

Analytical Investigations on Silver, Copper and the Earliest Tin Bronzes from Ur

Eveline Salzmann, Sabine Klein and Andreas Hauptmann

A key to understand economic and cultural relationships between Mesopotamia and other Early Bronze Age cultures lies in the analytical investigation of the related archaeological objects having the potential to answer specific archaeological questions. One is the question of the Bronze Age raw material supply of the region in question which may be traceable through the archaeological material. This may lead to conclusions about trading, organization, logistics and economic relationships. The present study is focused on the investigation of metal objects: particularly copper, arsenical copper, copper-tin alloys and silver objects excavated at the cemetery of Early Bronze Age Ur in Mesopotamia. One fifth of our samples were excavated from the so-called “Royal Tombs of Ur”, which provided a large number of finds and an amazing suite of precious metal objects (Woolley, 1934).

The University of Pennsylvania Museum of Archaeology and Anthropology in Philadelphia provided 89 mounted and 20 drilled samples for analytical investigations. The samples comprise 89 copper-based and 20 silver samples. This large amount is statistically relevant and gives a representative picture of the use of these metals in Ur.

Geochemical signatures such as elemental or isotope composition function as fingerprints of the metals which were produced in past times. This fingerprint is used here for the comparison of their geochemical signatures with various metal-rich mineral deposits.

The samples are currently under investigation at the laboratories of the Goethe-University Frankfurt am Main and Deutsches Bergbau-Museum Bochum. Preliminary to the analytical work, a portion of each drilled sample was mounted and polished in our laboratories for microscopy. The already mounted samples were re-polished to remove recent superficial oxidation. The analytical question requires spatial resolving techniques. To ensure representative bulk chemical compositions by point analysis, a statistically relevant number of measurement points was set randomly across the metal surface of the specimens. Characterizing the geochemical fingerprint

involved the determination of the main and trace element composition with wavelength dispersive electron microprobe analysis (EPMA) and single-collector laser ablation mass spectrometry (LA-ICP-MS). Regarding the analysis of copper and lead isotopes, multi-collector laser ablation mass spectrometry (LA-MC-ICP-MS) was used. For quality control of our spatial resolving methods a portion of each of the drilled samples was dissolved in aqua regia or nitric acid to perform homogenized chemical and isotope analysis by solution-based mass spectrometry.

Archaeological metal is not as pure as modern metal. It is therefore crucial to evaluate not only the main elements, but also all accessory (trace) elements of the metal composition. More than the main elements, the trace elements provide important information about the mineral sources exploited for the production of the metals or alloys.

Different potential types of copper and silver mineral deposits have to be taken into account for the discussion of raw material sources:

(1) Native copper and silver, which occur only rarely in nature (Muhly, 1989). (2) Copper sulfide minerals from deposits, which occur along ancient marine margins through volcanic activity. In these hydrothermal deposits, hot fluids containing different metal ions and sulfur permeate marine rocks underground and precipitate in contact with cold sea water (Mahfoud and Beck, 1997). Commonly occurring copper-rich sulfide minerals are chalcopyrite CuFeS_2 and chalcocite Cu_2S (3) Copper-rich oxide, carbonate and siliceous minerals such as malachite $\text{Cu}_2[(\text{OH})_2\text{CO}_3]$, azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ or cuprite Cu_2O are formed by weathering processes and occur in the alteration zones of sulfide deposits. (4) Silver occurs as argentite (Ag_2S) or cerargyrite (AgCl) in nature, but it was also extracted in Early Bronze Age from lead minerals such as galena (PbS) or cerussite (PbCO_3) by cupellation (Helwing 2014, Moorey 1994). Galena forms in various geological settings through

