NAA APPLIED TO HETEROGENEOUS LITHIC ARCHAEOLOGICAL ARTEFACTS - DIFFICULTIES AND ADVANTAGES FOR PROVENANCE ESTABLISHMENT

NEUTRONAKTIVÁCIÓS ANALÍZIS ALKALMAZÁSA RÉGÉSZETI KŐANYAGON – EREDMÉNYEK ÉS PROBLÉMÁK A SZÁRMAZÁSI HELY AZONOSÍTÁS VIZSGÁLATOKBAN

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Abstract

Instrumental neutron activation analysis (INAA) is a sensitive, precise and accurate technique, and allows obtaining simultaneously the concentration of a large number of chemical elements. The small amount of sample required for INAA is a huge advantage when dealing with Cultural Heritage materials. Nevertheless the chemical results obtained for these small samples analyzed must be representative of the object, which becomes difficult when dealing with heterogeneous materials like chert. INAA applied to very small flakes of the core from the same chert artefact has shown to be a promising methodology to identify chemical fingerprints contributing to the establishment of provenance and human mobility in ancient times.

Kivonat

A neutronaktivációs vizsgálat (INAA) érzékeny, pontos és megbízható összetétel vizsgálati módszer, amely egyszerre számos kémiai elem mennyiségi meghatározását teszi lehetővé. Kis mennyiségű mintát igényel, ami különösen fontos a kulturális örökség körébe tartozó tárgyak vizsgálatánál. Ugyanakkor fontos, hogy a kis mennyiségű minta kellőképpen reprezentatív legyen a tárgy egészére, ami inhomogén anyagok vizsgálata esetében kritikus lehet. Ugyanarról a magkőről származó apró pattintékok vizsgálatával teszteltük a módszer alkalmazhatóságát kova eszközök lelőhelyének azonosítására. Az eredmények hozzájárulhatnak a származási hely azonosításhoz és ezen keresztül az őskori mozgáskörzetek vizsgálatához.

KEYWORDS: LITHIC ARTEFACTS, INAA, CHEMICAL HETEROGENEITY, MICRO-INVASIVE METHODOLOGY, PROVENANCE

KULCSSZAVAK: KŐESZKÖZÖK, INAA, KÉMIAI HETEROGENITÁS, ALACSONY RONCSOLÁSI SZINTŰ VIZSGÁLAT, SZÁRMAZÁSI HELY VIZSGÁLAT

Introduction

Chert has been extensively used since pre-history to obtain tools as scrapers, hand axes and arrowheads due to its hardness and conchoidal fractures, which allows obtaining sharp blades. The identification of the geographical location where the raw materials occur may contribute significantly to trace human mobility.

Chert is a dense cryptocrystalline variety of quartz, slightly translucent to almost opaque (Brandl 2014). Inclusions of organic compounds, metal sulphides, and various metal oxides and hydroxides can cause the different colours (dark gray with shades of brown, red, or yellow, and sometimes white), and may lead to a heterogeneous chemical composition. So, besides a general low content of most chemical elements in chert, this heterogeneity may difficult the use of the chemical composition of these archaeological artefacts to distinguish chert from different sources. Therefore, it is important to evaluate the content differences of the larger number of chemical elements as possible within a same chert fragment. Due to the high value of cultural objects the amount of sample to be taken for analysis must be none (non-destructive techniques), or very small (micro-invasive techniques). Several works have been performed using a great variety of analytical methods to identify the sources of chert artefacts found in different archaeological contexts (Malyk-Selivanova et al. 1998; Costopoulos 2003; Allard et al. 2008; Kasztovszky et al. 2008; Crandell 2008; Bustillo et al. 2009; Hughes et al. 2010, 2012; Shackley 2011; Gauthier et al. 2012;).

Eixea et al. (2014) and Roldán et al. (2015) were able to discriminate two chert types from the Eastern part of Spain - the “Domeño type” (Villaverde et al. 2008), and the “Serreta type” (Molina et al. 2010, by using multivariate statistical analysis applied to data obtained by energy dispersive X-ray fluorescence spectrometry

(EDXRF), and the crystalline index of quartz obtained from the X-ray diffraction (XRD). However several sub-types previously identified macroscopically (Eixea et al. 2011) could not be differentiated by those methods. More recently Prudêncio et al. (2016) reported that instrumental neutron activation analysis (INAA) of small flakes from the same flint fragment of archaeological artefacts from archaeological sites from Eastern Spain allowed to differentiate flint types and variants.

In this work the methodology using INAA to evaluate the natural heterogeneity of chert fragments and its use to contribute for the establishment of chert provenance, is discussed.

