SMELTING SILVER

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Catherine M. Helm-Clark, Ph.D.

Summary

This project attempted to reproduce the lead reduction method of smelting silver, as is described in classical, medieval and renaissance sources on pyrometalurgy. The lead reduction smelting process involves two-steps: a fusion of the ore material with lead in a carbon-rich environment, followed by the separation of silver from the lead in an oxygen-rich environment. Period metallurgists used a variety of fluxes, elevated temperatures, and the principle of separation by density to achieve a final product of relatively pure silver.

The silver produced for this project was made by following the medieval smelting instructions, albeit using smaller quantities than a full-scale period smelting facility. A few modern substitutions were necessary in order to accommodate the furnaces available for this project, namely flour as a substitute for charcoal as a source of carbon, and natural gas or electricity as substitutes for charcoal as a fuel. All the furnaces used in this project were modern, since landlords take a dim view of building smelting furnaces in the middle of the apartment living room. Approximately a half pound of rock was smelted for a total yield of 4 milligrams of silver.

The Sources

There are four primary sources used for this study, **Pliny the Elder's** *Natural History*, **Theophilus's** *De Diversis Artibus*, **Biringuccio's** *Pirotechnia*, **and most importantly, Agricola's** *De Re Metallica*.   Agricola, Biringuccio, and Theophrastus are all available from Dover. The complete Pliny[1] is available as a ten volume set from Harvard University Press.

Pliny is the logical starting place for most inquiries into medieval material science since he was one of the most-frequently consulted sources in the middle ages. Both Biringuccio and Agricola quote him at length. Pliny wasn't the first to describe lead-reduction smelting, but his popularity with medieval metallurgists makes him the most important classical source.

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[1] The Penguin Classics abridgement of Pliny suffers from translation problems in name choices for minerals and other earth materials. I can't recommend its use for this reason.

Theophilus's description of cupellation (the second step in the smelting process) is the clearest of all the available primary sources, despite the fact that he's explaining how to refine silver for silversmithing. This is the consequence of a rather subtle fact, namely that refining silver is identical to the cupellation of silver for assay, which in turn is identical to the parting of silver and lead in the lead reduction smelting process. The only difference between these three things is one of scale. To quote Agricola (pp. 220-223):

> "The method of assaying ore used by mining people, differs from smelting only by the small amount of material used…. Both processes, however, are carried out in the same way, for just as we assay ore in a little furnace, so do we smelt it in the large furnace."

First, Take a Thousand Pennyweight of Rock
The very first item neede to smelt silver is some silver ore.[2]   I found my ore at the inactive Silverado silver mine, which is in a state park just north of Calistoga Hot Springs, CA. (Yes, I had a collecting permit.)

In Chapter 3 of De Re Metallica, Agricola describes how the live juices in the earth travel and then solidify near the surface to form *venae profounda,* enriched in ore-bearing minerals. In modern terms, many of Agricola's *vena profundae* are what we would call lode quartz or vein quartz deposits. The picture to the left was taken from the foot wall of the Silverado quartz vein, looking down ~150 ft to the base of the cut. The width of the dirt at base of the cut is approximately 30 ft. Before mining, the richest part of the quartz vein filled all of the cut seen in the photo. Most of this lode quartz vein was removed by 1875, but the miners at the time were "high-grading," and they left lower grades of ore in place. Since the mine is now part of a park, no one has attempted to go back and mine the rest of the deposit. These circumstances are responsible for preserving this Agricola-style *vena profunda* with silver ore rich enough to smelt using 15th to 16th century **methods.**
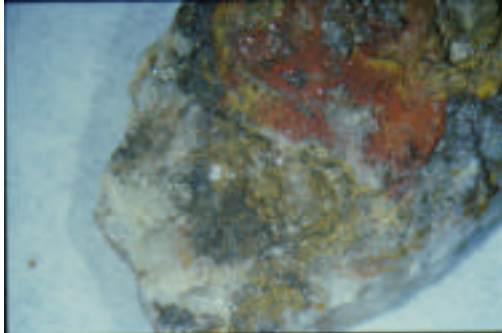

The Silverado Mine

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[2] "Ore" here is in a general sense, and not in the specialized sense used in mining.

