Lead isotope and trace element patterns of German and Polish Kupferschiefer – a provenance study of bronze artifacts

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ABSTRACT: The outstanding importance of the Early Bronze Age “Skydisk of Nebra” gave reason to investigate Central European copper occurrences in order to find out which occurrence might have been the source for its copper. Lead isotope ratios (by MC-ICP-MS) and trace element contents (Ag, As, Sb, Co, Ni, Bi, by energy-dispersive XRF) of German and Polish Kupferschiefer are presented and compared with data from the “Skydisk” and other artifacts found at Nebra. Trace element ratios and lead isotope data show clear differences between Kupferschiefer ore and Nebra artifacts. As a consequence, the investigated Kupferschiefer occurrences can be excluded as a copper source for the Nebra finds.

KEYWORDS: lead isotope, trace element, Kupferschiefer, “Skydisk of Nebra”

1 INTRODUCTION

The “Skydisk of Nebra”, found in 1999 at Mittelberg near Wangen (Saxony-Anhalt, East Germany), is the earliest astronomical illustration in Europe and thus one of the most important Bronze Age finds. It had been buried at Mittelberg in the Early Bronze Age (1600 BC) as part of a hoard together with two swords, two hatchets, and other bronze artifacts. At present, a DFG-financed multidisciplinary research group investigates a number of archeological, archeometallurgical, archeoastronomical, and geological questions connected with the “Skydisk of Nebra” and the associated artifacts.

One of the projects has the aim to find out which Mid European copper occurrence could have provided the copper for the “Skydisk” and the other finds from Nebra. The study is focused on occurrences, which crop out at surface and thus could have been easily exploited by Early Bronze Age miners. To characterize the different copper occurrences, lead isotopes and a number of trace elements (Ag, Co, Ni, As, Sb, Bi), which are not lost during smelting are used. Lead isotope compositions were measured by multicolonlector ICP-MS (Axiom, data corrected for Tl and Hg, 3 runs per sample). Trace elements together with the copper content are measured by energy-dispersive XRF (powder disks, detection limit for above mentioned trace elements about 10-50 ppm).

Amongst the investigated copper occurrences there are the Kupferschiefer outcrops at the southern rim of the Harz Mountains and Kyffhäuser, in the vicinity of Dobis and Könnern (Saxony-Anhalt, East Germany), and in the North Sudetic Syncline in Southwest Poland. The data of several Kupferschiefer samples from these localities is compared with trace element and lead isotope data of the “Skydisk” and the other Nebra finds (data taken from an unpublished Diploma thesis by Daniela Nickel at University Freiberg). The Kupferschiefer south of the Harz Mountains was seen as a possible copper source, due to its proximity to Nebra. Besides our own analyses, lead isotope data of the Kupferschiefer from the literature is compared with the Nebra finds.
2 SAMPLES

Field samples have been taken from five localities in Saxony-Anhalt and Lower Saxony (Fig. 1). From an outcrop at Dobis come two samples of mineralized Weißliegend Conglomerate and two samples of Kupferschiefer. At Könner, four Kupferschiefer samples from dumps have been taken. Five Kupferschiefer samples and one sample of “Sand Ore” are from underground at the “Röhrigschacht” in Wettelrode (near Sangerhausen at the southern rim of the Harz Mountains) and two Kupferschiefer samples are from an outcrop nearby. Three samples (two of mineralized Weißliegend Conglomerate and one of Kupferschiefer) come from a dump near Rottleberode further west. From Bad Lauterberg (Lower Saxony), the westernmost of the sample points, there are two Kupferschiefer samples from the entrance of a small gallery, immediately at the former outcrop of the Kupferschiefer.

Two samples have been obtained from the Mineralogical Collection of University in Freiberg (Germany). These are a sample of mineralized Weißliegend Conglomerate from Rottleben at the southern rim of the Kyffhäuser (Fig. 1) and one sample of copper marl from Leszczyna in the North Sudetic Syncline.

3 RESULTS AND DISCUSSION

Most of the 23 samples listed above have been measured for both trace elements and lead isotopes. The two samples from Kyffhäuser and from the North Sudetic Syncline have not yet been analyzed for lead isotopes.

