TESTING ORES FOR GOLD AND SILVER IN RENAISSANCE AUSTRIA: NEW TECHNIQUES, NEW DISCOVERIES

A. Mongiatti
M. Martinón-Torres
T. Rehren

1. INTRODUCTION

The Middle Ages were a period of increasing demand for metals in Europe, as the known ore deposits were fast exhausting. Then, since the Renaissance, noble metals started arriving in large quantities from the New World, competing with the metal production of the Old World. It became increasingly necessary for Old World miners to exploit low-grade deposits and develop more reliable quantitative systems of analysis to evaluate these poor ores (Rehren 1997). In this context, fire assaying developed greatly, as an analytical technique to fulfil these new requirements (Rehren & Eckstein 2002). The techniques for small-scale assaying and refining of precious metals improved significantly during the Renaissance, in the overlapping fields of mining, minting, alchemy, chemistry, etc. (Smith & Forbes 1969; Martinón-Torres & Rehren 2005a). Fire assay was common practice during the 16th century for various metals, and it became essential for gold and silver-bearing ores. The experiments and discoveries performed in laboratories of this period laid the foundations of modern chemistry and experimental science.

Though techniques for assaying and refining are explained in various 16th century texts, such as Agricola's *De Re Metallica* or Ercker's *Treatise on Ores and Assaying*, these are often unclear, and may in part reflect theoretical concepts that do not match actual laboratory practice. This paper outlines the results of a major project involving scientific analysis of high-temperature laboratory

CONTENTS

remains, with main focus on the 16th century assemblage from Castle Oberstockstall, Austria. This is the most comprehensive Renaissance laboratory ever recovered, with over one thousand technical instruments, amongst other chemical ceramic and glass ware, as well as slag remains (Von Osten 1998). Following the study of the manufacture, provenance and performance of these apparatus (Martinón-Torres et al. 2003; Martinón-Torres & Rehren 2005b), the focus is now on the metallurgical residues, to investigate experimental procedures, and the manipulation and understanding of metals. Thus, this study illustrates the laboratory processing of noble metals, but also has the potential to address the different perceptions leading to our modern understanding of matter.

2. THE MATERIAL FROM OBERSTOCKSTALL: A UNIQUE SET OF HIGHLY SPECIALISED INSTRUMENTS

The assemblage discovered in the 16th century laboratory of Oberstockstall includes ceramic and glass ware with specialised technical laboratory forms. Among the artefacts were found numerous vessels of several sizes used for distillation, assaying, small-scale melting and smelting, and further furnace equipment such as muffles. Ceramics constitute the major component of the assemblage, mainly triangular crucibles, scorifiers and cupels (Fig. 1), as well as a significant number of larger pots with less diagnostic shapes. These different types of technical ceramics were used in high-temperature operations: many of them show characteristic residues of use such as crystalline salts, metallic drops and slag; and traces of burning from the fire. The triangular crucibles are made of very refractory graphite-rich clay, allowing them to withstand heat and chemical reactions. The scorifiers are flat open vessels manufactured with alumina- and quartz-rich clay, relatively thin-walled and used in intermediate oxidising reactions within an assaying sequence. The bone-ash cupels are thick vessels with a porous body made of finely crushed bone ash and clay, and with a shallow depression on top. They were used for cupellation – a high-temperature process which separates noble metals from lead by oxidising the latter into litharge (PbO), which is absorbed by the cupels (Von Osten 1998; Martinón-Torres et al. 2003).

The study of the remains produced by high-temperature reactions will help to understand the specific utilisation of these various instruments. Besides residues adhering to the vessels, there are fragments of slag, metal and matte probably produced in some of these vessels, but later removed from them.

**Figure 1**: From left to right: bone-ash cupel, triangular crucible and scorifier from Oberstockstall

3. METHODOLOGY

The micro-structural and chemical investigation was primarily based on reflected-light optical microscopy and scanning electron microscopy with an attached energy dispersive spectrometer (SEM-EDS). Energy-dispersive X-ray fluorescence (ED-XRF) was also used as a semi-quantitative technique and to detect potential traces of gold and silver, which could not have been identified with the SEM-EDS, especially when in concentrations below 1000 ppm.

