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Study of archaeological samples via neutron techniques

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Summary. — The discovery of ancient artefacts and artworks usually raises a variety of questions such as the correct determination of their historical and cultural timeframe, the place and method of production, the choice of treatments and conditions for restoration and preservation. In the field of archaeometry, new perspectives are opened up by the use of neutron techniques. Results on a selection of archaeological samples, Etruscan bronzes coming from the *Museo Nazionale di Villa Giulia* and Roman marbles from *Villa Adriana* (*Tivoli*, Rome), are presented. ANCIENT CHARM project aims to develop a quantitative 3D imaging technique. This work presents some of results on a series of experimental investigation performed on test samples called "Black Boxes". Elements' and compounds' identification on the internal features of the boxes are obtained by the combined use of different neutron analysis methods. The presented studies successfully showed the high potential of neutron techniques in the study of ancient archaeological artefacts.

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The discovery of ancient artefacts and artwork usually raises a variety of questions such as the correct determination of their historical and cultural timeframe, the place and method of production, the choice of treatments and conditions for restoration and preservation.

In the field of archaeometry, new perspectives are opened up by the use of neutron techniques. Neutron is a very suitable means for the collection of information from the bulk of large cultural-heritage objects. In fact neutrons penetrate through objects without substantial attenuation, a property that makes them ideal for non-destructive testing.

Information on the artefacts is relative to composition, presence of alteration, crusts, inclusions, structure of the bulk, typology of the location of materials extraction, manufacturing techniques, refractoriness, porosity, firing temperature. Provenance and state of conservation of ancient objects are of key importance to address matters of attribution and restoration of archaeological objects.

A recent preliminary application of neutron techniques in the cultural-heritage field is a neutron diffraction study of marbles from *Villa Adriana* in *Tivoli* (Rome) [1, 2]

Fig. 1. – View of Villa Adriana site, Tivoli, Rome, Italy.

(see fig. 1). *Villa Adriana* is an exceptional complex of classical buildings designed and erected in the 2nd century AD by the Roman emperor Hadrian, and is recorded by the UNESCO in the World Heritage List. Analytical investigations on monumental complexes of the Roman Empire age complement the studies carried out on architectural and building engineering in order to achieve unitary views on this historical period. In this context, neutron diffraction techniques have been used for the characterisation of ancient Roman marble fragments from the *Edificio con Tre Esedre* palace, located in *Villa Adriana*. The marble decorations were built with a technique known as *opus sectile*, typical of Hadrian's time, with wall decorations belonging to the 2nd century AD. A reconstruction of the Palace's marble wall decoration positioning is shown in fig. 2. Fragments of such decorations (used as samples) are shown in fig. 3. Marble is one of the most common stones used for monuments, statues and other objects of archaeological interest and is typically composed of either calcite or dolomite or a combination of the two. The ongoing study aims at distinguishing different marble types on the basis of the mineral phase compositions and the crystallographic textures. Information obtained can be used to distinguish different types and hopefully identify the origin of the different marbles. The diffraction experiments on marbles were performed on the Time-Of-Flight (TOF) diffractometers GEM, INES and ROTAX located at ISIS Neutron Spallation source (UK). The use of multi-detector TOF neutron diffractometers allows us to perform quantitative analysis on stationary samples in a reasonably short time (from a few minutes to a few hours according to instrumentation and sample characteristics). This technique has many advantages: a stationary experimental set-up to collect a complete diffraction pattern can be used, objects of variable shapes or sizes can be illuminated

Fig. 2. – Reconstruction of the marble wall decoration of the Palace *Edificio con Tre Esedre*.

without prior preparation, and composition and preferred orientation or texture effects are easily recognised. Multi-phase and multi-bank analyses of the diffraction patterns were carried out with standard crystallographic public-domain software (GSAS [3] for quantitative phase analysis and MAUD [4] for texture analysis). An example of experimental data for marble 11, together with the final GSAS Rietveld refinement is shown in fig. 4.

