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The Richness of Silver Ore in the Middle Ages: A Comparative Study of Historical Descriptions and the Archaeological Evidence

Introduction

The archaeology of the Middle Ages is multifaceted in its methodology. Particularly in the early periods of the medieval age the historical records are sparse and lacking in detail. The deficiency of the written texts to describe the technical, economic and industrial practices has led researchers to adopt archaeological methods, such as archaeometallurgy, which is itself a discipline relying heavily on the methods of geology, mineralogy and material science. In order for interdisciplinary research to function properly, there should be active communication between the specialists, who come from diverse educational backgrounds and academic or scientific traditions. Often, however, this communication does not take place and groups form their own ideas based on their own methods leading to disjointed or even contradicting interpretations.

The clash of two traditions can be seen in recent debates on the use of argentiferous galena as a silver ore in the Middle Ages (Bartels, 2014; Téreygeol, 2002; Téreygeol, 2013). This highly active dispute has consequences not only for our understanding of the medieval mining of silver, but it has implications for our understanding of all silver production that came before it. The goal of this contribution is to explain the scientific and historical bases which have led to the development of these two conflicting traditions, and efforts are made to synthesize these two positions with an integrated and interdisciplinary approach to the problem.

Silver Ore and Silver Enrichment Processes

The place to start the discussion is with “ore”, the very word itself. In archaeometallurgy and mining archaeology the word is used rather loosely to describe anything that “could” or “might” have been used to make metal in the past. The true meaning of the word is inescapably intertwined with economics and the profitability of extraction (Shackelton,

1986, pp.2). The loose definition used by archaeologists is because it is often not known what the limit of profitability was nor is the ore that was used present; ore would have been turned into metal if it was economical to do so.

Therefore, when discussing silver ore, or the economic profitability of silver extraction, many factors must be considered, such as the political situation, security, infrastructure, accessibility of fuel and water, availability of skilled miners and metallurgists, and also the secondary products of silver production like copper, lead, litharge, etc. Ore does not simply consist of minerals in particular concentrations – it is the whole economic package.

So after law and order were established, infrastructure built, skilled workers found, then the minerals can be discussed. If one reads about silver mining in the American West from the early 20th century, it is clear that the profitability of silver mining, even up until quite recent times, was tied to the supergene, or secondary, enrichment process that can concentrate silver both by creating silver-rich minerals and increasing the abundance of these minerals (Emmons, 1913, pp.95, 114-125.).

The richest silver mineral is native silver and next is a relatively common mineral called acanthite, also known as argentite or silver sulfide (Tab. 1). Following these are cerargyrite, also known as silver chloride, and sulfosalts like ruby silver (proustite-pyrargyrite) and the silver-bearing fahlore minerals like freibergite. All of these minerals can contain silver concentrations above 50 weight percent, the purest and richest minerals can contain up to 90 or 99 percent silver (Ramdohr, 1980, pp.471, 562, 783-785, 1110).

To summarize the enrichment processes based on Emmons (Emmons, 1913, pp.114-118): silver chloride can only form from the weathering of an ore mineralization at or near the surface. All of the others can be in the primary ore or form from weathering and enrichment processes. For there to be silver enrichment, there must be quantities of silver in the primary ore minerals. Silver becomes increasingly water soluble and mobile when pyrite oxidizes during chemical weathering. As pyrite oxidizes, ferric sulfate is released, which is reactive with all forms of silver forming silver sulfate. Furthermore, the

Mineral	Other Names	Chemical Formula
Acanthite	Argentite, Silver Glance, Glaserz	Ag ₂ S
Cerargyrite	Horn Silver, Silver Chloride	AgCl
Cerussite	Lead Carbonate	PbCO ₃
Freibergite	Gray Copper, Fahlore	(Ag,Cu,Fe) ₁₂ (Sb,As) ₄ S ₁₃
Galena	Lead Sulfide	PbS
Jarosite	-	KFe ₃ (OH) ₆ (SO ₄) ₂
Native Silver	-	Ag
Polybasite	-	Ag ₉ SbS ₆
Proustite	Light Ruby Silver	Ag ₃ AsS ₃
Pyrargyrite	Dark Ruby Silver	Ag ₃ SbS ₃
Stephanite	Brittle Silver	Ag ₅ SbS ₄
Tetrahedrite	Gray Copper, Fahlore	(Cu,Fe,Ag) ₁₂ Sb ₄ S ₁₃

