Early Metal Technology

2. Silver and Lead

Silver

Native silver is rather rare. Not as rare as native copper (if one excludes the "anomaly" of the "old copper complex" in North America), but still rarer than native gold. Native silver has been used but, just like gold, relatively late. The oldest occurrence of silver comes from a "hoard" found in the famous cave in **Alepotrypa** / Greece, dated to the mid 5th to early 4th millennium BC. It is thus roughly contemporary to the first gold in Varna. However, the Greeks neglected to supply any pictures of that hoard (in the Net).

Native silver

Source. Photographed in the Metropolitan Museum NYC.

It appears that there aren't many artifacts around that were made from native silver. Hardly surprising considering how scarce it is. You can also get silver from "gold parting" but that was done rather late (roughly after 1500 BC) and does not produce elemental silver but a compound, same thing as an ore. So nothing helps:

If you want silver, you must smelt some ore

- Silver sulfides are the most easily found ores, and those are typically mixed up with the lead sulfide **galena** (PbS) or with lead carbonate called **cerrusite** ($PbCO_3$). The neolithic Anatolian towns knew galena because the people who lived there (in Çatal Höyük, to be exact) about 9000 years ago had made beads out of galena. They wouldn't have noticed the silver sulfide in there because even silver-rich galena rarely contains more than 0.5 % of the stuff.

Nevertheless, most of the silver produced in antiquity was from the little bit of silver sulfide or other silver compounds contained in the lead ores galena or cerrusite. The primary production of silver requires the smelting of these ores, producing a lead-silver alloy, and then the separation of the silver from the lead and the rest.

- The first thing to do is to find ore deposits. That is not as easy as finding gold deposits where you could see the gold. You don't see silver or lead when you look at galena or cerrusite containing ore. You see blackish stuff if you find galena, or whitish stuff if you find cerrusite, and sometimes well-developed transparent crystals:

Cerrusite veins and a cut crystal (the "light of the desert")

Source: Internet at large

- Cerrusite is rather fragile and very difficult to cut and thus no rival to diamond. The "light of the desert", the largest cut cerrusite single crystal, resides in Toronto's Royal Ontario Museum.

It would be good to have some idea (or "theory") of where it might pay to look for ores. We don't know how exactly early prospectors went about their business. Presumably they knew what they were doing but they weren't given to writing. **Aristotle** now, he was giving to writing in a major way and left us the first written record of ore deposit theory. He wrote that when the rays of the *sun* penetrate into the earths crust and interact with water in various proportions, metal or metallic ores form. His reasoning for this was that "a metal is a combination of the elements of earth and water with the presence of water told because metals are malleable and, when heated, will melt and flow". In the case of gemstones Aristotle believed it was light from the *stars* whose "pure, serene, and heavenly rays give birth to these bright and precious stones".

- **He was wrong**, as always. Aristotle defenders will argue that he couldn't know better. That argument was wrong when it came to the discovery of atoms, and it is wrong here. Witness **Plato's** theory, who also couldn't know better. He thought there was a great fire at the center of the earth, fueled by the sun, which gave off dense clouds of metal making vapors. The existence of this great fire was substantiated by the volcanoes. Not quite right either - but closer to the truth.

We still need to discuss why early humans wanted to have silver. After all, they weren't crazy about gold before 4500 BC, it appears. Silver is too soft for tools or weapons. It even tarnishes but doesn't turn a pleasant green like copper but a dull black so you must clean it ever so often. Silver is the very best electrical conductor, true enough, but that didn't concern stone-age man all that much. There are essentially two properties that might have been of value 6000 years ago:

- It was exceedingly rare and thus expensive. This is important as soon as societies have developed to a point where they have supreme leaders, kings, high priests or other VIPs that needed to distinguish themselves by touting expensive status symbols.
- Polished silver has the highest reflectivity of all surfaces and thus is ideal for a extremely important implement: the ubiquitous **mirror** essential for the well-being of the females and thus the survival of the species.

