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The publisher's version is available at:

https://doi.org/10.1016/j.apgeochem.2023.105764

When citing, please refer to the published version.

Antimony contamination sources and alteration pathways of Sb mineral phases in an abandoned mining area: the role of secondary mopungite [NaSb(OH)$_6$]

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ABSTRACT

Antimony pollution caused by mining activities is a current environmental concern. This study investigates the processes involved in the Sb release and mobility in the abandoned Sb mine of Su Suergiu (SE Sardinia, Italy). Analyses of outcropping rocks, mine wastes and foundry slags by means of X-Ray Powder Diffraction, Scanning Electron Microscopy - Energy Dispersive Spectroscopy and Electron Microprobe – Wavelength Dispersive Spectroscopy provided mineralogical and compositional data which contributed to the discussion about the oxidation pathways of Sb phases. The main Sb sources are metallic Sb and Sb_2O_3 (valentinite/sénarmontite), dumped in the foundry slag heaps as residues of metallurgical processes, and primary stibnite (Sb_2S_3) found in natural outcrops and mine wastes. These minerals, subjected to weathering processes, release Sb in solution where it is oxidized and remains as dissolved $Sb(OH)_6^-$. Carbonates and Na phases, like hydrate NaAl-silicate derived from metallurgical processes, influence the geochemical equilibria of the foundry slag heaps, where the precipitation of the rare mopungite, $Na[Sb(OH)_6]$, has been observed. At Su Suergiu, mopungite originates from a dissolution-precipitation process as the last forming mineral of the oxidation pathways, limiting the Sb mobility by bonding the $Sb(OH)_6^-$ in solution. Among the detected Sb secondary phases (e.g., Sb-oxides, FeSb-oxides, etc.), mopungite is the main Sb binder although it acts as a temporary sink because its stability is influenced by the hydrological regime, its solubility, and the water physicochemical parameters. Secondary Sb-bearing minerals can control the dispersion of Sb in contaminated area. At Su Suergiu the role of Fe-bearing compounds on Sb mobility is subordinate to that of mopungite due to the specific geochemical conditions linked to the metallurgical activities. The relevance of this study arises from the worldwide diffuse Sb mining, being in the top ten of the most mined elements worldwide, its toxicity and widespread

occurrence of Na-Sb-rich residues produced by Sb smelting plants.

Keywords: antimony mine, mopungite, Sb pollution, secondary minerals

1. Introduction

Antimony (Sb) is a non-essential element, and it is considered a potential human carcinogen. Although the knowledge about the toxicity of Sb compounds for the ecosystem is still lacking, high Sb concentrations are considered a serious environmental and health concern (Bagherifam et al., 2021; Filella et al., 2009; Gebel, 1997; Gurnani et al., 1994; He et al., 2019). For these reasons in the last decades Sb has gained environmental interest and, the World Health Organization (WHO, 2011) and the European Community (European Commission, 1998) have set, respectively, the thresholds of 20 μg L^{-1} and 5 μg L^{-1} of Sb concentration for drinking water.

Antimony concentration commonly ranges between 0.15 and 2 mg/kg in most rocks and it is usually below 1 μg/L in uncontaminated freshwaters (Filella et al., 2002b). Higher Sb concentrations in the environment can be due to both natural and anthropogenic sources, such as volcanism and ore minerals, shooting ranges, agricultural activities, transports, mining etc. (Hayes & Jr., 1991; He et al., 2019; Ngo et al., 2020; Okkenhaug et al., 2016). Being Sb in the top ten of the most mined elements worldwide, mining exploitation and foundry activities are supposed to be the greatest sources of Sb in the environment (Mitsunobu et al. 2009; Álvarez-Ayuso et al. 2013 and reference therein). These activities unearth ore minerals exposing them to oxidation, and produces huge volumes of highly polluting wastes such as primary ore, residues of metallurgical processes and secondary minerals (Biver & Shotyk, 2013; Filella et al., 2009; Ilgen et al., 2014; Multani et al., 2016). The reactivity of these materials, when exposed to surface/near surface conditions, depends on their mineralogical composition (Álvarez-Ayuso et al., 2013; Ashley et al., 2006; Cidu et al., 2018; He et al., 2019; Majzlan et al., 2011, and references therein), thus their characterization is fundamental to understand the processes occurring in mine areas and to evaluate the mechanisms leading to Sb release in a specific environment (Borčinová Radková et al., 2020; Courtin-Nomade et al., 2012; Filella, 2011; Filella et al., 2009; Roper et al., 2012; Wilson et al., 2004).

Antimony ore deposits are usually connected to hydrothermal activities where the primary ore is stibnite (Sb$_2$S$_3$) (Fowler & Goering, 1991). Common primary Sb minerals are sulphides, whereas oxides and sulphosalts may form especially in sulphur-deficient environment (Roper et al., 2012). Primary Sb sulphides are relatively insoluble at ambient temperature (Multani et al., 2016) however, in oxygen-rich environment, they tend to change to Sb(III) oxides that are further oxidized to Sb(V),

2

thereby allowing the Sb release in solution (Borčinová Radková et al., 2020). Weathering phases of stibnite oxidation are kermesite (Sb_2S_2O), sénarmontite/valentinite (Sb_2O_3) and stibiconite (Sb_3O_6OH) (Roper et al., 2012) plus other oxides, sulfosalts and hydroxides, the presence of which depends on the geological setting and local geochemical conditions (like circulating solutions enriched in Ca^{2+}, Pb^{2+}, Fe^{3+}, etc.) (Borčinová Radková et al., 2020, 2022; Majzlan et al., 2016).

In mine areas where residues of mining excavation are dumped together with tailings and residues of metallurgy, the oxidation pathways of Sb minerals become more complex. As an instance, tailings residual from flotation plants, still contain Sb and other elements commonly associated in primary ores (As, Fe, Pb, Zn, etc.), together with reagents used in flotation processes (Long et al., 2020; Multani et al., 2016). In addition, different metallurgical processes require the use of carbonates, alkali and other reagents that produce large amounts of complex wastes (Multani et al., 2016 and references therein). Several studies demonstrated that the potential to release toxic elements by these wastes depends on their mineralogy rather than their bulk chemistry (Guo et al., 2014; Majzlan et al., 2011; Su et al., 2021).

Secondary Sb(V) minerals may limit Sb dispersion and/or mobility in function of local geochemical condition and mineral solubility; minerals like the roméite group and tripuhyite (Roper et al. 2015 and references therein; Leverett et al. 2012) can incorporate Sb(V) in their structure in a stable way, whereas other phases like minerals with general formula $M^{x+}[(Sb(OH)_6]_x \cdot mH_2O$ ($M^{x+} = Ca^{2+}$, Na^+, Mg^{2+} etc.) like brandholzite [$Mg(H_2O)_6(Sb(OH)_6)_2$] and $Ca[Sb(OH)_6]_2$, might limit Sb mobility only temporarily (Diemar et al., 2009; Friedrich et al., 2000; Sejkora et al., 2010; Borčinová Radková et al., 2020; Johnson et al., 2005; Okkenhaug et al., 2011). Among these minerals, mopungite, $Na[Sb(OH)_6]$, a rare naturally occurring mineral, was detected in some sites either as a result of stibnite alteration in surface environment (Bittarello et al., 2015; Marzoni Fecia Di Cossato et al., 1987; Roper et al., 2018; Williams, 1985) or as a possible product of the interaction between primary Sb ore and reagents employed in the mineral processing (Protano and Riccobono, 1997). Roper et al. (2018) indicated that mopungite can exist as a precursor of brizzite ($NaSbO_2$), however studies focused on the role of mopungite on Sb mobility in mine areas are still lacking.