You need quartz with at least 10 parts per million silver in order to smelt it using pre-modern techniques. This number was derived by comparing silver yields from smelting with silver concentrations determined by x-ray fluorescence and atomic adsorption (Enderlin, 1993; Helm, 2000).

Samples came from the Silverado Mine and its environs. These were crushed by hand in an iron mortar. Historically, a variety of crushing techniques were available, including high-volume stamp mills, horse-driven rotary mills and hand grinding (Agricola, p. 319). For the relatively small amounts used in this study, buying a horse or building an iron-shoed, water-driven stamp mill seemed a bit like overkill, especially since a mortar and pestle would suffice.

Agricola (Chap. 8) and Biringuccio (pp. 141-142) discusses washing and roasting the ore prior to smelting, particularly for lower grades of ore. Biringuccio does not discuss why roasting can improve a marginal ore. The more verbose Agricola (p. 273) explains that roasting can soften the ore prior to crushing, and will drive off undesirable sulfur[3] and hydrocarbons.[4]

Washing the ore is more straight-forward: it dissolves all soluble salts[5] and many clays, most of which are unwelcome contaminants during smelting. Since silver minerals are relatively dense, they sink to the bottom of the bath. The dissolved salts and clays are then removed by pouring off the wash water. This cycle is repeated until the water is clear. The rocks collected from the Silverado mine are mainly quartz, with traces of native silver, silver sulfide, iron sulfide, and iron oxyhydroxide hydrates. I guessed that the sulfides and iron minerals were not abundant enough to justify roasting, so the only thing I did to prep my ore was to wash and crush it.

Quartz from the mine; bright spot near the center is native silver. Field of view is 1 cm.

Furnace Design
Once the ore has been mined and crushed to a powder, it is placed in a furnace to be fused along with lead and/or litharge (PbO), charcoal, and fluxes. The furnace itself is made of materials resistant to high temperatures like :

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3 Most precious metal deposits are rich in sulfide minerals, Roasting converts these sulfides to smelting-friendly oxides.

[4] **Tarry hydrocarbons are found** in **many types of ore deposits.**

[5] In the middle ages and the early modern period, the term salt referred a whole class of substances including alum, sal ammoniac, sal alkali, and modern table salt among others.

"certain infusible stones" which "resist fire very well, such as black flintstone flecked in white, or peperino, or a certain dead stratified stone that is almost half talc…for otherwise the violent, continuous, and long fires eat them and cause great expense to the patron and much annoyance and work to the laborers" (Biringuccio, pp. 146-147).

Agricola is much more detailed than this, and takes several chapters to discuss furnace design and construction.

Overall, however, there are only a few salient points worth mentioning about furnaces for the fusion step: they use fire-resistant materials in their construction, they are fired with charcoal, and there are means to provide a draft. The draft is needed to achieve a high-enough temperature to melt the silicates in the ore (1450° to 2000°C). The need for fire-resistant materials should be obvious. Using charcoal not only insures that the fire will be hot enough, it also insures that there is sufficient excess carbon available to reduce all the oxides in the furnace.

Small furnace from De Re Metallica

Any furnace we use must provide these things: sufficient heat to melt silicates, and sufficient carbon to reduce oxides. Initially, the furnaces used for this project were two natural gas-fired assay furnaces belonging to Sierra College in Rocklyn, CA. I later rebuilt a small electric muffle furnace someone was throwing out and installed it in a fume hood at my lab. Building a small charcoal-fired furnace for fusions was never an option, since city apartments are not great places for pyrometallurgy.

