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ANALYSES OF EARLY BRONZE AGE METAL OBJECTS FROM THE MUSEUM DEBRECEN, HUNGARY

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Introduction

The Early Bronze Age metal hoard of Nebra, which comprises the Nebra Sky Disc, two bronze swords decorated with gold cuffs, two flanged bronze axes, two bronze arm spirals and one bronze chisel, was discovered during an illegal excavation in 1999 AD on the Mittelberg in southern Sachsen-Anhalt, central Germany. Scientific investigations of the hoard and particularly of the Sky Disc initially concentrated on the authentication by mineralogical, trace element and lead isotope analyses of the bronze, the mineralogical and chemical composition of the corrosion layer and soil adhesions, as well as the technology of manufacture (Pernicka and Wunderlich, 2002; Pernicka et al., 2008; Pernicka, 2010). The gold inlays have been interpreted as a sun or full moon, a crescent-shaped moon, and 32 stars. Two of the stars were removed and the position of a third was changed when two horizon arches were later attached to the disk, followed by the final attachment of an arcuate boat or barge (Meller, 2003; Fig. 1). The constellation of the gold inlays suggests that the disk initially may have been used for calendrical purposes (Schlosser, 2003), making the Nebra Sky Disk the earliest astronomical representation of the night sky.

The archaeological context of the Sky Disc can be deduced from the accompanying finds in the hoard, which can all be dated to the Early Bronze Age in central Europe around 1600 BC, the classical Unetice Culture. This date of burial of the hoard was confirmed by ^{14}C analyses of a small piece of birch bark found in the handle of one sword. Of special chronological and culture historical importance was the typological parallel of the two swords of the Nebra hoard with the famous swords from Hajdúsámson. For this reason several objects from the Hajdúsámson hoard and chronologically and typologically similar one from Téglás and from Vámospércs were sampled on 30 April 2003 in the Déri Museum, Debrecen, Hungary.

Methods

The samples were analyzed by energy-dispersive XRF. Details of the procedure are described in Lutz and Pernicka (1996).

Lead isotope analysis was accomplished by multiple-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS). The sample was dissolved in diluted HNO_3 and lead was separated with ion chromatography resin from the matrix. The isotope ratios of lead were corrected for the mass discrimination by addition of Tl. A value of as ^{205}Tl / ^{203}Tl = 2.3871 was taken and an exponential relationship assumed. ^{204}Pb was corrected for the isobaric interference with ^{204}Hg by measuring ^{202}Hg and using a ^{204}Hg / ^{202}Hg ratio of 0.2293. The in-run precision of the reported lead isotope measurements was in the range of 0.02 to 0.08% (2σ) depending on the considered ratio.

Results and discussion

The results of the chemical and lead isotope analyses are summarized in Tables 2 and 3. As expected, all samples consist of low tin bronze with no other alloying components, especially no addition of lead which is important for the discussion of the lead isotope ratios in relation to the possible provenance of the copper, which was the major question here.

The hypothesis that trace element concentrations can be a guide to the provenance of ancient metals was formulated more than hundred years ago. One early example is Göbel (1842) with an extended title that reads like an abstract. In (my own) translation it reads: "On the impact of chemistry on the tracing of prehistoric peoples, or results of the chemical investigations of ancient metal objects, especially of those from

the Baltic region, to determine the peoples from whom they derive." He drew his conclusions from the geographical distribution of about 120 analysed objects and ascribed them to seemingly well-defined ethnic groups as was normal in those days. As soon as appropriate analytical methods became available in the 1930s very large analytical programs for ancient metal objects were performed along these lines. The largest one was undertaken by the Württembergisches Landesmuseum in Stuttgart (Junghans et al. 1960; 1968; 1974) with more than 20000 analyses of prehistoric metal objects from all over Europe. They were classified according to their chemical composition and the distribution of these metal groups was studied in time and space based on a frequency analysis of the concentration of As, Sb, Ag, Ni, and Bi.

With the application of lead isotope analysis to copper-based alloys (Gale and Stos-Gale 1982) chemical analysis of ancient metal objects seemed to have become obsolete. Indeed, it is often maintained that chemical analyses alone will not allow copper-alloy artefacts to be matched to their parent copper ores. Although this is correct in principle, there are cases where the trace element pattern may be more indicative of an ore source than lead isotope ratios. Some copper ore deposits are chemically rather homogeneous but show wide variations in their lead isotope ratios. This happens more often than initially thought so that it is obvious that a combination of both sets of data - lead isotope ratios and trace element concentrations - will provide better discrimination between different sources. With such a situation we are confronted in this study.

