# SOME INTERESTING APPLICATIONS OF RADIOCARBON DATING TO ART AND ARCHAEOLOGY

## A RADIOKARBON KORMEGHATÁROZÁS NÉHÁNY ÉRDEKES ALKALMAZÁSA

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## *Abstract*

*Radiocarbon dating is an important tool for the determination of the age of many samples and covers the time period of approximately the last 50,000 years. We can use radiocarbon dating to estimate the age of a wide variety of carbon-containing materials. Both organic or inorganic materials at the Earth's surface and in the oceans form in equilibrium with atmospheric carbon-14. This makes it an important tool for the understanding of processes during the time-scale of modern humans, from the last glacial-interglacial transition, to recent archaeological studies of art works. We present an overview of the technique, its advantages, assumptions and limitations. We also emphasize dating interesting objects. Radiocarbon has been applied to dating many historical artifacts and archaeological applications. Some specific examples including dating of famous artifacts of artistic, religious and scientific interest are discussed.*

## *Kivonat*

*A radiokarbon kormeghatározás az abszolút kronológiai adatok meghatározásának fontos eszköze, sokféle mintán alkalmazható és alkalmas az utolsó 50 000 év leleteinek datálására. A módszert sokféle, szenet tartalmazó anyag korának meghatározására használhatjuk. Szerves és szervetlen mintákat vizsgálhatunk a Föld felszínéről vagy az óceánok mélyéről, bárhonnan, ahol a C-14 izotóp mennyisége egyensúlyban volt a légköri szén izotóp összetétellel. Ennek következtében fontos eszköze a fejlődési folyamatok megismerésének a modern ember létezésének idején, az utolsó jégkorszakot megelőző interglaciális időszak végétől egészen napjainkig. A tanulmányban áttekintést adunk a kormeghatározási eljárásról, előnyeiről, feltételeiről és korlátairól. Esettanulmányokat mutatunk be érdekes műtárgyakon. A radiokarbon kormeghatározást számos történeti és régészeti tárgyon próbálták ki, amelyek között néhány különleges művészeti, vallási vagy tudományos értékkel is bír.*

KEYWORDS: RADIOCARBON DATING, ART, ARCHAEOLOGY

KULCSSZAVAK: RADIOKARBON KORMEGHATÁROZÁS, KÉPZŐMŰVÉSZET, RÉGÉSZET

## *Introduction*

Radiocarbon ($^{14}C$) is produced in the upper atmosphere by the action of secondary cosmic-ray particles, which are thermal neutrons on nitrogen. It has a half-life of 5,700 years and the amounts of $^{14}C$ produced naturally cover the time scale of approximately 50,000 years (Jull 2013a; Kutschera 2013; Fifield 1999; Tuniz et al. 1998). Of course, this is also the period of interest to archaeology and many other fields. There are a large and diverse number of applications of $^{14}C$ (Jull 2013b). Originally, $^{14}C$ was counted by decay counting of the nuclide, however this has now been largely replaced by direct measurement of $^{14}C$ atoms using accelerator mass spectrometry (AMS). Indeed, accelerator mass spectrometry has become the method of choice for most measurements of longer-lived radionuclides, of which the most well-known is carbon-14 (Jull and Burr 2013a). This method allows for much smaller samples of carbon to be measured than were previously possible using decay counting, since counting atoms directly is inherently more efficient than by counting radioactive decay particles. In practice, the measurement of samples of carbon of 0.05 to 0.5 mg is easily performed (Jull and Burr 2013b).

Radiocarbon dating relies on a basic assumption that organic or inorganic materials are in equilibrium with $^{14}C$, which is produced in the atmosphere and its removal into other reservoirs,

and which establishes a constant level of $^{14}C$ at any given time. This relies on the radioactive decay equation (Rutherford and Soddy 1902), where the decay rate is determined by the number of atoms:

$$\frac{dN}{dt} = -\lambda N \quad [1]$$

Where N is the number of atoms, t is time and λ is the decay constant of the nuclide. When an animal or plant dies, it is removed from the atmospheric equilibrium and so the level of $^{14}C$ decays according to equally recognizable equation:

$$\frac{N}{N_0} = e^{-\lambda t} \quad [2]$$

Where N0 is the number of atoms present at the time of formation of the material. One can therefore easily solve for the apparent "radiocarbon age" of the sample, by rearranging this equation:

$$t = -\lambda \ln(\frac{N}{N_0}) \quad [3]$$

Where t is the "radiocarbon age" of the material. This "radiocarbon age" is an approximate age of the material, since there are other effects on the $^{14}C$ production in the atmosphere (Burr 2013). Usually, radiocarbon ages are quoted in "years before present" (yr. BP), where "present" is defined as 1950AD. In practice, the production rate of $^{14}C$ in the atmosphere varies with time, so that it is important to calibrate raw radiocarbon ages derived from eqn. 3 to a true "calendar age". This is achieved by using a calibration of radiocarbon ages against true age from tree-ring records up to 12,700 before present. Beyond that time, calibration is achieved by cross-referencing $^{14}C$ ages of other records, such as annually-layered lake sediments or by cross-correlation of other dating methods such as U-Th in corals and speleothems (Reimer et al. 2013). An example of a calibration is shown in **Fig. 1**.

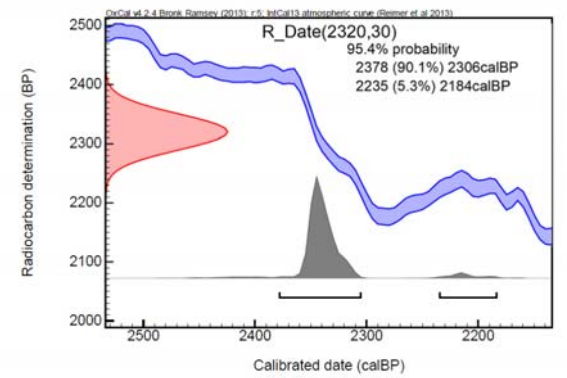


**Fig. 1.:** An example of a calibration of a radiocarbon age. The measured value is plotted on the vertical axis, with the 1σ error. The horizontal axis shows the combination of the analytical measurement with the calibration curve.

**1. ábra:** A radiokarbon koradat kalibrálása. A mért adatot 1σ hibával felvesszük a függőleges (y) tengelyre. A vízszintes (x) tengelyen leolvasható a kalibrációs görbe és a mért érték hibahatárral korrigált kombinációja.

The example shown is very precise, since the curve is very steep at this point. However, an intersect with a flatter or varying part of the calibration curve can obviously give much wider error ranges for the resulting calibrated age.

There are other effects that have changed the inventory of $^{14}C$ in the atmosphere. Fossil-fuel burning has raised the level of CO2 in the atmosphere from 280 ppm in the 18th century to almost 400 ppm today. This $^{14}C$-free carbon added to the atmosphere dilutes the original signal, so that the value today is considerably depressed. After 1950AD, we have a different effect on the radiocarbon curve. There is a large increase due to the atmospheric testing of nuclear weapons, which raised the atmospheric value in the northern hemisphere to 1.8 times the pre-bomb value. Since this testing mainly ceased after 1963, the level in the atmosphere has now decreased to about 1.04 times the pre-bomb value, due to both exchange with the ocean and the addition of more "dead" carbon from fossil-fuel burning. Indeed, the radiocarbon in the surface ocean is now exchanging bomb carbon-14 back into the atmosphere, as shown in **Fig. 2** (Hua et al. 2013). This radiocarbon "spike" allows us to identify recent material, post-1950AD, by its characteristic excess in carbon-14.

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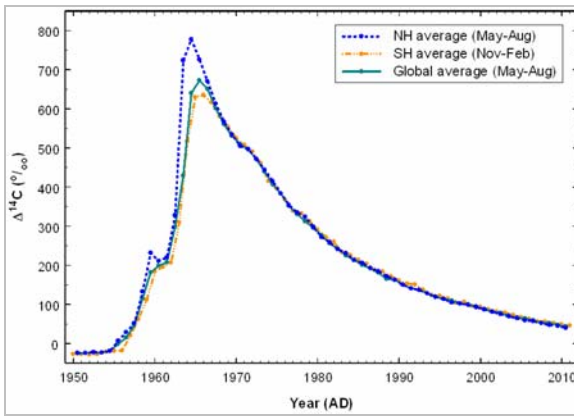


**Fig. 2.:** Average $^{14}C$ bomb pulse effect for the northern and southern hemispheres, from Hua et al. (2013)

**2. ábra:** Átlagos bomba impulzus hatás a $^{14}C$ értékekre az északi és a déli féltekén, Hua et al. (2013) alapján

In this paper, we will review the method, and then give some examples of applications that highlight the usefulness of these measurements to a wide variety of topics.

## *Basics of the AMS Method for adiocarbon*

AMS covers a wide range of different types of instruments, from very large accelerator systems, to the latest compact AMS systems, such as the one at ATOMKI in Debrecen, shown in **Fig. 3** (Molnár et al. 2013). The trend in AMS design over the last 20 years has led to smaller machines. Although they can vary a lot in detail (Jull and Burr 2013b), AMS systems all have the following basic components:

a.) an ion source which generates negative carbon ions (20 to 100 μA C-) by Cs sputtering from a graphite target. In some newer systems, ions can be generated from gas samples.

b.) an injection magnet, which performs the initial separation of the negative ions by mass. At this point, molecular ions such as hydrides of carbon (CH-) are also present. N- is unstable so an important possible interference is removed. Usually, the different isotopes are pulsed through the magnet rapidly.

c.) the accelerator, which may have a voltage of as little as 200 kV or perhaps as much as 3 MV, which accelerates the C- ions towards the “terminal”, which is located in the central part of the machine and is at high voltage.

d.) the terminal, that includes a gas canal, usually known as the "stripper". Negative carbon ions enter the canal and interact with a gas. Because they are

**Fig. 3.:** The MICADAS AMS system installed at Debrecen (courtesy Dr. M. Molnár).

**3. ábra:** A Debrecenben telepített MICADAS AMS rendszer.

moving so fast, they lose several electrons from their electron cloud, and as a result become positively charged. Depending on the design of the AMS, this can vary from the C+ to C3+ charge state.

e.) an electrostatic analyzer that allows us to select ions of one energy/charge ratio.

f.) a magnet to separate ions of the correct mass/charge ratio for the given design.

g.) a solid-state or gas ionization detector, which can discriminate between ions of $^{14}C$ and other isotopes.

h.) a data analysis and storage system. At Arizona, we use the procedures detailed by Donahue et al. (1990) to calculate the radiocarbon ages from the isotopic measurements.

## *Chemical Pretreatment*

It is important to use the appropriate chemical pretreatment scheme to clean the sample prior to extraction of the carbon in the form of graphite or CO2. In general, we use an acid-base-acid method for charcoal, wood, cellulose, plant material, animal tissue: After physical inspection, samples are cleaned with 1N HCl acid, 0.1% NaOH and 1N HCl (acid-base-acid (ABA) pretreatment), washed with distilled water until neutral, dried, and combusted to CO2 at 900oC with CuO. In contrast, carbonate samples are etched with H3PO4 to remove 50-85% of the carbonate, dried and hydrolysed with H3PO4 as discussed by Burr et al. (1992). More complicated cleaning is done for many kinds of art works, since the samples are also subjected to a Soxhlet extraction usually using hexane, then ethanol and finally methanol. Some laboratories also use acetone as an additional step in the Soxhlet protocol. All these steps are designed

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to remove various kinds of organic contaminants (Bruhn et al. 2001; Hatté and Jull 2013). For further details on sample pretreatment techniques for AMS analysis, the reader is referred to Hajdas (2009).

We have had some success dating iron archaeological artifacts by either melting the sample in an oxygen atmosphere and extracting CO2, or by using wet-chemical techniques (Park et al. 2010). In our laboratory, we use a radio-frequency induction furnace to melt the iron in a flow of oxygen. We have also had some limited success dating archaeological bronze items in this way (Jull, unpublished results).

An important material to consider for dating is bone. Bone degradation is a complex process and a lot of attention needs to be given to bone pretreatment because of the important role they play in archaeological studies. The basic method has remained unchanged for many years, which involves collagen extraction (Longin 1971). Collagen is a fibrous protein and the principal constituent of bone. This material degrades with time as a result of post-depositional alteration and eventually breaks down into individual amino acids. Because bone proteins break down over time, there is usually some type of pre-screening of bone samples, for example by measuring the elemental C/N ratio. Modern bone consists of ~22 wt% collagen and this value decreases with the age of the material. Samples with as low as 0.5% collagen may be datable, but often require specialized chemical pretreatment, such as the isolation and analysis of individual amino acids (Van Klinken 1999). Samples with <0.5% collagen are generally considered unsuitable for obtaining a useful date. Another refinement of the collagen extraction technique has become standard in the past decade, using ultrafiltration to isolate the >30 kD molecular weight fraction (Brown et al. 1988).

Groundwater and surface waters can be dated by extracting dissolved inorganic carbon by acid hydrolysis, in the same way as carbonates (Burr et al. 1992). We can extract dissolved organic carbon using either KMnO4 or K2Cr2O7 as an oxidizing agent, as well as in other ways (Leonard et al. 2013).

After cleaning and combustion, the carbon dioxide produced is converted to graphite using an iron catalyst. Finally, the graphite powder is pressed into a target holder and can be put into the accelerator ion source for analysis, along with other samples, known standards and blanks.

## *Some Aplications*

### Shroud of Turin

Perhaps the most famous example of radiocarbon dating involves the Shroud of Turin. This is a linen cloth which has the image of a crucified man. It is widely believed to be the burial cloth of Christ, although radiocarbon dating shows it to be of medieval age. Damon et al. (1989) reported a result of 691±31 radiocarbon years BP, which using the current calibration curve (Intcal13) gives a calibrated age of 1264-1388AD (95% confidence interval), the same range as originally reported. Freer-Waters and Jull (2010) discussed further characterization of the material. Intriguingly, there has been much discussion about these results and various challenges have been made to the original measurements. However, there has not been any reason to doubt the original studies. Many proposals have been made to do new dating measurements, however, so far none have been allowed by ecclesiastical authorities. Presumably, further work to confirm these results may be done in future.

**Fig. 4.:** The Book of Isaiah. This parchment is on display in the Shrine of the Book in Jerusalem. It dates to 209-59BC according to radiocarbon dating, or 150-125BC from studies of the writing style (Bonani et al. 1991; Jull et al. 1995). Image courtesy Israel Museum.

**4. ábra:** Ézsaiás Könyve. Ez a pergamen Jeruzsálemben látható a „Shrine of the Book" múzeumban. Kora a radiokarbon adatok szerint 209-59 BC, vagy 150-125 BC az írásmód vizsgálata alapján (Bonani et al. 1991; Jull et al. 1995).

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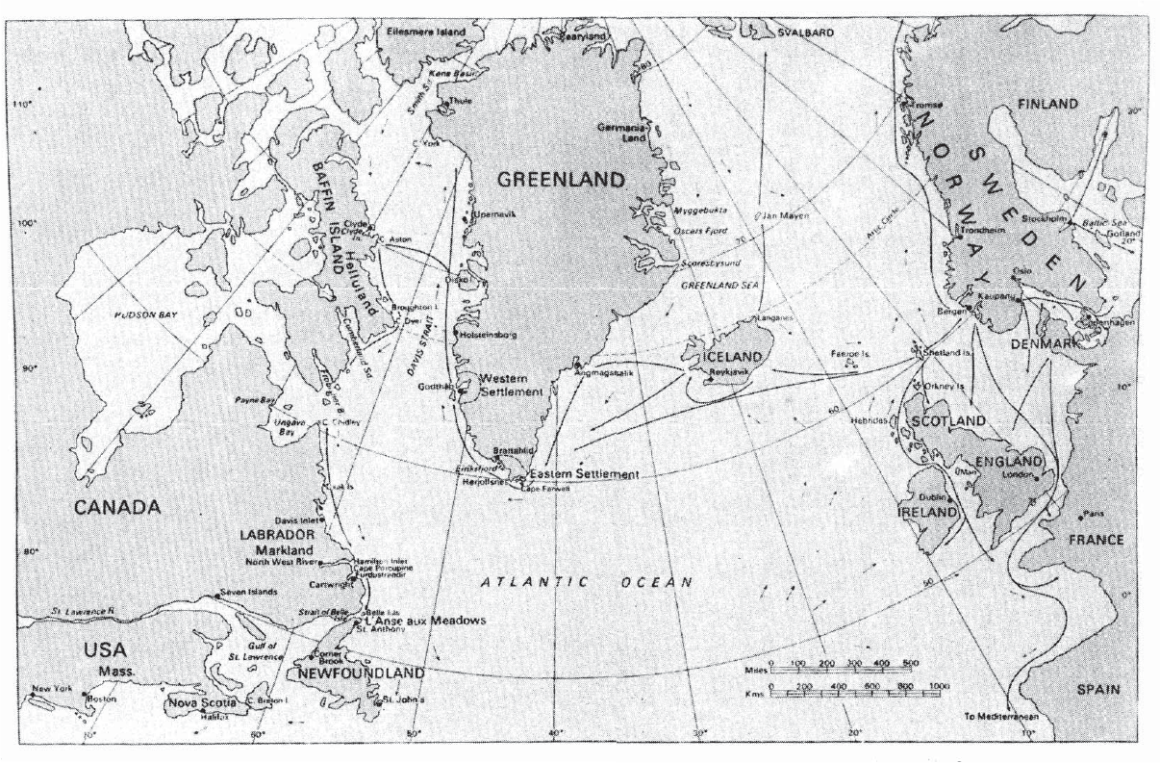


**Fig. 5.:** A map of Viking exploration routes, adapted from a drawing of G. Furuholmen (Canada Department of Mines and Technical Surveys) and reproduced by Nydal (1989) in Radiocarbon with permission.

**5. ábra:** A viking felfedezők utvonalainak térképe, G. Furuholmen (Canada Department of Mines and Technical Surveys) rajza alapján. (Nydal 1989 nyomán).

**Fig. 6.:** Vinland Map, dated by Donahue et al. (2002). Courtesy Beineke Rare Book Library, Yale University and Radiocarbon.

**6. ábra**: Vinland térképe, Donahue et al. (2002).kormeghatározása

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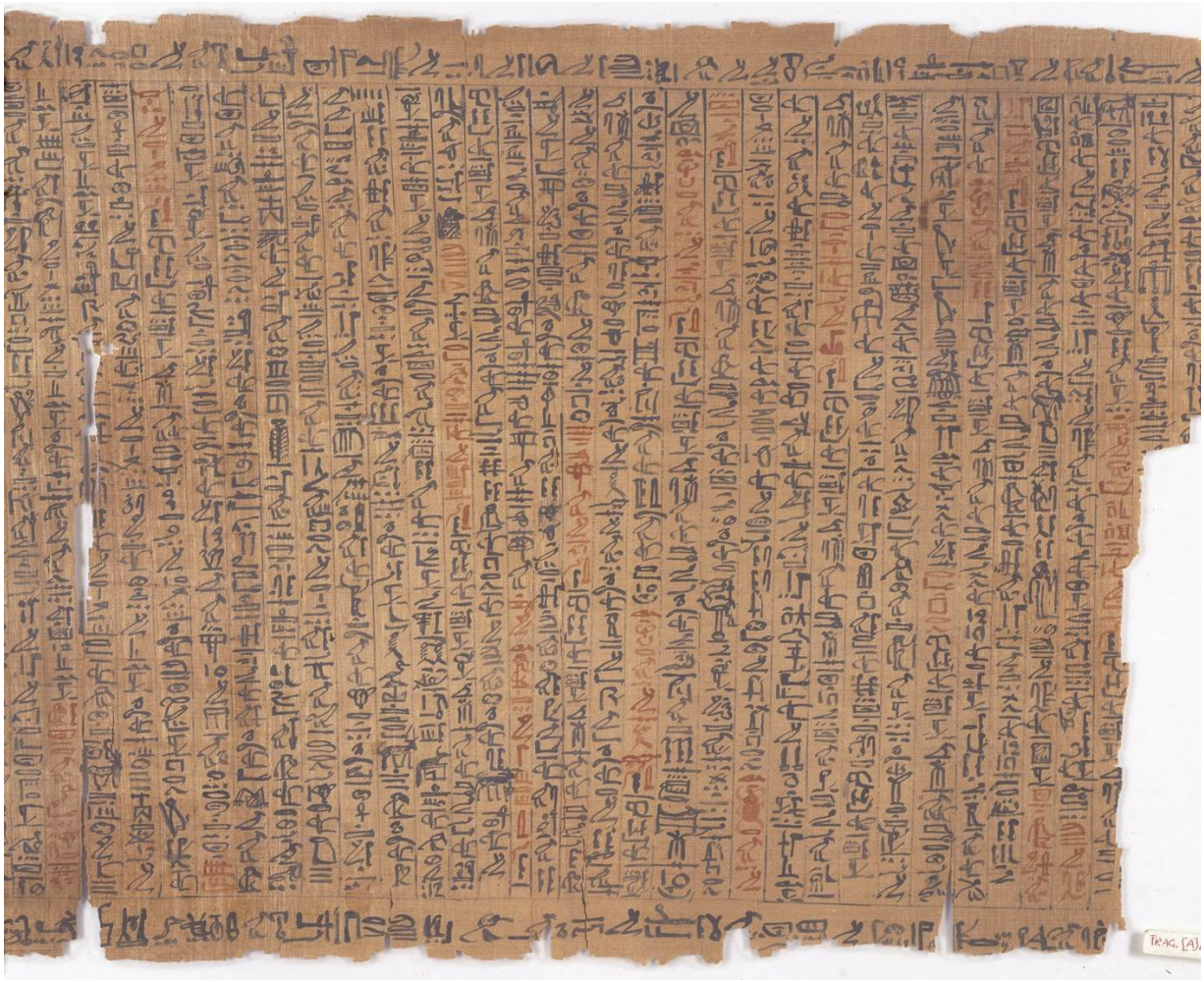

**Fig. 7.:** A papyrus page from the Egyptian Book of the Dead. Courtesy Brooklyn Museum.

**7. ábra:** Egy papirusz oldal a Holtak Könyvéből (Brooklyn Museum)

**Dead Sea Scrolls**

A remarkably uncontroversial example is the study of the Dead Sea Scrolls (Shanks 1993). These interesting documents, written on parchment or papyrus, contain detailed copies of books of the Old Testament, other religious commentaries on books of the Bible of an esoteric nature, as well as more mundane business documents, such as financial transactions. These documents date from the mid-2nd century BC, for example the Book of Isaiah shown in **Fig. 4**, to the first century AD. They are a fascinating depiction of some religious views from the Maccabean revolt to after the time of Christ, and are the subject of many discussions about their significance. The ages of these documents fit well with the expected results (Bonani et al. 1992; Jull et al. 1995).

