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Between the Bronze Age and the Middle Ages:

New Investigations of Slag from Panjhir, Afghanistan

ABSTRACT: *Fourteen slag samples from Panjhir were sectioned and mounted for optical and scanning electron microscopy. The microscopy of the slag samples is mostly consistent with previously analyzed polymetallic copper-lead-silver slag samples from Panjhir (Merkel, et al., 2015; Thomalsky, et al., 2015), but two slags are notably different. In one slag sample, a concentration of silver prills was identified and can be found in a highly oxidized region of the slag. These prills are interpreted originating from near a tuyère where blast of oxygen could have oxidized the argentiferous lead leaving the silver behind in form of metallic prills. The second unusual slag adheres to technical ceramic, possibly a crucible or furnace fragment, and is unique among the slags from Panjhir, entirely lacking lead, silver, and sulfur. Instead, copper-arsenic alloy prills were found. The copper-arsenic prills have an average arsenic content of 6 % which is a common alloy in the Bronze Age and may be an indication of prehistoric metal production at Panjhir. Additionally, three samples of argentiferous lead were taken from the slag for analysis. One argentiferous lead sample was cupelled to recover the silver, and the silver and lead samples were analyzed by inductively-coupled-plasma mass spectrometry. The argentiferous lead contains 2900 to 5400 ppm silver with larger quantities of bismuth and antimony. The cupelled silver contains bismuth above one percent and a gold content in the ppm range paralleling the composition of Islamic dirhams from the Panjhir region.*

KEYWORDS: POLYMETALLIC SMELTING, DIRHAMS, ARSENICAL BRONZE, CUPELLATION, BISMUTH, ARCHAEOMETALLURGY, LEAD ISOTOPE ANALYSIS.

Introduction

The silver mines of Panjhir are renowned for their unsurpassed productivity by Islamic writers of the 10th century AD (Ibn Hauqal and al-Hamdani), however, there are many unanswered questions about the role Panjhir played in the economy of not just the medieval period; its role in the pre-Islamic period is altogether unknown. The massive expansion of silver production in Central Asia and Afghanistan that occurred at the end of the 9th century AD has left its impact on the northern European landscape. Dirhams from the regions of Afghanistan and Transoxania, today Uzbekistan, are commonly found in 10th century hoards and settlements in Scandinavia, and the Viking-age emporium of Hedeby in northern Germany has numerous examples. Among the silver finds from Hedeby, coins struck at the mints of Samarqand, Al-Shash, Balkh, Andaraba, and even an example from Panjhir have been uncovered. The elemental and lead isotope analysis of such coins can give insight into the inner workings of the mining industries at the origin of the large-scale exodus of silver from Central Asia, but, from the European standpoint, it helps understand the recycling practices, and the dissemination of Asian silver and the chronology of its import. An exploratory study was carried out on the silver finds from Hedeby with these goals (Merkel, 2014). The analysis of dirhams from mining regions can serve as a proxy for the lack ore and slag available from the mines and production sites themselves, though, this may also give rise to erroneous conclusions, as will be explained.

Although mining region of Panjhir is celebrated by medieval authors like Ibn Hauqal (10th century AD, p.233) for its immense output of silver, there are a number of instances where the archaeological evidence points to the contrary. Firstly, when relating the quantities of dirhams minted in Central Asia and Afghanistan, the mints of Transoxania, particularly those of Al-Shash, they dwarf the minor amounts of dirhams minted in Balkh and Andaraba that are closer to the mines of Panjhir (Kovalev, 2002, p.3; Kovalev, 2003, p.58; Noonan and Kovalev, 2002, p.169) (Fig. 1). Based on the analysis of Samanid dirhams and slag from the Ilak region, Al-Shash, the most productive Samanid mint, seems to be supplied with silver from the Ilak region of Uzbekistan and is distinct from the coins of northern Afghanistan (Merkel, 2014). One could ask where the silver of Panjhir went, if it was not to be minted into coins.

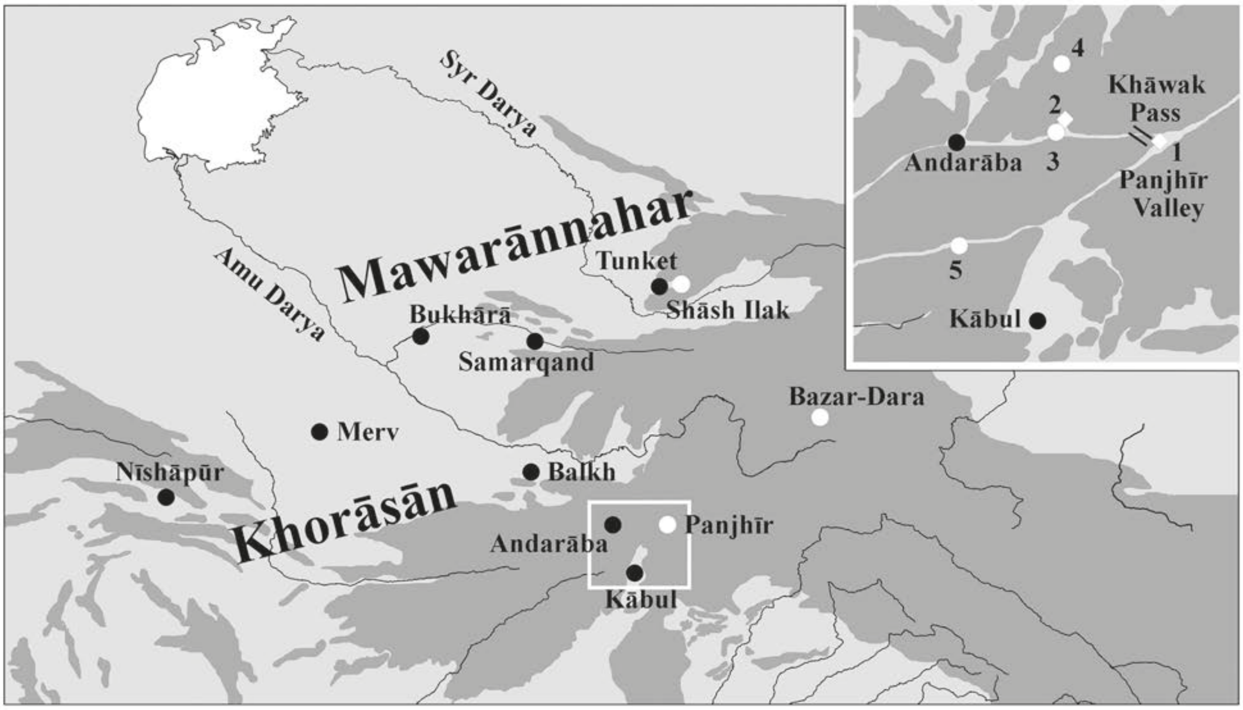

Fig. 1. Map of Central Asia and Afghanistan showing a selection of settlements (black) and mining regions (white). Detail of the Andarāba/Panjhīr region and polymetallic and lead-zinc ore deposits: 1 Chukri-Naw Fe-Ag (Polymetallic), 2 Unnamed F-Ag (Polymetallic), 3-4 Unnamed (Pb-Zn), 5 Farinjal (Pb-Zn). According to Merkel, et al. (2015, p.231).

A second important example are the contradicting lead isotope ratios of the polymetallic copper-lead-silver slag from the Panjhir Valley and the dirhams from northern Afghanistan (Merkel, et al., 2015). The slag was found where the valley leading to the Khawak pass meets the Panjhir river valley, and this location goes well with the 10th century AD description of Ibn Hauqal, who writes that the town of Panjhir is on the river with the same name and four days journey from Andaraba (10th century AD, pp.225, 231), which would require crossing the Khawak pass.[1] The polymetallic slag found at Panjhir is highly radiogenic, meaning they show a significant influence by the radioactive decay of uranium and thorium. The dirhams supposedly minted from Panjhir's silver do not share the same radiogenic isotope signature as the slag, yet, other elemental characteristics are consistent, chiefly the low gold content and the high bismuth content of the argentiferous lead. The difference in lead isotope ratios is not easy to explain, either other imported lead was used during refining or these copper-lead-silver slags from Panjhir have no relationship to the Samanid-era dirham production of northern Afghanistan.

