ARCHAEOMETRICAL ANALYSIS OF NEOLITHIC POTTERY AND COMPARISON TO POTENTIAL SOURCES OF RAW MATERIALS IN THEIR IMMEDIATE ENVIRONMENT – AN OVERVIEW

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Abstract: *The problem of pottery provenance and site endowments was investigated in the frame of a collaborative project between Tübingen University, Germany and the Hungarian National Museum, Budapest. Pottery, daub and soil samples from ten Neolithic sites throughout Hungary were investigated by mineralogical, petrological and geochemical methods, in this paper the focus lies on geochemical data from six selected sites (Vörs, Szarvas-Endrőd, Tiszalúc, Tiszaszőlős, Füzesabony, Felsővadász). Both pottery and soil samples have their typical chemical patterns, sometimes they are identical, sometimes different. Apart from the fact that pottery samples usually have a lower TiO_2/Al_2O_3 and Zr/V ratio compared to soil samples only few features can be found that all ten sites studied have in common. Each site has its specific problem, and has to be discussed separately as specific parameters apply.*

Keywords: *Archaeometry, Pottery, Clay, Soil, Neolithic, Hungary*

INTRODUCTION

Pottery is among the great invention of productive economies, as it contributed to storage, household and arts. Pyrotechnical innovations and their control (e.g. firing temperature) prepared the way to chemical and mineralogical alteration of a variety of raw materials resulting in specific material properties. The earliest phase of pottery use, during the Neolithic, is especially interesting (*Biró et al. 2007*). The problem of pottery provenance and site endowments was investigated in the frame of a collaborative project in 2005 and 2006 between Tübingen University, Germany and the Hungarian National Museum, Budapest (*Taubald & Biró 2007, Taubald et al. in press*). The project benefited substantially from the collaboration of scientists from archaeology, geology, petrology, geochemistry, mineralogy and archaeometry and represents a full interdisciplinary study (see also acknowledgements, *Zöldföldi et al. 2004*) – a fact that should not be underestimated.

Pottery, daub and soil samples from ten Neolithic sites throughout Hungary were investigated by mineralogical, petrological and geochemical methods (Vörs, Tihany, Kup, Aggtelek, Felsővadász, Borsod, Tiszalúc, Füzesabony, Tiszaszőlős and Szarvas-Endrőd, see **Fig. 1**). Clay deposits in the vicinity of each individual site were also sampled and studied in order to characterize potential sources of raw materials. In order to use chemical information as a tool in provenance studies, the key questions are: which elements are significant to do this study? How can we solve the problem of element mobility (alteration, weathering, etc.)? Can we distinguish pottery from different sites chemically? Can we do the same with soil samples? How similar or different soil and pottery are at the individual sites?

METHODS

More than 300 sedimentary/soil samples were taken by drilling and described macroscopically, about 130 were characterized petrographically. From 173 sherds and geological samples major and trace elements were analysed by XRF (X-ray Fluorescence Spectroscopy), partly also by INAA (Instrumental Neutron Activation Analysis). XRD (X-ray Diffraction) was carried out on about 100 samples for mineralogical information. Our investigations can be regarded as the first large scale comparative study on early pottery and its potential raw materials. In this paper geochemical results using XRF are presented and discussed.

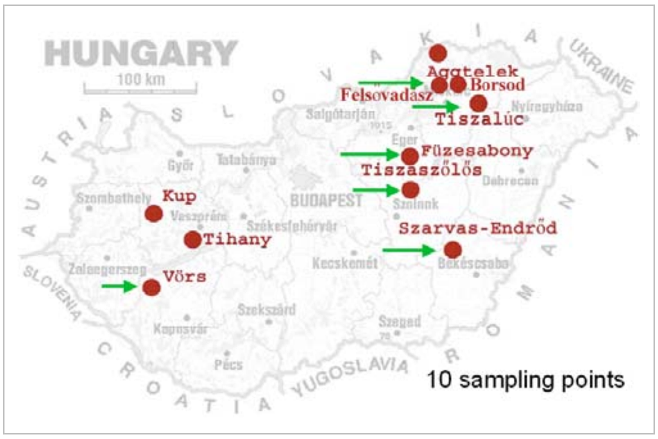

Fig. 1 Schematic map of Hungary showing the ten Neolithic localities sampled in the frame of the MÖB-DAAD exchange program in 2005 and 2006. Geochemical data from six selected sites are reported in this paper, the corresponding sites are highlighted with an arrow.

