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Silver production by cupellation in the fourth millennium BC at Tepe Sialk

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Until recently our knowledge of silver production in the Old World was based on ancient silver finds. This inventory allows three conclusions: i) Silver generally appears in the archaeological record in the fourth millennium BC, ii) contemporary is a significant increase in the number of lead objects, and iii) the geographical distribution of silver finds is limited to southwest Asia, Egypt and the Aegean. Contrary to the early copper metallurgy there is no indication that silver production and usage extended into southeast or central Europe. Already Prag (1978) has observed that the distribution of silver in the Old World is similar to the one of lapis lazuli.

For some time a ring from Beycesultan, layer XXIV, was held as the earliest known object of silver (Lloyd & Mellaart 1962) as this layer was dated by the excavators ca. 4300 BC. (s. also Wertime 1973; Prag 1978). However, two 14C dates from layers XXVI and XXVIII suggest that layer XXIV should rather be dated to the middle of the fourth millennium BC (Kohlmeyer 1994) or even towards its end (Moorey 1994). Therefore, according to present knowledge the earliest silver objects seems to come from Tepe Sialk, layer III:5 (Ghirshman 1938), which securely dates into the first half of the fourth millennium BC if not slightly earlier (Kohlmeyer 1994). A few dozens of silver objects from Uruk (van Ess and Pedde 1992), some from Susa (Tallon 1987), from Korucutepe (Brandt 1978) Alisar Hüyük (von der Osten 1937), and from predynastic contexts in Egypt (Prag, 1978) could be contemporary or somewhat later. Unfortunately the chronological position of the 233 silver objects from the late neolithic cemetery of Byblos is unclear; the excavators estimate a date of 3880-3200 BC (Dunand 1973). However, this estimate is in dispute and many archaeologists would rather date the cemetery into the third millennium BC (see Kohlmeyer 1994 for a discussion of those finds).

It was already mentioned that the first silver objects appear together with or at the same time as lead. This suggests the silver was produced from argentiferous lead ores right from the beginning, although it does occur as the native metal in nature as C. S. Smith (1967) pointed out, who also thought that cerargyrite (silver chloride, AgCl) could also have been used for the production of silver. Native silver and cerargyrite could relatively easily be reduced with charcoal which would result in the shiny white metal (native silver is often black or brown due to reaction with sulphur or chlorides on the surface). On the other hand, silver rarely forms big lumps of metal in nature but occurs predominantly in the form of thin wires. It could therefore have been overlooked by early metal workers. From antiquity until the eighteenth century AD most of the silver produced derived from argentiferous lead ores by cupellation. It is not important, if cerussite (lead carbonate, $PbCo_3$) was used as Wertime (1973) and Meyers (1988) have suggested, or galena (lead sulfiede, PbS). Both could have been easily reduced to argentiferous lead metal from which silver could be extracted by selective oxidation of lead and other base metals by a process called cupellation. Since lead usually contains less than 1% silver, it is indeed remarkable that this two-stage process was already discovered in the fourth millennium BC and systematically applied. But the chemical compositions of practically all Chalcolithic and Early Bronze Age silver objects seem to confirm this, since they contain small amounts of lead and differ in their general trace element pattern from native silver that is quite characteristic (Pernicka 1987).

Since a few years direct evidence for the cupellation process in the fourth millennium BC has come to light in the form of well dated litharge (lead oxide, PbO) from stratigraphically secure archaeological contexts in eastern Anatolia and at Habuba Kabira in northern Syria (Pernicka et al. 1998). Litharge does not occur in nature accordingly the presence of litharge is a secure proof of cupellation. It is the by-product or the "slag" of the cupellation process. It can be found, because initially it seems to have been discarded, because there was no practical use for lead in this period. Now numerous litharge samples from Arisman and Tepe Sialk demonstrate that cupellation was also practised on the Iranian plateau in the same period.

Concerning the provenance of the silver and litharge samples, it was so far not possible to identify any specific mine or even source region. Lead isotope analyses of litharge samples from Habuba Kabira (Pernicka et al. 1998))did not fit any of the large lead-silver deposits in the Taurus or the Trabzon region in Anatolia (Fig. 1). The situation seems much more clear in Iran. It has been long suspected that the lead-silver deposit of Nakhlak was an important production site for silver in antiquity. This can now be confirmed and even extended to the fourth millennium BC by the excellent agreement of lead isotope ratios in chalcolithic litharge samples from Arisman (Stöllner et al. 2004) as well as one sample from Tepe Sialk with lead slag and ores from Nakhlak (Fig. 2). Although an agreement of lead isotope ratios between ores and artefacts is a necessary but not sufficient requirement for the identification of an ore source the unusually and exceedingly small variation of lead isotope ratios in the Nakhlak deposit seems to provide sufficient evidence for a positive identification of Nakhlak as the source for the litharge from Tepe Sialk and Arisman.