This work is set in the abandoned Sb mine area of Su Suergiu (SE Sardinia, Italy) affected by serious Sb pollution, whose drainages impact the water bodies up to several kilometres downstream hence affecting the most important river (Flumendosa River) of SE Sardinia (Cidu et al., 2014, 2018). This work aims to shed light on the processes involved in the fate of Sb at the contamination sources. For this purpose, the mineralogy and chemistry of outcropping rocks, mine wastes and residues of metallurgical processes have been studied combining laboratory and synchrotron radiation X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-

EDS) and Electron Microprobe – Wavelength Dispersive Spectroscopy (EMP-WDS) to identify the Sb primary and secondary phases and to reconstruct the oxidation pathways. This study deepens the knowledge on Sb behaviour in mine-impacted areas and represents a useful tool in planning remediation actions, not only at Su Suergiu but also in other Sb mines worldwide.

2. Study area

2.1 Geological setting and mine history

The Su Suergiu abandoned mine is located in the Gerrei mine district (SE Sardinia, Italy) (Fig. 1 a-c). The geology of the region is characterized by low-grade metamorphic rocks belonging to allochthonous units emplaced during the Variscan orogenesis (Carmignani et al., 2001). The weakly metamorphosed outcropping succession consists of Cambrian to Lower Ordovician siliciclastic deposits followed by Middle-Late Ordovician volcanics and siliciclastic rocks, Silurian-Middle Devonian black shales and limestones, Middle Devonian-Lower Carboniferous limestones and Lower Carboniferous Culm-type deposits (Fig. 1c, RAS 2013).

The mineralization of Su Suergiu resulted from hydrothermal activity related to the late Variscan extensional tectonics (Funedda et al., 2018). The deposit mainly consists of sulphides- and scheelite [$Ca(WO_4)$]-bearing lenses and veins that follow the main foliation of highly deformed black shales and metalimestones belonging to the cataclastic Villasalto thrust zone (Carmignani et al., 1978). In detail, the ore mined at Su Suergiu is mainly made up by stibnite, arsenopyrite ($FeAsS$), scheelite, pyrite (FeS_2), with minor amounts of sphalerite (ZnS), chalcopyrite ($CuFeS_2$), berthierite ($FeSb_2S_4$), marcasite (FeS_2), pyrrhotite (FeS), tetrahedrite [$(Cu,Fe,Ag,Zn)_{12}(Sb,As)_4S_{13}$], galena ($PbS$), boulangerite ($Pb_5Sb_4S_{11}$), native gold ($Au$) and native antimony ($Sb$), in calcite ($CaCO_3$) and quartz ($SiO_2$) gangue (Funedda et al., 2005).

The Su Suergiu deposit was mined underground from 1880 to 1960, with an exploitation peak between the 1920's and 1930's. The foundry operated from 1882 to 1981, with alternating periods of stop and restart, processing local ores and, after the mine closure in 1960's, Sb-ores coming from Tuscany, China and Bolivia (Amat di San Filippo, 2014; Cidu et al., 2018; Contini et al., 2009; Secchi & Lorrai, 2001). In the early years of activity, the main products of the plant were liquated sulphide (Sb_2S_3) and Sb oxide (Sb_2O_3). From the first decade of XXth century, the foundry also produced metallic Sb (Contini et al., 2009; Secchi & Lorrai, 2001). In the first step of the process, carbonate gangue, metallurgical coke, flue dust and searing charcoal were added to Sb ore in the converters. During the reduction processes to obtain metallic Sb from the oxide, the reverberatory furnaces were charged with a mixture of oxide and charcoal with the addition of Na-carbonate as fluxing agent in

4

135 the percentage of 3.5% (Amat di San Filippo, 2014).

136 Waste materials deriving from the underground exploitation (hereafter referred to as mine waste) and

137 residues of metallurgical processes (hereafter referred to as foundry slags) were dumped within the

138 mine area (Fig. 2). When the mining and foundry activities definitively ceased, no actions addressed

139 to mitigate the contamination were realized due to the lack of environmental legislation. In the mine

140 area 14 mine waste dumps, for a total of 146,308 m^3 (IGEA, 2009), have been identified (Fig. 2).

141 They are mostly covered by vegetation and they show evidence of erosional processes only close to

142 the streams. The foundry slags, consisting of vacuolar slags, massive glass slags, rotary furnace slags

143 and various casting remains, were dumped in two main bodies (65,460 m^3), which also contain minor

144 amount of mine waste (Fig. 2) (Contini et al., 2009; IGEA, 2009). In this case the vegetation is absent

145 and, despite the presence of retaining walls on the heaps edge, the foundry slag heaps have been

146 subjected to considerable erosion, especially during episodic extreme hydrological events. It has been

147 estimated that about 18,400 m^3 (IGEA, 2009) of these wastes are accumulated along the riverbank

148 downstream the mine area up to the Flumendosa River.

2.2 Characteristics of the area and water geochemistry

151 The climate of the area is semi-humid with dry summers and variable rainfall mainly distributed from

152 October to April; the mean annual temperature and precipitations, based on data collected from 1955

153 to 1992, are 16°C and 670 mm, respectively (RAS, 1998).

154 The hydrology of the mine area is characterized by intermittent streams whose flow is strictly

155 dependent on rainfall. The mine area is drained by Riu Su Suergiu, whose waters flow into the Riu

156 Ciurixeda catchment (Figs. 1c and 2) which, in turn, flow untreated into the Flumendosa River, the

157 main river of SE Sardinia, used for agricultural and human consumptions.

158 Several hydrogeochemical surveys (from 2005 to 2015) were carried out over an area comprising the

159 Su Suergiu mine area, the Riu Ciurixeda catchment and a portion of the Flumendosa River (before

160 and after the confluence of Riu Ciurixeda).

161 These studies showed that waters flowing in the mine area are characterized by a Ca(Na)-sulphate

162 composition, oxidizing conditions and neutral or slightly alkaline pH. The dissolution of sulphide

163 minerals produces high concentration of sulphate; this is an acidifying process, but the presence of

164 carbonates buffers the solution pH. The drainage flowing downstream the foundry slag heaps often

165 shows high Na concentration (up to 600 mg/L), probably as a consequence of the water interaction

166 with the alkaline materials used during the Sb-ore metallurgy (Cidu et al., 2021, 2018, 2014).

167 Data of water samples collected in the mine area between 2012 and 2014 showed a wide variability

of Sb concentrations (detailed information on samples location and Sb concentrations are reported in Cidu et al., 2014). The highest values were determined in the slag drainage (up to 30,000 μg/L Sb; median value 13,000 μg/L Sb), while in the other samples (adits, spring and streams) the Sb concentration ranged between 48 – 4,020 μg/L (median: 323 μg/L), thus indicating the foundry slag heaps as the main source of dissolved Sb.

After the confluence with Flumendosa River, water still shows Sb concentrations above the thresholds set by the WHO (20 μg L^{-1}) (WHO, 2011) and the European Union (5 μg L^{-1}) (European Commission, 1998) for drinking water (Cidu et al., 2014, 2018). It was observed that, downstream the mine area, the natural Sb attenuation occurs mainly by dilution whereas attenuation linked to adsorption or precipitation of secondary Sb minerals has been considered negligible (Cidu et al., 2014, 2018). It is noteworthy that also weathered mine wastes and foundry slag dispersed downstream the mine area by runoff can contribute to increase dissolved Sb concentration in waters.

3. Materials and methods

3.1 Sampling and analyses

Different kinds of samples including outcropping rocks, mine wastes and foundry slags (Fig. 2), were collected within the mine area to perform mineralogical (XRD) and minerochemical (SEM-EDS and EMP-WDS) analyses. Further samples were collected along the Riu Su Suergiu riverbank, mainly waste runoff downstream from the foundry slag heaps (Fig. 2).

After collection, samples were air-dried at room conditions. To perform XRD analysis, samples were finely hand grinded in an agate mortar, then XRD patterns were acquired using a conventional θ-θ equipment (PANalytical X'Pert Pro) with Cu K$_\alpha$ wavelength radiation (1.54060 Å) and a Ni filter, operating at 40 kV and 40 mA, using the X'Celerator detector.

