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Stone artefacts and neutrons - Case studies from Hungary

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ABSTRACT

Many archaeometrical studies aim at identifying the provenance of various archaeological finds. For a large group of objects, e.g. for stone artefacts, the chemical composition might be characteristic for the supposed geological source. In the last 20 years, several projects on different scales have been launched, based on the non-destructive prompt-gamma activation analysis at the Budapest PGAA laboratory. Depending on the type of the raw material (such as obsidian, flint, radiolarite or metamorphic rocks), the success of the various neutron-based studies can be expected at different levels. In this paper, we demonstrate the potentials of the mostly applied neutron-based techniques through case studies.

1. Introduction

One of the most important question in archaeometry is to determine the provenance, i.e. the origin of raw material for various objects found with or without archaeological context. The provenance data, i.e. the association of the object with potential sources can help archaeologists to reconstruct the historical trade roots, social relations, movements of one-time communities and individuals etc.

Raw materials are necessarily different in respect of their complexity. Ceramics, glass or metals are typically composite materials; their chemical composition is modified intentionally and very often accidentally during the manufacturing process. Therefore, the provenance of these materials is difficult to determine, in most cases only the workshop can be identified with certain confidence.

On the other hand, the chemical (and mineralogical) composition of lithic material (various kinds of rocks) is not essentially affected during the prehistoric production and the “afterlife” of the object. Thus, provenancing of prehistoric lithic materials might bring success for tracing contacts. The prerequisite of the success, however, is to find fingerprint-like geochemical components on major-, minor- or trace level, with the help of which it is possible to assign the archaeological material to one or more geological sources. Needless to say, that all depend on the investigated material and the method applied. However, in the interest of the successful provenance study, statistically representative series of analyses are requested that give the preference of fast, low cost methods. On the other hand, the analytical result must be precise enough and representative for the investigated material. These requirements are often contradictory. It is obvious that there is no “omnipotent” analytical method; the application of complementary methods is recommended whenever it is possible. Efforts must be paid to preserve and document the studied samples precisely for possible further studies.

Certainly, in most cases only the non-invasive and non-destructive methods are allowed to apply on valuable objects. Most of the neutron-based methods are ideal tools for archaeometric studies, because the use of external beams does not require sampling and the induced radioactivity decays within a few days. Prompt-gamma activation analysis (PGAA) has been applied to determine the concentrations of the major and some trace elements in various kinds of rocks for about 20 years at the Budapest Neutron Centre for archaeometrical studies. PGAA, in principle is suitable to detect all the chemical elements, but, depending on the neutron-absorption cross-section, with very wide range of sensitivity. It is worth to mention that, since neutrons can move more centimeters in the samples, the composition obtained is characteristic for the bulk.

In addition to PGAA, neutron diffraction (ND) or small angle neutron scattering (SANS) can be in principle used to obtain structural (i.e. mineralogical) information of rocks. Neutron imaging (radiography or tomography) can be used as well, when we intend to visualize the parts of an object with different compositions. In case of rocks, however, usually we do not expect extra information from imaging, unless the porosity of the stone is of importance for the study. Finally, when (destructive) sampling is allowed, e.g. for fragmented objects, the most effective method to quantify a whole series of trace elements is the

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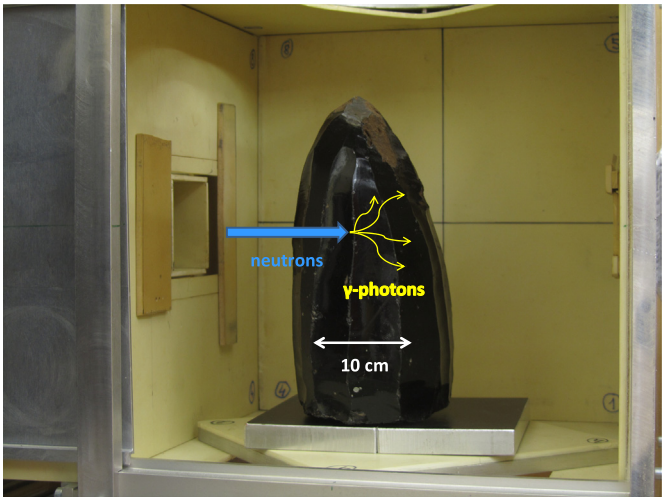

Fig. 1. Prompt-gamma activation analysis of a large obsidian core, found in Nyírlugos, Hungary – at the NIPS-NORMA station.

neutron activation analysis (NAA).

2. Experimental

Prompt-gamma activation analysis of stone objects has been done at the PGAA station at a horizontal cold neutron beam of $9.6 \times 10^7\,cm^{-2}\,s^{-1}$ intensity (Szentmiklósi et al., 2010). Objects of maximum 10 cm diameter can be placed in the sample holder. Objects of larger dimensions can be analyzed at the NIPS-NORMA station, see Fig. 1 (Szentmiklósi et al., 2010). A selected part of the object can be irradiated with the neutron beam, collimated to a cross-section between 5 mm^2 and 400 mm^2. The acquisition time was set to collect statistically significant counts in the spectra. Depending on the sample material, the sample amount and the elements of interest, the typical acquisition time was between 30 min and 720 min.

