



# Early Metal Technology



## 1. Gold

### Origin, Deposits and Recovery

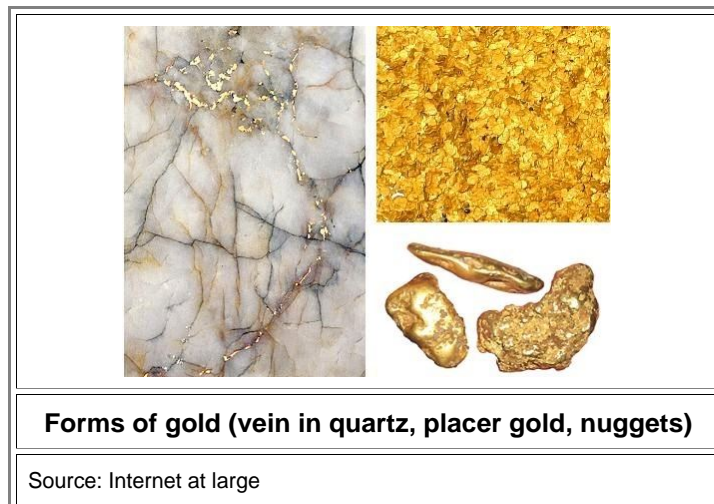
We find gold (Au) more or less on the surface of this planet (let's not get excited about a few miles below the surface here). The same is true for other "heavy" metals like platinum (Pt). This was a big puzzle. There shouldn't be any of that "heavy" stuff around. Why? Well, when this planet was formed some 4 billion years ago, all this heavy stuff was a (small) part of a liquid magma ball consisting mostly of iron and nickel. Gold and other heavy stuff in there did exactly what you would expect: it sunk to the center and stayed there. It's still there - at the very center of the still mostly liquid ball we call earth. Just the surface has solidified by now, forming a kind of thin crust or cross layer on the liquid inside. And that is still mostly iron and nickel.

Yes - there is a lot of gold, platinum, and so on, right at the center of the earth. No doubt about this, and no way of getting to it, and no puzzle there. The puzzle is: why was some of the stuff left back on the surface?

The answer is: There wasn't anything left back. The original gold is all deep down. The gold and platinum that we find *now* was deposited *later* by huge meteorites that crashed onto the already solidified surface of the earth. They struck the planet about 3.9 billion years ago, 200 million years after the earth had formed. M. Willbold and T. Elliott, of the Bristol Isotope Group in the School of Earth Science, figured that out by a rather complex and convincing analysis in 2011.

Interesting, but not all that helpful for getting large quantities of the stuff *now*. Mother Nature had plenty of time to close the impact craters, mix up the gold with other rocks, include it into mountains, sink it down and melt it, regurgitate it and erode what's left - several times all over. That's why now, almost 4 billion years later, we find it mostly in (quartz) veins or in what's left after erosion took everything apart and water washed it downhill.

In other words: Either look for gold-bearing veins in rocks - quite often quartz - or wash out the **placer gold**, tiny pieces of gold or gold dust, from sandy alluvial deposits. On occasion you also might get a bigger piece called a gold **nugget**. Gold-washing with a simple pan is easy to do and in the old times, when the stuff was more plentiful, was probably quite rewarding. Nowadays you can forget about that. Gold is recovered from "invisible" deposits with as little as 5 grams gold per ton of rock.



You could also spread a sheep skin or fleece into the river that "caught" the gold dust coming along so it could be removed later at leisure. That might be the origin of the golden fleece tale in the **Jason and the argonauts** myths. This method was used in antiquity, indeed, and the roots of the golden fleece tale thus are clear. That's what you and I think. "Archaeologists", however, says Wikipedia, "rejected these interpretations as ahistorical". The golden fleece rather represents: royal power, the flayed skin of some guy named Krios, a book on alchemy, a technique of writing in gold on parchment, the forgiveness of God, a rain cloud, and so on (there are at least 11 more of those obviously "historic" interpretations).

