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METALS AND SLAGGED RESIDUES FROM TEGEA: AN ANALYSIS AND METALLURGICAL NOTES

Introduction

This short report deals with analytical studies on 14 samples (12 metallic and two of slagged nature), from the excavation conducted at Tegea by the Norwegian Institute at Athens from 1990 to 1994. The main targets of the analytical work were to determine, both qualitatively and quantitatively, the metallic components of the corresponding objects, to assess the degree of corrosion, and to examine whether the two samples initially characterized as slag were technologically related to the metallic finds. After preliminary cleaning the samples were brought to the "Demokritos" Laboratory of Archaeometry in Athens. There the following processes were carried out:

1 – macroscopical observation and documentation under the stereomicroscope;

2 – preparation of polished sections;

3 – microscopical observations under the optical polarizing microscope;

4 – study of microphases under a scanning electronic microscope (SEM), Philips, model 515;

5 – chemical analyses (bulk) and microanalyses of particular phases with a micronanalytical system EDAX 9000 adapted to the SEM;

6 – microphotography with the SEM.

The chemical analyses are based on elements (as far as metals are analysed), unless a different method, such as oxide analysis, is indicated.

The total margin of error is less than 10% for the principal elements (or those which are present in quantities of more than 1%) and less than 20% for the secondary elements (or those present in quantities from 0.1–1%).

The laboratory work was carried out by the author, with the assistance of Ms Vasiliki Tsipopoulou, an advanced student from the section of archaeological conservation (TEI).

Samples from the temple sector

Mspl 1 (F. no. F1/3-2).

Bronze sheet, consisting of two corroded internal layers, covered on both sides by products of weathering.

Elements:	
Si	0.4
S	0.5
Cl	0.3
K	0.1
Sn	9.5
Ca	0.2
Fe	0.6
Cu	87.6
As	0.7
Total	99.9%

This is most probably an alloy of copper, with a moderate to low content of tin and a small content of arsenic, probably because of recycling.

Within the fabric of the sheet, globular concentrations of a different material with a stronger metallic shine and slightly lower content of tin were observed.

The external and internal corroded areas consist mostly of green copper oxides and siliceous aggregates, and there is very little tin present.

One of the external, dark-coloured surfaces most likely contains, in addition to products of corrosion (such as malachite), some metallurgical remains as well, since it includes sulphur and iron in addition to copper. These are probably remains of the metal sulphides which the ore once contained.

The analysis of this composite phase follows below:

Elements:	
Si	0.7
P	0.6
S	9.8
Cl	2.5
Fe	2.4
Cu	83.2
As	0.7
Total	99.9%

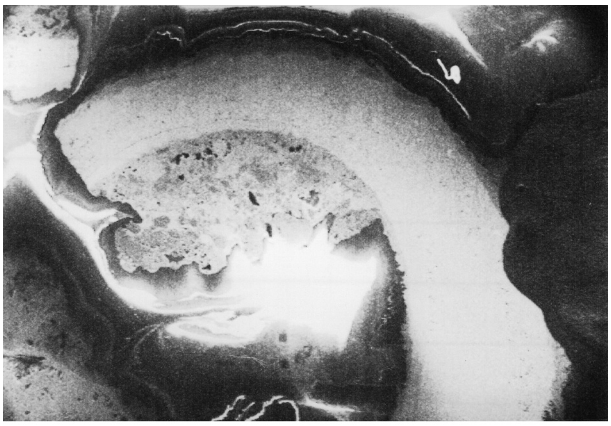

Figure 1. Surface of the sample **Mspl 1.** (Photo: Bassiakos)

