

# Electron Microprobe Investigations on the Copper Seal From Burial 10

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During the second campaign of excavations carried out in 1985 by a German-Italian expedition to Iraq at Tell Karrana 3 (north of Mosul), a strongly corroded metal seal was found in a tomb (Burial 10, cf. D. Stein in this volume). The seal was not allowed to be exported from Iraq. However, several very small particles less than 0.25 mm in size, which were removed from the corroded rim of the seal during restoration in the Mosul laboratory of the Iraqi State Organization of Antiquities, could be used for further investigations. As electron microprobes are suitable instruments for quantitative chemical analysis of microvolumes down to  $1\text{--}2\text{ }\mu\text{m}^3$ , a CAMECA SX50 microprobe was used for detailed work on the particles from the seal.

From art historical arguments, the seal can be dated into the so-called Jemdet-Nasr-Period around 2800 years B.C., a period attributed to the Early Bronze Age (Wilhelm, pers. com.). Therefore, it was of main interest to know if the seal was still produced from more or less pure copper, or if an alloy (i.e. bronze) was already used. Furthermore, the composition of different chemical compounds newly formed by corrosive alteration was analyzed. On 15 particles, the qualitative element composition was checked by a number of wave-length-dispersive scans. The content of the detected elements was determined by about 100 quantitative analysis.

## CHEMICAL COMPOSITION OF THE SEAL-METAL

The material used for the seal is certainly not classic Sn-bronze or As-copper, because the Sn-contents constantly scatter around the analytical detection limit of about 0.01 wt. % and neither Sn nor As could be identified by wavelength-dispersive scans. Those particles which were not obviously affected by intensive corrosion mainly consist of more or less pure Cu, which, however, oxidized to a different degree by secondary influence from the soil. Thus, varying Cu-contents between 86 and 97 wt. % have been found (for quantitatively oxidized Cu forming CuO or Cu<sub>2</sub>O, the Cu-concentration makes 79.9 and 88.8 wt. %, respectively). It cannot be completely excluded that the more or less pure Cu-particles are secondary products formed during corrosion processes from primary metal, but also in this

case some amount of As or Sn should have been detected if the primary metal was an alloy.

Apart Cu, several particles contain additional Pb in highly variable proportions, ranging from Cu-pronounced parts with about 86 wt. % Cu and 2 wt. % Pb to extremely Pb-dominated parts with up to 78 wt. % Pb and Cu-contents below 1 wt. %. This Pb-content in particles which are not much affected by corrosion points to an original relation of Cu and Pb, indicating either the use of primary ore from a Cu-Pb sulfide ore deposit or an intentional addition of Pb during smelting processes in order to produce a Cu-Pb-alloy.

## ALTERATION OF THE SEAL-METAL BY CORROSION

Most of the particles investigated consist of several secondary chemical compounds, mainly under participation of Cu, Cl and Si, as a result of corrosion processes during the last 4800 years. The interaction of the seal-metal with circulating soil-water in detail led to the formation of 3 different Cu-Cl-compounds and 2 Cu-Si-compounds, each confirmed by a series of analyses:

- A simple Cu-Cl-compound (I) with Cu-contents between 66 and 73 wt. % and Cl-contents between 27 and 34 wt. % is no stoichiometric CuCl (Nantokite), but shows the composition CuCl<sub>0.7-0.9</sub>.
- A further compound (II) consists of around 57 wt. % Cu and 16 wt. % Cl. The missing 27 wt. % can easily be explained with additional content of OH and/or H<sub>2</sub>O. A high amount of Cu-Cl-compounds with quite different proportions of additional OH and H<sub>2</sub>O is wellknown. The compound described here is approximately composed of Cu<sub>2</sub>(OH)<sub>3</sub>Cl (Atacamite-series).
- A third compound (III) with around 34 wt. % Cu and 16 wt. % Cl contains about 50 wt. % additional OH and H<sub>2</sub>O.
- Two different Cu-Si-compounds consist of around 27 wt. % Cu and 18 wt. % Si or around 37 wt. % Cu and 21 wt. % Si, respectively. The missing part to get 100 wt. % again can be

explained with additional OH and/or H<sub>2</sub>O in variable proportions.

