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CONTENTS

Metallurgical Residues from Late Chalcolithic and Early Bronze Age Liman Tepe

Ergun KAPTAN

The archaeometallurgical remains excavated in 1996 in Liman Tepe were studied in two main parts: 1- Pre-smelting processed ore finds; 2- Metallurgical remains.

1- Pre-smelting processed ore finds.

Atacamite, an oxidised copper mineral ($Cu_2Cl(OH)_3$ under the umbrella of pre-smelting processed ore finds. The other obtained three finds are mineral processing tools for ore dressing.

The x-ray determinations, the mineralogical studies and chemical analyses have been carried out on atacamite minerals. A green core is observed in the center of the mineral, then a gray coloured part covers this green core. Finally, again, a green part occupies the most outer part of the minerals. Ore microscopical studies show that the green parts are atacamite minerals while the gray parts are cuprites and limonites. The elements such as 36.5% Cu, 19.3 ppm. Au, 0.43% Pb, 0.02% Zn, 0.05% Ni, 0.24% Sn are determined in chemical analyses. However that elements such as Fe, Ag, Sb, As, Bi can't be detected. We can deduce that atacamite as a secondary mineral of copper, must have been carried from Buca Maden Tepe.

One of the ore dressing tools is a stalk handled ore grinding tool (L: 8cm). The other two materials are used for mineral grinding purposes. Used surfaces are circular shaped and caved in the center so as to grind ore. One of these tools is self stalk handled ore crushing tool (L. 8cm). Another one is a spherical shaped tool, but used surfaces are rather smooth with a grinding cave in its center (L. 7cm).

The ore dressing tools were used for communition purposes such as grinding and crushing. That is, these tools reduce grain size of oxidized copper minerals to an optimum grain size for further metallurgical treatment.

2- Metallurgical remains:

The slags belonging to pre-smelting processed ore finds have been found in five different locations. One of these slags belongs to the Late Chalcolithic Age. The others belong to the Early Bronze Age. The mineralogical - petrographical determinations and optical spectrographical semi-quantitative analyses have been conducted on the slags.

It is observed that ceramic crucible fragments are adhering to the slags. These slags occurred during metallurgical processes of the oxidised copper minerals in a ceramic pot. The required process temperature must be from 300-700^o C. The charcoal was put into the ceramic pot as a reducer to obtain the metallic copper.

Introduction

A number of interesting new archaeometallurgical finds have been discovered at the Liman Tepe excavations in 1996. In addition to the metallurgical slag found at Liman Tepe, important clues to metallurgical processes were recovered in unprocessed ores found at the site. Ores are often not found on slag deposits near metallurgical centers in Anatolia[1]. Slag is generally found in small numbers at excavations on urban sites. However, an exception is Kelenderis, where a great quantity of slag has been found[2].

Liman Tepe is a mound situated on a peninsula located in the Iskele neighbourhood of Izmir-Urla. The east-west highway from Izmir to Cesmealti cuts Liman Tepe in half (Fig. 1). The rocky summit of the peninsula situated in the northern part of the mound, extends to the south to the site of Klazomenai. The excavations at Liman Tepe began in 1980–1981. The excavations which continue through 1992 have been directed by Professor Dr. H. Erkanal.

The finds from Liman Tepe indicate that metallurgical activities play an important role at the site. Previous finds include a great number of moulds dating to the Middle Bronze Age and lead rings dating to the Early Bronze Age. In addition, a baked clay multi-faced mould, slag, copper ores and hammerstones used in ore dressing point to well developed metallurgical activities (Fig. 1). These materials have been

[1] Topkaya 1962.
[2] Kaptan 1994.

classified as pre-processing and metallurgical residues. Finds relating to a pre-processing phase include a copper mineral, atacamite ($Cu_2Cl(OH)_3$), and the ore dressing device while metallurgical residues include slag.