4. RESULTS AND DISCUSSION

The analysis of the various metallurgical and chemical remains allows a detailed reconstruction of several high-temperature processes. Most of the residues, however, can be ascribed to an operational sequence aimed at extracting noble metals from ore samples. This sequence started with the reducing fusion of fahlore or a similar complex sulphidic ore in a triangular crucible together with fluxes and other additives, followed by a refining step under oxidising conditions in a scorifier, and completed by cupellation on a bone-ash cupel, which would lead to the retrieval of the precious metals contained in the ore sample (Fig. 2). Of particular interest are the lumps of matte, which formed in the triangular crucibles during the reducing fusion of an ore, and for which no parallel is known.

CONTENTS
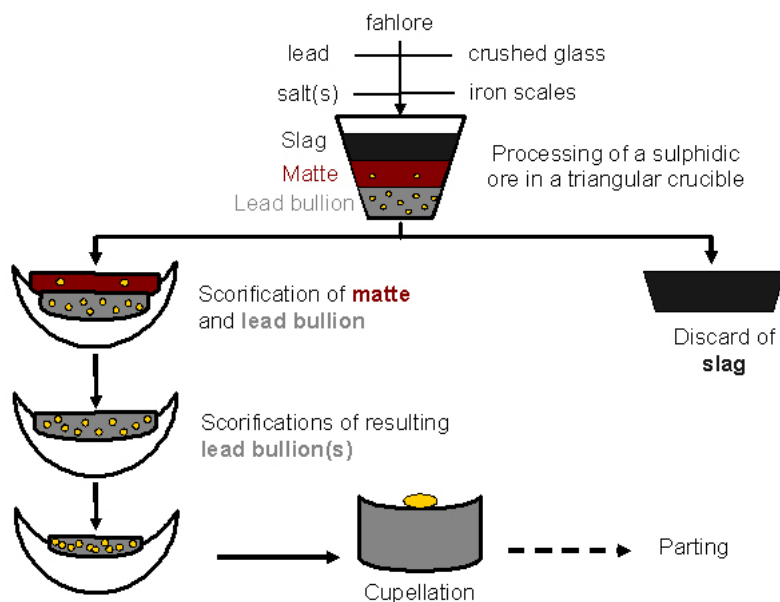
Figure 2: Diagram of the main technical sequence identified in Oberstockstall through the analysis of the residues of the various high-temperature stages.

4.1. The triangular crucibles: an apparently standard use

The residues within most triangular crucibles show broadly similar compositions. They include a silicate glass matrix, rich in alumina, soda, potash, lime, and iron oxide with minor amounts of zinc oxide and phosphates (Table 1). They also have variable quantities of magnetite crystals and sodium or potassium silicates; matte inclusions composed of sulphides of lead, antimony and/or copper; and usually metallic prills and matte particles mainly composed of antimony, copper and/or lead (Fig. 3). The material treated in these crucibles is likely to have been an ore, and not some metal or alloy, as too many elements, such as iron, calcium, zinc and antimony point towards a mineral origin and are very unlikely to come from the ceramic fabric (Martinón-Torres & Rehren 2005b). Some of these particular components were most likely part of the ore itself, and others were probably added as fluxes or collectors.

The matte inclusions in the crucible slag residues suggest the processing of a sulphidic ore, part of this sulphur not having oxidised during the reducing fusion in the crucible, and forming phases separate from the silica-rich system. The recurrent presence of antimony, copper, lead, bismuth and silver seems to suggest the assay of fahlore, a complex sulphidic ore (($Cu, Fe, Pb, Ag)_{12}(Sb, As, Bi)_4S_{13}$), for its content in precious metals. The high zinc concentration in the slag matrix fits this hypothesis, as sphalerite (ZnS) is a very common sulphide and frequently occurs with fahlore and other silver ores. The presence of matte and metallic inclusions (Fig. 3) in the slag residues also indicates that there were probably three layers in the crucibles separated by density: a lead-rich metallic bullion at the bottom, a sulphide-based system in between (the matte), and an oxide-based system on top (the slag).

