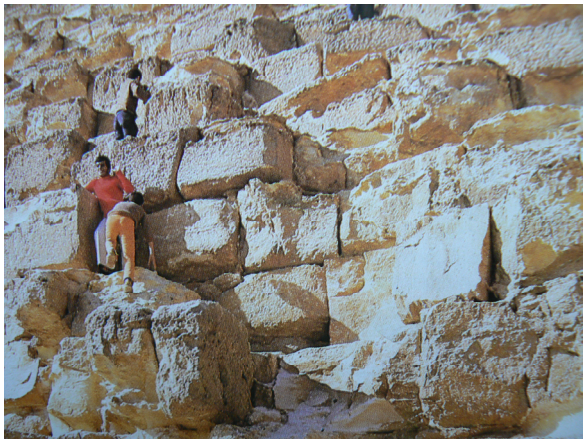

Figure 6: The huge blocks of the pyramid of Khufu with their rough vertical faces. (From the book of Jean-Philippe Lauer : Le Mystère des Pyramides - Presses de la Cité- 1989)

The main conclusion of this work indicates that the material is man-made and is close to the structure of a concrete. The arguments may be rapidly summarized as follows:

- (a) the elemental content of many of the 60 analyzed samples of the pyramid blocks is completely different from natural limestone. The Na, Mg, Al, and Si concentrations are sometimes so high that the Ca contribution is less than 5%. (9). The origin of Na is attributed to the use of natron whose main component is an hydrated sodium carbonate and which is abundant in the North of Giza. The origin of Mg, Al and Si could be the Nile silt.
- (b) Si- and Al-NMR measurements indicate that the material has been synthesized in a medium of high pH (probably NaOH).
- (c) recent work on the microstructure of pyramid samples compared with that of natural limestone samples collected in the quarries in the vicinity of pyramids shows that the pyramid blocks contain micro-crystals which are not natural but could have been only produced during a rapid solidification of a liquid solution.(10).
- (d) the presence of As in the coating of a limestone aggregate may find an explanation in the ancient report on the construction of pyramids by Herodotus who speaks about the use of an expensive ingredient which is related to a substance with a garlic taste (provisionally attributed to scorodite : $FeAsO_4\ 2H_2O$).

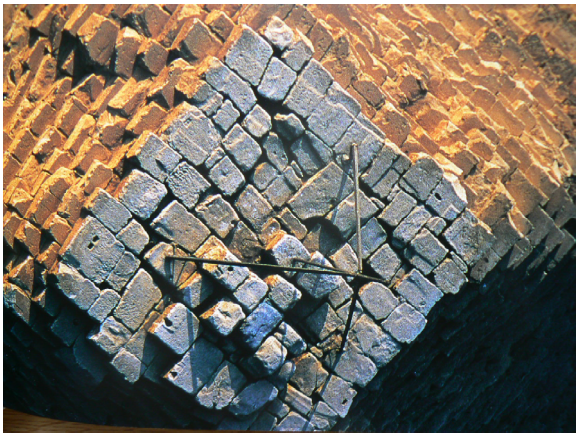

Figure 7 A: The horizontal faces of the blocks of the pyramid of Khufu. (Photography of Marcello Bertinetti published by National Geographic)

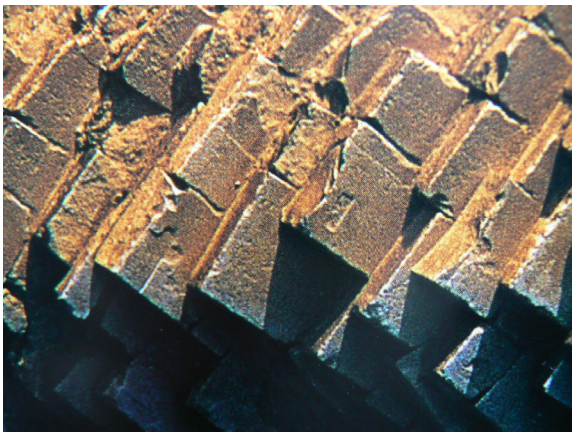

Figure 7.B : Detail of horizontal faces of the presently visible blocks of th pyramid of Khufu. Marks of some tool deposited on the surface before their complete drying are clearly visible on several blocks. No trace of carving is present

A visual argument may be easily seen if we compare vertical and horizontal sides of the blocks of the pyramid of Khufu. Figures 6 shows that the the vertical faces of the internal blocks (it is known that that the beautiful casing blocks have been robbed by the Arabs after the earthquake of 1356 to rebuild mosques and fortresses in the city of Cairo) exhibit a rough surface: roughness has been deliberately produced during the removal from the mould to allow the coupling of neighboring blocks. Even with those irregular faces the blocks appear perfectly fitted to each other. Dovetail joints are not used at that time and only appear in temples of the New Kingdom. They were necessary to link adjacent stones with flat surfaces of the external blocks. Wood or metal was inserted in those dovetails. On the contrary the horizontal faces of the blocks of Khufu are perfectly flat as can be seen figure 7. Their shape is original and did not suffer any damage from natural erosion. They are intact… and we cannot admit therefore that the vertical ones have also their original shape.