The third archaeological problem is the dating of silver production debris from the Panjhir Valley. The slag was not found in archaeological contexts but was deposited by erosion. Charcoal samples were found along with the slag providing two radiocarbon dates suggesting a Bronze Age exploitation (Thomalsky, et al., 2015). More recently, Julio Bendezu-Sarmiento, from the French National Centre of Scientific Research, visited the slag deposits at Panjhir and noted a high concentration of Kushan period ceramics (2nd c. BC to 3rd c. AD) as well as Islamic period ceramics, and no ceramics datable to the Bronze Age were found (J. Bendezu-Sarmiento, pers. comm. 1.12.2015). Although ceramic evidence seems to exclude a Bronze Age phase and the charcoal samples associated with the slag may have been impacted by contamination, properly conducted archaeological surveys have not been carried out and therefore, our knowledge of the archaeology is extremely limited. A multiphase exploitation of the mineralizations at Panjhir is certainly plausible; a number of examples exist from western Asia with both Bronze Age and Islamic period

DAI Sample	Material
Pa-15-12	Slag, Pb, and Ag
Pa-15-26	Slag and Pb
Pa-15-22	Slag and Pb
Pa-15-10	Slag
Pa-15-6	Slag
Pa-15-24	Slag
Pa-15-27	Slag
Pa-15-14	Slag
Pa-15-21	Slag
Pa-15-30	Slag and Ceramic
Pa-15-25	Slag
Pa-15-19	Slag
Pa-15-17	Slag
Pa-15-31	Slag

Tab. 1. List of slag samples from Panjhir analyzed in 2015.

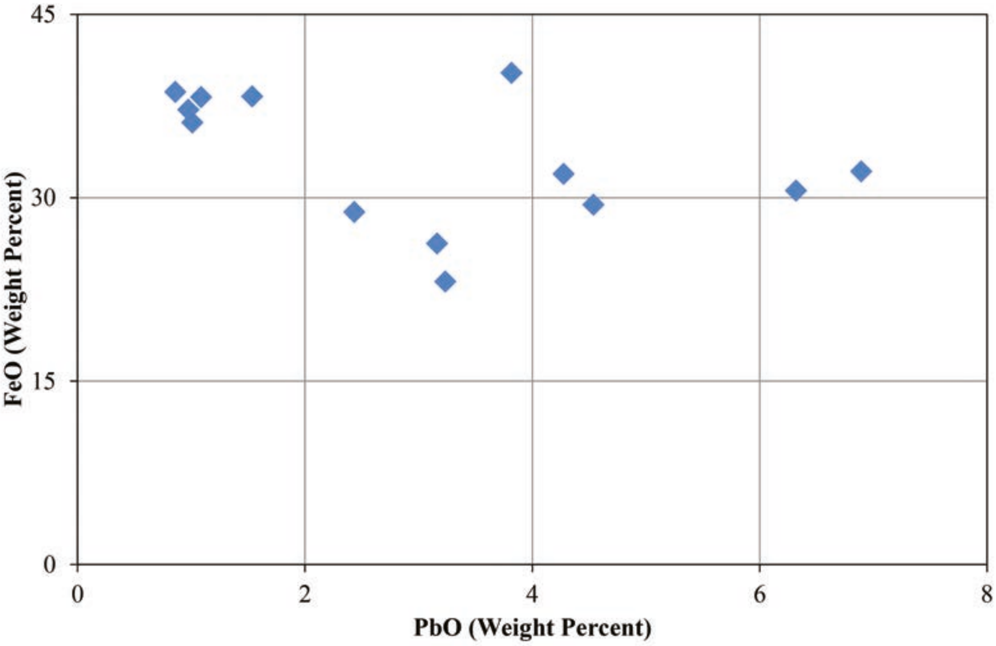

Fig. 2. The correlation between iron oxide and lead oxide in the semi-quantitative bulk slag compositions is weak (SEM-EDS). There is a small cluster of slags with FeO around 37 % and PbO at 1 %.

remains of copper exploitation at the same site (Hauptmann, 1985, pp.34-36; Hauptmann, 2007; Pigott, 1999, p.78; Stöllner and Weisgerber, 2004; Weisgerber, 1987).

In this conflicted setting, the analysis of the Panjhir slag samples remains an important task in characterizing the technical processes carried out and to understand their role in the developing archaeological picture. To augment the studies already undertaken in 2014 (Merkel, et al., 2015; Thomalsky, et al., 2015), fourteen slag samples collected from the Panjhir Valley were selected for microscopy, and three of them contained substantial amounts of metallic lead that could be analyzed with quantitative means, and one argentiferous lead sample was cupelled to recover the silver (Tab. 1). The main goals of this study are to explore the production technology, to identify technical differences that might be chronologically related, and to better characterize the richness of the ore used and the silver that would have been produced.

Methods

Several methods of analysis were used to study the slag, technical ceramic, lead, and silver from Panjhir. Ten mounted slag samples were prepared by setting the slag in epoxy resin and polishing it to the micron level. In addition, eight polished thin-sections were prepared for use under the optical microscope (Zeiss Galaxy Axiophot). Reflected and transmitted light microscopy were both used with a range of 2.5 to 40 times magnification. To complement optical microscopy, minerals and phases present and their morphology were analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). For this a Zeiss Gemini SEM combined with a Thermo UltraDry Silicon Drift X-ray Detector was used with a working distance of 10 mm and an energy of 20 kV. Samples were non-conductive so the SEM chamber was set to low vaccuum (ca. 30 – 50 Pascal) containing nitrogen gas. The quantification of the elemental spectra was performed using the Nora System Seven software fitted standard calibration and values obtained should be viewed as semi-quantitative.

Quantitative analysis of lead and silver samples was attained by single-collector inductively-coupled-plasma mass spectrometry (SC-ICP-MS) using a Thermo Scientific ELEMENT XR ICP-MS at the Deutsches Bergbau Museum Bochum. Three argentiferous prills from three different slags were extracted for quantitative analysis. Each prill weighed several grams, but the largest prill, weighing more than 12 g, was sufficient to perform the cupellation process to extract the silver (Section 3. 2). The lead and silver was dissolved in nitric acid (5 ml: 3 ml, H_2O: HNO_3) and diluted with ultra-pure water to create a 1000 ppm solution. For the cupelled silver sample, the sample was divided into two parts and a separate solution was prepared to dissolve the gold by first dissolving the silver in nitric acid and, secondly, by adding hydrochloric acid to form aqua regia. For the calibration of lead, the PG1-PG6 (Institute of Non-Ferrous Metals standards) were used and for silver the RAgP6 (Rand Refinery Ltd., MBH Reference Materials).

Type	Name	Formula
Metallic	Antimony	Sb
	Arsenic	As
	Bismuth	Bi
	Copper	Cu
	Gold	Au
	Lead	Pb
	Silver	Ag
	Speiss	Cu-Sb or Cu-Fe-As
Sulfide	Bornite	Cu_5FeS_4
	Chalcocite	Cu_2S
	Chalcopyrite	$CuFeS_2$
	Galena	PbS
	Pyrite	FeS_2
	Pyrrhotite	Fe(1-x)S
	Sphalerite	(Zn,Fe)S
Oxide	Cuprite	Cu_2O
	Delafossite	$CuFeO_2$
	Magnetite	Fe_3O_4
	Wüstite	FeO
Phosphate	Apatite	$Ca_5(PO_4)_3(F,I,OH)$
Silicate	Clinopyroxene	$(Ca, Na, Fe, Mg)(Al, Fe, Mg)(Si, Al)_2O_6$
	Hedenbergite	$CaFeSi_2O_6$
	Fayalite	Fe_2SiO_4
	Leucite	$K[AlSi_2O_6]$
	Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$
	Orthoclase	$KAlSi_3O_8$
	Plagioclase	$CaAl_2Si2O_8$
	Quartz	SiO_2
	Tridymite	SiO2

Tab. 2. List of minerals and phases mentioned in the text.

