Pursuing a Silver Standard for Sustainability

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INTRODUCTION

Silver is one of a handful of elements that has been known since antiquity. Mined by various civilizations since ca. 3000 BC (The Silver Institute, 2018), it has been used for many purposes including jewelry, medicine, clothing, tableware, art, solder, photography, and coinage. Perhaps because it has been part of our history for so long, it occupies a mostly unnoticed corner of people's lives—when they casually fasten a necklace around their neck or handle an old photograph to scan it into a digital existence. And yet, silver has arguably changed the course of history and made possible new technologies that come to permeate our everyday lives. As we have extracted silver from the earth, we have set in motion a new path for each atom through our surface environs and altered the available resource stock from which the trappings of civilization are built. But is our history with silver indicative of our future with this natural resource? Can we continue the present relationship indefinitely, and if not, how must it change?

PART I: MONEY MAKES THE WORLD GO 'ROUND

> *"We will now speak of metals, the very source of wealth and the prices paid for things, which diligent care seeks out within the earth in various ways. For indeed, in some places the earth is dug for wealth, when the way of life demands gold, silver, electrum, copper, and in other places for luxuries, when gems are wanted, and colours for painting on walls and timbers. Still elsewhere the earth is dug for the sake of rash boldness, when iron is wanted, which in the midst of wars and slaughter is more in demand even than gold. We search through earth's inner parts and live above the excavated hollows, astonished that she sometimes splits open or begins to shake, as if, in truth, this might not possibly be an expression of our sacred parent's indignation." -Pliny, Natural History 33.1-3 in* (Humphrey, 1998).

Acquiring metals means doing chemistry. Most metal deposits occur as minerals, in which metals are combined with oxygen, sulfur, and other elements from which they must be separated. Extractive metallurgy arose relatively early in human history, with evidence for smelting dating from the 6th millennium BC (Wertime, 1964). Limited metal working occurred before this time with metals found in their native form, such as gold. Silver, however, rarely occurs as a native metal and is more often encountered as a sulfide (Enghag, 2004). Ancient metal workers learned to separate silver from lead sulfide ores using cupellation, a process known since ca. 2500 BC. Still used today, cupellation involved heating the ore with a blast of air in a porous cup made of bone ash, called a cupel. Metals such as lead and iron are oxidized and absorbed into the cupel, leaving behind the noble metals silver and gold (Enghag, 2004; Weeks, 1968).

In the ancient kingdom of Lydia, sediments of the River Pactolus contained a different form of silver. There, deposits of electrum—an alloy of silver and gold—provided a source of precious metals for the first coins. These coins contained varying amounts of silver and gold, and thus the actual value of each coin could not be assured, despite the coin's face value. In the 6th century BC, under King Croesus, the Lydians learned to separate gold from silver by heating electrum with salt. Croesus subsequently issued the first pure silver and pure gold coins, increasing the currency's acceptance internationally (Browne, 2014) and driving up demand for silver (Craddock, 2009; Enghag, 2004), which, because of its lesser value, was more convenient for everyday trade (Browne, 2014).

The Wealth of Laurion

Near the end of the 6th century BC, with Athens's power ascendant, it began to mint its famous "owls", or tetradrachm coins (Browne, 2014). Their standard weight and value made them widely accepted for international trade (S. Encina, personal communication, November 8, 2017), and they served as a symbol of Greek power and influence throughout the Mediterranean (Browne, 2014). Much of the silver to produce the owls came from the mines at Laurion, some of the wealthiest known in the ancient world. The date of the earliest working of Laurion is debated; some scholars suggest that work began as early as ca. 3000 BC, while others suggest later dates of 2000-1500 BC (Shepherd, 1993). At Laurion, silver was found as argentiferous galena (silver-bearing lead sulfide), deposited during the Miocene (approximately 23-5 million years ago) (Bonsall et al., 2011) by hydrothermal fluids moving upward through interbedded layers of limestone and schist. The fluids permeated the porous limestone but slowed as they reached the much less porous schist, depositing ore at the contact between the two rock types. Thus, miners encountered several ore-bearing contacts as they worked deeper into the earth over time. Around 510 BC, the famous "third contact" was discovered (Healy, 1978; Shepherd, 1993), revealing the richest silver deposits to date and dramatically increasing silver output from the mines.