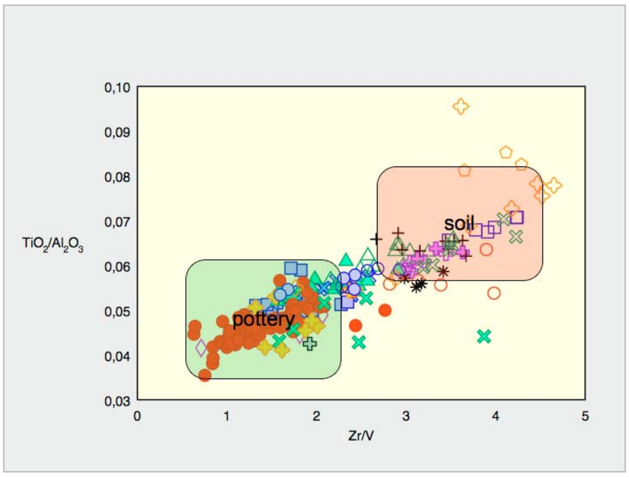

Fig. 2 TiO_2/Al_2O_3 and Zr/V ratios for all samples analysed in the frame of the project from all ten Neolithic sites. Pottery samples are marked with filled symbols, whereas soils (clay) are marked with open symbols. It is obvious that on the average pottery samples show a lower TiO_2/Al_2O_3 and Zr/V ratio compared to the soils as indicated by the two boxes. In contrast to Fig. 3 – 8 and details of the text here samples from the four sites not described here (Kup, Borsod, Tihany, and Aggtelek) are displayed in order to show the significant separation of the two fields.

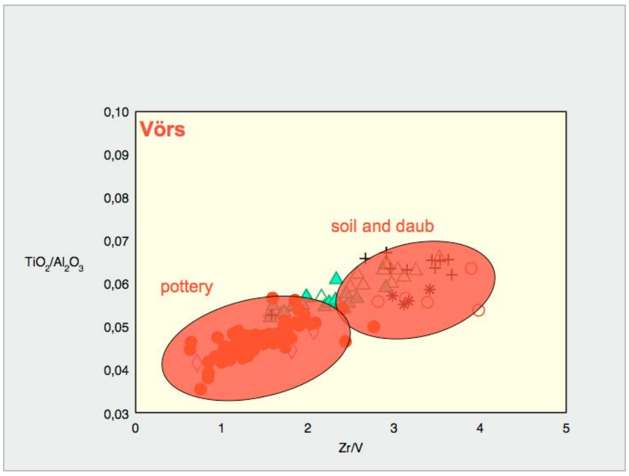

Fig. 3 TiO_2/Al_2O_3 vs. Zr/V ratios in a diagram displaying data points of samples from Vörs and Szarvas-Endrőd only. The shaded fields mark the position of pottery samples of Vörs and soil and daub samples of Vörs. Pottery samples are marked with filled symbols, whereas soils (sediment, clay) are marked with open symbols.

Major and trace elements were analysed with a wavelength dispersive XRF device (Hahn-Weinheimer et al. 1984). Prior to preparation the samples were ground with an agate mill for 10 minutes. Loss on ignition was determined at 1050°C externally and is displayed as LOI.

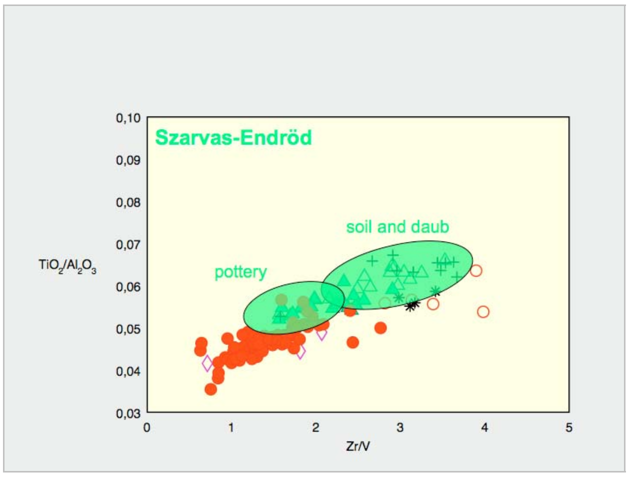

Fig. 4 TiO_2/Al_2O_3 vs. Zr/V ratios in a diagram displaying data points of samples from Vörs and Szarvas-Endrőd only. The overlapping shaded fields mark the position of pottery samples of Szarvas-Endrőd and soil and daub samples of Szarvas-Endrőd. Pottery samples are marked with filled symbols, whereas soils (sediment, clay) are marked with open symbols.