**The Gospel of Judas**

The Gospel of Judas is a Gnostic manuscript written on papyrus which has been compiled into a codex, or book. The original text was the subject of extensive criticism by the Christian scholar Irenaeus, who wrote a document called “Against all heresies” in about 180AD. The document gives a radiocarbon age of 1767±16 yr BP, which is consistent with a calibrated age range of 220-340AD.

**Voynich Manuscript**

A most intriguing document, the Voynich manuscript is currently in the possession of the Beineke Rare Books Library at Yale University in the USA. The document was known since about the 16th century, since it was at one time in the possession of the Holy Roman Emperor Rudolph II. The document is enigmatic in that it is written in an indecipherable language, which is assumed to also be encrypted. Many have tried to decipher this code, but none have succeeded. The document consists of strange drawings of astronomical features, botanical drawings of unknown plants and ritual bathing. The purpose of the document

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remains unclear. The manuscript was dated to the 15th century, to 1404-1438AD (Hodgins 2011).

### Vinland Map

Intriguingly, there is another document which is almost exactly the same age as the Voynich manuscript. This is called the Vinland Map, stored in the same library, which shows the New World on a map dated to the mid-15th century (1411-1468AD) (Donahue et al. 2002). This map (**Fig. 5**) used to be controversial, since it shows Newfoundland and Greenland on a map before the time of Columbus. However, we now know that there were earlier explorations to North America by the Vikings, well-dated by radiocarbon (Nydal 1989). There is a famous site at L'Anse aux Meadows in Newfoundland ("Vinland") giving ages of 975-1000AD, so the fact that Vinland appears on this map is not surprising. **Fig. 6** shows a map of Viking explorations shown by Nydal (1989).

### Egyptian Book of the Dead

One interesting object that we have dated was made on papyrus and features several pages of the Egyptian Book of the Dead. This is shown in **Fig. 7**. This object gave a very nice radiocarbon result of 1620-1430BC, and the calibration result is useful to show, as it gives some idea of the fit of this result to the calibration curve. In **Fig. 8**, one can observe that the smooth Gaussian curve of the "radiocarbon age" becomes more complex when passed through the complex function of the calibration curve, giving the result shown on the horizontal axis. The chronology of Egypt used to be based solely on dynastic chronologies and "king lists". However, Ramsey et al. (2010) have been able to cross-correlate the dating of Egyptian sites from historical records with radiocarbon dates on materials found in tombs with the radiocarbon calibration curve (Reimer et al. 2013).

## *Conclusions*

To conclude, dating art works is a fascinating topic that brings laboratory scientists into contact with a wide range of persons in different fields.

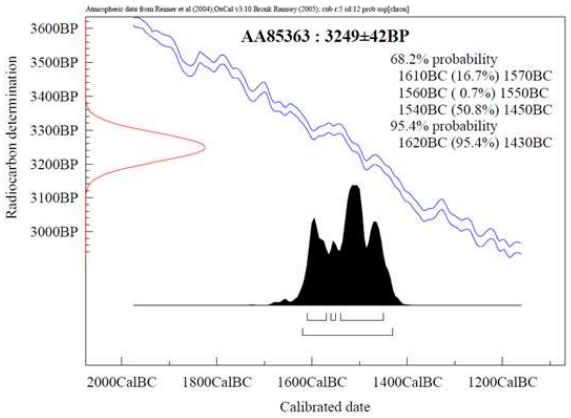


**Fig. 8.:** Calibrated age distribution for the papyrus page shown in **Fig. 7.**

**8. ábra:** A **7. ábrán** bemutatott papirusz kalibrált kora

Some are done for private individuals, so we cannot show those results here, although we do note that we also frequently receive art works for dating that turn out to be younger than expected. One example can be given which was dated both at Arizona and also in Debrecen. The result in both laboratories was the same and confirmed that the painting in question did not date from the early 16th century, as expected, but from the period of 1700-1950AD, when radiocarbon ages are subject to a number of fluctuations due to changes in solar activity and also the addition of "old" carbon due to the industrial revolution. Unfortunately, this is quite a common result. We attribute this to the copying of great works by later art students. Any visitor to an art gallery can observe enthusiastic students works on quite excellent copies of some great master's work. Hence, many copies of great art works circulate and the unsuspecting collector can be surprised when the expected Old Master turns out to be not quite so old. In any case, there are many excellent examples of radiocarbon dating applied to works of art and artifacts. We can only present a few of them here and we hope this brief introduction is helpful. Radiocarbon dating has an important place in the toolbox for the archaeologist and the art historian.

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## *References*


BONANI, G., IVY, S., WÖLFLI, W., BROSHI, M., CARMI, I., STRUGNELL, J. (1992): Radiocarbon dating of fourteen dead-sea scrolls. *Radiocarbon* **34/3** 843–849.

BROWN, T. A., NELSON, D. E., VOGEL, J. S., SOUTHON, J. R. (1988): Improved collagen extraction by modified Longin method. *Radiocarbon* **30/2** 171–177.

BRUHN, F., DUHR, A., GROOTES, P. M., MINTROP, A., NADEAU, M. J. (2001): Chemical removal of conservation substances by 'Soxhlet'-type extraction. *Radiocarbon* **43/2a** 229–237.

BURR, G. S. (2013): Causes of Temporal $^{14}C$ Variations. In: Scott A. ELIAS, ed. *Encyclopedia of Quaternary Science* (Second Edition). Elsevier. Oxford, England. 336–344.

BURR, G. S., EDWARDS, R. L., DONAHUE, D. J., DRUFFEL E. R. M., TAYLOR, F. W. (1992): Mass spectrometric $^{14}C$ and U-Th measurements in coral. *Radiocarbon* **34/3** 611–618.

DAMON, P. E., DONAHUE, D. J., GORE, B. H., HATHEWAY, A. L., JULL, A. J. T., LINICK, T. W., SERCEL, P. J., TOOLIN, L. J., BRONK, C. R., HALL, E. T., HEDGES, R. E. M., HOUSLEY, R., LAW, I. A., PERRY, C., BONANI, G., TRUMBORE, S., WÖLFLI, W., BOWMAN, S. G. E., LEESE, M. N., TITE, M. S. (1989): Radiocarbon dating of the Shroud of Turn. *Nature* **337** 611–615.

DONAHUE, D. J., LINICK, T. W., JULL, A. J. T. (1990): Isotope-ratio and background corrections for accelerator mass spectrometry radiocarbon measurements. *Radiocarbon* **32/2** 135–142.

DONAHUE, D. J., OLIN, J. S., HARBOTTLE, G. (2002): Determination of the radiocarbon age of the parchment of the Vinland Map. *Radiocarbon* **44/1** 45–52.

FIFIELD, L. K. (1999): Accelerator Mass Spectrometry and its applications. *Reports on Progress in Physics* **62** 1223–1274.

FREER-WATERS, R. A., JULL, A. J. T. (2010): Investigating a dated piece of the Shroud of Turin. *Radiocarbon* **52/4** 1521–1527.

HAJDAS, I. (2009): Applications of radiocarbon dating method. *Radiocarbon* **51/1** 79–90.

HATTÉ, C., JULL, A. J. T. (2013): Radiocarbon dating: Plant macrofossils. In: *Encyclopedia of Quaternary Science*, Second Edition. (eds. S. ELIAS and C. MOCK), Elsevier: Amsterdam. 361–367.

HODGINS, G. W. L. (2011): Forensic investigation of the Voynich manuscript. Presented at Conference: Voynich 100. Frascati, Italy. May 2011.

HUA, Q., BARBETTI, M., RAKOWSKI, A. Z. (2013): Atmospheric radiocarbon for the period 1950-2010. *Radiocarbon* **55/4** 2059–2072.

JULL, A. J. T., DONAHUE, D. J., BROSHI, M., TOV, E. (1995): Radiocarbon Dating of Scrolls and Linen Fragments from the Judean Desert. *Radiocarbon* **37/1** 11–19.

JULL, A. J. T. (2007): Radiocarbon Dating: AMS Method. In: Encyclopedia of Quaternary Science ed. Elias S (Amsterdam: Elsevier). 2911–2918.

JULL, A. J. T. (2013a): Overview of Dating Techniques. In: *Encyclopedia of Quaternary Science*, Second Edition (eds. S. ELIAS and C. MOCK), Elsevier: Amsterdam. 447–452.

JULL, A. J. T. (2013b): Radiocarbon Dating: AMS Method. In: *Encyclopedia of Quaternary Science*, Second Edition (eds. S. ELIAS and C. MOCK), Elsevier: Amsterdam. 316–323.

JULL, A. J. T., BURR, G. S. (2013a): 15.2 Mass Spectrometry Instruments VI: Accelerator Mass Spectrometry. In: *Treatise of Geochemistry* (eds. K. K. TUREKIAN and H. HOLLAND) Elsevier: Amsterdam. **15** 375–383.

JULL, A. J. T., BURR, G. S. (2013b): 14.4 Radiocarbon: Archaeological Applications. In: *Treatise of Geochemistry* (eds. K. K. TUREKIAN and H. HOLLAND) Elsevier: Amsterdam. **14**: 45–53

KUTSCHERA, W. (2013): Applications of accelerator mass spectrometry. *International Journal of Mass Spectrometry and Ion Physics* **349-350** 203–218.

LEONARD, A., CASTLE, S., BURR, G. S., LANGE, T., THOMAS, J. (2013): A wet oxidation method for AMS radiocarbon analysis of dissolved organic carbon in water. *Radiocarbon* **55/2–3** 545–552.

LONGIN, R. (1971): New method of collagen extraction for radicoarbon dating. *Nature* **230** 241–242.

MOLNÁR M., RINYU L., VERES M., SEILER M., WACKER L., SYNAL H.-A. (2013): EnvironMICADAS: A Mini $^{14}C$ AMS with Enhanced Gas Ion Source Interface in the Hertelendi Laboratory of Environmental Studies (HEKAL), Hungary. *Radiocarbon* **55/2-3** 338–344.

NYDAL, R. (1989): A critical review of radiocarbon dating at a Norse settlement in L'Anse aux Meadows, Newfoundland, Canada. *Radiocarbon* **31/3** 976–985.

PARK, J. S., BURR, G. S., JULL, A. J. T. (2010): A thermal and acid treatment for carbon extraction

from cast iron and its application to AMS dating of cast iron objects from ancient Korea. *Radiocarbon* **52/2-3** 1312–1321.

RAMSEY, C. B., DEE, M. W., ROWLAND, J. M., HIGHAM, T. F. G., HARRIS, S. A., BROCK, F., QUILES, A., WILD, E. M., MARCUS, E. S., SHORTLAND, A. J. (2010): A radiocarbon-based chronology for dynastic Egypt. *Science* **328** 1554–1558.

REIMER, P. J., BARD, E., BAYLISS, A., BECK, J. W., BLACKWELL, P. G., RAMSEY, C. B., BUCK, C. E., CHENG, H., EDWARDS, R. L., FRIEDRICH, M., GROOTES, P. M., GUILDERSON, T. P., HAFLIDASON, H., HAJDAS, I., HATTÉ, C., HEATON, T. J., HOFFMANN, D. L., HOGG, A. G., HUGHEN, K. A., KAISER, K. F., KROMER, B., MANNING, S. W., NIU, M., REIMER, R. W., RICHARDS, D. A., SCOTT, E. M., SOUTHON, J. R., STAFF, R. A., TURNEY, C. S. M., VAN DER PLICHT, J. (2013): Intcal13 and Marine13 radiocarbon age calibration curves 0-50,000 years cal. BP. *Radiocarbon* **55/4** 1869–1887.

RUTHERFORD, E., SODDY, F. (1902): The cause and nature of radioactivity. *Philosophical Magazine* **4** 370–396.

SHANKS, H. (1993): *Understanding the Dead Sea Scrolls: A reader from the Biblical Archaeology Review*. Vintage Books: New York. 1–384.

TUNIZ, C., BIRD, J. R., FINK, D., HERZOG, G. F. (1998): *Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science*. CRC Press: Boca Raton. 1–371.

VAN KLINKEN G. J. (1999): Bone collagen quality indicators for palaeodietary and radiocarbon measurements. *Journal of Archaeological Science* **26/6** 687–695.

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# ARCHAEOMETRY ON STONES. MULTI-METHOD APPROACH TO INVESTIGATE STONE PROVENANCE. STUDIED CASES FROM ROMAN HISPANIC MARMORA

## KÖVEK ARCHEOMETRIÁJA: TÖBB MÓDSZER EGYÜTTES ALKALMAZÁSA SZÁRMAZÁSI HELY VIZSGÁLATOKRA. ESETTANULMÁNYOK HISPANIAI RÓMAI MÁRVÁNYOKON

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### *Abstract*

*This contribution aims to expose a number of considerations regarding the reliability of the analytical results in the investigation of the quarry source of stones used as raw material in archaeological pieces. In many cases, a sequential selection of common petrological techniques achieves a positive result in provenance identification. Together with petrography and the determination of C and O stable isotopes, the study must often be complemented by the application of an additional technique to increase the rate of success, especially with certain white marbles. In some cases, however, even with a multi-method approach, the analytical results only guarantee an uncertain provenance between two possible marble sources. Additional remarks are reported after the archaeometric studies carried out on marble pieces found in Roman Hispania, where the presence of both, local and imported marbles, makes provenance study more difficult.*

### *Kivonat*

*Ez a tanulmány a bányahely azonosítás problémáival, az anyagvizsgálati eredmények megbízhatóságával foglalkozik. Sok esetben, különféle kőzettani technikák megfelelő sorrendben történő alkalmazása jó eredményeket hozhat a származási hely vizsgálatok tekintetében. A kőzettani vizsgálatokkal együttesen alkalmazott stabil izotóp vizsgálatok mellett további technikák alkalmazására is sort kell keríteni a hatékonyság növelése érdekében, különösen bizonyos fehér márvány típusok esetében. Egyes esetekben azonban még a többféle vizsgálati technika is csak bizonytalan azonosítást tesz lehetővé, például két lehetséges márványbánya azonosítása tekintetében. További példákat mutatunk be a római kori Hispánia márvány leletein, ahol mind a helyi, mind a távolsági eredet felmerülhet a márványok tekintetében, ami a vizsgálatok körét kiszélesíti és megnehezíti.*

KEYWORDS: MARBLE, QUARRY, ARCHAEOMETRY, IBERIAN MARBLES

KULCSSZAVAK: MÁRVÁNY, KŐBÁNYA, ARCHEOMETRIA, IBÉRIAI MÁRVÁNYOK

## *Introduction and aims*

Stone and stone artefacts are common in archaeological remains, not only from Roman times, but also from many other periods. It is clear that a wide variety of stones were used for artefacts at different times and in different parts of the world. In general terms, throughout History, man has taken advantage of stone resources that were readily available. Since prehistoric times, man has known how to select stone depending on its quality to be used as a tool, a noble decorative element or perhaps for its special symbolic value. The archaeometrical study of stone pieces helps to understand the way of life of the ancient communities as the results can be of considerable value in establishing the provenance of artefacts and in elucidating exchange mechanisms, as well as providing geographical and chronological evidence of man's activities.

The study of the original geological source, or provenance study, is approached using different petrological, physical and chemical methods, depending on the stone element being under investigation. Dealing with building and decorative stones, it is undertaken through petrographical analyses that make it possible to determine their origin and to identify the quarry from which they were extracted. In general and for economic reasons, local stones were always widely used. The macroscopic and petrographical description of the stone provides a detailed characterization of the lithology, which is indispensable to address a successful identification. The extensive field survey around the archaeological site allows for checking the existence of the stone extraction fronts or locating previously unknown quarries. The type of quarry, number of extraction fronts, tool marks, type and size of the obtained elements, quarrying techniques, are all aspects that facilitate an

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understanding of the implications of stone resource exploitation.

In recent years the scientific community has been paying great attention to the archaeometrical study of archaeological marble pieces from the Hellenistic-Roman world (Maniatis, 2009; Gutiérrez Garcia-M et al., 2012 and other Asmosia proceedings). This survey focuses on the identification of the original stone raw material through the comparative analyses of rocks from ancient quarries. The results not only help to certify their authenticity, but contribute to the identification of copies, to match fragmented pieces and help with the planning of the work of conservation and restoration. In addition, they provide a better historical knowledge of the taste for certain varieties of marble, the preference of use by the sculptural workshops and the intercultural connection of the different artists, not to mention the economic impact arising from the exploitation and trading networks, including the use and distribution of local marbles.

In the sphere of Roman stone artefacts found in Hispania, not only the classical marbles were imported but also different white and coloured marbles were quarried from local sources, increasing the difficulty in discriminating the stone provenance (Àlvarez et al, 2009a; Lapuente 1995; Lapuente et al, 2014). In most cases, the statuary quality of Iberian marbles cannot compete with that of the classics. However, those marbles exploited in the SW of the Iberian Peninsula, particularly from different districts of the Ossa Morena geological unit, were highly appreciated in Roman times with excellent results of carving (Nogales & Beltrán, 2008; Nogales et al, in press). They are the so-called marbles of the Estremoz Anticline district, located in Lusitania, and those from the Almadén de la Plata district, in the Baetica Roman province (**Fig. 1**). Being originally from the same geological unit, the Ossa Morena of the Iberian Massif, both exhibit similarities in physical and compositional parameters, which make it more difficult to ascertain the marble origin of Hispanic artefacts. Additionally, in the Alpine Betic Chain, south of Iberia, pure dolomitic marbles were exploited in Mijas-Coín (quarries of the Málaga district). Their compositional and textural parameters are similar to those of Thasos dolomitic (Lapuente et al, 2000; 2002), increasing even more the complexity of provenance identification. Furthermore, Estremoz, Almadén de la Plata and Coin-Mijas together with other minor quarries from the Malaga district, have recently been identified in archaeological remains outside Iberia (Antonelli et al, 2009; 2015; Origlia et al, 2011). These identifications in the North of Africa open a new perspective for consideration in marble provenance analyses, as until now, these marbles were thought to be destined exclusively for local markets. A wide variety of physical and chemical techniques exist today to establish the nature and provenance of the stone artefacts. Databases, such as The Miss Marble database, (Zöldföldi et al, 2009) of combined mineralogical as well as chemical and physical parameters aim to help discriminate between ancient quarrying areas.

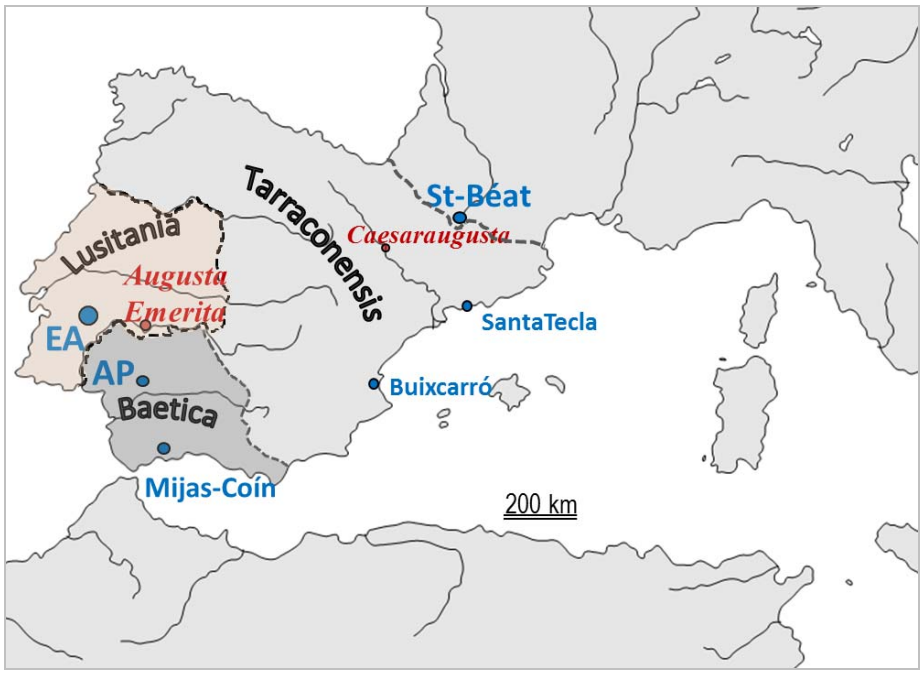


**Fig.1.**

Geographical setting of the Hispanic archaeological sites, the Roman provinces and the principal Iberian quarries named in the text. EA: Estremoz Anticline district. AP: Almadén de la Plata.