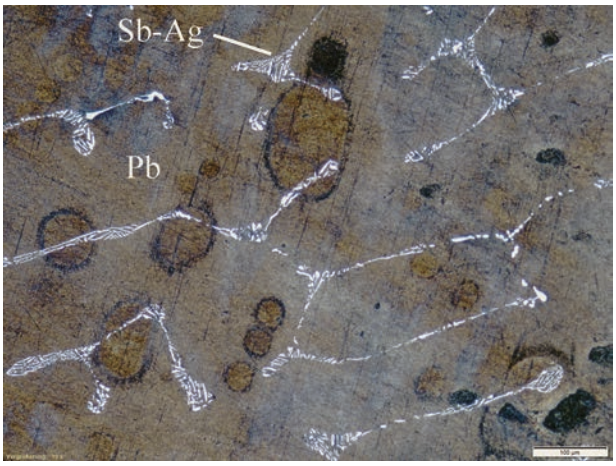

Fig. 3. Argentiferous lead showing the silver-antimony-lead eutectic infill in slag sample Pa-15-27. Polarized light microscope image, scale bar is 100 µm.

Results

The results are split into two parts, one focussing on the microscopy of the mounted samples and thin sections and the second on the mass spectrometry of the argentiferous lead and the cupellation results.

Microscopy of the Slag and Argentiferous Lead

Polymetallic Smelting Slags – Copper-Lead-Silver

Macroscopically, the slag fragments are black to dark gray in color and have blue, green, and white incrustations. Their texture is heterogeneous, ranging from bubbly to dense, from coarse with rock fragments to smooth. Microscopically, all but one sample contain copper, lead, and silver-rich phases; one very special slag (Pa-15-30) has copper-arsenic alloy prills, is clearly unrelated to lead-silver production and will be discussed separately (section 3.1.3). The majority of samples shows similar characteristics to previous slag samples analyzed from Panjhir (Merkel, et al., 2015), but there are some important differences, which will be outlined in this section.

The slags primarily contain phases like fayalite and calcium-iron bearing clinopyroxenes similar to hedenbergite (see Tab. 2 for list of phases and minerals). Potassium alumosilicate phases similar to leucite in composition and spinels like magnetite are common. Euhedral magnetite phases can be present in the slag in large quantities either well dispersed throughout the slag or occasionally in form of large inclusions up to 7 mm in size with small (< 50 µm) inclusions of copper and lead-bearing phases. The bulk slag compositions are presented in table 3. There is a weak inverse correlation between the iron oxide and lead oxide (Fig. 2) and there is an apparent cluster of compositions with ca. 37 weight percent iron oxide and ca. 1 percent lead oxide. Although they are elementally similar, they do not form a cohesive group microscopically; they all have dense non-porous textures with well distributed spinel and silicate slag phases, but the relative amounts of the different types of phases and inclusions vary. In many of the slags, partially reacted or unreacted silicates can be found; most common is quartz, but remains of potassium-rich feldspars are numerous.

All slags, with exception of the atypical Pa-15-30, contained prills of argentiferous lead, but all slags contain various copper phases. In the present samples the argentiferous lead prills can be as large as 15 mm and are almost always associated with copper sulfides and copper antimonides. Most lead prills are in the lead-antimony-silver-system, which was thermodynamically described by Lee, Oh, and Lee (1994). A segregation of metallic antimony and silver antimonide phases formed between the lead grains during cooling (Fig. 3). The argentiferous lead prills tend to contain more antimony than copper and silver (Fig. 4) and there does not seem to be a clear relationship among the three elements. The analysis of 64 lead prills (> 50 µm) showed an average silver content of 1.7

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	S	K_2O	CaO	MnO	FeO	Cu_2O	Sb_2O3	PbO
Pa-15-12	2.2	2.0	8.0	33.7	-	-	2.2	9.2	1.2	38.3	0.6	-	1.5
Pa-15-26	0.9	1.9	8.4	40.3	0.6	-	2.7	9.4	0.1	29.4	0.6	1.1	4.5
Pa-15-22	2.0	2.4	8.6	32.3	0.5	0.5	2.4	11.1	1.8	36.1	0.5	0.7	1.0
Pa-15-10	2.1	2.3	6.5	37.3	0.6	-	2.0	7.4	1.4	32.1	0.6	0.8	6.9
Pa-15-6	2.7	2.8	10.8	42.6	-	-	2.6	9.2	0.9	23.1	0.9	0.5	3.2
Pa-15-24	2.2	2.5	7.8	30.3	0.5	1.0	2.5	10.7	1.9	38.6	0.8	-	0.9
Pa-15-27	3.1	2.1	6.6	31.4	0.5	-	2.1	7.3	1.8	40.2	0.6	-	3.8
Pa-15-14	2.0	2.5	7.9	34.8	0.6	-	2.5	8.6	2.0	30.6	1.0	1.2	6.3
Pa-15-21	2.6	2.5	9.0	32.3	0.7	0.9	3.2	7.5	2.6	37.2	-	-	1.0
Pa-15-25	2.8	2.5	9.9	40.9	0.6	-	2.7	9.3	1.2	26.3	-	0.6	3.2
Pa-15-19	2.2	2.2	10.0	40.3	0.5	-	2.9	9.2	1.0	28.8	-	-	2.4
Pa-15-17	2.1	1.7	8.9	33.4	0.6	0.5	2.2	8.9	1.0	38.2	-	0.8	1.1
Pa-15-31	2.6	2.5	7.6	37.8	-	-	2.6	7.2	1.1	31.9	0.8	1.0	4.3

Tab. 3. Semi-quantitative bulk slag compositions determined by SEM-EDS area analysis. The analyses are averages of three or more 2 mm^2 areas of homogeneous slag matrix. Oxygen was calculated stoichiometrically and carbon was excluded. The "-" means not detected or the value was under 0.5%. Values are normalized to 100 % and given in weight percent.

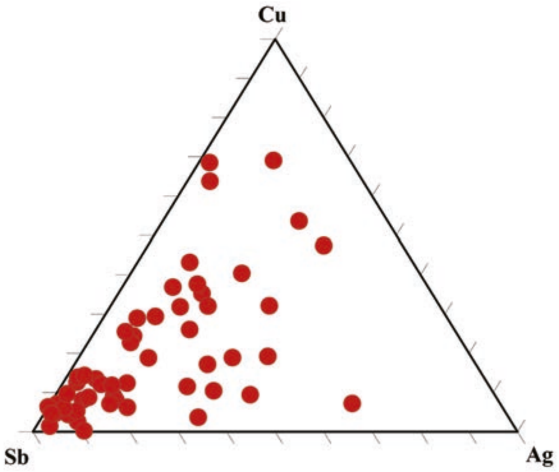

Fig. 4. Relative amounts of antimony, copper and silver in the argentiferous lead prills determined by SEM-EDS. The plotted points have combined total Sb-Ag-Cu contents above 5 wt. % and below 35%. Bismuth was excluded because it was difficult to measure, due to peak overlap with lead and other elements.

weight percent, however, the SEM-EDS has a tendency to overestimate the levels of silver, antimony and copper.[2]

The sulfide inclusions have a range of compositions. Slag sample Pa-15-19 has clusters of sulfides containing iron sulfides (pyrrhotite) and zinc sulfides, galena, and an eutectic/co-eutectic intergrowth of galena and copper-iron sulfide (Fig. 5a). Iron sulfides like pyrrhotite have not been identified in the other slags from Panjhir. The copper-iron sulfides in this sample are bright yellow under the optical microscope and appear to be chalcopyrite. There is little metallic lead in this slag; the lead tends to be present as sulfides. In contrast, the majority of slags from Panjhir has copper sulfides with less iron such as bornite or chalcocite. Slag Pa-15-22 has bornite-chalcocite phases forming an eutectic with galena and is associated with a prill containing lead and copper antimonide (Fig. 5b). The large argentiferous lead prills are all accompanied by a layer of copper sulfide matte of about 1 to 2 mm thickness. A thin layer of speiss separates the matte and the lead. This speiss typically contains copper antimonides. Copper-iron arsenide speiss lathes are found together with copper antimonide in Slag Pa-15-24, but in general, arsenides are not commonly found in the copper-lead-silver slags from Panjhir.