Prompt- and delayed gamma photons produced in the (n,γ) reactions are detected with a special detector system, which includes a 27% efficiency HPGe detector surrounded by a BGO annulus. The spectra are collected in a 64 k multichannel analyzer. The prompt-gamma spectra are evaluated using the Hypermet PC software (Révay et al., 2001). The element identification and the determination of quantitative composition is done on the basis of our PGAA library (Révay & Molnár, 2003), applying the prompt k_0-method (Molnár et al., 1998). In most of the geochemical studies, concentrations of the major components are given in weight% of the oxides, while trace elements are given in weight% or μg/g. Since oxygen is a poorly detectable element with PGAA, the amounts of the oxides are calculated on the basis of the typical oxidation number of a given element. In the following, we discuss the applicability of PGAA for the study of archaeological stone objects through some significant examples from Hungary. During the provenance studies, we are looking for similarities and differences between the compositions of the groups of the archaeological objects and those of the comparative raw materials.

2.1. Data treatment

The ideal case for the treatment of data would be, undoubtedly, open access databases for all analytical results on Cultural Heritage items. This is, however, practically impossible right now. Researchers are pushed to produce new data and new results in publications. Whereas everybody is happy to use existing high-quality datasets, the compilation and maintenance of such sources of information is supported, in the best case, on the level of individual projects and/or research centres with restricted access. This means a lot of extra work, production of clones with the danger of introducing errors and misunderstanding. Results of different laboratories and different measurement types are especially difficult to compare and require special round robin test projects. For the time being, the analytical results are typically evaluated among themselves within measurement series in the same laboratory.

3. Results and discussion

In most cases, when bulk compositions of various rocks are determined, we can quantify the major components of Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and H. Depending on the type of rock, however, some of the above elements might be under the detection limits of the PGAA system. From the trace components, B, Cl, Sm and Gd, those with high neutron-absorption cross-section can almost always be determined in the spectra. Others, like S, P, Sc, V, Co, Cr, Nd and Eu occasionally can be determined. Finally, other geochemically important trace elements like Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and U are typically below the detection limits of the PGAA. As an initial step in the identification of the lithic raw material, in most cases we can differentiate between the major types (i.e. between obsidian, silex, felsitic porphyry or carbonates) with the help of PGAA data (Fig. 2).

3.1. Fingerprinting Carpathian obsidians

Obsidian is one of the most frequently investigated prehistoric raw materials. Thanks to the significant geochemical differences between the different sources in the World due to the specific formation process, one can easily classify the various obsidian sources, based on certain major and trace elements. In order to measure the key elements for fingerprinting, various destructive or non-destructive methods, such as NAA (Kilikoglou et al., 1996), XRF (Milič, 2014) – recently a portable variant – ICP-MS (Yi & Jwa, 2016) and also PGAA (Kasztovszky et al., 2008) can be used.

With PGAA, it was possible to quantify the major geochemical components, except MgO, which was found to be below the quantification limit. We have observed that from the detected major and trace elements, B, Cl and Ti are the best discriminative elements that can be measured by PGAA. When comparing PGAA with the portable XRF results, we have concluded that PGAA gives reliable composition data representative for a few cm^3 bulk sample, whereas XRF provides information on the near-surface composition, and the result is somewhat influenced by sample geometry. We have shown too, that grouping on the basis of B, Cl and Ti content measured by PGAA is in a few points more detailed than on the basis of Rb, Sr and Zr measured by portable XRF using the built-in “Soil” mode (Kasztovszky et al., 2017a).

Since 2003, we have analyzed around 200 archaeological obsidian pieces and around 150 geological reference samples. In our research, we have focused on the distribution of archaeological obsidian in the Carpathian Basin and its surroundings. Thanks to the opportunities offered by CHARISMA, IPERION-CH and bilateral research projects, pieces from Romania (Astalos & Kasztovszky, 2009), Croatia (Kasztovszky & Težak-Greg, 2009), Serbia, Bosnia-Herzegovina (Kasztovszky & Težak-Greg, 2009) and Poland (Kabaciński et al., 2015) have been analyzed at the Budapest PGAA laboratory. Reference geological material have been obtained partly from the Lithotheca of the Hungarian National Museum and also from bilateral co-operations. With the selection of representative geological reference samples, we tried to cover all the archaeologically significant geological sources, such as the Carpathian sources (including C1, C2E, C2T and C3 subtypes), as well as obsidian from Lipari, Sardinia, Melos, Antiparos, Pantelleira, Palmarola, Armenia and Anatolia.

As a very first result, we were able to unambiguously separate obsidian from other, sometimes macroscopically similar material using PGAA (Kasztovszky & Biró, 2004). Furthermore, all the studied archaeological pieces could be assigned to one of the above raw material