Table 1. Objects investigated.

Lab no.	object	site	museum inventory no.
FG-030621	Nackenscheibenaxt	Vámospércs	D 1; S 2.1910.973
FG-030622	Nackenscheibenaxt	Hajdúsámson	D 2; 1907.1206
FG-030623	Nackenscheibenaxt	Hajdúsámson	D 3; 89.5.1
FG-030624	Schaftlochaxt	Hajdúsámson	D 4; 1907.1210
FG-030625	Schaftlochaxt	Hajdúsámson	D 5; 1907.1216
FG-030626	Schaftlochaxt	Hajdúsámson	D 6; 1907.1214
FG-030627	Nackenscheibenaxt	Téglás	D 7; 78.17.2 (356)
FG-030628	Schwert, Griff	Téglás	D 8; 78.17.1, Griff
FG-030629	Schwert, Klinge	Téglás	D 9; 78.17.1, Klinge

Table 2. Chemical composition of the samples as determined with energy-dispersive XRF. All values are given in mass percent. Mn, Zn, Se, Te and Bi were below the detection limit of 0,01 % in all samples.

Lab no.	Cu	Sn	Pb	As	Sb	Ag	Ni	Fe	Co
FG-030621	95	3,7	0,03	0,71	0,117	0,009	0,62	0,13	0,025
FG-030622	94	7,0	0,02	0,60	0,082	0,028	0,48	< 0,05	0,021
FG-030623	94	7,0	0,09	0,27	0,041	0,012	0,27	< 0,05	< 0,005
FG-030624	96	3,6	0,03	0,23	0,017	< 0,005	0,18	< 0,05	< 0,005
FG-030625	94	5,1	0,03	0,52	0,111	0,015	0,51	0,09	< 0,005
FG-030626	97	2,1	0,02	0,30	0,046	0,009	0,36	< 0,05	< 0,005
FG-030627	93	4,0	0,06	1,05	0,61	0,094	1,40	< 0,05	0,031
FG-030628	95	6,1	0,06	0,24	0,091	0,013	0,36	0,12	0,014
FG-030629	94	5,4	0,05	0,76	0,37	0,046	1,28	0,22	0,048

Table 3. Lead isotope ratios in the samples investigated. The precision of measurement is ± 0,005% for ratios with ^{206}Pb in the denominator and up to ± 0,01% for $^{206}Pb/^{204}Pb$.

Lab no.	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
030621	2,0653	0,83065	18,880
030622	2,0440	0,82478	19,009
030623	2,0633	0,83167	18,804
030624	1,9863	0,78685	20,089
030625	2,0142	0,80405	19,523
030626	2,0377	0,81646	19,246
030627	2,0981	0,85335	18,365
030628	2,0494	0,82652	18,948
030629	2,0381	0,82330	18,963

Since there are no copper mineralisations in the vicinity of Hajdúsámson it is essential to obtain an idea of possible source regions. Furthermore, it is necessary that ore deposits suspected of being a metal source have already been investigated chemically and in view of their lead isotope ratios. This is usually not found in the geological or geochemical literature, because the trace elements used for provenance discussion are often not reported. In addition, very few geological reports contain any information on ancient or at least "old" mining. In Fig. 1 those regions are outlined, where all these conditions for a reasonable discussion of the provenance of the copper are fulfilled. There may be more smaller occurrences of copper in this large area but in the developed Early Bronze Age one can safely assume that the amount of copper produced was already quite substantial that could only be supplied by larger deposits.

Before going in to details of the discussion of the analytical results it may be worthwhile to recall the basics of the use of lead isotope ratios for provenance studies. Lead is a common trace element in most natural rocks. It occurs in nature in four stable isotopes, that is in four different varieties which all have the same chemical behaviour, but slightly different mass. Three of these isotopes form continuously through the radioactive decay of uranium and thorium, two other trace elements present in most rocks. Through this process the relative proportion of the four lead isotopes changes over geological time as the three radiogenic isotopes increase in quantity, while the fourth one (^{204}Pb) remains unchanged and, accordingly, relatively decreasing in abundance. During ore formation, the lead is removed from the parental rock and concentrated together with other metals such as copper or silver, but typically separated from uranium and thorium; at this stage, the lead isotope abundance ratio in the ore is therefore effectively fixed, while the lead isotope ratio in the surrounding rocks continues to evolve due to their remaining contents of uranium and thorium.