Atacamite ($Cu_2Cl(OH)_3$)

One of the most important finds from the 1996 season include the secondary copper mineral, atacamite. These finds were found in Level V dated to the Early Bronze II period and measure 4.4 x 2.9 x 1.9 cm. One half has been analysed (photo 1). This is the first time atacamite has been found in Anatolia. Geological investigations in Turkey have not found atacamite either.

This mineral is named after the copper mineral found in the Atacama desert in Chili. Atacamite occurs as a result of the alteration of copper sulphide at oxidation zones in deserts[3]. In general this mineral occurs in North and South America, Australia, South Africa and Central Asia. In addition Sardinia's Nurra mines have similar alteration zones[4]. However, in Turkey, it had been thought that natural conditions that would create this mineral do not exist. However, some mineral specialists have suggested that such natural conditions do exist in copper deposits in Turkey. Despite the earlier lack of finds, the 1996 atacamite finds necessitates a more detailed investigation into the natural conditions that created it. Atacamite, or hydro copper chlorine occurs as a result of the alteration of copper sulphide at oxidation zones in deserts[5]. It occurs naturally as a secondary mineral in oxidation zones. One of its important characteristics is that atacamite changes to malachite ($CuCO_2(OH)_2$) and vice versa. This occurs under chlorine conditions in subsurface areas. Archaeometric analyses have noted the formation of atacamite on bronzes and copper when deposited in chlorine rich soils[6]. However the finds from Liman Tepe are not atacamite formed on the surface of bronzes and copper artifacts, but an ore.

Geologists from MTA specializing in mineralogy have noted that it is possible that occurrences of atacamite are possible under certain conditions in copper deposits. For exemple chlorine and fluorine containing ground waters will alter copper veins containing malachite. Chalcopyrite ($CuFeS_2$) which undergoes alteration by iron and sulfiphides. Thus malachite, azurite and atacamite and in some areas, cuprite is formed. In some cases gold inclusions in chalcopyrite get retained in the secondary copper mineral[7].

X-ray diffraction and chemical analyses of polished cross sections have been performed on Liman Tepe finds. Results of the x-ray diffraction indicate that the ore is atacamite ($Cu_2Cl(OH)_3$).

Polished Cross Section Investigations with a Metallurgical Microscope[8]

The sample can be macroscopically defined as dull green in parts and, slightly red-gray with a metallic sheen. The other is slightly reddish gray in color with a metallic lustre. Limonite shows gray under parallel nicole, and yellowish brown, brownish red colors under a polarizing lens having a reflection that covers the whole surface of the mineral. Cuprite is light-bluish gray in color. Characteristics is a bluish gray-olive green anisotropy colors and blood-red internal reflection. Generally, cuprite is replaced by the others, especially atacamite. Atacamite is distinguished by showing reflection pleocroism and by its characteristic internal reflection. Cuprite minerals showing selection structures are observed in atacamite, which are mostly replaced by atacamite. Sometimes replaced cuprite is in acicular form. Under cross-nicole cuprite is observed as back stains in atacamite. Strong internal reflection of atacamite masks cuprite's color. Most probably grains of gold are observed in one or two

3 Gümüş 1974.
4 Mottana et al. 1995.
5 Ďuďa-Rejil 1990; Mottana et al. 1995.
6 Doeringer et al. 1970.

7 Pehlivan 1997.
8 A summary of the metallurgical microscopic analyses is given. The complete report can be found at the MTA Museum report no.44 and the director of the Liman Tepe excavations Professor Dr. Hayat Erkanal. In addition one half of the sample is on display in the MTA Museum Mineralogical department. Photographs taken under the microscope have not been included in this article since they are in color.

localities showing foliated texture and high reflection. The thickness of these grains are about 2-3 micron.

Chemical Analysis

Cu 26.5 % 0.43 % Pb 0.02 % Zn 0.05 % Ni 0.24%Sn 19.3 ppm Au

Fe not detected Sb not detected Ag not detected As not detected

Ore Dressing Device

Three ore dressing devices which were used for ore beneficiation were found in the 1996 Liman Tepe excavations. Two are similar and have stalk handles, the other is square in shape. The square shaped ore dressing device dates on the beginning of the Early Bronze I period and comes from Level VI (Fig. 1 and photo 2). The working surface has been flattened and there is a shallow hollow in the center. The hollow was used to crush ore to the required size. The device measures 7 cm high, the hollow is 2,7 cm in diameter and 0,5–0,7 cm deep. The artifact has been carefully crafted however, it was not used extensively.