Figure 1. Laurion (Laurium) lies approximately 27 miles southeast of Athens, Greece. Map produced using Mapbox. © Mapbox © OpenStreetMap

Although mining has always been dirty and dangerous work, conditions within Laurion were abysmal. Connecting tunnels between shafts were too low to stand up in. Ventilation was so poor and the mines so hot that miners probably had to work naked. Oil lamps provided dim light and generated smoke, making it difficult to breathe (Shepherd, 1993). Slaves—as many as 20,000 at the height of production during the 5th century BC (Shepherd, 1993)—supplied the necessary labor, and the work was so difficult that most died within four to five years (Patterson, 1972).[1]

Invasion

Silver production from Laurion peaked in 483 BC—none too soon to save Athens from invasion. In 490 BC, Athens had defeated the Persians, led by Darius I, at the Battle of Marathon. Aware that Athens could be attacked again, Themistocles, an Athenian politician and general, convinced the citizens of Athens to give up their individual shares of the profit from Laurion and pour the money into building up Athens's defenses. These funds allowed the harbor at Piraeus—a port city approximately 7 miles from Athens's city center—to be completed and 200 ships constructed. In 480 BC, Darius's son Xerxes I attacked Greece, attempting to complete the subjugation that his father had failed to accomplish. The Persians were ultimately unsuccessful and with the aid of the Athenian navy and an alliance with Sparta, Xerxes was defeated at the Battle of Salamis, ensuring Athens's autonomy and its status as the most important regional power of the time (Shepherd, 1993).

Decline and Aftermath

By 150 BC, Laurion was exhausted. Extant slag heaps testify to the massive amounts of silver extracted over five centuries: around 1800 metric tons were produced between 650 and 100 BC, with approximately three-quarters of the output attributed to the 5th century BC (Patterson, 1972). Evidence of the impact of Laurion silver exists not only in the golden years of Athens and its owls, but also in the environmental degradation left behind. Pollution from mining and smelting activities is recognized in the geologic record (Nriagu, 1996). Roasting and smelting of sulfidic ores produced large amounts of sulfur dioxide (Craddock, 2009), a toxic gas now regulated as a criteria pollutant by the U.S. Environmental Protection Agency. Lead-silver ore smelting also released copious amounts of lead to the atmosphere which is documented in Greenland ice cores (McConnell et al., 2018; Rosman, Chisholm, Hong, Candelone, & Boutron, 1997). "Our sacred parent" might well have cause for indignation.

PART II: THE TWO-PERCENT SOLUTION

> *"Proponents of colloidal silver have claimed or advertised that the compound can treat or cure 650 different diseases or disease organisms; eliminate all pathogens in the human body in 6 min or less; and kill every destructive bacterial, viral, and fungal organism in the body including anthrax, Hanta, Ebola, and flesh-eating bacteria."* (Marx & Barillo, 2014)

Blue Man (No Group)

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[1] Although the Athenian state owned the mines, concessions were leased to individuals, who rented slaves from their owners. Athens itself owned no slaves, but the Greek philosopher Xenophon later suggested in his *Ways and Means* that this was a missed opportunity to earn additional money: "If my proposal were adopted, this alone would be new: just as private individuals have managed a permanent income for themselves by acquiring slaves, so also the city would acquire state-owned slaves until there were three for each Athenian citizen." In: (Humphrey, 1998)

Paul Karason was known as "the blue man." After an appearance on the Today show in 2008, Karason gained internet fame for the dramatic blue-grey color of his skin. He had been taking colloidal silver that he had produced at home. Ingesting the silver caused a condition called argyria, in which silver particles deposit in the skin and internal organs[2]. He became truly and irreversibly blue, an unfortunate side effect of his self-medication activities. Humans have no nutritional requirement for silver, but neither is silver generally toxic, except possibly in large doses. Nevertheless, some purveyors of alternative medicine tout the benefits of silver, and colloidal silver products are widely available. (Reputable sources of medical information state that colloidal silver is not safe or effective.)