Archaeologist bashing is sometimes not much fun. They make it too easy.

Whatever. Those ancient guys treasured gold and wanted to have some, and that is what the tale definitely tells us.

Humankind definitely wants gold, especially one of its genders. However, that wasn't always the case. Before 4500 BC, it seems, nobody cared much about the stuff. That's because beer hasn't been invented yet, [I believe](#). The name "gold", by the way, goes back to Proto-Indo-European "g(h)el", meaning yellow/green. The chemical symbol Au comes from Latin: *aurum*, meaning "gold". Not a very good joke but it seems to be disputed what precisely "aurum" means in this context.

Getting gold in the old times was not all that difficult, especially if you had an unlimited supply of slaves. Working your gold dust and particles into something desirable was more involved. For that you needed people who knew a trick or two, nowadays called engineers.

Several tasks come to mind:

1. Purifying, i.e. taking out the unwanted alloy elements.
2. Compacting the stuff without melting it.
3. Melting and casting.
4. Alloying, i.e. putting in the wanted alloy elements.
5. Goldsmithing, i.e. making pretty objects.

### Compositions and Purifying

Let's start with purifying, a term that contains "parting" and "refining" as special techniques. What one needs to know first is:

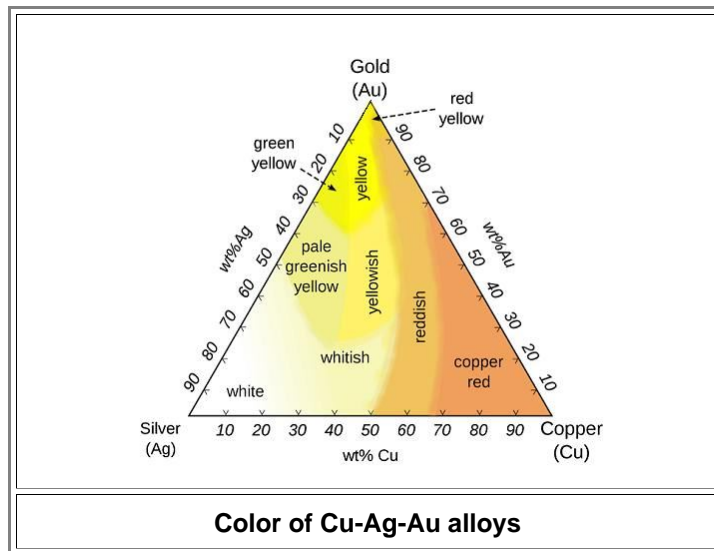
**Native Gold (Au) is always an alloy**

Native gold may contain large amounts of silver (Ag; up to 40%) and smaller but still substantial amounts of copper (Cu, up to 1%) and iron (Fe; up to 5%). Other noble metals might be present, in particular platinum and palladium, and a lot of "trace" elements like mercury and tin. In fact, naturally occurring **electrum** is an alloy of gold and (at least) 10% to 30% silver (Ag) plus some copper and whatever else.

So what! Do I, the ancient gold user care? Do the alloy elements change the properties of the material in a way that makes it less attractive to me? This is actually not one but two questions:

1. *Do the alloy elements change the properties of material?* Answer: Certainly!
2. *Are the changed properties bad for me?* Answer: It depends.

The properties that change noticeably already with a few percent of silver or copper (let's forget the rest) are color, hardness, melting point, price and corrosion resistance. Harder is better for wear and tear but not so good for easy workability. A lowered melting point makes casting easier but the color may not be to your liking. So pure gold has the best color? Not if you prefer "rose" or "red" gold (ca. 25% - 50% copper) to "gold" gold. It's a matter of taste - and red gold is cheaper!