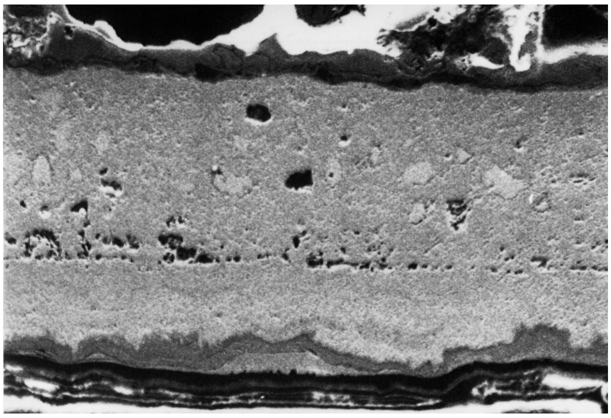

Figure 2. Surface of the sample **Mspl 1**. (Photo: Bassiakos)

In a different part of the same area there is a higher content of iron. In this sector the siliceous aggregates are not present.

On the outside of the transformed area the expected corroded area is present.

The surface, where it has not been created by corrosion, also has an external accumulation which can be observed in certain places and consists only of a combination of copper and chlorine phases. (See *Figs 1–2)*

Analysis of the ring-shaped composite:

Elements:

Si	0.1
P	< 0.1
S	< 0.1
Cl	0.4
K	< 0.1
Sn	4.6
Ca	0.1
Fe	0,7
Cu	88.9
Pb	4.8
Total	99.6%

This is a peculiar alloy of copper, lead and tin. However, such a composition is not uncommon, since the addition of lead in Cu-Sn alloys makes the bronze easier to cast. The corroded surface contains copper and silicium oxides, as analyzed below.

Elements:

Al	5.5
Si	39.5
P	0.3
S	0.2
Cl	0.9
K	0.9
Sn	0.5
Ca	0.4
Ti	0.3
Mn	0.2
Fe	2.2
Cu	46.5
As	0.3
Pb	2.1
Total	99.8%

Mspl 2 (F. no. E1S/5-1).

Observations from the optical microscope:

Completely oxidized alloy of copper and tin, where an extensive, layer-like area has been preserved; it probably corresponds to the metallic sheet which has been transformed into malachite. On both sides of this sheet other copper oxides spread out; malachite of darker colour dominates, and iron is probably present.

Study under the SEM:

Elements:

Al	4.4
Si	28.0
P	1.3
S	1.6
Cl	0.2
K	1.0
Sn	13.8
Ca	2.9
Ti	0.3
Mn	0.1
Fe	2.3
Cu	44.0
Total	99.9%

This is a completely disintegrated metal object which has not maintained its shape and is totally corroded.

Mspl 3 (F. no. E1S/15-2).

Observations from the optical microscope:

Object of copper or bronze, completely transformed by weathering to fragile cuprite which is in some places covered by a thin layer of malachite and other, green copper oxides. These products coexist to a large extent with clay minerals and iron hydroxides, which enclose the oxidized object.

Optical observations under the SEM:

The compact, earthy substance which encloses the oxidized archaeological copper object consists of silicium dioxide, calcium and iron; copper is also present in the oxidation products.

Elements:

Al	8.0
Si	38.3
P	0.9
S	1.5
Cl	1.1
K	2.0
Sn	3.7
Ca	5.3
Ti	1.0
Mn	0.1
Fe	14.0
Cu	24.0
Total	99.9%

Mspl 4 (F. no. E1S/15-3).

Observations from the optical microscope:

This is a completely oxidized iron object which does not retain any of the original tissue and appearance of the metal, and consists only of iron oxides and hydroxides.

Study under the SEM:

Elements:

Al	6.4
Si	22.0
P	1.7
S	1.4
Cl	0.6
K	1.5
Ca	6.3
Ti	1.1
Fe	56.0
Cu	2.8
Total	99.8%

Part of the detected elements (*e.g.* Al, Si, Cl, Ca, K) derives from the earthy substances which enclosed the objects while they were buried in the soil. This soil did not necessarily contain iron.

The iron oxides have taken the form of hematite, but hydroxides (limonite etc.) are also present; the latter, along with silica and calcium that are also present to a large extent, comprise the natural soldering material surrounding the corroded object.