Minor amounts of bismuth are difficult to be detected in the metallic inclusions by SEM-EDS because of a peak overlap with lead, which tends to be a major element. Only in rare cases, significant quantities of bismuth are present so that clear bismuth peaks can be detected. It has been noted previously that extremely silver-rich bismuth-bearing agglomerations have been found in slags from Panjhir (Merkel, et al., 2015, p.241-243), and in Slag Pa-15-24 one such inclusion was found (Fig. 5c-d). In the inclusions of this type, there is a phase separation between bismuth-poor and bismuth-rich lead together encased in layers of copper antimonides and copper-iron sulfide matte. Within this type of agglomeration, inclusions larger than 100 μm can be found containing mostly silver with minor amounts of antimony.

Silver Prills in Polymetallic Smelting Slag

Among the polymetallic copper-lead-silver slags, sample Pa-15-14 has unsusual characteristics that have not been seen before, chiefly metallic silver inclusions of up to 0.5 mm in size. The slag can be divided into two regions, based on the redox conditions: a reduced region with fayalite and hedenbergite and argentiferous lead/copper sulfide inclusions similar to many of the slags previously discussed, but there is a region of the sample that is oxidizing with high amounts of metallic silver and copper oxide and lead oxide. In the oxidized region, phases like copper-iron oxides (delafossite) and magnetite are common and there are lesser quantities of hedenbergite, leucite, calcium-silicates similar to wollastonite and an unknown antimony oxide-rich phase containing

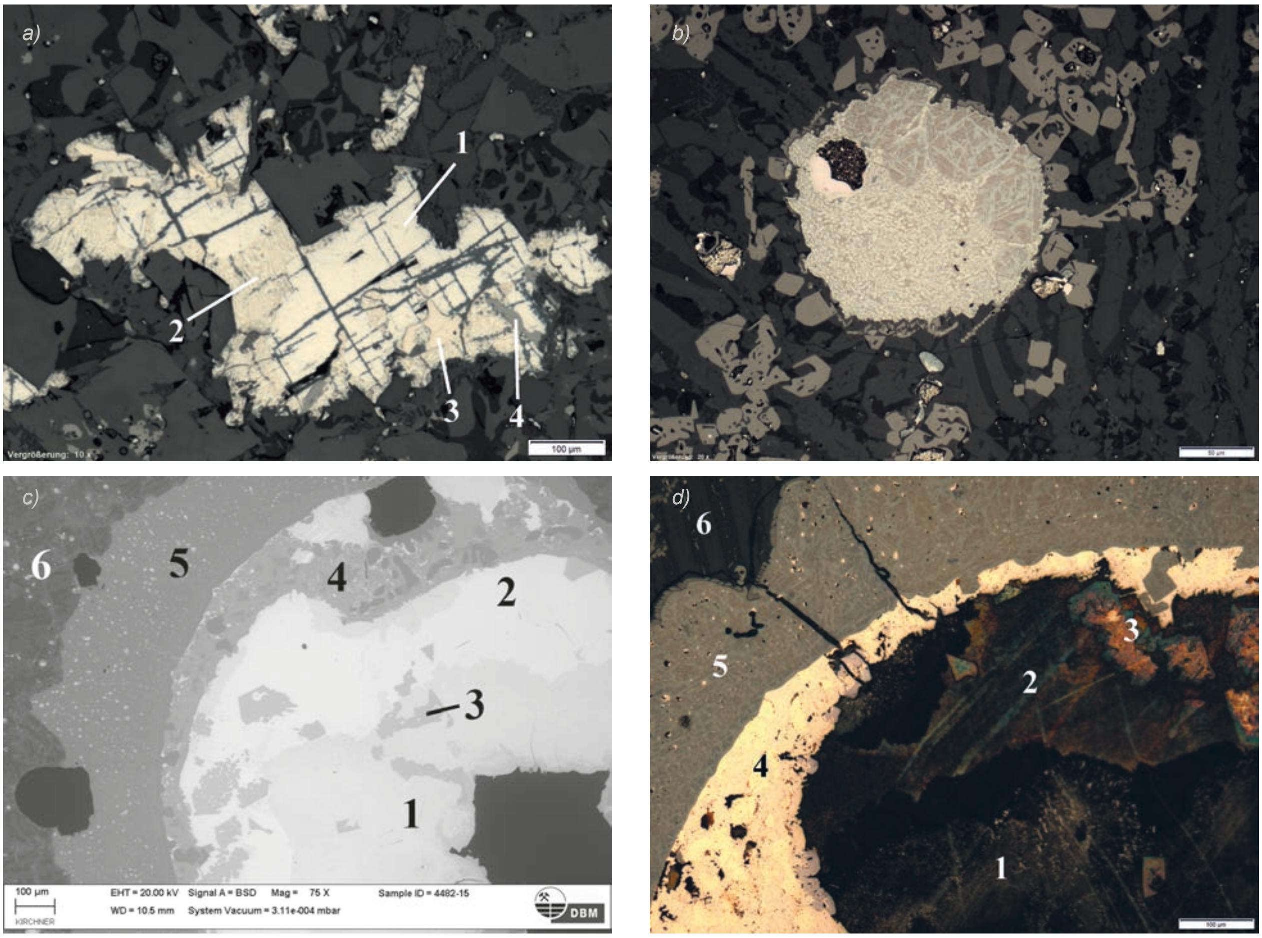

Fig. 5. a) Slag Pa-15-19 multiphase sulfide inclusion containing galena (1), an eutectic mixture of copper-iron sulfide and galena (2), pyrrhotite (3), and zinc sulfide (4). Polarized light microscope image, scale is 100 µm. b) Slag Pa-15-22 with multiphase sulfide/metal inclusion. The inclusion consists of bornite-chalcocite intergrowth together with an eutectic/co-eutectic intergrowth with galena surrounding a prill containing metallic lead (black) and copper antimonide (purple). Polarized light microscope, scale bar is 50 µm. c) Slag Pa-15-24 with multiphase sulfide/metal inclusion. Lead (1), bismuth-rich lead (2), silver with antimony (3), speiss with copper and antimony (4), copper-iron sulfide matte (5) and slag (6), SEM backscatter image, scale bar is 100 µm. d) The same inclusion under the polarized light microscope, scale bar is 100 µm.

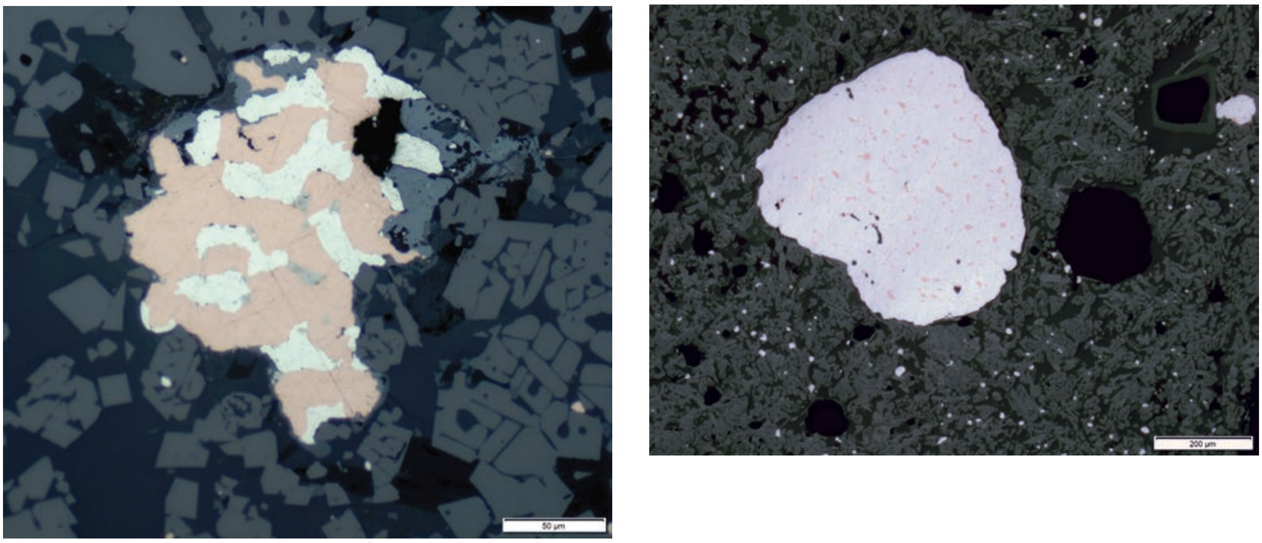

Fig. 6. a) Prill containing metallic copper and silver with cuprite in slag Pa-15-14. Polarized light microscope image, scale 50 µm. b). Large silver prill with small amounts of copper in slag Pa-15-14. Polarized light microscope image, scale 200 µm.

