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PIXE Analysis of Artifacts from Radiocarbon Dated Archaeological Contexts

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Abstract. A set of obsidian rock samples from the archaeological site of Mersin-Yumuktepe, Turkey, were submitted to PIXE-PIGE analyses at CEDAD, the AMS-IBA facility of the University of Salento, Lecce, Italy. Paired ^{14}C-AMS analyses performed on organic materials associated with the rock samples were used to obtain an absolute reference chronological framework. The analyses led to the separation of the samples in two compositional groups and to the identification of the sources of the raw material.

Keywords: PIXE, PIGE, Cultural Heritage, Accelerator Mass Spectrometry, Radiocarbon dating

INTRODUCTION

In recent years accelerator-based analytical techniques have achieved an important role in the field of Cultural Heritage diagnostics as testified by the increasing number of accelerator-based facilities having an intense research activity in the field of archaeometry [1-3].The two main areas where the major contribution of nuclear-based techniques can be recognized are, with no doubt, AMS (Accelerator Mass Spectrometry) radiocarbon dating and analysis of materials by mean of IBA (Ion Beam Analysis) methods [4]. The availability at CEDAD (Centro di Datazione e Diagnostica) at the University of Salento, Lecce, Italy of an accelerator equipped with beam lines for AMS ^{14}C dating and IBA analyses has given the possibility to explore the potentialities resulting from the combined application of the two techniques in the same archaeometric problem. In particular we will show the results obtained in the PIXE (Particle Induced X-Ray Emission) and PIGE (Particle Induced Gamma Ray Emission) analysis of obsidian rocks recovered in neolithic levels of the archeological site of Mersin-Yumuktepe, Turkey. The ages were determined by mean of ^{14}C-AMS analyses performed on associated organic materials.

THE CEDAD ACCELERATOR BASED FACILITY

The CEDAD is a multidisciplinary research facility devoted to the development and the application of nuclear-based methods in different research fields such as cultural heritage diagnostics, environmental, material and Earth sciences [5]. The center is based on a 3 MV 4130HC Tandetron^{TM} accelerator, manufactured by High Voltage Engineering Europa B.V., and equipped with five experimental beam lines for: AMS (Accelerator Mass Spectrometry) radiocarbon dating, high energy ion implantation, in vacuum and in air IBA (Ion Beam Analysis) and μ-PIXE.

The AMS Beam Line

The accelerator mass spectrometry ^{14}C dating beam line is in operation at CEDAD since 2003 and a detailed description of its features is reported elsewhere [5]. The AMS spectrometer is essentially constituted by a Cs sputtering ion source (HVEE 846B), a low energy sequential injector and a high energy mass spectrometer. A 20-30 μA, 35 keV C^- carbon beam, extracted from a 2 mm large solid graphite cathode in the ion source, is energy and mass

analyzed in the low energy mass spectrometer before being injected into the accelerator where it is accelerated by a 2.5 MV terminal voltage towards the high energy spectrometer. Along the high energy spectrometer the most abundant 3^+ charge state is selected and the 10 MeV carbon ions are analyzed by a 110°, double focusing magnet. $^{12}C^{3+}$ and $^{13}C^{3+}$ beam currents are then measured by two Faraday cups while the $^{14}C^{3+}$ ions are further energy and mass analyzed by a 33° electrostatic deflector and a 90° magnet before being counted in a gas ionization detector. The system has shown, over the years, reproducible precision levels of 0.3%–0.4% and 0.05%–0.1% on the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ determinations, respectively, reaching in 2006 a total sample throughput of ~1000 measured samples [6].

The external beam set-up at CEDAD

In the low energy side of the system a multipurpose injector, formed by two ion sources (a HVEE Mod. 358 Duoplasmatron ion source and a HVEE mod. 860A sputtering ion source) and a 90° analyzing magnet are used to produce and inject into the accelerator the ion beams to be used in the IBA and ion implantation beam lines. In particular protons and He beams are produced in the 860 source by sputtering of TiH cathodes and in the Duoplasmatron source, respectively. A detailed description of the external-beam set up has been given elsewhere [7]. The beam in firstly collimated in vacuum by mean of a 2 mm graphite nozzle and then extracted in air through an extraction window (typically a 8 μm tick Kapton foil) . The X-Ray detection apparatus is formed by two detectors: a Si(Li) SSL 30150 Canberra detector (active area 30 mm^2) and a Si(Li) Mod. 80160 Canberra (active area 80 mm^2) detector optimized for the detection of low (≤ 7 keV) and high energy X-Rays (≥ 7 keV), respectively. The PIGE analyses are performed by mean of a GC6022 Ge detector from Canberra.

PROVENEANCE STUDIES OF THE OBSIDIAN TOOLS FROM MERSIN YUMUKTEPE-TURKEY

As an example of the potentialities given in archaeological investigations, by the combination of AMS ^{14}C-dating and IBA methods, we report on the PIXE-PIGE analyses performed on a set of obsidian artifacts recovered in ^{14}C dated archaeological contexts. Aim of the study is to identify the sources of the raw material and to reconstruct the chronological evolution of their exploitation.