Selected samples were analysed at the MCX (Materials Characterisation X-ray diffraction) (Rebuffi et al., 2014) line at the Elettra synchrotron light source (Basovizza, TS, Italy) using an incident monochromatic beam with a wavelength of 0.95373Å. XRD patterns were acquired using a step scanning diffractometer in the 6-70° 2θ range with 0.012° 2θ step size. Sample powders were mounted in thin windows glass capillaries that were kept spinning during acquisition to reduce preferential orientation effects.

The phase identification was performed using the software X'Pert HighScore Plus (PANalytical B.V., Almelo, The Netherlands) following the previous steps of Kα$_2$ stripping, trace smoothing and manual peak finding. Rietveld structure refinement was performed using GSAS-II software (Toby & Von Dreele, 2013) based on the mopungite structural file Sb07 from Palenik et al. (2005) and an iterative

process until the best values of Goodness of Fit (GoF) and wR were reached (Toby, 2006). The three-dimensional structure visualization was performed using VESTA 3 software (Momma & Izumi, 2011) and the structural file built from the refined data using GSAS-II.

To better understand the relationship among the Sb-bearing phases detected by mineralogical analysis and to assess the alteration path of Sb, SEM-EDS analysis was performed on different types of foundry slag samples. SEM analysis was performed using a FEI Quanta 200 equipped with a ThermoFisher UltraDry Energy EDS detector at the CeSAR laboratory (University of Cagliari).

Quantitative microanalyses were performed at the Dipartimento di Scienze della Terra (Università Statale di Milano, Italy) by a JEOL JXA–8200 electron microprobe (EMP) equipped with five wavelength-dispersive spectrometers (WDS). The list of analysed elements, with the relative standards, spectral lines, and monochromators (in brackets) are here reported: Zn (Zn, Kα, LIFH), Fe (fayalite, Kα, LIFH), Ni (nickeline, Kα, LIFH), Co (Co, Kα, LIFH), Mn (rhodonite, Kα, LIFH), Sn (Sn, Lα, TAP), Sb (Sb, Lα, TAP), Ca (grossular, Kα, PETH), Si and Al (grossular, Kα, TAP), Na (omphacite, Kα, TAP), K (K-feldspar, Kα, PETH), Mg (olivine, Kα, TAP), Ti (ilmenite, Kα, PETJ), Cr (Cr, Kα, PETJ), W (W, Lα, LIFH). The electron beam was set to 15 kV accelerating voltage, 5 nA beam current, 1-2 μm beam diameter, and each element was determined after counting time of 30 seconds on peak and 10 seconds on background. Element concentrations were determined after applying $\varphi(\rho z)$ algorithm and corrections for X-ray fluorescence, absorption, atomic number (Z) and matrices, and by evaluating spectral interferences. The requirement of $I_{xstd}/I_{std} = 1.00 \pm 0.01$ was checked for each element before the analysis (where, I_{xstd} intensity of the analysed standard, and I_{std} the intensity of the same standard after calibration).

The Eh-pH diagrams were performed using the Hydra-Medusa software with its internal database complex.db and complex.elb (Puigdomènech, 2010). The Hydra-Medusa database was modified adding the solubility constant (K_s) of mopungite (logK_s -4.996) (Blandamer et al., 1974; Ilgen et al., 2014). Concentrations used for the calculations were taken from Cidu et al., 2018, and Na and $Sb(OH)_6^-$ values were varied to allow mopungite precipitation.

4. Results

4.1 XRD analysis and structural refinement

The mineralogical characterization reveals remarkable differences between the outcropping rocks, the mine waste samples, and the foundry slags (Table 1).

In agreement with the geology of the study area, the mineralogy of outcropping rocks is mainly made up by quartz and calcite with minor amounts of phyllosilicates, probably chlorite and/or illite and

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muscovite (Table 1). Efflorescences and patinas were locally found onto the surface of natural outcrops, resulting from the oxidation of metal-sulphides. These efflorescences mainly consist of metal-sulphate hydrate as halotrichite ($FeAl_2(SO_4)_4 \cdot 22H_2O$), kalinite ($KAl(SO_4)_2 \cdot 11H_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$), plumbojarosite ($Pb_{0.5}Fe_3(SO_4)_2(OH)_6$), hexahydrite ($MgSO_4 \cdot 6H_2O$) and other sulphates with mixed metal cations and different hydration degree (Table 1, Fig. S1). However, except some small amount of pyrite (Fig. S1), other sulphur-bearing phases related to the mineralization event cannot detected by XRD, likely due to their poor crystallinity and/or low concentration.

The samples collected in the mine waste dumps show a mineralogical composition matching that of the surrounding rock outcrops, since mine waste hosts the gangue and the overburden resulting from excavation. The mineralogical composition consists of quartz, calcite, dolomite and phyllosilicates in different proportions (Table 1 and Fig. S1). In some cases, the presence of the primary mineral stibnite was observed; gypsum (and rarely hematite) is linked to the alteration of primary sulphides.

Slag samples collected at the foundry slag heaps show different colour, texture, consolidation degree and a complex mineralogy attributable to the different metallurgical treatments employed during the foundry activity and to the subsequent weathering processes (Table 1). Macroscopically, it is possible to distinguish residues of rotary furnaces, casting residues and vacuolar or glassy massive slags, in addition to metallic Sb (hereafter referred to as MET) found as encrustations on mould fragments formerly used to cast the Sb ingots (Fig. 2).

The XRD patterns of samples representative of the different types of foundry slags are reported in figure S1. The mineralogical composition of most samples consists of quartz, calcite, dolomite and phyllosilicates belonging to the host rock; in some samples, minor amounts of ankerite $[Ca(Fe^{2+},Mg)(CO_3)_2]$ and arsenopyrite, probably derived from the primary mineralization are detected (Table 1).

Diverse Na phases are commonly found as NaAl-silicate hydrate, NaAl-carbonate, and NaCa-sulfate or carbonate. High-temperature minerals belonging to the sodalite-cancrinite group, as nosean $[Na_8Al_6Si_6O_{24}(SO_4)]$ and hauyne $[(Na,Ca)_{4-8}Al_6Si_6(O,S)_{24}(SO_4,Cl)_{1-2}]$, and mullite ($Al_{(4+2x)}Si_{(2-2x)}O_{(10-x)}$ where x=0.17-0.59) and cuspidine ($Ca_4Si_2O_7(F,OH)_2$) rarely occur. The abundance of Na minerals is attributable to the Na-rich additives employed in the reduction processes (mainly $NaCO_3$: Contini et al. 2009). The high-temperature silicates are byproducts of the foundry processes, where the silica was probably provided by the gangue and, supposedly, from the quartz sand used for ingot coating. The presence of cristobalite is also attributable to the high temperature of metallurgical processes (Piatak & Ettler, 2021), as observed in the vitreous slags showing the typical background of amorphous materials together with quartz and cristobalite peaks (e.g., sample SUMA 5_3, Fig.

8

268   S1).

269   Diverse Sb-bearing phases occur, such as metallic Sb or (rarely) metal alloy (Fe_2Sb), oxides

270   (sénarmontite, and valentinite, Sb_2O_3; rarely schafarzikite, $FeSb_2O_4$) and sulphides (tetrahedrite

271    $(Cu,Fe)_{12}Sb_4S_{13}$) (Table 1, Fig. S1). Of particular interest is the diffused presence of mopungite

272    $Na[Sb(OH)_6]$, always detected in the XRD patterns of altered casting residues and residues of rotary

273   furnaces. These samples often show crumbliness, powdery surfaces and patinas. Among them, two

274   samples of patinas scraped from highly altered casting residues (sample SUMA 5_6, Fig. 3a),

275   consisting of pure mopungite (Fig. S1), were analysed at the MCX line at the Elettra synchrotron light

276   source in order to perform the structural refinement. The obtained XRD patterns do not show peaks

277   of phases other than mopungite, the strongest reflections being [hkl – d (Å) – (I)]: [(111 – 4.6 – 100)

278   (020 – 4.01 – 67) (022 – 2.81 – 36) (002 – 3.94 – 27.8)] (Figs. 3b and c). The structure of the analysed

279   samples belongs to the tetragonal system, space group $P4_2/n$, face-centered unit cell. The unit-cell

280   parameters obtained by the structural refinement are close to those reported by (Schrewelius, 1937),

281   and in general agreement with the more recent literature, slightly larger than those reported by Palenik

282   et al. (2005) and smaller than data from Bittarello et al. (2015) and Asai (1975). The results of the

283   Rietveld refinement and the structural parameters for the unit cell are reported in Table 2, whereas

284   the lists of reflections are reported in Tables S2 and S3.