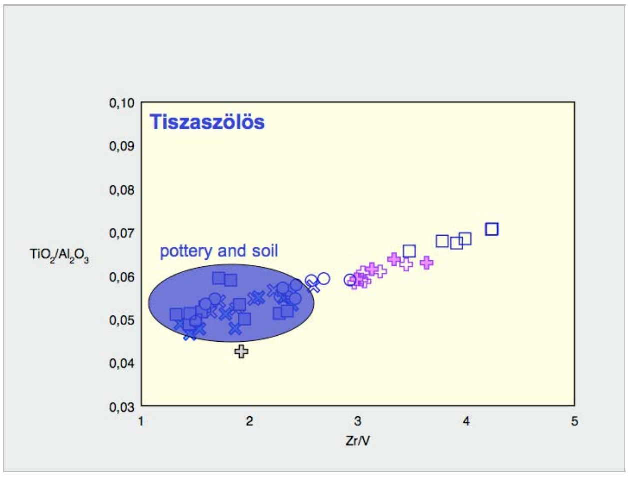

Fig. 5 TiO_2/Al_2O_3 vs. Zr/V ratios in a diagram displaying data points of samples from Tiszaszőlős, Füzesabony, Felsővadász and Tiszalúc only. The shaded field marks the position of pottery and soil samples of Tiszaszőlős. Pottery samples are marked with filled symbols, whereas soils (sediment, clay) are marked with open symbols.

For the fused beads 1,5000 g of dried sample powder (at 105°C) was mixed with 7,5000g MERCK spectromelt A12 (mixture of 66% Li-tetraborate and 34% Li-metaborate) and melted at 1200°C to fused beads using an Oxiflux system from CBR analytical service.

Measurements were done using a Bruker AXS S4 Pioneer XRF device (Rh-tube at 4kW) with 32 standardised samples. Analytical error and detection limits vary and depend on element and sample composition.

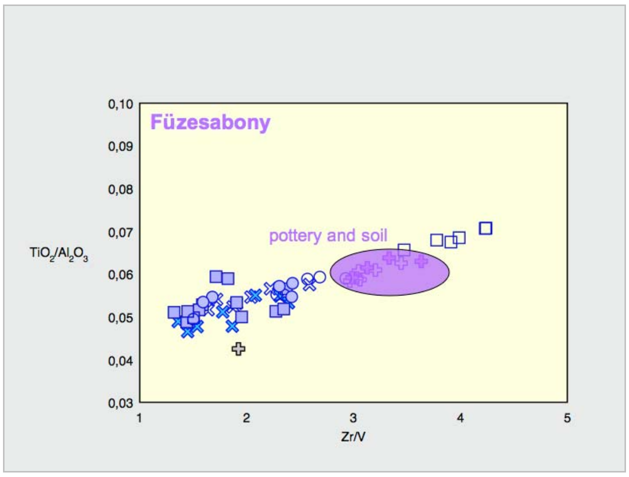

Fig. 6 TiO_2/Al_2O_3 vs. Zr/V ratios in a diagram displaying data points of samples from Tiszaszőlős, Füzesabony, Felsővadász and Tiszalúc only. The shaded field marks the position of pottery and soil samples of Füzesabony. Pottery samples are marked with filled symbols, whereas soils (sediment, clay) are marked with open symbols.

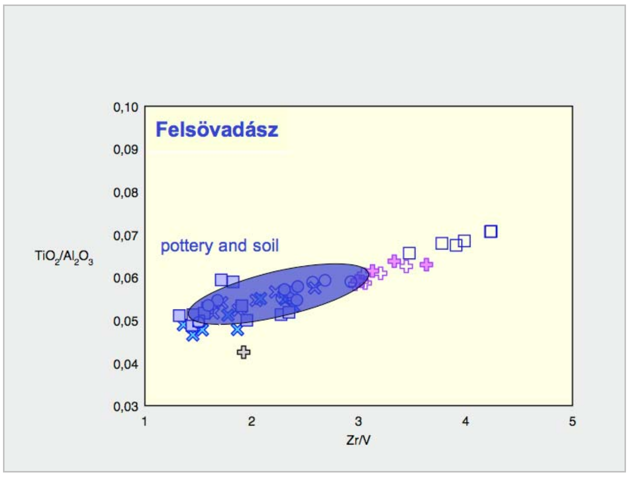

Fig. 7 TiO_2/Al_2O_3 vs. Zr/V ratios in a diagram displaying data points of samples from Tiszaszőlős, Füzesabony, Felsővadász and Tiszalúc only. The shaded field marks the position of pottery and soil samples of Felsővadász. Pottery samples are marked with filled symbols, whereas soils (sediment, clay) are marked with open symbols.

