DISCOVERING NEW INFORMATION FROM HISTORICAL ARTEFACTS USING ELECTROMAGNETIC RADIATION AND CHARGED PARTICLES AS A PROBE

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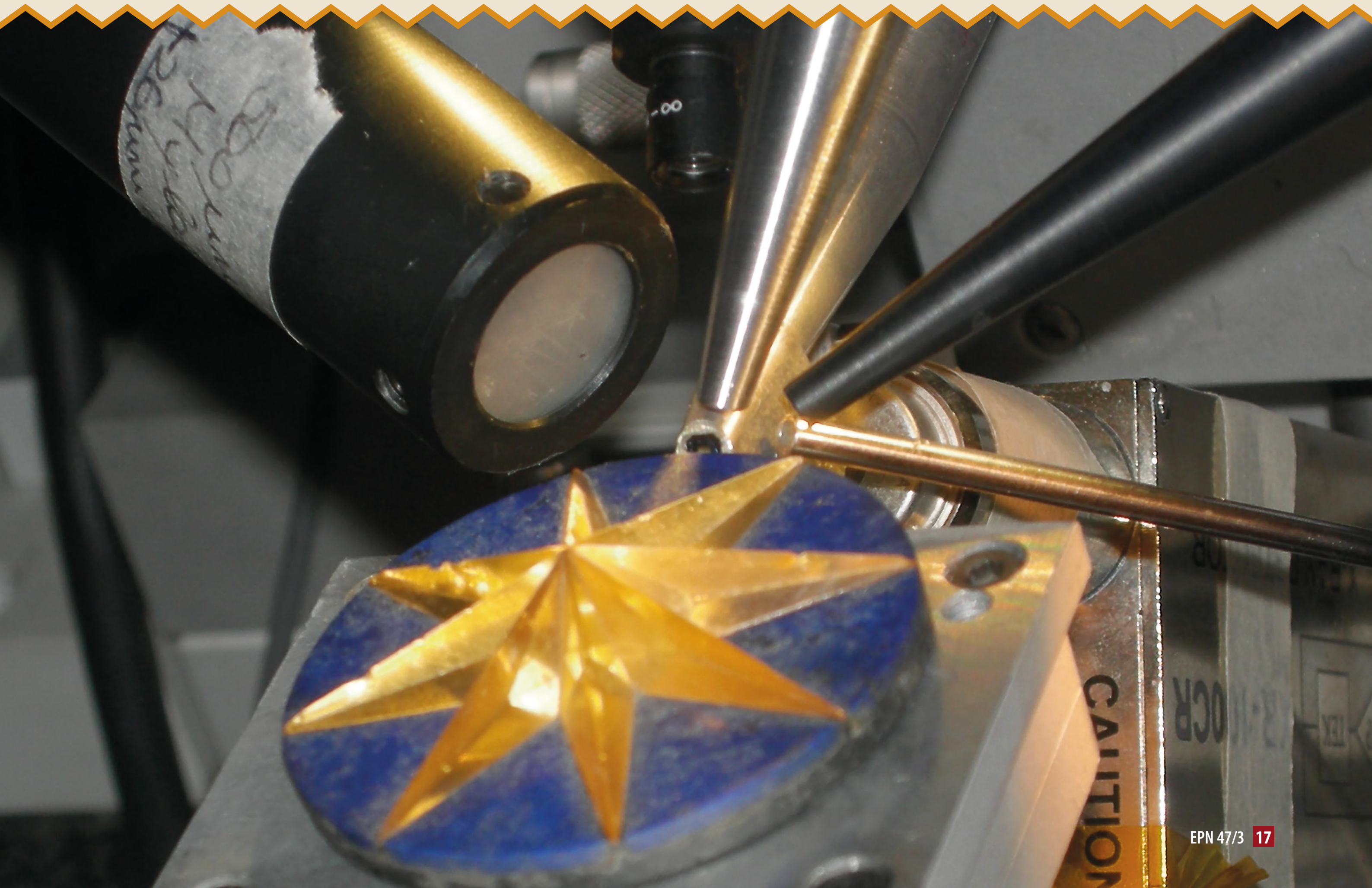
Archaeological artefacts included in cultural heritage contribute to the knowledge of our roots, which may help us to learn about our future. Although the connection between ancient times and nuclear technology seems farfetched, this paper will try to show how nuclear radiation of various kinds can be irreplaceable in the elemental composition analysis of an archaeological find.