Natural gas furnace at the assay lab at Sierra College

Using an assay furnace is not really a substitution since, as Agricola pointed out (p. 220), the only difference between assay and smelting is one of scale. The heat

sources used here do differ, however, with natural gas in Sierra College's furnace, and electicity in my rebuilt muffle furnace.

Fluxes

> I have decided to explain those things which mining people call fluxes because they are added to ores not only for assaying, but also for smelting.
> (Agricola, p. 232)

All silver ores need to be fluxed for smelting.[6] In Pliny's day, when almost all the ore smelted was high-grade, the addition of lead or lead ore (galena, PbS) was sufficient for fluxing (book XXXIII, sec. XXXI). By the time that Biringuccio and Agricola are writing in the 16th century, the art of fluxing has advanced in complexity but not in clarity. Biringuccio suggests nothing better than a trial-and-error approach to find the right flux[7] recipe for any given ore (pp. 143-144). Agricola, on the other hand, has a set recipe for fluxing silver ore (p. 244). If the simple addition of lead is not sufficient to melt the ore, then he suggests adding "powder of the first order of fluxes" until everything melts in the crucible. Agricola's first order of fluxes (pp. 232-234) include litharge (PbO), galena (PbS),

furnace slags (mostly amorphous silica), soda (sodium bicarbonate), saltpeter (KNO3), burnt alum (anhydrous alkaline aluminum sulfates), vitriol (iron, copper or zinc sulfate hydrates), salt (NaCl), sand (SiO2 source) and soft tophus[8] (CaCO3).

Litharge and soda being measured into a crucible

I find it very interesting that borax is missing from Agricola's list. Agricola, Biringuccio and Theophilus all discuss it as a flux to aid the melting of precious metals in contexts other than silver smelting. Agricola mentions borax (p. 247) for the assay of lead minerals.[9] Biringuccio included it in his general list of fluxes (p. 143). Considering that borax was a well-known flux in period, I think it's reasonable that it was used in the fusion step for smelting silver.

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[6] For sufficiently pure silver and gold in quartz, amalgamating with mercury was preferred over smelting. Pliny mistakenly believed that amalgamation worked only for refining gold (book XXXIII, sec. XXXII). Neither Theophilus nor Agricola mention Ag/Hg amalgams, but Biringuccio describes amalgamation in detail (pp. 142-143).

[7] Both Agricola and Biringuccio use the term flux in a much broader sense than the modern definition of an additive used to reduce melting temperature.

[8] Hoover and Hoover (1912, p. 233) opine that tophus is probably tufaceous limestone.

I determined my flux mix using basic inorganic chemistry and trial-and-error.[10]

The Reduction and Fusion of Lead and Ore

> "In the crucible where metals are tested, be they gold,
> silver, copper or lead, they are mixed in precisely the
> same way as they are mixed in the blast furnace when
> they are smelted" (Agricola, p. 222)

For large amounts of ore, fusion takes place in the blast furnace. For small amounts of ore, fusion takes place in a crucible inside a small furnace. The only difference between the two is one of scale.

Melted ore and fluxes boiling in the crucible
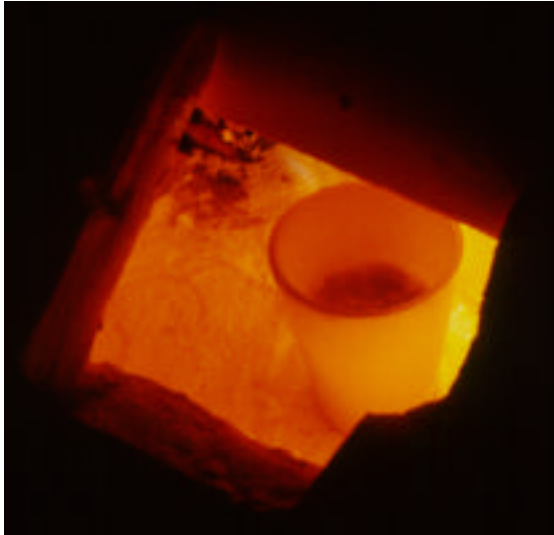
As mentioned earlier, high temperatures and excess carbon are indispensable for period silver smelting. In a furnace fired by natural gas, the heat source provides no excess carbon to bond the oxygen. The fusion will not succeed if there is insufficient carbon available. The way around this is to add a carbon source to the fluxes. I used flour as my carbon source, though any solid organic material such as wood chips will serve. Flour has the virtue of already being a powder, so no further preparation of a carbon source is required. Agricola (p. 245) and Biringuccio (p. 139) used coal or charcoal placed inside the crucible. In general, flour is easier to find and cheaper to buy than true charcoal.[11]

