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# TIN SMELTING AT THE ORIENTAL INSTITUTE

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Several experimental smelting procedures were tested both in the field in Turkey and at the Oriental Institute by our metals specialist, Bryan Earl from Cornwall, with additional analysis by Dr. Hadi Özbal of Istanbul. A video camera documented both experiments, while photographs and slides were also taken for future publication. The courtyard of the Oriental Institute served as the setting for the smelting experiment, which was widely witnessed by faculty, staff, and students from the Oriental Institute. Scientists from other departments of the University of Chicago such as chemistry, geophysics, Enrico Fermi Institute, as well as researchers from the Field Museum and the Illinois Institute of Technology also joined the demonstration. The experiment was successfully conducted on November 11, 1994.

The archaeological excavations at Kestel and Göltepe in the Taurus Mountains of Turkey, led by Professor Aslıhan Yener of the Oriental Institute, have disclosed an early Bronze Age tin mining and processing operation. There is at least one ancient mine in the area of the excavations, now named Kestel Mine, but there are undoubtedly more yet to be found. The experiments aimed at establishing production techniques and were designed to determine the magnitude of tin production at the site of Göltepe.

Tin metal does not quickly spring to mind as being of great archaeological importance, but a moment's thought brings one to the problem of bronze. Bronze is normally taken to be some alloy based on copper, particularly the tin-copper bronzes, and the development of such alloys is of great significance. The use of bronze shows that there was a realization that it had valuable properties, which reveals the possession of considerable metallurgical skills. Tin is the key to a host of important archaeological considerations.

**Bryan Earl smelting tin in the courtyard of the Oriental Institute**

Because of the problems associated with the finding, mining, and smelting of tin, any assessment of tin work at an ancient site should be based on a highly practical examination. It is necessary to apply a wide range of very refined techniques to gain an understanding of the details of the operation, any significant conditions that controlled what had happened, and the character of the materials resulting from the work. The trial at the Oriental Institute demonstrated the methods that had been adopted for the initial assessment of the Kestel and Göltepe sites in Turkey. Using material from Göltepe, it was shown that tin mining and smelting, using methods that had been deduced by examination of the archaeological evidence, were entirely practical. Material quite suitable for the production of tin-bronze was produced.

In the Chalcolithic period (ca. fifth–fourth millennium B.C.) either naturally occurring native copper or copper smelted from some ore by some form of furnace was used. The furnace smelting process needed the development of considerable mining and smelting skills. Some of the copper used was fairly pure metal. The earliest bronze is usually differentiated from copper as having a small amount of arsenic and sometimes iron added, which gave a metal that had superior mechanical properties to copper alone, such as increased hardness. It is difficult to judge whether the additional arsenic was a deliberate addition or a lucky impurity. Many copper ore deposits, such as the sulfide ores, do have an arsenic ore content. It is possible that the early metallurgists found that adding arsenic ore to their copper gave the desired effect, but so far there does not appear to be any evidence that this was intentional.

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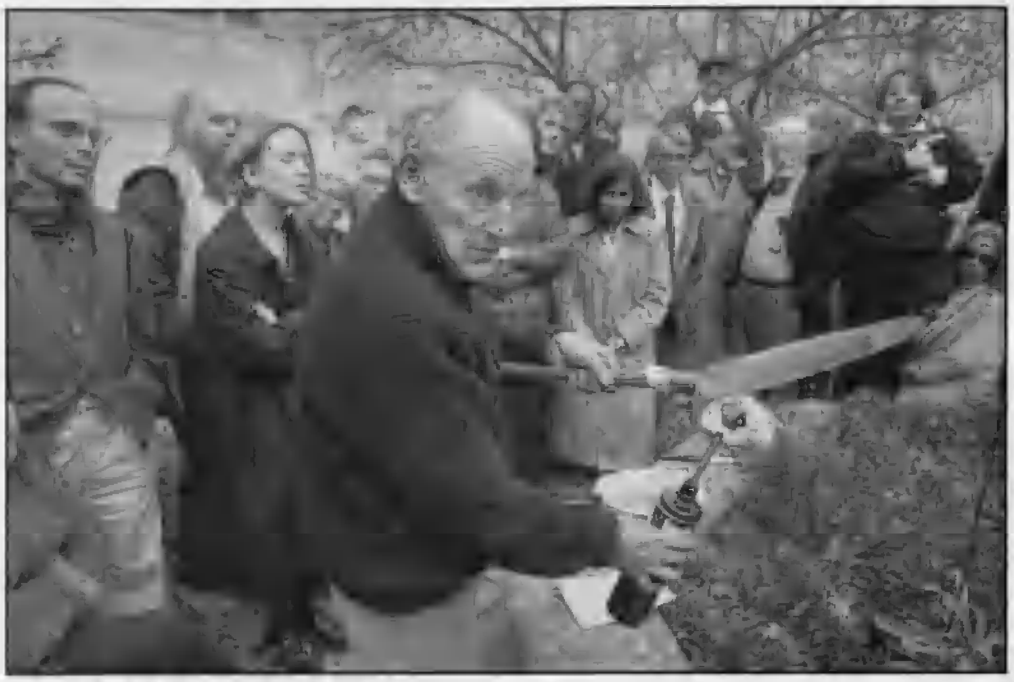