The lead isotope abundance ratios in ore deposits therefore provide a means for determination of the geological age of the formation of the ore deposit. During smelting, this isotope ratio is transferred without change into the metal, where lead occurs again as a trace or minor element in the copper, so that the lead isotope ratio of a copper artefact represents the lead isotope ratio of the ore deposit from which it was smelted as long as no lead is added to the metal. Different ore deposits form at different geological times and in different geological environments which enables one to distinguish them and the metals that were produced from different deposits by their lead isotope ratios. However, ore formation is a ubiquitous process, and can happen at the same time in different parts of the world, leading to geographically unrelated ore deposits which may have the same lead isotope signature. In addition, there are copper ore deposits which are relatively poor in lead but contain relatively high concentrations of uranium and thorium which can lead to a highly variable lead isotope signature. Such lead is usually called radiogenic. All these circumstances can lead to overlapping lead isotope characteristics of different ore deposits. A useful approach is to exclude in a first step those ores that do not match the archaeological artefacts isotopically and then check, if the remaining (isotopically overlapping) ore deposits can be discriminated by their trace element pattern.

Figure 1. Location of Hajdusamson and major copper mineralisations in central and southeastern Europe together with one minor one (Aibunar) that was already exploited in the fifth millennium BC.

Fig. 2 shows the lead isotope ratios in the artefacts analyzed and the ore deposits outlined in Fig. 1. Not shown are the data for Majdanpek and Aibunar which would plot around 206Pb/204Pb = 18.5 and 207Pb/204Pb = 15.6 so that they can safely be excluded as possible sources for the objects under study. The chalcolithic copper mine at Aibunar in Bulgaria can be furthermore be excluded, because it is a rather small deposits but, more important, its ores contain only arsenic at similar concentrations as the objects investigated but have much lower nickel concentrations (Pernicka et al. 1997). From the Medni Rid region in Bulgaria there are presently only few analyses available so that it is also not included in the discussion. Majdanpek in Serbia is one of the largest copper deposits in Europe and was exploited already in the fifth millennium BC (Pernicka et al. 1993, Radivojević et al. 2010) but it seems to have produced only rather pure copper in prehistoric times and it can be clearly distinguished form the eastern Alps by lead isotope ratios (Höppner et al. 2005). This leaves only the central European ore regions in focus of which the Slovak Ore Mountains is geographically closest. From Fig. 2 one can also conclude that the copper ores from the Saxo-Bohemian Ore Mountains are an unlikely source for the artefacts analyzed so that we need only to distinguish between the remaining two regions that are not so clearly separated in the lead isotope diagram. Silver and nickel are those trace elements in copper, which are most indicative of the ores used, because they behave in a similar way during the smelting processes. In Fig. 3 the concentrations of these two elements are plotted together with the analyzed artefacts. Although there is still some slight overlap between the two ore regions the fit with the copper ores from the Mitterberg area in Salzburg is much better.

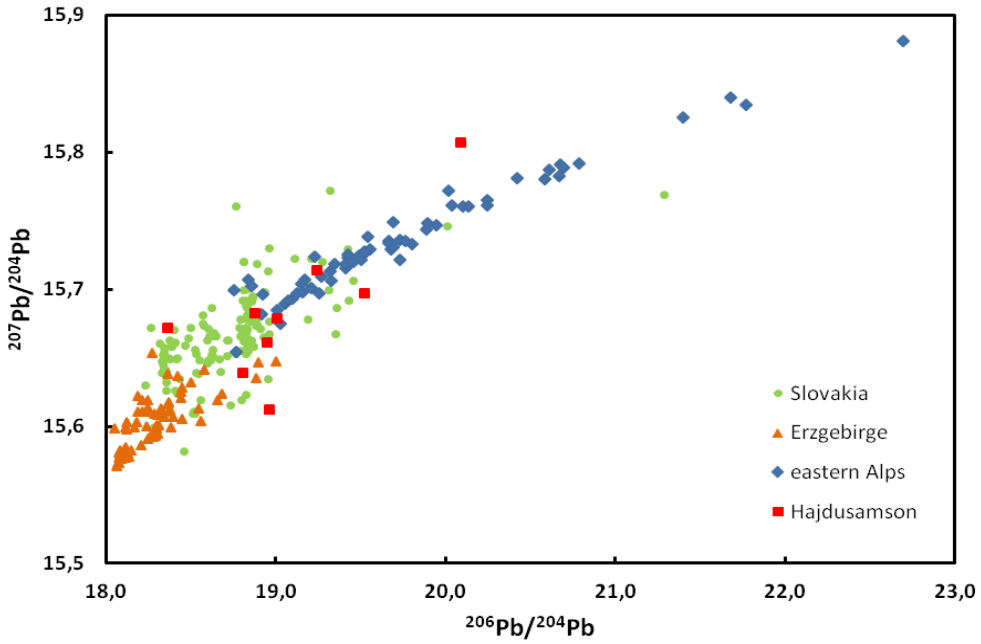

Figure 2. Lead isotope ratios of the archaeological objects analyzed (red symbols) and of copper ores from the eastern Alps, the Slovak Ore Mountains, and the Saxo-Bohemian Ore Mountains. Data are taken from Niederschlag et al. (2003) and Schreiner (2007). The data for the eastern Alps are as yet unpublished. The analytical errors are smaller than the symbols.