Liquid lead is an extremely efficient scavenger of other metals, especially silver and gold. As the melted lead trickles through the molten slag, it picks up noble

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[9] Borax was commonly called chrysocolla in period since chrysocolla was any mineral used to solder gold. Period chrysocolla includes the modern mineral chrysocolla, malachite, chalcanthite, and borax among others (Hoover and Hoover, p. 560).

[10] My final recipe used 15 grams of ore, 36 grams litharge, 5 grams flour, 15 grams soda, 10 grams anhydrous borax and 30 grams silicate sand. In the furnace, litharge is reduced to melted lead. The sand and ore are reduced to molten slag. The sand also increases the viscosity of the slag, which makes density separation at the end of the fusion easier. Soda is completely soluble in the slag, where it counteracts the acidic nature of the silicates; if the acidity of the slag is not neutralized, then some of the silver may be trapped in the slag. Borax lowers the melting temperature of the silver. Flour prevents oxidization by providing carbon to react the liberated oxygen to make CO and CO_2.

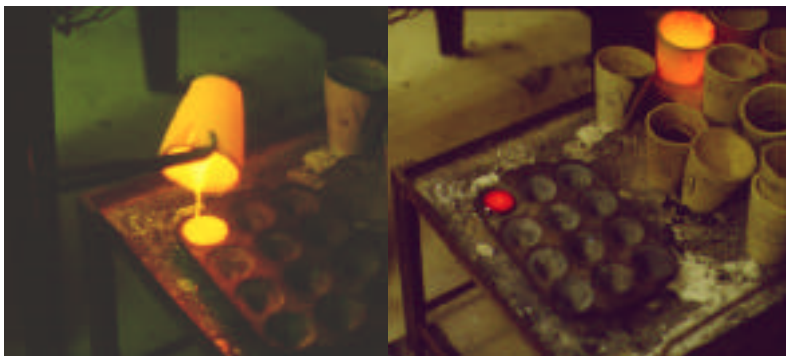[11] Using flour is not my idea. Most modern assay labs use flour as a carbon source.

metals in its downward path to the bottom of the furnace or crucible, stripping the slag of its metal content. The combination of heat and high-carbon insures all the oxides, sulfides and silicates in the mix are chemically reduced. If a reducing environment is not achieved in the mix of ore and fluxes, then the lead would oxidize to litharge, preventing it from scavenging noble metals from the slag.

Separation by Density

> "pour out the metal in a liquid state, or, when it has cooled, break the crucible and clean the metal from slag; and in the same way the smetler, as soon as the metal flows from the furnace into the forehearth, pours in cold water and takes the slag from the metal with a hooked bar." (Agricola, pp. 222-223)

During the fusion, as the lead and precious metals sink to the bottom, the less-dense slag floats on top. In a blast furnace, the smelter would poke a tap hole into the side of the furnace to drain off the slag. Once most of the slag had been removed by density separation (much like skimming fat scum off the top of homemade chicken soap), the metals in the bottom of the furnace were then tapped, and allowed to collect in a "forehearth" at the exterior foot of the furnace. The now-argentiferous[12] melted lead was poured into a mold (Agricola, pp. 282-283) in preparation for the next step in the smelting process.