The texture information is displayed in pole figures. Pole figures are the "maps" of the crystal grains orientations, caused in marbles by geological processes, and can be used as a fingerprint to identify them. In fig. 5 a sketch of a pole figure reconstruction from the diffraction measurements for marble fragments is shown. Pole figures indicate deviations from a random crystallite orientation distribution (*e.g.*, in sample n. 17).

Another recent application of neutron techniques was performed on bronze samples (figs. 6 and 7) coming from the *Museo Nazionale di Villa Giulia*, Rome, Italy. Non-destructive Neutron Diffraction (ND) on VIII century BC laminated Etruscan bronzes was performed with the aim of collecting information related to the main composition of the artefacts, the presence and nature of alterations or inclusions and the bulk structure. The experiments were carried out at ISIS spallation neutron source. The bronze vases are part of an Etruscan collection discovered in the necropolises of *Osteria-Poggio Mengarelli* and *Cavalupo* in the outskirts of Vulci (Viterbo, Italy).

The samples, 14 fragments, were analysed with regard to chemical-phase compositions and corrosion products. Bronze is composed of copper, tin (Cu, 85–95%, Sn, 5–15%) and small quantities of other metals. The determination of the exact copper/tin/lead relative composition provides important information on the working process and technologies adopted and, indirectly, on the authenticity of the artefacts. Furthermore the presence of other components, like corrosion products, is linked to the past environment and to the

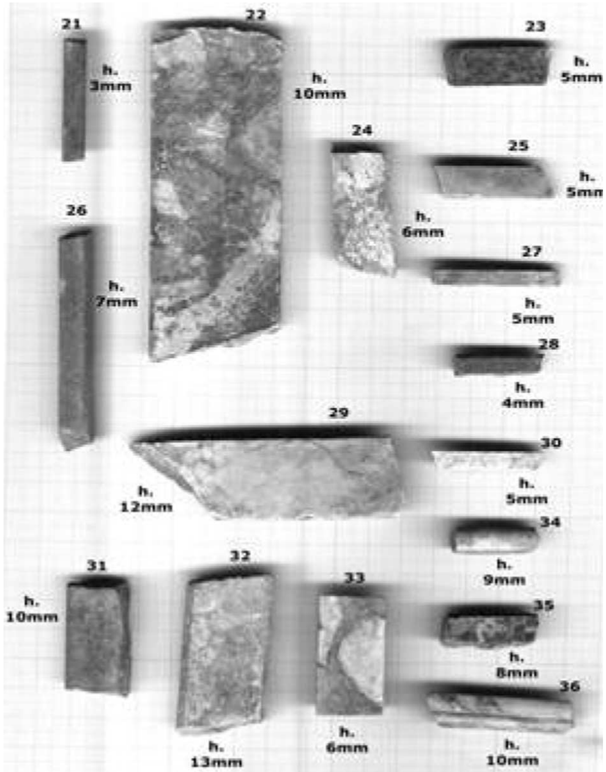

Fig. 3. – Marble fragments coming from Villa Adriana site.

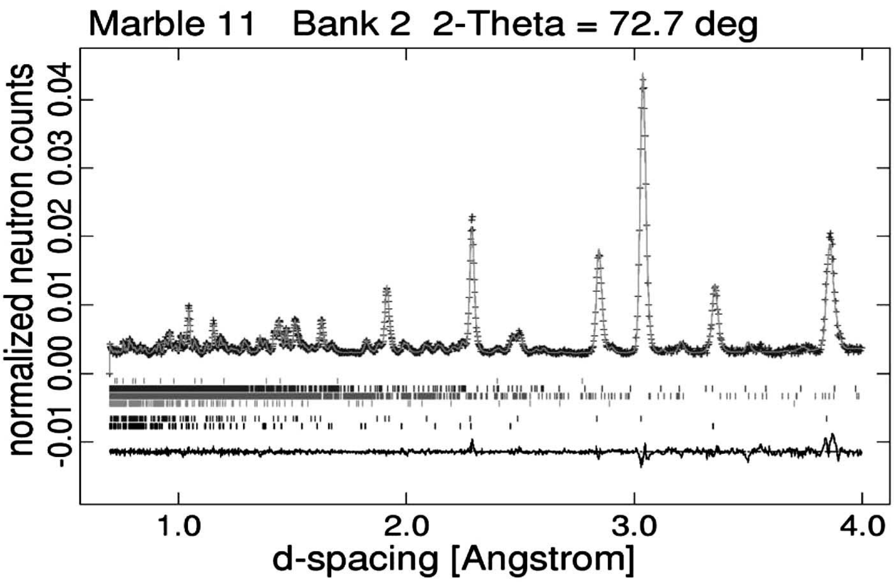

Fig. 4. – Example of final GSAS Rietveld refinements plot for one of the marble samples (no. 11).

