ARCHAEOMETRICAL ANALYSIS OF NEOLITHIC POTTERY AND COMPARISON TO POTENTIAL SOURCES OF RAW MATERIALS IN THEIR IMMEDIATE ENVIRONMENT - APPLICATION OF NEW ANALYTICAL, NON-DESTRUCTIVE X-RAY TECHNIQUES AND SR ISOTOPE MEASUREMENTS

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Kivonat

A Tübingeni Egyetem és a Magyar Nemzeti Múzeum együttműködésében régészeti és geológiai mintákat vizsgálunk több újkőkori lelőhelyrőlegy új MÖB-DAAD program keretében, amely 2005-2006 folyamán valósul meg. Valamennyi vizsgálandó lelőhely magyarországi, a közelmúltban végzett ásatások eredménye, és jelentős leletanyagot szolgáltatott. Ebben a tanulmányban a kerámia vizsgálatára alkalmazható természettudományos módszereket foglaljuk össze, amelyeket a program során megvalósítunk. Vizsgálataink elsődleges célja a kerámia előállítás kérdéseinek vizsgálata, miszerint helyben és helyi nyersanyagból készültek-e az edények, esetleg a hozzávalókat vagy a kész edényeket kisebb-nagyobb távolságból szállították. Vizsgáljuk a nyersanyagfelhasználást, a lelőhelyek talajának, a környező agyagos üledéselk és a kerámia kémiai összetételének és kőzettani jellemzőinek összefüggését és az előállítási folyamatot (pl. égetési hőmérséklet és soványító adalékanyagok).Részletesen foglalkozunk a Sr-izotóp vizsgálatok alkalmazási lehetőségével és egy új, roncsolásmentes XRF technikával. Továbbá, összehasonlítjuk a különböző XRF módszereket, beleértve a roncsolásmentes technikát is.

KULCSSZAVAK: KERÁMIA VIZSGÁLATOK, ÚJKŐKOR, XRF, SR-IZOTÓP VIZSGÁLATOK

Abstract

In collaboration of Tübingen University and the Hungarian National Museum, archaeological and geological samples from different Neolithic excavation sites and their geographical surroundings will be investigated, the a new MÖB-DAAD project lasts from 2005 to 2006. All sites are located in Hungary and have ample scientific evidences. State of the art analytical methods will be applied to evaluate the history of pottery production (question of on-site production or transportation), usage of raw material (geochemical and/or petrological correlation between clay deposits and pottery) and production processes (e.g. firing temperatures, temper). Analytical details and applicability of Sr-isotope method and a new non destructive XRF technique are described. In addition, different XRF methods are compared, including a non destructive method.

KEYWORDS: POTTERY ANALYSIS, NEOLITHIC PERIOD, XRF, SR-ISOTOPE ANALYSIS

Introduction

In course of former DAAD-MÖB collaboration, we have established excellent working connection between Hungarian and German partners (Tübingen University, Hungarian National Museum, Eötvös Loránd University and the Geochemical Research Laboratory of the HAS). The program "Archaeometrical study of Roman and Mediaeval Marbles in Hungary" was successful in clarifying the provenance of the marble relics found at Heténypuszta Roman fortress, and has completed our knowledge on marble quarries in and around the province of Pannonia. The idea and necessity of a new joint research devoted to pottery emerged already during the former joint project. In continuation to this very successful exchange project in the years of 2001 and 2002, we are glad to have financial support by German DAAD and Hungarian MÖB for a new project to be carried out in 2005 and 2006. The new project's objective is prehistoric study of ancient pottery and its raw materials in Hungary.

Pottery production is one of the most important crafts of prehistoric communities. Most of the archaeological evidences were recovered from sherds and different ceramics, which were excavated on habitation sites as well as cemeteries.

Therefore, pottery has served for long as the basic starting point of archaeological analysis of a site. Material characteristics of the ceramics may depend on many complex factors: technological, regional, cultural and functional ones. Our project intends to deal mainly with regional factors, comparing local sediments with the material of early ceramics all over Hungary.

Our planned analysis is aimed at a systematic study of the regional factor, as one aspect of problems connected with prehistoric pottery production. By this, we hope to get closer to solving archaeometrical, petrological and historical problems emerging in the study of pottery.

The scientific approach of our work is to compare the mineralogical, petrological and geochemical composition of ceramics and local sediments (clay, silty clay, sand, etc.). The latter are supposed to be raw materials for pottery making in five selected localities (see Fig. 1): Vörs (SW-Hungary), Kup (W-Hungary), Szarvas-Endrőd (SE-Hungary), Aggtelek-Baradla (N-Hungary), Tiszaszőlős-Domaháza (E-Hungary). These sites were selected in the planning phase of the project; in the implementation phase, we have completed them by further important localities (see Map). These sites represent different geological areas in the Carpathian-Basin. Raw materials around Vörs, Szarvas-Endrőd and Tiszaszőlős can be characterised by young river sediments of two different water catchment areas (gathering grounds of river Danube and Tisza), while Aggtelek-Baradla and Kup are situated in piedmont areas characterised by Mesozoic sedimentary and Palaeozoic sedimentary and low grade metamorphic rocks. All of the samples originate from modern excavations with ample scientific evidences (soil samples for silting included). The pottery is characteristic on regional level in respect of style and form.