**1. ábra**

A szövegben említett lelőhelyek, a római provinciák és bányahelyek térképe. EA: Estremoz Antiklinális körzet. AP: Almadén de la Plata.

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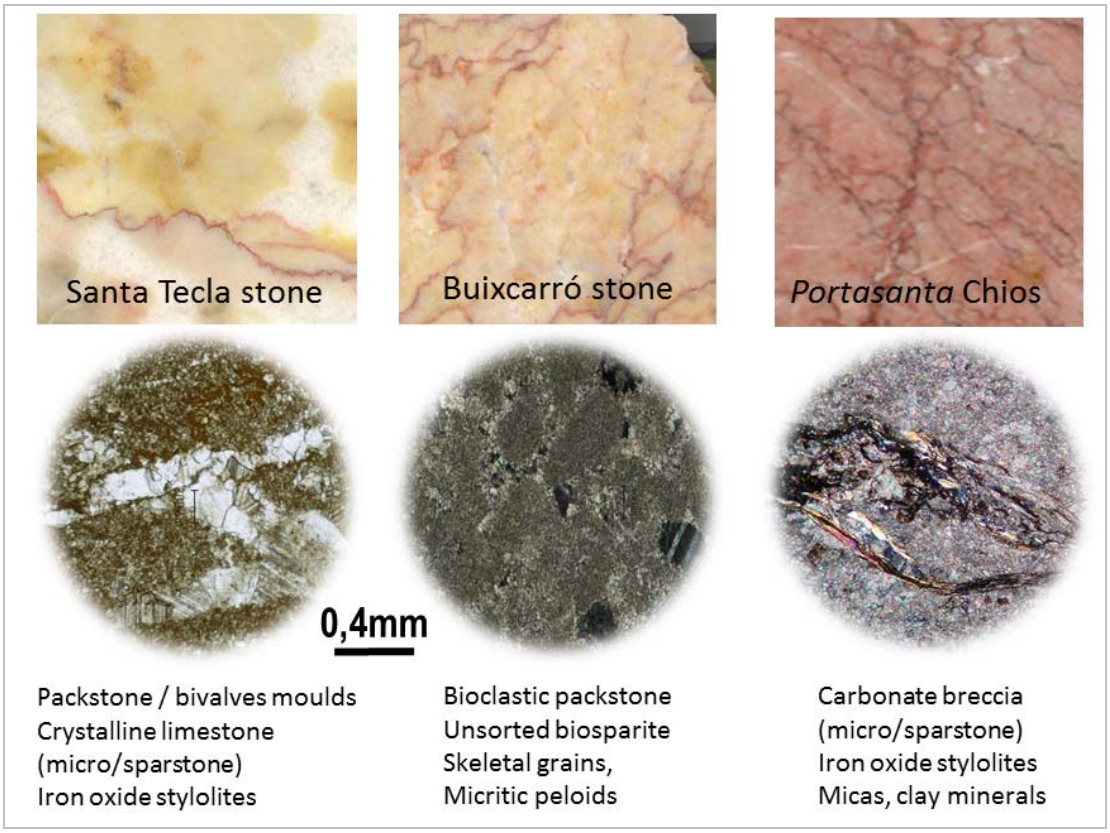


**Fig. 2.:** The yellow variety of Santa Tecla, exploited by Romans in the city of Tarraco visually resembles the appreciated *Giallo antico*, or *marmor Numidicum* from Tunisia. Additionally, the pink variety of Santa Tecla is quite similar not only to other Hispanic stone, the Buixcarró (*marmor Saetabitanum*) exploited near Xativa in Barxeta (Valencia), but also to the *Chium marmo*r known as Portasanta from the island of Chios. As both classical marmora were usually imported into Hispania, the petrographic approach is needed to discriminate the imported from the local stones. All these carbonate varieties are well identified using optical microscopy (Àlvarez et al, 2009a,b).

**2. ábra:** A Santa Tecla típusú kőzet sárga változata amelyet Tarraco környékén bányásztak a római időszakban szabad szemmel erősen hasonlít a tunéziai *Giallo antico*, más néven *marmor Numidicum*-ra. A Santa Tecla rózsaszín változata emlékeztet más hispániai bányászott kőzetekre, pl. a Xativa környéki Buixcarró márványra (*marmor Saetabitanum*), de a Chios szigetéről származó Portasanta vagy *Chium marmo*r-ra is hasonlít. Miután mind a két területről importáltak márványokat Hispániába, a megfelelő forrásterületek elkülonítéséhez kőzettani mikroszkópos vizsgálat szükséges

Macro- and microscopic examinations are always recommended as a starting point, yielding the basic information related to the nature of the stone being studied, on which to build a plan for more detailed examination. Rather than the methodological aspects, widely commented elsewhere (Attanasio, 2003; Lazzarini, 2004), this paper means to offer a series of guidelines intended to serve as a clarification for those not familiar with the archaeometrical study of marbles and who consider that the fact of having analyzed a piece is always sufficient guarantee to certify their quarry of origin.

## *Marble, marmor in Roman times*

The term "*marmor*" used by the Romans, has a similar meaning to that of commercial marble, today. Mainly a proper metamorphic marble, but also whatever sedimentary carbonate rock, even stones of another nature such as serpentines, alabasters, basalts, granites, porphyries, jaspers, etc., which have enough quality to exhibit attractive coloured patterns after polishing. Pompey, Caesar, Cicero all succumbed to the fascination for the architectural and sculptural Hellenistic marbles. During and after Augustus, there was great enthusiasm for marble monuments and ornaments in both public and private spaces as a symbol of the power and image of the Empire. Coloured *marmora* were quarried from many different places around the Mediterranean. Most of their quarries were the property of the Emperor himself and their exploitation and stone trading was kept under strict administrative control.

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The accessibility of the quarries to the nearest port for sea transport was obviously essential. They are well known to scholars because they were documented by the classic sources such as Pliny and even their high prices are known through Diocletian´s edict. *Marmora* used as pavements, opus sectile or walls covered with slabs became synonymous of power and richness, all over the Roman territories. The most important *marmora*, including white marbles, were exploited from the eastern Mediterranean area of Greece and Asia Minor, including their islands, together with Carrara in Italy. Other quarries were those of the conquest territories in the North of Africa, Gallia and Hispania (Àlvarez et al, 2009a).

## *The archaeometrical study of coloured marmora*

The provenance study of coloured *marmora* can be a relatively easy task after a first visual inspection and a later comparison with well-known catalogues (Mielsch, 1985; Gnoli, 1988; Borghini, 1992; Napoleoni, 2001, etc). Additionally, the approach can be carried out by checking historic collections like that of Faustino Corsi found on display at the Museum of Natural History in Oxford and recently available on-line (www.oum.ox.ac.uk/corsi/).

However, the heterogeneity of colour patterns, the state of fragmentation, the existence of diverse varieties extracted from the same quarry and also the imitation with local stones, makes their study more difficult. It is in these cases where petrography is essential to avoid misidentification (**Fig. 2.**).

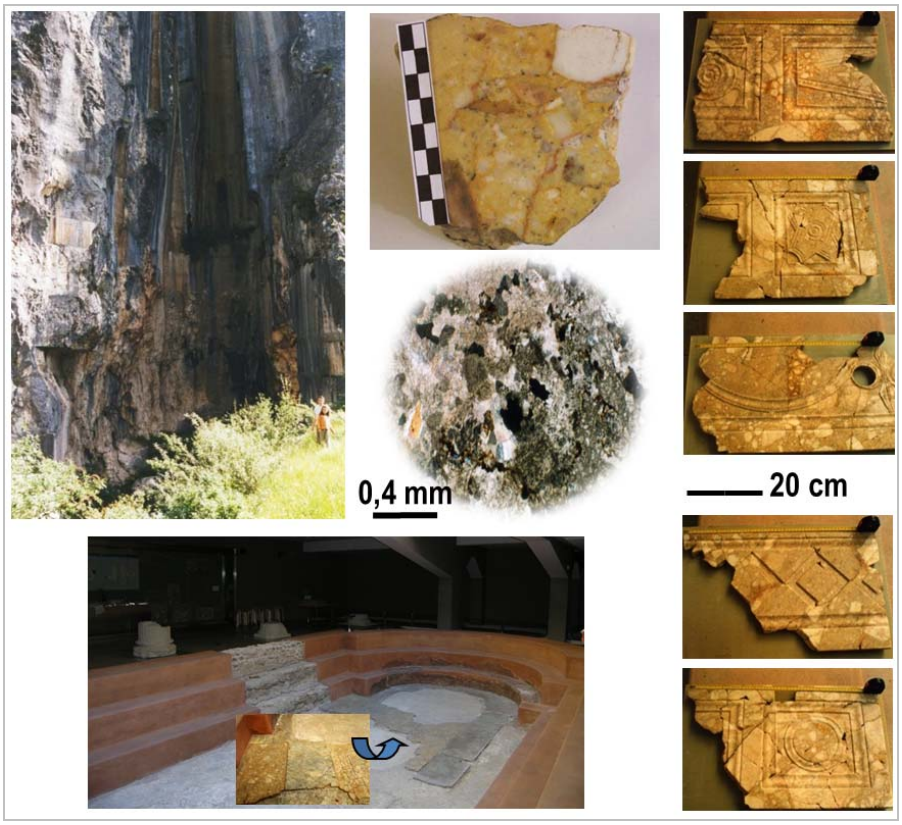


**Fig. 3.:** In Caesaraugusta, a yellow breccia with some golden shades which recall the precious Giallo antico brecciato was used in different buildings. In the public baths, rectangular slabs of this material covered the ground of a large open air swimming pool and also, with ornamental geometric figures, veneering the south wall. After macro and microscopic examination the stone was identified as the Roman breccia from Saint Béat (place called "La Péne-Saint-Martin) in the French Pyrenees, a marble district where white, grey and banded marbles were also exploited in Roman times.

**3. ábra**: Caesaraugusta-ban a Giallo antico brecciato-ra emlékeztető sárga breccsát használták a különféle épületeknél; pl. a közfürdőkben Makroszkópos és mikroszkópos vizsgálatok szerint a kőzet Saint Béat-ból származik (Francia Pireneusok, La Péne-Saint-Martin környéke), ahol fehér, szürke és szalagos mintázatú márványok egyaránt előfordulnak..

A guideline to take into account in the provenance study is the association of different *marmora*. White and coloured marbles jointly exploited from the same area reinforce their mutual identification when both were used in the same architectural decorative programmes. This is the case of certain white and coloured marbles used in Caesaraugusta. An enormous range of several *marmora*, in large and small slabs, covered the orchestra of its Roman Theatre. Their provenance was studied to discover the source area, which at first was only known not to be local. A yellow breccia with some golden shades which recall the precious *Giallo antico brecciato* from Tunisia, but quarried in the French Pyrenees, was the key to identifying many other varieties in white, grey and banded marbles exploited in the same district (**Fig. 3.**).

## *White marbles*

Regarding white marbles, a multi-method approach must be applied in order to discriminate their provenance. A previous step is needed, a database with as many identifying parameters or «finger prints» as possible of the ancient quarry marbles obtained through the application of the same techniques. The identification of the marble source used in one archaeological piece involves a parallel analytical study which may be more or less complex, depending on different factors, from which the existence of local-regional marbles increases the uncertainty. Unlike the multicoloured *marmora,* white marbles need to be analysed following a step by step protocol and even their determination may be unsettled despite applying different analytical methods.

## *Analytical databases with quarry marbles*

The initial phase of the provenance study is based on the elaboration of an analytical database of ancient marble quarries. Each research group works mainly with their own samples and their own analytical database, complemented with additional information from literature. However, not all databases include the same samples and the same methods, while some are based on mineralogical X-ray power diffraction (XRD), optical microscopy (OM) and stable C-O isotopic data; others deal with electron paramagnetic resonance (EPR) data, stable isotopes and certain petrographical parameters such as the maximum grain size (MGS). Cathodoluminescence (CL) microscopy, combined with stable isotopes, has been used for known classical quarrying areas (Barbin et al, 1989, 1992), as well as in Central Europe (Jarč & Zupančič, 2009; Št'astná et al, 2009) and in Iberia (Lapuente et al, 2000, 2014).

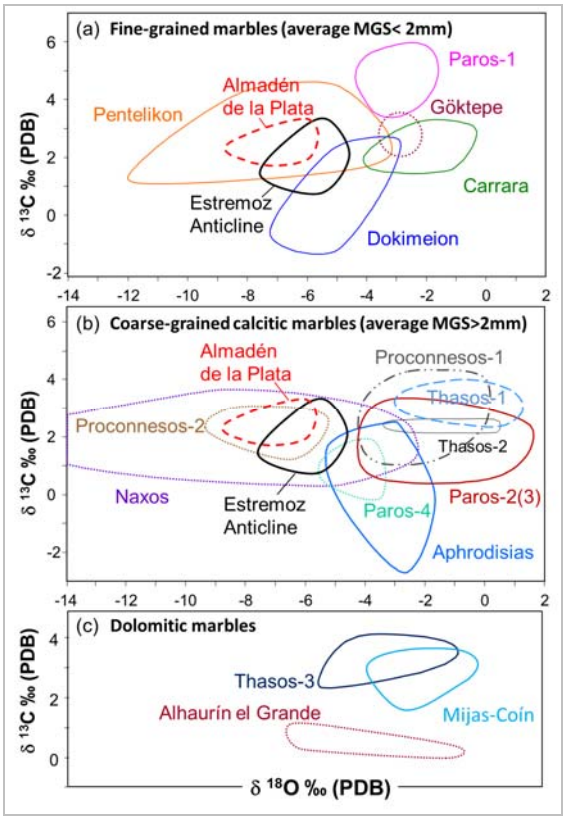


**Fig. 4.:** Isotopic signature of the most important Roman Hispanic white marble quarries compared with the classical marbles.

**4. ábra:** A legfontosabb római kori hispániai fehér márvány bányahelyek stabil izotóp adatai a klasszikus antik márványokhoz hasonlítva

Although it is true that each research team applies their available methods, most of them select the parameters established from a common group of techniques, (OM, XRD and stable C and O isotopes), which are the basis of the characterization of many marbles used in antiquity (e.g. Lazzarini et al, 1980; Herz, 1987; Moens et al, 1992). Marbles from one district of quarries usually have an isotopic signature distinctive from the rest of the marble sources. To improve comparison and discrimination, two different isotopic signature diagrams are commonly used (Gorgoni et al, 2002), one for fine grained marbles (MGS<2mm) and another for the coarse grained ones (MGS>2mm). Although much overlapping is common, especially for the coarse grained marbles, it is by far one of the most popular techniques, whenever it is combined with other techniques like thin-section microscopy. The recent discovery of ancient quarries of Göktepe, in Asia Minor (Attanasio et al., 2009) offers an additional marble source to be considered in the study of marble origin, whose isotopic signature partially overlaps those of Carrara and Dokimeion (Attanasio et al, 2015). Regarding the stable C and O isotopes of the most important Hispanic quarry marbles, updated

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isotopic diagrams for the Estremoz Anticline district in Lusitania and for Almadén de la Plata in Seville, have been reported (Lapuente et al, 2014). In both marble districts, the intra-quarry variation of features affects from macro- to microscale and it is not unusual to find different petrographical characteristics in one single marble block.

In **Fig. 4.**, both Iberian Estremoz Anticline and Almadén de la Plata isotopic fields are plotted in the reference isotopic diagrams for the classical marbles according to Gorgoni et al, (2002) in which the Göktepe field has also been included after data by Attanasio et al (2009, 2015). Pure dolomitic marbles from Mijas-Coín and dolomitic from Alhaurín el Grande together with Thasos dolomitic are also drawn in the same figure. Both Malaguese white marbles have been recently identified in archaeological pieces from Banasa, Morocco (Antonelli et al, 2015).

Secondly, other additional techniques such as the CL or EPR have been applied with success to identify classical marbles (Barbin et al, 1992; Attanasio et al, 2000; 2006; Polikreti & Maniatis, 2002). The use of additional CL features facilitates the discrimination of both mentioned Hispanic districts, whose marbles are similar –looking metamorphic rocks derived from comparable carbonate sequences subjected to a complex structural tectono-metamorphic evolution. Recent studies focused on the characterization of Hispanic marbles, lead us to draw attention to the similarity in visual and petrographical characteristics of white and coloured marbles of Estremoz Anticline and Almaden de la Plata. However, the combined use of Almadén de la Plata with dolomitic marble of Mijas-Coin found (Málaga), in different archaeological remains along the Guadalquivir Valley (Beltrán & Loza, 2008) facilitates their identification. The association of both Baetican materials gives great advantage to address the marble database comparison (Origlia et al, 2011; Antonelli et al, 2015). On the other hand, although both types of marble from the Ossa Morena unit share physical and compositional parameters, the additional combination of CL and isotopes is proving advantageous in their discrimination helping to improve knowledge about the dissemination of both types of marble and corroborating the minimal use of marbles originally from a different administrative Roman province (Lapuente et al, 2014).

Finally, despite this battery of techniques, certain marbles like some varieties of the recently discovered quarries of white Göktepe in Asia Minor (Attanasio et al, 2009) require additional parameters to be distinguished from Carrara marbles (Lapuente et al, 2012). Fortunately, the combination of different content of strontium seems to be useful for their discrimination (Attanasio et al, 2015).

## *The application of the database*

In determining the marble quarry origin of one archaeological artefact, the analyst is faced with a number of difficulties that may affect the final interpretation of the results. On the one hand, sampling the archaeological artefact can be a difficult task and to avoid defacing the piece, a sample is not always taken from the most representative area to identify the marble source. The visual inspection of the complete piece is always recommended to observe any macroscopic characteristic not registered on the sample taken. The natural patina and even the sulphurous smell when being crushed can be useful qualitative features to help in the provenance study.

On the other hand, the more parameters the database contains, more likely it becomes to find the match, though at the same time, more difficult is the step by step comparison due to the common overlapping of features. The results sometimes fail to match well with the comparative parameters due to the lack of certain samples in the databases, either because some ancient quarrying sources still remain undiscovered or because they have become erased after years of intensive quarrying activity. In addition, some “finger prints” may not be exclusive to a single quarry and conversely, the intra-quarry variation from macro to micro-scale, can negatively affect the study of fragmented pieces, especially if great differences are detected in one single marble block. Moreover, the multiplicity of databases and the diversity of analyses with a different presentation of results make the correlation and comparison difficult among samples of different research groups.