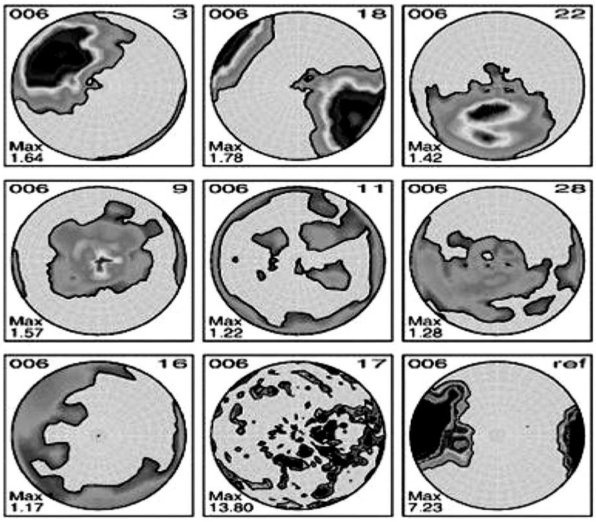

Fig. 5. – Marbles from Villa Adriana: texture reconstruction along the (006) axis. Pole figures. Samples n. 3, 18, 22, 9, 11, 28, 16, 17.

physical and chemical events that transformed the object into a partially corroded matrix (*e.g.*, burial environment or exposure to the atmosphere, marine conditions and laboratory environment) [5]. An example of experimental data for bronze samples, together with the final GSAS Rietveld refinement is shown fig. 8.

Results obtained from ND investigation of objects show that 60% to 95% by weight is uncorroded alloy that presents a composition ($Cu = 90 \pm 4\%$) which is typical of low-tin

Fig. 6. – Etruscan bronze cup coming from Museo Nazionale di Villa Giulia.

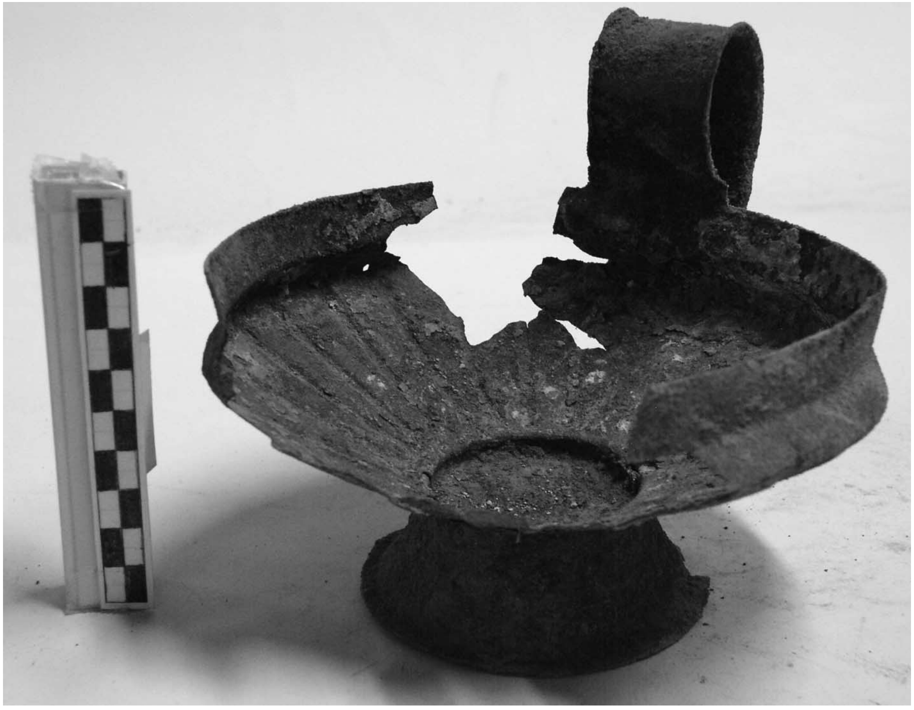

Fig. 7. – Etruscan bronze vase coming from Museo Nazionale di Villa Giulia.