A Silver Bullet for Bacteria

Claims about colloidal silver as a cure for various conditions probably relate to its well-known antimicrobial properties. Silver ion (Ag^+) is toxic to most bacteria and to algae (Marx & Barillo, 2014; Ratte, 1999). Persian kings reportedly would only drink water that had been transported in silver containers because the water would stay fresh for years (Alexander, 2009). Likewise, pioneers in North America were said to have dropped silver coins into containers of water and milk to prevent spoilage (Alexander, 2009; Barillo & Marx, 2014). Prior to the introduction of antibiotics, silver nitrate was widely used to prevent infection. In the late 19th century, obstetrician Carl Siegmund Franz Credé began treating newborns with eye drops containing 2% silver nitrate to prevent neonatal conjunctivitis. During the 20th century, burn care was revolutionized by the use of new silver compounds for treatment (Barillo & Marx, 2014), and wound dressings were significantly improved by the addition of silver compounds that reduced infection (Marx & Barillo, 2014).

Although antibiotics have largely replaced silver nitrate for fighting bacterial infection, silver has not entirely gone away. Attempts to overcome antibiotic resistance might in the future be bolstered by adding silver to antibiotic treatments, though any new medicines will have to contend with silver's potential to make patients a little blue.

PART III: DON'T SWEAT IT

In 2018, anti-odor clothing was widely available, from shirts to socks to underwear. The wearer was promised that, after a hard day at work or at the gym, he would still feel fresh and dry. Such a claim could be made because these products contain silver embedded into the fabric—often referred to as nanosilver or silver nanoparticles—which inhibits the growth of bacteria responsible for smelly gym clothes. In theory, clothes need to be washed less often, saving water and energy. However, concern has been mounting about the environmental and health effects of silver nanoparticles.

Nanoparticles are commonly defined as particles between 1-100 nanometers (nm) in size, and their use in consumer products has continually increased since 2005. Silver became the most

[2] For a recent investigation of the chemical transformations of silver in the human body that lead to silver particle deposition, see Liu, J., Wang, Z., Liu, F. D., Kane, A. B., & Hurt, R. H. (2012). Chemical transformations of nanosilver in biological environments. ACS Nano, 6(11), 9887–9899. https://doi.org/10.1021/nn303449n.

cited nanomaterial in a consumer products database in 2007 (Vance et al., 2015). Nanoparticles are commonly presumed to have properties unlike those of the bulk material, although research is ongoing and whether this is true may depend on the specific material in question. It also may be that we know more about nanosilver than any other nanoparticulate material, and therefore we have less reason to suspect unknown harm. For example, colloidal silver has been used as medicine for almost a century (Nowack, Krug, & Height, 2011), and the condition argyria is well documented from the early 20th century.