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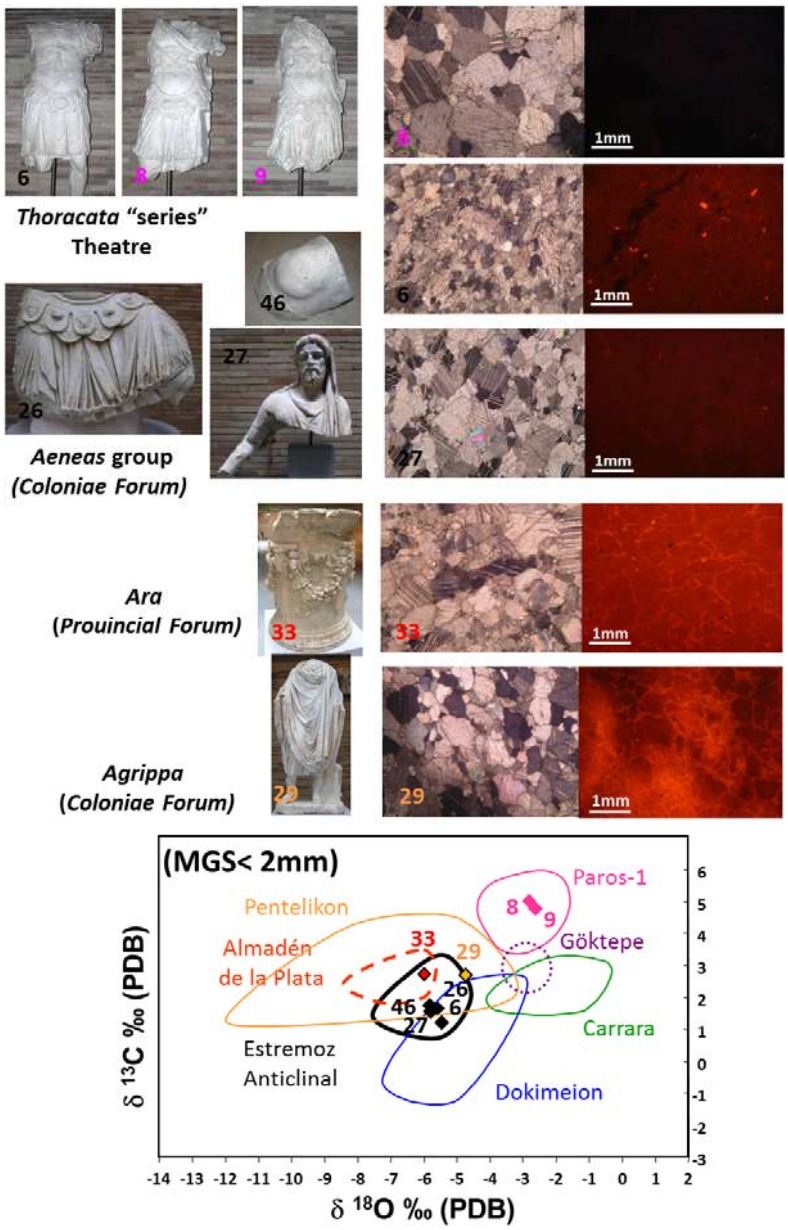


**Fig. 5.**:Three fragmented pieces of the Aeneas group from the Coloniae Forum of Augusta Emerita (capital of Roman Lusitania) were assigned to the same type of fine grained marble of the local Estremoz Anticline district, confirming the hypothesis of being a replica sculpture following a model from the Metropolis (Samples 26, 17 and 46). In the «series» of Thoracata Emperor from the scaenae frons of the Theatre of Augusta Emerita, only the archaeometric analyses reveals which marbles were local and which were imported. In this case, the quality of the local Estremoz Anticline marble allowed the skilful artist to achieve an excellent result, following the style of the other pieces carved in marble from the island of Paros (lychnites) (Samples, 6, 8 and 9). In sample 33, the petrographic features and the moderately strong CL intensity are compatible with two Iberian marble sources, Estremoz Anticline and Almadén de la Plata. Both provenances are also possible through its isotopic signature. Both marble sources are located in the same geological unit, the Ossa Morena, but in a different Roman administrative province, Estremoz in Lusitania and Almadén de la Plata in the Baetica province. Both were widely used in the SW part of Hispania, but each one was particularly used in each respective administrative province. In sample 29, the petrographic and CL features along with the isotopic signature are compatible with a local marble (Estremoz Anticline) and an imported marble (Pentelikon).

**5. ábra:** Három töredék Lusitania Augusta Emerita forumáról, amelyet a helyi Estremoz Antiklinális márványaihoz kötöttek.. További vizsgált márvány töredékek, ahol archeometriai vizsgálat tisztázta a márványok eredetét.

In general, over the last decade, studies on the origin of marbles have progressed with great success. In principle, the implementation of the first group of techniques (OM, XRD and stable isotopes) may be enough to find the origin of the marble used for an archaeological piece. The combination of mineralogical-petrographical features with the isotopic, works relatively well to discriminate a lot of classical marbles and many Hispanic marbles. This is the case applied to distinguish certain archaeological pieces from Augusta Emerita with common petrographical parameters, but their different isotopic signatures serve to be assigned to a different marble source, one local (Estremoz Anticline district) and the other a Lunense marble (Lapuente et al, 2000; 2014).

The presence of local marbles in addition to the imported increases the difficulty of discovering marble provenance of Hispanic artefacts. Moreover, the high quality of the finished sculpture work should not presuppose the idea of an imported marble having been used. Conversely, the technical quality of certain Iberian white statuary marbles made excellent carving works possible in the hands of skilful sculptors. Even using a combination of different techniques, certain doubts arise with the marble provenance of some cases, such as an *ara* from the Prouincial Forum of Augusta Emerita or the case of the Agrippa Statue (**Fig. 5.**).

## *Conclusions*

Although there is no single reliable satisfactory method for matching the marble source of an artefact, the puzzle of information to distinguish one marble from another is gradually being completed using a combination of techniques. The provenance of Hispanic white marble artefacts is an even more difficult task. Not only does it require the application of several techniques, but also the archaeological criteria must not be overlooked since, together with imported marbles, extensive use was made of high quality local marbles such as those from the Estremoz Anticline district.

The interdisciplinary study with an archaeological hypothesis, regarding the nature of local or imported from the piece, based on the association's materials, their chronology, style, iconography, together with knowledge about the geographical distribution of local material, lies in a better interpretation of analytical results. Research involving new discriminating parameters has been leading towards the strontium isotopes and others more specific such as fluid inclusions. But currently, C and O isotopes combined with petrography and CL holds our greatest attention due to its successful application in many cases.

## *Acknowledgments*

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## *References*

ÀLVAREZ, A., DOMÈNECH, A., LAPUENTE, P., PITARCH, A., ROYO, H. (2009a): Marbles and stones of Hispania. Exhibition Catalogue. ICAC. Tarragona. 1–143.

ÀLVAREZ, A., Gutiérrez, A., Lapuente, P., Pitarch, A., Rodà, I. (2009b): The *Marmor* of Tarraco or Santa Tecla Stone (Tarragona, Spain). In: Ph. JOCKEY (ed.) *Interdisciplinary Studies on Mediterranean Ancient Marble and Stones. Proceedings of the VIIIth International Conference of ASMOSIA*. Aix-en-Provence, Collection L´atelier méditerranéen. Maison méditerranéenne des sciences de l´homme. Maisonnueve & Larose. 129–140.

ANTONELLI, F., LAZZARINI, L., CANCELLIERE, S., DESSANDIER, D. (2009): *Volubilis* (Meknes, Morocco): Archaeometric study of the white and coloured marbles imported in the Roman age. *J. Cultu. Herit.* **10** 116–123.

ANTONELLI, F., LAPUENTE, M.P., DESSANDIER, D., KAMEL, S. (2015): Petrographic characterization and provenance determination of the crystalline marbles used in the Roman city of *Banasa* (Morocco): New data on the import of Iberian marble in Roman North Africa. *Archaeometry* **57** 405–425.

ATTANASIO, D. (2003). Ancient white marbles. Identification and analysis by Paramagnetic Resonance Spectroscopy. L'Erma di Bretschneider, Roma. *Stud. Archaeol.* **122** 1–284.

ATTANASIO, D., ARMIENTO, G., BRILLI, M., EMANUELE, M.C., PLATANIA, R., TURI, B. (2000): Multimethod marble provenance determinations: the Carrara marbles as a case study for the combined use of isotopic, electron spin resonance and petrographic data. *Archaeometry* **42** 257–272.

ATTANASIO, D., BRILLI, M., OGLE, N. (2006): The isotope signature of Classical marbles, L'Erma di Bretschneider, Roma. *Stud. Archaeol.* **145** 1–336.

ATTANASIO, D., BRUNO, M., YAVUZ, A. B. (2009): Quarries in the region of Aphrodisias: the black and white marbles of Göktepe (Muğla). *J. Roman Archaeol.* **22** 312–348.

ATTANASIO, D., BRUNO, M., PROCHASKA, W., YAVUZ, A. B. (2015): Multi-Method Database of the Black and White Marbles of Göktepe (Aphrodisias), including Isotopic, EPR, Trace and Petrographic Data. *Archaeometry* **57** 217–245.

BARBIN, V., RAMSEYER, K., DÉCROUEZ, D., HERB, R. (1989): Marbres blancs: caractérisation par cathodoluminescence, *Comptes-Rendus Acad. Sci. Paris* **308**/**II** 861–866.

BARBIN, V., RAMSEYER, K., DÉCROUEZ, D., BURNS, S.J., CHAMAY, J., MAIER, J.L. (1992): Cathodoluminescence of white marbles: an overview. *Archaeometry* **34** 175–183.

BELTRÁN, J. & LOZA, M.L. (2008): La explotación romana del mármol de la "Sierra de Mijas" (Málaga). Un estado de la cuestión. In: T. NOGALES BASARRATE & J. BELTRÁN (ed.): *Marmora* Hispana: explotación y uso de los materiales pétreos en la Hispania Romana, *Hispania Antigua, Serie Arqueológica* **2** Roma 313–337.

BORGHINI, G. (ed.), (1992): *Marmi antichi*. Edizioni de Luca, Roma, 1–342.

GNOLI, R. (1988): *Marmora Roman*a. 2ª ed, Edizioni dell'Elefante. Roma, 1–183.

GORGONI, C., LAZZARINI, L., PALLANTE, P., TURI, B. (2002): An updated and detailed mineropetrographic and C-O stable isotopic reference database for the main Mediterranean marbles used in antiquity. In: J.J. HERRMANN JR., N. HERZ & R. NEWMAN (eds.): ASMOSIA 5. Interdisciplinary Studies on Ancient Stones. Archetype Pub., London, 115–131.

GUTIÉRREZ GARCIA-M. A., LAPUENTE, P., RODÀ, I. (eds.), (2012): Interdisciplinary studies on ancient stone. Proceedings IX ASMOSIA Conference (Tarragona 2009). ICAC. *Documenta* **23** 1–800.

HERZ, N. (1987): Carbon and oxygen isotopic ratios: a data base for Classical Greek and Roman marble. *Archaeometry* **29** 35–43.

JARČ, S. & ZUPANČIČ N. (2009): A cathodoluminescence and petrographical study of marbles from the Pohorje area in Slovenia. *Chemie Der Erde-Geochem.* **69** 75–80.

LAPUENTE, P. (1995): Mineralogical, petrographical and geochemical characterization of white marbles from Hispania. In Y. MANIATIS, N. HERZ & Y. BASIAKOS (eds.): *The study of marble and other stones used in antiquity,* Archetype, London. 151–160.

LAPUENTE, P., TURI, B., BLANC, Ph. (2000): Marbles from Roman Hispania: stable isotope and cathodoluminescence characterization. *Appl. Geochem* **15** 1469–1493.

LAPUENTE, P., PREITE-MARTINEZ, M., TURI, B., BLANC, Ph. (2002): Characterization of dolomitic marbles from the Malaga province (Spain). In: J.J. HERRMANN Jr., N. HERZ & R. NEWMAN (eds.): *ASMOSIA 5. Interdisciplinary Studies on Ancient Stones.* Archetype Pub., London, 152–162.

LAPUENTE, P., LEÓN, P., NOGALES-BASARRATE, T., ROYO, H. PREITE-MARTINEZ, M., BLANC, Ph. (2012): White sculptural materials from Villa Adriana: Study of provenance. In: A. GUTIÉRREZ GARCIA-M., P. LAPUENTE, I. RODÀ, (eds.). Interdisciplinary Studies on Ancient Stone. Proceedings IX ASMOSIA Conference (Tarragona 2009). ICAC. *Documenta* **23** 364–375.

LAPUENTE, P., NOGALES-BASARRATE, T., ROYO, H., BRILLI, M. (2014): White marble sculptures from the National Museum of Roman Art (Mérida, Spain): sources of local and imported marbles. *Eur. J. Miner.* **26** 333–354.

LAZZARINI, L. (2004): Archaeometric aspects of white and coloured marbles used in antiquity: the state of the art. *Per. Mineral.* **73** 113–125.

LAZZARINI, L., MOSCHINI, G., STIEVANO, B. M. (1980): A contribution to the identification of Italian, Greek and Anatolian marbles through a petrological study and the evaluation of the Ca/Sr ratio. *Archaeometry* **22** 173–183.

MANIATIS, Y. (2009): ASMOSIA VII. Proceedings of the 7th International Conference of Association for the Study of Marble and Other Stones in Antiquity. Thasos 15-20 septembre 2003. École française d´Athènes. *Bull. Correspondance Hellénique.* **Suppl. 51** 1–829.

MIELSCH, H. (1985): *Buntmarmore aus Rom im Antikenmuseum Berlin.* Staatliche Museen Preussischer Kulturbesitz, Berlin.

MOENS, L., DE PAEPE, P., WAELKENS, M. (1992): Multidisciplinary research and cooperation: keys to a successful provenance determination of white marble. in M. WAELKENS, N. HERZ, L. MOENS (eds.). Ancient Stones: Quarrying, Trade and Provenance, *Acta Archaeol. Lovaniensia Monogr.* **4** 247–254.

NAPOLEONE, C. (2001): *Delle Pietre Antiche di Faustino Corsi romano. Grafiche Milani.* Franco Maria Ricci (ed.). Milano, 1–167.

NOGALES BASARRATE, T. & BELTRÁN FORTES, J., (eds.), (2008): Marmora Hispana: explotación y uso de los materiales pétreos en la Hispania Romana. *Hispania Antigua. Serie Arqueológica,* **2**. L´Erma Di Bretschneider. 1–543.

NOGALES BASARRATE, T., LAPUENTE, P., ROYO, H. PREITE-MARTINEZ, M. (2015): Stone materials in Lusitania reflecting the process of Romanization. Proceedings X ASMOSIA Conference, Rome. In: P. Pensabene & E. Gasparini (eds.) "L´Erma" di Bretschneider. 233–242.

ORIGLIA, F., GLIOZZO, E., MECCHERI, M., SPANGENBERG, J.E., TURBANTI MEMMI, I., PAPI, E. (2011): Mineralogical, petrographic and geochemical characterisation of white and coloured Iberian marbles in the context of the provenancing of some artefacts from *Thamusida* (Kenitra, Morocco). *Eur. J. Mineral.* **23** 857–869.

POLIKRETI, K. & MANIATIS, Y. (2002): A new methodology for marble provenance investigation based on EPR spectroscopy. *Archaeometry* **44** 1–21.

ŠŤASTNÁ, A., PŘIKRYL R., JEHLIČKA J. (2009): Methodology of analytical study for provenance determination of calcitic, calcite-dolomitic and impure marbles from historical quarries in the Czech Republic. *J. Cult. Herit.* **10** 82–93.

ZÖLDFÖLDI, J., HEGEDÜS, P. & SZÉKELY, B. (2009): MissMarble: Online Datenbanksystem über Marmor für Naturwissenschaftler, Archäologen, Denkmalpfleger, Kunsthistoriker und Restauratoren. In: HAUPTMANN, A. & STEGE, H. (eds.) *Archäometrie und Denkmalpflege* 2009. Kurzfassungen. Metalla Sonderheft 2. München,161–163.

Corsi Collection of Decorative Stones, Oxford University Museum of Natural History, www.oum.ox.ac.uk/corsi/, 28th November 2014.

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# ANALYSIS OF HISTORIC GLASS BY ION-BEAM METHODS

## TÖRTÉNELMI ÜVEGEK VIZSGÁLATA IONNYALÁB-ANALITIKAI MÓDSZEREKKEL

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## *Abstract*

*Analytical methods, based on irradiation of samples with MeV ion beams, notably particle induced X-ray (PIXE) and gamma ray (PIGE) emission analysis can be used to provide complete chemical analysis of glass objects in a non-destructive way. A review of applications is given that were performed at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana, which involve glass of the first centuries BC, Roman and late Antique glass, as well early medieval and Venetian glass till the glass of the late 19th and early 20th centuries. Historical questions like the origin of raw materials and classification of glass compositional groups according to individual workshops are addressed.*

## *Kivonat*

*Azok az analitikai módszerek, amelyek a minták MeV-es ionnyalábbal való besugárzásán alapulnak – nevezetesen a részecske-indukált röntgen-, ill. gammaemissziós (PIXE, ill. PIGE) módszerek –, alkalmasak üvegtárgyak kémiai (elem-) összetételének roncsolásmentes meghatározására. A cikkben áttekintjük a ljubljanai Jožef Stefan Intézet Tandetron gyorsítójánál, Kr. e. I. századi római és késő antik, valamint korai középkori, velencei és 19-20. századi üvegeken végzett vizsgálatokat. A kutatás során a megválaszolandó kérdések voltak: a nyersanyag eredetének meghatározása, összetétel szerinti csoportok felismerése és azonosítása az üveggyártó műhelyekkel.*

KEYWORDS: PIXE, PIGE, GLASS ANALYSIS, ROMAN GLASS, EARLY MEDIEVAL GLASS, VENETIAN GLASS

KULCSSZAVAK: PIXE, PIGE, ÜVEGEK ANYAGVIZSGÁLATA, RÓMAI ÜVEG, KORAI KÖZÉPKORI ÜVEG, VELENCEI ÜVEG

## *Introduction*

Chemical analysis by ion beam methods is based on excitation of characteristic X-rays and gamma rays. As quite many elements can be analyzed simultaneously, it is aptly used for the analysis of glass. Its main advantage is non-destructive way of measurements and simple handling of the investigated objects, provided their surface is not covered by a thick corrosion layer. Typical penetration depth of 3 MeV protons in glass is about 90 μm, and the main fraction of X-rays usually comes from about one third of this thickness. Representative measurements of the bulk composition can still be obtained if surface modification, like selective leaching of alkaline elements, reaches depths of 1-2 μm.

Glass is essentially made of silica whose melting point is lowered by flux; alkaline oxides are used for this purpose. Oxides of alkaline earths are added for chemical stability. As the agents encountered in nature are not chemically pure, small amounts of decolorants are added to the glass batch for obtaining clear transparent glass, or opacifiers and pigments for obtaining opaque or colored glass. It is the flux that exhibits largest variation through history. For the glass of Bronze Age Egypt and Mesopotamia, during the second millennium BC, alkalis were obtained from the ash of halophytic plants, harvested at sea shores and in deserts (Rehren 2008). The period between 800 BC and 800 AD is characterized by an extensive use of alkalis from the sediments of dry Egyptian lakes, known as natron (Sayre & Smith 1961). Glassmaking of natron-based raw glass then intensified in the eastern Mediterranean and dominated in Greek, Roman and Late Antiquity worlds. After the 6th c. AD several political disturbances in Egypt limited access to natron sources, and in the quest of alkalis the use of halophytic plants was resumed (Shortland et al. 2006). In the transition period between the 9th and 12th centuries, glass from the ash of halophytic plants gradually superseded natron-based glass that still participated in glassmaking as a recycling material. The new technology spread from the East, most likely Islamic or Byzantine world (Freestone 2005). After the 12th century, glassmaking in Northern Italy, notably in Venice directed the glass technology and glass trade (Verità & Zecchin

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2009). Due to the high demand of the Venetian glassware, glassworks were formed also in other European towns that fabricated glass products in the Venetian style. In the 17th century, several improvements in treating raw material were introduced: purer silica sources and refined alkalis came into use, and arsenic started to be used as decolorant. In Northern and Central Europe, wood ash was used for making potash, which resulted in production of forest glass.

What are the open questions regarding production of historic glass? For Greek and Iron Age glass it is certainly the location of glassworks. This question is also important for Roman glass, although largely answered by strontium and neodymium isotope ratios measurements: in the Roman Imperial era, between the 1st and 4th c. AD, glass was produced in the Eastern and Western part of the Mediterranean, but production was concentrated in the Eastern part during Late Antiquity (Ganio et al. 2012). For Venetian and Venetian-like glassmaking, it is important to distinguish between the imported and locally produced objects (De Raedt et al. 2001). In the present review, we show measurements performed on Greek glass from Bulgaria, on Roman glass from several sites in the Eastern Balkans and Slovenia, on Venetian-type glass from Ljubljana and Slovenian castles, and on examples of modern glass. For each type of glass, compositional groups are determined by statistical methods and historical or provenance information for each group is sought.

## *Experimental methods*

The measurements were performed at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana, using in-air proton beam of 3 MeV nominal energy. The beam was extracted into air through a thin metal foil; aluminum of 8 μm thickness was used for PIXE, and tantalum of 2 μm for PIGE measurements. Different materials were used to avoid undesired background: no hard X-rays are induced in aluminum window during PIXE measurements, while aluminum gamma rays are undesirable for PIGE; using a high Z window (like tantalum) for PIGE results in low gamma energies, typically below 300 keV. Three spectra were taken in each measuring point: soft X-ray with a 5.7 cm air gap as the only absorber, hard X-ray with 0.1 mm Al as an additional absorber, and gamma spectrum. The beam current was a few tenths of nA for the first case and 1-3 nA for the latter two; typical X-ray spectra were measured for 5 minutes and gamma spectra for 20 minutes. The proton number was measured for PIGE only, using a thin wire mesh intersecting the beam in vacuum (Jezeršek et al. 2010). Some measurements were performed in a time-optimized way: tantalum exit window was used for all measurements, and hard X-ray and gamma spectra were measured simultaneously. The disadvantage of this type of measurement was the presence of Ta L X-rays in the spectra. The soft X-ray spectrum involved elements from silicon to iron, and the hard X-ray spectrum from iron till highest Z. The X-ray line intensities of the two spectra were recalculated into a single data set according to the iron line using calculated transmission of absorbers. For modern glasses, the content of iron was too low to enable reliable statistics. The hard X-ray spectra were then measured with an additional absorber of 700 μm kapton, and the two spectra were compared according to the calcium line. The size of air gaps between the exit foil and target and between target and detector were determined from the measurements of a few elemental and simple chemical compound targets. The elements Na, Mg and Al were determined from the gamma spectra using the lines excited by inelastic proton scattering: 440 keV for Na, 585 keV for Mg, and 844 and 1014 keV for Al (Hirvonen et al. 1995). The most critical measurement was that of Mg, as its line coincides with the line of 583 keV from natural background. Using a lead shielding around the gamma detector and a sufficient count rate of PIGE it was possible to achieve the lowest detection limit of 0.2 % MgO. The detection limits for other minor and trace elements obtained by PIXE are significantly better: about 100-50 μg/g for the elements between calcium and iron, and about 5 μg/g for iron and heavier elements in its vicinity. The detection limits then decrease with Z and are about 10 μg/g around Sr and Zr and about 100 μg/g around Sn and Sb. The detection limit of Pb that is determined according to its L-lines is about 5 μg/g. The interference of particular X-ray or escape lines reduces sensitivity for P (about 1%), Co (about 100 μg/g) and Ba (about the same level as the content of Ti).