285   The mineralogy of samples collected along the Rio Su Suergiu riverbank is quite similar to that of

286   the foundry slag heaps, but it is worth to note that, even if the samples are altered, the mopungite was

287   never detected (Table 1).

288

4.2 SEM and EMP analysis

290   SEM analyses performed on casting residues sampled at the foundry slag heaps, in agreement with

291   XRD results, show an elemental composition of the matrix (Si, Al, Ca, O, Na) compatible with the

292   presence of NaAl-silicate hydrate and calcite (Figs. 4 and 5). The local presence of Mg and Fe (sample

293   SUMA 5_7, Fig. 4a), in addition to Si, Al and K agrees with the presence of phlogopite, also detected

294   by XRD.

295   The sample SUMA5_1 (Fig. 2, Table 1), observed by backscattered electrons (BSE), consists of dark

296   grey grains (the abovementioned Si-Al-Ca matrix) on which brighter micrometric particles, mainly

297   constituted by heavy elements, are finely dispersed (Fig. 4b-d). EDS spectra indicate variable

298   proportions of Sb, O, Ca and Fe; matching the EDS semiquantitative analyses with the XRD on the

299   same samples (Table 1), the presence of Sb oxides (senarmontite and valentinite), Sb-Ca oxides and

300   schafarzikite can be assessed. The mopungite is recognizable as pale grey encrustation.

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Before SEM analysis, the sample SS7 was treated in order to analyse separately the powder forming a patina of alteration and the underlying surface (Fig. 2). For this purpose, the powder was gently withdrawn with a spatula then the sample was immersed in ultrapure water (Millipore, Milli-Q$^{©}$, 18.2 MΩ cm^{-1}) for 20 minutes and successively washed with ultrapure water. The EDS spectra of both powder and washed SS7 samples show an elemental composition of the matrix compatible with the presence of NaAl-silicate hydrate and calcite in agreement with mineralogical results (Fig. 4e-g). Iron is widely detected in both powder and washed samples, maybe due to its presence as impurities or as rare crystallographic disordered phases not revealed by XRD analysis. BSE images of washed sample highlight numerous fractures and holes of dissolution on the surface, reasonably linked to alteration processes (Fig. 4g). These discontinuities are often filled up by microcrystals of Sb-oxides and mopungite that rarely show a proper habitus, while in the dissolution cavity euhedral crystals of mopungite (~ 100 μm) are well visible (Figs. 4h and i).

A semi-quantitative estimate based on EDS analysis performed on several samples, indicates variable proportions of Na and Sb for the mopungite, which can be attributable to the different local availability of Na and to different precipitation/crystallization conditions.

BSE image of casting residue SS5, sampled in the Riu Su Suergiu riverbank, shows dark flakes with lamellar structures covered by euhedral grains likely bearing heavier elements (more pale grey) (Fig. 5a). The EDS spectra (Figs. 5b and c) indicate the presence of Sb, mainly concentrated in the pale grey grains, in addition to Na, Al, Si e O and minor amounts of Fe and Zn, suggesting that the sample is composed by a matrix of silicates with minor Sb phases. These findings agree with XRD patterns indicating the presence of quartz and high-temperature silicates derived from metallurgical processes (mullite, moissanite and cristobalite) and, subordinately, Sb-bearing phases. In this case, mopungite was not detected, neither by XRD nor by SEM analyses.

Differently from the other types of metallurgical residues, the sample MET has a shiny surface (Fig. 2): the XRD patterns indicate that the sample is almost completely composed by metallic Sb with minor amounts of quartz and other silicates (Fig. S1). BSE imaging shows a light grey surface made up by compactly packed lamellae, in direct contact with a porous and irregular surface consisting of aggregates of euhedral crystals (Fig. 5d). Results of EDS analysis indicate that the lamellar part is mainly composed of metallic Sb whereas the porous zone, consisting of Sb oxide, represents an oxidation surface (Figs. 5e and f). Traces of Si, Al, Na, Ca, K and O, likely due to the presence of silicates, were observed in EDS spectra (not shown).

Quantitative chemical analyses were performed by EMP on samples selected after SEM observation. The results are reported in Tables 3, 4 and 5 showing the composition of metallic Sb, mopungite-like phases and Na-Ca silicates, respectively. The exact position of the spot analyses is shown in figures

S4 and S5. EMP analyses confirm the reliability of the results obtained by XRD and SEM investigations.

Metallic Sb is almost pure with small amounts of Sn (0.41-0.46 wt.%): it has been found in the samples MET as well as in SS7 and SUMA-5_4, as small droplets. The sample MET hosts also small inclusions of a Sb-Fe alloy with a ratio of about 80:20 and Sb oxides as surficial encrustations (Table 3, Fig. S4). Among the Sb oxides, both Sb_2O_3 and Sb_2O_4 were identified by calculating the stoichiometric oxygen required to fulfil the cations amount, up to reach approximately 100 wt.% ox. This finding supports the XRD analyses that detected senarmontite, valentinite and schafarzikite.

Several spot analyses were performed on mopungite crystals found by SEM-EDS investigation in three samples of foundry slags (SUMA_5_4, SS7, SUMA_5_1). As already observed by EDS spectra, the relative proportions of Sb and Na vary from one crystal to another with Sb_2O_5 ranging 70.44-79.55 wt.% and Na_2O 7.64-10.84 wt.%. Minor amounts of other oxides, especially SiO_2 (0.25-1.62 wt.%) and FeO, Sn_2O, ZnO, Al_2O_3 (< 1 wt.%) were also detected (Table 4, Fig. S5). Interestingly, none of the dozens analysed points have a composition closely matching that of an ideal mopungite that, according to its stoichiometry, should be 65.54 wt.% Sb_2O_5, 12.56 wt.% Na_2O and 21.90 wt.% H_2O. Indeed, all points are more or less enriched in Sb and deficient in Na and have a water content (estimated as the difference between the ideal oxides sum of 100 wt.% and the measured one of about 80-90 wt.%) lower than expected (see discussion below).

Further analyses were performed on the silicate phases in the attempt to characterize the complex matrix of the slags (Table 5, Figs. S4-5). The identification of several phases is complicated by their low total cations sums, likely due to the presence of hydroxyl and/or carbonate and/or sulphate groups. For instance, the Na-rich alumino-silicates are recognized as cancrisilite or kyanoxalite (cancrinite group) based on the contents of the main cations and by the oxides sum (about 90 wt.%) compatible with the presence of about 10 wt.% of H_2O + CO_2. Likewise, Ca-silicates have been identified as spurrite or hillebrandite, both characterized by approximately 30 wt.% SiO_2 and 60 wt.% CaO, and with about 10 wt.% CO_2 and H_2O, respectively. Many other analytical spots provided chemical compositions with variable contents of SiO_2, Al_2O_3, CaO and Na_2O and with low oxides sums, but a clear match with known minerals could not be established. However, by comparing EMP analyses with the XRD mineral identification, some further constraints on slags mineralogy can be provided. For instance, minerals like nosean and hauyne were not precisely identified by EMP but their presence is reliably inferred by some spot analyses, showing compositions close to these phases, and by their finding through XRD.