The presence of copper (2.8%) indicates that archaeological objects of copper or copper alloys (such as bronze) were in contact with this object while it was buried.

Mspl 5 (cat. no. **Br-Mi 4**; Tex no. 718, F. no. E1S/67-1).

Analysis in area A: Elements:		Analysis in area B: Elements:	
Si	0.4	Si	0.3
Sn	22.2	Sn	20.5
S	0.5	S	0.4
Cl	0.9	Cl	0.5
Fe	0.2	Fe	0.2
Cu	75.2	Cu	77.3
As	0.7	As	0.8
Total	100.1%	Total	100.0%

This material is a fairly compact bronze (alloy of copper and tin) with a high content of tin, about 20%, and an area of corrosion with a high level of oxides.

In the area where the alloy is intact, diversified, kidney-shaped areas with a lower content of tin appear again, surrounded by bands or nets of slightly darker surfaces which contain more tin. The dark areas contain oxides from copper only (probably after the progressive transformation into malachite), not from tin.

Samples from the northern sector

MsplN 1 (from D6/08).

Elements:

Si	0.4
Sn	7.4
Fe	0.2
Cu	91.4
As	0.5
Total	99.9%

This is a bronze alloy, probably recycled. It has a rather low content of tin and evident traces of corrosion because it was buried in the earth, and cavities created by the disintegration where secondary materials, probably malachite, have developed from the bronze.

Morphologically, there is a difference between the appearance of the alloy in some dominating areas with a strong metallic shine, and in less shiny areas where the oxides are also visible.

In the very shiny areas there is also a visible alternation between shiny, irregular areas and a "net" of less shiny threads. The "nets" contain slightly more tin (about 10%) than the irregular areas, which also contain tin.

In the less shiny areas, with oxides, there is hardly any tin at all, an indication that there is mostly copper in the oxides.

A second analysis of the same sample was made at a different, solid spot:

Elements:

Si	0.3
Sn	8.5
Fe	0.2
Cu	91.0
Total	100.0%

MsplN 2 (from D6/08).

Analysis in an area of strong, metallic shine without corrosion (bulk analysis):

Elements:	
Si	0.6
S	0.3
Cl	4.1
Sn	18.5
Fe	0.3
Cu	75.5
As	0.7
Total	100.0%

Analysis of a sample without chlorine (indicative):

Elements:	
Si	0.6
S	0.3
Sn	19.1
Fe	0.3
Cu	78.9
As	0.8
Total	100.0%

Analysis from a corroded, more central area:

Elements:	
Si	0.6
S	0.3
Cl	8.8
Sn	17.3
Fe	0.3
Cu	72.2
As	0.6
Total	100.1%

In the analysis of the external surface, where the green coating (probably malachite) dominates, no presence of chlorine was observed at least internally. This signifies that the chlorine did not come from the soil that surrounded the object, but either it existed in the alloy in the shape of admixtures or impurities containing chlorine located in the less solid areas of the alloy, or it came from atacamite (copper chloride hydroxide) as a corrosion product from older bronze objects melted down for the new object.

The analyzed sample from the corroded area located at the margin of the sane metal consists of green oxides, probably malachite.

Elements:	
Al	0.9
Si	5.2
P	0.5
S	0.2
Cl	< 0.1
K	0.2
Sn	0.2
Ca	0.2
Fe	0.6
Cu	91.7
As	0.3
Total	100.0%