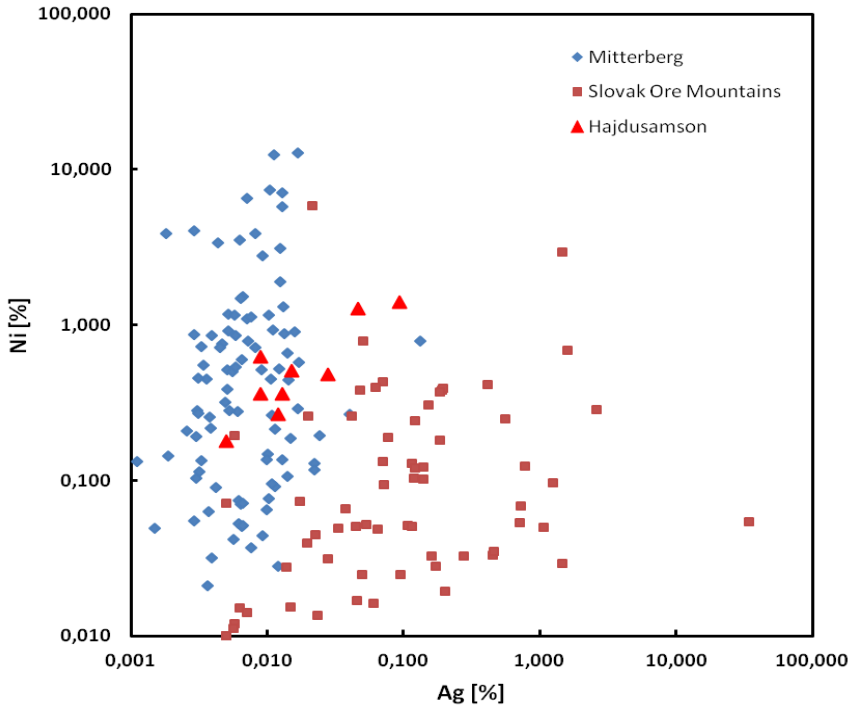

Figure 3. Concentration of silver and nickel in the archaeological objects analyzed (red symbols) and of copper ores from the eastern Alps and the Slovak Ore Mountains. Data are from Schreiner (2007) and unpublished for the eastern Alps. The analytical errors are smaller than the symbols.