|	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	MnO	FeO	CuO	ZnO	Sb2O3	PbO	SO2
OB 307/S2	5,1	0,1	9,5	45,9	0,5	3,1	6,5			13,2		7,9	0,5	6,9	0,8
OB 345/S1-S2	3,9	2	13,4	55,2	0,9	3,3	8,4	5,7		6,5		0,1			0,6
OB 461/S1	9,9	1,7	18,6	54,1	0,1	2,7	4,2	1,4		6,3		0,4			0,6
OB 479/S1	6,2	1,3	5,6	28,3		6,9	3,5	0,9		6,6			40,7		
OB 494/S1-S2	4,3	2,1	12,7	39,1	1,3	4,2	13,1	0,5		16,4	0,4		5,6		0,3
OB 498/S1	7,3	1,1	12,7	39,7	0,4	1,7	6,7	0,2		18,7		0,1	9,8		1,6
OB 509/S1	4,1	1,7	5,5	36,1	0,3	2,7	6,6	0,4		7,8		0,1		34,7	
OB N001/S1	0,1	1,9	3,8	25,3	2	2,9	13,9			17,1	4,6	0,4	21	6,5	0,5
OB N001/S2	0,1	2,3	7,6	45,7	0,7	4,7	6,1			14,5	4,2	0,1	12	1,5	0,5
OB N003/S1	9,8	1,4	8,3	35,1	0,5	2,6	10,3	1,2		26,2		0,1			4,5
OB S004/S1	7,2	1,1	2,9	50,7	0,7	6,7	1	2,4	0,8	23,9					2,6
Average of ceramic matrices	0,2	0,7	32,4	57,3	0,3	2,1	0,7	1,3		5					

Table 1: Average chemical composition by SEM-EDS, normalised to 100 wt%, of glass matrices of inner crucible slag residues.

The formation of crucible slag may find its origin in various components: the slag may simply be some molten ceramic, which introduces elements such as silica, alumina and potash in the slag (Table 1); but it may also derive from the various compounds of the charge, particularly the gangue of the ore and any added fluxes, or of the interaction between these and the ceramic fabric. The chemical composition of these slag residues, the relative proportions of their different elements and the comparison of these ratios with those of the ceramic, inform about the ceramic contribution to the slag formation, and the potential raw materials and additives processed in the vessel.