Geochemical characterisation of sediments from these geological areas has not been done yet. The results of sediments analysis will be compared to the petro-archaeological results obtained from prehistoric pottery. We will apply state of the art analytical facilities to get the best information possible about the investigated samples:

- NAA (Neutron Activation Analysis for chemical composition)

- PGAA (Prompt Gamma Activation Analysis for chemical composition)

- XRD (X-ray Diffraction for mineralogical phase analysis)

- EPMA (Electron Probe Micro Analysis for chemical composition, if necessary)

- Isotope geochemistry (Sr-isotope analysis for identification of source materials)

- XRF (X-ray Fluorescence analysis for chemical composition)

Intensive personal scientific exchange between Budapest and Tübingen will help to make use of the analytical measurements, as much as possible.

Sr-isotope techniques:

Strontium isotope measurements in this project will be one particular application of radiogenic isotope techniques to solve archaeological problems. Strontium isotopic data presumably will help in differentiation/comparison between various sherds and raw materials. (for further details regarding the application of Sr see PINTÉR, 2005).

Fig. 1:

Localities of archaeological excavations in Hungary, selected for sampling in the frame of the project.

The first pioneering work is also reported by the Geochemical Laboratories in Tübingen in the 90s, a project that focused on chemical and isotopic studies of Trojan sherds. Applying Rb-Sr, Sm-Nd and REE techniques, one was able to distinguish between different localities of production and proved the import of Mycenaean ware to Troy (KNACKE-LOY, 1994).

For detailed isotope analysis about 50 mg of powdered sample is required (applicable for Sr as well for Nd, or other isotope systems). The samples are digested over night with HF-HClO$_4$ and then kept at 170°C for another 6 days to dissolve also accessory minerals. Sr is then separated from the solution by adding 5 ml sample solution to a cation-chromatography resin (see Fig 2). The separation of Sr from other elements is necessary to avoid peak overlapping, caused by other isotopes with the same atomic mass in the mass spectrometer (e.g. ^{87}Rb and ^{87}Sr). Since Sr is usually present in the samples in a relatively low concentration (few ppm), all chemical steps are carried out in an ultra-clean lab (see Fig. 3), in order to avoid contamination.

Strontium isotopic ratios (^{87}Sr/^{86}Sr ratio) are measured with a Finnigan MAT 262 Thermion-mass-spectrometer, calibrated with international standards. Four Sr isotopes, namely Sr-84, Sr-86, Sr-87 and Sr-88 naturally exist.

Fig. 2: Cation exchange chromatography resin in cigarette-like columns, de-signed especially to separate Sr from other elements. The carousel is placed in an ultra-clean fume hood in the clean lab.

A portion of Sr-87 is formed by β-decay of primordial radioactive Rb-87, thus Sr-87 is called radiogenic isotope in Geochemistry. It implies that due to different original Sr and Rb concentrations and formation times, different clay sources presumably have different ^{87}Sr/^{86}Sr ratios. These isotopic ratios are not influenced by transport of raw material, fabrication or firing of sherds and thus can provide a not erasable fingerprint for a clay source (Knacke-Loy, 1994).


Fig. 3: One of the working benches in the geochemistry clean-lab at Tübingen University. In this laboratory the amount of air particles is reduced with filter systems to a minimum, the fume hood inside the lab provide even better conditions in order to avoid contamination of Sr (or Nd) from the sample to be analysed by other sources.

It has been used in Geosciences for a long time. It has proved its performance for generations of geologists and geochemists, as it is suitable for measurement of a couple of interesting elements. Of course, not all the elements can be analysed with the same precision and accuracy with all methods, but with the variety of analytical facilities to be applied in this project we might have a chance to get almost the complete system of elements, since the different chemical methods complement one another in a perfect way.

Conventional XRF methods, however, were destructive, where at least 1.5 g sample powder was required to fabricate a fused bead on which the chemical composition was analysed. For more than five years now, there is the possibility to get quantitative chemical information with XRF in a non-destructive way. All you need is a specimen small enough to fit in your sample holder (about 4 cm in diameter) and even enough to cover an 8 mm aperture homogeneously (see Fig. 4 and 5).