The first steps and the present days

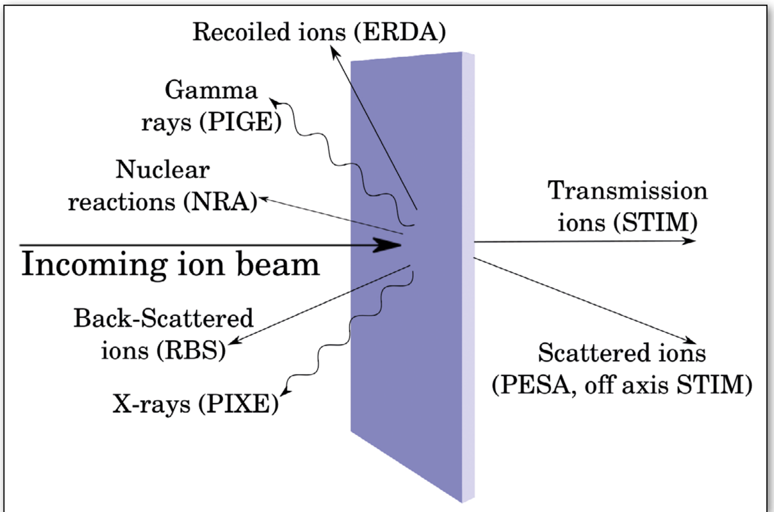
Scientific methods in archaeology and art began to be systematically applied in the late eighteenth century by the German scientist Martin Heinrich Klaproth (1743–1817), who published the first-ever quantitative analysis of an alloy of some Greek and Roman metal coins. Much later, in the early 1960s, various types of ion beam analyses (IBA) were developed and put into routine use. Further developments of IBA-based analytical methods were related to progresses in low-energy accelerators, in detectors for particle, X-ray and γ-ray and in systems for processing experimental data [1].

Ion beams of several MeV, produced by small accelerators, penetrate into matter, interact with the atoms of the sample and produce, among other phenomena, X-rays and γ-rays, which carry information about the investigated artefact. The small accelerators can provide a wide range of ion beams (protons, alphas and heavy ions), with flexible energy range (and thus adjustable probed depth) and diameter of the beam (from millimetre to micron size). They can thus provide tailored tools for the study of the diverse objects of Cultural Heritage.

Nuclear analytical methods successfully applied in archaeometry

Archaeometry involves non-invasive surveys of the terrain, science-based dating methods and analytical techniques for object characterization. Nuclear physics contributes significantly to the dating methods (radiocarbon dating) and to analytical methods with techniques sensitive to practically all the elements of the periodic table and capable of reconstructing the spatial distribution of the elements present in the sample [2, 3].

It should be emphasized that applications of nuclear analytical methods on the cultural heritage have recently been collected for a new, topical paper published by the Nuclear Physics Board of the European Physical Society publication, of a few highlights of which we would like to present here.



▼ **FIG 1:** A schematic description of ion elastic and inelastic ion collisions with solid matter inducing different phenomena. Their products are elastically scattered ions and/or elastically recoiled light nuclei, X-rays produced in ion inelastic collision with the target atoms, and products of nuclear reactions.