Recent PIGE results obtained at CEDAD with protons of 3.5 MeV on the previously studied material and on new samples show that numerous fragments contain the elements identified in our previous measurements but also a large amount of S and Cl. Those elements have been also analysed by PIXE, simultaneously.

PIXE results refer only to the surface content due to the large absorption of the low energy X-ray lines, but PIGE results concern regions at least 10 times thicker. Those measurements have been performed on grinded material to obtain pellets with very flat surface as well as on original irregular small fragments. The results are certainly not identical but they give perfectly compatible semi-quantitative data. Variations in the range of 20% are sometimes observed but they are attributed to the non-homogeneity of the samples. The sizes of the grains even after collapsing in micro-crystals are certainly greater than the range of the incident particles. The presence of Na, S and Cl is a clear evidence that natron has been used to produce the binding medium. Natron is essentially a hydrated sodium carbonate, but natural natron is a mixture, in various concentrations, of sodium carbonate and bicarbonate, but it contains also chlorides and sulphates. A complete determination of the stoichiometry would only be possible by including in the measurements the concentrations of carbon and oxygen which cannot be determined by PIXE but could be quantitatively analysed by nuclear reactions induced by deuterons or ^{3}He. The next steps of the study would be the use of an internal beam facility to perform the simultaneous determination of all the elements using NRA, PIGE and PIXE. All the measurements are to be made simultaneously in the same sample region to be sure of the good stoichiometry. Additionally the radiocarbon dating of straw or any other organic material expected to be present in the mortars at the bottom of several blocks would give a definitive proof to our model of construction. Unfortunately the permission of sampling new materials and to export them in a sufficiently equipped laboratory is not yet accepted.

Obsidian tools

AMS measurements of the organic material (mainly charcoal) surrounding obsidian tools found in the strata of the excavation performed in the region of Mersin-Yumuktepe (South of Turkey) give a very good estimate of the period (6000-7000 BC) of use of these tools (8). Elemental maps for all major elements using the CEDAD PIXE microprobe indicate a sharp increase of Si and other major and minor components

on a distance of more than 200 microns from the edges of these tools. On the other hand, no decrease of some other observable element has been observed in the PIXE maps. One example is given in figure 8. This increase cannot be attributed to some shadow effect in the detection procedure of the low energy K-lines of Si but could be due to the presence, at surface, of light elements like C, N and O whose analysis was not possible by PIXE. The Microprobe investigation using incident deuterons or ^{3}He to induce nuclear reactions on these light elements is in project. The analysis of those elements would help our interdisciplinary team to understand the use of these tools.

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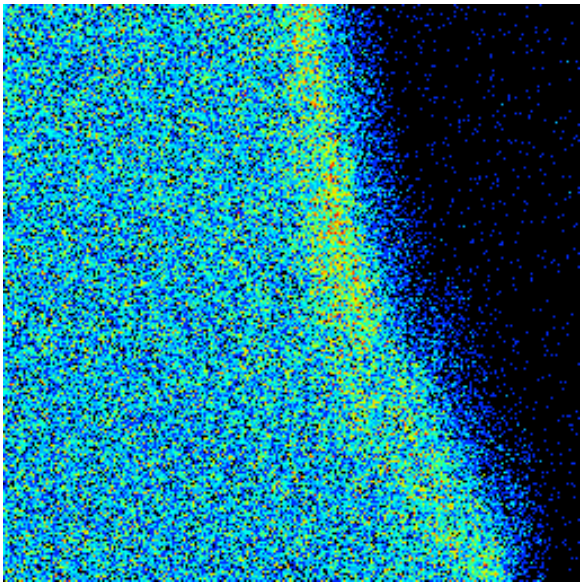

Figure 8: The Si map obtained with the PIXE microprobe of CEDAD (size of the map : 500 µm x 500 µm).
Yellow for high concentration, blue for low concentration.

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