

SMELTING OF GOLD AND SILVER ORES IN RENAISSANCE AUSTRIA

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ABSTRACT

The gold and silver smelting area of the Angertal valley is located in the Gastein region, in the south west of Austria, and is linked to the Bockhart mining area, where there is evidence for mining of gold and silver ores. The principal minerals containing the noble metals are galena and pyrite, with variable amounts of sphalerite, chalcopyrite and arsenopyrite. Extensive mining of the Bockhart gold- and silver-bearing veins started during the fourteenth century and ended at the end of the nineteenth century, with a peak of activity, according to written sources, in the second half of the sixteenth century. Excavation of one site in the Angertal valley revealed several well-preserved furnaces, used for smelting ores, and a vast amount of smelting slag, pieces of ore, furnace wall fragments, and charcoal. Their nature, quantity and degree of preservation made this site ideal to investigate the large-scale smelting technology of noble metal ores during the Renaissance, as a contribution to a larger project reconstructing the socio-economic dimensions of the metallurgical activity in this region. This paper presents the first results of the ongoing analytical study by optical microscopy, SEM-EDS and ED-XRF of ore, matte and slag. The slag is mostly fayalitic, and the presence of matte links the smelting process to the sulphidic ores from the region. A preliminary reconstruction is presented of the high-temperature processes performed to extract the noble metals from their ores.

KEYWORDS

Gold, silver, pyrite, galena, smelting, slag, matte, Austria, Renaissance.

LOCATION AND HISTORY

The introduction to the early modern smelting site of the Angertal, Austria, is mainly based on two publications [1, 2]. Further accounts of the history and geology of the Hohe Tauern region are also considered to place the technology of this metallurgical site within its broader context in the sixteenth century [3-6].

The gold smelting area of the Angertal, the valley of the river Anger, is located in the Gastein region, south of the *Bundesland* Salzburg in Austria. The Angertal is close to the Bockhart mining area, which is part of the Hohe Tauern and where there is historical and archaeological evidence for late medieval to Renaissance mining of gold and silver ores. In a previous study of the ores, the main minerals containing gold were identified as quartz, pyrite and arsenopyrite [7]. The present study, however, shows slightly different results (see below). Gold-rich silver is mainly found in the galena ore. This mining area of the Hohe Tauern was connected to smelting sites in the valley through established pathways; this was also the case for those located in the Angertal. While the mining of the various ores in the Bockhart took place all year round, the smelting operations occurring in the Angertal were seasonal. According to the historical records, the ore was transported from the mines to the smelting sites in the valley using bags made of pig skin, which were slid down the slopes of the mountains. The tracks left by such transportation are still visible today.

The first period of gold exploitation seems to occur between the middle of the first millennium BC and the end of the fifth century AD. During this time, the gold is likely to have been extracted from river sand and placers. Even though the region was known to be rich in gold and silver, the extensive mining of the gold- and silver-rich Bockhart veins only started during the fourteenth century and ended at the end of the nineteenth century. Although this is a rather long chronological sequence, the peak of mining activity was found from written sources to be in the 1550s-1560s. The scale of production is indicated by the production for the year 1557, which was 830 kg of gold and 2723 kg of silver [2].

The earliest written reference to the smelting site of the Angertal goes back to the end of the fourteenth century. Smelting of ores extracted from mines in the Gastein valley, such as those located in the Bockhart, took place from that period until the end of the sixteenth century. The smelting site of the Angertal was probably abandoned around that time due to a lack of wood, which was needed to produce the charcoal used as fuel in the smelting furnaces. Another possibility for this halt of the activity in this smelting area could also be the exhaustion of the rich veins up in the mines.

ARCHAEOLOGICAL CONTEXT AND MATERIAL

In 1996, a comprehensive geophysical prospecting of the Angertal smelting area, combined with other archaeometric and archaeological methods, was undertaken to draw detailed maps of the region, and precisely locate the smelting sites. The archaeological study was combined with a review of historical documents. Several smelting installations were identified in various states of conservation. One of these smelting areas, which presented very good preservation, was selected for further excavation, which took place between 1996 and 1998 [1].