The concentrations were calculated by an iterative method that considers matrix elements for X-ray and gamma ray spectra simultaneously. The method of independent atomic parameters was used for PIXE, while the PIGE values were normalized according to the values measured in glass standard NIST 620, using the surface approximation. The sum of metal oxides was normalized to unity, but for the control purposes it was also calculated independently using the argon line induced along the proton beam in air as an internal standard. The measurements with the sum differing much from unity were considered with caution. Glass standards NIST 620 and 621 were also measured periodically and treated as unknown targets. The accuracy of major elements was within ±5%; however, for trace elements and values close to detection limits it may deteriorate to 10-20%. An example of NIST 620 measurement is shown in (Marić Stojanović et al. 2015).

## *Results and discussion*

Natron is a much purer agent than ash of halophytic plants, so the natron-made glass can easily be recognized according to its low contents of magnesium and potassium, typically below 1.6% MgO and 1% $K_2O$ (Sayre & Smith 1961; Zucchiatti et al. 2007). Glass from the Greek colony Apollonia Pontica on the Black Sea coast in the present Bulgaria dated to the 5th and 4th c. BC undoubtedly contained natron (Ljubomirova et al. 2014). The glass composition is similar to that of other Greek cities, which points to a centralized glasswork. A location on the Rhodes Island is supposed, which is sufficiently close to the raw material sources in the Levantine area (*op.cit.*).

Roman glassworks produced raw glass in huge blocks weighting several tons, which were splintered in chunks and distributed commercially for reworking into objects. A glass chunk of this type was discovered close to Roman municipium Nauportus (today's Vrhnika near Ljubljana) as early as 1886; yet it was the recent chemical analysis that confirmed its manufacture with natron, and therefore its Roman origin (Istenič & Šmit 2012).

Roman glass was commonly recycled that may partly obscure its primary origin. Our principal knowledge of glass composition came form two shipwrecks, loaded with cargos of broken glass: Ouest Embiez close to Marseilles dated from the end of the 2nd till the beginning of the 3rd c. AD, and Iulia Felix close to Grado, dated to the first half of the 3rd c. AD. Statistical analysis of glass from south France identified 12 groups (Foy et al. 2003), two of them being Roman: glass of group 3 was used in a broad time interval between the 3rd c. BC and 9th c. AD; it was discolored by manganese oxide and its origin is Levantine. Glass of group 4 was used in a much narrower time period of the 2nd and 3rd c. AD; it was discolored by antimony oxide, while its origin is still unknown. Statistic analysis of glass from Iulia Felix produced two groups of colored and two groups of clear glass (Silvestri 2008; Silvestri et al. 2008); the colored glass agrees well with group 3, while one group of the clear glass agrees with group 4. The second group of clear glass from Iulia Felix embraces both group 4 and a large fraction of group 3.

The Roman glass of the Imperial period analyzed in the lab originated from Albania (1st-4th c. AD), Bulgaria (1st-7th c. AD) and Serbia (Marić Stojanović 2015; Šmit et al. 2013; Lesigyarski et al. 2013). The MgO-$K_2O$ plots with low magnesium and potassium concentrations confirmed that the glass comprised natron; but it was for the Albanian glass that the plot revealed several groups (**Fig. 1a**).

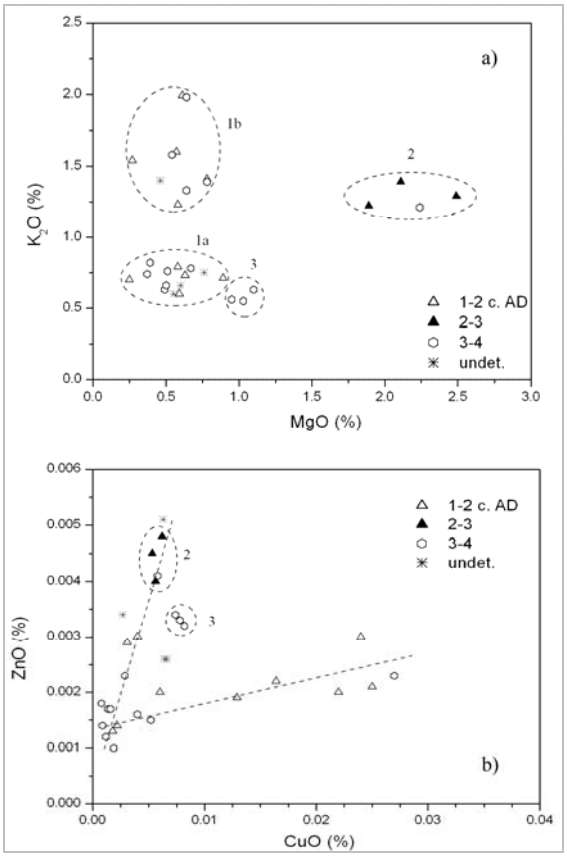


**Fig. 1.:** Roman glass from Albania shows individual features according to its MgO and $K_2O$ contents (a), which may result due to different mineral impurities in the primary raw material, but may also be consequence of repeated recycling process, as shown in the distribution according to CuO and ZnO (b). Based on archaeological dating, the glasses were distributed into four groups: 1st-2nd c. AD, 2nd-3rd c. AD, 3rd-4th c. AD and undetermined (after Šmit et al. 2013).

**1. ábra:** Az Albániából származó római üvegek MgO és $K_2O$ tartalmuk szerint jellegzetes összetételt mutatnak (a), ami lehet a felhasznált nyersanyag ásványi szennyező anyagainak következménye, de oka lehet ennek a többszöri újraolvasztás is, amint ezt a CuO és ZnO megoszlás mutatja (b). Régészeti kormeghatározás szerint az üvegek négy csoportba sorolhatók: i.sz. I-II. sz., i.sz. II-III. sz., i.sz. III-IV. sz. és ismeretlen korú üvegek (Šmit et al. 2013 nyomán).

Such groups may confirm that the minerals used for making raw glass came from different locations, which is consistent with the present model that production of raw glass during the Imperial period was dispersed (Ganio et al. 2012). However, such conclusions have to be made with caution, as specific mineral imprint can also be made during the recycling process and alloying with scrap glass. Copper and zinc are typical indicators of the recycling process (Freestone 2005), which is result of accidental mixing of colored and transparent

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glass in the recycled batch. **Fig. 1b** indeed shows the same groups as observed in the MgO-$K_2O$ plot, which is a supporting argument of the glass differentiation in the secondary working process. The magnesium and potassium concentrations also increase with recycling on account of the impurity input, which results in the fact that the objects produced during recent centuries of the Roman era have higher concentrations of these two elements. It is tentative to use this effect for provisional dating: glass from the Kosmaj Mountain in Serbia lacks precise archaeological dating, but as its MgO and $K_2O$ concentrations are below 1%, it can be dated to the first half of the Imperial period with high confidence. Recycling process also introduces elements that are related to mineral impurities, such as aluminum, titanium and iron. Higher levels of these elements are evident in the younger period glass from Bulgaria (Lesigyarski et al. 2013).

High levels of impurities, such as titanium, manganese and iron mark the new type of glass that appears in the fourth century AD and whose origin is yet unknown, though Egypt is strongly supposed as its production site (Freestone 2005). Known as the HIMT glass – an acronym indicating high iron, manganese and titanium, it is a wide-spread glass type in the Western Europe. Its occurrence in the eastern Mediterranean is modest, as the glass trade and production was still dominated by Levantine glassworks. The glass they produced was similar to the glass of group 3 from south France and is designated as Levantine I. In comparison with the Imperial period glass it contains slightly increased levels of calcium and aluminum oxides. Our measurements identified HIMT glass both among the 4th c. AD samples from Bulgaria and among the glass inventory of the Late Antique site Tonovcov grad from western Slovenia (Šmit et al. 2014). The site exhibits traces of all historic periods, the most prominent being a hilltop settlement with a complex of early Christian churches. Its population is divided into two phases, the older during the second half of the 4$^{th}$ and beginning of the 5$^{th}$ century, and the younger extending between the end of the 5$^{th}$ and the beginning of the 7$^{th}$ century. The majority of glass finds belongs to the younger period, though the glass inventory also contains a few examples of blue-green glass from the older period. The older glass contains smaller amount of MgO than the younger one. According to the origin of the sand component, glass of the younger period is of the type Levantine I, with a few examples of HIMT glass (**Fig. 2**). Some HIMT glasses have a lower amount of impurities, which suggests the glass was recycled with a certain amount of older glass.

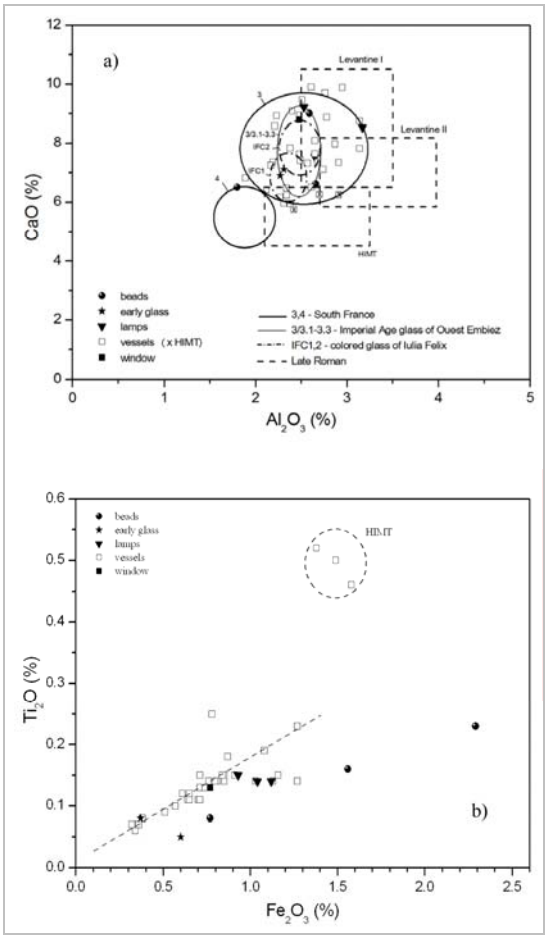


**Fig. 2.: a)** Distribution of glass from Tonovcov grad according to the sand composition reflected in CaO–$Al_2O_3$ plot (after Šmit et al. 2014). Lines show the accepted glass types. The group 3/3.1-3.3 represents Roman Imperial glass of south France and was obtained from Foy et al. 2003 subtracting the Late Roman groups 3.1 – 3.3 from the group 3. Data for colored glass of Iulia Felix are from Silvestri 2008 and for Levantine I and HIMT glass from Zucchiatti et al. 2007. (b) Only three examples of HIMT glass were found, which were well distinguishable according to their iron- and titanium content. (They are marked by × on Fig. 2(a)).

**2. ábra: a)** Tonovcov grad-ból származó üvegek megoszlása a homok összetétele szerint, CaO–$Al_2O_3$ diagramon (Šmit et al. 2014 nyomán). A vonalak az elkülönített üvegtípusokat mutatják. A 3/3.1-3.3 csoportok dél-francia római császárkori üvegeknek felelnek meg Foy et al. 2003 adatai alapján, kivonva a későrómai 3.1 – 3.3 csoportokat a 3. csoportból. A Iulia Felix-ből származó színes üvegek adatait Silvestri 2008 munkájából vette át a szerző, míg az I. levantei csoport és a HIMT üvegek adatai Zucchiatti et al. 2007. munkájából származnak. **b)** Összesen három HIMT üveget találtak, amelyek jól elkülönülnek vas- és titántartalmuk alapján (ezeket a 2(a) ábrán ×-szel jelöltük).

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Glass inventory, containing Levantine I glass with a few examples of HIMT glass is characteristic also for some other sites in the Eastern Mediterranean (Arletti et al. 2010), which may be interpreted as an indicator of particular trade connections in the eastern part of the Empire.

Since the 6th c. AD there is a decline in the use of natron. There are several explanations – also climatic and political – for the diminished availability of natron sources. The latter seem most probable as several political disturbances inflicted Egypt between the 7th and 9th c. AD (Shortland et al. 2006). The shortage of natron was overcome with the ash of halophytic plants. The new technology spread from the Byzantine or Islamic East where it was practically never abandoned. The commercial items that are easy to disseminate are glass beads. Production of glass beads is well documented and certain types are historically well explored. For example, we know that beads with mosaic eyes, which are frequent finds in central and northern Europe, were produced in the Bagdad caliphate during the first third of 9th c. AD (Andrae 1973).

During our measurement of Late Antique glass from the hilltop settlement Gradišče nad Bašljem in northern Slovenia we also encountered beads made with the ash of halophytic plants (Šmit et al. 2009). The site was populated in Late Antiquity and during the Carolingian period. Archaeological finds show that its end was an abrupt military event – either related with a rebellion of Slavs against the Franks in 819 or connected with Hungarian incursions. There were numerous glass finds at the site – beads, pins and earrings with glass heads and also several ingots or cullet of raw glass. The majority of objects were made of natron glass. The cullet showed a more uniform composition than the objects, which excluded production of the objects at the site. Two glass beads were found to be made using plant ash, which is consistent with the dating of the second population phase into the Carolingian period. The small percentage of plant ash also demonstrates that glassmaking still relied on the supplies of the old glass from Antiquity, while influx of the new material was modest. One glass bead made of plant ash was also discovered at the site Tonovcov grad (Šmit et al. 2014).

As the composition of glass beads can be an important time indicator, a systematic study was performed for the glass beads discovered in early Slavic graves (Šmit et al. 2012). Their selection involved graves around Ptuj in eastern Slovenia and graves around the Bled Lake in the central part of the country – the two different locations lay along the axis of Slavic migrations, which spread from the east. The analysis showed that the beads formed two groups: beads made of natron-type glass and beads made of glass using ash of halophytic plants (**Fig. 3a**).

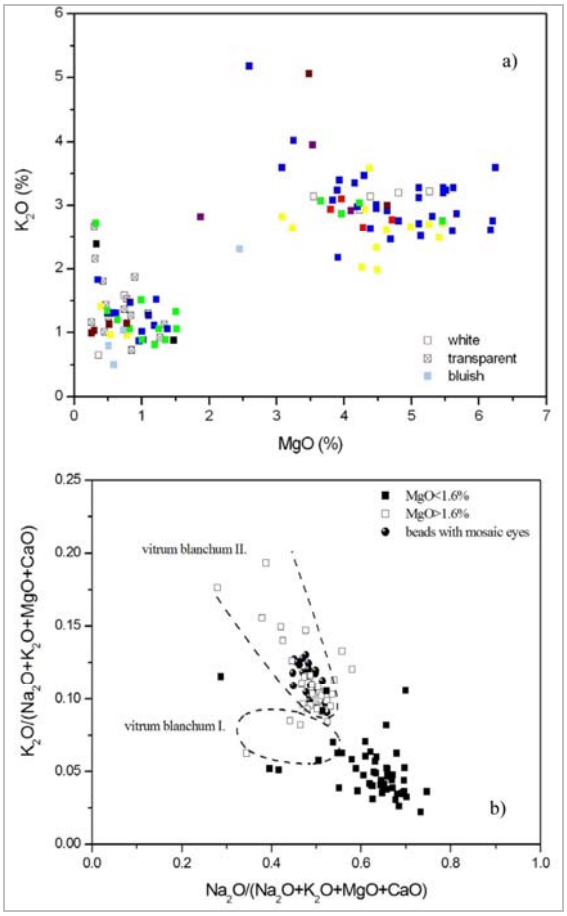


**Fig. 3.:** Beads from the early Slavic graves in Slovenia were made from the glass made of natron (low MgO and $K_2O$ values) and from the glass made of the ash of halophytic plants (a). The latter group shows alkali composition similar to one group of Venetian glass (b) (after Šmit et al. 2012).

**3. ábra:** A szlovéniai korai szláv sírok gyöngyei a nátron típusú üvegből készültek (alacsony MgO és $K_2O$ tartalmú alapanyag) és sótűrő növények hamujának felhasználásával készültek (a). A későbbi csoport gyöngyei a velencei üvegekhez hasonló alkália összetételt mutatnak (b) (Šmit et al. 2012 nyomán).

The latter groups also contained beads with mosaic eyes and knuckled beads, which were documented to be of Islamic origin. For dating the graves it can safely be assumed that the presence of beads made of halophytic plants assigns a date after 800 AD. Such beads appeared in the graves both from the central and eastern part of Slovenia, which has important consequences for dating of the Köttlach culture in Slovenia (Korošec 1979). The graves around Ptuj were dated to the end of the 8th and beginning of the 9th c. AD with respect to ceramics, which is consistent with the occurrence of glass beads. The difference occurs for the graves in the central and western Slovenia, which were traditionally dated to the 7th and 8th centuries, but are dated later, to the first half of the 9th c. by

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European archaeologists (Giesler 1980). The identification of plant-ash glass beads in these graves provides strong arguments for the later dating.

Alkalis produced from the ash of halophytic plants are less pure than natron, so the contents of impurities can be used to identify their source. A useful indicator is the relative fraction of sodium and potassium oxides normalized to the sum of alkaline and earth-alkaline oxides (de Raedt 2001). The composition of glass beads made of ash of halophytic plants is similar to the glass produced in Iraq and around the Aral Sea (**Fig. 3b**), which confirms their oriental origin (Šmit et al. 2000). However, this type of glass is also common among the much later Venetian glass, which shows a very long exploitation of specific alkali sources. Scientific interpretations about this source are conflicting, which we learn on the example of Venetian glass.

The largest set of Venetian glass analyzed by IBA methods is from Ljubljana (Šmit et al. 2000; Šmit et al. 2002). There is documented glass industry in the city during the 16th century, including a detailed list of glass products, which is part of the last will of the glasswork lease holder Kristof Prunner (1564). There are also numerous glass finds from Ljubljana; 800 samples obtained from excavations are held in the National Museum of Slovenia (Kos 2007). The analysis using the combined PIXE-PIGE method involved more than 300 specimens. Beside the Venetian glass, several contemporaneous glass pieces from the castle ruins and examples of Roman and forest glass were analyzed for comparison and for checking the reliability of the statistical methods. Venetian-like glass from Ljubljana formed two distinct groups, which distinguished mainly due to the content of potassium oxide (Šmit et al. 2002).

We learned more about the Venetian glass when the measurements from Ljubljana were compared with the analytical results from Antwerp (Šmit et al. 2004). The city was a significant glassmaking center during the 16$^{th}$ and 17$^{th}$ centuries. Considering the relative fractions of sodium and potassium oxides, two groups of Venetian white glass (*vitrum blanchum*) were found (**Fig. 4a**). An independent group was formed by the more qualitative *cristallo* glass. The composition of *cristallo* manufactured in Venice and Antwerp found to be different: the Antwerp-made contained more potassium than sodium, so the two elements showed inverse correlation. Of the two groups of Venetian white glass, the one with more potassium also gives impression of inverse correlation. This fact inspired some researchers (Cagno et al. 2012) that only the group with low potassium content (v.b. I in **Fig. 4**) represents the true Venetian glass, while the high potassium group (v.b. II in **Fig. 4**) is glass made *à façon de Venise*.

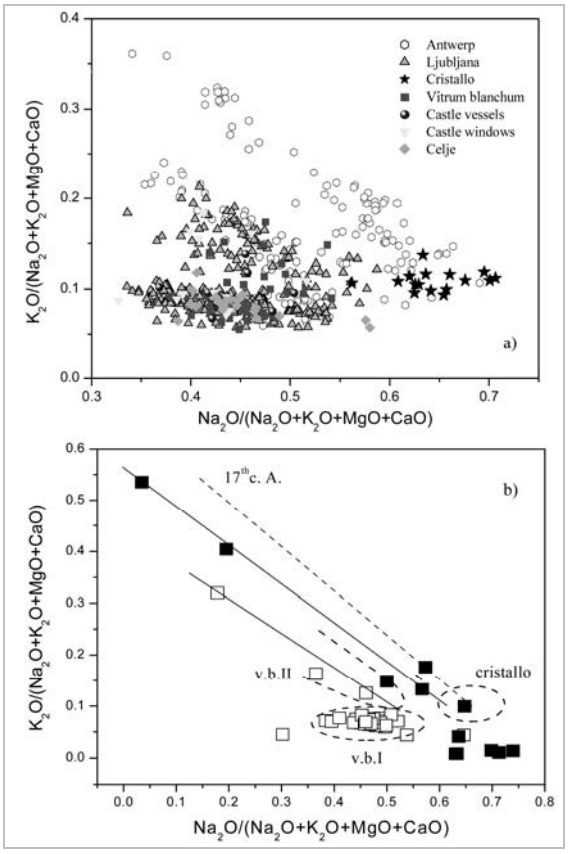


**Fig. 4.:** (a) Distribution of Venetian and *façon-de-Venise* glass from Slovenia (cities of Ljubljana and Celje and castle ruins) and Antwerp according to the composition of the flux (after Šmit et al. 2004). Two groups of Venetian white glass (*vitrum blanchum*, v.b. I and v.b. II) and a group of cristallo glass were found. (b) The same three groups also appear in the Albanian city of Lezha (after Šmit et al. 2009), indicating a technological step that was very likely adopted in the 17$^{th}$ century.