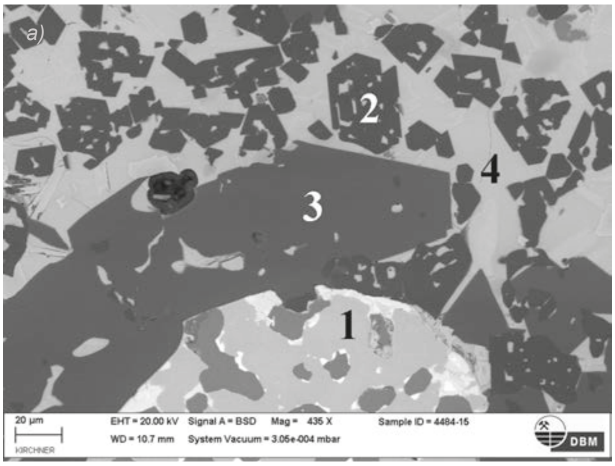

Fig. 7. Slag Pa-15-14, SEM-Backscatter image of silver prill (1), magnetite (2), delafossite (3) in lead oxide-rich slag (4). There are elementally dense phases present in the slag, containing the oxides of antimony, iron and lead. The silver prill contains bismuth (white) and cuprite inclusions (dark gray).

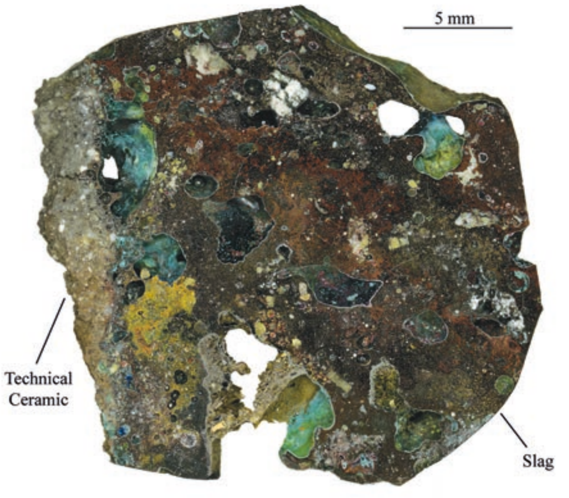

Fig. 8. Polished section of slag Pa-15-30 showing slag and adhering technical ceramic.

lead oxide and/or iron oxide. It is in this region of the slag where there are prills of metallic silver with varying quantities of metallic copper and cuprite (Fig. 6a-b). The general oxidizing conditions of the melt are confirmed by the presence of delafossite and the combination of metallic silver and cuprite and the entire lack of metallic lead and antimony (Fig. 7). The steep gradient from the normal reducing smelting slag to the oxidizing conditions described seems to indicate that this slag may have been close to a tuyère, which could have created localized highly oxidizing conditions. The conditions are so oxidizing in this part of the slag that the oxides of lead, antimony, and copper reacted with the surrounding slag leaving metallic silver or silver-copper prills with bismuth inclusions; bismuth is found in the silver in the percentage range.

Copper-Arsenic Smelting

On the macroscopic scale, slag Pa-15-30 is black with reddish undertones, has a coarse bubbly texture, and adheres to a ceramic material that is gray in color (Fig. 8). The slag was sawn and revealed numerous metallic prills ranging from coppery-red to pale whitish-yellow, and was clearly different from the typical copper-lead-silver slags from Panjhir. A polished thin-section and polished mounted sample were prepared for microscopy. The slag is mostly glassy, with partially reacted granitic rock fragments and small and finely distributed cuprite and spinel phases (magnetite) throughout, but there are magnetite inclusions that are up to 1 mm in size. There are regions of the slag that have small pleochroic brown-green clinopyroxene prisms up to 100 µm but most of them are smaller than 50 µm.Tridymite was detected by both optical and scanning electron microscopy and is infrequent. There are partially reacted quartz grains and relics of potassium-rich feldspars. The slag adheres to technical ceramic, either a crucible fragment or furnace lining and has got a coarse texture, with microscope inclusions of quartz, orthoclase, plagioclase, heat-altered muscovite, apatite, iron oxides and titanium oxides, and does not seem to be specifically selected because of its refractory characteristics. The largest inclusions are quartz grains and typically under 500 µm in size. The morphology within the technical ceramic indicates a lack of vitrification that would be expected of an externally heated crucible, and, therefore, it is more likely that the heat originated from the inside of the vessel or furnace. When comparing the bulk slag composition and the technical ceramic (Tab. 4), the slag has a higher silica to alumina ratio and has elevated iron oxide, and lime contents. The slag is a true smelting slag and is not simply melted ceramic.

The most striking feature of this slag are the copper-arsenic prills with lead contents close to or below the detection limit of the SEM-EDS. In strong contrast to the other slags from Panjhir, only copper-arsenic prills were found in the slag and no sulfides or lead-bearing compounds were identified. Arsenic has been found in the metallic prills ranging from 2 to 13 percent by weight. In the prills with higher arsenic contents, there are two phases that form (Fig. 9 a-b; compare Mehofer, 2014, p.467). The large prill in figure 9 b was analyzed by SEM-EDS and the two Cu-As phases (α, α+γ) have ca. 5 and 17 weight percent arsenic respectively.[3] Under the optical microscope, the α-phase appears silvery-yellow and the α+γ-phase is bluish-gray. Small micron-sized bismuth-rich phases can be found in the prills often occurring at the joint between the two Cu-As phases. The average compositions of 49 prills (> 30 µm) analyzed by SEM-EDS is 92 wt. % Cu, 5.8 wt. % As, 1.4 wt. % Sb, and 0.6 wt. % Bi. There is a clear linear relationship between the several of the Periodic Table group 5 elements (As, Sb, and Bi). Arsenic versus antimony are plotted in figure 10. The ratios based on the prill compositions are roughly 100 parts As to 24 parts Sb to 12 parts Bi. Elevated iron contents seem

	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Cu_2O	ZnO	As_2O_3	Sb_2O_3
Bulk Slag	2.4	9.2	37.8	2.6	9.5	28.4	6.4	1.4	1.3	1.2
Glass	1.5	9.9	41.2	2.8	13.7	14.5	7.4	0.8	5.0	2.3
Ceramic	4.2	20.5	54.6	4.0	7.8	8.8	-	-	-	-

Tab. 4. Semi-quantitative bulk compositions of slag sample Pa-15-30 determined by SEM-EDS area analysis. The bulk slag and ceramic analyses are averages of five representative 2 mm^2 areas and the glass is an average of three 0.025 mm^2 areas without phases or minerals. Oxygen was calculated stoichiometrically and carbon was excluded. The "-" means not detected or the value was under 0.5%. Values are normalized to 100 % and given in weight percent. Lead oxide and sulfur were sought, but could not be detected.