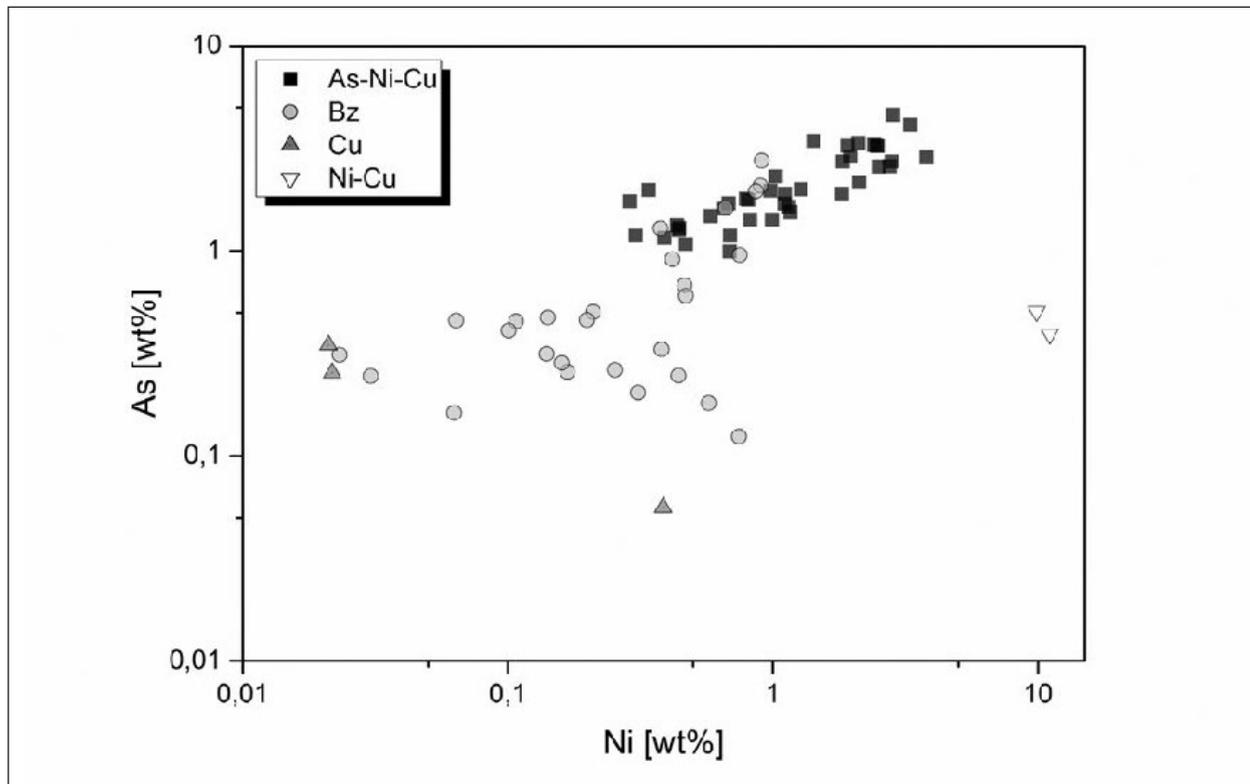


Figure 1. Scatter plot of arsenic and nickel content in the copper-based metals of Ur. We distinguished between copper rich in arsenic and nickel (As-Ni-Cu), tin bronzes (Bz), “pure” copper, and copper rich in nickel (Ni-Cu). Note the positive correlation of copper rich in arsenic and nickel, while tin bronzes are widely dispersed.

magmatic, sedimentary or metamorphic processes and is therefore commonly found. (5) Tin occurs mostly as cassiterite (SnO_2) in placer deposits or primarily near igneous intrusions, mostly granite. Other tin minerals occur in mixed copper-tin hydrothermal deposits where stannite (Cu_2FeSn_4) and corresponding secondary minerals occur.

The analysis of the main elements in the metal samples allows the classification of the copper-based metals by their arsenic, nickel and tin contents. Samples containing more than 2 wt. % tin are commonly defined as tin bronzes (Stech, 1999). The tin bronzes from Ur contain 7 - 12 wt. % tin, which is considered an ideal alloy composition range for cold and hot working and casting due to their physical properties.