Quartz, calcite, dolomite and gypsum were detected by EDS spectra but not analysed by WDS. Although recognized by XRD analyses, no phyllosilicates were found by EMP likely due to the

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369 different sample preparation required by the two techniques. Indeed, grinding the whole sample for
370 XRD analyses allow to include its external surface, whereas cutting and polishing the slabs for EMP
371 analyses imply the loss of the external surface where phyllosilicates are likely concentrated as
372 alteration patinas.
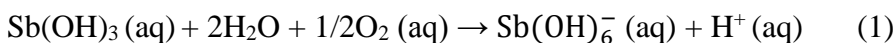
373

5. Discussion

374 *5.1 Case study*

375

376 The ore minerals hosted in the mine waste (and subordinately in the natural outcrops) and the Sb-
377 bearing phases in the foundry slag heaps represent the main sources of Sb from Su Suergiu area. The
378 mineralogical associations, detected by XRD analysis, suggest that Sb is released through i) oxidation
379 of primary Sb sulphides (in mine wastes and natural outcrops) and ii) weathering of Sb-bearing phases
380 dumped in the foundry slag heaps (Fig. 6).
381 Previous authors (Ashley et al., 2003) indicated two main pathways of stibnite oxidation in contact
382 with circumneutral waters under oxidizing conditions: the direct oxidative dissolution and the
383 formation of Sb(III)-oxides which successively dissolve. In both cases, Sb(III) is released in solution
384 where is present as dissolved $Sb(OH)_3$. Under oxidizing conditions and near-neutral pH values,
385 typical geochemical conditions of surface waters, $Sb(OH)_3$ is oxidized to $Sb(OH)_6^-$ (Eq.1) (Oorts et
386 al., 2008) that is stable in solution and can be transported for a long distance downstream from the
387 contamination source.

388

389 $$Sb(OH)_3 \text{(aq)} + 2H_2O + 1/2O_2 \text{(aq)} \rightarrow Sb(OH)_6^- \text{(aq)} + H^+ \text{(aq)} \qquad (1)$$

390

391 At Su Suergiu, the presence of gypsum in mine wastes (and outcropping rocks) indicates sulphide
392 oxidation due to exposition to surface environment. The mineralogical association linked to the
393 stibnite oxidation (Ashley et al., 2003) is not observed, suggesting the occurrence of direct oxidative
394 dissolution, as simplified in Eq. 2 (Cidu et al., 2018):

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396 $$Sb_2S_3 + 7O_2 + 10H_2O \rightarrow 2Sb(OH)_6^- + 3SO_4^{2-} + 8H^+ \qquad (2)$$

397
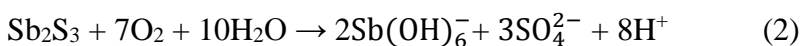
398 The dissolution of sulphides (not only stibnite, but also pyrite, arsenopyrite, etc.) is also proved by
399 the high concentration of SO_4^{2-} (Cidu et al., 2021, 2018, 2014) in the water draining the mine area
400 (up to 1900 mg L^{-1}). Carbonates present in both natural outcrops and in the gangue (Table 1),
401 neutralize the acidity of solutions to circumneutral - slightly alkaline pH, promoting further oxidation

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and Sb mobilization.

The high Sb concentration, up to 30,000 μg/L Sb in waters draining the Su Suergiu mine area, indicates the foundry slag heaps as the main source of Sb released in the environment (Cidu et al., 2021, 2018, 2014). This finding agrees with data reported by Contini et al. (2009) showing mean value of 1% Sb in solid samples collected along the Rio Su Suergiu and Rio Sessini, and dramatically higher Sb content, from few unit % up to about 17 wt% Sb in samples collected in the foundry slag heaps. The high variability observed within the foundry slag heaps, is probably due to the inhomogeneity of the foundry products dumped there. This is supported by the abundance and variability of Sb mineralogical phases observed in foundry slag samples in our study (Table 1, Fig. S1).

The mineralogical associations observed in different foundry slag samples suggest complex alteration schemes, whose simplified examples are reported in figure 6. The metallic Sb and Sb-oxides are recognized as the primary minerals of Sb contamination, however Fe-Sb alloy and tetrahedrite are also rarely detected. The primary metallic Sb can be dissolved to $Sb(OH)_3$ (Eq. 3) (Ilgen et al., 2014) or oxidized to valentinite (Eq. 4) (Lide 2005, modified). The valentinite can dissolve and release $Sb(OH)_3(aq)$ (Eq. 5) (Biver & Shotyk, 2013; Oorts et al., 2008), or be further oxidized to cervantite that successively releases $Sb(OH)_3$ (and presumably $Sb(OH)_6$) by dissolution.

$$4\ Sb^0(s) + 3O_2\ (aq) + 6H_2O \rightarrow 4Sb(OH)_3\ (aq) \qquad (3)$$

$$Sb^0(s) + 3H_2O \rightarrow Sb_2O_3(s) + 6H^+ + 6e^- \qquad (4)$$

$$Sb_2O_3(s) + 3H_2O(l) \rightarrow 2Sb(OH)_3\ (aq) \qquad (5)$$
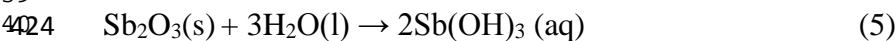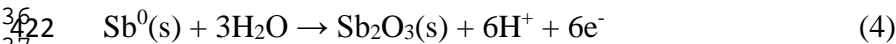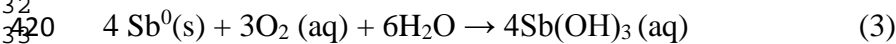
In the same way, primary sénarmontite/ valentinite can follow the direct dissolution or the oxidation to cervantite. Once in solution, the $Sb(OH)_3$, at oxidizing conditions and slightly alkaline pH of draining water (7.1< pH < 8.5) (Cidu et al., 2021, 2018, 2015), quickly oxidize to $Sb(OH)_6^-$ (Eq.1). The mopungite is the last-forming mineral of the proposed weathering schemes. The abundant presence of this mineral is the peculiarity of the studied system, in fact mopungite has been reported only in seven locations around the world (data from www.mindat.org/show.php?id=2777&ld=1), because it forms in presence of high concentrations of $Sb(OH)_6^-$ and Na^+ (> 20 mM) (Blandamer et al., 1974; Ilgen et al., 2014).

Figure 7a displays an Eh-pH diagram of Sb for the system Na-Sb-S-H-O, built by using the composition of the slag drainage sample SU2 (30.10.2012) (Fig.2) from Cidu et al. (2014). According

to thermodynamic equilibrium conditions, despite the high Sb (30,000 μg L^{-1}, i.e. 0.25 mM) and Na (600 mg L^{-1}, i.e. 26.10 mM) concentrations, mopungite precipitation is not predicted at the oxidizing conditions characterizing drainages from the investigated area (red circle), while the Sb(OH)$_6^-$ species is stable in solution (Filella et al. 2002). In agreement, mopungite was not detected in the XRD patterns of samples collected downstream the foundry slag heaps. Apparent mopungite formation was found by increasing either 1.7 times the Na concentrations (Fig. 7b) or 1.8 times that of Sb (Fig. 7c). These findings suggest that the apparent formation of mopungite is related to local water chemistry and cannot be predicted based on bulk water chemistry downstream to foundry slags. The favourable conditions for precipitation can likely be reached during drying of foundry wastes that lead to local and variable Na and Sb concentrations.