Tab. 1: List of minerals mentioned in text.

presence of ferric sulfate in water increases the solubility of silver sulfate and allows it to migrate upwards or downwards in the ore deposit. Under reducing conditions it can be deposited as native silver that can react with chloride-bearing water to form silver chloride, which under normal conditions is stable. Silver sulfate can react with hydrogen sulfide released by sulfur-bearing minerals like galena, sphalerite and pyrite during weathering and can form acanthite and replace these minerals. If acanthite replaces galena, then argentiferous galena can be formed (Fig. 1). If antimony, arsenic, or copper is in the solution, minerals like ruby silver or argentiferous fahlore can be formed. The sulfides of silver are the most stable and chlorides and native silver will form sulfides if hydrogen sulfide is present. Under certain conditions silver sulfide can be reduced to form native silver. The enrichment processes basically stop when there is either no ferric sulfate available or if there is no source of oxygen in the system.

For these reasons, the surface and cementation zones of silver-bearing deposits can be extremely rich. Starting with silver halides like cerargyrite at the top particularly in the gossan and followed by native silver and the range of silver sulfosalts below in the enrichment zone. Below this is the primary unweathered ore, which will often have significantly less silver.

Historians' Perspective

Though nowadays these rich deposits are mostly gone, based on the medieval accounts the rich silver minerals could be found and seem to have had a paramount role in production. The account of Albertus Magnus in the 13th century (Albertus Magnus, pp.181 and 220) describes the four types of silver ore found in Germany: 1. whole stone,

with silver distributed throughout the rock, it is separated from the rock by roasting, crushing and milling and heating such as how gold is produced, 2.-3. there are two types of veins – one as a column in the earth and the other as string-like veins – both consisting of firm, dry and almost pure silver, possibly silver sulfide or native silver, and 4. veins found in the earth like a soft but firm mush, which based on his descriptions appears to be silver chloride. The lumpy substance he describes is so pure it can be burned directly to silver. There is no mention of galena or even lead in conjunction to silver ore.

To move from Central Europe to the Arabian peninsula, Al-Hamdani says that in Yemen in the 10th century, silver ores, meaning specifically the stone in which silver is extracted, has a silver content between 50% at the richest and 0.8% at the poorest (Al-Hamdani, pp.272-274). Here he describes the silver ore as containing a darkness that becomes bright through fire, likening this to the darkness of the moon whose brightness can be seen only with the shine of the sun (Merkel, et al., 2016, pp.111; Al-Hamdani, pp.128-129). He may be referring to the dark silver minerals acanthite or cerargyrite, which respectively have blackish and purplish-grayish hues.

If we go later to the post-medieval account of Agricola (1950, pp.111-114):

“When considering silver ores other than native silver, those ores are classified as rich, of which each one hundred librae contains more than three librae of silver. The quality comprises of rudis silver [a general term for naturally occurring silver compounds], whether silver glance or ruby silver, or whether white, or black, or grey, or purple, or yellow, or liver-coloured, or any other. Sometimes quartz, schist, or marble is of this quality also, if much native or rudis silver adheres to it. But that ore is considered of poor quality if three librae of silver at the utmost are found in each one hundred librae of it. Silver ore usually contains greater quantity than this.”

For Agricola, Glaserz, also called acanthite, silver glance and silver sulfide, is one of the most important silver ores (Fig. 2). He describes ten by ten meter long, 20-30 cm wide veins of silver sulfide that could be found at Joachimsthal / Jáchymov in Bohemia. The experienced miner could tell the silver sulfide from the other minerals with the strike of a hammer or by eyesight alone. Upon refining, for every 100 pounds of this ore, 90 pounds of silver were produced (Lehmann, 1810, p.289-291). Malleable high-grade silver ore, which includes native silver, acanthite and some types of *rudis* silver, was hammered into sheets and cut with shears 6 feet long in preparation for refining by cupellation (Agricola, 1950, p.269). These descriptions give the impression that such rich silver ores were not a rare occurrence and played an important role in the overall silver production. These rich minerals like native



Fig. 1: Argentiferous galena from the Czech Republic. This galena was roasted, smelted and the silver was purified using analytical cupellation. The silver content of the smelted lead is 0.7 % (Photo: S. Merkel).