A large number of samples contain significant amounts of arsenic (1 - 4 wt. %) (instead of tin) and nickel (0.4 - 4 wt. %) (Figure 1). Both elements show strong correlation to each other, predominantly for the arsenic and nickel-rich copper alloys as well as for few tin bronzes. All samples including the arsenic and nickel-rich copper contain small amounts of tin. Two samples of a dagger (PG 737) contain very high amounts with bulk concentrations of nickel around 10 wt. %. Small amounts of antimony, cobalt, lead, iron and sulfur are associated

with the arsenic-nickel copper. Whereas the tin bronzes low in arsenic and nickel are relatively poor in trace elements. High arsenic combined with high nickel occurs in ultramafic rocks as it is found in ophiolite belts. Ophiolites are uplifted oceanic crust (ultramafic rocks) that has been emplaced onto continental crust (Moghadam, et al., 2012).

Our silver samples are characterized by high copper contents from 0.1 to 7 wt. % followed by lead contents of 0.1 to 1.5 wt. %. The gold levels are below 1000 ppm except one silver bracelet containing 5000 ppm gold. The concentration of other elements (Sb, As, Cr, Pt, Sn, Pd, Ni, Co, Fe, Mn < 100-500 ppm) is low. Copper shows correlations with lead, arsenic and nickel. The silver was most probably produced from a cupellation process of argentiferous lead minerals mixed with fahlore (Pernicka and Bachmann, 1983).

The sulfur content of 0.01 to 1 wt. % as well as the non-ferrous metals in the copper-based artifacts already indicated a hydrothermal sulfide deposit as a potential source for the collection of copper-based metals from Ur. This fact is strengthened by the identified copper isotope signature given as $\delta^{65}\text{Cu}$. Copper isotope ratios have the potential to differentiate between various types of mineral deposits from which the artifacts derive. $\delta^{65}\text{Cu}$