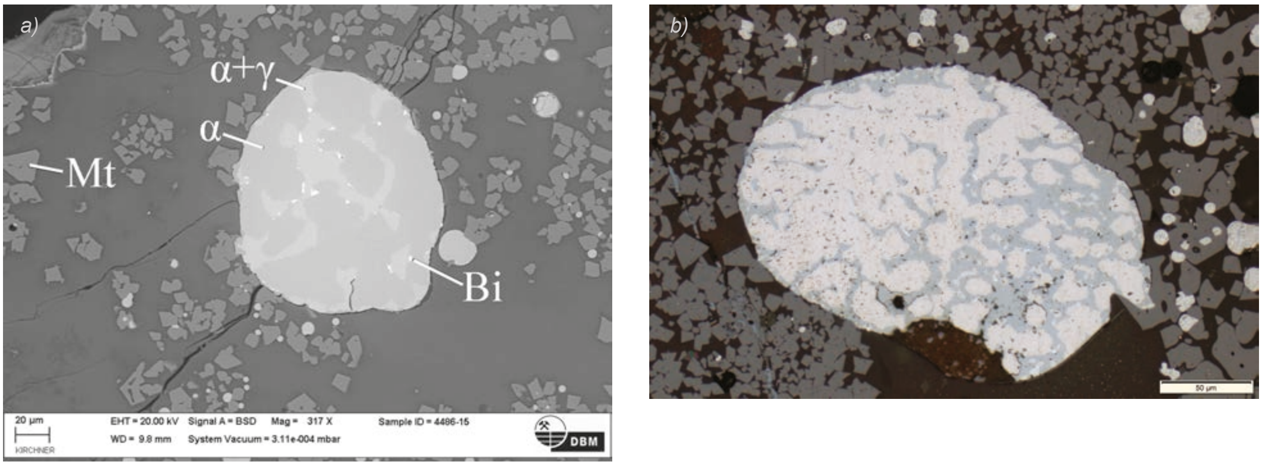

Fig. 9. a) Copper-arsenic alloy prill in slag Pa-15-30. The prill is composed of three phases: a bismuth-rich phase (Bi), two copper-arsenic phases, one with more than 10 % As (α+γ) and one with less (α). The surrounding slag matrix contains spinel phases similar to magnetite (Mt). SEM backscatter image, scale is 20 µm. b) Prill in slag Pa-15-30 showing two copper-arsenic phases. The α-phase (light gray) has got ca. 5 % As and the α+γ-phase (blue-gray) has got ca. 17 % As. Polarized light microscope, scale 50 µm.

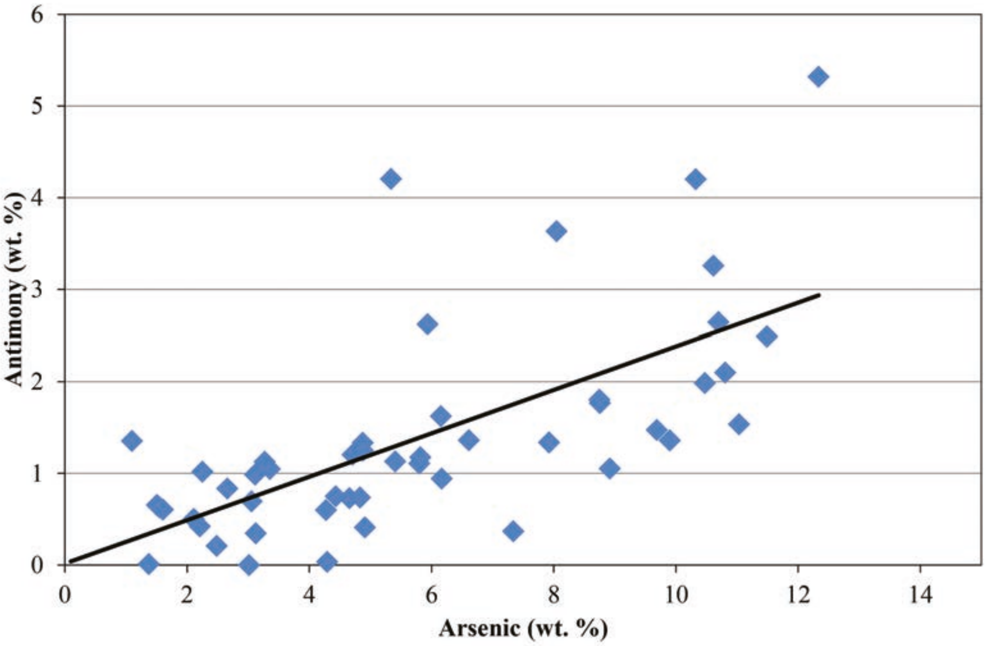

Fig. 10. In the SEM-EDS analyses of 49 metallic prills in slag Pa-15-30, a positive relationship can be observed between arsenic and antimony.

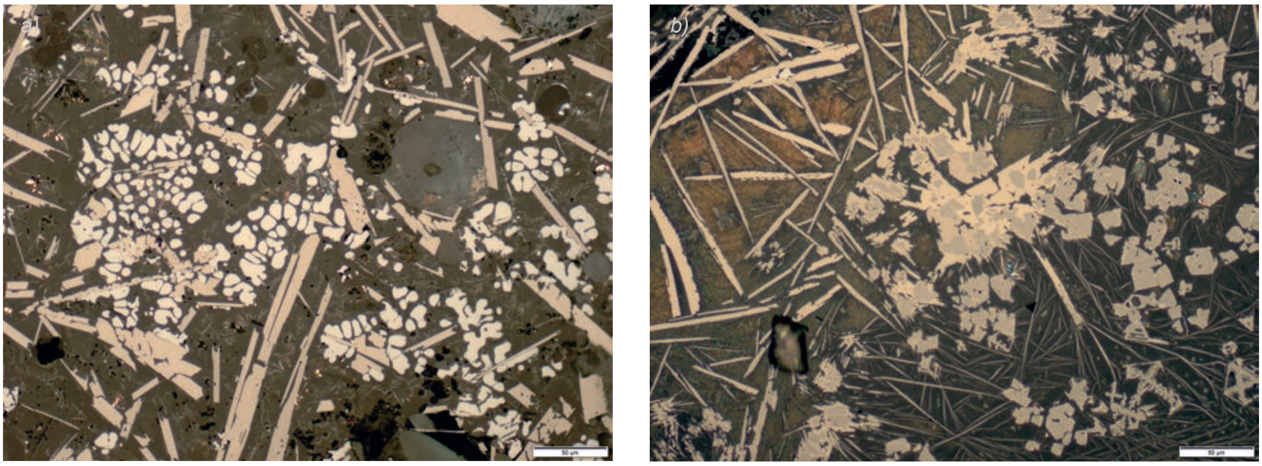

Fig. 11. a) Globular cuprite and needle-like crystals of delafossite in slag Pa-15-30. Polarized light microscope image, scale is 50 µm. b) Magnetite, delafossite and cuprite in slag Pa-15-30. Delafossite encases many of the magnetite phases. Polarized light microscope image, scale is 50 µm.

	Pa-15-12	Pa-15-26	Pa-15-22	Pa-14-S2d
Pb	95.1 (%)	94.5 (%)	95.4 (%)	96.2 (%)
Sb	18700	18400	20800	9500
Bi	9200	4100	25900	25900
Ag	2900	3000	5400	6000
P	5	5	5	10
S	250	270	890	25
Fe	80	110	25	150
Co	0.6	2.4	0.1	0.3
Ni	55	210	10	6
Cu	16700	15800	890	2800
Zn	10	10	10	40
As	1200	4400	690	45
Cd	3	3	3	n.m.
Sn	7	3	15	12
Te	5	8	10	12

Tab. 5. Quantitative mass spectrometry (SC-ICP-MS) of four argentiferous lead from Panjhir. Pa-14-S2d was previously published (Merkel, et al., 2015). The results are presented in parts per million (ppm) with exception of lead, which is weight percent.

to be related to the arsenic content of the prills, but due to possible contamination from surrounding slag matrix and adjacent magnetite or delafossite inclusions, it is difficult to quantify by SEM-EDS. The prills with the highest arsenic contents may have a maximum of 2 to 3 weight percent iron, which is an estimate based on surpluses of iron in relation to the typical alumina: silica: lime: iron oxide ratio of the surrounding slag matrix.

There seems to be a slight gradient of redox conditions based on the relative amounts of metallic copper, cuprite, and delafossite present. The least reducing conditions are near the ceramic-slag seam with high amounts of delafossite, cuprite, cuprite-encased copper prills, and lower arsenic contents in the copper (Fig. 11a-b) and the ratio of metallic copper to copper oxide properly increases in the slag, but cuprite dendrites can be found throughout the slag. Interestingly, and in opposition to what is known about arsenical bronze production (Lechtman and Klein, 1999; Mehofer, 2014; Thornton, Rehren and Pigott, 2009), no sulfides or iron arsenides were detected.

Argentiferous Lead and Cupellation Experiment

Three slag samples had argentiferous lead prills, large enough to divide, one part to be analyzed by microscopy and the other one to be extracted and measured quantitatively by SC-ICP-MS. The microstructure of the argentiferous lead inclusions are similar with lead being the main phase with an antimony-silver-lead eutectic intergrowth and there are sporadic inclusions of copper antimonide speiss and copper-iron sulfides that failed to separate. The results of the quantitative analysis of the three new prills and one previously published analysis can be found in table 5. The analyses show that the average silver content of the argentiferous lead is between 0.29 and 0.6 percent with larger but variable amounts of antimony and bismuth.