**4. ábra:** (a) Velencei és velencei típusú üvegek elterjedése, valamint antwerpeni típusú üvegek elterjedése Szlovéniában (Ljubljana és Celje városából, illetve várromokból), a folyósító anyag összetétele szerint (Šmit et al. 2004 nyomán). A velencei fehér üveg két csoportja (*vitrum blanchum*, v.b. I és v.b. II) valamint a *cristallo* üveg egy csoportját találták meg. (b) Ugyanez a három csoport jellemzi az albán Lezha város leleteit (Šmit et al. 2009 nyomán), ami arra utal, hogy a szükséges technológiai fogásokat a XVII. század folyamán sajátították el.

However, the latter groups also contain examples of original Venetian glass, so the two groups rather represent two different sources of alkalis that were used in Venice, but also in other glassmaking centers. It is tempting to identify the two groups with *alume catino*, harvested in the Levantine area, and barilla from Spain (Turner 1999). But if we consider again that the glass of the type v.b. II was also used for glass beads produced in Iraq and in

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the regions north of it, alkalis from v.b. II might rather be made of dessert-like plants, like *Kalidium caspicum*.

As the true Venetian and Venetian-like glass were made from the same type of alkalis, distinction between the home production and Venetian import is tedious. For Antwerp, home-produced glass contains more zirconium and hafnium impurities, as the silica used had a different geological background than in Venice (de Raedt et al. 2001). For Ljubljana, no distinction according to the two elements was found as both cities used silica from Alpine rivers (Šmit et al. 2005). The rare earth elements may also characterize the origin of silica.

It was the 17th century that brought a significant change of technology. The Albanian city of Lezha was under strong Venetian influence since the 15th century and excavations in the city revealed many pieces of Venetian glass. Its analysis showed three characteristic groups (Šmit et al. 2009). Two of them were the Venetian white glass, while the third group was different: its alkalis were of similar composition than the 17$^{th}$ c. glass from Antwerp and Netherlands (**Fig. 4b**). A rather pure silica source was used with low concentrations of iron, titanium and aluminum, and arsenic replaced manganese as decolorant. The glass then represents a new technological step following the Venetian glassmaking of the 15$^{th}$ and 16$^{th}$ century. This type of glass was not found in Ljubljana as its glassworks stopped operating before the early 17$^{th}$ century.

Forest glassworks that were active in the 18$^{th}$ and early 19$^{th}$ century used a rather uniform technology: abundance of wood was used for heating and producing ash that was precipitated into potash. Arsenic was used for discoloration. By the end of the 19$^{th}$ century new types of pigmentation were introduced. Our analysis included glass pigmented with uranium salts and glass colored red with colloidal particles. For both types of glass kept in the National Museum of Slovenia we identified three separate groups (Fajfar et al. 2013). One is very likely original production in the present Czech Republic, whereas two groups supposed to be local. One of them could possibly be located in the area of Pohorje in northern Slovenia where several forest glassworks were operating during the 19th century, and the other may represent products of the glasswork in Hrastnik in central Slovenia. The red-pigmented glass has a two-layered structure. The outer layer is typically engraved up to the transparent substrate. Pigmentation of the outer layer was achieved with copper; no gold according to the Egermann's technique was found.

## *Conclusion*

Ion beam analytical methods can be successfully applied for the characterization of historic glass. In comparison with certain chemical methods they are surpassed in sensitivity that cannot reach below μg/g, which makes them incompetent for measuring the whole range of trace elements. They are also not able to provide isotopic information. However, these methods require sampling and pre-processing of samples with wet chemical methods. The main advantage of ion-beam analysis is non-destructive way of measurement in selected points of the integral glass objects. A wide range of elements can be measured simultaneously, which allow identification of the flux and determination of major impurities in the silica matrix, such as aluminum, titanium, iron, strontium and zirconium. The methods are also efficient for determination of decolorants, opacifiers and pigments. All this information is collected to give meaningful historic interpretation.

## *References*

ANDRAE, R. (1973): Mosaikaugenperlen. Untersuchungen zur Verbreitung und Datierung karolingzeitlicher Millefioriglasperlen in Europa. *Acta Praehistorica et Archaeologica* **4** 101–198.

ARLETTI, R., GIACOBBE, C., QUARTIERI, S., SABATINO, G., TIGANO, G., TRISCARI, M., VEZZALINI, G. (2010): Archaeometrical investigation of Sicilian early Byzantine glass: chemical and spectroscopic data. *Archaeometry* **52** 99–114.

CAGNO, S., FAVARETTO, L., MENDERA, M., IZMER, A., VANHAECKE, F., JANSSENS, K. (2012): Evidence of early medieval soda ash glass in the archaeological site of San Genesio (Tuscany). *J. Arch. Sci.* **39** 1540–1552.

DE RAEDT, I. (2001): Composition of 16$^{th}$-17$^{th}$ century façon-de-Venise glass excavated in Antwerp and neighbouring cities, *Ph.D. dissertation*, University of Antwerp. Antwerp, I. p. 23–24, II. p. 124–127.

DE RAEDT, I., JANSSENS, K., VEECKMAN, J., VINCZE, L., VEKEMANS, B., JEFFRIES, T.E. (2001): Trace analysis for distinguishing between Venetian and façon-de-Venise glass vessels of the 16$^{th}$ and 17$^{th}$ century. *J. Anal. At. Spectrom.* **16** 1012–1017.

FAJFAR, H., ŠMIT, Ž., KOS, M. (2013): PIXE-PIGE analysis of colored historic glass. *Glass Technol.: Eur. J. Glass Sci. Technol*. **A 54** 218–225.

FOY, D., PICON, M., VICHY, M., THIRION-MERLE, V. (2003): Caractérisation des verres de la fin de l'Antiquité en Méditerranée occidentale: l'emergence de nouveaux courants commerciaux. In: Foy, D. & Nenna M.-D., eds., *Échange et*

*commerce du verre dans la monde antique. Actes du colloque de l'Association Française pour l'Archéologie du Verre*, *Aix-en-Provence et Marseille 2001,* Éditions Monique Mergoil, Montagnac, 41–85.

FREESTONE, I.C. (2005): The Provenance of Ancient Glass through Compositional Analysis. *Periodical of Material Research Society Symp. Proc*. **852** 1–14.

GANIO, M., BOYEN, S., BREMS, D., SCOTT, R., FOY, D., LATRUWE, K., MOLIN, G., SILVESTRI, A., VANHAECKE, F., DEGRYSE, P. (2012): Trade routes across the Mediterranean: a Sr/Nd isotopic investigation on Roman colourless glass. *Glass Technol.: Eur. J. Glass Sci. Technol*. **53** 217–224.

GIESLER, J. (1980): Zur Archäologie des Ostalpenraumes vom 8. bis 11. Jahrhundert. *Archäologisches Korrespondenzblatt* (Mainz) **10** 85–98.

HIRVONEN, J.-P. & LAPPALAINEN, R., (1995): Particle-Gamma Data. In: TESMER, J.R. & NASTASI M. eds., *Handbook of Modern Ion Beam Materials Analysis*, Materials Research Society, Pittsburgh, 573–613.

ISTENIČ, J. & ŠMIT, Ž. (2012): A raw glass chunk from the vicinity of Nauportus (Vrhnika). In: Lazar, I. & Županek B., eds., *Emona: between Aquileia and Pannonia,* Annales Mediterranei, Univerza na Primorskem, Koper 301–309.

JEZERŠEK, D., ŠMIT, Ž., PELICON, P. (2010): External beamline setup for plated target investigation. *Nucl. Instr. and Meth. B* **268** 2006–2009.

KOROŠEC, P. (1979): Zgodnjesrednjeveška arheološka slika karantanskih Slovanov / Archaeologisches Bild der karantanischen Slawen in fruhen Mittelalter, [Early medieval archaeological image of Karantanian Slavs]. (in Slovenian, German summary) *Dela / Slovenska akademija znanosti in umetnosti, Razred za zgodovinske in družbene vede [Works of the Slovenian Academy of Sciences]* **22**, Ljubljana, 1–248.

KOS, M. (2007): 15th and 16th Century Glass, *Collection of the National Museum of Slovenia*. National Museum of Slovenia, Ljubljana, 40–139.

LESIGYARSKI, D., ŠMIT, Ž., ZLATEVA-RANGELOVA, B., KOSEVA, K., KULEFF, I., (2013): Characterization of the chemical composition of archaeological glass finds from South-Eastern Bulgaria using PIXE, PIGE and ICP-AES. *J. Radioanal. Nucl. Chem*. **295** 1605–1619.

LJUBOMIROVA, V., ŠMIT, Ž., FAJFAR, H., KULEFF, I. (2014): Chemical composition of glass beads from the necropolis of Apollonia Pontica (5th-3rd century BC). *Archaeologia Bulgarica* **18** 1–17.

MARIĆ STOJANOVIĆ, M., ŠMIT, Ž., GLUMAC, M., MUTIĆ, J. (2015): PIXE-PIGE investigation of Roman Imperial vessel and window glass from Mt. Kosmaj, Serbia (Moesia Superior). *J. Arch. Sci. Reports* **1** 53–63.

REHREN, Th. (2008): A review of factors affecting the composition of early Egyptian glasses and faience: alkali and alkali earth oxides. *J. Arch. Sci.* **35** 1345–1354.

SAYRE, E.V. & SMITH, R.W. (1961): Compositional categories of ancient glass. *Science* **133** 1824–1826.

SHORTLAND, A., SCHACHNER, L., FREESTONE, I., TITE, M. (2006): Natron as a flux in the early vitreous materials industry: sources, beginnings and reasons for decline, *J. Arch. Sci.* **33** 521–530.

SILVESTRI, A. (2008): The colored glass of Iulia Felix. *J. Arch. Sci* **35** 1489–1501.

SILVESTRI, A., MOLIN, G., SALVIULO, G. (2008): The colourless glass of Iulia Felix. *J. Arch. Sci.* **35** 331–341.

ŠMIT, Ž., PELICON, P., VIDMAR, G., ZORKO, B., BUDNAR, M., DEMORTIER, G., GRATUZE, B., ŠTURM, S., NEČEMER, M., KUMP P., KOS, M. (2000): Analysis of medieval glass by X-ray spectrometric methods, *Nucl. Instr. and Meth*. **B 161-163** 718–723.

ŠMIT, Ž., PELICON, P., HOLC, M., KOS, M. (2002): PIXE-PIGE characterization of medieval glass, *Nucl. Instr. Meth. Phys. Res*. **B 189** 344–349.

ŠMIT, Ž., JANSSENS, K., SCHALM, O., KOS, M. (2004): Spread of façon-de-Venise glassmaking through central and western Europe, *Nucl. Instr. Meth. Phys. Res*. **B 213** 717–722.

ŠMIT, Ž., JANSSENS, K., BULSKA, E., WAGNER, B., KOS, M., LAZAR, I. (2005): Trace element fingerprinting of façon-de-Venise glass, *Nucl. Instr. Meth. Phys. Res.* **B 239** 94.

ŠMIT, Ž., JEZERŠEK, D., KNIFIC, T., ISTENIČ, J. (2009): PIXE-PIGE analysis of Carolingian period glass from Slovenia, *Nucl. Instr. and Meth*. **B 267** 121–124.

ŠMIT, Ž., STAMATI, F., CIVICI, N., VEVECKA-PRIFTAJ, A., KOS, M., JEZERŠEK, D. (2009): Analysis of Venetian-type glass fragments from the ancient city of Lezha (Albania), *Nucl. Instr. Meth. Phys. Res.* **B 267** 2538–2544.

ŠMIT, Ž. KNIFIC, T. JEZERŠEK, D. ISTENIČ, J. (2012): Analysis of early medieval glass beads – Glass in the transition period. *Nucl. Instr. and Meth*. **B 278** 8–14.

ŠMIT, Ž., TARTARI, F., STAMATI, F., VEVECKA-PRIFTAJ, A., ISTENIČ, J., (2013): Analysis of Roman glass from Albania by PIXE-PIGE method. *Nucl. Instr. and Meth.* **B 296** 7–13.

ŠMIT, Ž., MILAVEC, T., FAJFAR, H., REHREN, TH., LANKTON, J.W., GRATUZE, B. (2014): Analysis of glass from the post-Roman settlement Tonovcov grad (Slovenia) by PIXE-PIGE and LA-ICP-MS. *Nucl. Instr. and Meth*. **B 311** 53–59.

TURNER, G. (1999): Allume Catina and the aesthetics of Venetian cristallo. *J. Design History* **12** 111–122.

VERITÀ, M. & ZECCHIN, S. (2009): Thousand years of Venetian glass: the evolution of chemical composition from the origins to the 18th century. In: JANSSENS, K. DEGRYSE, P. COSYNS, P. CAEN, J. VAN'T DACK L. eds., *Annales du 17e congrès de l'AIHV* (Antwerp 2006), University Press Antwerp, Antwerp, 602–613.

ZUCCHIATTI, A., CANONICA, L., PRATI, P., CAGNANA, A., ROASCIO, S., CLIMENT FONT, A. (2007): PIXE-analysis of V-XVI century glasses from the archaeological site of San Martino di Ovaro (Italy). *J. Cult. Herit.* **8** 307–314.

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# RÉGÉSZETI FÉMTÁRGYAK KUTATÁSÁNAK ÚJ EREDMÉNYEI ÉS KÉRDÉSEI MAGYARORSZÁGON

## RECENT RESULTS AND QUESTIONS OF METAL FINDS FROM ARCHAEOLOGICAL CONTEXT IN HUNGARY

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### *Abstract*

*The research of iron objects and history of smelting in the Carpathian Basin run back over two hundred, while the analysis of copper, gold and bronze artefacts over one hundred years. Here I attempt to give an overview of the results of the recent decade with the help of the archaeometry case studies of metal finds from Hungary published in the Archeometriai Műhely and other journals. These papers reflect recent research trends that investigate the metal finds from two aspects: on the one hand they analyse the raw material composition of the artefacts, and they also study the phases of production technique on the other, with the application of destructive sampling and non-destructive methods as well.*

### *Kivonat*

*A Kárpát-medencéből előkerült vastárgyak és a kohászat történetének kutatása immár kétszáz, a réz-, arany- és bronztárgyak vizsgálata több mint egy évszázados múltra tekint vissza. Az alábbiakban az utóbbi tíz év eredményeit, az Archeometriai Műhelyben és más folyóiratokban közölt, a hazai régészeti fémtárgyakat érintő újabb archeometriai esettanulmányokat tekintem át röviden. Ezek jól tükrözik a jelenlegi kutatási trendeket, melyek két fő irányból közelítik meg a fémtárgyakat: egyrészt a nyersanyag-összetétel elemzésére, másrészt a készítés-technikai lépések megismerésére irányulnak, roncsolásos mintavételek és roncsolás-mentes módszerek alkalmazásával egyaránt.*

KEYWORDS: ARCHAEOMETALLURGY, GOLD, COPPER, BRONZE, IRON, RAW MATERIAL ANALYSIS, PRODUCTION TECHNIQUE

KULCSSZAVAK: ARCHEOMETALLURGIA, ARANY, RÉZ, BRONZ, VAS, NYERSANYAG-VIZSGÁLAT, KÉSZÍTÉS-TECHNIKAI VIZSGÁLAT

### *Bevezetés*

A Kárpát-medencéből előkerült vastárgyak és a kohászat történetének kutatása immár kétszáz, a réz- és bronztárgyak vizsgálata több mint egy évszázados múltra tekint vissza. A hazai kutatás fejlődéséről az elmúlt másfél évtizedben több összefoglalás született Gömöri János, illetve Czajlik Zoltán és Szabó Géza tollából (Gömöri 2000; Czajlik 2012a; Szabó 2013). Az alábbiakban az utóbbi tíz év új eredményeit és kutatási programjait tekintem át röviden, különös tekintettel a 10 éves fennállását ünneplő Archeometriai Műhelyben megjelent, a réz-, arany-, bronz-, és vastárgyakhoz kapcsolódó esettanulmányokra.

Az Archeometriai Műhely 2004. évi első megjelenésétől 20 tanulmány foglalkozott a fémművességgel (Ilon 2014). Olvashattunk üreges fejű bronztű endoszkópos vizsgálatáról, különböző roncsolásmentes, neutronbefogáson illetve neutronszóráson alapuló technikák (neutrontomográfia, neutronaktivációs analízis, prompt-gamma aktivációs analízis, vagy repülési-idő neutrondiffrakció), és röntgenanalitikai módszerek (köztük proton-indukált röntgen-emissziós analízis: PIXE, és pásztázó elektronmikroszkóppal kiegészített elektronsugaras mikroanalízis: SEM-EDX) alkalmazásáról. A hazai elemzések a Budapesti Kutatóreaktorban (Budapesti Neutronközpont, BNC), az ATOMKI Ionnyaláb Alkalmazások (Ion Beam Applications: IBA) laboratóriumában, az Eötvös Loránd Tudományegyetemen és a Budapesti Műszaki Egyetemen készültek, néhány esetben külföldi együttműködésben, részben az Európai Unió Ancient Charm és Charisma programjaihoz csatlakozva (Dúzs et al. 2005; Kasztovszky & Belgya 2006; Uzonyi 2007; Kasztovszky 2011). Az Archeometriai Műhelyben és más, hazai és nemzetközi folyóiratokban, valamint tanulmánykötetekben közölt, a Kárpát-medencei régészeti fémtárgyakat érintő újabb esettanulmányok jól tükrözik a jelenlegi kutatási trendeket, melyek két fő irányból közelítik meg a fémtárgyakat: egyrészt a nyersanyag-összetétel elemzésére, másrészt a készítés-technika megismerésére irányulnak.

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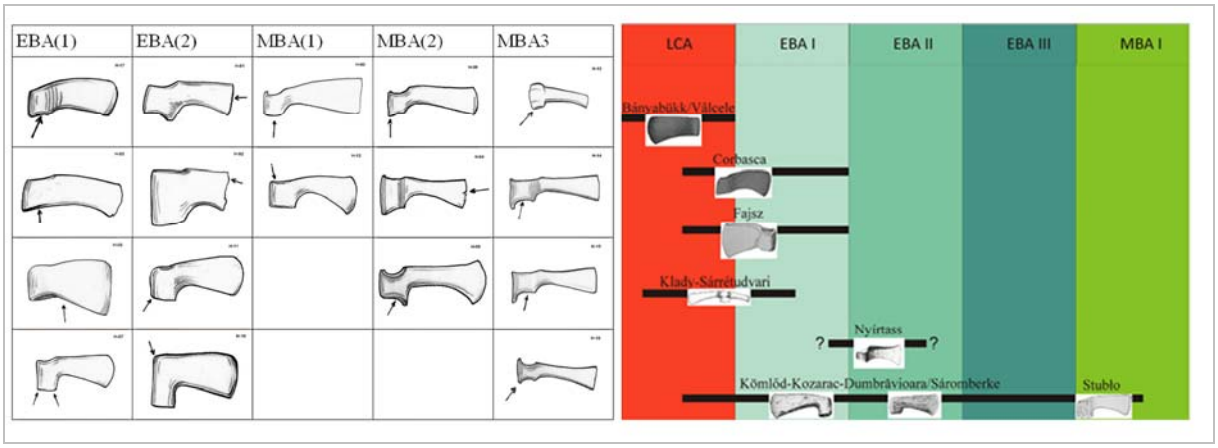



**1. ábra:** A Kárpát-medencei nyéllyukas balták időrendje: 1. Shalev, Kovács, T. Biró 2012 nyomán (a nyilak a baltákon végzett nyersanyag-elemzések mintavételi helyeit jelzik), 2. Dani 2013 nyomán
**Fig. 1.:** Chronological table of the shaft-hole axes in the Carpathian Basin: 1. after Shalev, Kovács, T.Biró 2012 (arrows indicating sampling points), 2. after Dani 2013

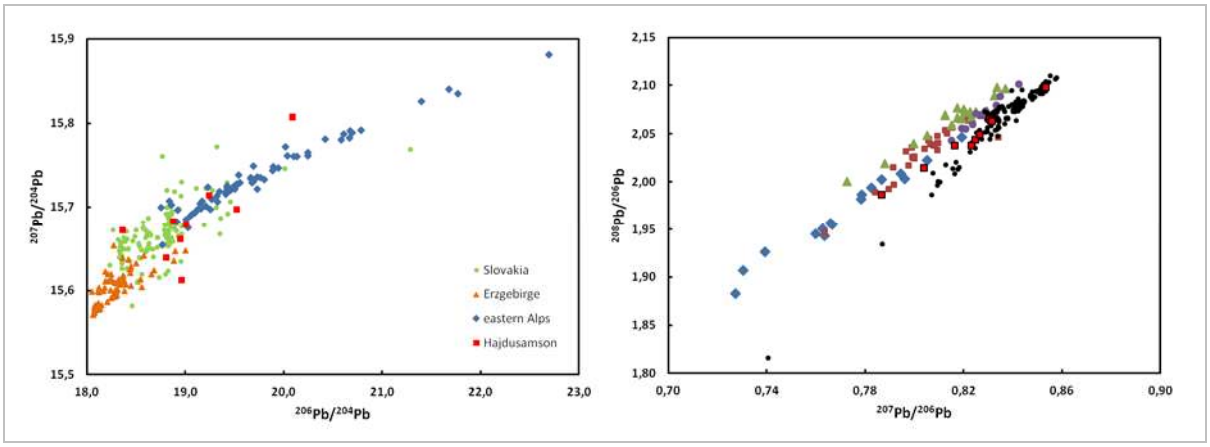
## *Nyersanyagok elemzése*

A nyersanyagok felől közelítve Czajlik Zoltán tanulmányára kell felhívnunk a figyelmet, aki a Kárpát-medence tágabb térségében a réz és vas nyersanyag őskori kohósításának nyomait foglalta össze. Az ércfeldolgozó műhelyek azonosítása általában az ismert geológiai adottságokból következik. Természetes rezek hasznosítása esetén (pl. Rudna Glaván) a horpák és bányagödrök bizonyítják a kitermelést, és ércpörkölési, kohósítási nyomokra nem számíthatunk. Néhány ismert őskori rézbánya környezetében viszont nagy számban kerülnek elő meddőhányók és salakhányók. Először többnyire a középkori, a népvándorláskori, vagy a római császárkori salaklelőhelyek részletesebb vizsgálata vezethet el az őskori kovácsolási, vagy pörkölési/kohósítási nyomok megismeréséhez. Fontos a kohászati és a kovácssalak egyértelmű elkülönítése, amit középkori vas anyag esetében Molnár Ferenc végzett el (Molnár 2011). A Kárpát-medencében egyelőre csak kevés és főként vaskori kohósításra vonatkozó adatot sikerült összegyűjteni. Az arany és a réz ércek feldolgozásáról jórészt közvetett adatok állnak rendelkezésre (Czajlik 2012b).