The international standards are compiled in *Govindarau (1989)*. On a routine basis the following elements were measured on each individual sample: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, LOI (determined externally), Ba, Ce, Co, Cr, Eu, La, Nb, Nd, Ni, Rb, Sm, Sr, V, Y, Yb, Zn, Zr.

In order to account for the problems mentioned above in this paper only variation diagrams using the immobile elements TiO_2, Al_2O_3, Zr and V as ratios (TiO_2/Al_2O_3 and vs. Zr/V) are displayed (see **Figs. 2-8**).

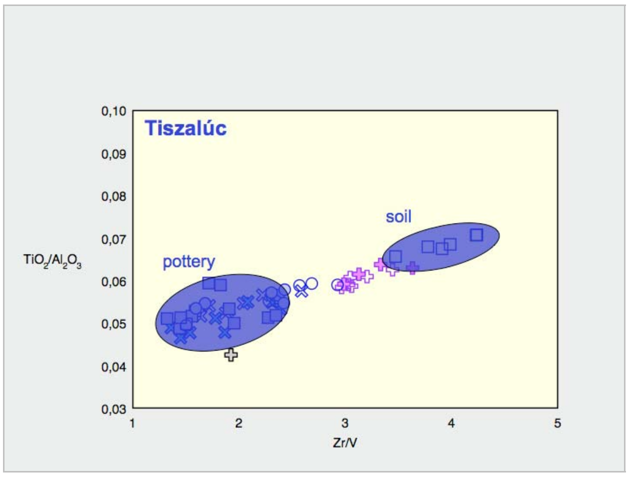

Fig. 8 TiO_2/Al_2O_3 vs. Zr/V ratios in a diagram displaying data points of samples from Tiszaszőlős, Füzesabony, Felsővadász and Tiszalúc only. The two shaded fields mark the position of pottery from Tiszalúc and soil samples from Tiszalúc. Pottery samples are marked with filled symbols, whereas soils (sediment, clay) are marked with open symbols. For Tiszalúc there is a clear separation of the chemical composition of pottery and soil (clay, sediment).

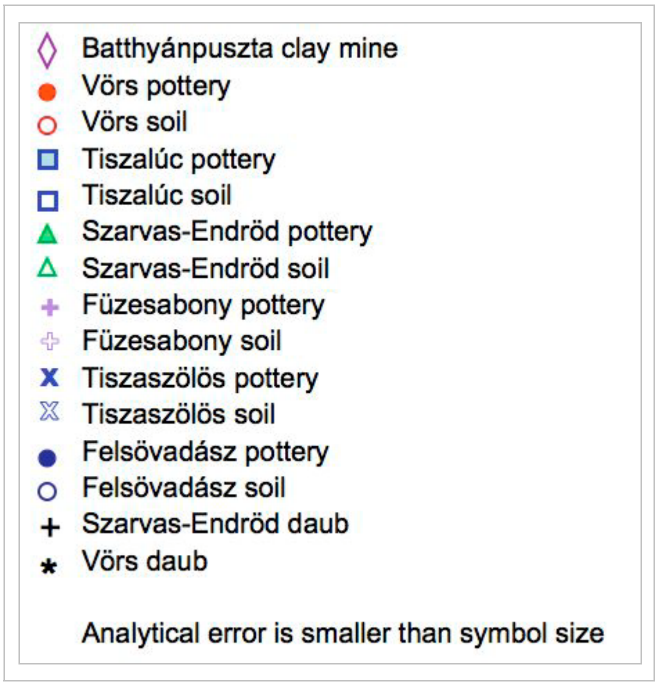

Fig. 9 Legend with the explanation of the symbols used from Fig. 3 throughout Fig. 8. Symbols of samples from the four Neolithic sites Kup, Borsod, Tihany, and Aggtelek are not explained in this Figure as they are not subject of this paper. However, they are shown in Fig. 2, where the complete data set of the project is displayed.

However, several other element concentrations or element ratios are also suitable, as long as they can be regarded as immobile, e.g., P_2O_5, Fe_2O_3, Ni, Cr, Sm, Nd.