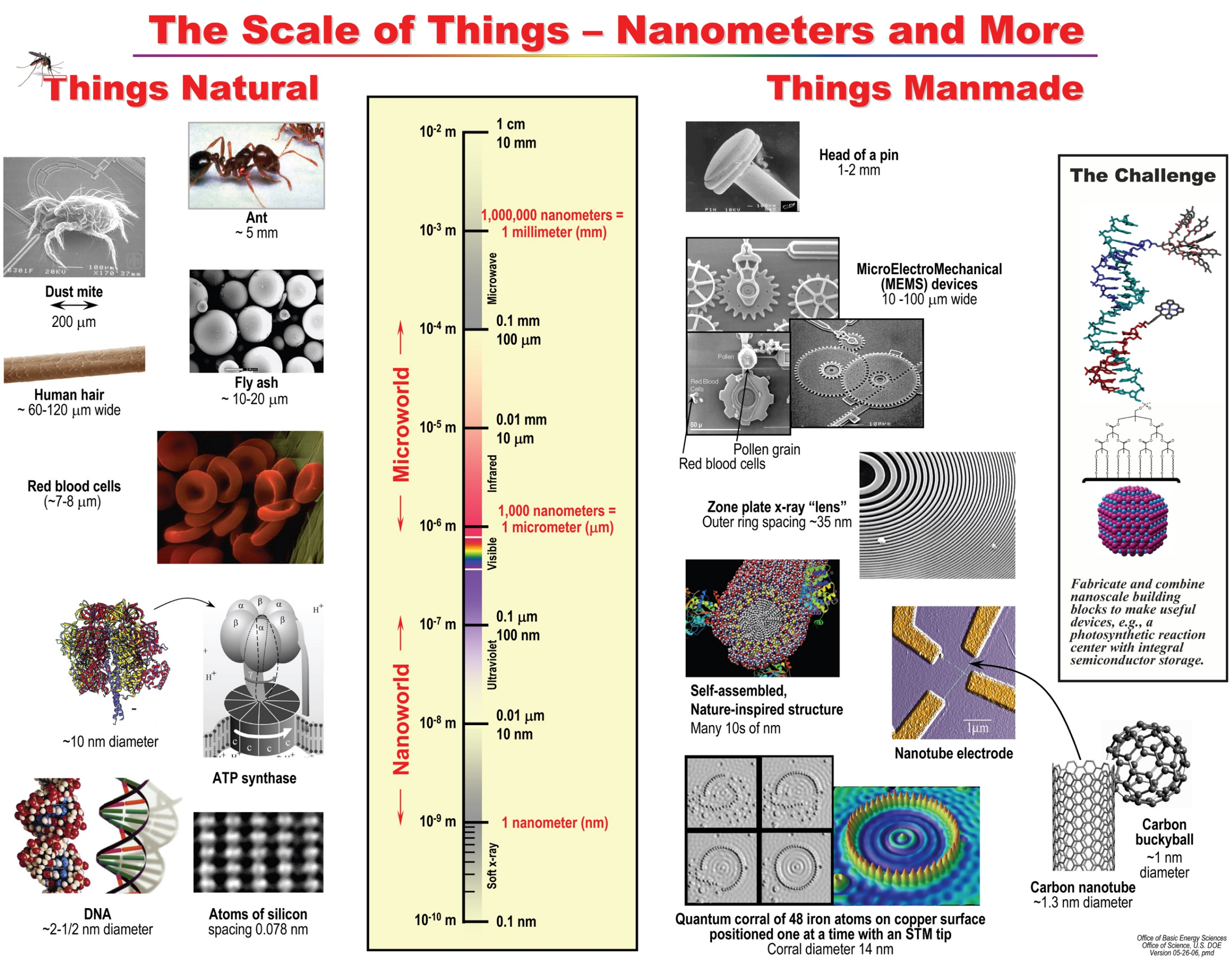

Figure 2. Conceptualizing the nanoscale. Credit: U.S. Department of Energy, Office of Basic Energy Sciences.

What is clear is that some silver is released into the environment when anti-odor clothing is washed. Eventually, even silver-enabled underwear has to come down to Earth. Imagine that pair of underwear is put into the laundry: Some silver dislodges from the fabric and enters the wash water, with the total amount released dependent on the silver incorporation method and initial amount loaded onto the fabric (Reed et al., 2016). As the washer drains, the wash water becomes wastewater and travels through underground pipes to a wastewater treatment facility. At that facility, the wastewater undergoes primary and secondary treatment in preparation for eventual return to a waterway. Most silver in the influent wastewater (more than 90%) is efficiently removed to sludge, meaning it does not exit the facility with the treated wastewater. The small portion of silver that remains is discharged as effluent into a receiving stream or river, where it becomes incorporated into sediments and carried downstream (Shafer, Overdier, & Armstrong, 1998). The sludge can be treated in various ways, including being landfilled, incinerated, or spread on agricultural fields to return nutrients to the soil. Although the silver species present in sludge are much less toxic than silver ion (Ag^+), silver can potentially enter the soil, subsoil, and groundwater after disposal of the sludge (Blaser, Scheringer, MacLeod, & Hungerbühler, 2008).