In Oberstockstall, these slag samples are relatively rich in iron and calcium when compared to the composition of the crucible fabrics: there is approximately three to four times more iron and about ten times more calcium than expected, if the slag were simply fused ceramic (Table 1). The iron may originate from pyritic ores, the most common sulphides. Gold often occurs disseminated in veins of pyrites or arsenopyrite; some of these minerals have been identified in the Oberstockstall assemblage (Soukup & Mayer 1997). It may be worth noting that, due to its apparent similarity with gold, pyrite is widely known as the fool's gold or the gold of the alchemists. However, iron could also have been added as a flux to drive the ore to melt: for instance, Ercker advises the addition of iron if the ore does not contain enough (Sisco & Smith 1951: 114). The calcium could find its origin in the gangue: Biringuccio mentions limestone as a gangue of copper ores and silver- or gold-bearing lead ores (Smith & Gnudi 1990: 53) and modern geology knows calcite as the gangue of many copper ores and complex sulphidic ores such as fahlore.
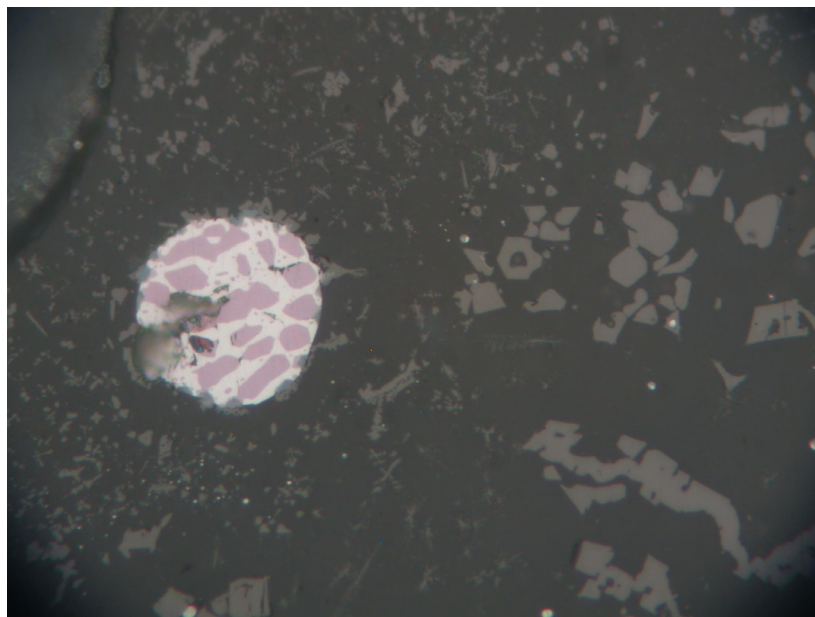
Figure 3: Microstructure of a crucible slag sample: cubic magnetite crystals (brown) and metallic inclusion of copper (white) and copper antimonide (pink) in a dark grey glassy matrix, enriched in calcium oxide, iron oxide, potash and soda (OB 494/S2, optical microscope, plain polarised light, 1000x, long axis ~150 μm).
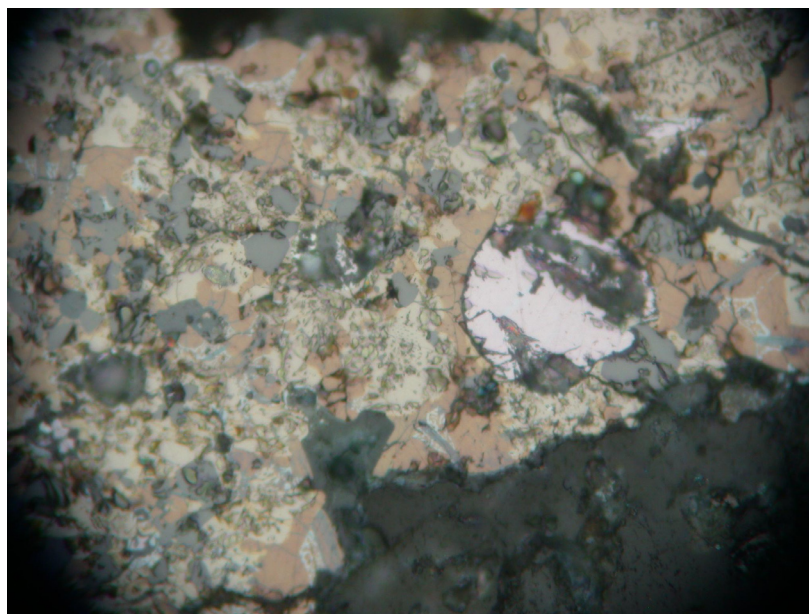
Figure 4: Microstructure of a matte cake: a complex sulphidic system composed of pyrrhotite (light cream colour) a mixture of chalcopyrite (light yellow) and bournonite (flesh/brown); with crystals of magnetite (light grey) and a large corroded prill of antimony (white and grey). (OB S002/S2, optical microscope, plain polarised light, 500x, long axis ~300 μm).

	Na2O	MgO	Al2O3	SiO2	K2O	CaO	TiO2	FeO	CuO	As2O3	Sb2O3	PbO
OB 268/S1			5	17,2	0,5	0,9		5,4	0,8			70,3
OB 269/S1			2,5	8,2								89,4
OB 270/S1		0,3	2,4	9,6		0,1		10,6	1,5	0,1		75,4
OB 271/S1			1	2,9							92	4,1
OB 273/S1			5,9	20,9	0,5	0,5	0,4	1	0,8	0,6		69,5
OB 274/S1			3,2	11,1	0,5				0,2			85
OB 276/S1			4,8	16,5		0,1		2,2				76,4
OB 277/S1			4,4	16,9				2,1	3			73,6
OB 279/S1			2,8	9,7	0,5	0,7		1,7		8,5		76,1
OB 281/S1			3,2	11				4,9	2,2	0,4	6,1	72,3
OB 284/S1			2	6,4		1,3		5,3		1,4	65,6	18,1
OB N006/S1		0,9	4,6	13,8	0,2	2,3	0,1	2	4,1			71,9
Average of ceramic matrices	0,4	0,5	31,2	58,6	1,6	0,8	0,9	4,7				

Table 2: Average chemical composition by SEM-EDS, normalised to 100 wt%, of the matrices of the scorifier slag samples.