In the foundry slag heaps of Su Suergiu, the abundance of Na phases derived from metallurgical processes explains the enrichment of Na$^+$ in solution and allows the mopungite precipitation, that limit the Sb dispersion by bonding Sb(OH)$_6^-$. SEM imaging (Fig. 4) shows that mopungite can precipitate as euhedral crystals, as microcrystal in veinlets within the NaAl-silicates hydrate matrix and as encrustation on altered surfaces of grains. This variability can be due to local differences of geochemical and kinetic conditions at the microscale. For example, in the dissolution cavities the precipitation of euhedral crystals might be promoted by the stagnation of concentrated solution. The velocity of circulation/percolation of solutions within the foundry slag heaps can influence the local concentration (linked to the contact time solid/solution) and the migration of the elements leading to the precipitation of secondary minerals with different composition and crystallinity, as supported by the variability of relative proportion of Na and Sb detected by WDS analyses. The common Na deficiency observed in mopungite-like phases suggests that the Na availability in the slag matrix is the limiting factor in the mopungite formation. On the contrary, the high Sb contents in mopungite is the result of the availability of this element in the slags, as testified by the widespread occurrence of micro disseminations of metallic and oxidized Sb. The inconsistency between XRD refinement data, indicating a perfect mopungite, and chemical analyses, pointing to a non-ideal phase, may depend on the position of the analysed phases within the slag fragments. XRD analyses were performed on powder grasped from the surface of slag fragments whereas EMP analyses, requiring the samples cut into polished slabs, were unavoidably performed on crystals intersected in the inner part of the samples. This difference in mopungite composition can shade a light on its formation mechanism. Antimony released in solution from the Sb droplets reacts with Na-rich silicates in the surrounding matrix resulting in the formation of mopungite-like phases. The Na enrichment increases as fluids migrate toward the surface of the slags where alternating dry-wet cycles, due to the weather conditions, enhance the precipitation of a "real" mopungite.

14

Metallic Sb is far from equilibrium conditions (Fig. 7, red circle), and it is probably easily oxidized or dissolved in the investigated system, representing a considerable source of Sb. In agreement with the thermodynamic prediction, we identified Sb oxidation surfaces on metallic Sb in MET sample by EDS-SEM analysis (Fig. 5d-f).

The stibnite field extends from acidic to alkaline conditions (pH 8.7) at anoxic conditions, but an increase in Eh values can lead to the formation of Sb oxides or to a direct dissolution. As stated above, the direct oxidative dissolution (*sensu* Ashley et al., 2003) seems to be the prevalent process at Su Suergiu, since the mineralogical association linked to the stibnite oxidation was not found.

The abundance of mopungite observed through both XRD and SEM analyses indicates that it is the main trap of dissolved $Sb(OH)_6^-$ for which represent a (temporary) sink in function of the change of geochemical and hydrological conditions. In fact, it must be considered that under high flow condition, the dilution can lead to the mopungite dissolution and thus to the re-mobilization of Sb. This could explain the high Sb concentrations in waters reported by Cidu et al. (2014, 2018) after storm events, despite the dilution linked to the consistent increase of water flow. The role of metal oxy-hydroxides in limiting the Sb mobility, often reported in literature (Beauchemin et al., 2012; Craw et al., 2004; Ilgen et al., 2014; Ritchie et al., 2013; Wilson et al., 2004), does not seem to be very effective at Su Suergiu; indeed, the rare occurrence of phases like FeSb-ox and CaSb-ox can just subordinately contribute to Sb immobilization due the local availability of metals.

5.2 Broader implications

The role of secondary Sb minerals on Sb mobility in supergene and anthropic environments is examined in several studies and can be useful to understand the apparently ambiguous behaviour of Sb. As highlighted by Majzlan et al. (2016), mineralogical studies consider Sb as a low mobile element since it tends to form poorly soluble phases such as tripuhyte ($FeSbO_4$), while many geochemical studies report a high Sb mobility inferred by its high concentrations in the surrounding waters. The key to understand such a contrasting behaviour is to consider the role of secondary phases, especially their stability in specific environmental conditions, the oxidation pathways and the conditions limiting or enhancing their crystallization, and the kinetics of formation/dissolution reactions. As an instance, some secondary minerals can bind Sb only in specific conditions, thus they do not have relevance in the Sb retention where these conditions are not fulfilled (Roper et al., 2015). Several papers document that Sb released in the environment, due to oxidation of stibnite and other Sb-bearing minerals, can be adsorbed onto metal oxy/hydroxides (Fe, Mn, Al) or co-precipitated with secondary minerals (Beauchemin et al., 2012; Craw et al., 2004; Ilgen et al., 2014; Ritchie et al.,

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2013; Wilson et al., 2004) thus contributing to natural attenuation of $Sb(OH)_6^-$. Also jarosite, by means of the substitution of Fe with Sb, appears to be efficient for Sb immobilization (Courtin-Nomade et al., 2012). In tailings enriched in Fe compounds, the immobilization of Sb by means of adsorption or coprecipitation with Fe phases, results more effective and stable than the precipitation of Sb secondary minerals (Ashley et al., 2003; Borčinová Radková et al., 2020).

The role of mopungite in Sb mobility at Su Suergiu mine seems to be a peculiar case study since mopungite has been found in few localities worldwide. On the contrary, it could be a process more common than expected since alkali, especially Na-compounds, are largely used in Sb smelting processes, resulting in the production of huge amounts of hazardous wastes called alkali residues (Guo et al., 2014; Long et al., 2020; Su et al., 2021). These wastes are a source of contamination and are currently studied with the aim to estimate the potential release of toxic compounds (Guo et al., 2014), to reduce the environmental impact (Salihoglu, 2014), but also to recovery Sb, As, and sodium bicarbonate to be reused in smelting processes (Long et al., 2020; Su et al., 2021). Thus, understanding the processes affecting the Sb fate in Na-rich residues of metallurgical plants is a current and worldwide concern.

6. Conclusions

In this study, the peculiar conditions allowing the mopungite formation at Su Suergiu are described, providing a new insight on its role on Sb mobility. At Su Suergiu, mopungite precipitation is due to alteration of the natural thermodynamic equilibria induced by past mine and metallurgical activity, and it acts as temporary sink for Sb contributing to reduce Sb dispersion in solution. The high Na availability to solution in Su Suergiu slags favours mopungite formation. These findings are fundamental to understand the mineralogical and geochemical processes occurring in the investigated area, and they shed light on the mechanisms responsible for Sb mobility, representing a fundamental tool to plan future remediation actions at Su Suergiu and elsewhere.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure Captions

Fig 1. Location of the study area (a, b) and schematic geological map of the Gerrei mine district (c) (RAS, 2013, modified).

Fig. 2. Photos of representative samples of different types of metallurgical residues sampled at the foundry slag heaps and waste runoff in Su Suergiu, and location of water and solids sampling point.

Fig. 3. Photo of the selected foundry slag SUMA 5_6 (a); synchrotron XRD patterns, after Rietveld refinement performed by GSAS-II, of patinas scraped from the surface (b, c); the unit cell of mopungite obtained by VESTA 3 software (d).

Fig. 4. SEM analysis: BSE images of casting residues SUMA 5_7 (a) and SUMA 5_1 (b, c and d), the superficial powder withdrawn from SS7 sample (e and f) and the SS7 washed surface (g) with the detail of mopungite microcrystals in the dissolution cavities (h and i). The labels refer to the composition determined through the EDS spectra.

Fig. 5. BSE image (a) and the EDS spectra (b and c) of the casting residue SS5 sampled along the Riu Suergiu riverbank, and BSE image (d) of MET sample, metallic antimony, with the EDS spectra (e and f).

Fig. 6. Schematic representation of different alteration schemes proposed for the different Sb contamination sources at Su Suergiu mine area.

Fig. 7. Eh vs pH diagrams for Sb in the system $Sb - Na - S - H - O$ built by the chemical-equilibrium-diagram-tool Hydra-Medusa (Puigdomènech, 2010). The red circle represents the water sample SU2 (30.10.2012) from Cidu et al. (2014).