Fig. 2: Silver ore from Freiberg, Saxony (Beschert Glück). The dark areas are primarily the mineral acanthite (DBM Mineral Collection, Photo: S. Merkel).

silver and acanthite were fully anticipated and integrated in the production system as late as the time of Agricola (16th century). Despite this focus on the richer ores, with the proper furnace design and smelting procedure, even very poor ores with under 0.1 % silver could be smelted and the silver extracted (Tab. 2A).

Archaeometallurgists' Perspective

The current perspective on silver ore by archaeometallurgists has developed out of roots based in modern economic geology and extractive metallurgy. This is clearly seen in the grams per ton unit used to express the concentration of silver. The fundamental works of archaeometallurgy have had a strong and resilient influence on the way silver ore continues to be seen within the field. According to Hans-Gert Bachmann, silver was mostly produced from silver-bearing lead ores containing half a percent and rarely up to 1 to 3 percent silver (Bachmann, 1993, p.489). This ore grade is thought to be representative for Roman silver production, and R. F. Tylecote, very influential in archaeometallurgy, has put the limit of economical extractability of silver from argentiferous lead at 0.06 % silver during the Roman period (Tylecote, 1986, p.61). For him, silver production in the Middle Ages based on lead minerals containing 0.1 % silver was realistic and probable (Tylecote, 1986, p.71).

Paul Craddock (1995, p.212) states in a standard archaeometallurgical work:

"Native silver, together with dry ores [cerargyrite, acanthite, ruby silver] so rich that they could be smelted directly with no cupellation, may have been major sources at the inception of silver production, but by the Iron Age at the latest they must already have been insignificant in the Old World. The major sources were argentiferous lead, with significant contributions from the jarosites and possibly from the de-silvering of copper ores."

It is commonly accepted in the field of archaeometallurgy that starting as early as in the Bronze Age, silver was produced primarily from argentiferous lead ores,

A)						
	0.5-1 Unciae Silver	≈	12.2-24.3 Troy Ounces	≈	378-756 Grams	≈ 417-837 ppm
	1 Centumpondium Ore		1 Short Ton		0.907 Ton	≈ 0.04-0.08 %
B)						
	3.5 Unciae Silver	≈	85 Troy Ounces	≈	2643.8 Grams	≈ 2915 ppm
	1 Centumpondium Lead		1 Short Ton		0.907 Ton	≈ 0.29 %

Tab. 2: The units and amounts given by Agricola and the conversion into grams per ton, parts per million and percent. A) Value given for the lowest quantity of silver extractable from ore by smelting (Agricola, 1950, p.388) and B) the figure given for the silver content in argentiferous lead in the context of cupellation (Agricola, 1950, p.475).

chiefly silver-bearing cerussite and galena. Silver-bearing lead ore was smelted and an alloy of lead and silver was produced. Lead is the main collector of silver during smelting and lead can be easily separated from silver using the cupellation process. The cupellation process is the separation of noble metals from lead through the selective oxidation of lead above the melting temperature of lead oxide (c. 900°C). Two immiscible liquids are formed, and the liquid lead oxide (litharge) can be drained off or absorbed into an inert porous hearth material leaving behind the non-reactive precious metals in metallic form.

If one assumes that silver production was based on argentiferous lead ores, then it only follows logic that the concentration of silver in the lead from smelting slags would give us an impression of the richness of the original lead-silver ore. In truth, however, it may be more complex than this. The validity of this statement will be discussed further in the paper.

Going through the various studies of ores and slags from prehistory to the Middle Ages a growing pattern emerges.

- At Sifnos, with important metal production in prehistory and in the antique period, analyzed lead-silver ore contained up to 0.5 % silver, but was often half of that or less (Vavelidis, et al., 1985, p.69; Weisgerber, 1985, p.115).
- At Thasos, Early Iron Age to medieval silver production was again attributed to the mining of argentiferous galena with silver contents up to 0.4 %; the silver content in analyzed argentiferous lead from slags was in the range of 0.1 to 0.2 % (Hauptmann, Pernicka und Wagner, 1988, pp.88-102).
- Similar values are given for famous antique silver mines of Laurion, in Greece, the Roman mines of Riotinto in Spain and the late Roman lead-silver mines of Mount Kosmaj in the Balkans (Merkel, 2007, pp.46, 67).
- An example of early medieval silver mining is Melle in France. It is thought that the mine was based on the extraction of argentiferous galena that contained typically 0.15% silver and up to a maximum of 0.5 % (Téreygeol, 2002). Argentiferous lead from experiments using galena from Melle contained 0.24 % silver (Téreygeol and Arles 2014, p.208). The mint of Melle was one of the most important in the Carolingian period and its high output of silver coins can only be explained by the productivity of its silver mines (Sarah, 2014, pp.186-187).
- The high medieval polymetallic smelting of Ramelsberg ore at Huneberg, in Germany, has again repeated the pattern. The argentiferous lead produced from smelting was shown to contain on average around 0.2% silver (Asmus, 2012, pp.230, 253).
- At the late Antique / medieval mine of ar-Radrad in Yemen, recent studies have shown that the silver content of lead-silver ore fragments from the mines