Apart from the described compounds, Cu is combined with Cl as well as Si ( $\pm$  OH, H<sub>2</sub>O) in some cases. Particles containing Cu and Pb as primary metal may also be corrosively altered to Cu-Pb-Cl-(and/or)-Si-OH-H<sub>2</sub>O-compounds, however, with high compositional variability. Additional Fe up to 3 wt.% and Al up to 2 wt.% have been detected for a few analysis points.

## CONCLUSIONS

Although the seal is dated into the Jemdet-Nasr-Period (around 2800 years B.C.) which can be attributed to the Early Bronze Age, it was made from more or less pure Cu instead of Sn- or As-bronze. This matches first results of running investigations on a large amount of early metallic objects from Mesopotamia (Lutz et al. 1992; Lutz, pers. com.), showing that more or less pure Cu is the material which was commonly in use up to the beginning of ED III around 2600 years B.C., when it has been largely replaced by Cu-Sn-alloys.

On the other hand, Cu-based alloys, especially As-copper, are known even from the fourth millennium (Müller-Karpe 1991). As-bronze is considered typical for early metallic art objects of Mesopotamia around the Jemdet-Nasr-Period (e.g. with a composition of 88.8 wt.% Cu, 7.4 wt.% As and 3.6 wt.% Ni for a Mesopotamian seal which is dated into the Jemdet-Nasr-Period too; see Moortgat-Correns 1985). Müller-Karpe (1990, 1991) describes the use of As-copper in Mesopotamia between the Uruk-Period and ED III. As-coppers are also known from the prehistoric metalwork of Anatolia (De Jesus 1980).

Variable Pb impurities in the Cu may be explained in two different ways (if an unintentional contamination of Cu by Pb during smelting processes is excluded):

1. The people who produced the seal intentionally added a certain amount of Pb for the production of an alloy of Cu and Pb. The so-called Pb-bronze with or without additional Sn-contents is a well-known material for special applications in modern technology (e.g. Schumann 1974), but was already in use during the Bronze Age when it was discovered that Pb facilitates the casting of Cu-melts and that valuable Cu may be diluted with Pb (Tylecote 1966).

In Mesopotamia, "Cu-Pb-alloys occur in Susa rather frequently in the fourth and third millennia (Malfoy & Menu, 1987)" (Müller-Karpe 1991). A lion figurine of the Late Uruk-Period or the Jemdet-Nasr-Period from Uruk and a pin of

the Late Uruk-Period from Susa, consisting of Cu with 9 and 14.3 wt.% Pb, respectively, are mentioned in the same paper. In general, Pb-contents of sometimes more than 7 wt.% seem to be typical for a lot of Mesopotamian metal objects (Lutz, pers. com.).

First sporadic use of Pb in combination with Cu is also known from the Egyptian Pre-Dynastic Period, but it became somewhat more common during the time of the 3. and 4. Dynasty (2800 - 2300 B.C.). During the Late Bronze Age around 1000 years B.C., Sn-bronze with Pb-contents between 2 and 15 wt.% was in use in Mesopotamia, Iran, Turkmenistan and China (Tylecote 1966).

Almost 500 Cu-based metallic art objects of the Late Chalcolithic as well as EB I, EB II and EB III periods of Anatolia have been compiled by De Jesus (1980), including information on their qualitative chemical composition. The metal types commonly used here are pure Cu, Cu-Sn-bronze with Sn-contents usually between 1 and 10 wt.%, Cu-As-bronze with As- contents usually between 1 and 5 wt.%, and, to a certain extent, Cu-As-Sn ternary alloys. Pb occurs as a common trace element. For 35 of these objects, Pb is constituent of the major element composition, forming Cu-Sn-Pb, Cu-As-Pb, or sometimes Cu-Sn-As-Pb alloys. In only two cases, however, Pb is combined with pure Cu. This demonstrates that simple Pb-coppers were not really in use for prehistoric metalwork in Anatolia.