The stalk handled ore crushing tool dates on the Early Bronze II period and was found in level V (Fig. 1). The tool was well made and used to prepare ore (photo 3.L8). The tool has a handle and the working surface is oval. It is possible that it was used in the first phase of ore preparation, although this is not known for sure since there are no traces of crushing on the surface. It is possible that it was made for ore crushing but only used infrequently or not at all (photo 3.L9). The tool measures 9,9 – 9,1 cm high, tha handle diameter, 5,6 – 3,8 cm, and the diameter of the work surface 7,2 – 6,3 cm.

Metallurgical Slag Finds

The slag finds from the 1996 season at Liman Tepe deserve special notice. These materials can determine the metallurgical activities at the site. These copper oxide slag samples were found inside a baked clay crucible which was used during mineral processing. Slag samples from Liman Tepe were found in different locations on the mound. Four smaller samples of slag were probably as a result of casting the ingots. The other samples are ore metallurgical processing slags. In addition in 1996 a baked clay mold with three surfaces were probably used for casting ingots (Fig. 1, photo 4).

Copper Slag (L.1)

Copper slag was found in Early Bronze II, level V (Figure 1.L.1). The slag sample measures 16–14,5 cm and it is only sample from 1996 that measures that size. The slag fragment was the result of smelting copper oxide minerals in order to obtain an ingot. The slag has a high level of silica which was used as a fluxing material. Baked clay fragments have adhered to the outer surface of the slag in a concave form. This is due to its being crucible slag, similar to the 16 cm example already found. When the slag was fractured, the interior is black and milimeter sized spaces. In addition there were charcoal bits measuring 0,5 – 0,3 cm in size in some parts of the slag sample as well as green colored copper oxide structures (photo: 5). The slag is light which suggests that the metal processing was successful at Liman Tepe. It is also important to note that a stalk handled hammerstone was found near the slag (Fig. 1, L.9)

Results of the Optical Spectographic Semi-Quantitative Analyses

Cu 0.0015 % Fe>1 % Si>10 %. The following are the detection limits for not detected elements: Pb 0.004 % Ag 0.0004 % Au 0.004 % Zn 0.1 % Ni 0.004 % Sb 0.1 % Sn 0.004 % As 0.4 %

Copper Slag (L.2)

This sample is from Early Bronze III, level V. (Fig. 1, L.2). It measures 7–6,5 cm. When broken, the slag has similar spaces both internally and externally (photo 6). It resembles pumice and when mineralogical petrographic analysis was conducted, it was determined that it was metallic slag. The sample is very light in weight. The spaces measures 0,3 – 0,2 cm. No copper contamination was found from metallurgical processes.

Semi Quantitative Optical Spectrography Analyses

Cu 0.003 % Fe>1 % Si> 10 %. Detection limits for the undetected elements are as follows: Pb 0.004% Ag 0.0004 % Au 0.004 % Zn 0.1 % Ni 0.004 % Sb 0.1 % Sn 0.004 % As 0.4 %

Copper Slag (L.3)

This sample was found in Early Bronze II, level V. These are four small sized fragments measuring 2 – 1,5 cm. One of the slag samples has green copper oxide particles. These four small samples are matte black to gray in color and have millimeter sized spaces. Most probably these are the results of casting copper into ingot shape.