If the fusion is confined to a crucible, the contents can be poured into a mold. If the slag is sufficiently viscous, the denser and more-fluid metal will flow out of the crucible first and collect in the bottom of the mold. Once the poured material cools off, the argentiferrous lead can be separated from the slag using a hammer or mallet. In mining, the post-fusion argentiferrous lead is called a button.

Pouring the crucible contents into a mold

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[12] This is an assumption since we don't really know yet if the lead picked up any silver.
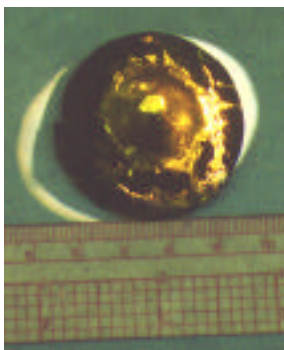
The photo to the left demonstrates what can happen if the slag is not viscous enough. Some of the metal did not collect in the button, but is trapped within the slag

The photo to the right shows two buttons separated from their slag. The button to the left of the hammer has been shaped into a cube, making it easier to insert into a cupel. The button to the right of the hammer has not been shaped

Cupellation: Parting Lead and Silver by Controlled Oxidation

In a furnace whose contents can be isolated from sources of carbon, the buttons and cakes of argentiferrous lead are placed in porous containers called cupels, or placed on a thick porous "cupellation" hearth, respectively.[13] The cupels and the porous hearth are made of ashes mixed with water and compacted (Biringuccio, p. 159; Theophilus, p. 96). The ashes are sometimes mixed with other materials
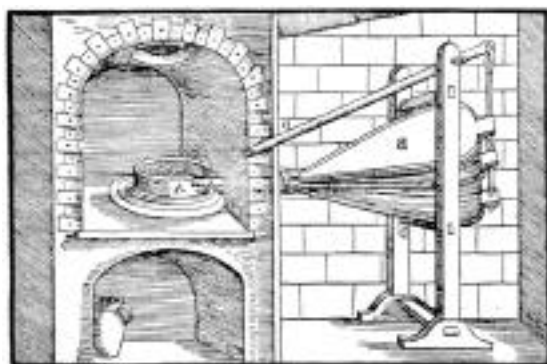

in order to improve cohesion or hardness in the cupels or hearth (Biringuccio, p. 162). Agricola, true to form, takes more than 10 pages to discuss the making of cupels and the sorts of ashes to use. He also states his own preference for boneash (p. 230). Biringuccio prefers to use wood ash left over from doing the laundry (p. 162). Theophilus doesn't specify what flavor of ashes to use.

*Cupellation furnace with an iron ring to separate the argentiferrous lead from the charcoal*

No one sells boneash cupels. Modern assay labs use cupels made out of magnesium oxide, which are superior in every way except in price. I made my own cupels out of boneash with a small amount of mortar added to improve cohesion. The mold I used was scavenged from an abandoned gold mine in the

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[13] Archeological research in the last two decades seems to indicate that boneash cupels and hearths were actually uncommon prior to the 16th century, and that a variety of porous ceramics were used instead for small volume cupellation. This seems a little problematic to me in light of Theophilus's instructions to use ashes for cupellation, but try and tell an archeologist that… (Bayley, 1995, p. 1)