Methods

A number of different analytical techniques have been applied to characterize archaeological materials with varying degrees of success, but all of them need to have multi-element capability and sufficient sensitivity to detect traces of elements in the various matrices. Among these techniques the analytical method with one of the longest and most successful histories of application for provenance research has been instrumental neutron activation analysis (INAA) (Julig 1995; Glascock 2004; Glascock and Neff 2003; Glascock and Speakman, 2008; Prudêncio 2009). INAA is a sensitive technique useful for quantitative multi-element analysis of major, minor, and trace elements. This technique involves the irradiation of a sample by neutrons to make the sample radioactive followed by gamma spectrometry to determine the amounts of different elements present in the sample. INAA has a number of advantages over most other analytical methods when investigating archaeological specimens. In fact the preparation of archaeological materials for analysis by INAA is extremely easy in most instances a representative sample may be only a portion of the sample weighed and place in an appropriate container (100-200 mg) (micro-invasive technique), which is very important when dealing with cultural materials that must be preserved.

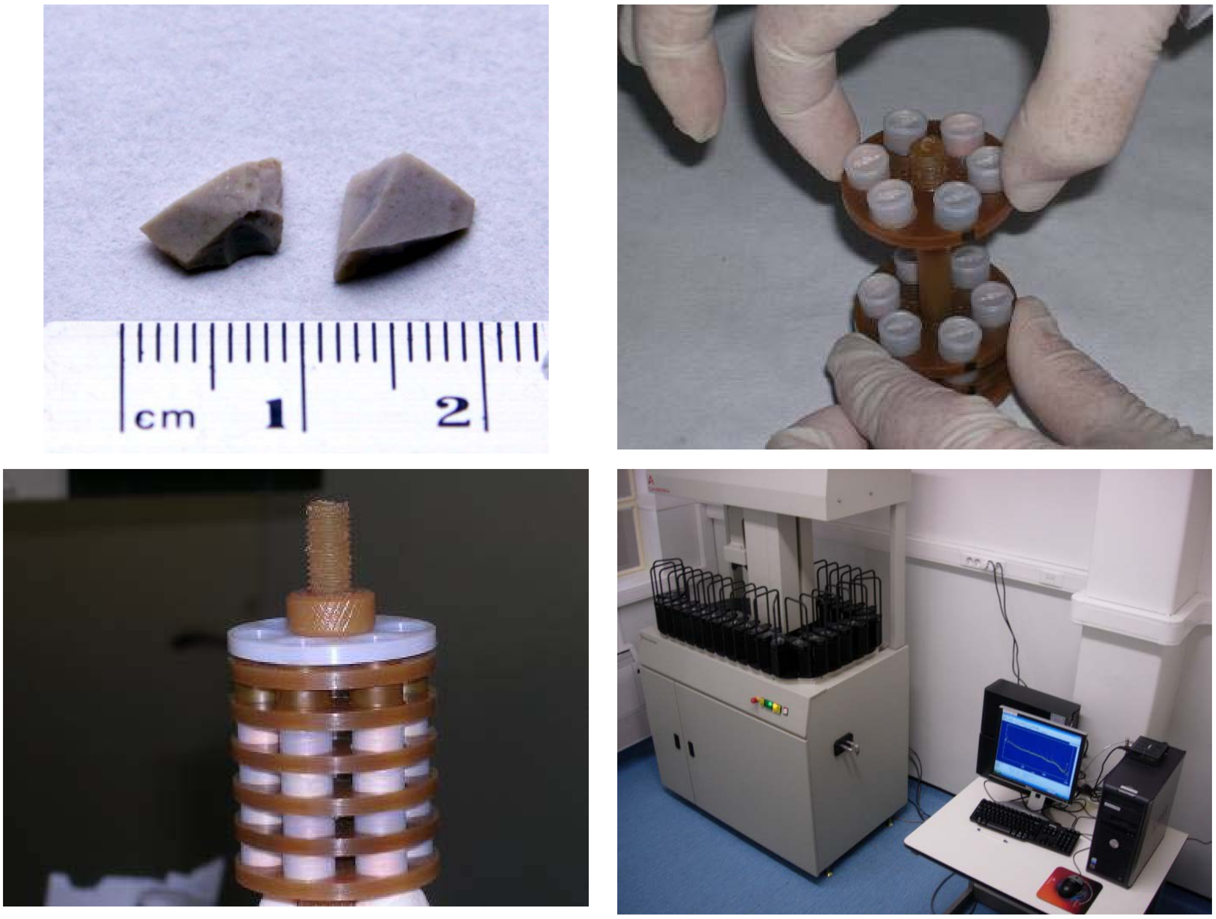

Fig. 1.: Photographs of: flakes of the core of a chert fragment; polyethylene vials with samples and reference samples powders; container ready to be used for long irradiations in the Portuguese Research Reactor (CTN, IST); counting room of the INAA laboratory of CTN.