Semi Quantitative Optical Spectrography Analyses

Cu 0.4 % Pb 0.007 % Fe>1 % Si 10 %. Detection limits for the undetected elements are as follows: Pb 0.004% Ag 0.0004 % Au 0.004 % Zn 0.1 % Ni 0.004 % Sb 0.1 % Sn 0.004% As 0.4 %

Copper Slag (L.4)

This sample was found in Early Bronz Age level V (Fig. 1, L.4). Four samples meauıre between 2,5 – 1,5 cm. These slag pieces are matte black on the exterior, and when broken are shiny glassy black on the interior (photo 7). This is similar to other glassy slag samples found in slag deposits in Anatolia. The reason behind the glassy consistency of these samples from Liman Tepe is that a great deal of silica was used as a flux during processing. This is corroborated by x-ray diffraction and mineralogical-petrographic analyses. Malachite was also detected in the slag.

Results of the x-ray diffraction: trydymite (SiO_2), Crystobalite (Sio_2), Malachite ($CuCo_2Cu$ (OH)x. Mineralogical- petrographic determination: glassy slag. Microscopic analysis indicates that the glassy slag resulted from the presence of trydymite and crystobalite minerals.

Copper slag (L.5)

This sample is from Late Chalcolithic I, level VII (Fig. 1, L.5). The analyzed samples measure 1.502 cm in size. It was found with a baked clay fragment adhering to the surface, which was probably a part of a crucible. It has a great many spaces and is a shiny black color, characteristically glassy.

Semi Quantitative Optical Spectrographic Analyses

Cu 1 % Pb--1 % Ni 0.1 % Sn 0.2 % Fe>1 % As 0.4 % Si>10 % Detection limits for the undetected elements are as follows: Ag 0.0004 % Au 0.004 % Zn 0.1 Sb 0.1 %

On the basis of the analyses this copper ore comes from another source than the Early Bronze Age samples.

Metal Sources near Liman Tepe

There are no copper workings that are in operation today in the state of Izmir and neighboring states. However, there are copper and lead deposits and veins which are not important for today, but do exist here (Fig. 2). A map showing the distribution of copper and lead sources in the Izmir area and which would be important to Liman Tepe has been prepared[9]. This map will be important for metallurgical residues from other settlements in the Izmir area as well.

Late Chalcolithic - Early Bronze Age miners had tapped into the surface gossan deposits. They obtained copper oxide ores from the cracks and faults of the gossan and brought to Liman Tepe. Copper ingots are easily made from copper oxide minerals (atacamite, malachite, cuprite). This is because high temperatures and furnaces are not necessarily to smelt these minerals. The closest copper-lead-zinc deposits and veins important to Liman Tepe are Buca Maden Tepe, Kemal Paşa Yeni Kurudere, Ovacık Yayla, Bayındır Sarıyurt-Ilıcadere, Menderes Efen Çukuru and Gümüldür Gümüşü (Fig. 2). These are economically unimportant today.

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9 This map has been prepared by mineralogy engineer Yunus Lengeranlı, Assistant General Director of the MTA.

Processing Copper Oxide Ores

It is important to note that before smelting processes with charcoal and wood, the Liman Tepe process started with a well designed ore preparation procedure. This is corroborated by the three ore dressing tools found at the 1996 excavations. After ore dressing, the copper oxide minerals (atacamite and malachite) would be placed inside a baked clay crucible with semi processed charcoal. Atacamite, malachite smelts at 300 ^{o}C and CO_2 is produced. The smelted material turns into copper oxide at 600–700 ^{o}C. Inside the crucible, after the heat has been achieved with the charcoal, the second phase of processing begins. This is the reduction of copper oxide to metallic copper (copper ingot) with the charcoal.

Conclusions

The finds relating to ore dressing and metallurgical processing residues come from Late Chalcolithic I and Early Bronze Age I - III at Liman Tepe. It has been determined that copper smelting was practiced at Liman Tepe using copper oxide ores without the use of a furnace. This is because furnaces are used for high temperature sulphide smelting. The metallurgical processes at Liman Tepe used crucibles since copper oxide ores do not require high temperatures. In addition the Liman Tepe metallurgists used the charcoal knowingly for reduction of atacamite-malachite during the smelting of the ores.

The small quantities of slag are natural for crucible smelting processing of oxide ores of malachite and atacamite. In addition the analyses of the slags have indicated that the smelting process at Liman Tepe was a successful operation.