3.1 Trace elemental characterization

The trace elements Ag, Co, Ni, As, Sb and Bi are typically used for determining the provenance of bronze artifacts because these elements pass from ore into crude copper during smelting (Pernicka 1987). However, bronze artifacts, consisting of 90% to 97% copper and up to 10% tin cannot be directly compared with copper ores. For this reason the metal ratios Ag/Cu, As/Cu, Sb/Cu, Co/Cu, Ni/Cu and Bi/Cu are used.

Figure 2 shows these trace elements to copper ratios for all samples (black triangles). There is a relatively large variation between different localities and also between samples from the same locality. This gives an insight into the strong lateral and vertical variability in the chemical composition of the Kupferschiefer. For comparison with the Nebra finds, the variation within the group of artifacts (including the “Skydisk”) is indicated by rectangles of different spread. It can be seen that there is almost no overlap. The As/Cu ratios of some samples fall into the variation of the artifacts but in most cases the Kupferschiefer tends to have higher relative trace element contents, especially for Ag and Co. It is important to note that a number of values are omitted in the diagram because the trace element contents are below detection limit and thus are difficult to display on a logarithmic scale. This includes for the artifacts (total number is 30) 8 values for Co, 11 values for
Ag, 9 values for Sb, and all except one value for Bi (resulting in a small rectangle for the Bi/Cu values of the artifacts). For the Kupferschiefer samples (total number is 23) 13 values for As, 11 values for Sb, and 18 values for Bi are affected. So especially for Bi, there are values both from samples and artifacts below detection limit. But nevertheless, the trace element pattern of the Kupferschiefer is clearly different from the Nebra finds.

3.2 Lead isotopical characterization

Smelting of copper ores does not cause an isotope fractionation of lead (Pernicka 1987). As a consequence, the isotope ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ can be used to characterize bronze artifacts. Lead isotope ratios of 21 Kupferschiefer samples (and samples from mineralized Weißliegend Conglomerate) have been analyzed. The results are displayed in the following diagrams. Figure 3 and 4 compare lead isotope ratios of samples from the different localities to those of the “Skydisk” and the other Nebra finds. Similar to the XRF data, the lead isotope ratios show a clear difference between Kupferschiefer ores and the Nebra artifacts. However, the samples seem to form two clusters, one including the samples from Dobis, Könern and Wetzelrode, the other one including samples from Rottleberode and Bad Lauterberg. One sample of Weißliegend Conglomerate from Dobis and the sample of “Sand Ore” from Wetzelrode are characterized by higher $^{206}\text{Pb}/^{204}\text{Pb}$ contents (Fig. 3 and 4).

In the following two diagrams (Fig. 5 and 6) lead isotope data from literature is additionally shown. This includes data from the Kupferschiefer at Mansfeld (Niederschlag et al. 2003; Wedepohl et al. 1978), Eisleben (Wedepohl et al. 1978), Sangerhausen (Hammer et al. 1987; Wedepohl et al. 1978), Bad Lauterberg (Leveque and Haack 1993), from “Richelsdorfer Gebirge”, “Weserbergland” and Lubin (Wedepohl et al. 1978), and also from the Zechstein at Kyffhäuser (Leveque and Haack 1993).
Figure 6. $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of artifacts, Kupferschiefer samples and Kupferschiefer data from literature.

Most of this literature data (with Lubin tending to higher $^{206}\text{Pb}/^{204}\text{Pb}$ contents) plots in the same range as our measured Kupferschiefer samples. The signature of the published data is also different from that of the Nebra finds.

4 CONCLUSIONS

Trace element data as well as lead isotope data of the Kupferschiefer at the southern rim of the Harz Mountains and near Dobis and Königern (Saxony-Anhalt, East Germany) is clearly different from data of the “Skydisk of Nebra” and its associated artifacts. As a consequence, these occurrences can be excluded as a copper source for the Nebra finds. XRF data of the Kupferschiefer at the southern rim of Kyffhäuser and in the North Sudetic Syncline (Southwest Poland) suggests that these localities can also be excluded, but this still has to be confirmed by lead isotope measurements. Lead isotope data from literature also shows no correlation with the “Skydisk” and the other artifacts from Nebra.

The present data is available for provenance studies of other artifacts and thus offers an excellent opportunity for future metallurgical comparisons.

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