The excavation brought to light three well-preserved furnace bases; several slag heaps of different sizes; a dry stone wall, which separates one slag heap from the furnaces and probably protected the latter from land and rock sliding; and a few wooden beams and post holes, which were interpreted as remnants of a water-powered bellows system (Fig. 1). The bulk of the material uncovered mainly consisted of a vast amount of various smelting slag, ore and matte fragments and charcoal pieces. These are all metallurgical remains characteristic of the technology performed at this site.

The slag fragments collected from the site macroscopically show a wide range of variation in shape, size, colour, texture, and degree of corrosion. Most of these are black, platy, more or less porous and/or rusty, with different surface textures (Fig. 2, left). Others are bulky, grey, with orange or green areas of corrosion products, indicative of the potential original metals composing the bulk (Fig. 2, right).

The nature, quantity and degree of preservation of the remains made this site ideal to investigate the large-scale smelting technology of gold and silver ores during the Renaissance. It was hoped that the analytical study would shed light on the potential ores, fluxes and techniques employed, together with the degree of efficiency and standardisation of this smelting installation. This information can then be placed in the wider context of the region, where the historical metallurgy of noble metals has had a huge socio-economic importance. In addition, the technological reconstruction based on the archaeological and archaeometric data will allow for comparisons between texts and materials as sources of information.