Acknowledgments:

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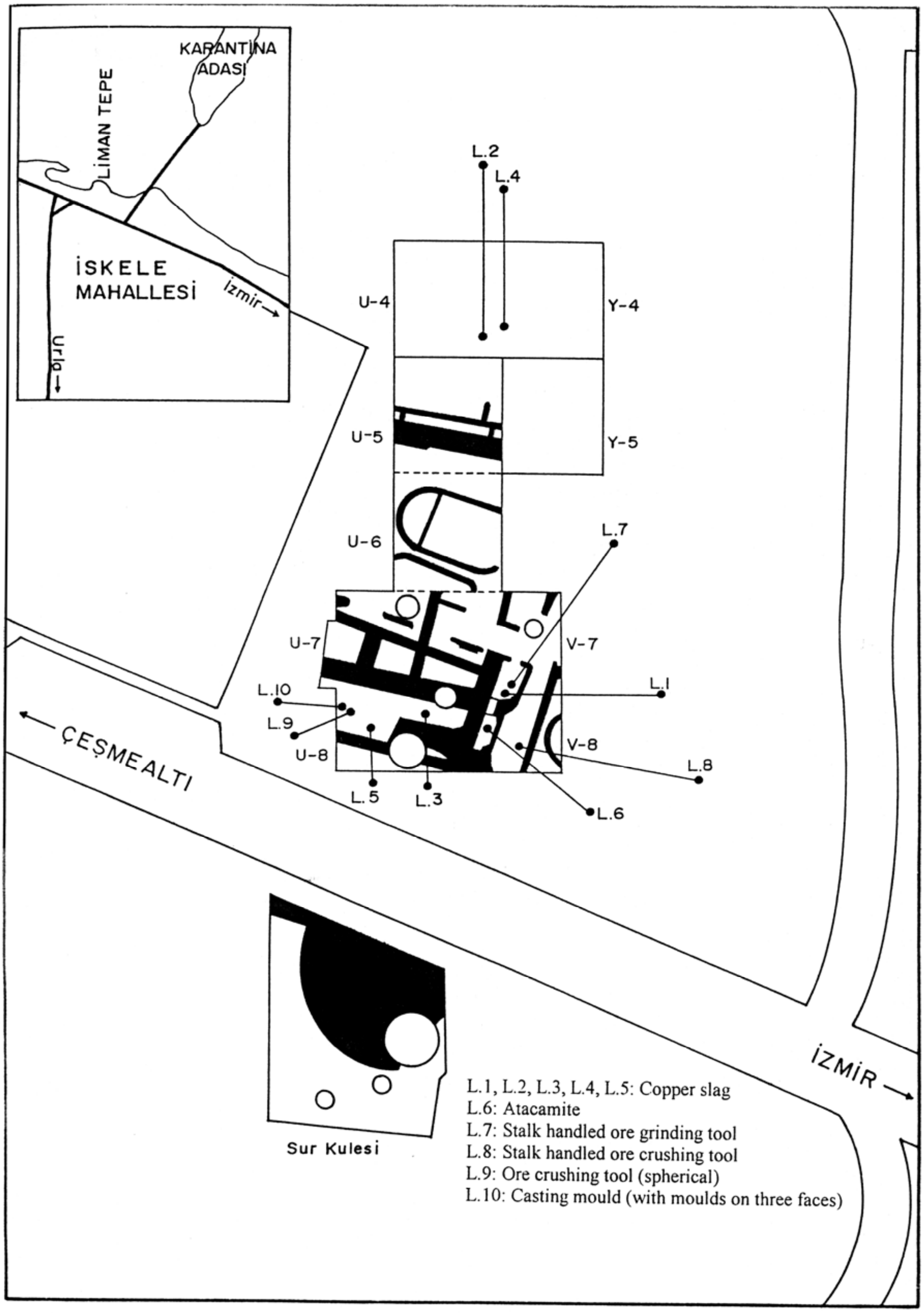
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Sur Kulesi
L.1, L.2, L.3, L.4, L.5: Copper slag
L.6: Atacamite
L.7: Stalk handled ore grinding tool
L.8: Stalk handled ore crushing tool
L.9: Ore crushing tool (spherical)
L.10: Casting mould (with moulds on three faces)