Due to the significant variability of the geological background of the individual sites, however, the four elements used in this publication proved themselves as the only ones being suitable for an overview paper. Furthermore, related to this problem, in this paper the focus lies on six selected sites only (Vörs, Szarvas-Endrőd, Tiszalúc, Tiszaszőlős, Füzesabony, Felsővadász) as the inclusion of all ten sites would have complicated the discussion and extended the paper – both is beyond the scope of this presentation as it should be an overview. Six out of ten sites with the most comprehensive and significant database were selected for this paper.

RESULTS

The complete database with all chemical information in the frame of this project is accessible on the project homepage (www.ace.hu/daad). In **Fig. 2** all samples from all ten localities analysed with XRF within the frame of this project are shown, **Fig. 9** displays the symbols that are used throughout **Figs. 3-8** for the Neolithic sites selected for this paper. The combination of two immobile element ratios (TiO_2/Al_2O_3 vs. Zr/V) reveals, that pottery and soil differ in their chemical composition, with the majority of pottery samples (filled symbols) grouping in the lower left part, whereas most soil samples (open symbols) plot in the upper right field of the diagram, however, there is also an overlapping of both fields. Due to the many data points it is not evident at first sight, but the soil samples (raw material of pottery and burnt wall debris, daub) are characteristically different for most of the localities. Soil samples are represented mineralogically by sandy clays, with variable amount of quartz grains and variable concentration of double layer and triple layer clay minerals. Also, the geochemical pattern of pottery at individual sites ("fingerprint") is different by sites and regions. Pottery is completely of Neolithic age, but different in culture and style. This implies, that each site has to be discussed separately as specific parameters apply. Some of the sites have already been reported individually in respect of soil and pottery petroarchaeology, others are currently under inspection (*Gherdán et al. 2004, Biró et al. 2007, Szakmány & Starnini 2007, Szilágyi & Szakmány 2007*). The present paper is concerned with the overall geochemical features.

In **Fig. 3** and **Fig. 4** - for simplicity - only data points of soil and pottery/daub samples from Vörs and Szarvas-Endrőd are shown (see also Symbols in **Fig. 9**). As can be seen in **Fig. 3** at Vörs the possible raw materials of the pottery, i.e. the soil samples, are different in chemical composition from the pottery and cluster in the upper right field of the diagram. Pottery is more heterogeneous in chemical composition, probably due to the variable amounts of different clay minerals. Furthermore the database for Vörs pottery is the largest in the frame of this project, reflecting the high variability regarding Neolithic pottery at Vörs. In **Fig. 4** samples from Szarvas-Endrőd show a similar situation, but with less chemical variation in the pottery samples and an overlap with the soil samples. Additionally, for these two sites there are also findings of daub fragments. These do overlap chemically completely with the soil samples, indicating a direct origin from a local raw material.

In **Figs. 5-8** samples from Tiszalúc, Tiszaszőlős, Füzesabony and Felsővadász are shown. Similarly, as in **Fig. 3** for the Vörs samples, **Fig. 8** (Tiszalúc) again shows a site, where Neolithic pottery and local soil, which is the possible raw material, are chemically completely different. This is no surprise, because the soil samples show the highest TiO_2/Al_2O_3 ratio of all soil presented in this paper, indicating a lower clay mineral concentration and thus a raw material less suitable for pottery production, whereas the pottery signature is very similar to that of the Vörs pottery.

In contrast, **Figs. 5-7** represent the localities of Füzesabony, Tiszaszőlős and Felsővadász showing that pottery and soil samples overlap and are not distinguishable chemically, which is a special phenomenon especially for Füzesabony, as the pottery samples show chemical features that are typical for soils and in the frame of this project represent the pottery samples with the highest TiO_2/Al_2O_3 ratio, showing features otherwise typical for soil samples.

DISCUSSION AND CONCLUSION

Using immobile elements and element-ratios instead of element-concentrations allows to distinguish chemically between pottery and soil for each individual site studied in the frame of this project. Both materials, pottery on one side, and soil samples as their potential raw materials on the other side display typical chemical patterns. At some localities they are identical (Tiszaszőlős, Felsővadász, Füzesabony, partly Szarvas-Endrőd), at some are different (Vörs, Tiszalúc, partly Szarvas-Endrőd). The immobile elements used here also make it possible to distinguish and fingerprint the pottery samples from each of the ten sites, and the same is possible for the soil samples.