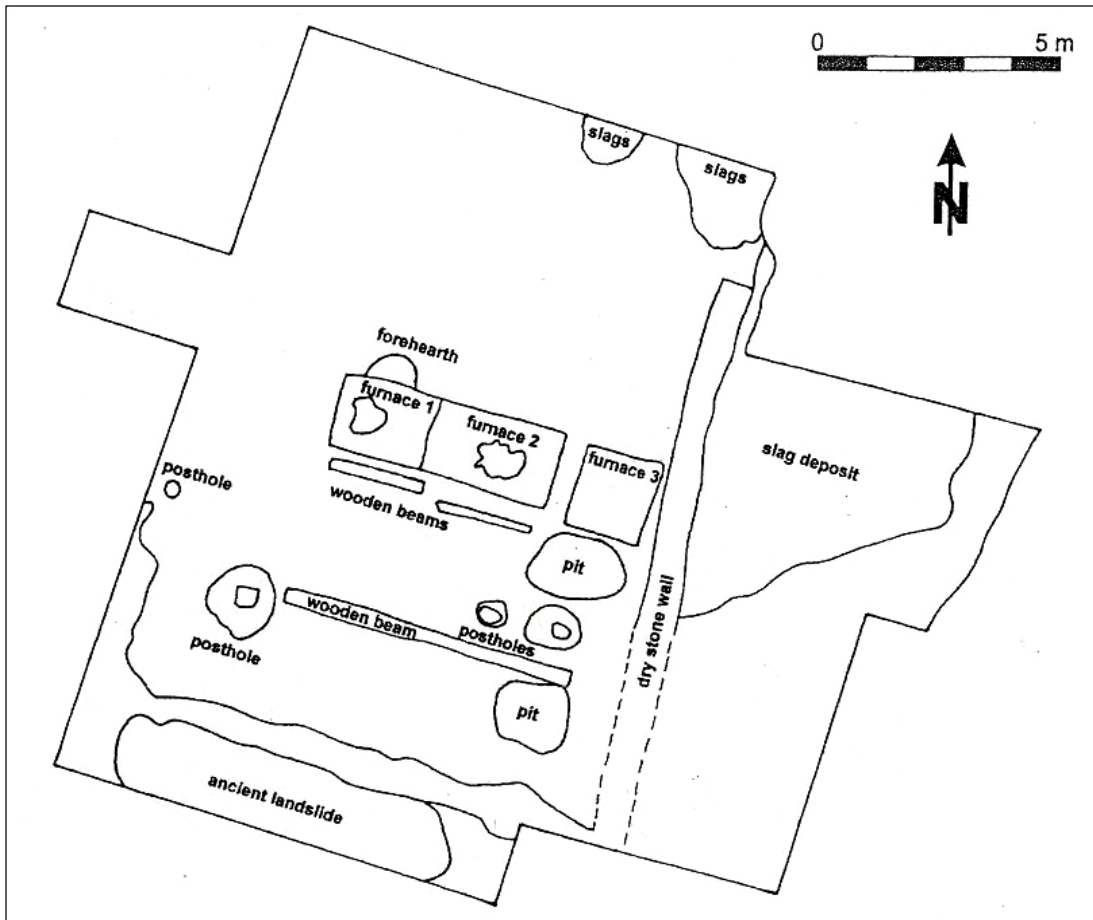


Fig. 1. Map of the Angertal smelting site after excavation (after [1]).

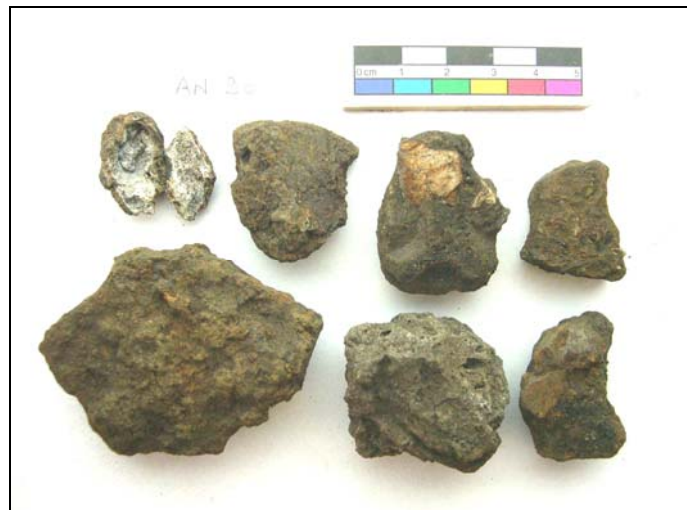


Fig. 2. Two macroscopically different groups of slag fragments: black and platy with a surface texture characteristic of a solidified liquid (left); bulky and rusty (right) (scale bars 5 cm).

METHODOLOGY

The material selected for this project has been analysed on a microstructural and chemical level, using optical microscopy, ED-XRF, SEM-EDS and SEM-WDS. Pieces of ores and slag have been mounted in epoxy-resin as polished blocks for microscopic and microanalytical studies, while homogeneous lumps of several slag fragments have been crushed and mounted as pressed pellets for quantitative XRF studies. Unless otherwise noted, the compositional data reported here is from the SEM-EDS and SEM-WDS.

ANALYTICAL RESULTS

Although arsenopyrite had previously been identified as one of the main ores, it seems from the present analyses that most of the ores comprise a mixture of sulphidic minerals, principally rich in pyrite and galena, and containing variable amounts of sphalerite, chalcopyrite and arsenopyrite (Fig. 3, 4). The gangue of these ores is generally composed of a manganese-rich iron carbonate and/or quartz. One main feature of all these ore fragments, which have so far been studied by optical microscopy and SEM-EDS, is their relative poverty in noble metals. This aspect is currently being further explored through the bulk quantitative analyses of ore samples by ED-XRF.