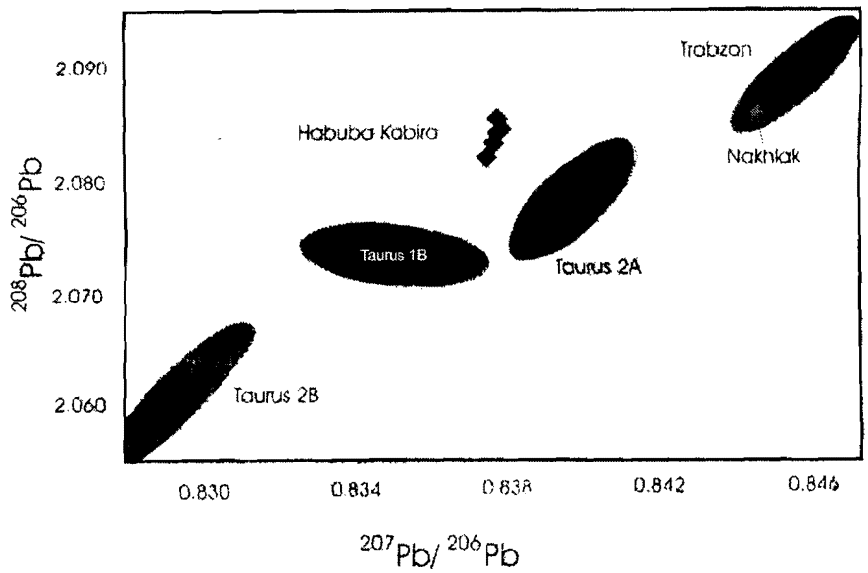

Fig 1: Isotopic comparison between lead silver ores of Anatolia (Wagner et al.1979, Seeliger et al, 1985, Yener et al, 1991) and Nakhlak, and with litharge samples from Habuba Kavira (Pernicka et al. 1992) and the prehistoric mine of Kevam located to the east of Anatolia a.T the contents of the isotopic percentage is totally different and out of the present diagram.

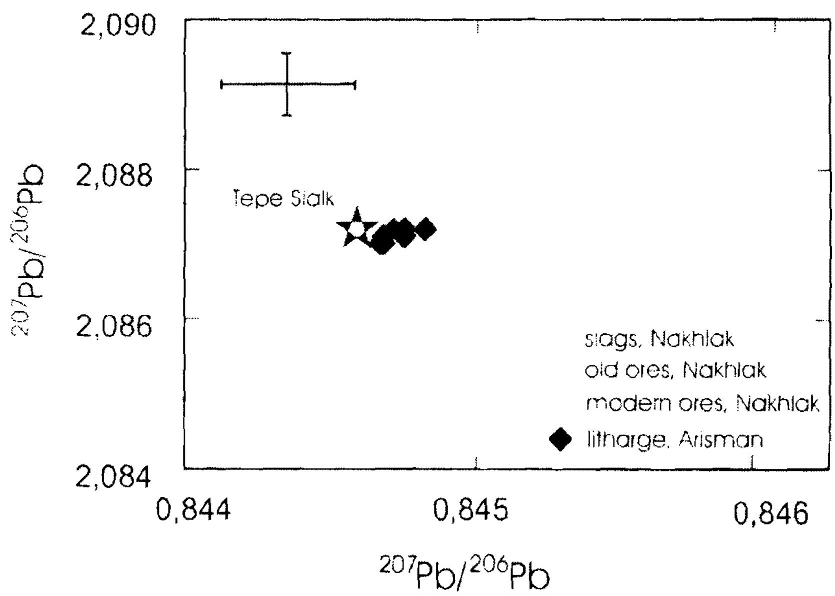

Fig 2: Lead isotope ratios in lead-silver in lead slag and ores from Nakhlak and in litharge samples from Arisman and Tepe Sialk indicated by a star. The "modern ores" derive from deep mining at Nakhlak at a depth of 50 to 200m. The "old ores" are scattered pieces of ore from the surface in the vicinity of old structures and from the ancient mines near the surface. The cross indicates the standard error of two sigma in the Freiberg laboratory. Note that the total variance of the data is only about .1% in this plot.

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