Do you like what you see?
Link to elaborate Greek mirror

Indian lady; apparently not too pleased with what she sees. Wiki; Soham Banerjee	Greek Lady on red-figure pot, ca. 470 BC – 460 BC, quite pleased with herself. National Archaeological Museum, Athens

So let's make silver now. Smelting silver was standard procedure since the early fourth millennium BC in southwest Asia and done with what one calls "argentiferous ore". The "ferous" in this word, by the way, has nothing to do with iron. It's just kind of Latin for the "y" in "silvery". Large scale efforts to mine and smelt silver began sometime after 3000 BC. The major source was galena, containing typically far less than 1 % of silver sulfide.

The ore was processed before smelting. First it was broken up to small bits and the promising pieces collected. "Sluicing", i.e. using water to separate the heavier pieces from the lighter ones also has been used. Smelting produced lead (see below) with the silver dissolved in it. The actual smelting is relatively easy - provided you got everything right. Just note that for smelting sulfides you typically first turn them into oxides so you need an oxidizing atmosphere, at least in the beginning. If all goes well you end up with elemental silver dissolved in elemental lead. You might also first "roast" your ore in a regular fire to drive out the sulfur.

- It only remained to get the the little bit of silver out of the large amount of lead. That's actually what "**cupellation** ", the process already discusses for parting gold, was really invented for. Look up the basics in the gold module. The Chaldeans, it appears at present, were the ones who invented "cupellation" around 2500 BC for extracting the silver from the lead-silver alloy, a smart if wasteful process that was used for millennia.
- In short, the liquid metal mix was exposed to air, and that oxidized everything except the silver. Lead oxide (PbO or "litharge") was formed, containing some of the other oxides, the rest evaporated. Everything not silver - mainly lead oxide - is also called litharge and soaked into the special porous container called a *cupel*, forming what one calls a litharge cake. They are usually circular, concavo-convex, typically around 15 cm in diameter, and about the most common archaeological evidence of cupellation in the Early Bronze Age.

Piece of a silver litharge cake (found in Great Britain)

Source: The Dornoch Historylinks Image Library; with friendly permission

- By 1000 BC so much silver was being produced from lead ores that its price relative to gold had dropped to about 1/12th (it used to be more like 1/4th). Large-scale cupellation must have gone on an industrial scale and a lot of waste in the form of lead ores or slag was produced - several 100.000 tons in central Iran alone, a number given in **Wertime's** famous report of his "metallurgical expedition" [1)].
  A lot of people died in making the stuff. Simply from hard slave labor in the "lead mines", or because all this lead, and in particular the lead-bearing vapors during smelting, are rather poisonous. Forests disappeared because a lot of fuel was needed, and the atmosphere got polluted for the first time. That is not a joke. The residues of ancient lead / silver smelting can be found in the **ice cores** from Greenland or in other strata like lake sediments. This actually offers a new way of **dating human activities**.

In monetary value silver was second only to gold, and whole empires depended on it. Around 1500 BC it was used for making the first coins. A present-day **dollar** is simply a messily pronounced "**Taler**", the true name for the silver coins that were major currency in central Europe for quite a while. "Taler" is just short for "Joachimstaler", the silver coins from the town Joachimstal (the valley (= Tal) of St. Joachim; the father of the Virgin Mary) in the Harz region, the major silver mining district of Germany in the Middle Age.

- Silver thus mutated from a status metal announcing wealth to one of the media actually measuring wealth. Besides making coins, you could also use it for art or elaborate show-off items:

Proto-Elamite antelope and mountain goat from Susa, Iran. Around 3000 BC

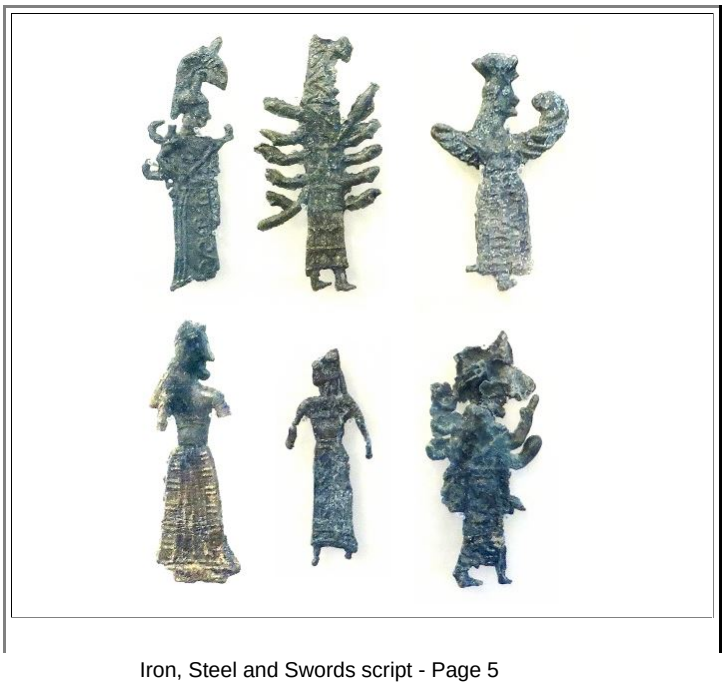
Source: Photographed at the Metropolitan Museum NYC and Boston Fine Art museum.

- The old Susanites obviously knew how to work with silver (and gold) some 5000 years ago. The goat goes nicely with this bull; here is a larger version of the bull.
- The ancestors of the Vikings up North also treasured silver, as evidenced by the **Gundesstrup cauldron** ; now in the Copenhagen museum. The cauldron is a rather large affair from around 300 BC or so. It is richly decorated and from the style of these decorations one might conclude that it contained special beverages that caused mind enlargements.

Detail of Gundestrup silver cauldron
Large format

Lead

- Silver is pretty, lead is useful. A fashion model is pretty, engineers are useful. It shouldn't come as big surprise that nobody cared much for lead for a few thousand years after it became known. It was the Roman empire that used the stuff on a large scale. Lead also kills you eventually if you live long enough to fall for its long-term effects but nobody then cared much either.
  What is lead good for? First, anything faintly electric or electronic (there is a difference) is hard to imagine without solder, and solder used to be a tin-lead alloy for the last 100 years or so. Only recently lead solder was banned and we now must do with inferior stuff. It is also great in batteries. The overwhelming majority of cars still has a lead battery for running the electric system. Lead is also great for making the slugs for all those guns we like to have around.
  At present lead comes in as No. 5 (after iron, aluminum. copper and zinc) on the production scale.
  I guess all these lead applications didn't quite convince the Romans. I'll try again further down.
  - Even so nobody really cared for it, lead may well have been the first metal smelted by humankind. The last word isn't in, we have to wait if the famous lead bracelet from the sixth millennium BC, found at Yarim Tepe is really made from lead. If yes, it must have been (accidentally) smelted lead because there is no native or elemental lead around.
- So let's smelt some lead. It's easy. I've said so and everybody else seems to share that point of view. But majority votes mean nothing in science. A majority in a parliament may pass a law that π = 3.0 because that makes math so much easier, but the areas of circles will not suddenly get smaller because of that (this has almost happened, by the way; check for "Indiana Pi Bill"). North Carolina has just (2013) passed a law making the ongoing climate change illegal.
  - Is it easy to smelt lead? Yes or No? How the hell should I know? All I can say is that quite a few things have to come together. If you throw galena into a fire, it will simply oxidize. If the temperature reaches about 600 ^{o}C (1112 ^{o}F) you get lead oxide (PbO) - our old friend "litharge". In serious lead smelting you do exactly that first as a separate process - it is called *roasting* the ore - after you carefully broke down your ore into small particles that were washed and sluiced in order to get out the "gangue", all the stuff not galena (or cerrusite, as the case might be). One of the reasons for doing that is that the presence of some copper ore, or - worse - zink sulfide (ZnS) would make successive smelting rather difficult.
    Then you smelt your "clean" lead oxide. That is not too difficult, mildly reducing conditions and medium temperatures below 800 ^{o}C (1472 ^{o}F) are sufficient. Of course, you need to make sure that your freshly produced liquid lead (its melting point is a sissy 327 ^{o}C (622 ^{o}F) doesn't oxidize right away again because it falls into the hot lower part of the furnace. Protecting it by some liquid slag that sits on top might be a good idea; maybe you should add some *flux* to the mix.
  - If you are lucky (or know exactly what you do), you might get lead just so by putting rather pure galena into a fire. First you oxidize some but not all lead sulfide, and next you make elemental lead by reacting lead oxide and lead sulfide according to: $2PbO + PbS \Rightarrow 3Pb + SO_2$. You don't even need reducing conditions for that.
    There are reports that American Cowboys produced their lead this way.
- So, yes, it can be easy to smelt lead - if everything happens to be just right. Given a millennium or two, plus a lot of people making fire and fooling around with early pyrotechnolgy, it is almost sure that it happened on occasion. It is also almost sure that nobody cared.
  Large-scale smelting of lead ores, as outlined above, was done for a long time only because of the silver. For every kilogram of silver, a few tons of lead "slag" was produced so people eventually wondered if lead was good for something non-electrical, since electricity hadn't been invented yet. Guns hadn't been invented either so nobody needed slugs. What could one do with the dense and ugly stuff - besides using it for the cupellation of noble metals, of course?
  - You could make little "votive" figurines, i.e. some trinkets offered to the Gods to obtain some favor. Most Gods are not very smart and might not notice that this is not silver. It's always worth a try.