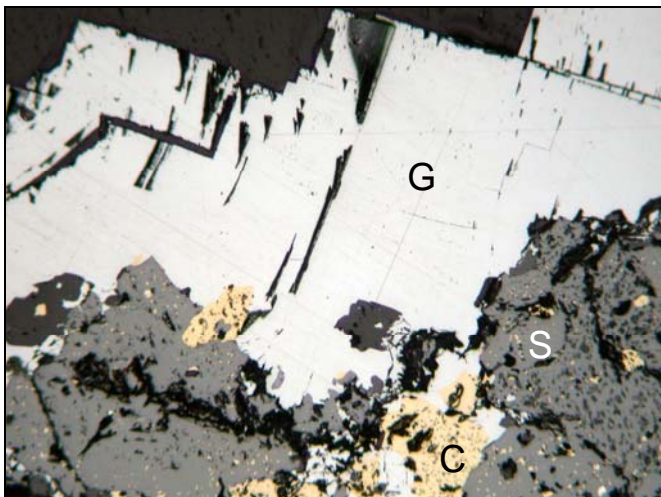


Fig. 3. Photomicrograph of an ore fragment from the Bockharttal mining site, showing crystals of galena (G), sphalerite (S), and chalcopyrite (C) (BO 991-07/S1, optical microscope, plain polarised light, 100x, long axis ~250 μm).

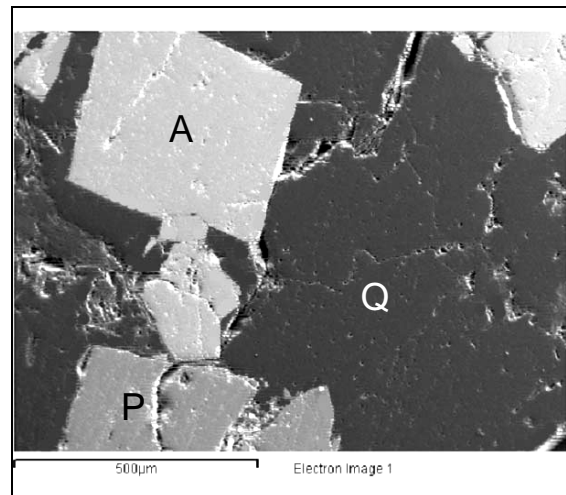


Fig. 4. Crystals of arsenopyrite (A) and pyrite (P) in a gangue of quartz (Q) (BO 152-01/S1, SE, 100x).

The bulk chemical compositions of the platy slag specimens are dominated by iron oxide and silica, and are mainly rich in alumina and the oxides of lead, manganese, sulphur and zinc, with lower concentrations of soda, potash, calcium oxide, magnesia, and arsenic oxide (Table 1). Their microstructure is generally very homogeneous, with numerous crystals of iron-rich olivines (42-65 wt% FeO, 27-36 wt% SiO₂), containing various amounts of zinc oxide (1-5 wt% ZnO), manganese oxide (4-18 wt% MnO), magnesia (1-6 wt% MgO), alumina (1-3 wt% Al₂O₃), and lower quantities of potash (1 wt% K₂O) and calcium oxide (1 wt% CaO). These olivine crystals are usually highly acicular and oriented perpendicular to the direction of the cooling front (Fig. 5). This, together with the flow texture exhibited by some of the slag fragments, confirms that the slag had a relatively low

viscosity and was tapped out of the furnace, where it solidified fairly quickly. The slag fragments analysed also present some crystals of magnetite and many inclusions of matte, i.e. a mixture of sulphidic compounds (Fig. 6). In addition, lead prills appear occasionally entrapped in the slag phase.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	MnO	Fe ₂ O ₃	CuO	ZnO	PbO	As ₂ O ₃
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	ppm
AN 113-01/S1	b.d.l.	1.3	4.7	28.3	1.4	1.3	3.3	4.0	36.1	0.4	4.0	15.1	1062
AN 117-02/S1	b.d.l.	0.2	1.6	14.5	16.2	0.5	0.5	2.1	48.4	1.8	6.3	7.8	306
AN 130-01/S1	b.d.l.	1.4	4.6	23.9	3.7	1.1	2.6	10.9	43.1	0.2	3.8	4.6	312
AN 130-10/S1	b.d.l.	1.4	4.3	23.3	3.9	1.1	2.5	10.8	43.4	0.2	4.0	5.0	728
AN 134a-02/S1	1.2	1.4	4.1	24.4	2.6	1.0	2.3	7.3	44.1	0.4	1.2	9.7	2807
AN 148-01/S1	b.d.l.	0.5	3.0	19.7	7.9	0.8	1.0	2.4	58.4	1.4	2.2	2.7	134
AN 170-03/S1	1.2	0.6	4.6	29.3	5.1	1.1	1.1	1.3	53.1	0.4	1.3	0.9	308
AN 187-02/S1	0.6	0.7	4.3	33.0	5.3	1.0	1.5	2.0	50.4	0.1	0.7	0.3	176
Average	0.4	0.9	3.9	24.6	5.8	1.0	1.9	5.1	47.1	0.6	2.9	5.8	729