How should we respond to these silver-enabled products? The environmental effects of silver nanoparticles are not fully known, and previous experience with wastewater contamination by the photographic industry has provoked caution (Luoma, 2008). Dilution, in some ways, is still treated as the solution to pollution—intentionally or not.

CONCLUSION

> *"Treacherous treasure,*
> *avarice tarnishing us,*
> *photos claiming souls."*
> (Lee, 2017)

In theory, metals can be infinitely recycled, transforming from one product to the next. At greater than 50%, silver has one of the better end-of-life recycling rates among metals (Graedel et al., 2011). A 2006 estimate suggests that silver stocks will be sufficient to meet global demand for at least 50 years (Gordon, Bertram, & Graedel, 2006). But every year, tons of silver are lost as waste. An atom of silver mined by a Greek slave at Laurion could conceivably be making its way to the ocean this very minute as a component of wastewater. From there, the endless journey through and across our planet continues, but when will it again reach the rock from which it came? Or will it remain beyond our reach forever? Will we notice the silver in the soil, water, and creatures with which we share this planet?

ACTIVITY: SILVER CYCLING AND SUSTAINABILITY

Biogeochemical cycling is defined as the mass of a given element stored in a given reservoir at any one time coupled with its rate of transfer to a different reservoir. A reservoir is any system that can store an element, such as rocks, the ocean, living things, or soil. All the elements of the periodic table are constantly cycling through all of Earth's reservoirs, though human activity has altered the rates at which they cycle. In this activity, you will explore what this means for our continued ability to use natural resources, explore potential consequences, and propose solutions.

ACTIVITY PART I: GETTING FAMILIAR WITH THE MODEL

Open the Insight Maker model "Silver Biogeochemical Cycling" found at https://insightmaker.com/insight/109267/Silver-Biogeochemical-Cycling-v2. Make a copy of this model (i.e. clone the Insight) to use for your own explorations. In this model, silver mass in reservoirs is given in Gg (gigagrams) and flow rates are given in Gg/yr (gigagrams per year).

1. Identify the:
    a. Three largest silver reservoirs by mass.

    b. Three smallest silver reservoirs by mass.

2. Click on "Settings" and set the following:

    Simulation start = 0;
    Simulation Length = 1000;
    Time Units = Years;
    Pause Interval = No Pause;
    Analysis Algorithm = Fast (Euler);
    Simulation Time Step = 20

    Click Apply. Press the button that says Simulate to run the model. You can set the run speed of the model in the lower right-hand corner of the graph that appears. When the model run finishes, click on Configure. Under Data, select "OceanCrust". Set the minimum value for the y-axis to zero. For the Secondary Y-axis Data, select "TerrBiomass". Again set the minimum value for the secondary y-axis to zero. Give the graph a descriptive title and click Apply.

    Describe the results for OceanCrust and TerrBiomass. Why are they so different?

3. Close the graph. Click on the flow SoiltoFreshwater. The flow rate should be set at 71 Gg/yr. Change this flow rate in any way you wish and run the model (i.e. click Simulate). Make sure your graph displays the results for Freshwater and Soil. Describe how you changed the flow rate and the results of your change.

4. Reset the SoiltoFreshwater flow rate to 71. Add a flow into or out of the Freshwater reservoir. To do this, let your mouse pointer hover over the box labeled Freshwater. A blue arrow should appear in the center. Click this arrow and drag outside the box. You now have a new flow. To change the direction of the flow, click the button at the top of the workspace showing two arrows pointing in opposing directions. Give the flow a name, a flow rate, and units of Gg/yr. Run the model, then describe below the flow you added and the results of your change. Make sure your graph displays the results for Freshwater and any other reservoirs that interest you.

ACTIVITY PART II: SOCIO-ENVIRONMENTAL IMPACTS ON SILVER CYCLING

5. Now let's explore the effects of silver mining and use in products. Create a new stock called ResourcePool, and create a flow from the Upper Cont Crust to the ResourcePool. Label this flow Extraction. Set the initial value of ResourcePool at 345 Gg. Set the initial flow rate for Extraction at 20 Gg/yr and create a value slider. Set the value slider max at 200 and the slider min at 0.