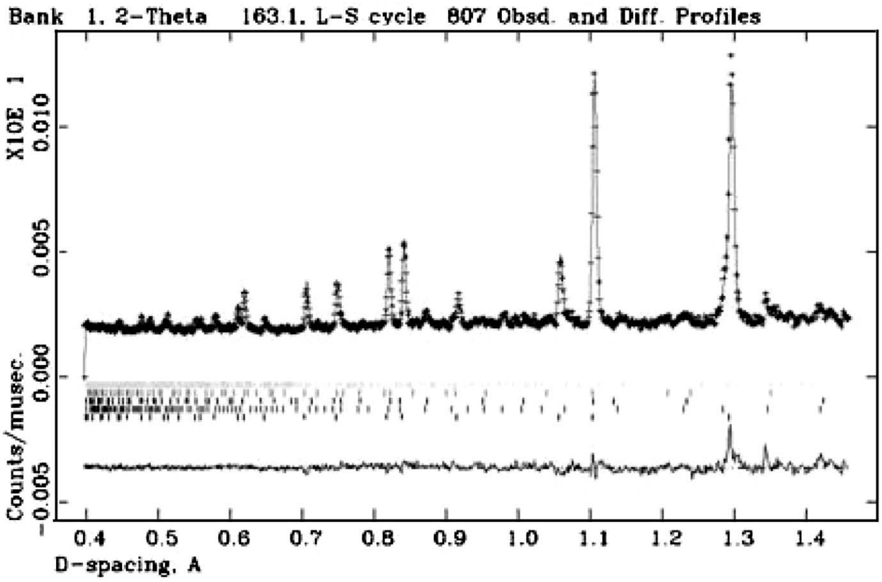

Fig. 8. – Example of final GSAS Rietveld refinements plot, sample no. 6, detector bank no. 1 at $2\theta = 163$. Components: bronze (Cu/Sn), cuprite (Cu_2O), lead, tenorite (CuO), nantokite (CuCl).

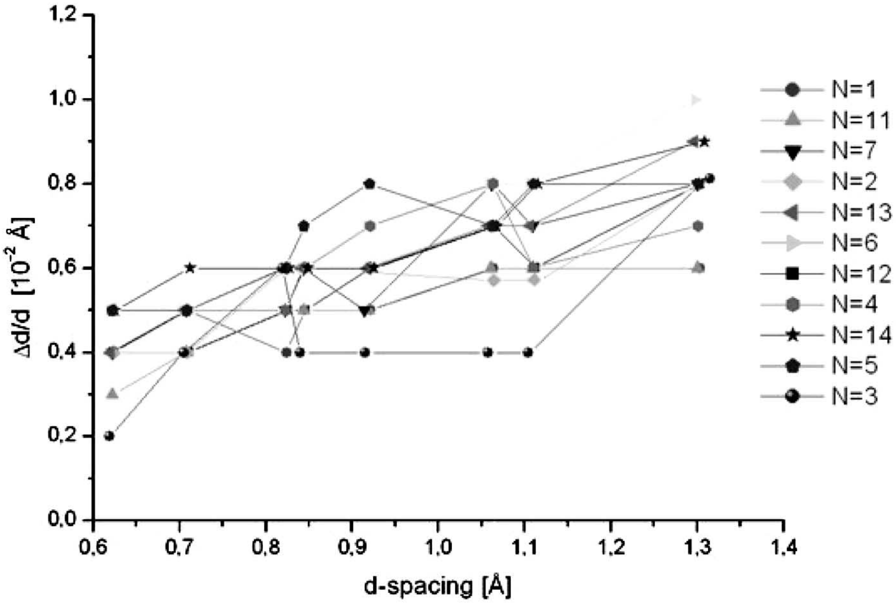

Fig. 9. – Relative variation of the bronze-Bragg peak width for the different samples.