Table 1. Bulk chemical composition of slag fragments by ED-XRF (data normalised to 100%, b.d.l.: below detection limit, of about 0.1 wt% for Na₂O).

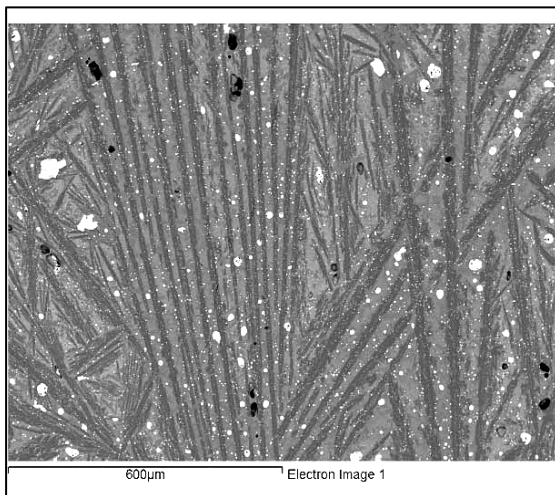


Fig. 5. Photomicrograph of a typical platy slag sample, showing the acicular fayalitic crystals in a glass matrix. Note the numerous bright inclusions of matte (AN 113-01/S1, BSE, 100x).

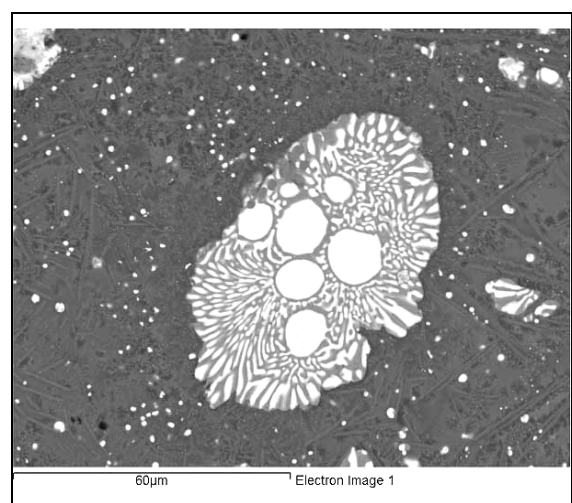
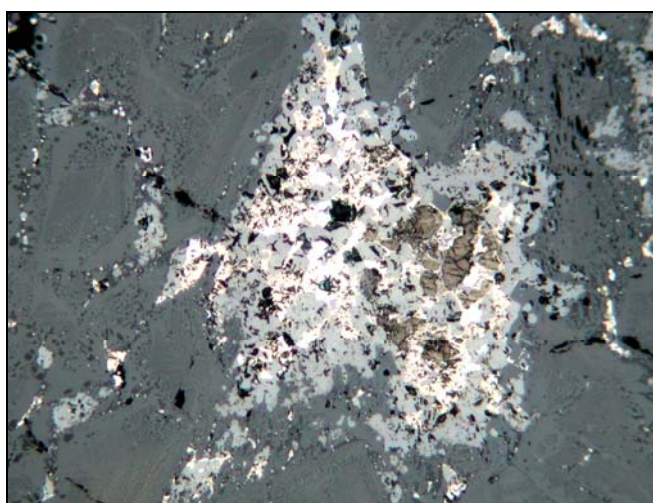


Fig. 6. Detail of matte inclusions within slag samples, composed of different sulphides (left: AN 117-02/S1, optical microscope, plain polarised light, 200x, long axis ~500 µm; right: AN 113-01/S1, BSE, 1000x).