California Mother Lode, which resembles the molds shown by Biringuccio (p. 138) and Agricola (p. 231) closely. Even with the addition of mortar, however, most boneash cupels fall apart when kept for more than two years. I have made over 50 cupels by hand; the last survivor crumbled to powder in 1999.
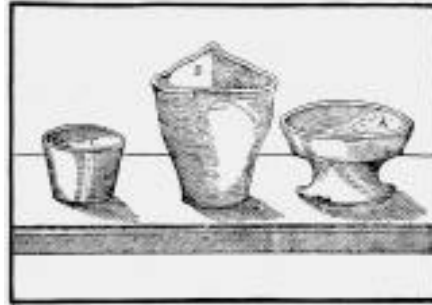
A cupel, a crucible, and a scorifier (not discussed here) from De Re Metallica
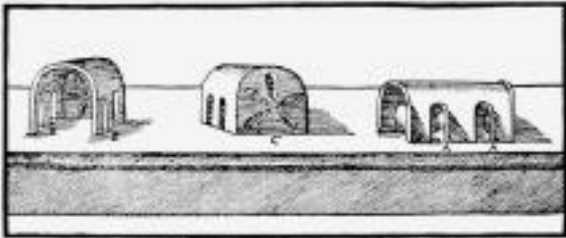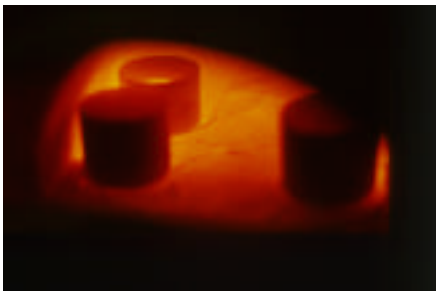

Removable muffles

Cupellation takes place either in a muffle or on a cupellation hearth. For an assay furnace, a muffle is traditionally arched like a miniture portable quonset hut, which can be inserted or taken out of the furnace as needed. Its sole function is to prevent the carbon from the fuel source from reacting with the contents of the muffle. A fixed furnace which is heated by, but isolated from the fuel source, is usually referred to as a cupellation or muffle furnace Most of the cupellation for this study happened inside the muffle furnaces at Sierra College.

Once the furnace is up to temperature (~900°C), the argentiferrous lead is placed in a cupel or on the cupellation hearth. Since lead is a base metal, in the presence of heat and oxygen (but not carbon), it will


Muffle furnace isolated from the reducing conditions underneath

oxidize to red or yellow litharge. This litharge will be in the liquid state due to the elevated temperature of the furnace, and will be adsorbed by the porous cupel or hearth. The temperatures needed to melt lead and litharge

Cupel with melted lead in the muffle

A cupel just out of the muffle furnace. The staining on the left side of the cupel is adsorbed litharge

are not sufficient to melt silver. When all the lead is converted to PbO and adsorbed by the cupel, the only solid left in the cupel or on the cupellation hearth is the silver. The mining term for the round bit of precious metal left at the end of cupellation is a doré..
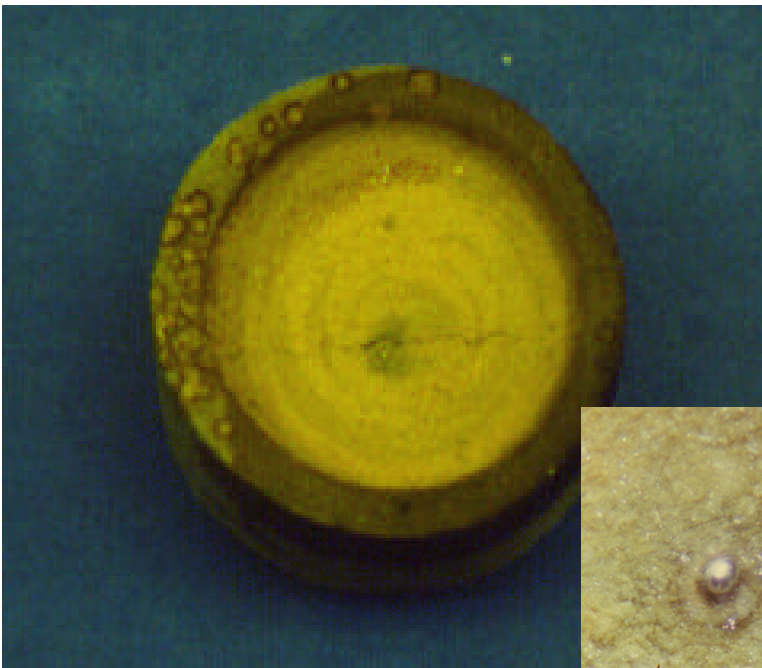
To the left is a photo of a cupel after all the lead has been oxidized to PbO and adsorbed. The yellow color is from the litharge. The spots on the left rim are from spattering by impurities during the cupellation (probably arsenic). In the middle of the cupel is a grey spot, and in the middle of that is a bright speck which is the silver doré. The inset photo is a blow-up of the doré.
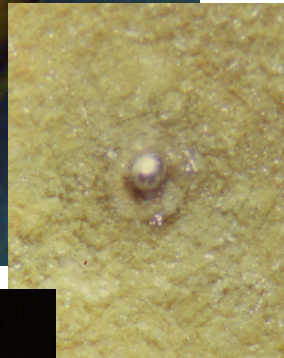
When the lead initially melts in the oxygen-rich atmosphere of the muffle, it may immediately form a crust of litharge (PbO) if the temperature isn't high enough. Crust formation will effectively stop the smelting process since any liquid lead under the crust is now isolated from the oxygen