ancient bronzes, thus supporting the authenticity of the samples. ND measurements also provided information about working methods of bronzes through the analysis of relative bronze peaks width $\Delta d/d$ as a function of d-spacing (see fig. 9): annealing and two different types of cooling dynamics (fast and slow) are present while hammering could also be present. Furthermore ND data analysis showed that the combination of corrosion products in the single samples is in agreement with possible environmental conditions in which the objects were in contact. Most of the samples were buried. Some of these were in contact with salted water. This could come from seawater percolation or simply salted food contained in the vases. Additionally it has been possible to trace probable quantitative values for the concentration of certain environment components such as CO_2 and NaCl present in the tombs.

In this context ANCIENT CHARM (Analysis by Neutron resonant Capture Imaging and other Emerging Neutron Techniques: new Cultural Heritage and Archaeological Research Methods) is a research project funded by the European Commission under the "New and Emerging Science and Technology" programme. The aim of the project is to develop non-invasive 3D tomographic imaging of the elemental and phase composition based on established neutron techniques as Neutron Resonant Capture Analysis (NRCA), Prompt Gamma Activation Analysis (PGAA) and Neutron Diffraction (ND) [6] for cultural heritage.

In order to develop a protocol with the aim of combining Tomography, Prompt Gamma Activation Analysis (PGAA) and Neutron Diffraction (ND) data collected on the same archaeological object, test samples of varying complexity were constructed and analysed by the different neutron methods. Two series of closed and sealed "Black Boxes" have been constructed by Bonn University, Germany and by the Hungarian National Museum. The first set consists of ten hollow aluminium cubes of 40 mm edge length that

TABLE I. – *Results coming from prompt gamma activation analysis (PGAA) measurements (a) and from neutron diffraction (b). The numbers identificate the zone of neutron irradiation and are the same of fig.* 10 *(a,b).*

a)

1	Cu, **Fe**, Na, Cl, Ca, Si	**6**	**Fe**, Na, Cl, Si, Ca
2	Cu, Fe, Na, Cl, **Al**, Si, Ca	7	**Fe**, Na, Cl, Ca, Si
3	**Cu**, Na, Cl	**8**	**Fe**, Na, Cl, Ca, Si
4	**Cu**, Na, Cl	**9**	**Cu**, Na, Cl
5	Na, Cl, **Al**, Si, Ca	**10**	**Cu**, Na, Cl

b)

1	NaCl, Cu-type=fcc: steel (Fe) or copper (Cu)
2	Fe-type=bcc: ferrite + cementite, in calcite+quartz
3	NaCl, small fcc peaks
4	calcite ($CaCO_3$), quartz (SiO_2) („failed shot")
5	NaCl
6	calcite (75 wt%), quartz(25 wt%)

contain 2D or 3D arrangements of materials that are relevant for archaeological samples. The second set consists of similar pieces yet made of iron and with edge length of 50 mm. The inner composition and the distribution of the filling materials were initially known exclusively by the creators. The aim of such "blind" investigations is to assess potentialities and limitations of each technique and the effects of technique combinations [7].

In fact ND provides information about compounds while PGAA about elements. The combination of both techniques gives a good picture of the inside of the objects. As an example table I a,b reports the ND and PGAA results on Bonn Al4 "Black Box" (fig. 10).

The final interpretation of the resulting data is that the box is divided into two parts with different filling materials: salt (NaCl) and clay consisting of quartz (25 wt% SiO_2) and calcite (75wt% $CaCO_3$). The objects in the two chambers are made of different materials: two of these are made of a f.c.c.-structure of Cu-type and two of a b.c.c. lattice specifically made of ferrite (Fe). Therefore, the main components are identified by TOF-ND. PGAA is required to unambiguously detect the f.c.c.-material by providing the elements it is made of. The clay is composed by two main components which were identified with approximately the correct proportions, also an extra phase (the cementite) was observed in the ferrite.