The few matte fragments analysed so far show a bulk composition rich in iron (35-40 wt% Fe), copper (15-20 wt% Cu), and lead (10-20 wt% Pb), the balance being sulphur. They are structurally composed of different sulphidic phases, mainly pyrrhotite (FeS), which results from the partial burning of pyrite (FeS₂) during the melt, and has partly further oxidised to form crystals of magnetite (Fe₃O₄). Also present are complex iron-copper sulphides of various compositions (20-50 wt% Fe, 10-45 wt% Cu, 25-35 wt% S) and iron-zinc sulphides (37 wt% Fe, 27 wt% Zn, 2 wt% Cu, 34 wt% S), sometimes partially oxidised (Fig. 7). These matte samples also have lead prills trapped in their bulk.

The bulk composition of one matte sample analysed by ED-XRF revealed high concentrations of iron (47.3 wt% Fe), copper (22.2 wt% Cu), lead (14.3 wt% Pb) and sulphur (12.5 wt% S), with lower amounts of zinc (2.3 wt% Zn), silver (0.4 wt% Ag), silicon (0.3 wt% Si), manganese (0.3 wt% Mn), arsenic (0.3 wt% As) and antimony (0.1 wt% Sb). These results corroborate the phase study carried out by optical microscopy and SEM-EDS.

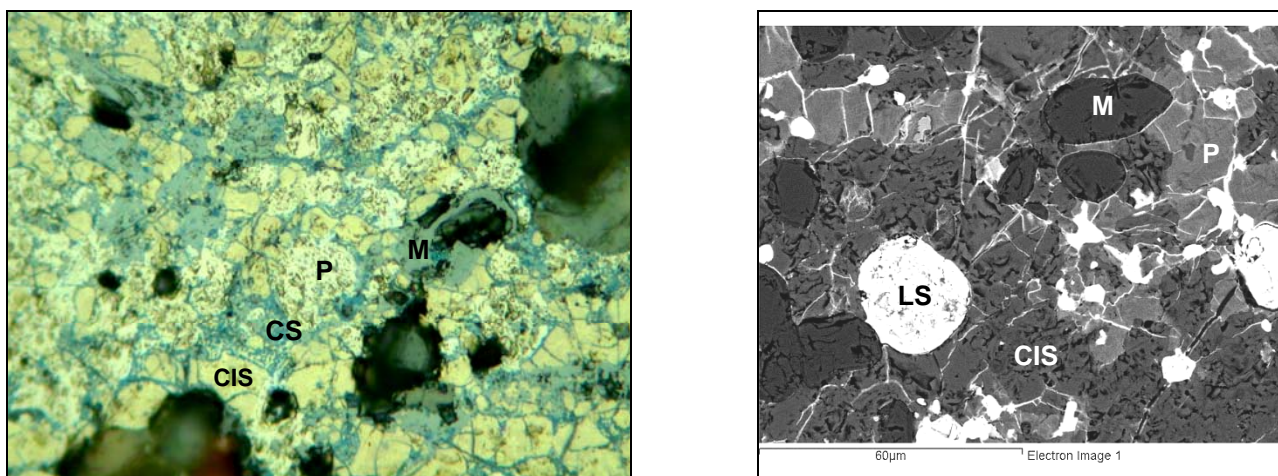


Fig. 7. Microstructure of two different pieces of matte, exhibiting phases of magnetite (M), pyrrhotite (P), a complex copper-iron sulphide (CIS), lead sulphate, which has formed from the corrosion of lead sulphide (LS), and copper sulphide (CS), which has probably formed as a secondary phase and deposited in cracks and grain boundaries during burial (left: AN 198-01/S1, optical microscope, plain polarised light, 100x, long axis ~1 mm; right: AN 108-06/S1, BSE, 1000x).