The high SiO_2/Al_2O_3 ratio in the slag could result from either a selective melting of the ceramic fabric and/or an additional source for silica. Quartz, for instance, is a common gangue mineral for gold ores and several sulphidic ores. In addition, other sources of the silica in the slag may be considered, in the light of recommendations by 16th century authors: for example, the deliberate addition of quartz (Hoover & Hoover 1950: 380), or even of crushed glass, as a flux to melt a relatively refractory ore (Hoover & Hoover 1950: 238; Wickoff 1967: 224). This latter possibility in particular would explain the combined high concentrations of silica, potash and lime in the slag. Early modern glass, readily available in the Oberstockstall laboratory, typically contains more lime than alkali oxides, and more potash than soda (Wedepohl 1997). Nonetheless, although potash-lime glass was the main type in Northern Europe, soda-lime glass was extensively imported from France and Italy. The high amount of sodium oxide in the slag could therefore be due to the addition of such type of glass. This would be in conformity with the presence of fragments of Venetian glass objects in the assemblage from Oberstockstall (Von Osten 1998: 70). However, the high soda content could also have its origin in the addition of rock salt (NaCl), sodium nitrate or carbonate, as recommended by the main Renaissance authors. These salts would act either as a cover for the charge, which would help prevent projections and therefore losses at the beginning of the reaction, or as a flux, because they would melt immediately in a hot crucible and drive the rest of the charge to melt.

The single isolated piece of slag recovered (OB S004) shows a similar composition, a silica-, iron oxide-, soda- and potash-rich glass with large inclusions of iron sulphides, confirming that this slag was produced in one of the triangular crucibles as a result of the fusion of an ore, and that matte was probably formed during this operation.

In summary, it appears that a relatively large number of triangular crucibles in the laboratory assemblage from Oberstockstall were used for the fusion of sulphidic minerals, such as tetrahedrite ($(Cu, Fe)_{12}Sb_4S_{13}$), pyrite, galena, etc, which probably contained antimony and noble metals; as well as calcite and/or quartz as gangue. Most likely, several reagents were added to the charge and contributed to the simultaneous formation of metal, matte and slag. Some, if not most, of the lead oxide, iron oxide, potash and soda of the slag were probably not present in the ore, and almost certainly part of additional compounds. Lead was used as precious metal collector in the crucible, as suggested by lead-rich metallic remains; and fluxes such as glass, iron filings and salt were probably added to the ore to perform this first stage of the metallurgical sequence, most likely under neutral to reducing conditions. Some crucibles exhibit some differences in their composition, suggesting some variability in the processes taking place in this laboratory, e.g. the use of antimony as metal collector instead of lead, resulting in an antimony silicate glass (OB 479). There is, however, not the space here to elaborate on this further.

4.2. Matte: an unexpected product

Several matte cakes and fragments have been recovered in Oberstockstall. They exist in relatively small numbers compared to the hundreds of reaction vessels. However, they are almost the only surviving proper products resulting from the high-temperature operations carried out in these ceramics, except for one fragment of slag, and a single piece of bullion (see above); all other remains are present as relatively thin films attached to crucibles. Their occurrence in the laboratory suggests that they may have been kept for further treatment, while the slag was thrown away elsewhere. These matte finds are thus the best-preserved physical representation of actual 16th century practice, and their study is crucial to further understand the chemical reactions, the ore and the potential fluxes utilised in Oberstockstall.

The characteristic triangular shape of one particular matte cake confirms it was produced in one of the triangular crucibles during the first step of the sequence, confirming the development of a three-layer system in this reaction vessel. Most of these matte lumps, however, exhibit what remains of circular sections, indicating that the melt was either poured into a different container and left to cool, or solidified at a low height in the crucible, where the inner section is not triangular but rounded.