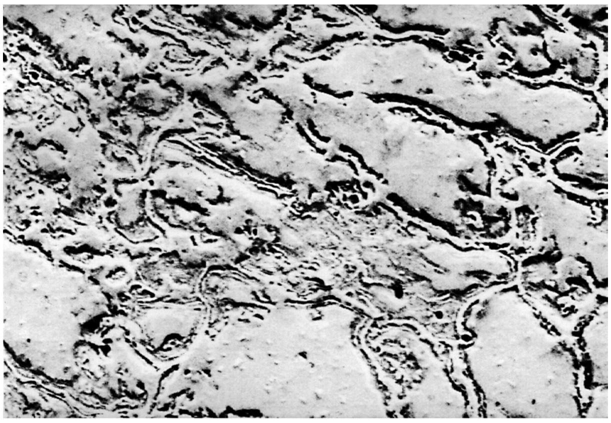

Figure 3. Surface of the sample **MsplN 2**. (Photo: Bassiakos)

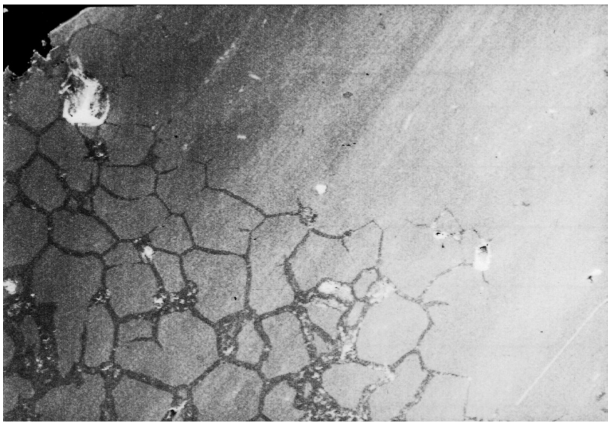

Figure 4. Surface of the sample **MsplN 2**. (Photo: Bassiakos)

The different analyses of dark and light sectors in the corroded area demonstrated the presence of siliceous material, probably quartz or amorphous silica, enclosed in the mass of copper oxide. Inside the object with metallic shine (the light areas) a difference was observed between the kidney-shaped or irregularly shaped areas, and other areas, also those irregular, but with less metallic shine. (See *Figs 3–4)*

The first area consists mostly of copper and only a little tin, in the proportion 10 : 1, while the second contains tin in a proportion of 2 : 1.

MsplN 3 (from D6/08).

Elements:	
Si	0.4
S	0.1
Cl	1.7
Sn	7.8
Fe	0.3
Cu	88.3
Pb	1.4
Total	100.0%

In this sample there is an area with oxides from corrosion consisting mostly of copper and tin in aggregates, and some solid metal with clear traces of corrosion (copper oxides) on one side.

In the solid metal, differentiated bodies/phases or small globes with a higher content of copper and somewhat darker material with more tin appear. (See *Fig. 5*)

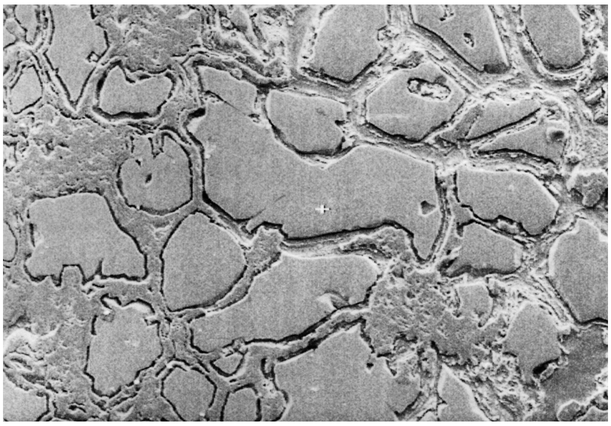

Figure 5. Surface of the sample **MsplN 3**. (Photo: Bassiakos)

MsplN 4 (F. no. C6/43-1).

Elements:

Mg	0.7
Al	15.2
Si	71.1
K	2.0
Ca	1.3
Ti	1.2
Fe	8.3
Total	99.8%

This is probably a piece of dissolved pottery (waster), with a high proportion of siliceous material in grains of quartz and as amorphous matter. The data so far obtained do not indicate any metallurgical relationship between the analysed metal samples and this slag material.