may be as high as 1% silver when normalized to lead, but others are less. In the argentiferous lead from smelting slags, the silver is well below 1% with an average content of 0.17% (Merkel et al., 2016, p.120; Téreygeol, 2014, p.164). This is obviously in conflict with the economic limit described by Al-Hamdani, who praised the mine of ar-Radrad for its enormous silver yield that was unparalleled in the Islamic world (Al-Hamdani, pp.144-147, 272-274).

- The slags from Panjhir, a prolific silver mining region known for its vivid historical descriptions from the Middle Ages (Weisgerber, 2004, pp.202-204), have been analyzed. They are certainly tied to silver production because argentiferous lead was the main smelting product found in the slags. Four large inclusions of argentiferous lead found in different slags were analyzed by quantitative mass spectrometry in Bochum and contain c. 0.3 to 0.6 % silver (Merkel, 2017, p.279).

Based on the archaeological evidence from slags and the ore samples available for study, it appears that much of the silver production in the Middle Ages, as well as in earlier periods, was based on argentiferous lead or polymetallic ore with silver concentrations between 0.1-0.5 % and rarely higher.

Discussion

Seeing the two lines of argumentation side by side demonstrates how far apart the two positions are. Regarding the historical accounts of silver ore, certainly there is some element of sensationalism in the descriptions, but despite this there must be some core of veracity. It is evident from the three historical examples mentioned above that Craddock's emphasis on lead-based silver production from the Iron Age onward is not entirely correct. It is important that he stresses that silver ores pure enough to be smelted directly to silver without cupellation may have been rare, but the use of cupellation is no proof that the majority of silver was produced from argentiferous lead ores. As Agricola says, even the highest grade silver ores such as native silver and acanthite were purified by cupellation.

As we do not have the ores that were smelted, any silver produced directly by refining and by cupellation would be nearly, if not entirely, invisible in the archaeological record. Even ore geologists, with their partial, modern views on mining, seem to underestimate the significance and extent of ore enrichment in the past. Since the widespread use of explosives in mining, ore is generally seen a certain number of tons of rock with a certain number of grams of silver and whether this silver is found as veins of native metal or acanthite or as micro-inclusions of silver minerals in galena is of secondary importance. The pre-modern miner who dug and removed the rock

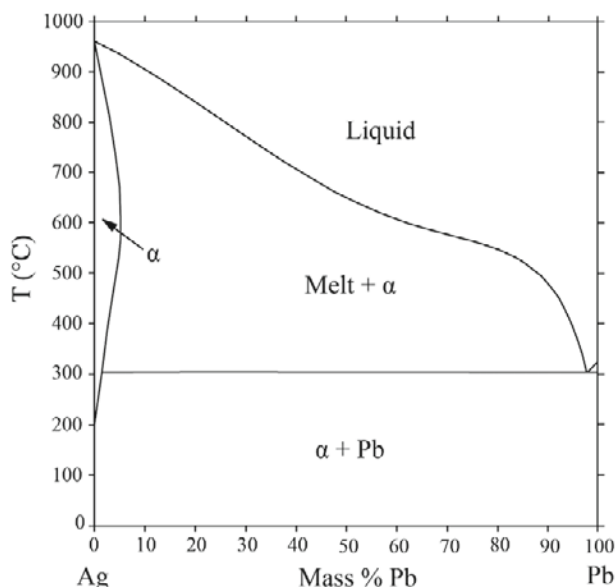


Fig. 3: Silver-Lead phase diagram redrawn from Lee, et al., 1994. Silver forms a liquid solution with lead and the melting point lowers with increasing amounts of lead. The eutectic forms at 305° C at 95.7 % lead.

by hand also collected and sorted the most important ore minerals by hand.