All the matte lumps present similar microstructures: a complex mixture of sulphur-dominated phases, mainly composed of antimony, lead, copper and iron, with many magnetite crystals and slag particles, as well as numerous corroded antimony-rich prills (Fig. 4). Two matte fragments mainly show antimony- and lead-rich phases, such as bournonite ($PbSbCuS_3$), tetrahedrite ($(Cu, Fe)_{12}Sb_4S_{13}$) and galena, while the other matte cakes are essentially composed of iron-rich phases, such as pyrrhotite (FeS), chalcopyrite ($CuFeS_2$), tetrahedrite, and bornite (Cu_5FeS_4), adding up to between 30 and 40 wt% in the bulk compared to ca. 15 wt % for the former two samples. This varia-

tion may be the result of the processing of different ores, some variability in the redox conditions, or the use of different fluxes. These hypotheses again point towards the experimental nature of the various metallurgical procedures carried out in Oberstockstall. Tetrahedrite, pyrite and galena may have been some of the tested ores, having partially reacted in the melt and then recrystallised.

The high iron content of most of the matte cakes, together with the numerous inclusions of magnetite, calcium and sodium silicates relates them to the crucible slag residues, further corroborating the idea that they formed in the triangular crucibles. In addition, this high concentration of iron is also connected to the scorifier slag remains – a matter discussed below.

Matte is typically undesired in fire assaying, as it retains some of the noble metals, which are then lost for the lead bullion, leading the assay to return an inaccurate result. This is probably why Renaissance writers recommended that sulphidic ores were thoroughly roasted beforehand, which would drive off the sulphur and prevent the formation of matte. Hence, matte cakes such as those found in Oberstockstall are not mentioned in any of the books reviewed (Sisco & Smith 1951: 46-48, 218). In contrast, the person working in Oberstockstall did not roast the ore samples, and had instead to routinely refine this sulphur-rich material in successive scorifications and cupellations, in order to extract the noble metals it held. This practice also differs from that documented in the contemporary Frobisher's ore-assaying site, in Canada, where no matte has been identified even though part of the ore was galena (Beaudoin & Auger 2004).

4.3. The scorifiers: a potentially wide utilisation

Scorification literally means "slag making", and it typically involves an oxidising reaction aimed at concentrating the noble metals within lead-based bullion. The oxide-rich slag and traces of use on the Oberstockstall scorifiers differ very much from the slag formed in the triangular crucibles, and show that these vessels indeed underwent a high-temperature oxidising reaction. As with the crucibles residues, most of the slag samples from these dishes show a relatively similar chemical composition: their main matrix is a lead silicate with variable amounts of silica and other oxides, mainly iron oxide and alumina (Table 2). The lead-dominated glass probably results from the oxidation of the lead metal added earlier to the raw material(s) in order to collect the noble metals, as advised in contemporary books. The composition of the glass also confirms that the substance scorified was not a raw ore, but the products of the previous reducing stage: the slag is lacking typical gangue components, such as alkali and earth alkali oxides, in stark contrast with the crucible slag remains.

A few matte inclusions and metallic prills are found in these scorifier slag specimens. These inclusions, and the relatively high iron oxide levels, indicate that the material scorified was not just metal bullion, but also contained matte. The scorification of matte cakes with the metal is documented here for the first time, giving new insight into small-scale, high-temperature processes. The lead metal bead resulting

from this operation, presumably containing the gold and/or silver of the original ore sample, would be either refined by further scorification or, when clean and small enough, subjected to cupellation.

Two exceptional samples (OB 271, OB 284) are mainly composed of antimony oxide. Briefly, these suggest that the scorified material was an antimony-rich bullion or matte layer, resulting from the addition of antimony as metal collector in the crucible (see above), and that antimony was further used as an alternative metal collector during the scorification step.

4.4. The bone-ash cupels: a final refining step

The analyses of cupels from Oberstockstall indicate they are made of a mixture of bone ash and some clay, with a pure bone ash lining on the central depression. The bodies of used cupels are soaked with lead oxide, now mostly transformed into secondary carbonates, which filled the pores; varying amounts of metals such as gold, silver, copper, antimony and bismuth have also been detected, relating these to the previous metallurgical residues (Rehren 1998; Martinón-Torres & Rehren 2005b). Thus, cupellation would constitute the last high-temperature operation necessary to obtain a clean button of noble metals, completely free of lead. If both gold and silver where alloyed in this final product, they could be parted using mineral acids, which would explain the presence of distillation equipment and glassware in the assemblage.