Bryan Earl drying vanned material

The most important development in the making of bronze was the evolution of the tin-copper alloys. Depending on the tin content, these bronzes provide a wide range of valuable properties, such as hardness, toughness; or ease of casting. To make them requires a deliberate addition of tin to the copper metal. To make a significantly valuable tin-bronze, about five percent of tin is required—more if various specific properties are desired. The tin can be introduced into the copper in several ways. The simplest method is by "cementation," i.e., adding tin ore of reasonably high grade to molten copper along with charcoal. The most controllable method is to add the tin as metal to the copper.

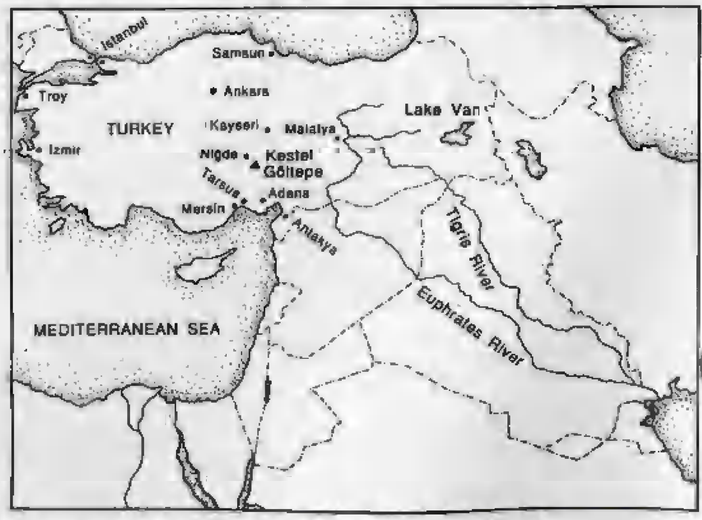
Tin is not widely distributed and is really a semiprecious metal. Tin hardly ever occurs "native" as metal. Its only really significant ore is cassiterite ($SnO_2$), which is normally a dull drab brown material that is difficult to distinguish from ordinary rock unless sensitive methods are used. Cassiterite has two specific properties that are useful for its separation and identification. It is very dense and if crystals of the ore are present it can have a bright sparkle because of its high refractive index. Occasionally a lump of cassiterite is found in a lode, but this is not at all common. Rich ore holds about 5.0% metal, good ore about 2.0%, and skilled miners in western England work down to about 0.2% from stream detrital deposits. Tin also occurs in the mineral stannite ($Cu_2SnFeS_4$), but this is quite rare and is not considered an important ore. Tin ore is virtually always found associated in some way with an "acid"—high silica content—rock. The density of cassiterite ranges from ca. 6.99 to 7.0 g/cc, gold from 12.0 to 20.0 g/cc, and hematite (an iron ore [$Fe_2O_3$] that is found associated with the Turkish tin ore) 5.26 g/cc. The typical waste—gangue—minerals with this ore are quartz, 2.65 g/cc, and calcite, 2.71 g/cc. These densities indicate the relative ease of separation by a "washing" process.