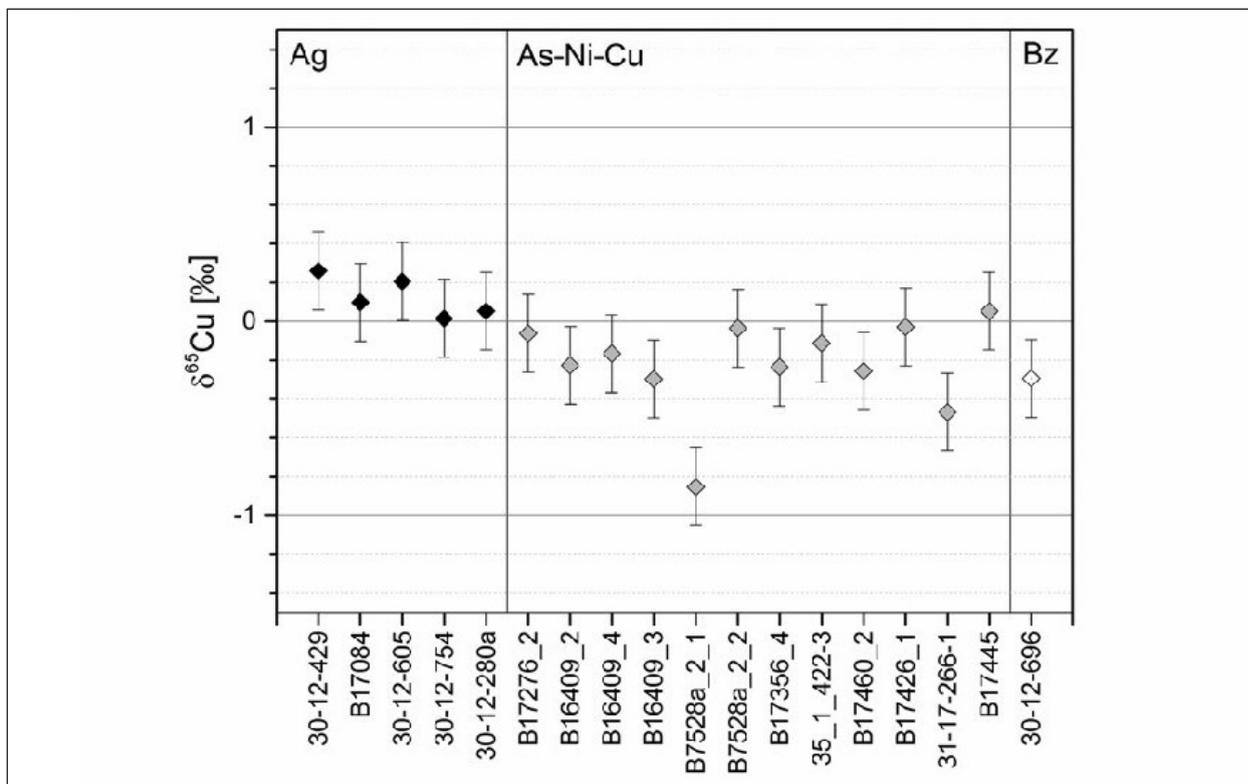


Figure 2. Results of copper isotope measurements with femtosecond-laserablation mass spectrometry. Data are mass bias corrected with Ni spike. All artifacts (silver – Ag, arsenic nickel copper – As-Ni-Cu, tin bronze – Bz) show typical copper isotope ratios for a primary sulphide deposit. Sample B17528a_2_1 was tested on a corroded surface and shows alteration of $\delta^{65}\text{Cu}$ by corrosion.

values fluctuating around zero represent primary sulfide minerals as crystallized during a hydrothermal event. Negative $\delta^{65}\text{Cu}$ values show the relics of altered supergene sulfide minerals and positive $\delta^{65}\text{Cu}$ values indicate secondarily oxidized minerals, which occur in alteration zones (Markl, Lahaye and Schwinn, 2006). As the samples from Ur have $\delta^{65}\text{Cu}$ values around zero (Figure 2), the metal most probably originates from a primary hydrothermal sulfide mineral deposit.

The silver samples show $\delta^{65}\text{Cu}$ ratios close to those of the copper artifacts, but with a tendency to slightly positive values. This indicates secondary oxide mineral deposit as a source. Combined with the results of their chemical analysis the argument for silver metal produced from argentiferous lead ores of a Pb-Ag-Zn-Cu-mineralization is strengthened.

To summarize the preliminary thoughts on the provenance of the copper and silver metal, it must be stated that there are no metal deposits in the vicinity of lower Mesopotamia and Ur. It is thus obvious that the metal had to be imported from elsewhere (Zettler and Horne, 1998). Based on the analysis of the material so far, there is evidence for a hydrothermal arsenic and nickel bearing copper source, and, due to the geographic situation, an ophiolite belt has to be considered as a potential candi-

date. Second a more pure copper source (likely an oxide mineral deposit, due to the chemical purity of the bronzes) and is probably associated with a tin mineralization due to the association of tin and this type of copper. And third, a Pb-Ag-Zn-Cu-type deposit may be the origin for the investigated silver artifacts.

The *Tethyan Eurasian Metallogenic Belt (TEMB)* runs from Cyprus and Taurus Mountains across the Zagros Mountains to Oman bearing ophiolitic rocks and polymetallic ore deposits (Jankovič, 1997). There is archaeological evidence for large-scale copper production in Oman in the 3rd and 2nd millennium BC (estimated 2000 – 4000 tons) (Hauptmann, 1987). It is known by cuneiform texts that the land of copper *Magan* traded copper to southern Mesopotamia (Weisgerber, 2007). It has been well established that Oman is the ancient *Magan* (Prange, et al., 1999). The Omani copper shows similar arsenic and nickel contents, both up to 4 wt. %.

Begemann, et al. (2010) measured and compared lead isotope data from Oman with Mesopotamian artifacts (including Ur, Figure 3). They found that a number of artifacts they measured match the copper ores from Oman. Despite to the evidence of large-scale copper production in Oman, the geographic situation and the cuneiform texts deliver strong arguments for a copper