Wood chip in cupel to aid melting

draft. Theophilus's (p. 97) trick of adding a small piece of charcoal on top of the lead will temporarily create a reducing environment, discouraging the formation of a litharge crust and promoting melting (p. 97).

Stuff I Skipped

Silver vs. Gold
The process described here for smelting silver is the same as for gold. Most silver contains a little gold, and most gold contains a little silver. At the Silverado mine, the ratio of silver to gold is 74:1 (Enderlin, 1993). If the proportion of gold were higher, it would be worthwhile to part the silver and gold. There are a number of ways to do this, but we will confine ourselves here to a method most people are familiar with, i.e. parting with nitric acid. Agricola (pp. 443-445) calls his nitric acid *aqua valens*, whereas Biringuccio (pp. 190-200) prefers the term *aqua fortis*. The terminology for period acids is actually quite confused, and it is usually necessary to look at the original recipes to determine what sort of acid is being produced (Hoover and Hoover, pp. 441-444).   Gold is impervious to dissolution by nitric acid, whereas silver is not. By placing the doré in nitric acid, the silver goes into solution and the gold stays behind. The silver is later recovered from the acid by precipitation in the presence of elemental copper.

How Much Rock?
Volumes can be deceiving when working with rocks. A softball-sized piece of quartz weighs approximately four pounds (slightly less than 2 kilos). A bowling ball made of quartz would break your arm. The amounts smelted for this project were much smaller, though after hand crushing all the rocks, it seems like a whole lot more. The small pill vial with the grey powder in it (see display) is 15 grams of crushed quartz from the Silverado mine. It's grey because of small amounts of other minerals mixed in with the quartz (e.g., iron oxyhydroxides, silver sulfide, silver chloride, pyrite, etc.). If this sample were smelted, it would yield approximately 1 milligram of silver.

How much is one milligram of silver? The flattened doré in the septum bottle (see display) weighs 1.08 milligrams. This is marginal ore by period standards, where precious metal contents were measured in parts per hundred or thousand (Hoover and Hoover, p. 242). By modern measures, the silver concentration in the crushed quartz on display is ~75 parts per million, or 2.2 troy ounces per short ton. If this were gold, we'd be in business. Since this is silver, it's not worth the cost of mining and smelting. If silver is valued at 5 dollar per troy oz., a reasonable average price for the last 10 years, then the ~1 mg of silver in the bottle on display has a value of approximately 16 thousandths of a cent.