Apart from the fact that pottery samples usually have a lower TiO_2/Al_2O_3 and Zr/V ratio compared to soil samples, only few chemical features can be found that all ten sites studied have in common (also interesting in this context: P_2O_5, Fe_2O_3, Ni, Cr, Sm, Nd). This makes it especially difficult to summarize from a geochemical point of view. Each site has its specific problem, and has to be discussed separately as specific parameters apply. Some to mention are geological parameters of the catchment area as concentration of quartz and feldspar grains, type of clay minerals, alteration of clays, anthropogenic influence like temper and levigation, usage of pottery, biological influence, e.g. bat dung in cave.

Where we have findings of daub, net-weights and wall debris fragments (Vörs, Szarvas-Endrőd), their chemical composition is identical to that of the local soil, a fact that indicates that for this purpose obviously soil of lower quality was accepted.

At some sites local soil and pottery are very similar chemically (Füzesabony, Tiszaszőlős and Felsővadász), which is an evidence that the local sediments might be used without any further pre-selection or treatment (temper, levigation, etc.). Apart from Füzesabony this is mainly the case, when the local sediments plot in the lower and left side of the diagram TiO_2/Al_2O_3 vs. Zr/V. This observation suggests that the sediment was of good quality for pottery use anyway. In contrast at some sites pottery and sediment are different chemically (Vörs, Szarvas-Endrőd and especially Tiszalúc). The question here is, whether clay was selected, treated (through tempering, grain size selection) or transported from other sites.

All results and conclusions presented here are based on geochemical data. However, this is only one aspect in archaeometry. Further analyses, especially petrography and XRD for mineralogical information are essential to prove the assumptions made here (or to re-interpret them). In order to make "the big picture" a cooperation between geologists – and above all – archaeologists is indispensable.

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REFERENCES

BIRÓ, K.T., GHERDÁN, K. & SZAKMÁNY, Gy. (2007): Ceramic sequence of 7000 years: archaeometrical study of pottery finds from Vörs, Máriaasszony sziget (SW Hungary). In: Waksman, Y., Archaeometric and Archaeological Approaches to Ceramics. Papers presented at EMAC '05, 8th European Meeting on Ancient Ceramics, Lyon 2005 BAR International Series Oxford 1691 25-31.

GHERDÁN, K., BIRÓ, K.T. & SZAKMÁNY, Gy. (2004): Petrologic studies on Early Neolithic Pottery from Vörs, SW Hungary ActaMinPetr 45 / 2 41-48.

GOVINDARAU, K. (1989): Compilation of working values and sample description for 272 geostandards, Special Issue of Geostandards Newsletter, Vol. XIII.

SZAKMÁNY, Gy. & STARNINI, E. (2007): Archaeometric research on the first pottery production in the Carpathian Basin: manufacturing traditions of the Early Neolithic, Körös Culture ceramics / Archeometriai vizsgálatok a Kárpát medence első kerámia készítői körében: Körös kultúra, DK-Magyarország. Archeometriai Műhely 2007 IV/2, 5-20.

SZILÁGYI V. & SZAKMÁNY Gy. (2007): Petrographic and geochemical study of ceramics of Neolithic settlements on the northern boundary of the Great Hungarian Plain – Tiszaszőlős-Domaháza (Körös Culture) and Füzesabony-Gubakút (ALP Culture, Szatmár Group) / Az Alföld északi határán található neolit telepek – Tiszaszőlős-Domaháza (Körös-kultúra) és Füzesabony-Gubakút (AVK-kultúra, Szatmár-csoport) – kerámiáinak kőzettani és geokémiai vizsgálata. Archeometriai Műhely 2007 IV/3, 31-46.

TAUBALD, H., BIRÓ, K., KASZTOVSZKY, Zs. & BALLA, M. (in press): Early Neolithic Pottery and its Environment in Hungary. In press for the proceedings of the 36th ISA Symposium, Quebec 2006.

TAUBALD, H. & BIRÓ, K.T. (2007): Archaeometrical analysis of Neolithic pottery and comparison to potential sources of raw materials in the immediate environment of the settlements – a first summary of the MÖB-DAAD exchange program. Archeometriai Műhely 2007, IV/2, 1-4.

ZÖLDFÖLDI, J., PINTÉR, F., SZÉKELY, B., TAUBALD, H., T. BIRÓ, K., MRÁV, Zs., TÓTH, M., SATIR, M., KASZTOVSZKY, Zs. & SZAKMÁNY, Gy. (2004): Római márványtöredétek viszgálata a Magyar Nemzeti Múzeum gyüjteményéböl. (Provenance studies on Roman Marble Fragments in the Hungarian National Museum, Budapest) Archeometriai Műhely 2004, I/1, 40-46.