Obsidian is a natural glassy volcanic rock produced during the rapid cooling of lava with a high silicon content (SiO_2 content higher than ~ 65 wt %). Obsidian was widely used from the end of the Paleolithic to the Bronze age, when it was gradually replaced by metals, for the production of both artifacts of every day use and luxury objects. Obsidian was, thus, a precious raw material testifying long distance (sometimes several thousands kilometers) trades and exchanges whose reconstruction is of a fundamental importance for archaeologists. Thus the identification of the geological sources of the raw material by mean of physico-chemical analyses is a very active research field since a long time [8].
In particular in the Mediterranean and Near East several sources have been identified and compositionally characterized around Italy (Lipari, Pantelleria, Sardinia, Palmarola), Turkey, Iran and Armenia [9-11].
From the experimental point of view, several different techniques have been used for the compositional characterization of obsidians such as ICP-AES (Inductively Coupled Atomic Emission Spectrometry), ICP-MS (Inductively Coupled Mass Spectrometry), NAA (Nuclear Activation Analysis) and XRF (X-Ray Fluorescence). More recently several studies have explored the potentialities of IBA-based methods in this field. In particular the possibility given by a combined PIGE-PIXE approach to determine both light (F, Na, Li, Al, Si, B), by PIGE, and heavy (Cl, K, Ca, Ti, V, Mn, Fe, Zn, Ga, As, Rb, Sr, Y, Zr), by PIXE, element concentrations in an external beam mode without any sample processing and in a non destructive way can be regarded as the crucial advantages of the methods [12-14]. Here we present the results of the PIXE-PIGE analysis of obsidian tools recovered in Neolithic levels in the archeological site of Mersin-Yumuktepe, Southern Turkey (Figure 1), one of the most important archaeological sites in the near East showing an unbroken stratigraphy spanning more than 8000 years from the Early Neolithic to the Middle Age [15].

FIGURE 1. Map of Anatolia.

Sample Selection and chronological framework

A set of 27 obsidian tools, recovered during the excavations performed by the Italian Archaeological mission in Mersin-Yumuktepe were submitted to PIXE-PIGE analyses at CEDAD in order to obtain information about the provenance of the raw material.
At the same time 9 organic samples, charcoal and bones, were submitted to ^{14}C-AMS analyses. The selected samples allowed to obtain an absolute age for different excavated contexts from the end of the 7th millennium BC (Middle Neolithic) to the 11th-12th century AD (Byzantine Age) (Figure 2). In particular all the studied obsidian samples were selected from contexts Early-Middle Neolithic levels for which the ^{14}C analyses gave a calibrated age between the second half of the 7th millennium BC (Sample YT EBA61h: 6269-6016 cal BC) and the first half of the 6th millennium BC (Sample YT03 E6d1: 5903-5645 cal BC).

PIXE-PIGE Experimental

The obsidian samples were irradiated in air by using 3.7 MeV protons, extracted in air through a 8 μm thick Kapton foil and impinging perpendicularly on the sample surface. The beam current and the spot size were ~ 1 nA and 2 x 2 mm, respectively. In order to attenuate the contribution of low-energy X-Rays a "funny" 100 μm thick polyethylene collimator with a 1 mm hole 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 .
The use of 3.7 MeV allowed to have protons impinging on the sample surface, after crossing the Kapton exit window and the ~1 cm in air, at an energy of ~ 3.5 MeV as obtained by the SRIM2003 (Stopping and Range of Ions in Matter) code. This beam energy was chosen in order to: i. increase the sensitivity for trace elements as the results of higher PIXE cross sections; ii. be above the resonance at 3.1 MeV for the reaction ^{28}Si(p,p'γ)^{28}Si resulting in the possibility to detect silicon by PIGE using the 1778 keV gamma line [14,16]. Obsidian samples already measured by LA-ICP-MS (Laser Ablation Inductively Coupled Plasma-Mass Spectrometry) at the Centre de Recherches Ernest Babelon, Orléans, France and by micro-PIXE and PIGE at the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary were used as reference standard [17]. In particular a sample from Lipari Islands (Italy) and From Erdöbénye, Tokaj Mountains were used for the present study.

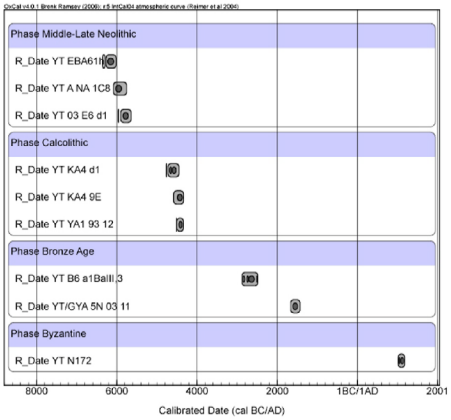

FIGURE 2. AMS radiocarbon dating results in calibrated, calendar ages.