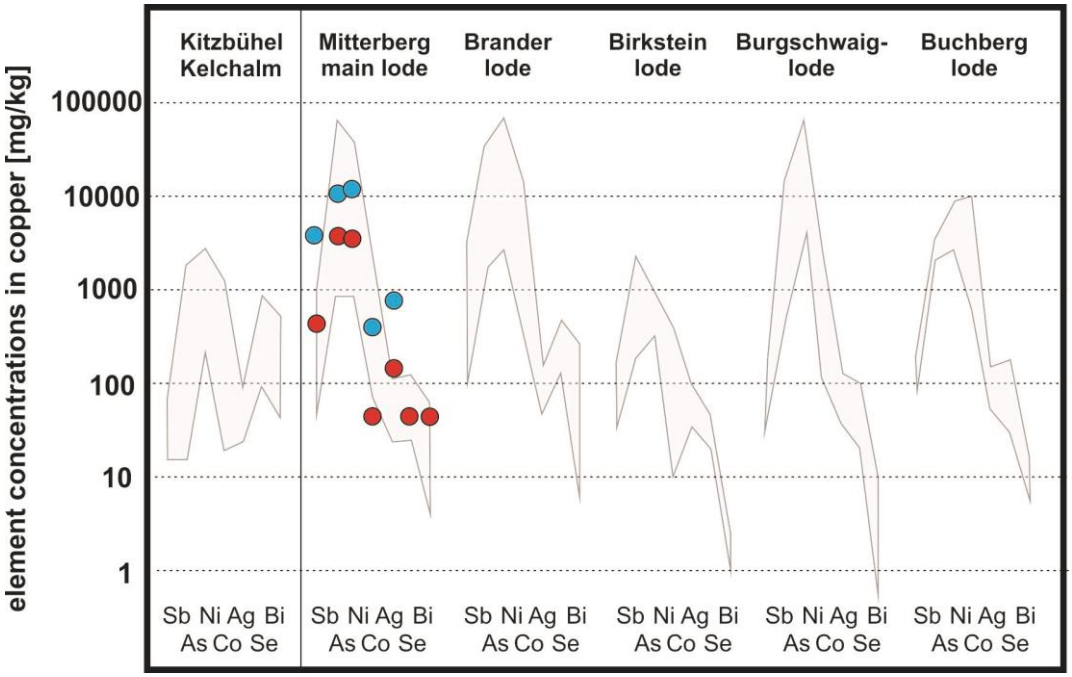

Figure 4. Trace element patterns of copper ores from Kitzbühel, Tirol, and from different lodes in the Mitterberg area in Salzburg, Austria (Lutz et al. 2011). Most objects analyzed in this study (red) match the pattern of the main lode almost perfectly, while two samples from Téglás (blue) are different in their silver and antimony concentrations.

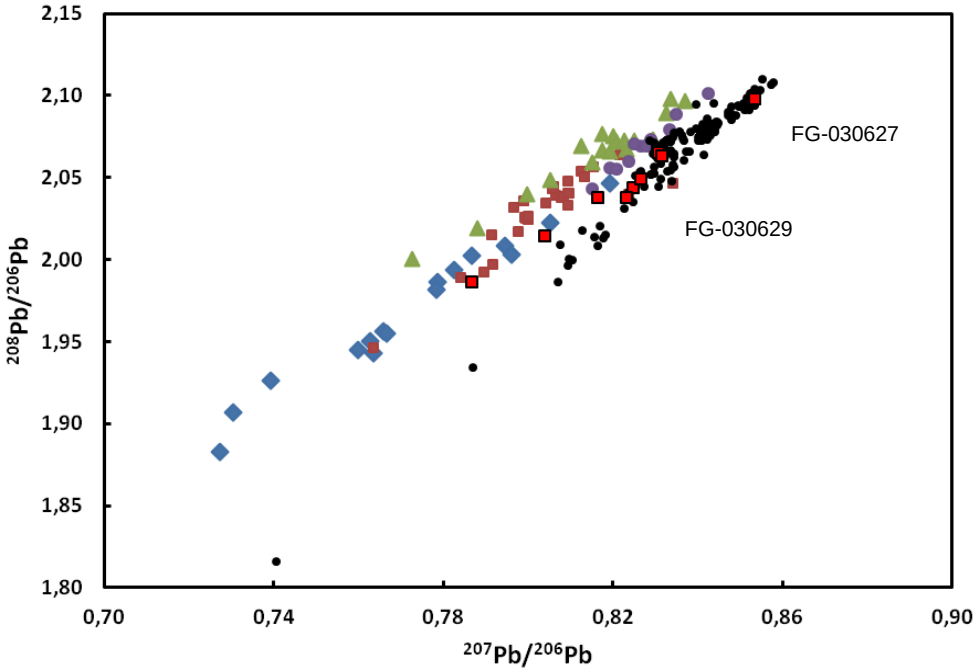

Figure 5. Alternative presentation of the lead isotope ratios of the archaeological objects analyzed (red symbols) and of copper ores from Mitterberg and the Slovak Ore Mountains. Data from Schreiner (2007) and unpublished data for Mitterberg. The analytical errors are smaller than the symbols.

We can even go further and compare the trace element pattern with more elements that are considered to be useful for discussing a possible relationship between copper ores and smelted copper (Pernicka 1999). It has been shown that within the Mitterberg area different lode systems can also be differentiated (Lutz et al. 2010). These patterns are now compared with the analyzed object in Fig. 4, whereby six of the eight objects are more or less plotting on top of each other. Only two samples, an axe (FG-030627) and a sword blade (FG-030627), both from Téglás, are different in two elements, namely silver and antimony.If we go back to the lead isotope ratios and use a different type of diagram then we see that the copper ores from the Mitterberg and Slovakia define different trends, which overlap in the upper right hand corner. The two samples that are chemically different from the Mitterberg copper ores indeed plot along the trend of the Slovak Ore Mountains.

In conclusion it seems almost certain that the copper for the Hajdúsamson axes, the axe from Vámospércs and the hilt of the sword from Téglás derives from the Mitterberg area in Salzburg, Austria, while the blade of the sword and the axe from Téglás may derive from the copper ores in the Hron valley in Slovakia although the eastern Alps cannot be totally excluded.

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