Nothing helps. We need to first take our native gold apart into its constituents, and then make the alloys we want from the pure stuff. Following the development of the techniques, we do that in two steps:

1. **Gold parting:** Separating the silver from the gold, i.e. separating two noble metals.
  2. **Gold refining:** Separating the gold from "**base metals**", i.e. metals that do not belong to the noble metal family.
- After we made pure gold, we can alloy it with whatever we like - as long as we can melt it. If we want to make gold-platinum (Pt) alloys like some South-American civilizations, we have a problem. Platinum melts at 1772 °C (3221 °F), definitely not within reach for pretty much all ancient cultures. I'm not going into that, suffice it to mention that they essentially "glued" together platinum particles with liquid gold.

## 1. Gold parting

Separating the silver from the gold was done by "**cementation**". This is a rather unfortunate word because it is used for several different things, including a technique for getting carbon into iron in order to make steel or for making [brass](#). It typically refers to solid-state processes where the material to be processed is immersed into (powdered) solids followed by heating the ensemble. Then an alloy might be formed without melting.

The basic technique here is to turn the silver into a salt, typically silver chloride (AgCl) or sulfate (AgSO<sub>4</sub>), that is "caught" or dissolved in some part of the total package. In modern times (say 17th century and beyond) gold parting was done with other methods, for example by exposing the granulated stuff to acids like nitric acid, by bubbling chlorine gas through the molten alloy, or by electrolysis. In the antique world this kind of chemistry did not exist and the silver was turned into a salt by the cementation method..

Gold parting by cementation was definitely used in the 6th century BC in Sardis, Lydia (Turkey). It might have been used earlier but in Lydia it became necessary because King Alyattes (the guy who ruled Lydia around 610 BC - 550 BC, and whose son **Croesus** became famous for unlimited wealth), struck the first silver and gold coins as legal tender. In other words: the guy invented real **money** (as opposed to the bits in some computer memory we call money these days). Of course people immediately came up with falsifications that contained less of the noble metal and some copper instead. Thus the need to have pure gold and silver (and to prove that) arose.



- How is gold parting by cementation actually done? Just turn your gold-silver-copper-whatever alloy into thin sheets or granules in order to maximize the surface area. Then put it into a closed container together with common salt (NaCl), some brick dust or burnt clay. Add [eye of newt and toe of frog](#), [Wool of bat and tongue of dog](#), pee on it to add some urine, and say a prayer, invocation or spell. Don't forget to sacrifice a banker or two. Now heat the container for a while (24 hours, say) to 800 °C (1472 °F) or so, but keep below 1000 °C (1832 °F) to avoid melting the gold.

Most of the latter ingredients aren't really needed but add mystery and make you appear more important, allowing to charge a higher fee. However, a little mystery is still associated with the process. It will work - it is just not very clear how, exactly, AgCl is formed by a reaction with NaCl. It is not so easy to split NaCl, and there is a heated debate in chemist circles of what kind of reactions really occur.

- Whatever happens, in the end you have relatively pure gold and some silver compound akin to a silver mineral that is contained in the remaining dross. Feed that stuff into a suitable smelter and you regain the silver. What you also have is a considerable reduction in the weight of your gold since the silver contained in the original "gold" is now somewhere else. This caused a lot of concern in ancient treasuries.

## 2. Gold Refining

**Base metals** can be easily *oxidized* - in contrast to gold or other noble metals. That is the basic property employed to separate gold (and other noble metals) from base metals. In antiquity and for a few thousand years after that, this was done in a tricky process called **cupellation**.