There are considerable similarities in the initial stages of the mining and dressing (concentrating) of tin and gold. Similar to gold, cassiterite is usually found entrapped in gangue mineral if it is in the original lode containing the ore. A lode occurs like the cheese in a sandwich, where the cheese is the orestuff and the bread on either side the surrounding country rock. The lodestuff has to undergo several treatments. To be worked it must first be mined out, crushed to release the valuable material, and then dressed, usually by using moving water to displace the lighter gangue minerals leaving a rich head of the heavy particles of cassiterite or gold.

If the tin-gold ores have been broken down out of the lodes by weathering, the material is often carried to a stream along with the gangue, usually in gravel or sand-like debris. Often the ores can be obtained by washing, but in some cases crushing is needed to release them.

The washing can be done in a number of ways. Using a pan or similar vessel such as conical bowl—a batea—is one method, or the orestuff can be thrown into running water flowing in some form of trough or inclined plane, often with a prepared surface so that the heavy ore particles settle out of the water apart from the waste. In very dry districts winnowing can be used to make an initial separation.

While gold can be easily seen, cassiterite is far from easy to detect. Nowadays, a range of very sensitive techniques, such as X-ray fluorescence assaying, is used. However, in the past simple but surprisingly delicate methods for assaying had evolved. A much used assay for cassiterite developed in western England's metalliferous region: a powdered sample of orestuff is swirled with water on the blade of a shovel and then given a series of upward flicking motions. The heavy cassiterite is tossed up through the water and appears as a cres-



Map showing location of Göltepe and Kestel cent shaped patch at the top of the charge with the lighter waste below. The size of the cassiterite head indicates the richness of the ore. This technique, known as "vanning," was still in use at a major tin mine until 1985. It was a highly practical assay. It had the advantage of separating the cassiterite that could actually be recovered by washing techniques. A skilled vanner can detect down to 0.1% cassiterite in the lodestuff. The introduction of the very effective tin flotation dressing method has shown that vanning undervalues the ore.

For examining ancient archaeological material it is prudent to use old methods when making an evaluation of possible mineral values. Such techniques are probably similar to those that could have been used by the ancient miners. If cassiterite could be found in significant quantity by vanning at an archaeological site, there is a high probability that the ancient worker could have detected it.

Bryan Earl indicating vanned cassiterite

Once the cassiterite has been found and concentrated, it has to be smelted to metal. Smelting is done by heating under suitable reducing conditions. Classically, charcoal was both the fuel and the reducing agent.

Kestel Mine was mined by firesetting: working out the rock by first building a fire against it to weaken it and then breaking it out, probably with stone tools. By vanning out the charcoal from the debris remaining in a fireset pocket it has been determined by accelerator dating that one fireset can be dated to about 2600 B.C. Although the mine is located in calcite/dolomite country rock, there is also quartzitic rock both in the mine and outcropping nearby. By sampling and vanning it was found that cassiterite is present in lode structures and in some cases has formed an accessory in the adjacent rock. This, and the patchy distribution of the ore, is typical of cassiterite mineralization. Gold, in small particles, also occurs in the mine. Such an occurrence with cassiterite is not uncommon. Some of the cassiterite crystals from Kestel are of a somewhat unusual and notable red color, which tends to make them stand out in a panning or vanning assay. The value of the ore is too low and the mine gives an appearance of having been worked out.

It is likely that the ancient miners were initially attracted by the small gold content of the orestuff. On working the gold they then also found the heavy cassiterite. It is a matter of considerable interest how they recognized the tin, especially as it was in the nonmetallic oxide that had to be smelted to produce a metal.

Many thousands of stone tools have been found during the archaeological excavations at Göltepe, a small hill about 2 km distant from Kestel Mine. The tools are typical of those used to powder ore. Many of these tools are hand held pounding and rubbing stones, which have a typical flat face from the grinding action on a stone slab, with a characteristic "dimple" in the middle. It is interesting that this appearance exactly duplicates that of the iron tools used to the present day for bucking (crushing and powdering) ore ready for assaying in western England. During the excavations some ground ore powder was excavated from Early Bronze Age pithouse structures at Göltepe. The powders were differentiated in color from the surrounding materials. Hadi Özbal, Professor of Chemistry at Bosporus University, assayed these by atomic absorption techniques and found that some had tin contents of over one percent. The minerals associated with this tinstuff have been identified as those found in Kestel Mine and not from the Göltepe rock, which is a flysch. These powders gave every indication of being orestuff in process. As only one small speck of gold has been found in them so far, it seems they represent material that was destined to go forward to be concentrated ready for smelting to tin. The ore has an unusually high hematite content, and this is partially concentrated with the cassiterite because of its high density. It seems the gold had been removed.