MsplN 5 (F. no. C6/46-8).

Elements:

Mg	3.0
Al	18.2
Si	56.1
K	2.3
Ca	13.1
Ti	0.9
Cr	0.2
Mn	0.2
Fe	6.0
Total	100.0%

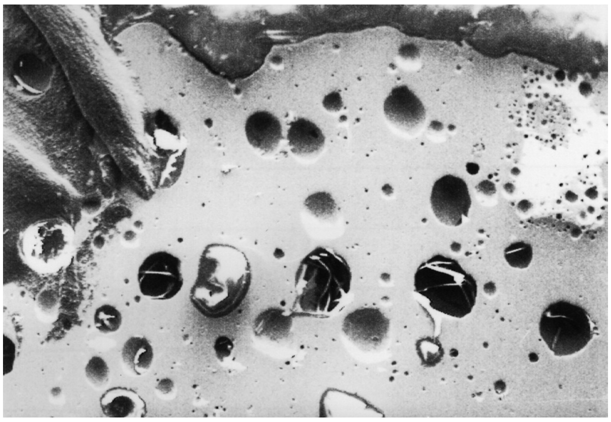

Figure 6. Surface of the sample **MsplN 5**. (Photo: Bassiakos)

This is a pottery waster, created by a temperature above 1250° C. The shape of the pottery has collapsed and created a glassy compound with a spongy and porous look, with black colour.

The presence of this sample indicates that there probably was a pottery workshop nearby with a functioning furnace. (See *Fig. 6*)

MsplN 6 (from C7/80).

Elements:

Si	0.5
S	0.2
Cl	0.2
Sn	10.2
Fe	0.4
Ni	0.1
Cu	87.7
Pb	0.7
Total	100.0%

This is an alloy of copper and tin (bronze) which retains a metallic core; visually it is homogeneous.

MsplN 7 (from C6/107).

Elements:

Mg	0.4
Al	0.6
Si	4.4
K	0.1
Ca	0.4
Ti	0.1
Cr	0.1
Mn	0.4
Fe	93.4
Total	99.9%

This is a piece of oxidized iron with a few internal irregularities which are organized in lines and irregular patterns in a very open distribution.

The object has been oxidized to such depth that metallurgical observations and microphase characterization on a microscopical scale are not possible.

MsplN 8 (F. no. C7/107a-17).

This is an object with an internally compact core of copper, enveloped by a corroded area.

Internally:		In the external parts:	
Elements:		Elements:	
		Cl	0.8
Si	0.3	Si	0.4
S	< 0.1	S	0.1
Sn	0.2	Sn	12.8
Fe	0.1	Fe	0.2
Ni	0.1	Ni	0.2
Cu	98.9	Cu	84.1
Pb	0.5	Pb	0.5
Total	100.1%	Total	99.1%

The covering, corroded area consists of bronze, with an external and an internal zone. It is fairly porous, and has an internal differentiation with lighter and darker zones.

In the different areas there are visible concentrations where there is more tin than copper. They are darker in colour than other, lighter areas where there is far less tin than copper, in a proportion about 1 : 10.

Generally, however, the entire covering is corroded, with areas of oxidized copper (probably malachite).

MsplN 9 (F. no. C7/113-4).

Elements:	
Si	0.3
S	0.1
Sn	8.6
Fe	0.3
Cu	90.6
Total	99.9%

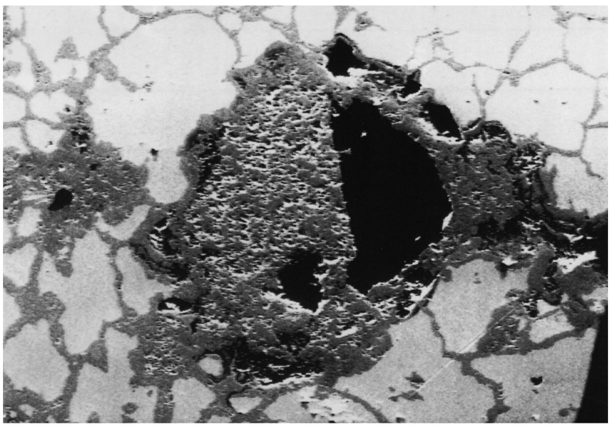

Figure 7. Surface of the sample **MsplN 9**. (Photo: Bassiakos)