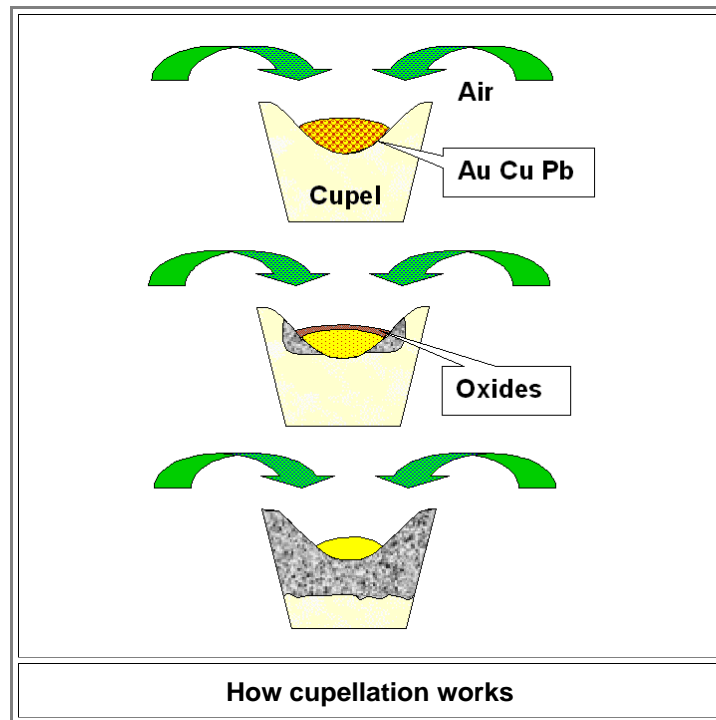
The problem is that just heating your impure or debased noble metal in air won't do the trick. The oxygen of the air would like to oxidize the base metals but can't get to them because they are inside a solid. You need to add lead (Pb). All noble metals dissolve readily in lead, so when you *heat up* the mix the lead melts rather quickly and dissolves the rest. Moreover the lead and the base metals, now dissolved in the liquid, oxidize readily if air /oxygen is available. In particular lead oxide (PbO) called **litharge** readily forms and that helps to oxidize the rest. The metal oxides are either dissolved in the lead oxide, evaporate, or form a kind of slag or dross on the much denser liquid, making removal possible.

- It remains to get rid of the lead oxide plus whatever it contains. Now you need the **cupel**, a "little cup" that named the process and in which you do all the processing. It must be made from a porous material that absorbs lead oxide (and the other oxides and whatever else is dissolved in the lead oxide) but *not* the molten noble metals. It also shouldn't react with the litharge, and that excludes most silicate-based "clays" typically used for pottery. There are many ways to make a suitable cupel, simply take magnesia (Magnesium oxide; MgO) for example. The ancients didn't have that, so they went for *adder's fork and blind-worm's sting, lizard's leg and owlet's wing*, or more

prosaically for bone ashes, fish spines or burnt horn, ground into a powder, mixed with a binder, shaped, and fired. That worked if everything was done [just right](#).

The lead oxide dispersed in the cupel will also contain some of the base metal oxides and traces of the noble metal (gold in our case), and this mixture is then called "gold litharge". The cupel soaks up the litharge (and some of the noble metal if you are not careful) and eventually you are left with the pure noble metal, gold in our case.

Here is a schematic rendering of what happened



What exactly is going on in cupellation is rather complex chemistry. When cupellation was first used or invented back in the third millennium BC, the chemistry background of the ancient practitioners was just a little bit better than that of the average contemporary American: very close to zero. Nevertheless, cupellation worked and developed into a fine empirical art during the next 4000 years or so until other (and better) methods took over.

- Cupellation was also used for *assaying*, the art of judging purity and composition of some metals or ores. Then it was done with small specimens on a small scale. Archaeologists on occasion find old cupels soaked with litharge. Analyzing those finds allow to get a good idea of what kind of metals were cupellated in antiquity.

### Working Gold

Now we have some gold - native or pure - and need to work with it. It's always dust or small pieces, so the first thing to do is compacting. Melting and casting - point 3 on our [list above](#) - is the obvious way to do this, but not necessarily the easy way.

Hammer welding, if possible at all, won't work for obvious reasons (try to hammer fine dust into shape!). So [powder metallurgy](#) comes to mind. Glue the dust together with a little binder (wood resin or honey, for example), pour the paste into a form, and heat it for a while at moderate temperatures of a few hundred °C, burning of the binder and sintering together the gold particles. That is what was done in early gold working, and the work of Ch. Raub [1](#) must be mentioned in this context.

- It's easy to distinguish between cast and sintered gold. Cast gold shows the typical [dendrite structures](#) whereas sintered gold looks more like an ensemble of particles, see below. There are just not many pictures around, probably because the self-proclaimed owners of gold artifacts - museum curators - are loath to loan their priced possession to ruthless scientists who might take them apart.