A legkorábbi, az újkőkor végén megjelent rézgyöngyök vizsgálata a tárgyak nyersanyaga és állagmegóvása szempontjából is fontos adatokkal szolgált. Kasztovszky Zsolt és munkatársai a Polgár-Csőszhalmon előkerült 148 db rézgyöngyből álló gyöngysor két gyöngyén roncsolásmentes PGAA, röntgen-pordiffrakciós és neutron-diffrakciós elemzést végeztek. Megállapították, hogy a gyöngyök korróziója folyamatos, és az eredeti természetes fázis már nyomokban sem volt jelen a tárgyakban. Az elemzések az állapotromlás kezeléséhez is segítséget nyújtottak (Kasztovszky et al. 2010).

A hencidai rézkori aranykincsen végzett energiadiszperzív röntgen-fluoreszcens (ED-XRF), pásztázó elektronmikroszkópos, PIXE és más módszereket alkalmazó komplex méréssorozat azt bizonyította, hogy a 12 aranycsüngő legkevesebb 3 (vagy 5) csoportba sorolható összetétel alapján. Az elemtérképezés a csüngők homogén elemeloszlását mutatta, mely készítésük során öntéstechnika használatára utal (Csedreki et al. 2010; Csedreki & Dani 2011). Fontos adatokkal szolgált az eddig csak néhány esetben vizsgált kora és késő bronzkori aranytárgyak elemösszetételének meghatározására irányuló, az MTA TTK Műszaki Fizikai és Anyagtudományi Intézetben elvégzett elektron-sugaras mikroanalízis (Endrődi 2012; Ilon 2012).

Nemrégiben került közlésre a kora bronzkori fémművesség fejlődését kutató izraeli–magyar projekt adatsora, melynek során a MNM-ban őrzött baltákon történt mintavételezés (Shalev, Kovács, & T. Biró 2012). E vizsgálatsorozatot kiegészítik azok az újabb megállapítások, amelyek szerint a kora bronzkorba sorolt balták egy részét inkább a rézkor végére keltezhetjük (**1. ábra;** Hansen 2011; Dani 2013; Szeverényi 2013, további irodalommal). E megfigyelések a nyersanyagokkal összevetve is érdekes tanulságokat hordoznak: a rézkori és kora bronzkor elejére keltezhető balták tiszta rézből készültek, míg a kora bronzkor fejlettebb időszakaiban gyakoribbá vált az arzéntartalmú nyersanyag, a középső bronzkor hajnalán pedig megjelentek az ónbronzok.




**2. ábra:** 1. A hajdúsámsoni kincs vizsgált tárgyai (pirossal jelezve), valamint a Keleti Alpok, a Szlovák Érchegység és a Cseh-Szász Érchegység rézérceinek ólomizotóp-arányai; 2. a vizsgált tárgyak (pirossal jelezve), valamint Mitterberg, és a Szlovák Érchegység rézércei ólomizotóp-arányainak alternatív bemutatása. Pernicka 2013, Fig. 2, Fig. 5 nyomán

**Fig. 2.:** 1. Lead isotope ratios of the archaeological objects analyzed (red symbols) and of copper ores from the eastern Alps, the Slovak Ore Mountains, and the Saxo-Bohemian Ore Mountains; 2. Alternative presentation of the lead isotope ratios of the archaeological objects analyzed (red symbols) and of copper ores from Mitterberg and the Slovak Ore Mountains, after Pernicka 2013, Fig. 2, Fig. 5

A rézkori, kora és középső bronzkori fémtárgyak vizsgálata során az utóbbi években számos módszer alkalmazására került sor. Barkóczy P., Kovács Á. és P. Fischl K. néhány, az 1960-as években végzett stuttgarti elemzési sorozatban (vö. Junghans, Sangmeister & Schröder 1968, 1974; Krause 2003) is vizsgált réz- és bronzkori tárgyat elemeztek újra a Miskolci Egyetem Anyagtudományi Intézetének LISA laboratóriumában. A metallográfiai vizsgálatokra a tárgyak már meglevő sérüléseinek helyénél került sor, itt végezve a szövetszerkezeti elemzéshez szükséges roncsolást. A tárgyak elemösszetételére vonatkozó eredmények részben a korábbi, stuttgarti adatoktól eltérő eredményekkel szolgáltak, ami a módszerek finomodásával és a korabeli tárgyak inhomogén anyagszerkezetével magyarázható. Mind a mikroszerkezetet, mind a zárványokat részletesen megvizsgálták pásztázó elektronmikroszkóppal: a borsodgeszti kartekercs esetében például a réz mellett ónt, antimont és nikkelt mutattak ki. A zárványok rézszulfidból, valamint az ón és az antimon kénnel alkotott vegyületeiből állnak; eszerint az alapanyag a réz szulfidos érceiből kohósodott, az ón és az antimon kísérő ásvány formájában volt jelen (Barkóczy, Kovács & Fischl 2011).

A dunántúli középső bronzkorra keltezhető zalaszabari kincs tárgyainak egy részénél roncsolásos mintavétellel járó energiadiszperzív röntgen-fluoreszcens (EDXRF) spektrometria segítségével 14 elem koncentrációját vizsgálták (Fe, Co, Ni, Cu, Zn, As, Se, Ag, Sn, Sb, Te, Au, Pb, Bi; a módszer leírásáról ld. Lutz & Pernicka 1996) a tübingeni egyetem kisebb mintavétellel járó vizsgálatsorozatához kapcsolódva. Az *Untersuchungen zur Vermittlung der Zinnbronze nach Mitteleuropa über das Karpatenbecken* projekt során T. Kienlin és E. Pernicka vezetésével közel 400 magyarországi és további több mint 200, a mai Románia nyugati részének múzeumaiban őrzött tárgyból is mintákat vettek; egyelőre csupán néhány tárgy elemösszetétel eredménye került közlésre (Kiss et al. 2013, 74, 3. ábra, 1. táblázat; Kiss et al. 2014, 2. táblázat). A nyersanyag az arzén, az ezüst és az antimon magasabb aránya miatt fakóérces ércteleprő származhat, ahol – amint azt az egyik tárgy vastartalma mutatja – kalkopirites ércek is lehettek (vö. Czajlik 2012a, 41). A nyersanyag összetételében megfigyelt különbségek arra utalnak, hogy a tárgyak zöme nem egyszerre készült, ami fontos megállapítás a bronzkincsek tárgytípus-összetételére és a deponálási szokásokra vonatkozóan.

A Szegedi Tudományegyetem, a debreceni ATOMKI és a Ljubljanai Egyetem együttműködő munkatársai a Charisma program keretében az alföldi halomsíros kultúra fémtárgyainak komplex vizsgálatát végezték el. A legtöbb tárgy jellemző nyomeleme az arzén és a nikkel. E nyersanyagot R. Pittioni kelet-alpi réznek nevezte, D. Liversage részben erdélyi eredetűnek tartotta (Pittioni 1957; Liversage 1994). Sánta G. szerint a Kárpát-medencében csak néhány olyan lelőhely van, melynek szulfidos ércei kohósítás után ilyen összetételt adnak; ezek főleg Dobsina (Dobšina, Szlovákia) környékére, a Szepes-Gömöri Érchegységre jellemzőek, ahol a kontakt metaszomatikus vas- és rézérctelep kalkopirit és

fakóércek mellett jelentős mennyiségű gersdorffitot (NiAsS) tartalmaz (Sánta 2011).

Félkész nyersanyagöntvények vizsgálata alapján Czajlik Zoltán több regionális nyersanyagforrás használatát valószínűsíti a késő bronzkor későbbi időszakaiban is (Czajlik 2006, 2013).

Amint az eddigi eredmények bemutatásából láthattuk, a felhasznált nyersanyagok konkrét forrásának, bányahelyének meghatározására a tárgyak vizsgálata önmagában nem alkalmas (vö. még Kiss 2009; Kiss 2012). A Kárpát-medencei rézbányák őskori kitermelésének kérdését több kutatási program is érintette az elmúlt évtizedben. M. Schreiner a szlovákiai, Garam völgyi őskori bányák, valamint a térség rézkori és bronzkori fémművessége komplex vizsgálatát végezte el: az elemösszetétel és ásványszerkezet elemzéshez röntgen-diffraktometriát és ólomizotóp-elemzést alkalmazva (Schreiner 2007; Schreiner et al. 2012). A délkelet-magyarországi régióban amerikai-magyar együttműködéssel folyó bronzkori településkutatási program és ehhez kapcsolódva a nyugat-romániai régióban fekvő bányahelyek vizsgálata is elkezdődött *(Arizona–Timisoara Early Metallurgy project)*. Az elemzés során a településekről származó fém tárgyakon, salakokon és az érc mintákon egyaránt végeztek összetétel elemzést, röntgen-diffrakciós, továbbá optikai és pásztázó elektronmikroszkópos vizsgálatokat (Papalas 2008; Duffy 2014). A nyugat-romániai réz- és bronztárgyak kutatásába a bochumi Bergbau-Museum is bekapcsolódott (vö. Hansen 2005). Az említett szlovákiai elemzések mellett eddig csupán a Fertő-tó térségének ausztriai oldaláról rendelkeztünk a Kárpát-medence térségét érintő ólomizotóp-adatokkal (Duberow et al. 2009). Emiatt rendkívül fontosak a Dani J.és E. Pernicka együttműködése nyomán elsőként publikálásra került magyarországi ólomizotóp vizsgálatok (**2. ábra**). A hajdúsámsoni kard és a térség valamivel későbbi leleteinek elemzési eredményei arra utalnak, hogy a Felső-Tisza-vidéki műhelyek a középső bronzkor derekán, virágzásuk kezdetén Közép-Európa nyugatabbi részéből importált nyersanyagból dolgoztak, majd a helyi fémművesség a nyersanyagforrások tekintetében is önállóvá vált, minden bizonnyal a mai kelet-szlovákiai nyersanyagforrásokra alapulva (Dani et al. 2013; Pernicka 2013). További új adatokat várhatunk a folyamatban levő, egyelőre közöletlen vizsgálatoktól (ld. az említett tübingeni projektet, illetve Siklósi et al. in prep.).

## *Készítés-technikai megfigyelések*

A LISA laborban végzett metallográfiai vizsgálatoknak a készítés-technikára vonatkozó megállapításai szerint a középső bronzkori zalaszabari bronzkincs tárgyai közül néhány öntéssel készült, míg másoknál az öntést követő utólagos megmunkálás látható, esetenként az alakításnak megfelelően elnyújtott zárványokkal, de leggyakrabban a megmunkálást követő hőkezelésből adódó újrakristályosodás mutatható ki (Kiss et al. 2013; vö. még P. Fischl et al. 2013). Emellett roncsolás-mentes (neutron radiográfiás, PGAA és repülési-idő neutron-diffrakciós: TOF-ND) vizsgálatok is készültek az MTA BTK Régészeti Intézet és a BNC együttműködésével (Kiss et al. 2014) réz- és bronztárgyakon, többek között a zalaszabari bronzkincs peremes baltáján. Mivel hasonló formájú balták gyakran kerülnek elő a Közép-Európa nyugatabbi részéből ismert rézbányák környezetében megtalált, azonos tárgyak sorozatát tartalmazó kincsleletekből, a kutatók egy része arra következtet, hogy ezek formaöntött félkész termékként/standard tömegű nyersanyag-öntvényként („előpénzként") értelmezhetők. Számos peremes balta metallográfiai elemzése során az él öntés utáni megmunkálására utaló, újrakristályosodott szövetszerkezetet lehetett kimutatni, emiatt T. Kienlin inkább eszközként való használatukat tartja fontosabbnak. A TOF-ND elemzés a zalaszabari peremes baltánál is kimutatta az utólagos megmunkálást. Örökségvédelmi szempontból nagyon fontos tény, hogy az említett vizsgálat a balta élének öntés utáni edzését a tárgy megsértése nélkül igazolta, és a balta korábbi kis roncsolással járó mintavétele nyomán végzett ED-XRF elemzés óntartalom adatával jól korreláló eredménnyel is szolgált (Kiss et al. 2014).

M. Mödlinger szintén a Charisma program keretében vizsgálta a késő bronzkori támadó és védő fegyvereket. A támadó fegyvereket vizsgáló munka 80 késő bronzkori kard röntgen-fluoreszcenciával, elektron mikropróba analízissel és 3D-CT-vel történt vizsgálata során fontos megfigyeléseket tett az öntéstechnika módjáról és hibáiról, a kardok edzéséről, élezéséről és használatáról (Mödlinger 2011). A védő fegyverek kutatása többek között magyarországi sisakok, páncélok és lábvértek készítésének technikájára, valamint a harc közbeni sérülésekkel összefüggő használati nyomokra fókuszál. A BNC roncsolás-mentes módszerei, valamint metallográfiai elemzés alkalmazásával nyert eredményei alátámasztják Szabó Géza korábbi megállapításait, amelyek szerint a bronzsisakokat az alapanyagul szolgáló öntött lemezből kalapálással és hőkezeléssel formálták meg; a tetejükön elhelyezett gomb pedig viaszveszejtéses módszerrel készült (Szabó 1994, 2013; Mödlinger et al. 2013, 2014).

Szabó Géza kora vaskori bronzedényeken végzett vizsgálatai a tárgyak műhelykörzetekhez való kapcsolásának lehetőségét mutatták ki; a műhelyek adott esetben a Hallstattól Regölyig nyúló térséget láthatták el sorozatban gyártott készletekkel (Szabó 2012).

A késő vaskori bronz karikaékszerek archeometallurgiai vizsgálata során Molnár Ferenc és munkatársai több nyersanyagtípust és eltérő készítéstechnikával dolgozó műhelykörzeteket különítettek el (Molnár et al. 2012).

Áttérve a vastárgyak kutatására az avar- és Árpád-kori vasművesség az iparrégészeti feldolgozásoknak köszönhető jobban ismert adatai (összefoglalóan: Gömöri 2000; Török 2011; Thiele & Török 2011, Thiele et al. 2013) mellett újabban a szkíta és kelta kor vastárgyainak kutatása is megélénkült. A Duna-Tisza közén fekvő Bátmonostor-Szurdok lelőhely megelőző feltárása során talált, feltehetően temetkezéshez köthető, szkíta kori leletegyüttesből hat vasfegyver komplex archeometriai vizsgálatát végezték el a Miskolci Egyetem LISA Laboratóriumában, számítógép-vezérelt tárgyasztalos optikai mikroszkóppal, energiadiszperzív röntgen-mikroszondával felszerelt pásztázó elektronmikroszkóppal (SEM-EDS), illetve mikrokeménység-mérővel. Az ordacsehi-cserefőldi kelta kori tárgyak vizsgálatsorozatának fő célja a salakminták és a fémtárgyak kémiai, ásványtani és anyagszerkezeti jellemzőinek feltárása volt. Az elemzett vaskori tárgyak általában relatíve lágy, inhomogén szövetszerkezetű, ferrites, ferrit-perlites vasból készültek (Török et al. 2013a, 2013b).

Czajlik Zoltán és Molnár Ferenc a sajópetri kelta településen a vasművesség munkafázisaihoz kapcsolódó emlékanyagot dolgozták fel, és egy kohók nélküli technológia lehetőségét vetették fel (Czajlik & Molnár 2007; Czajlik 2012b, 1. ábra).

A közelmúltban Budaörsön feltárt római kori kocsi sírokból előkerült vasalkatrészének archeometriai vizsgálatát (metallográfiai, mikrokeménység-mérését és elektronsugaras mikroanalízisét) Thiele Á. és munkatársai végezték el a BME Anyagtudomány és Technológia Tanszék laboratóriumában. Megállapításaik szerint a kocsi alkatrészek ötvözetlen szénacélból készültek, s többségüknél a gyártástechnológia tekintetében a korszak kovácsai az igénybevételekkel szemben általában megfelelő anyagot, de nem mindig megfelelő technológiát (megmunkálást és hőkezelést) választottak (Thiele et al. 2011).

Egy pusztataskonyi 6. századi germán sírból előkerült kard archeometallurgiai vizsgálatát is elvégezték a Miskolci Egyetem Anyagtudományi Intézetében. Az ötvözetlen acél kard ferrit-perlites szövetszerkezete arra utal, hogy egyazon bucavasból készült. Török B. és Kovács Á. munkája fontosságát kiemeli, hogy a tanulmányt megelőzően az alföldi gepidák vaselőállítási technikájáról nem álltak rendelkezésre ismeretek (Török & Kovács 2011).

Thiele Á. és munkatársai a díszítő kovácshegesztés kísérleti régészeti módszerrel és metallográfiai vizsgálatokkal való tanulmányozása során maratási kísérleteket is végzett különféle sav fajtákkal. Az eredmények szerint a korabeli kardkészítők minden bizonnyal a természetben könnyebben elérhető, relatíve gyenge savakat használták rendszeresebben, mint például az ecetsavat, a megsavanyodott sört, a vizelet savtartalmát, a borkősavat, illetve a csersavat, amely az igen hatásos, kék-fekete színű sávokat eredményezi és egyfajta rozsdásodás-gátlásként is szolgált Thiele et al. 2014).

A vasművesség későbbi történetének új eredményei között kell megemlíteni a szigetvári csatatéren előkerült 16. századi öntött acél ágyú technikatörténeti szempontból fontos vizsgálatát, hiszen a korábbi ismeretek szerint Európában a 19. század második feléig nem készültek ilyen fegyverek (Szabó et al. 2013).

## *Összefoglalás*

A bemutatott esettanulmányok arra hívják fel a figyelmet, hogy többféle módszer kombinációjával lehet a nyersanyag és a készítés-technika körvonalazásához közelebb jutni. A tudományterületek specializáltsága, ugyanakkor a régészeti tárgyak vizsgálata során felvetődő komplex kérdések megoldása csak munkacsoportok, különböző tudományágak együttműködő szakemberei számára lehetséges. A vizsgálat helye és a mintavétel kijelölésében a régészeti kérdésfelvetés és a műtárgyvédelmi szempontok összehangolása, valamint a mintavételi helyek dokumentálása és publikálása révén egyre gyarapodó archeometriai adatbázisok jöhetnek létre. Ennek segítségével az úttörő tematikai és módszertani munkákból a jövőben tendenciák rajzolhatók ki, újabb kérdések megválaszolására sarkallva a kutatókat.

## *Irodalom*

BARKÓCZY P., KOVÁCS Á., P. FISCHL K. (2011): Réz és bronz leletek metallográfiai és metallurgiai vizsgálatai – Metallographical and Metallurgical Investigation of Prehistoric Copper and Bronze Finds. *Archeometriai Műhely* **8** 293–304.

CZAJLIK Z. (2006): La distribution du cuivre des origines à la fin de l'âge du Bronze en France. Essai de comparaison des demi-produits provenant de France orientale et de l'Europe centrale. *Acta Archaeologica Academiae Scientiarum Hungaricae* **57** 47–65.

CZAJLIK Z. (2012a): *A Kárpát-medence fémnyersanyag-forgalma a későbronzkorban és a vaskorban.* Tálentum könyvek. Eötvös Loránd Univ., Budapest, 1–172.