Table 1

Table 1. Mineralogical phases recognized through XRD analysis in outcropping rock and efflorescences and patinas, mine waste heaps and foundry slag heaps samples collected at Su Suergiu abandoned mine area. (abbreviations: Ank= ankerite; Apy= arsenopyrite; Ar= aragonite; Cal= calcite; Ccn= cancrinite; Cer= cervantite; Crs= cristobalite; Cus= cuspidine; Dol= dolomite; Fds= feldspar (group); Gr= graphite; Gy= gypsum; Hal= halotrichite; Hyn= hauyne; Hm= hematite; Hx= hexahydrite; Jar= jarosite; Kal= kalinite; Kie= kieserite; MgFe= magnesioferrite; Mt= magnetite; Mois= moissanite; Mop= mopungite; Mul= mullite; Nj= natrojarosite; Nsn= nosean; Pbj= plumbojarosite; Phy= phyllosilicates; Py= pyrite; Qtz= quartz; Sb= metallic Sb; Sck= schafarzikite; Sen= senarmontite; Stbn= stibnite; Td= tetrahedrite; Val= valntinite).

samples	description	mineralogical phases
Outcropping rocks		
	1A - yellowish efflorescence	Sulphate hydrate (mainly Fe) Hal, Kal, Jar/Pbj, Hx
SUMA 1	1B - fine grained material blue-grey	Qtz, Gy, Nj, Phy[1]
	1C - brown massive	Qtz, Gy, Phy[2], Py, Cal
SUMA 2	white patina	Qtz, Phy[3], Cal, Ar
SS11		Qtz, Cal, Phy[4]
SS12		Qtz, Gy, Al-sulphate-hyd, Ca-Al-sil-hyd, Jar, Phy[5]
SS13	patina on black schist	Qtz,Gy, Phy[6]
SS14		Qtz, Cal, Gy, Phy[7]
SS15		Qtz, Cal, Gy, Phy[8], Py-Cpy

[1] = muscovite, clinochlore; [2] = muscovite, clinochlore, illite; [3] = clinochlore, muscovite; [4] = biotite, illite, clinochlore, muscovite; [5] = illite, muscovite; [6] = illite, clinochlore; [7] = illite, muscovite, clinochlore; [8] = clinochlore-Fe, muscovite

samples	description	mineralogical phases
Mine Waste		
SUMA 3	dark grey consolidated fine grainsize clasts, with quartz vein	Qtz, Phy[1], Cal, Dol
SUMA 4	dark fine grainsize clasts	Qtz, Gy, Phy[2]
SS1	consolidate dark-grey clasts	Stbn, Qtz, Cal, Hm, Dol(Fe)
SS10	poorly consolidated fine grain size dark grey wastes	Qtz, Gy, Phy[3]

[1] = muscovite, clinochlore; [2] = muscovite, clinochlore; [3] = illite, clinochlore

Foundry slag heaps

Residues of rotary furnace

samples	description	mineralogical phases
SUMA 5A	massive poorly consolidated grey-dark fine grain size materials (5A) covered by friable red alteration crust (5A_red)	(5A) Qtz, Mop, Cal, NaAl-CO$_3$, Phy[1], Td, metal-ox; (5A_red) Mop, Apy, Qtz, Phy[2] and Fe compounds derived from alteration
SUMA 5_4A SUMA 5_4B	yellowish-brown consolidated lags, slightly altered	(5_4A) Mop, Val, Sen, Qtz, NaAl-CO$_3$, Cal, Nsn, Phy Hyn, metal-ox (5_4B) Mop, Sen, Sb, Sb$_2$Fe, Qtz
SUMA 5_5	dark-brown slag, with red-yellowish patina	Mop, NaAl-silicate hyd, CaSb-ox, Qtz, Cal, Phy[2], Mul, Apy

Casting residues

samples	description	mineralogical phases
SUMA 5_1	slight brown foliated shell	Mop, Val, Sen, CaSb-ox, NaAl-silicate hyd, Mt(?), Sck
SUMA 5_2	yellowish granular patina on casting residues	Mop, Qtz, Cal, metal-ox
SUMA 5_6	yellowish and red patinas onto highly altered casting residues	Mop
SUMA 5_7	grey nodule partially consolidated, slightly altered	Mop, Cal, Phy[3], NaAl-silicate hyd, Apy, Na-Mg/Al sulphates, Ank, Cus(?)
SS7	yellowish altered casting residues	Mop, Cal, Cer, NaAl-silicate hyd, Kie (?)
SS8	massive casting residues, slightly covered by yellowish patina of alteration	Mop, Val, Sen, Sb-ox, Dol, NaCa-sul, Phy[4], Ccn (?)

Slags

samples	description	mineralogical phases
SUMA 5_3	black massive glassy slag, with brown elements	disordered carbon, Qtz, hight temperature SiO$_2$
Metallic Sb		Sb, Qtz
SS9	foliated dark residue with yellowish patina (uncertain origin)	Mop, Mois, Ccn (?), Gr

[1] = muscovite, clinochlore; [2] = clinochlore, phlogopite; [3] = clinochlore; [4] = illite-montmorillonite, vermiculite; [4] = muscovite

samples	description	mineralogical phases
Waste runoff		
SS2	vacuolar /glassy brown slag	Qtz, Gy, Phy(?)
SS3	glassy slag	Qtz, Gy, Crs
SS4	vacuolar slightly glassy foundry slag	Qtz, Dol, Crs, Sb-ox, Fds, Phy(?), Sck
SS5	dark fine grain size (casting residues)	Qtz, Mul, Crs, Mois, Sb, Val
SS6	massive casting residues, slightly altered	Sb-ox, NaCa-silicate, MgFe

Table 2

Table 2. Results of Rietveld refinement on two monomineralic samples within the *P 4₂/n* space group. Cell parameters, Caglioti parameters and refinement quality parameters are reported (in brackets the uncertainty of the last decimal number). The atomic coordinates, occupancy, Thermal parameter (U_{iso}) and Wyckoff positions are also listed for the sample SUMA_5_6B.

	a=b (Å)	c (Å)	V (Å³)	α= β= γ	U	V	W	GoF	wR
SUMA_5_6A	8.0184(1)	7.8872(1)	507.117	90	40.956	3.129	3.078	1.34	13.537
SUMA_5_6B	8.0219(1)	7.8887(1)	507.643	90	52.196	-7.316	3.711	1.45	12.903
	Structural details of SUMA_5_6B sample								
			x	y	z	Occ.	U_{iso}	Site	Sym.
1	Sb	Sb	0	0	0	1	0.008	4c	-1
2	Na	Na	0	0.5	0	1	0.013	4d	-1
3	O	O1	0.0590	0.2206	0.0981	1	0.013	8g	1
4	H	H1	0.0318	0.2352	0.1938	1	0.019	8g	1
5	O	O2	-0.0872	-0.0695	0.2215	1	0.013	8g	1
6	H	H2	-0.2012	-0.088	0.2252	1	0.020	8g	1
7	O	O3	0.2231	-0.0761	0.0707	1	0.012	8g	1
8	H	H3A	0.2342	-0.1967	0.0641	0.5	0.018	8g	1
9	H	H3B	0.2351	-0.0664	0.1906	0.5	0.018	8g	1

Table 3

Table 3. Selected analyses of metallic Sb, Sb-Fe alloy, and Sb-oxides

phase	Sb^0				SbFe-alloy			Sb^{III}-ox		$Sb^{III}Sb^V$-ox	
sample	MET		SS7	SUMA-5_4	MET			MET	SUMA-5_4	MET	SUMA-5_4
Wt el% / Point	1	2	7	8	3	5	Wt ox%	6	9	4	10
Sb	100.09	99.99	100.72	99.20	79.10	80.02	Sb_2O_3 *	98.4	98.53	99.06	87.07
Fe			0.08		20.18	20.09	FeO	0.11			0.21
Sn	0.41	0.46	0.43	0.42	0.29	0.33	SnO_2	0.41	0.56	0.41	0.37
Zn				0.13			ZnO		0.2		0.2
Ni					0.41	0.13	NiO				
Co					0.11	0.15	CoO	0.085			
Mn				0.07			MnO				0.1
Si						0.03	SiO_2	0.094	0.16	0.98	2.82
Ca							CaO				3.01
Na	0.04	0.04	0.06	0.10			Na_2O	0.1	0.13	0.19	5.11
Tot	**100.54**	**100.49**	**101.29**	**99.92**	**100.09**	**100.76**	**Tot**	**99.2**	**99.59**	**100.63**	**98.89**

Table 4

Table 4. Selected analyses of mopungite-like phases from the inner part of the slag fragments.