5. CONCLUSIONS

This unique assemblage allows a glimpse of real chemical and metallurgical 16th century laboratory practice. The main operational sequence identified here, involving the crucible fusion of a fahlore with lead as metal collector and iron filings, crushed glass and salt as fluxes, seems to be in accordance with the description of the procedures given by Agricola and Ercker. There are, however, two significant but closely related deviations from the standard given in books: first, the lack of roasting; and second, the scorification and refining of matte, which would not form as a separate phase if the ores were first roasted. In addition, the processing or use of antimony and bismuth – metals "unknown" as such to most 16th century writers – and other experiments present a more colourful picture than the "canon" given in written treatises.

This contextual study aims first at the understanding of past metallurgical processes and the related technologies, through the analysis of archaeological remains. However, wider implications are explored in our ongoing work. On the one hand, the understanding of the technical texts, combined with the archaeometric study of contemporary material, may provide a measure of the influence of books on practitioners. On the other hand, by identifying *chaînes opératoires* and interpreting

them in their context, this study will contribute not only to a narrow history of technicalities, but to a wider and richer history of science and technology that is much more relevant to us.

ACKNOWLEDGMENTS

REFERENCES

Beaudoin G, Auger R, 2004. Implications of the mineralogy and chemical composition of lead beads from Frobisher's assay site, Kodlunarn Island: prelude to Bre-X?. Canadian Journal of Earth Sciences, vol. 41: 669-681.

Hoover HC, Hoover LH, 1950. De Re Metallica, Georgius Agricola, Translated from the first Latin edition of 1556, Dover Publications Inc, New York.

Martinón-Torres M, Rehren, Th, 2005a. Alchemy, chemistry and metallurgy in Renaissance Europe: a wider context for fire-assay remains. Historical Metallurgy, vol. 39, no. 1: 14-28.

Martinón-Torres M, Rehren Th, 2005b. Ceramic materials in fire assay practices: a case-study of 16th-century laboratory equipment. In: Understanding people through their pottery - Proceedings of the 7th European Meeting on Ancient Ceramics (EMAC'03), Instituto Portugues de Arqueologia, Lisbon: 139-149.

Martinón-Torres M, Rehren Th, Von Osten S, 2003. A 16th century lab in a 21st century lab: archaeometric study of the laboratory equipment from Oberstockstall (Kirchberg am Wagram, Austria). Antiquity, vol. 77, no. 298.

Rehren Th, 1997. Metal Analysis in the Middle Ages. In: Material Culture in Medieval Europe. Papers of the Medieval Europe Brugge 1997 Conference, vol. 7 G. De Boe & F. Verhaeghe, eds., Instituut voor het Archeologisch Patrimonium, Zellik: 9-15.

Rehren Th, Eckstein K, 2002. The Development of Analytical Cupellation in the Middle Ages. In: Archaeometry 98: Proceedings of the 31st Symposium Budapest, April 26 -May 3, 1998, vol. 2 E. Jerem & T. B. Katalin, eds., Archaeolingua, Oxford: 445-448.

Sisco AG, Smith CS, 1951. Lazarus Ercker's Treatise on Ores and Assaying. Translated from the German edition of 1580, The University of Chicago Press, Chicago IL.

Smith CS, Forbes RJ, 1969. Metallurgy and Assaying. In: A History of Technology. vol 3: From the Renaissance to the Industrial Revolution, c,1500-c.1750, C. Singer et al., eds., Clarendon Press, Oxford UK: 27-71.

Smith CS, Gnudi MT, 1990. The Pirotechnia of Vannoccio Biringuccio. The Classic Sixteenth-Century Treatise on Metals and Metallurgy, 1st edn. 1959 edn, Dover Publications Inc, New York.

Soukup RW, Mayer H, 1997. Alchemistisches Gold. Paracelsistische Pharmaka. Laboratoriums-technik im 16. Jahrhundert, Böhlau, Wien.

Von Osten S, 1998. Das Alchemistenlaboratorium von Oberstockstall. Ein Fundkomplex des 16. Jahrhunderts aus Niederösterreich, Universitätverlag Wagner, Innsbruck.

Wedepohl KH, 1997. Chemical composition of medieval glass from excavations in West Germany. Glastechnische Berichte - Glass Science and Technology, vol. 70, no. 246, 255 p.

Wickoff D, 1967. Albertus Magnus, Book of Minerals, Clarendon Press, Oxford.

CONTENTS