The metal prills identified in the pieces of slag and matte are mainly composed of lead (75-90 wt% Pb), which has a thin superficial oxide layer (ca. 10 wt% O). Many of these prills have a fairly high silver content (1-4 wt% Ag), with local concentrations up to 36 wt% (WDS), and usually combined with antimony to form silver antimonide (Ag₃Sb). This silver generally contains relatively high quantities of gold (1-4 wt% Au, WDS). Several prills also show very high levels of arsenic (27 wt% As).

DISCUSSION

The analytical results obtained so far contribute towards a preliminary image of the extractive technology of gold and silver at the Angertal smelting site. It seems clear that the smelting process produced three main phases: a lead-rich bullion, matte, and slag. These phases are immiscible and have different densities; however, the small metal globules found within slag and matte, and the sulphidic inclusions within the slag, both due to incomplete mechanical separation, suggest that all three formed in a single smelting step and were in close contact. Therefore it can be assumed that

they formed three different layers within a single furnace. The bottom layer, dominated by lead metal, probably collected the noble metals and would have been processed by cupellation – hence its absence from the archaeological record. Matte and slag were tapped out of the furnace, where they solidified as distinct layers, before being discarded.

The existence of the matte phase is indicative of the smelting of sulphide-rich ores, and gives information regarding the redox conditions in the furnace. The presence of lead, copper and iron sulphides, and of silver, antimony and arsenic within prills and sulphidic phases, point towards the processing of galena and pyrite, the two main ores which have been identified at this site, and probably chalcopyrite and more complex silver- and gold-bearing fahlores containing iron, antimony, copper, lead and arsenic. However, the overall low levels of arsenic in the various metallurgical products do not support the processing of arsenopyrite-rich ores, as previously suggested by the identification of this mineral as one of the main ores [7].

The lead content of the slag for many of the samples is typical of a medieval to early modern galena smelting [8]. Besides, the lead concentration of the pieces of matte is generally high. This suggests, first, that the various sulphidic ores were smelted for their lead content and not for copper; and second, that the galena ore contained lead in sufficient quantity to act as a collector for the noble metals, without requiring any further addition of metallic lead to the charge.

Further chemical and mineralogical analyses, as well as mass balance calculations, are currently under way, and aimed at determining whether any fluxes were used, more specifically whether iron or quartz were added to the charge to help form the fayalitic slag. The contribution of clay and fuel ash to the formation of slag is also investigated. Additional work is required to estimate more precisely temperature and redox process parameters.

Pieces of ores from both the mining and smelting areas are being analysed by ED-XRF at this time, in order to determine more accurately their content in precious metals, since so far these have not been identified by SEM-EDS in any of the analysed samples. The particular ore fragments from the mine could date to the final phase of mining at the Bockhart, and be an indication of the impoverishment of the veins in gold and silver towards the end of the sixteenth century. This could have led to the smelting sites of the Angertal to be abandoned due to a lack of ore. The pieces of ores found at the smelting site may, however, have been left aside after some beneficiation treatment, not being rich enough in the economically valuable minerals, and may thus not reflect a contemporary impoverishment of the ores.

The analysis of a larger number of samples will allow more detailed inferences as to the extent of standardisation and metallurgical skill in the Angertal smelting site. The degree of homogeneity and leanness of all the slag samples analysed so far are indicative of a fairly standardised and efficient process. However, as noted above, some gold and silver remain trapped in metal and matte inclusions. Although we have not found evidence of the further processing of matte in order to retrieve the noble metals within, the relatively high silver level in the analysed matte sample brings up the question of whether the Angertal smelters were aware of that loss. This raises the issue of whether it would have been worth assaying the matte – a process only recently identified by us on a small scale at the contemporary laboratory of Oberstockstall [9] – and thereby processing it further so as to recover the noble metals. Assaying matte is not part of the general canon of metallurgical practice at the time, as established in most of the Renaissance literature. However, the need to adapt to changing geological and/or economic conditions may have been an incentive to the local metallurgists for the development and application of innovative technologies in the smelting industry of sixteenth-century Austria, thus contributing to the long process of changing metallurgy from an art to a science.

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