A total of fifteen batches of rock were smelted, not counting failures while finding a flux recipe that worked. The average yield for each smelting batch was 0.25 milligrams of silver. The input for each smelting batch was 14.7 grams. There are 31.1 grams in a troy oz. To accumulate 1 troy oz., therefore, would take 124414 smelting batches using the small assay furnaces, where each smelting charge was 14.7 gm of rock. The total amount of ore to get 1 troy oz. would be 1829 kg, which is 4024 ordinary English-system pounds. The volume of this rock is 0.684 cubic meters, which is approximately slightly more than two thirds of a cubic yard. This is about the size of your average domestic dishwashing machine. (I was going to say that this was approximately the size of your average dishwasher, but if my dishwasher thought I was accusing him of gaining that much weight, I'd be doing my own dishes in short order…)

Old Used Clichés: DON'T DO THIS AT HOME

There were at least four different ways of getting silver out of rocks by the 16th century. The two most prevalent methods were the lead reduction process recreated here, and the mercury amalgam process, which not even I am nuts enough to try.

The problem with the lead reduction method is the lead. Everyone has a clue these days that lead paint and lead pigment used to make that paint are not things we want around anymore. What many do not realize is that lead fumes liberated by heat sources are just as bad or worse. Note the chimney on the furnace in the photo. Both the lower chamber and the muffle on the furnace are vented. There are venting pathways built into the fire brick which line the furnace. The draft for pulling the lead fumes out of the furnace and up the chimney is a gigantic squirrel-cage fan the size of a VW bug on the roof of the lab building at Sierra College.

When I moved to St. Louis and rebuilt the small electric muffle furnace, I installed it into a fume hood in the lab where I worked. I managed to finish four batches of fusions and

cupellations in the electric furnace, and then it died. Despite the fact that the resistance element was embedded in the ceramic lining of the rebuilt furnace, the lead fumes were sufficiently corrosive to eat the element and short it out (the manufacturer of the element concurred after I shipped them the element for inspection). The manufacturer said they had never intended their heating elements to be used in the presence of corrosive atmospheres, like acids or lead fumes. Furthermore, they would never recommend any electric element, whether protected by embedding or otherwise, to be used in an application which liberated lead fumes. They also suggested that I check the dust catcher for fan attached to my fume hood, wherein I found a bright yellow layer of PbO.

Oxidizing the lead back to litharge liberates a lot of lead fumes, which then precipitate and/or coat most of the surfaces inside the furnaces to the bright yellow seen on the cupels and around the rim of the muffle shown on page 11.

While it is certainly possible to build my own furnaces for smelting in the manner suggested by Theophilus, Agricola, and Biringuccio, there really isn't any decent way to contain the lead fumes safely without a well-designed ventilation and dust catchment system. I did my silver project in geochemical labs with good safety equipment. It never even crossed my mind to attempt this project without such precautions.

Interesting ramblings not necessary for this documentation:
The crucible on the left was used three times before I retired it. Note the dark line that the arrow points at. Also note that the ceramic below the line is a lighter color than above the

line. That's because the reduction of litharge to melted elemental lead is a corrosive process and it eats the crucible.
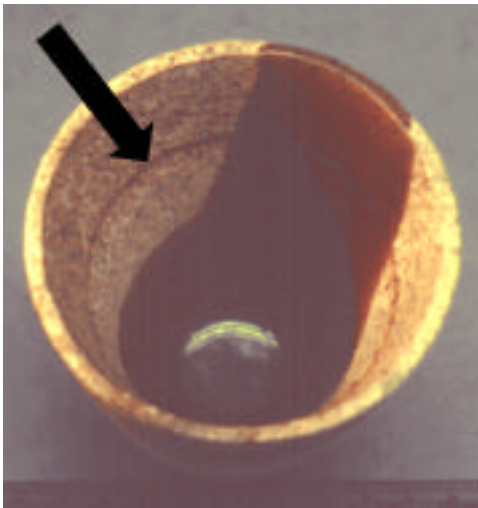
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Pliny the Elder, *Natural History : A Selection*, trans. By Healy, J. F., 1991, Penguin USA, 399 pp., ISBN: 0140444130. [This is the edition I DON'T recommend, due to bad word choices in the translation in the sections covering mining and minerals]

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