Up to now only qualitative analysis was possible this way; recently, due to improved analytical performance as well as software skills (complex matrix correction with variable α-parameters) also quantitative measurements can be done without destroying the specimen. α-parameters are required to correct the results for significant analytical effects produced by variable matrices (e.g. SiO$_2$-rich or poor, heavy or light, liquid or solid, etc.). Formerly a certain α-parameter was required and has to be determined for each individual matrix.
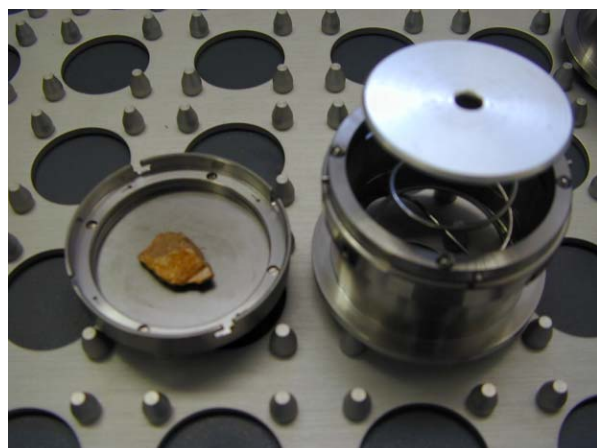
Fig. 4: Small archaeological sample (1.5 cm in diameter) in an open sample holder for XRF analysis.

Fig. 5: Three XRF sample holders (closed, upside down), one with a conventional 34 mm window, the other two with 8 mm window, containing a rock-specimen (left) and a gold-foil (right) inside.

Due to improved software capacity XRF machines are now able to calculate a specific α-parameter within a few seconds by an iterative mathematical process, applicable only to your individual sample. This advantage allows for the quantification of data that could formerly only be used in a qualitative way. However, as the analytical precision usually is better for the conventional, standardized method, these new application is also called "semi-quantitative. Detection limits and precision of the instrument depend on acquisition time. For most elements heavier than Na detection limits are usually 50 – 100 ppm, some elements however go down to 5 ppm. Corresponding analyses times vary between 10 min and approximately 3h, also depending on how many elements are of interest.

In order to show the differences, the analysis of a fused bead of one sample (PF1) measured with three different methods is displayed in Table 1. In the table, "standard 1.5h" stands for the conventional calibrated method, whereas "std.less 30 min" means the same sample (fused bead) measured with a standard less, 30 min-method in 1/3 time, and "std.less 30 min powder" means the same sample, but this time as rock-powder, measured with a standard-less, 30 min method in 1/3 time. One can see that for the major elements, as well as for many trace elements all three methods give values that are in good agreement with each other, which also certifies the applicability of the standard less methods.

Conclusion

Archaeological and geological samples from five selected Hungarian Neolithic localities will be analysed with state of the art analytical facilities in order to compare products and raw materials. Two of them are described in detail in this paper. Unfortunately no results from samples of this project are available yet at the time of writing. New data will be published here soon.

References:

PINTÉR, F. (2005): Provenance study of the Early Iron Age Knobbed ware in Troia, NW Turkey and the Balkans: Petrographic, geochemical and isotope geochemical evidence. *PhD-thesis, University of Tübingen*, Germany, 242 pages (in English).

KNACKE-LOY, O. (1994): Isotopen-geochemische, chemische und petrographische Untersuchungen zur Herkunfstbestimmung der bronzezeitlichen Keramik von Troia. *Heidelberger Geowissenschaftliche Abhandlungen*, 77, Heidelberg 1994, 193 pages (in German).

Sample	SiO2 (%)	TiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MnO (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	P2O5 (%)	LOI (%)
PF1 std.less 30 min.	62,56	0,63	16,78	3,67	0,06	1,54	4,45	3,61	4,28	0,41	1,20
PF1 std.less powder 30 min.	61,58	0,68	17,64	4,08	0,07	1,68	4,87	3,87	4,77	0,53	
PF1 standard 1,5h	63,59	0,63	16,65	3,81	0,07	1,80	4,32	3,71	3,96	0,50	1,20

Sample	Ba (PPM)	Co (PPM)	Cr (PPM)	Ni (PPM)	Rb (PPM)	Sr (PPM)	V (PPM)	Y (PPM)	Zn (PPM)	Zr (PPM)	Ce (PPM)
PF1 std.less 30 min.	1284	0	0	0	114	594	3	10	1	513	122
PF1 std.less powder 30 min.	1156	0	0	0	120	550	46	12	84	324	72
PF1 standard 1,5h	1140	11	41	10	117	480	56	29	49	332	113

Sample	Eu (PPM)	La (PPM)	Nb (PPM)	Nd (PPM)	Pb (PPM)	Sm (PPM)	Th (PPM)	U (PPM)	Yb (PPM)	Sum (%)
PF1 std.less 30 min.	0	61	0	37	64	0	0	18	0	99,45
PF1 std.less powder 30 min.	0	35	33	32	19	8	0	0	0	100,00
PF1 standard 1,5h	1	63	0	47	32	6	5	1	2	100,49

Table 1: Comparison of different XRF methods applied of the same rock specimen. One can see that for most elements they are in good agreement. For further details see text.