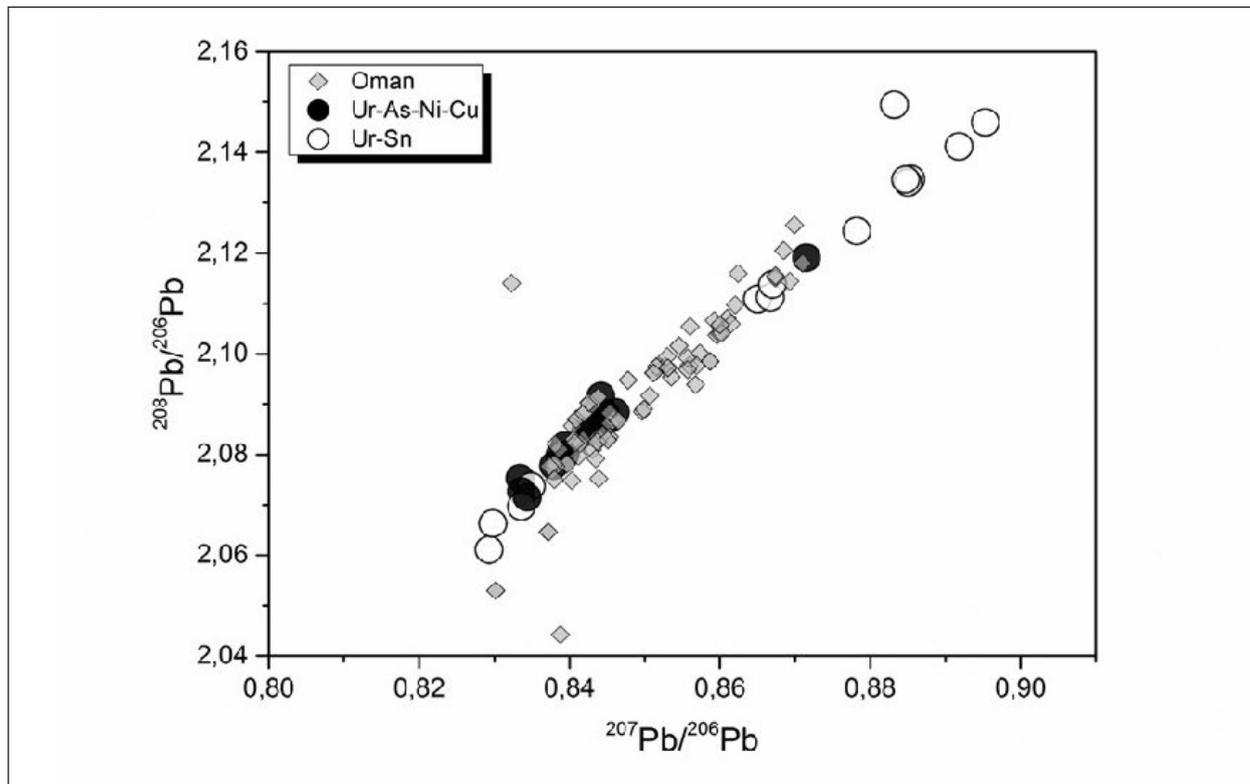


Figure 3. Lead isotope ratios $^{207}\text{Pb} / ^{206}\text{Pb}$ and $^{208}\text{Pb} / ^{206}\text{Pb}$ of arsenical nickel copper and tin bronzes of Ur measured by Begemann and Schmitt-Strecker in comparison with data from Oman (Begemann and Schmitt-Strecker, 2009; Begemann, et al., 2010).

trade from *Magan* / Oman to Mesopotamia (Begemann and Schmitt-Strecker, 2009), the lead isotope signature of Oman overlap with the Anarak region in the Iranian Plateau, where a Cu-As-Ni mineralization occurs, as well (Bagheri, Moore and Alderton, 2007). As a result, Oman is not the exclusive candidate, and Iran and others within the TEMB also have to be taken into consideration as potential suppliers for Ur.

The present results already point to the geological setting, in which the source regions for copper and silver from Ur are located. To identify the true metal sources of the Ur objects, further lead isotope analyses will be performed in future studies. Our results shall contribute to a refined understanding of structures, logistic, economy and policies of trade and exchange in the Early Bronze Age Middle East.