Next to ore that can be found today, the second line of investigation is of the ancient slags associated with silver production. According to the traditional model of silver production, i.e. that silver is produced from argentiferous lead ore, the analysis of silver collected in the lead metal inclusions in the slag should give an indication on the quality of ore or otherwise a silver-to-lead ratio of the original material. Several studies undertaken have shown that the content of silver in smelted lead tends to contain well under one percent silver and more generally correspond to the 0.1 - 0.5 % silver found in argentiferous lead ores, thus confirming the use of such ores as the basis for silver production archaeologically. Although Agricola mentions that 3% silver is the boundary between poor and rich ores (and that most silver ores are the rich kind), in the context of cupellation Agricola gives the example of the silver content in argentiferous lead as being c. 0.29 % silver (Tab. 2B), also corresponding to the amounts expected in argentiferous lead ores.

However, this chain of logic is problematic for two reasons. Firstly, slag is a waste material, and the information obtained from its study probably reflects the poorest quality of ore used. Slags that contained higher concentrations of silver could have easily been recycled and only the silver poor slags were likely disposed of. The richest ores would have by-passed this smelting step and went directly to the cupellation furnace and thus evidence of their existence would not be found in smelting slag. Secondly, it is not clear that the silver-to-lead ratio in the metallic lead in the slag reflects the ratio of the original ore. The ratio may have been intentionally suppressed to

prevent loss of silver in the slag by adding lead, litharge or lead ore. By maintaining a hyper-eutectic relationship of silver to lead (Fig. 3), thus impeding the silver from crystallizing before the lead during cooling, silver loss in the slag and other metallurgical by-products / waste material may have been reduced.

Lastly, the economic factors such as the price of silver, the cost of skilled labor and the availability of fuel influenced the profitability of silver mining and would dictate the lower limit of ore quality in the Middle Ages just as it is today. In areas with political stability, abundant fuel resources, sufficient access to labor and in times of high silver prices, silver may have been produced from ores that in other periods and other regions would have been uneconomical. There certainly is a danger in oversimplification and trying to force silver production into a linear chronological development, from high-grade silver ore to relatively silver poor galena. Furthermore, it should not be forgotten that in the 9th and early 10th century AD there was a large-scale import of silver dirhams to the Baltic region from Central Asia and the Middle East (Merkel, 2016; Noonan, 2001); and however irrational this may seem, there must have been economical reasoning behind it, and it must have been connected to the price and availability of silver in Europe. Although there were many silver-bearing deposits in Central Europe mined extensively later in the Middle Ages which are geographically much closer to the Baltic, these were either unknown or could not have been mined cost-effectively at that time.

Conclusions

The historical accounts focus on the rich ores and the archaeological record only gives us indications for poor or seemingly poor ores. Although numerous questions remain to be unanswered, some assumptions and remarks can be made regarding the quality of silver ore used in the Middle Ages:

1. The focus on rich ores in the historical texts may reflect only a small, but economically important, part of the total production. A significant portion of the ores used were not of the rich kind. The combination of rich ores and poor ores would have together financed the mining operation.
2. Very rich ores were not smelted in furnaces and their traces would probably not be found in slags. They would have been cupelled directly and, thus, remain invisible.
3. As Agricola explains, rich and moderately rich silver ores could have been diluted with lead during smelting in order to collect as much of the silver as possible (Agricola, 1950, pp.379-391). Once the silver is in the lead, nearly all of it can be recovered by cupellation and reprocessing the cupellation debris. This means that depending on the smelting technol-

ogy, the silver-to-lead ratio does not have to reflect the original ore and may have been manipulated for technological reasons.

4. The slags and ore that we find are refuse. Slags can easily be recycled and the ore we find today may not be representative of the richness used in the past.
5. Lastly, the role of economics should not be underestimated. The price of silver was not constant over time. It is clear that inefficient technologies, from our viewpoint, could have been economical at certain points in time. For example, if a rich new deposit is discovered, it could put a long-standing industry based on poorer quality ore out of business.

It is clear from the historical records that minerals like native silver, acanthite and silver halides were encountered by medieval miners. It is a fortune that such descriptions survived because in the archaeological record, these extremely rich silver minerals are near to invisible.

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