   Now create a flow from ResourcePool to Atmosphere. Label the flow in a meaningful way and set the initial flow rate at 0.44 Gg/yr.

   Create a flow from ResourcePool to Freshwater. Label the flow in a meaningful way and set the initial flow rate at 1.137 Gg/yr.

   Create a flow from ResourcePool to Soil. Label the flow in a meaningful way and set the initial flow rate at 9.93 Gg/yr.

   Create a flow from ResourcePool to Ocean. Label the flow in a meaningful way and set the initial flow rate at 0.72 Gg/yr.

   Run the model. How do the long-term evolutions of Atmosphere, Freshwater, Soil, and Ocean compare to Part I, without Extraction?

6. Which reservoir(s) is(are) most affected by extraction of silver from Upper Continental Crust? Which reservoir(s) is(are) least affected? Explain why this is the case.

7. Some parts of the silver cycle have been omitted for clarity and simplicity in the model. For example, the Insight Maker model shows no inputs to Upper Cont. Crust. In reality, input from the mantle does occur. Ocean crust that re-supplies the mantle is returned on the timescale of plate tectonics, or tens of millions of years. Regeneration of silver resources in the upper continental crust is therefore dependent on plate tectonics. What does this mean for our continued ability to extract new silver resources?

8. Silver extraction rates have not been constant through time. For example, advances in mining techniques during the 20th century greatly increased silver production. In contrast, in times of war silver production has decreased. Using lead (Pb) isotopes measured in a Greenland ice core, researchers have pinpointed a number of events that affected Roman silver output during antiquity (McConnell et al., 2018). In this question you will explore how society, economics, and technology can affect resource extraction.

    a. Add (a) variable(s) to the model modifying the extraction rate accordingly for each scenario below.

    b. Decrease the Extraction flow to 1 Gg/yr as a baseline value to simulate the lower overall extraction rates during antiquity. Extensive Roman silver mining activities occurred in southern Spain during the Roman Republic and Imperial periods. Warfare in Spain between 196 and 182 BC dropped annual lead flux in the ice core to roughly 10% of its pre-war level at some points. Assume that silver production dropped accordingly to 10% of its pre-war level (baseline value). How do the Atmosphere, Freshwater, and Ocean reservoirs change in response to warfare?

    c. The Pax Romana was a long period of peace and prosperity during Imperial Rome. During this time lead emissions imply that silver production was high, and Roman currency, the denarius, consistently showed high silver bullion content. At maximum, lead flux increased approximately 30 times over its prior level. Increase silver extraction 30-fold over your imposed baseline. How do the Soil, Freshwater, and Ocean reservoirs change in response?

    d. The Pax Romana ended with the Antonine Plague, which again lowered silver production (how can you mine silver without slaves, er, workers?). Decrease silver extraction to 30% of its baseline value. How do the Soil, Freshwater, and Atmosphere reservoirs change in response?

    e. Imagine that the Romans began to melt down old denarius coins and re-use the silver. How would this affect the ResourcePool reservoir? How would this affect downstream environmental reservoirs such as Ocean?

ACTIVITY PART III: SYNTHESIS

Write a narrative describing the natural and anthropic components of the silver biogeochemical cycle. How do these systems interact? What are the important components, flows, and feedbacks?

ACTIVITY PART IV: ENVISIONING SUSTAINABLE SOLUTIONS

Imagine that it is the year 2137 and silver supplies are running low. As a crucial component of electronics, it is impossible to manufacture these items without silver and it cannot easily be substituted by another metal. Working in groups of 3, create a 10-minute presentation describing your solution for using silver sustainably—in other words, so that we can ensure an adequate supply of silver for the foreseeable future that considers social, environmental, and economic impacts. Each student should investigate one of the three aspects (social, economic, or environmental) and how it relates to the proposed solution. Your solution does not have to be technologically feasible today, but it must be possible, e.g. it cannot violate the laws of physics.

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