Slag Pa-15-12 contained a particularly large lead inclusion (Fig. 12). A 7.34 g piece of an argentiferous lead prill from this slag was heated in a commercially available magnesite cupel to extract the silver. The experiment was carried out using an electric oven. The empty cupel was placed in a cold oven, which slowly warmed up to 900 °C. The argentiferous lead was placed in the pre-heated cupel and put back into the oven. The oven was heated to 950 °C; this temperature was then held stable. The oven door was periodically opened to check the progress of the cupellation. The cupel was removed from the oven immediately once no more traces of smoke could be seen and the metal became still and shiny, the so-called '*Silberblick*', and cupellation was complete (Fig. 13). The resulting silver bead weighed 21.9 mg which relates to an original silver concentration in the argentiferous lead of 2980 ppm and is directly comparable to the 2900 ppm

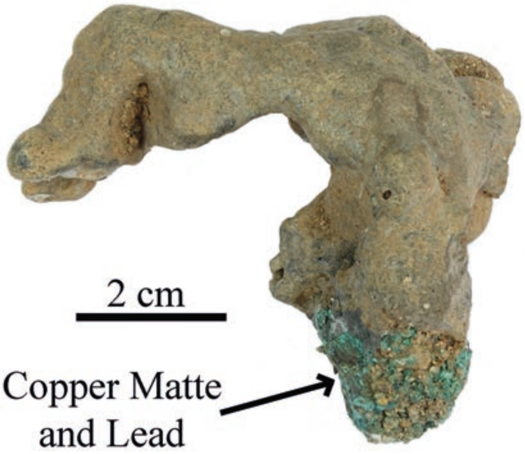

Fig. 12. Slag sample Pa-15-12. The greenish area is the corrosion of copper matte that surrounds a large piece of lead. The lead inclusion is more than 12 g of metal.

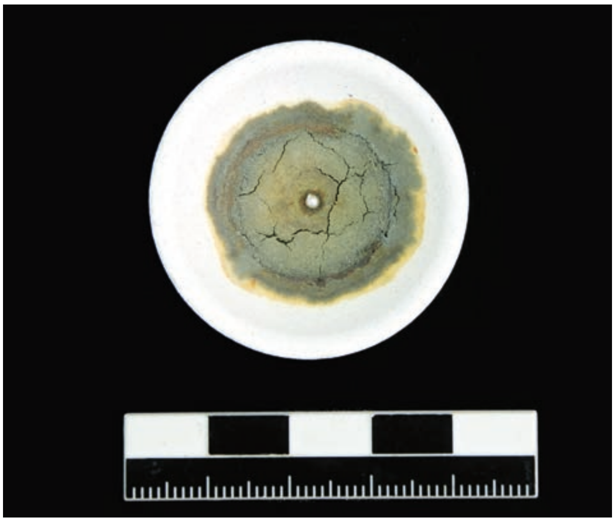

Fig. 13. Cupelled silver from the argentiferous lead of slag sample Pa-15-12.

		Ag	Sb	Bi	Cu	As	Au	Pb
Argentiferous Lead		0.29	1.87	0.92	1.67	0.12	n.m.	95.1
Cupelled Silver		98.3	0.09	1.27	0.12	0.003	6	0.20
Dirham. Panjhir*		98.7	<0.01	1.18	0.10	<0.001	3	0.36
Dirhams. Andaraba*	x5	98.0	<0.01	1.78	0.18	<0.001	38	1.56
Dirhams. Balkh*	x3	97.3	<0.01	1.91	0.80	<0.001	93	2.23
Dirhams. Al-Shash*	x15	97.6	<0.01	0.56	1.51	<0.001	747	0.59
Dirhams. Samarqand*	x13	97.3	<0.01	0.49	1.78	<0.001	758	0.60

Tab. 6. Comparison before and after cupellation of the argentiferous lead from Panjhir (Pa-15-12) and a dirham from Panjhir. The compositions of the argentiferous lead and cupelled silver were determined by SC-ICP-MS at the Deutsches Bergbau-Museum Bochum. All values are in weight percent except gold, which is in ppm. The "n.m." means not measured.
**The dirhams are from the last quarter of the 9th century to the middle of the 10th century AD and were analyzed with regard to their elemental composition by laser ablation ICP- Quadropole MS at the Leibniz Universität Hannover (Merkel, 2014).*

silver measured in a piece of the same argentiferous lead by mass spectrometry. Comparing the cupelled silver to the original argentiferous lead (Tab. 6), the antimony, arsenic, copper, and lead contents were reduced to the trace element level, but about one percent bismuth remained in the silver; that corresponds well to previous studies of the behavior of elements during cupellation (Pernicka and Bachmann, 1983). In the cupellation process, the ratio of gold to silver remains unchanged; the gold content of the original lead was not measured, but the final silver contains 6 ppm gold.

Discussion

All but one slag analyzed in 2015 belong to a polymetallic smelting technology connected to silver production, but the one sample that seems not to be related to this process profoundly impacts the current understanding of metallurgy at Panjhir. The discussion will be divided into two parts: firstly the polymetallic smelting technology and secondly the lead-poor slag with copper-arsenic alloy prills and its implications for the metallurgy at Panjhir.

Polymetallic Copper-Lead-Silver Production at Panjhir

The vast majority of slag samples analyzed in this study and in prior studies (Merkel, et al., 2015; Thomalsky, et al., 2015) indicate that a smelting technology was implemented to extract argentiferous lead and copper-sulfide matte. By the present study, some more details related to the process could be clarified, and the addition of new samples allows a reassesment of previously made interpretations.

Ore Type: The new analyses have shown that, in addition to the lead sulfides and copper-iron sulfides, zinc sulfides and iron sulfides can also be present in the slag. The pyrrhotite found in a small number of the mixed sulfide inclusions probably stems from the decomposition of pyrite (FeS_2) and not as a relic from the original ore. The most common sulfides in all polymetallic slags are galena and copper sulfides ranging from bornite to chalcocite; chalcopyrite is present but not commonly found. No sulfides contained detectable amounts of silver, arsenic, antimony, or bismuth; these elements are found particularly concentrated in the metallic lead prills and associated intermetallic phases (speiss). This means that the original ore cannot be determined; it can be assumed that the ore contained fahlore minerals and silver sulfosalts which quickly decomposed upon smelting.

Smelting Technology: The smelting technology of these samples conforms to the previously analyzed slags; a discussion is outlined in Merkel, et al. (2015). Regarding the question of the smelting process, the analyzed slags do show a tendency that the clinopyroxene-rich slags have less or no iron-bearing copper sulfides and less lead sulfides than the fayalite-rich slags allowing a delineation of two groups based on the redox conditions and the iron content of the copper sulfides. However, this does not necessarily mean that they represent a two-stage smelting system. The fayalite slags may simply represent slightly more reducing conditions leading to better preservation of iron-bearing copper sulfides while the slags lacking fayalite are perhaps more oxidizing favoring the break-down of iron-bearing sulfides into their oxides. It has been shown with sample Pa-15-14 that the redox conditions can drastically change within a centimeter, and the heterogeneity of the larger slag pieces has yet to be assessed.

Products: The new samples and the cupellation experiment have provided a much better insight into the possible outcomes of the extractive metallurgical processes. The four large prills of argentiferous lead analyzed quantitatively indicate that silver contents around 4000 ppm are the norm. As silver is concentrated and collected by the lead, the raw ore, due to its polymetallic nature, would have had a lower concentration of silver. A galena sample from the Panjhir area was analyzed by pXRF; this analysis resulted in a value of 2500 ppm silver (Thomalsky et al., 2015, p.219) and is roughly analogous to the concentration of silver in the argentiferous lead from the smelting slags.