Lead votive figurines; Laconia / Greece; around 600 BC

Source: Photographed in the Metropolitam Museum NYC.

- On a less flimsy side, you could make lead anchors for your fleet. Or even better, coat your ships with it. That kept those barnacles from clinging to your wooden ships and and in particular the shipworm (actually a clam with nothing on) from drilling holes in the hull.
  Burying your dead in sealed lead coffins is an idea that caught on. You don't want to know exactly why one does this, but it became customary with the Romans and is still done today (look up "Lady Di coffin").

Roman lead sarcophagus

Source: Archeology Museum Istanbul

- The Romans were big on having running water and decent plumbing. The words "plumbing" or "plumber" have their origin here, the Roman / Latin word for lead is plumbum, short Pb, because the Romans used lead in a major way for making pipes and plumbing hardware. If you look a the pictures below, Roman plumbing was pretty good. After the end of the empire it took about about 1300 years to get back to their standards again in the more advanced parts of Europe

Roman plumbing implements

Source: About any museum in Italy

Roman loo with running water - in and out

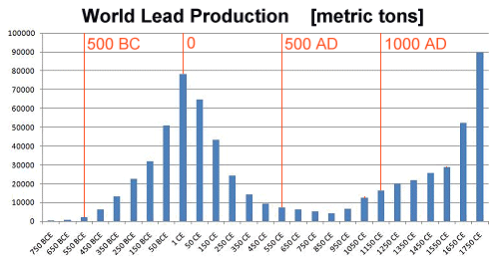
Source: Photographed at Ephesus, Turkey

- Then you needed quite a bit of lead to clamp those big stone constructions together. An iron clamp was inserted into holes in the two stone blocks to be joined, and fixed in place by filling the space with molten lead. A similar procedure was used for connecting the drums of tall columns.

Top: Lead-encased iron clamp keeps masonry stones together
Bottom: Vandalized wall with clamps removed

Source: Photographed at Ephesos; Turkey

- The metals were valuable so these constructions were routinely vandalized and the metal taken out as soon as things declined.
  The Greeks and others also used this technology (the pictures above are from a Greek city) but the Romans did it on a large scale. Look at the worldwide lead production below to get an idea of what lead meant to the the Romans.



World production of lead

Source: Wikipedia

- What else can you do with lead? A lot: tickets for the circus, seals and inlays for teeth (the German word for both is "Plomben"), weights, pans for salt production, urns and balls for shooting at the enemy with whatever you had for that. You also can put it on the roof of your house (still done a lot) or falsify gold coins (no longer done; we have bankers now for cheating you moneywise).

Finally, it is necessary to point out once again that humankind insisted in mixing up lead with something else. I've already covered the mix-up with graphite ("Plumbago") and galena, but people also confused it with **tin**. Up to the 17th century they called it: plumbum candidum or "bright lead", in contrast to plumbum nigrum or "black lead", the real stuff

- A lead-silver alloy was known as "**stannum**". Later this term was transferred to tin, hence its chemical symbol "Sn"

[1)] T. Wertime: Metallurigal Expedition through the Persian Desert", Science , Vol. 159 (1968) p 927