2. The Pb impurities point to the use of primary ore from a Cu  $\pm$  Pb sulfide deposit. As attempts to find evidence for a definite source deposit by chemical comparison are accompanied by different uncertainties, a discussion about the source of the ore is more or less speculative:

In Mesopotamia itself, no important ore deposits are known which could be used for Cu supply, except some smaller Pb and Cu deposits in the Mountains north of Mosul described by Layard (1849, cit. in Müller-Karpe 1991). It is questionable whether these deposits have been exploited during prehistoric times. Thus, import of smelted Cu or Cu ore was necessary. It seems reasonable to suppose an origin of the Cu from ore deposits of East-Anatolia, especially the stratiform sulfide deposit of Ergani Maden in the upper reaches of the Tigris. This deposit contains Cu-rich pyrite-chalcopryrite-bornite ores with a certain proportion of galena (Pb-sulfide) and sphalerite (Zn-sulfide) (Wolf 1981; De Jesus 1980). Ergani Maden, still today one of the largest Cu deposits of Anatolia, seems to be a very old Cu-mine and is assumed to have been exploited also during prehistoric times, although there is no direct evidence. Beside East-Anatolian deposits, Iran and also the region of the Arabian Gulf and Oman must be taken into account for supporting Mesopotamia with Cu (De Jesus 1980; Müller-Karpe 1991). The sulfidic Cu deposit of Chale Ghar in West-Central Iran, for example, was exploited during the time of the Jemdet-Nasr-Period in Mesopotamia, as dated by ceramics from the mine (Holzer et al. 1971, cit. in De Jesus 1980). "T. Berthoud

(1979) maintained that metal used for objects in the early third millennium from the Hamrin Basin (southeast of Mosul, the author) was from the Iranian Plateau (Anarak area)" (Müller-Karpe 1991). Especially "Southern Mesopotamia could have drawn technology as well as copper from sources linked to cultures in the Arabian Gulf", because "trade and cultural links between these two areas were stronger than was once thought" (De Jesus 1980). In this context, Oman should be mentioned as a possible source, because prehistoric Cu-mining is well-known from that area (Hauptmann 1985), which maintained trade relations with Mesopotamia during the 3rd millennium (Wilhelm, pers. com.). Chemical investigations also point to Oman as a source for part of the Cu which was used in Mesopotamia (several authors, cit. in Müller-Karpe 1991).<sup>1</sup>

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**Cu-contents of pure Cu-grains:**

wt. %	grain 2	grain 2	grain 2	grain 2	grain 2	grain 2	grain 2	grain 2
Cu	87.6	73.6	65.9	88.7	90.1	93.2	87.6	86.2
wt. %	grain 2	grain 2	grain 2	grain 2	grain 2	grain 2	grain 2	grain 2
Cu	87.7	86.7	96.1	95.7	95.8	95.9	87.8	87.1
wt. %	grain 4	grain 4	grain 4	grain 4	grain 4	grain 5	grain 5	grain 5
Cu	90.1	89.8	90.6	88.5	95.7	88.0	88.7	87.8
wt. %	grain 9	grain 9	grain 11	grain 13	grain 13	grain 13	grain 13	grain 15
Cu	87.9	96.1	87.4	77.5	75.6	86.1	86.6	88.0
wt. %	grain 15	grain 15	grain 15	grain 15				
Cu	89.3	91.4	90.1	97.0				

**Compositional range of Cu-Pb combinations:**

wt. %	grain 5	grain 5	grain 5	grain 5	grain 5	grain 13
Cu	78.9	86.1	0.2	0.4	0.4	71.1
Pb	9.5	2.2	77.7	68.9	78.0	2.0
total	88.4	88.3	77.9	69.3	78.4	73.1

**Cu-Cl-compound I:**

wt. %	grain 4	grain 4	grain 4	grain 4	grain 4	grain 4	grain 9	grain 9
Cu	69.8	75.6	69.4	65.7	70.3	70.6	65.9	66.6
Cl	30.4	29.5	32.1	29.7	30.0	27.9	33.6	32.9
total	100.2	105.1	101.5	95.4	100.3	98.5	99.5	99.5
wt. %	grain 9	grain 15	grain 15	grain 15	grain 15	grain 15	grain 15	grain 15
Cu	69.1	70.3	71.4	68.9	72.2	73.5	72.1	68.6
Cl	30.0	30.9	31.7	33.5	32.7	30.3	32.3	32.8
total	99.1	101.2	103.1	102.4	104.9	103.8	104.4	101.4