PIXE-PIGE Results

In Figure 3 typical PIXE and PIGE spectra are shown (Sample 14). Eleven elements: K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Y, Zr and Nb were determined by PIXE and four elements: F, Na, Al and Si were determined by PIGE.

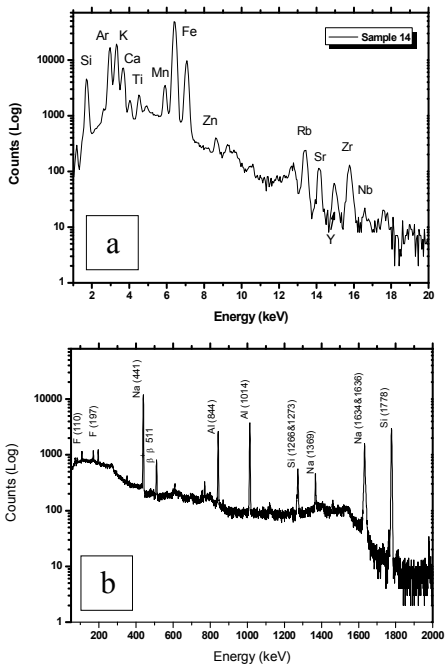

FIGURE 3. Typical PIXE (a) and PIGE (b) spectra obtained on one of the analyzed samples (Sample 14). Gamma ray energies between brackets are expressed in keV (E_{proton} = 3.7 MeV).

The Na, K and Si concentrations were then used to petrografically classify the samples according to the TAS diagram (Figure 4): all the studied samples can be regarded as rhyolite. The analysis of the binary Sr-F diagram (Figure 5) clearly shows that the samples can be distinct in two geochemical groups (Group 1 and 2).

For the identification of the two sources the Sr-Zr diagram and the comparison with published data for the known obsidian sources in Anatolia has been used (Figure 6) [9, 11, 17]. The diagram shows that the samples belonging to the group 1 and 2 can be attributed to the East Göllü Dag and Nenezi Dag sources, respectively.

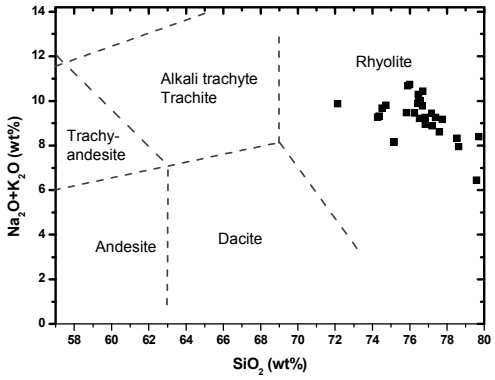

FIGURE 4. Position of the studied samples in the TAS diagram.

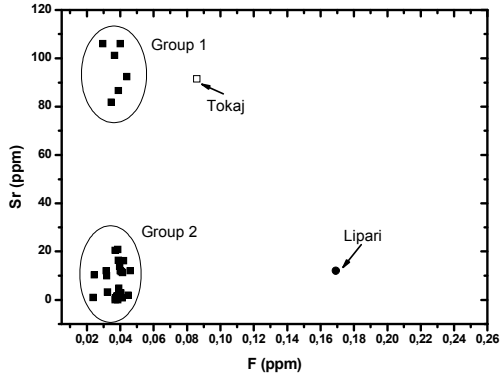

FIGURE 5. Distribution of the studied samples in the Sr-F diagram.

CONCLUSIONS

A set of 27 obsidian samples from the archaeological site of Mersin Yumuktepe, Southern Turkey were analysed by PIXE and PIGE. The samples were all selected from Neolithic levels dated by ^{14}C-AMS analyses to the 7th-6th millennium BC. The PIXE-PIGE analyses showed to be fully capable in the identification of two compositional groups in the analyzed rocks corresponding to two sources of the raw materials identified by the comparison of the obtained data with published data for known obsidian sources in Anatolia.

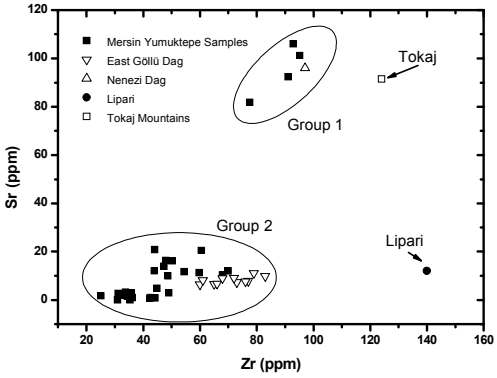

FIGURE 6. Distribution of the studied samples in the Sr-Zr diagram.

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