Fig. 1

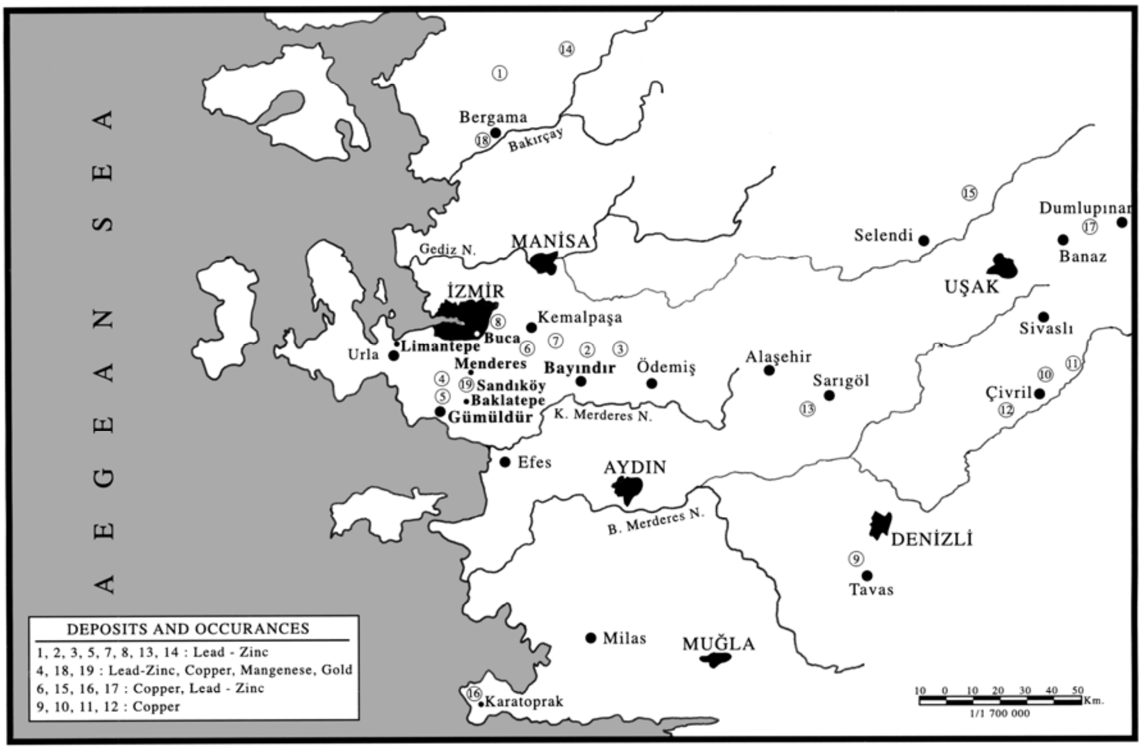


Fig. 2

Photo 1

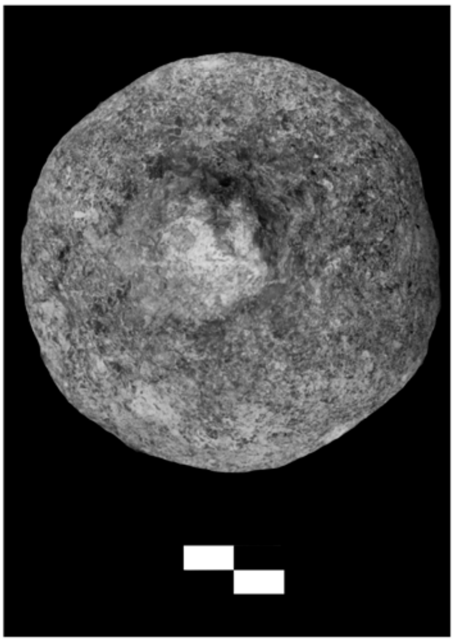
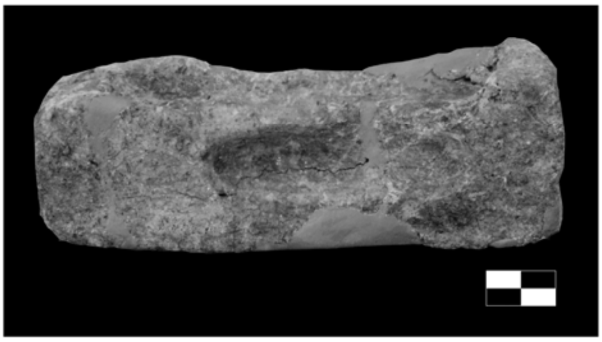