Göltepe also holds many curious ceramic sherds. These have no domestic association but give every indication of being vessels in which tin smelting took place. They have been loosely termed "crucibles." Microprobe examination by M. Adriaens of the fabric of these crucibles shows patches of very light tin content—probably as oxide—in the inner section. Smelting cassiterite for tin metal in such a container buried in the ground is well known and was practiced in Japan until the beginning of this century. The fuel and reducing agent was charcoal and an air blast was arranged to urge the fire to a sufficiently high temperature for the smelting to take place.

Enough of one of the powder samples was recovered to enable a quantity of cassiterite to be vanned that produced suf-

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ficient concentrate for a smelting trial. The concentrate was found to hold 10.2% tin as metal. Investigations of tin smelting in Africa indicate that low concentrations such as this had been used by early smelters.

A small replication experiment was set up, using the method that it was surmised had been used in the past from a study of the material remains. Some clay nozzles ("tuyeres" to the iron smelter) had been found and it appeared that they had been used to provide an air blast to fire the smelting charge held in the clay crucibles. Bellows may not have been available to the ancient miners, so it was decided to use air blown through a pipe, as depicted in the wall painting in tomb 386 of Thebes, ca. 2000 B.C.

By studying the crucible sherds it was evident that they had been made by mixing clay with chaff to give a vessel the properties needed to withstand the thermal shock of high temperature gradients. They all had notably thick walls and it later appeared that this gave good thermal insulation properties so that the heat could be well confined. Three experimental crucibles were fabricated from clay and chaff obtained from Celaller, a mountain village near Göltepe. The crucibles were constructed using a slab construction technique, replicating the size and technique of the crucibles excavated from Göltepe. One of the crucibles was used in the Oriental Institute smelt.

For the trial in Turkey local charcoal broken to ca. 2.0 cm sieve aperture was put into a dried crucible, ignited, and then blown by mouth until a good bright red heat was reached. Small portions of the tin concentrate were then put on the glowing charcoal and then immediately covered with fresh charcoal. This whole operation was then repeated until all the concentrate had been used up. The blowing was kept up for a further twenty minutes and then everything was allowed to cool. The charge was tipped out onto a vanning shovel, the remaining light charcoal and ash were washed off, and a highly magnet attracted fused gray slag was left. The slag was crushed and beautiful round "prills" (globular beads) of tin metal, up to 2.0 mm diameter, were vanned clear. "Prill" tin was similarly smelted, according to Thomas Beare, in sixteenth century A.D. England.

With a feed of ca. 5.0 g the tin prill yield was ca. 0.175 g. Although the feed for the smelt held a considerable amount of hematite unavoidably tossed up with the cassiterite, the resulting tin metal was quite malleable, indicating a reasonably good purity. By theoretical considerations, particularly considering the temperatures achieved, there should have been high iron phase, normally termed "hardhead"—a tin/iron complex—making the product far less pure. However, the smelting conditions encountered in such furnacing have not only very high temperature gradients but are also dynamic enabling the highly mobile molten tin to separate remarkably clean, although it is still contaminated with iron to a certain degree.

*Kate Luchini, Oriental Institute Assistant Museum Preparator, blowing air into the red hot crucible*

Even though the fine prill tin concentrate could have been remelted with some flux and poured to an ingot, it is quite possible that the prills were taken to the bronze founder. There was no need to have the tin in block form. Although the iron content of the tin produced in this manner could make it unsuitable for making materials such as pewter and solder, the iron impurity is not particularly objectionable if such tin is alloyed with copper because the iron would be largely rejected into a dross and a good bronze could be produced.

The trial smelting at the Oriental Institute duplicated the methods that had been used at Göltepe. Both the identification and concentration of material from the site and its smelting to tin metal were attempted. Th trial provided further material for study from the scarce archaeological samples. An addition to the Turkish firing scheme was a small scale "fire assay."

A sample of the Göltepe ore powder was concentrated by vanning, which showed the cassiterite that separated above the lighter waste as a light brown head. It was dried and divided into two portions. The top segment, which was made up of the cleaner (high grade) cassiterite and weighed approximately 50.0 mg by area estimation, was set aside. The lower segment, which had notable hematite contamination, was estimated to weigh 150.0 mg.