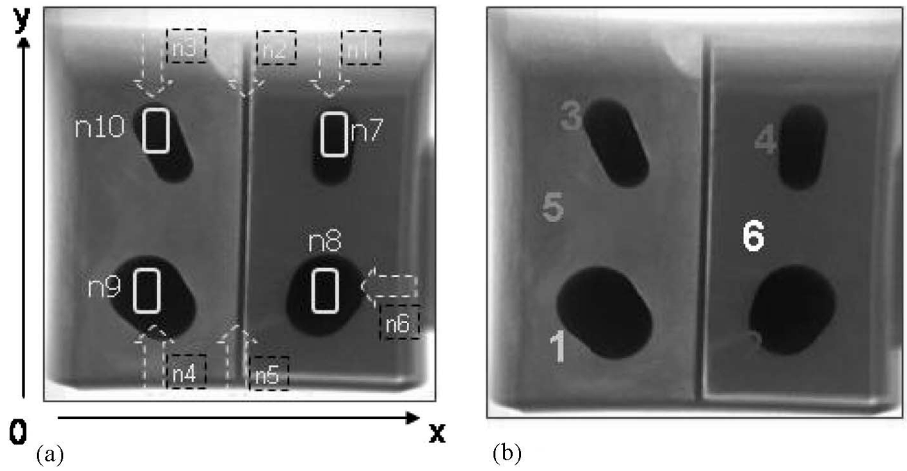

Fig. 10. – X-ray radiographies of test sample (Al4 "Black Box"). There are evident the points of irradiation during the different measurements: (a) prompt gamma activation analysis, (b) neutron diffraction. The numbers of the points are the same of table I (a,b).

The study was completed through the identification of the spatial distribution of the internal objects in the "Black Boxes" via X-ray radiography and neutron tomography.

Conclusions

Neutron techniques are very suitable for non-destructive investigation of bulky archaeological samples. With regard to such diverse objects interesting results were observed.

Marbles and stones coming from *Villa Adriana* were studied via ND obtaining compositional and textural information related to the geological characteristics.

Etruscan bronzes coming from the *Museo Nazionale di Villa Giulia* were analysed with the aim to determine the corrosion products which are directly related to conservation environment, alloy composition and working methods.

Studies on test samples ("Black Boxes"), within the Ancient Charm European research project, were performed. These studies successfully showed the high potential of neutron techniques in the study of ancient archaeological artefacts.

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REFERENCES

[1] Filabozzi A., Pietropaolo A., Andreani C., De Pascale M. P., Gorini G., Kockelmann W. and Chapon L. C., *Nuovo Cimento C*, **29** (2006) 252.

[2] Filabozzi A., Andreani C., De Pascale M. P., Gorini G., Pietropaolo A., Perelli-Cippo E., Senesi R., Tardocchi M. and Kockelmann W., *J. Neutron Res.*, **14** (2006) 55.

[3] Larson A. C. and Vondreele R. B., *GSAS: Generalized Structure and Analysis Software*, http//www.ccp14.ac.uk.

[4] Lutterotti L., *MAUD.: Material Analysis using Diffraction*, http://www.ing.unitn.it/∼luttero/maud/index.html.

[5] Festa G., Caroppi P. A., Filabozzi A., Andreani Carla, Arancio M. L., Triolo R., Fabrizio Lo Celso, Benfante V. and Imberti S., *Composition and corrosion phases of Etruscan Bronzes from Villanoviano Age*, in *Measurements Science and Technology*, **19** (2008).

[6] Gorini G. and Ancient Charm Collaboration, *Nuovo Cimento C*, **30** (2007) 47.

[7] Kasztovszky Zs., Kis Z., Belgya T., Kockelmann W., Imberti S., Schooneveld E. M., Festa G., Filabozzi A., Andreani C., Kirfel A., Biró K. T., Dúzs K., Hajnal Zs., Kudejova P., Tardocchi M. and the Ancient Charm Collaboration, *Promt Gamma Activation Analysis and time of flight neutron diffraction of 'Black Boxes' in the 'Ancient Charm' project*, *12th International Conference on Modern Trends in Activation Analysis (Sep. 16-21 2007), Tokyo Metropolitan Univ., Hachioji-shi, Tokyo, Japan.*