**Cu-Cl-compound II:**

wt. %	grain 8	grain 8	grain 8	grain 8	grain 8	grain 9	grain 9	grain 9
Cu	57.0	56.5	56.7	57.1	56.9	58.1	58.3	57.1
Cl	16.1	16.2	16.0	15.9	16.2	16.1	15.8	16.0
total	73.1	72.7	72.7	73.0	73.1	74.2	74.1	73.1
wt. %	grain 11	grain 11	grain 11	grain 11				
Cu	56.9	57.6	57.3	58.9				
Cl	16.0	15.9	16.0	15.5				
total	72.9	73.5	73.3	74.4				

**Cu-Cl-compound III:**

wt. %	grain 1	grain 1	grain 1	grain 1	grain 1	grain 1	grain 1	grain 1
Cu	32.1	32.4	32.2	32.1	35.4	35.8	33.9	34.8
Cl	15.9	15.6	16.0	16.0	15.9	16.0	15.4	16.3
total	48.0	48.0	48.2	48.1	51.3	51.8	49.3	51.1

Quantitative electron microprobe analysis  
of different spots on different grains from the seal.

wt.%	grain 1	grain 15	grain 15	grain 15	grain 15	grain 15	grain 15
Cu	34.8	33.2	34.8	35.2	36.1	32.2	35.2
Cl	15.5	15.8	15.9	15.6	15.8	15.8	15.8
total	50.3	49.0	50.7	50.8	51.9	48.0	51.0

**Cu-Si-compound I:**

wt.%	grain 3	grain 3	grain 3	grain 3	grain 7	grain 14	grain 14	grain 14
Cu	27.2	25.6	29.6	27.3	27.7	27.2	28.7	30.5
Si	19.1	17.5	18.0	18.8	15.7	18.3	18.2	15.9
total	46.3	43.1	47.6	46.1	43.4	45.5	46.9	46.4

**Cu-Si-compound II:**

wt.%	grain 7	grain 7	grain 7	grain 7	grain 7
Cu	42.8	31.3	37.0	36.5	38.1
Si	22.8	19.4	20.1	19.7	21.1
total	65.6	50.7	57.1	56.2	59.2

**Cu-Si-Cl-compounds:**

wt.%	grain 11	grain 11	grain 11
Cu	21.4	31.2	30.8
Si	19.1	11.5	12.2
Cl	0.2	9.1	8.2
total	40.7	51.8	51.2

**Cu-Pb-Si-Cl-compounds:**

wt.%	grain 6	grain 6	grain 6	grain 12	grain 12	grain 12	grain 12	grain 12
Cu	6.4	11.4	8.6	18.5	29.7	37.9	39.3	36.9
Pb	66.8	55.8	61.8	42.6	16.7	11.0	12.1	19.1
Si	1.8	5.1	2.5	6.6	9.5	10.1	11.3	13.5
Cl	0.2			1.8	0.6	0.3	0.5	0.6
total	75.2	72.3	72.9	69.5	56.5	59.3	63.2	70.1

wt.%	grain 13	grain 13	grain 13	grain 13
Cu	53.3	54.7	48.3	35.3
Pb	1.1	2.0	6.3	24.5
Si	12.2	13.2	0.9	0.9
Cl	0.2	1.1	7.9	11.2
total	66.8	71.0	63.4	71.9

wt.%	grain 6	grain 6	grain 6	grain 6
Cu	10.3	19.7	21.3	21.6
Pb	21.4	17.1	11.8	4.8
Si	7.9	3.8	2.3	19.0
Cl	9.7	14.6	15.1	0.1
Fe	2.9	2.2	1.7	1.8
Al	1.4	0.3	0.2	1.9
total	53.60	57.73	52.40	49.20

Quantitative electron microprobe analysis  
of different spots on different grains from the seal.