How ion beam methods work

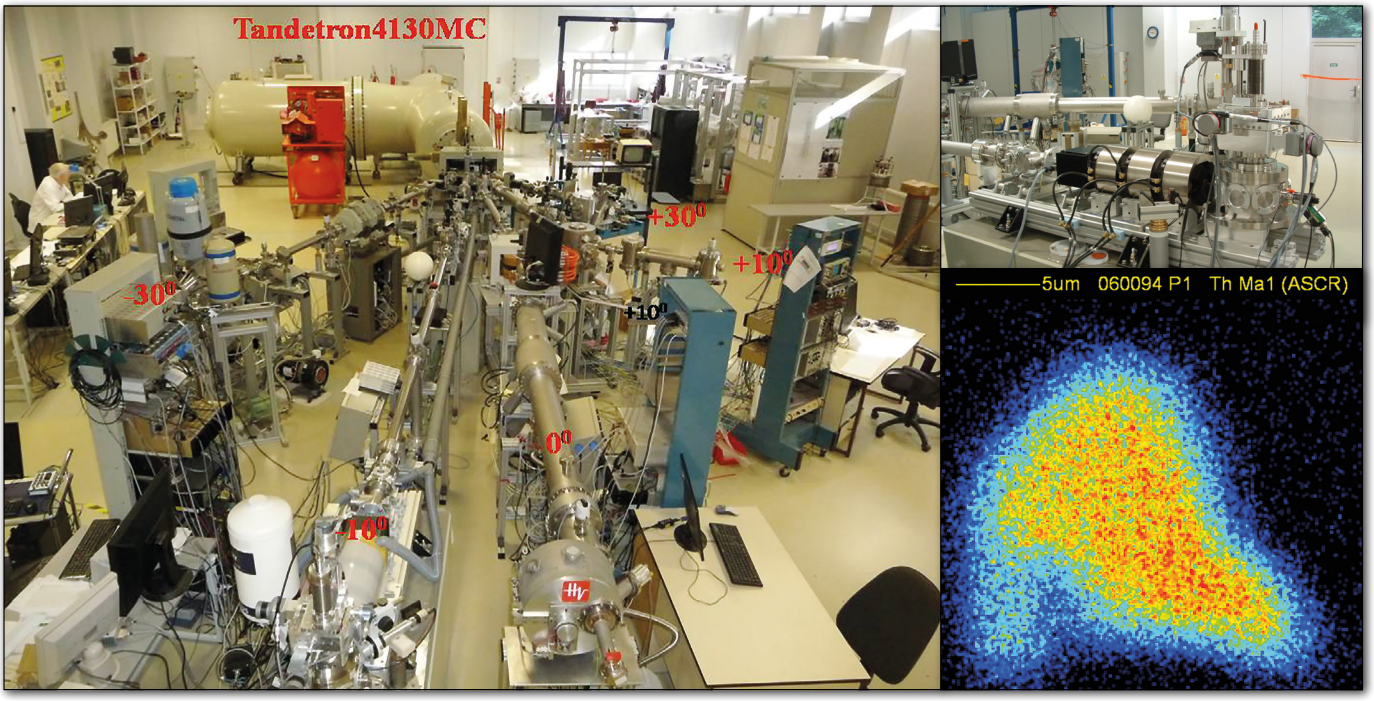
Rutherford backscattering spectrometry (RBS) is an analytical non-destructive method which is based on the measurement of the energy spectra of MeV ions (protons, He^+, Li^+, or heavier ions) elastically scattered from solid samples [2, 3]. From the analysis of the backscattered particles' energy distribution it is possible to determine the elemental amounts in the sample and their depth distributions.

When ions and matter interact via nuclear reactions, charged particles and/or γ-rays are produced (see Figure 1). The **Nuclear Reaction Analysis** (NRA) technique is based on the study of the energy spectrum of these charged particles and γ-rays. The yield of nuclear reaction products is proportional to the reaction cross sections (which define the probability of each type of interaction) and the density of target atoms in the sample. Most frequently used reactions are (p,α), (d,p), and (d,α), which allow indicating the presence and the concentration of several isotopes typically from ^{1}H to ^{32}S, such as ^{2}D, ^{12}C, and ^{16}O [2-4], just to name a few. Energy loss by the incident ion can be used to determine depth profiles by resonance scanning using a (p, γ) reaction, where γ-rays are detected. **Particle-Induced Gamma Emission** (PIGE) is based on nuclear reactions, most typically (p, γ), induced in specific isotopes. The energy of the γ-ray lines indicates the elements, while the intensity is related to their concentrations.