**Microstructure of sintered (left) and cast (right) gold**

Source: Maria Filomena Guerra and Thomas Calligaro: "Gold cultural heritage objects: a review of studies of provenance and manufacturing technologies" *Meas. Sci. Technol.* 14 (2003) p.1527–1537 but going back to Ch. Raub's work [1](#)

- ▶ I do not need to go deeply into melting and casting; I covered that for copper and so on in [some detail](#). By the time gold became popular - around 4500 BC - [pyrotechnology](#) was advanced enough to allow simple casting. The only problem with gold was (and is) that the stuff is precious. You typically don't get to melt large amounts of it and thus you can only cast small solid objects. You can cast large objects with little material if you make them hollow or generally thin-walled. The thinner the better, because you get large surfaces and thus a lot of gold to be seen this way. The only catch is that for casting thin-walled stuff you have to make precision molds - and that you couldn't do in 4500 BC.

  - So in the end you forge your gold objects by hammering and maybe annealing in between, just as your ancestors did with copper some [4000 years earlier](#). Look at the [first gold objects](#) unearthed so far and you can pretty much "see" it.
- ▶ If you can melt pure gold, you can make alloys with all the other metals that have a lower or comparable melting point. The melting point of the alloy then will [tend to be lower](#) than the melting point of the metals involved and you have no problem. As I stated in the link, this is a basic property of almost all alloys for very basic thermodynamic reasons called "[entropy](#)". However, the "*almost all*" refers to the few cases where metals are fully miscible, i.e. can be mixed in any proportion without changing the fundamental structure. In a gold (Au) - platinum (Pt) alloy, for example, you have a simple fcc type crystal with either gold or platinum atoms at the lattice points, randomly occupying the available sites according to their concentration. The effect is that the melting point of gold alloyed with some platinum actually goes up!

  - What that means is that you may run into problems with alloying if you mess around with platinum - as the early South-Americans did. They found ways to deal with the problem but I won't go into that here.
- ▶ If you take all the techniques and tricks from above, add a few more (like wire making, soldering, and making filigree (look it up yourself)) we are discussing **gold smithing**, an ancient craft or art, still very much appreciated by all and sundry. Look at your Fabergé egg to appreciate this. If you don't have one, send me large amounts of money and I will send you one or something else.





Master pieces (one from a goldsmith)



Detail from above

Source: Museum in Goslar / Germany; "Bergkanne" from 1477.

### Specialties

Gold is an extraordinary material with a lot of special or unique properties - and no technical uses to speak of. Where it might be of some interest - electrical contacts, for example - it is simply too expensive for large scale uses. Take platinum as counter-example. It is just as noble and expensive as gold but whole branches of industry would collapse without it (find out for yourself why). Even silver is technologically far more important than gold; not to mention copper or the "base metals" iron and aluminum.

Yet gold has some special properties worthwhile to mention.

#### 1. Gold leaf

Pure gold, or gold alloyed somewhat with other noble metals, is not only rather soft but also extremely malleable. You can easily shape a "nugget" with a hammer, for example into a thin sheet. Not just thin but ultra-thin - like  $0.1 \mu\text{m}$  or  $100 \text{ nm}$ ! A little piece, about the size of a lentil bean can be beaten into a foil half a square meter in size!

I'm not saying it is easy. It is rather tricky - look it up. But now you can cover large things with goldfoil by gluing it on, also not too simple but possible. This is one way for **gilding** things. You can't get more luster out of something expensive.

You can also use gold leaf to cover a Hamburger if you like junkfood but find it too common because it is too cheap. Gold leaf is edible and not poisonous. Or you put it into liquor. I'm not making this up.

You just can't do anything really useful with it.

## 2. Nanogold

Make some gold dust with really small-sized particles - 100 nanometer at most - and embed them in ordinary glass. Bingo! You have created stained glass with a deep red color as shown below:



**Stained glass from the 12th century or earlier**

Source: Museum in Goslar / Germany.