CZAJLIK Z. (2012b): A fémnyersanyagok őskori kohósításának nyomai a Kárpát-medencében -

Traces of prehistoric smelting workshops in the Carpathian Basin. *Archeometriai Műhely* **9** 97–104.

CZAJLIK, Z. (2013): Lokaler, regionaler oder Fernhandel? Probleme der spätbronzezeitlichen Metallversorgung am Velem–St. Veit Berg (Westungarn). In: Rezi, B., Németh, R., E., & Berecki, S. (eds): Bronze Age Crafts and Craftsmen. Proceedings of the International Colloquium from Târgu Mureş 5–7 October 2012. *Bibliotheca Mvsei Marisiensis* **6** Târgu Mureş , 167–180.

CZAJLIK Z. & MOLNÁR, F. (2007): Sidérurgie. In: Szabó, M. (dir.) & Czajlik, Z. (ass.): *L'habitat de l'époque de La Tène à Sajópetri-Hosszú-dűlő*. L'Harmattan, Budapest, 263–270.

CSEDREKI L. & DANI J. (2011): A hencidai rézkori aranykincsen végzett pixe vizsgálatok tanulságai – Experiences of the pixe analyses performed on the copper age gold treasure of Hencida. *Archeometriai Műhely* **8** 285–192.

CSEDREKI L., DANI J., KIS-VARGA M., DARÓCZI L., & SÁNDORNÉ KOVÁCS J. (2011): A hencidai aranykincs interdiszciplináris vizsgálatai (új szempontok, új eredmények). *A Debreceni Déri Múzeum Évkönyve 2010-ről*, 35–52.

DANI, J. (2013): The Significance of Metallurgy at the Beginning of the Third Millennium BC in the Carpathian Basin. In: Heyd, V., Kulcsár, G., & Szeverényi, V. (eds): *Transitions to the Bronze Age. Interregional Interaction and Socio-Cultural Change in the Third Millennium BC Carpathian Basin and Neighbouring regions*. Archaeolingua, Budapest, 203–231.

DANI, J., TÖRÖK ZS., CSEDREKI L., KERTÉSZ ZS., & SZIKSZAI Z. (2013): A hajdúsámsoni kincs PIXE vizsgálatának tanulságai. *Gesta* **12** 30–47.

DUBEROW, E. PERNICKA, E. & KRENN-LEEB, A. (2009): Eastern Alps or Western Carpathians: Early Bronze Age Metal within the Wieselburg Culture. In: KIENLIN, T. L. & ROBERTS, B. W. (eds.): *Metals and Societies. Studies in honour of Barbara S. Ottaway*. Universitätsforschungen zur prähistorischen Archäologie 169. Bonn, 336–349.

DUFFY, P. (2014): *Complexity and Autonomy in Bronze Age Europe*: *Assessing Cultural Developments in Eastern Hungary (Prehistoric Research in the Körös Region*. Archaeolingua, Budapest, 1–402.

DÚZS, SZATHMÁRI, & T. BIRÓ (2005): Régészeti tárgyak endoszkópos vizsgálata – Investigation of archaeological objects by industrial endoscope. *Archeometriai Műhely* **2** 62–66.

ENDRŐDI, A. (2012): Early Bronze Age headdress. Markers of the social status in the Bell Beaker–Csepel group. *Archaeológiai Értesítő* **137** 7–26.

GÖMÖRI J. (2000): Az avar kori és Árpád-kori vaskohászat régészeti emlékei Pannoniában *(Magyarország iparrégészeti lelőhelykatasztere I. Vasművesség. – The archaeometallurgical sites in Pannonia in the Avar (7th–9th c. A D.)- and early Árpád period (10–12. c. A. D.)*. Soproni Múzeum és MTA VEAB Iparrégészeti és Archaeometriai Munkabizottság, Sopron, 1–373.

HANSEN, S. (2005): Neue Forschungen zur Metallurgie der Bronzezeit in Südosteuropa. In: Ü. Yalcin (Hrsg.), *Anatolian Metal 3*. Der Anschnitt, Beiheft 18. Bochum, 89–104.

HANSEN, S. (2011): Metal in South-Eastern and Central Europe between 4500 and 2900 BCE. In: Yalçın, Ü., Wirth, Ch. (eds): Anatolian Metal 5. *Der Anschnitt*, Beiheft **24** Bochum, 137–150.

ILON G. (2014): 10 éves az Archeometriai Műhely (AM) – Ten years of Archaeometry Workshop. *Archeometriai Műhely* **11** 77–80.

JUNGHANS, S, SANGMEISTER, E. & SCHRÖDER M. (1968): *Kupfer und Bronze in der frühen Metallzeit Europas. Die Materialgruppen beim Stand von 12000 Analysen*. Studien zu den Anfängen der Metallurgie 2. 1-3. Mann, Berlin, 1–174.

JUNGHANS, S, SANGMEISTER, E. & SCHRÖDER M. (1974): *Kupfer und Bronze in der frühen Metallzeit Europas.* Studien zu den Anfängen der Metallurgie 2. 4. Mann, Berlin, 1–406.

KASZTOVSZKY ZS. (2011): A Budapesti Neutronközpont szerepe az európai kulturális örökség kutatásában – Charisma. *Magyar Tudomány* **10** 1238–1246.

KASZTOVSZKY ZS. & BELGYA T. (2006): Non-Destructive Investigations of Cultural Heritage Objects with Guided Neutrons: The Ancient Charm Collaboration. *Archeometriai Műhely* **3** 12–17.

KASZTOVSZKY ZS., SZILÁGYI V., & SAJÓ I. (2010): Neolitikus rézgyöngyök vizsgálata Polgár-Csőszhalom lelőhelyről – előzetes eredmények / Scientific investigation of Neolithic copper beads from Polgár-Csőszhalom – Preliminary result. *Archeometriai Műhely* **7** 137–140.

KISS V. (2009): A fém nyersanyag-felhasználás kérdései a Dunántúl kora és középső bronzkorában – Questions of the use of metal as raw material in the Early and Middle Bronze Age of Transdanubia. In: Ilon G. (Szerk.) *ΜΩΜΟΣ VI. Őskoros Kutatók VI. Összejövetele. Nyersanyagok és kereskedelem.* Szombathely, 197–212.

KISS V. (2012): Arany, réz és bronztárgyak kutatása a középső bronzkorig. Az

archeometallurgia aktuális kérdései – The study of gold, copper and bronze artefacts until the Middle Bronze Age. Current questions of archaeometallurgy. *Archeometriai Műhely* **9** 61–74.

KISS V., BARKÓCZY P., & VÍZER ZS. (2013): A zalaszabari bronzkincs archeometallurgiai vizsgálatának előzetes eredményei. *Gesta* **13** 3–13.

KISS, V., FISCHL, K.P., HORVÁTH, E., KÁLI, GY., KASZTOVSZKY, ZS., KIS, Z., MARÓTI, B., & SZABÓ, G. (2014): Bronzkori fémtárgyak roncsolásmentes neutron analitikai vizsgálatának eredményei. *Gesta* **14** in press.

KRAUSE, R. (2003): *Studien zur kupfer- und frühbronzezeitlichen Metallurgie zwischen Karpatenbecken und Ostsee*. Vorgeschichtliche Forschungen 24. Rahden/Westfalen, 1–203.

LIVERSAGE, D. (1994): Interpreting composition patterns in ancient bronze: the Carpathian Basin. *Acta Archaeologica* (*København*) **65** 57–134.

LUTZ, J., & PERNICKA, E. (1996): Energy dispersive X-ray analysis of ancient copper alloys: empirical valuesfor precision and accuracy. *Archaeometry* **38** 313–323.

MOLNÁR F. (2011): Salakok és fémek archeometriai vizsgálata. In: Müller R. (szerk.): *Régészeti kézikönyv*. Magyar Régész Szövetség, Budapest, 510–524.

MOLNÁR, F., CZAJLIK, Z. & MASSE, A. (2012): Analyse archéométallurgique des bracelets et anneaux de chevilleceltiques en bronze mis a jour à Ludas. In: Szabó, M. (dir.), Tankó, K. et Czajlik, Z. (ass.) : *La nécropole celtique à Ludas–Varjú-dűlő*, L'Harmattan, Budapest, 249–265.

MÖDLINGER, M. (2011): Ritual object or powerful weapon – the usage of Central Europe Bronze Age swords. In: Uckelmann, M., Mödlinger, M. (eds): *Bronze Age Warfare: Manufacture and Use of Weaponry*. BAR IS **2255**. Oxford, 153–166.

MÖDLINGER, M., KÁLI, G., KASZTOVSZKY, Z., KOVÁCS, I., PICCARDO, P., SZILÁGYI, V., & SZŐKEFALVI-NAGY, Z. (2013): Archaeometallurgical characterization of the earliest European metal helmets. *Materials Characterization* **79** 22–36.

MÖDLINGER, M., KASZTOVSZKY, Z., KIS, Z., MARÓTI, B., KOVÁCS, I., SZŐKEFALVI-NAGY, Z., KÁLI, Gy., HORVÁTH E., SÁNTA, Zs., & EL MORR, Z. (2014): Non-invasive PGAA, PIXE and ToF-ND analyses on Hungarian Bronze Age defensive armour. *Journal of Radioanalytical and Nuclear Chemistry* (in press). DOI: 10.1007/s10967-014-3064-7

P. FISCHL K., KISS V., & KULCSÁR G. (2013): "Ahány ház, annyi szokás"? Specializált háztartások a Kárpát-medencei kora és középső bronzkorában. In: ΜΩΜΟΣ VII. Őskoros Kutatók VII. Összejövetele. 2011. március 16–18. Százhalombatta, Matrica *Múzeum. Őrségészeti Levelek / Prehistoric Newsletter* **13** 255–269.

PAPALAS, CH. (2008): *Bronze Age Metallurgy of the Eastern Carpathian Basin: a holistic exploration*. Unpublished Ph.D Thesis, Arizona State University, Tucson, 1–286.

PERNICKA, E. (2013): Analyses of Early Bronze Age metal objects from the Museum Debrecen, Hungary. *Gesta* **12** 48–55.

PITTIONI, R. (1957): Urzeitlicher Bergbau auf Kupfererz und Spurenanalyse. Beiträge zur Relation Lagestätte–Fertigobjekt. *Archaeologica Austriaca* Beiheft 1. Wien, 1–76.

SÁNTA G. (2011): Koszideri és halomsíros bronztárgyak komplex vizsgálata–összetétel, fázisok és korróziós felületek – Complex study of bronze objects from Koszider and tumulus period–composition, phases and corrosion. *Archeometriai Műhely* **8** 305–320.

SCHREINER, M. (2007): *Erzlagerstätten im Hrontal, Slowakei: Genese und prähistorische Nutzung*. Forschungen zur Archäometrie und Altertumswissenschaft, 3, Rahden/Westfalen, 1–292.

SCHREINER, M., HEYD, V. & PERNICKA, E. (2012): Kupferzeitliches Metall in der Westslowakei. In: Kujovský, R. & Mitáš, V. (eds): *Václav Furmánek a doba bronzová. Zborník k sedemdesiatym narodeninám*. Archaeologica Slovaca Monographiae – Communicationes 13. Nitra, 355–366.

SHALEV, S., KOVÁCS, T., & T. BIRÓ, K. (2012): Investigation of early copper-based alloys from the collection of the Hungarian National Museum – Korai rézötvözetek vizsgálata a Magyar Nemzeti Múzeum gyűjteményéből. *Archeometriai Műhely* **9** 105–116.

SIKLÓSI, ZS., PRANGE, M., KALICZ, N., ANDERS, A. & RACZKY, P. (in prep.): New data for the provenience of early copper finds from the Great Hungarian Plain. In: Anders, A., Hansen, S. & Raczky, P. (eds.): *Chronologies, Lithics and Metals. Late Neolithic and Copper Age in the Eastern Part of the Carpathian Basin and in the Balkans. Proceedings of the international workshop organised by the Institute of Archaeological Sciences, Eötvös Loránd University, the Eurasien-Abteilung des Deutschen Archäologischen Instituts, and the Römisch-Germanische Kommission des Deutschen Archäologischen Instituts, Budapest, 30th March 1st April, 2012*. Berlin–Budapest in prep.

SZABÓ G. (1994): A Kárpát-medencei későbronzkori sisakok készítésének problémái egy újabb lelet alapján (Probleme der Herstellung Spätbronzezeitlichen Helme im Karpatenbecken). In: Lőrinczy G. (szerk.): *A kőkortól a középkorig*. Csongrád Megyei Múzeumok Igazgatósága, Szeged, 219–227.

SZABÓ G. (2010): Az archaeometallurgiai kutatások gyakorlati és etikai kérdései – Practical and ethical issues of archaeometallurgical research. *Archeometriai Műhely* **7** 111–122.

SZABÓ G. (2012): A Kárpát-medencei archaeometallurgiai kutatások eredményei, aktuális kérdései a 21. század elején, különös tekintettel a bronz- és vasgyártás társadalmi hátterének változásaira / Recent advances and new questions of archaeometallurgical research in the Carpathian Basin at the begining of the 21st century, with special emphasis on the change in the social background of bronze and iron artefacts. *Archeometriai Műhely* **9** 75–96.

SZABÓ G. (2013): *A dunántúli urnamezős kultúra fémművessége az archeometallurgiai vizsgálatok tükrében – The metallurgy of the Transdanubian Urnfield Culture in the light of a Archaeometallurgical Investigations*. Specimina Electronica Antiquitatis – Libri 1. PTE-BTK-TTI, Ókortörténeti Tanszék, Pécs, 1–134.

SZABÓ G., KOVÁCS Á. & BARKÓCZI P. (2013): A Szülejmán kori harcászat és haditechnika a szigetvári ágyú és lövedékek archaeometallurgiai vizsgálatának tükrében. *Gesta* **13** 83–115.

SZEVERÉNYI, V. (2013): The Earliest Copper Shaft-Hole Axes in the Carpathian Basin: Interaction, Chronology and Transformation of Meaning. In: Anders, A., Kulcsár, G., Kalla, G., Kiss, V., Szabó, G. (eds): *Moments in Time: Papers Presented to Pál Raczky on His 60th Birthday, Prehistoric Studies I.* Budapest, 661–669.

THIELE Á., LENGYEL B. & MRÁV ZS. (2011): Római kocsi vasalkatrészeinek archeometriai vizsgálata –Archaeometrical Analyses of Iron Parts of a Roman-Age Carriage. *Archeometriai Műhely* **8** 321–328.

THIELE Á. & TÖRÖK B. (2011): Vastermelés, vaskihozatal és a kohósított gyepvasércek minimálisan szükséges vastartalma az avar és Árpád-kori vasbucakohászatban – Iron production, iron yield and the minimal iron content of bog iron ores regarding avar and Árpád-age bloomery iron smelt. *Archeometriai Műhely* **8** 345–450.

THIELE Á., TÖRÖK B., HARAMZA M., & JUHÁSZ G. M. (2014): A díszítő kovácshegesztés (pattern-welding) szerepe 2-10. századi kard- és késpengékben–korhűen rekonstruált vasanyagok maratási vizsgálata – The role of pattern-welding in 2-10th century knife and sword blades–etching tests on reconstructed materials. *Archeometriai Műhely* **11** 126–136.

THIELE Á., TÖRÖK B., & KÖLTŐ L. (2013): A foszfor szerepe a vas somogyi archeometallurgiájában – avar és Árpád-kori vaskohászatból származó somogyi salakok SEM-EDS vizsgálata – The role of phosphorus in the archaeometallurgy of iron: SEM-EDS analysis on slag samples from Avar and Árpád-age bloomery workshops of Somogy County. *Archeometriai Műhely* **10** 13–22.

TÖRÖK B. (2011): Vasérc, vasbuca, vastárgy. *Bányászattörténeti Közlemények* **12** 3–29.

TÖRÖK B. & KOVÁCS Á. (2011): Kora középkori gepida kard archeometallurgiai vizsgálata –Archaeometallurgical investigations of an Early Medieval Gepidic sword. *Archeometriai Műhely* **8** 337–344.

TÖRÖK B., BARKÓCZY P., KOVÁCS Á., GYUCHA A., & GULYÁS GY. (2013): Szkíta kori vasfegyverek mikroszerkezete és készítési jellemzői. *Gesta* **12** 56–66.

TÖRÖK B., KOVÁCS Á., BARKÓCZY P., & KRISTÁLY F. (2013): Ordacsehi-Cserefölđ kelta településéről származó vassalak és vastárgyak anyagvizsgálata és készítés-technológiai vonatkozásai – Materials testing and production technology investigation of iron tools and slag from a Celtic settlement of Ordacsehi-Cserefölđ. *Archeometriai Műhely* **10** 23–32.

UZONYI I. (2007): Ionnyaláb és röntgenanalitikai módszerek alkalmazása műtárgyak és régészeti leletek vizsgálatára – Application of Ion Beam and X-Ray Analytical Techniques for the investigation of Art and Archaeological objects. *Archeometriai Műhely* **4** 11–18.

# KÖZLEMÉNYEK


## *Beszámoló*

**a Synchrotron Radiation and Neutrons in Art and Archaeology 2014 (SR2A-2014) konferenciáról**

Helyszín: Párizs, Franciaország

Időpont: 2014. szeptember 9 – 12.

Első alkalommal vettem részt a kétévente megrendezett konferencián, amelyet az idén a párizsi Louvre Múzeum előadótermében tartottak. A konferencia fő profilja a szinkrotron- és neutronsugárzáson alapuló technikák alkalmazása műtárgyak és régészeti leletek vizsgálatában. Ezen belül túlsúlyban voltak a szinkrotronos vizsgálatokról szóló előadások, neutronos kutatásokról jóval kevesebb beszámoló hangzott el. Az előadások többsége mikro-szerkezetvizsgálati (XRD), mikro-elemanalitikai (XRF, aktivációs analitika), elemtérképező, képalkotó (radiográfia, tomográfia) módszereket mutatott be, amelyeket festmények, szobrok, egyéb műtárgyak vizsgálatára használnak főként állagmegóvás, konzerválás céljából.

A konferencia honlapja:

http://ipanema.cnrs.fr/spip/scientific-events/synchrotron-radiation-and-neutrons/sr2a-2014/article/synchrotron-radiation-and-neutrons-163?lang=en

Az egyes szekciók címe:

Conservation and Alteration / New methods and analytical processes / Processes and Chaînes opératoires / Palaeontology and Palaeo-environments

Az egyik szekció ún. „public session” volt, azaz nyilvános minden „külső” érdeklődő számára. A „public session”-nal párhuzamosan zajlott a poszterek bemutatása.

A konferencia végén kerekasztal beszélgetést tartottak a szakma aktuális kérdéseiről, a perspektívákról. Ezen kívül ifjúsági díjakat adtak át, továbbá szakmai vezetést is szerveztek a múzeumban.

Összesen kb. 250 résztvevő volt jelen, mintegy 40 szóbeli előadást és 80 posztert mutattak be.

Magyar szerzőktől származó poszterek a konferencián:

Zs. Kasztovszky, K. T. Biró, V. Szilágyi, A. Hajnal, K. Özvegy, Á. Szekeres: Provenance study of archaeological obsidian using non-destructive Prompt Gamma Activation Analysis

J. Corsi, A. Lo Giudice, A. Re, A. Agostino, A. Scherillo, F. Grazzi, Zs. Kasztzovszky, B. Maróti, L. Szentmiklósi, F. Barello: Characteriszation of silver pre-Roman coins from northern Italy with neutron-based techniques

V. Kiss, K. P. Fischl, E. Horváth, Gy. Káli, Zs. Kasztovszky, Z. Kis, B. Maróti, G. Szabó: Non-destructive analyses of bronze artefacts from hoards and graves of the Bronze Age in Hungary

Gy. Káli, E. Horváth, Zs. Siklósi, M. Bondár, V: Kiss: Non-destructive and Non-invasive Archaeometallurgical Investigations on Copper Age Artefacts from the Carpathian Basin

L. Rosta: Neutrons and complementary methods for archaeometallurgy investigations

G. Festa, E. Perelli Cippo, D. di Martino, R. Senesi. C. Adreani, E. Schooneveld. W. Kockelmann, N. Rhodes, K. T. Biró, G. Gorini: Neutron resonance transmission imaging for 3D elemental mapping at the ISIS spallation source

A konferencián bemutatott előadások és poszterek egy része közlésre került a Journal of Analytical Atomic Spectrometry (i.f.: 3,2) c. folyóiratban.

Hazai szerzőktől a következő közlemények jelentek meg:

- Corsi J, Maroti B, Re A, Kasztovszky Z, Szentmiklosi L, Torbagyi M, Agostino A, Angelici D, Allegretti S, Compositional analysis of a historical collection of Cisalpine Gaul's coins kept at the Hungarian National Museum, JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY 30:(3) pp. 730-737. (2015)

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- Kiss V, Fischl KP, Horváth E, Káli G, Kasztovszky Zs, Kis Z, Maróti B, Szabó G Non-destructive analyses of bronze artefacts from Bronze Age Hungary using neutron-based methods, JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY 30:(3) pp. 685-693. (2015)

A következő SR2A konferencia 2016-ban lesz Chicagóban.

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