1. ábra: Kova szilánkok; műanyag fiolák a porított mintákkal és referencia anyagokkal; a Portugál Kutató Reaktornál használt mintatartó, előkészítve a hosszúidejű besugárzáshoz; a Portugál Kutató Reaktor Neutronaktivációs Laboratóriumának számláló helyisége

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Despite the small amount of sample required for INAA, the sample analyzed must be representative of the artefact, which becomes very difficult if the cultural objects are made of heterogeneous materials. Thus, when dealing with cultural heterogeneous materials like chert three issues are important: (1) to use the fewer amounts of sample as possible; (ii) to assess eventual heterogeneity; and (iii) to identify chemical fingerprints. The big question is: how to solve this issue? Recently, Prudêncio et al., 2016 presented a methodological approach applying INAA to small samples (in a micro-invasive way) from heterogeneous chert fragments. The analytical method applied included (**Fig. 1.**): (i) 2-3 small portions (less than 1g) of the core of each chert fragment prepared separately; (ii) powder samples for analysis of the geological and archaeological fragments obtained by drying for several hours at 30ºC, and ground in a corundum mortar to avoid contamination; and (iii) INAA – irradiation and gamma-spectrometry. Gamma spectra were obtained with measuring times of 6 hours per sample and standard in order to reduce the error associated with the peak areas determination. The chemical contents of Na, K, Fe, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U were obtained. Instrumental errors are in general to within 5%, and occasionally within 15%. Details of the analytical method may be found elsewhere (Gouveia et al., 1992; Prudêncio, 2009). Corrections are made for the interference from uranium fission. It is well known that the presence of U in samples interferes in the determination of several elements concentration by instrumental neutron activation analysis. This is partly due to the identity of some 235U fission products with radionuclides formed by radioactive capture of neutrons on those elements (nuclear interference), and also to the fact that the γ-rays emitted by some fission products cannot be resolved from γ-rays emitted by radionuclides of interest produced by (n,γ) reaction (spectral interference). The extent to which the interference may affect the accuracy of the determination depends on the ratio of the concentrations of the element to be determined and of U in the sample, as well as on the irradiation conditions and cooling time. So corrections for the determination of rare earth elements (REE), zirconium and barium must be done (Gouveia et al. 1987; Martinho et al. 1991).

Discussion

The results obtained by Prudêncio et al. (2016) for chert fragments of archaeological artefacts and geological outcrops has shown that INAA applied to small samples (circa 150 mg) of the core of the fragment (micro-invasive technique) appears to be a suitable method to characterize and differentiate chert from different sources in a micro-invasive way. In fact, analyzing 2 - 3 samples of the same fragment, the relative standard deviation of the chemical contents obtained for each element may reach very high values, reflecting how the concentration of some elements may vary within the core of the same chert fragment (**Fig. 2.**).

Also the same element may be homogeneously distributed in some chert cores, and very heterogeneously distributed in other chert cores (for example Zr and Hf).

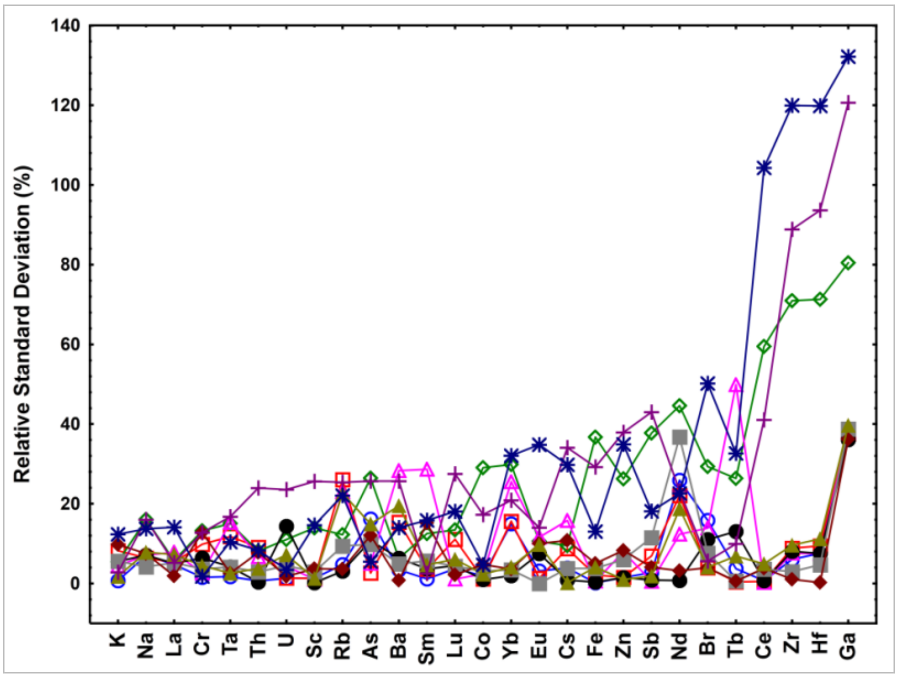

Fig. 2.: Relative standard deviation (RSD) for the concentration obtained of 27 chemical elements in flakes (n=2-3) of the core of chert fragments (data from Prudêncio et al. 2016)

2. ábra: Magkövekből származó minták méréséből meghatározott 27 kémiai elem koncentrációjának relatív szórása (relatív standard deviációja – RSD), n=2-3 megismételt mérés esetén (Prudêncio et al. 2016 nyomán)

Thus this micro-invasive methodological approach, with a careful analysis of the chemical results obtained by INAA for each lithic archaeological artefact or geological fragment, and the identification of chemical fingerprints (chemical elements homogeneously distributed inside the core of a certain type of chert) may contribute significantly for the establishment of chert sources.

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