Actually you haven't; at least not for the example show above. Nevertheless, gold nanoparticles of the right size that are embedded in a transparent medium make for vivid colors. So do nanoparticle of other metals. What kind of color exactly, and how that depends on all the variables of the system - kind of metals, size, shape and density of the particles, nature of the host material - you definitely don't want to know if you are not conversant in quantum mechanics and advanced solid state physics.

The fact is that ancient craftsmen did somehow manage to produce glass containing metal nanoparticles, producing some color effects that we only understood recently, with the advent of nanotechnology and things like "plasmonics". Here is an example:



**Lycurgus cup; illuminated from the outside and the inside**

[Large picture](#)

Source: British Museum; free image service.

The famous Lycurgus cup was probably made in Rome in the fourth century AD. It was a rare masterpiece and not everyday Roman glassware - and it made use of silver-gold alloy nanoparticles! Actually, a lot of color on ceramics or in stained glass and so on comes from "nanotechnology".

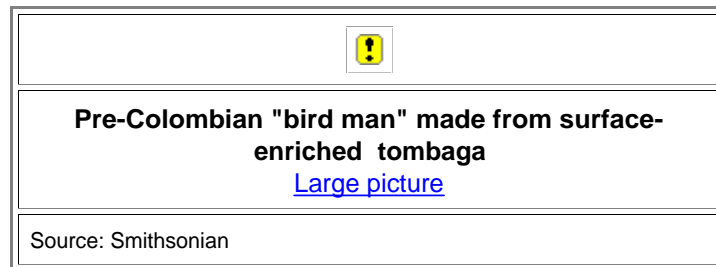
I won't go into how one makes nanoparticles and embeds them in glass or the glazes of certain ceramics. I'm just saying that there is a rich field that was ploughed in the past with some good results and no understanding whatsoever. Now we do understand, and the results are often amazing if not recognized by the public at large. If you don't believe me, I'm sentencing you to read [this book 2](#).

### 3. Nanocheating

If you dilute your gold with a lot of copper, you can make sizeable objects for less money compared to pure gold. Unfortunately the [color](#) changes from "gold" to "rose" or "reddish". You can plate or gild your contraptions (for example a coin) with pure gold if you know how to do this, but you can also employ nanotechnology to do your cheating. All you need to do is to remove the copper (or silver if you are a more stylish cheater) from a surface layer of your cheap alloy. What's left is nanoporous pure gold that looks nice and golden.

The technique is also called "surface enrichment" or "depletion gilding" and has been practiced for more than 2000 years. Just throw your alloy in some suitable chemistry along the [lines](#) of: *scale of dragon, tooth of wolf, Witches' mummy, maw and gulf Of the ravin'd salt-sea shark, Root of hemlock digg'd i' the dark, Liver of blaspheming Jew, Gall of goat, and slips of yew*. Nitric acid also works. Or ammonium carbonate (the stuff in smelling salts) soaked in urine. The pre-Colombian cultures of Central and South America also knew the technique; they used it on a large scale, in fact.

- One of their favored materials was a gold-copper alloy with up to 70 % copper known as "**tumbaga**", not to be mixed up with "tombak" which is a kind of brass or copper-zinc alloy. It has a significantly lower melting point than gold or copper alone, is harder than copper but still easily forged. Heat it a bit, oxidizing the surface-near copper, and etch out the oxide with fruit juice (= citric acide and the like). Repeat until satisfied. What you get looks rather convincing:



Enough about gold now. If you send me some, I will do some scientific investigations with it (like how it can be used to make that woman up there look even better). I'll let you know the results.

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<sup>1)</sup> Raub Ch 1995 The metallurgy of gold and silver in prehistoric times Prehistoric Gold in Europe (NATO ASI Series vol 280) ed G Morteani and J P

<sup>2)</sup> V. Kochergin, H. Föll: "Porous Semiconductors: Optical Properties and Applications", Springer 2009