References

- Bagheri, H., Moore, F., and Alderton, D., 2007. Cu-Ni-Co-As (U) mineralization in the Anarak area of central Iran. *Journal of Asian Earth Sciences*, 29(5-6), pp.651-665.
- Begemann, F., and Schmitt-Strecker, S., 2009. Über das frühe Kupfer Mesopotamiens. *Extrait d'Iranica Antiqua*, 44, pp.1-45.
- Begemann, F., Hauptmann, A., Schmitt-Strecker, S., and Weisgerber, G., 2010. Lead Isotope and chemical signature of copper from Oman and its occurrence in Mesopotamia and sites on the Arabian Gulf Coast. *Arabian Archaeology and Epigraphy*, 21, pp.145-179.
- Hauptmann, A., 1987. Kupfer und Bronzen der Südostarabischen Halbinsel. *Der Anschnitt*, 39, pp.209-218.
- Helwing, B., 2014. Silver in the early societies of Greater Mesopotamia. In: H. Meller, R. Risch, and E. Pernicka, eds. 2014. *Metalle der Macht – Frühes Gold und Silber*. 6. *Mitteldeutscher Archäologentag. Internationale Tagung*. Halle: Sachsen-Anhalt Landesmuseum für Vorgeschichte. pp.411-421.
- Janković, S., 1997. The Carpatho-Balkanides and adjacent area: a sector of the Tethyan Eurasian metallogenic belt. *Mineralium Deposita*, 32(5), pp.426-433.
- Mahfoud, R. F., and Beck, J. N., 1997. Copper mineralizations in the ophiolite of Oman: The genesis and emplacement relationship with the orogenic movements of serpentized peridotite. *International Geology Review*, 39, pp.252-286.
- Markl, G., Lahaye, Y., and Schwinn, G., 2006. Copper isotopes as monitors of redox processes in hydrothermal mineralization. *Geochimica et Cosmochimica Acta*, 70(16), pp.4215-4228.
- Moghadam, H. S., Stern, R. J., Kimura, J.-I., Hirahara, Y., Senda, R., and Miyazaki, T., 2012. Hf-Nd isotope constraints on the origin of Dehshir Ophiolite, Central Iran. *Island Arc*, 21(3), pp.202-214.

- Moorey, P. R. S., 1994. *Ancient Mesopotamian Materials and Industries. The Archaeological Evidence*. Oxford: Clarendon.
- Muhly, J. D., 1989. Çayönü Tepesi and the Beginnings of Metallurgy in the Ancient World. In: A. Hauptmann, E. Pernicka and G. A. Wagner (eds.), *Archäometallurgie der Alten Welt. Beiträge zum Internationalen Symposium „Old World Archaeometallurgy“ Heidelberg 1987. Der Anschnitt, Beiheft, 7*. Bochum: Deutsches Bergbau-Museum. pp.1-11.
- Pernicka, E., and Bachmann, H. -G., 1983. Archäometallurgische Untersuchungen zur antiken Silbergewinnung in Laurion. Das Verhalten einiger Spurenelemente beim Abtreiben des Bleis. *Erzmetall*, 36(1983), pp.592–597.
- Prange, M. K., Götze, H. -J., Hauptmann, A., and Weisgerber, G., 1999. Is Oman the Ancient Magan? Analytical Studies of Copper from Oman. In: S. M. M. Young, A. M. Pollard, P. Budd and R. A. Ixer, eds. 1999. *Metals in Antiquity. BAR International Series, 792*. Oxford: Archaeopress. pp.187-192.
- Stech, T., 1999. Aspects of Early Metallurgy in Mesopotamia and Anatolia. In: V. C. Pigott (ed.), *The Archaeometallurgy of the Asian Old World. University Museum Monograph, 89*. Philadelphia: University Museum, University of Pennsylvania. pp.59-71.
- Weisgerber, G., 2007. Copper from Magan for Mesopotamian Cities. In: S. Cleuziou and M. Tosi, ed. 2007. *In the Shadow of the Ancestors: The Prehistoric Foundations of the Early Arabian Civilization in Oman*. Muscat: Ministry of Heritage & Culture, Sultanate of Oman. pp.195-196.
- Woolley, C. L., 1934. *Ur Excavations, Volume 2: The Royal Cemetery. A Report on the Predynastic and Sargonid Graves Excavated between 1926 and 1931*. London / Philadelphia: British Museum / Museum of the University of Pennsylvania. [online] available at <<http://www.etana.org/sites/default/files/coretexts/20263.pdf>> [Accessed 15 March 2016].
- Zettler, R., and Horne, L., 1998. *Treasures from the Royal Tombs of Ur*. Philadelphia: University of Pennsylvania Museum of Archaeology and Anthropology.