Particle-Induced X-ray emission (PIXE) exploits X-ray emission for elemental analysis [2, 3]. The energy of a peak in the X-ray spectrum is specific for a particular element, and its intensity is proportional to the elemental concentration. PIXE has a very low detection limit, down to several ppm in standard practice.

A big technological progress was made after the **ion microbeam** development. In a microbeam, the ion beam from the accelerator passes through a lens (a combination of magnetic quadrupoles with alternated polarities) focusing the high energy ions. The samples are irradiated with an ion beam focused onto a spot that can be as small as a few hundreds of nm in diameter. Standard IBA techniques are used to characterize the irradiated object. By raster-scanning the beam over the sample surface, a 2D or 3D distribution of elements can be determined with nm depth resolution and lateral resolution limited by the size of the beam spot, see Figure 2 [4, 5, 6].

Some archaeological artefacts cannot be placed in a vacuum chamber because of their large size or the presence of volatile components. Such samples can be analysed using an **external ion beam**. The beam is extracted from the evacuated beam line into air through a thin window, made of thin metal foils, strong plastic materials like kapton, or Si_3N_4. Practically all setups now allow the scanning measurement mode that produces elemental

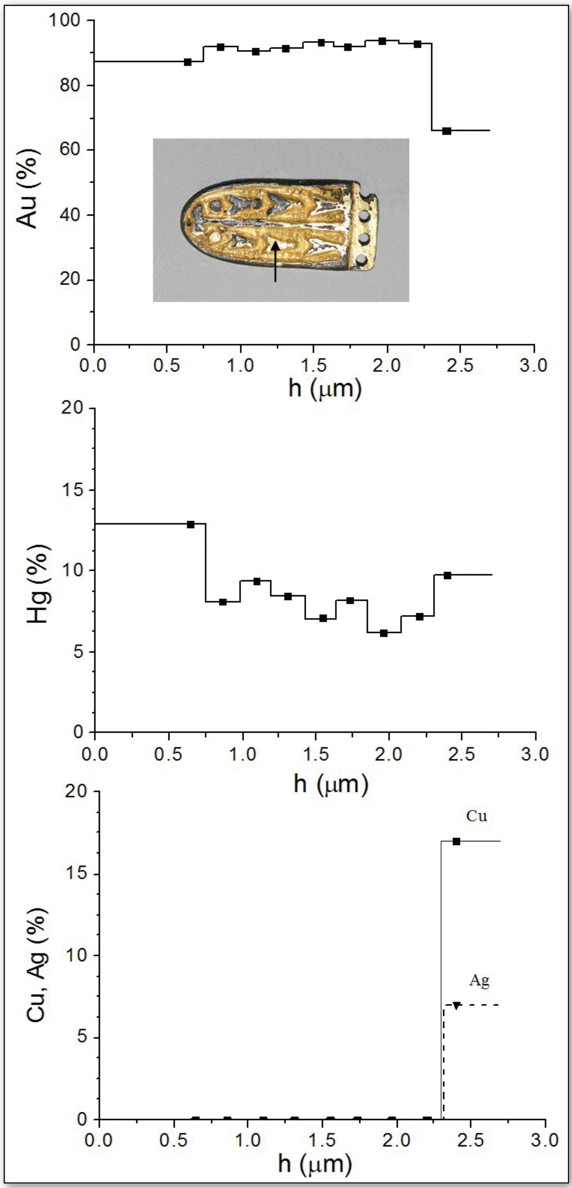


concentration maps. The target is surrounded by an array of detectors. Normally there are at least two X-ray detectors, one with a thin window detector for soft X-rays and a detector with a large solid angle (but equipped with an additional absorber) for hard X-rays. The external microbeam set-up can be improved to be versatile and allows all IBA techniques to be used individually or in combination [6], namely PIXE–PIGE–RBS with protons, PIXE–PIGE–NRA with deuterons, PIXE–RBS with He^{+} ions [1-6].