The high grade portion of the cassiterite was incorporated with approximately equal volumes of charcoal dust and mixed sodium/potassium carbonate flux (mixed carbonates to ease fusion). The mixture was then placed into a small porcelai crucible with a second larger crucible placed in it to act a cover. This crucible was now prepared for the main smelt. On a very small scale, this preparation closely followed the fire assay for tin practice in western England.

A crucible that had been made in Turkey was used for the main smelt. Some American hardwood charcoal was crushed to about 2.0 cm sieve aperture size and ignited before dropping into the npty crucible. A single mouth blown pe of 0.7 mm bore was then placed in the charcoal, through which air was continually blown, with more charcoal added to keep the crucible full, until the core was seen to be at a bright red heat. The lower grade hematite-contaminated cassiterite was then run onto the top of the glowing charcoal, with no added flux, and immediately covered with more charcoal pieces. Air was blown through the tube into the glowing mix throughout the addition of the material. When the main "furnace" was seen to be well alight, the small fire assay crucible was placed on top and covered with additional charcoal. As the assay settled into the charge and was seen to heat to bright red, more charcoal was added to maintain the fire. After about fifteen minutes, blowing was stopped and the furnace allowed to cool.

***Tin prill smelted in courtyard of Oriental Institute fused to fragment of crucible***

The small crucible was taken out. On breaking open, two tin metal prills were found in the slag. The main charge was treated as in Turkey. After tipping it out onto the vanning ovel, the light fractions were removed, leaving a small residue of ash and matte gray fused slag. One of the larger pieces of slag was separated for study later; the remainder was crushed and vanned under water in order to separate the small prills of tin metal. This main crucible smelt duplicated the Turkish trial in a most satisfactory manner. With a charge of only about 200.0 mg, it was apparent that the method was entirely practical, bearing in mind the losses that can be expected such as the reoxidization of tin to volatile oxide.

The small crucible fusion was included to gain a sample of the highest grade tin that might be expected from the Kestel/Göltepe feed. There was also some concern that the main smelt would not produce tin, given the very small charge and the obvious basic nature of the big crucible smelt. It is not suggested that any such assay method was used by the ancient miners.

Variation in the charcoal effected the success of the smelt tremendously. The use of commercial charcoal briquettes resulted in unsuccessful smelts, while wood charcoal completed the smelt efficiently and resulted in tin metal prills. The test run utilizing a micro-crucible was only partially successful. Even though we did manage to produce prills (tin metal globules), they penetrated the fabric of the micro-crucible and made them impossible to extract. The iron rich charge sample, ich was not vanned and thus enriched, fared poorly as well. n metal prills were easily produced by using a simple blowpipe and wood charcoal, after having enriched the ore with a vanning shovel to approximately ten percent tin content.

Other variables during the tests were the number of simultaneous blow pipes, the crucible with or without cover, and the nature of the fuel used. A surprisingly high temperature can be reached by the simple method of blowing air through tubes into the "furnace." A replica smelt made in Cornwall, U.K., where a platinum/rhodium thermocouple probe was used, showed that 1100°C and over was easily maintained and was sufficient for smelting the ore. Under these conditions it was found that no cassiterite reduction occurred until well over 650°C was attained. When more than one person blew air through tubes into the glowing charge, far higher temperatures were achieved. An experiment with three blowpipes made the fire so hot that it melted a metal blowpipe and vitrified a micro-crucible, indicating a temperature in excess of 1100°C.

It is probable that the ancient miners at Kestel used the smelting process to get a tin that was sufficiently cleaned of gangue to be used in the production of bronze. The products of the Oriental Institute smelt are now being subjected to a barrage of tests—from thin section optical petrography to gallium ion microprobe—to unravel further mysteries. The ancient miners would surely have been fascinated.

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*For more information on the Oriental Institute's archaeological excavations at Göltepe, Turkey, see K. Aslıhan Yener's "Managing Metals: An Early Bronze Age Tin Producing Site at Göltepe, Turkey" (N&N No. 140, Winter 1994) and "The 1993 Excavation Season at Göltepe, Turkey" (The Oriental Institute Annual Report 1993–1994, pp. 31–40).*

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*Photographs by Lloyd DeGrane*