The next task is the comparison of the silver produced through cupellation and the Islamic period silver dirhams from mints in Northern Afghanistan and Transoxania. As it is shown in table 5, the single dirham analyzed that was struck at the mint of Panjhir is nearly identical to the cupelled silver from the slag in elemental composition. As one goes further to the north of Panjhir the gold and copper contents of the dirhams gradually increase. The average elemental compositions of the dirhams from the two major mints of Transoxania, Samarqand and Al-Shash, are nearly undistinguishable and seem to indicate that they may have a common source distinct from Panjhir. Interestingly, there seems to be a time dimension, too; the dirhams from northern Afghanistan, Balkh for example, made before the last third of the 9th century AD, rarely share the characteristics of the silver from Panjhir and have significantly higher gold contents and lower bismuth contents (Ilisch, et al., 2003, pp.92-94; Merkel, 2014), and this possibly marks a shift in mining towards the end of the 9th century AD.

The dirhams from Samarqand and Al-Shash have differing lead isotope ratios, although a common source is suggested by the elemental compositions. The Shash-Ilak is one of the most important mining regions in medieval Central Asia and probably supplied the mints of Transoxania with silver. As the lead isotope ratios of the Al-Shash dirhams are consistent with polymetallic copper-lead-silver smelting slags in the Shash-Ilak region (Merkel, et al., 2013), the differing lead isotope ratios between Al-Shash and Samarqand may be related to the refining of silver at Samarqand with lead from another source, and this can be inferred because Samarqand had no major silver mines of its own. It can be established that the provenancing of silver in the Islamic period may be more complex than previously thought, and the lead isotope ratios do not necessarily provide information about the source of the silver, instead, one must consider all the occasions by which the silver could have been alloyed, either during recycling or during refining.

An explanation, albeit speculative, was put forth to justify the discrepancy between the lead isotope ratios of the dirhams and the slag in which imported lead may have been used during the final refining steps to purify the bismuth-bearing silver from Panjhir (Merkel, et al., 2015). The elemental composition of the cupelled silver closely mirrors the Panjhir dirham composition, creating a further link between dirham production and the polymetallic slag, but the reasons behind the inconsistency of the lead isotope ratios have yet to be answered to a satisfactory degree.

Copper-Arsenic Smelting and its Implications

The slag sample Pa-15-30 is unique among the samples investigated and raises a multitude of questions: At first, what is happening in the slag? This requires a closer look at the mineral and phase assemblage in the slag. The presence of cuprite throughout the slag and localized concentrations of delafossite indicates mildly reducing conditions and this is confirmed by a lack of fayalite and wüstite, which require the formation of FeO. The mild redox conditions of the slag account for the relatively high loss of copper as oxides in the slag, but also the oxides of arsenic and antimony (see Tab. 3). The slag mostly consists of glass with small clinopyroxene prisms and euhedral magnetite crystals. Besides, it contains fragments of granitic rock with residual and highly fractured quartz grains, and the feldspars were mostly melted and occasionally there are magnetite inclusions comparable in size to the granite fragments. The characteristics of the slag indicate that it is truly a smelting slag that was produced under moderately reducing conditions.

This leads to the second question, whether the copper-arsenic alloy in the slag was intentionally produced. The Gales report on Bronze Age copper slags from the island of Kythnos (Aegean) containing copper prills with 0.2 to 6.6 percent arsenic, and argue that the alloy produced is accidental due to the smelting of mixed ores containing oxidized copper and arsenic minerals (Stos-Gale and Gale, 1988, pp.25-26). An important difference between the slags from Kythnos is that the slags found there are fayalitic and not comparable to the mild redox conditions seen in the present slag.

The copper-arsenic prills are not in accordance with the redox conditions of the surrounding silicate slag. The calculated Gibbs free energy formation for arsenic oxide (As_2O_3) for 1100 °C shows that the high level of reduction required to reduce arsenic to metal from its oxide[4] is inconsistent with the mildly reducing conditions in the slag. This implies that the alloy could not have been formed without the original presence of sulfur or without at least some of the ingredients initially being in a highly reduced state. A direct reduction of oxide copper-arsenate ores can tentatively be ruled out. Possiblities of producing copper-arsenic alloys have been studied experimentally or through archaeometallurgical remains, and a slag containing copper with high arsenic contents could be a result of several processes:

1. That the arsenic alloyed with the copper originated as a sulfide, e.i. co-smelting with mixed As-containing oxide/sulfide ore (see Lechtman and Klein, 1999),
2. That the arsenic came from the alloying with iron-arsenic speiss, e.i. co-smelting with speiss (see Hauptmann, Rehren and Schmitt-Stecker, 2003; Thorton, Rehren and Pigott, 2009),
3. Or that a previously produced copper-arsenic alloy was refined under mildly reducing conditions to oxidize excess iron, thus oxidizing a portion of the copper and arsenic as well.

Due to the lack of sulfides and speiss phases in the slag, it is not possible to identify what kind of metallurgical process was carried out; for that a larger sample size is needed.

The question of the age of the slag is of interest though difficult to answer. Two charcoal samples associated with the Panjhir slags provided dates in the Bronze Age, but could this unusual slag fragment be a remnant of such an early metallurgical phase? Copper-arsenic alloys are the most common copper alloy used on the Iranian Plateau during the Bronze Age and only looses its importance at the beginning of the Iron Age when its position is replaced by tin bronze; less is known about the Bronze Age alloys in northern Afghanistan, though Pigott suggests that the tin deposits in Afghanistan may have been the earliest suppliers in southwest Asia (Pigott, 1999, p.81). Several characteristics of the slag from Panjhir are paralleled in the Early Bronze Age slag cakes from Shahr-i Sokhta in Iran (Hauptmann, Rehren and Schmitt-Stecker, 2003), namely the poorly reducing and inefficient smelting conditions and the presence of cuprite, magnetite and hedenbergite, but there are some important differences in the Shahr-i Sokhta slag like the presence of copper sulfides and the lack of arsenic. It is perhaps not productive to speculate further concerning the age of slag Pa-15-30, but what can be said is that it shows a complete departure from the typical polymetallic copper-lead-silver slags found at the site and that there is more than one metallurgical technology or tradition to be found at the Panjhir.

Conclusions

The new archaeometallurgical investigations of slag from Panjhir have widened the sample basis and broadened our knowledge of the metallurgical processes carried out, and they have allowed a reassessment of some of the previously made interpretations concerning the polymetallic copper-lead-silver smelting. The discovery of copper-arsenic-related extractive technology changes the prior perceptions of the metallurgy at the site, and although the age of these remains are unknown, just the possibility that this unusual slag with adhering technical ceramic may be of old age warrants further archaeological investigations.

Concerning the silver production at Panjhir, the additional quantitative analyses of lead recovered from the slag has shown that the silver content of the smelted argentiferous lead is nearly half a percent, and not richer, and that bismuth contents are significantly higher. The sulfide inclusions in the slag point to the smelting of a mixture of sulfidic ore minerals, but the form the silver, antimony, and bismuth originally took could not be determined. It can be concluded from the comparison between the quantitative analysis and SEM-EDS of the same argentiferous lead samples that the SEM-EDS systematically overestimates the silver content by a factor of up to four, in part, due to the relief created by polishing and therefore has repercussions on the use of microscopy in determining silver contents. The cupellation of argentiferous lead has produced a silver alloy that is directly comparable to the elemental composition of a dirham minted at Panjhir in the late 9th century AD, a composition that seems to be characteristic of numerous examples of dirhams from Andaraba and Panjhir (Ilisch, et al., 2003); however, the discrepancy between the lead isotope ratios of the slags from Panjhir and the silver dirhams of northern Afghanistan remains difficult to resolve.

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Notes

1 The shortest overland route from Andaraba to the Panjhir River is approximately 80 km and crosses the Khawak pass. If one reckons 20 km a day, then it would take four days to get from Andaraba to the Panjhir Valley.

2 The comparison of the mass spectrometry (see section 3.2) and SEM-EDS results of the same prills indicates that the SEM-EDS results for silver are about four times higher than it is actually present in the lead. One possible reason for this may be the relief caused by polishing; since the lead is softer than the antimonide inclusions, the lead is selectively abraded increasing the surface area of the harder phases exposed.

3 For phase diagram of the Cu-As system and description see Scott (2012, pp.112-116).

4 Calculated to be -349.6 kilojoules/mole O_2 based on the coefficients for arsenic oxide gas/arsenic gas and the free energy equation provided by Weast and Astle (1981, p.D-45).

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