Examples of the archaeological artefacts analyses

The example of metal analysis demonstrates the identification of the gilding technique, see Figure 3. The object studied comes from the Early Medieval Age, which favoured gilded silver or bronze jewellery. The methods applied were differential PIXE and RBS with in-air proton beam [6]. Differential PIXE is based on the sequential measurement in the same spot such that protons reach different target depths. This is achieved by the variation of the proton incident angle or by the variation of proton energy. The results of the de-convolution procedure are concentration profiles, which can reach up to a few tens of microns below the target surface. Figure 3 shows the elemental concentration profiles of a gilded strap end [7, 8].

▲ **FIG 2:** Typical ion beam lines arrangement at the Tandetron accelerator (Center of Accelerators and Nuclear Analytical Methods NPI CAS, Rez, Czech Republic) with the microbeam facility at -10°. Shown are the ion beam line (left panel), the microbeam vacuum chamber for placing specimen in the upper right corner, and elemental map (Th visualized) of the inclusion in the granitic rocks in the lower right corner.



▶ **FIG 3:** The elemental concentration profiles of the gilded layer on a gilded strap end from the from the Early Medieval Age obtained obtained by differential PIXE; *h* denotes the distance from the surface.

> **Ion beams of several MeV interact with the atoms of the sample and produce X-rays and γ-rays, which carry information about the investigated artefact**

▲ **FIG 4:** An artwork from the 'Collezione Medicea' during IBA analysis carried out at the external microbeam at INFN-LABEC in Florence.

The amount of additional elements (Cu, Hg) in the gold layer undoubtedly reveal the amalgamation gilding technique used.

Examples of elemental composition study of precious stones

PIGE was very efficiently used for light elements and PIXE for medium and heavy elements in qualitative and quantitative analysis of emeralds and garnets, popular among Romans and their barbaric successors. Emeralds contain a known fraction of beryllium, which can be measured either directly or taken into account numerically for the calculation of matrix effects. The provenance sites of the precious stones are certainly of interest as they indicate the extent of trade routes established by the Romans [9, 10] and can be determined via various trace element concentrations in the precious stone. The fluid channels in a set of emeralds excavated in a Roman grave from Slovenia point to a source in Egypt, while emeralds from another grave may be traced to Afghanistan.

Another interesting application is the study of the origin of Lapis lazuli. Lapis lazuli is a semi-precious blue stone widely used for different purposes since the antiquity. However, at present there are still some lacking pieces of information about its trade in ancient times [11, 12, 13]. An external proton microprobe was used, as the external beam allows for non-invasive, multitechnique (PIXE, PIGE and ionoluminescence IL) study of objects of almost any shape and dimension, see Figure 4. For the provenance discrimination the study focused on markers, such as for example the presence or absence of the trace elements in the stone of a specific mineral phase. After this study, some of the markers found on rocks have been successfully used to identify the origin of six precious artworks.

Conclusions

The application of atomic and nuclear techniques in the study of archaeological objects provides a historian or archaeologist with 'material' information that can help in the understanding of the way of life in ancient times. This knowledge is necessary for the testing of the authenticity and provenance of artefacts and for the preparation and implementation of the necessary restoration work. All of these objectives are common to the very large community of people working in the field of archaeometry, *i.e.* the 'application of science to art and archaeology'.

About the Authors

Anna Macková is currently the Head of the Tandetron Laboratory, an instrument responsible for the CANAM (Centre of Accelerators and Nuclear Analytical Methods) infrastructure, a part of the Nuclear Physics Institute of the Czech Academy of Sciences, v. v. i., Czech Republic. She is a nuclear physicist dealing with ion beams of a wide range of masses and energies for the development of new progressive materials, nanostructure deposition and characterization, microbeam applications *etc.* She is an Associate Professor at J. E. Purkynje University.

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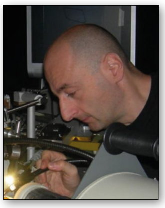

Lorenzo Giuntini is an applied nuclear physicist, one of the founders of the LABEC, the Florence laboratory of the National Institute of Nuclear Physics for the study of cultural heritage and environment by nuclear techniques. He has been the initiator of the Florence microbeam and his main expertises are external microprobe, IBA and XRF. He presently serves as one of the two responsible of the Tandem laboratory in Florence and is associate professor of experimental physics at the University of Florence, Italy.

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