Photo 2

Photo 3



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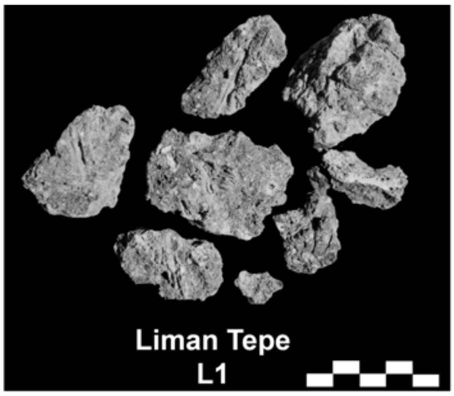

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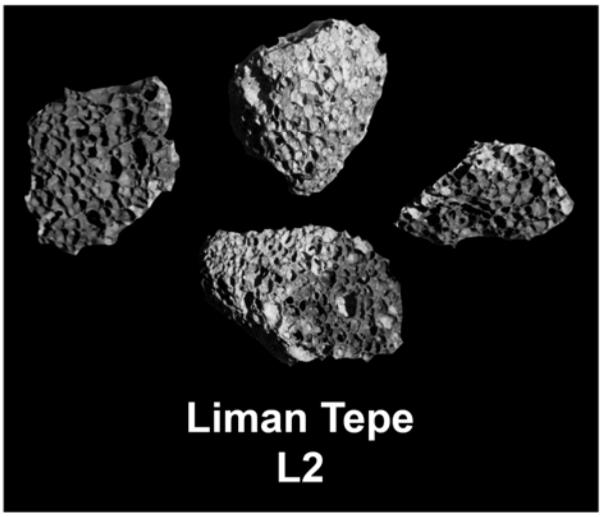

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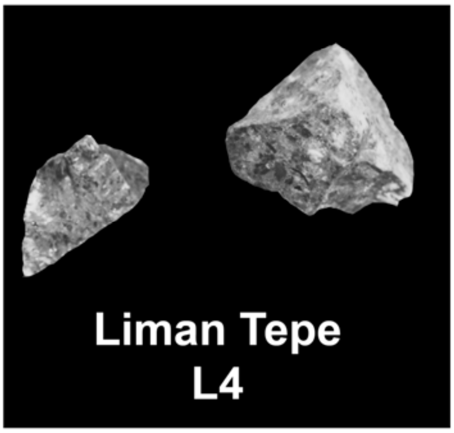

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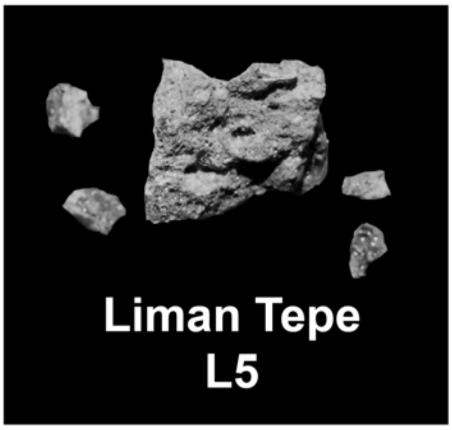

Photo 8