This is an alloy of copper and tin with less than 10% tin, and an internal structure consisting of irregular crystals with a relatively lower content of tin, enclosed in a fine net of metallic material with a relatively higher content of tin.

The sample is enveloped by areas of earthy material, but also by oxides of the alloy (weathering products) consisting almost entirely of copper, probably malachite. (See *Fig. 7*)

Concluding remarks

According to the analytical data (microscopic and chemical), the 14 analysed samples, derived both from the temple and the northern sector, can be classified in the following categories: a) ten samples (**Mspl 1–3, 5; MsplN 1–3, 6, 8, 9**) correspond to bronze objects, most of them corroded; b) two samples (**Mspl 4, MsplN 7**) correspond to iron objects, totally corroded; and c) two samples of slag (**MsplN 4–5**) correspond to ceramic wasters.

The two iron samples are totally corroded and do not allow for microscopic observations of their internal tissues. Most of the bronze samples are also corroded. Such an increased degree of corrosion is to be expected for the area of Tegea, where the semi-arid Mediterranean conditions dominate and the metallic objects, buried for millennia in that environment, have been retrieved almost totally corroded and surrounded by weathering products. Here we must recognize the oxidizing role of the element chlorine, which along with oxygen participates in the composite weathering products. However, chlorine might also have pre-existed in any earlier bronze object that may have been recycled, as described for the sample **MsplN 2**.

Lead is present in some bronze samples (**Mspl 1, MsplN 3, 6, 8**), and its content varies from traces to a few percent. This phenomenon is not common, but not rare in the bronzes of the Greek mainland and the Aegean. As already noted, the addition of lead in bronzes during the casting stage increases its ductility, although lead cannot be incorporated in the bronze alloy; it creates minute prills. Thus, in cases where earlier cast bronzes have been used as a "source" of bronze and recycled, the addition of some lead might be justified. The same explanation, the recycling of earlier bronzes, seems valid for the small amounts of arsenic detected in most bronze samples. A few analytical data, derived from the sample **Mspl 1**, could also support the probability of local metallurgical activity; the metallurgical workshop in front of the early cult buildings provides evidence for this in the Late Geometric period.[1] The two almost vitrified ceramic wasters (**MsplN 4–5**) are not connected with any metallurgical activity, but provide fair indications for pottery production in the surrounding area, which has also

[1] See for this discovery the report section **ii** (Nordquist), 157–78.

been supported by recent archaeological discoveries.[2]

In the bronze samples where a metallic core is retained we can note a variation in the tin content; in most core-retaining bronze samples (**Mspl 1, MsplN 1, 3, 6, 9**) the tin content varies from 7.2–10.2%, and such tin content, though somewhat lower than the more common 11–13% for the Greek Cu-Sn bronzes, seems adequate; even with 7% tin the ancient bronze-smith could have manufactured bronzes for particular requirements. However, the addition of tin in the Cu-Sn alloy at levels as high as 18.5–22% in **Mspl 5** and **MsplN 2** represents a needless waste of tin and certainly would have made the produced alloy less easy to work: it would become brittle. Such high percentages of tin in bronze objects could serve only a decorative purpose. In fact, with this alloy the shine of the final product is substantially increased, imitating the colour and the shine of gold! Therefore, before we proceed to any final conclusion regarding this important issue, further analytical work on more samples will be required.

[2] See for this the paper by V. Cracolici, "Pottery from the Norwegian Arcadia Survey: A preliminary report," in Østby (ed.) *Arcadia,* 123–7.