Sample	SUMA_5_4		SS7	SUMA_5_1				
Point analysis	15	16	17	18	19	20	21	22
	Wt ox%							
Na_2O	8.79	10.84	7.64	10.33	8.01	11.82	9.71	9.25
Sb_2O_5	79.55	73.99	70.44	74.66	75.58	76.55	77.76	72.10
FeO	0.16	0.11	0.22			0.12	0.09	0.36
SnO_2	0.32	0.29	0.29	0.30	0.26	0.20	0.21	0.28
SiO_2	1.62	0.25	0.81	0.46	0.63	1.07	1.12	1.45
ZnO	0.14				0.12	0.21		0.49
Al_2O_3	0.36		0.43				0.11	0.37
MgO	0.06	0.08						0.08
TiO_2								0.08
WO_3		0.32	0.31					
K_2O	0.03							
Tot	**91.03**	**85.87**	**80.14**	**85.74**	**84.61**	**89.98**	**89.00**	**84.46**

Table 5

Table 5. Selected analyses of Ca-rich and Na-rich silicates from the slag fragments matrix

Sample	SUMA-5_4			
Point analysis	*11	*12	**13	**14
	Wt ox%			
SiO_2	31.32	31.31	40.10	39.48
Al_2O_3	0.06	0.03	27.93	27.38
TiO_2		0.08		
FeO	0.33	0.26	1.31	1.19
MgO	0.14	0.16	0.12	0.09
CaO	59.13	59.04	0.44	0.09
Na_2O	0.20	0.18	19.31	20.46
K_2O		0.01	0.26	0.28
ZnO	0.30	0.18	0.09	
NiO	0.06		0.05	
Cr_2O_3		0.05	0.05	
Sb_2O_5	0.44	0.87	0.09	0.15
SnO_2		0.09		
WO_3			0.28	
Tot	**91.98**	**92.26**	**90.02**	**89.52**
* Good match with phases like Hillebrandite [$Ca_6Si_3O_9(OH)_6$] or Spurrite [$Ca_5(SiO_4)_2(CO_3)$]; total oxides at about 92% is acceptable considering 9% of H_2O or CO_2, respectively				
** Good match with phases like cancrisilite or kyanoxalite, both belonging to cancrinite group; total oxides at about 90% is acceptable considering 6% H_2O and 5% CO_2.				

Figure_1

Click here to access/download;Figure;Figure_1.jpg ⬇

Legend

Eluvial and colluvial sediments, landslide (HOLOCENE)	
Pala Manna Complex limestones, sandstones and quartzites (LOWER CARBONIFEROUS)	
Calcari di Villasalto nodular limestones (MIDDLE DEVONIAN - LOWER CARBONIFEROUS)	
a) *Limestone* siltstones and gray limestones; b) dark and nodular limestones; c) *Tentaculites shales* siliciclastic rocks, siltstones and quartzites (SILURIAN - MIDDLE DEVONIAN)	
Ryholites and dacites volcanic rocks (MIDDLE ORDOVICIAN)	
Arenarie di San Vito - micaceous sandstones, quartzites and siltstones, conglomerate (CAMBRIAN - LOWER ORDOVICIAN)	

stratigraphic contact

cataclastic and milonitic rocks

main trust — fault

stream — main river

town — abandoned mine

Figure_2

Click here to access/download;Figure;Figure_2.jpg ⬇

Figure_3

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Figure 3

Figure_4

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Figure_5

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Figure_6

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Sb contamination pathways at **Su Suergiu mine area**

(I)

(II)

Mine wastes and subordinately natural outcrops **Sb sulphides**

Foundry slag heaps **Sb-bearing phases (Sb-ox, Sb⁰)**

Stibnite (Sb_2S_3)

Senarmontite/Valentinite $(Sb^{(III)}_2O_3)$

Metallic antimony (Sb^0)

Valentinite $(Sb^{(III)}_2O_3)$

Cervantite $(Sb^{(III)}Sb^{(V)}O_3)$

$Sb^{(III)}(OH)_3^0 \ (aq)$

$Sb^{(V)}(OH)_6^- (aq) \longrightarrow + Na^+ (aq)$

Streamwater **dispersion in solution**

Mopungite $Na[Sb^{(V)}(OH)_6]$

Figure_7

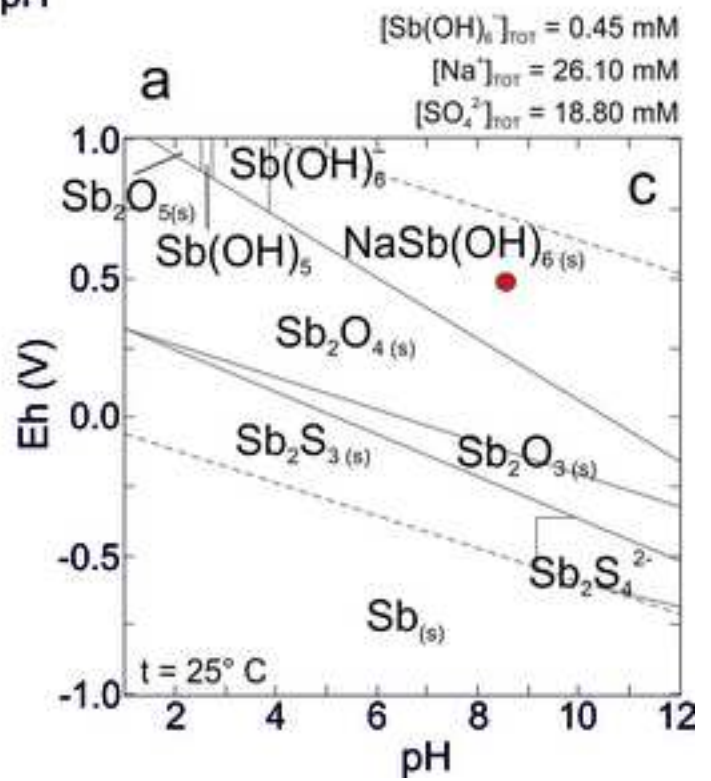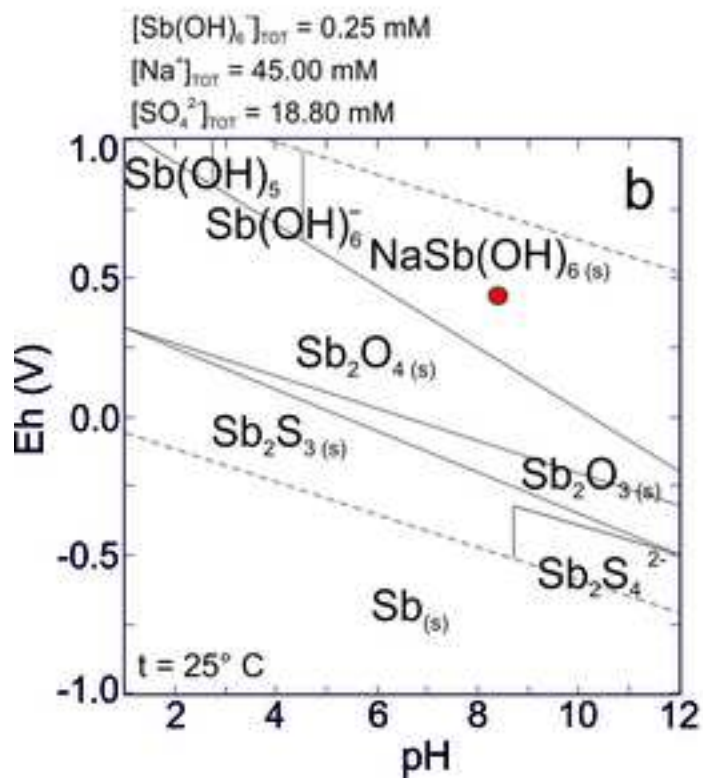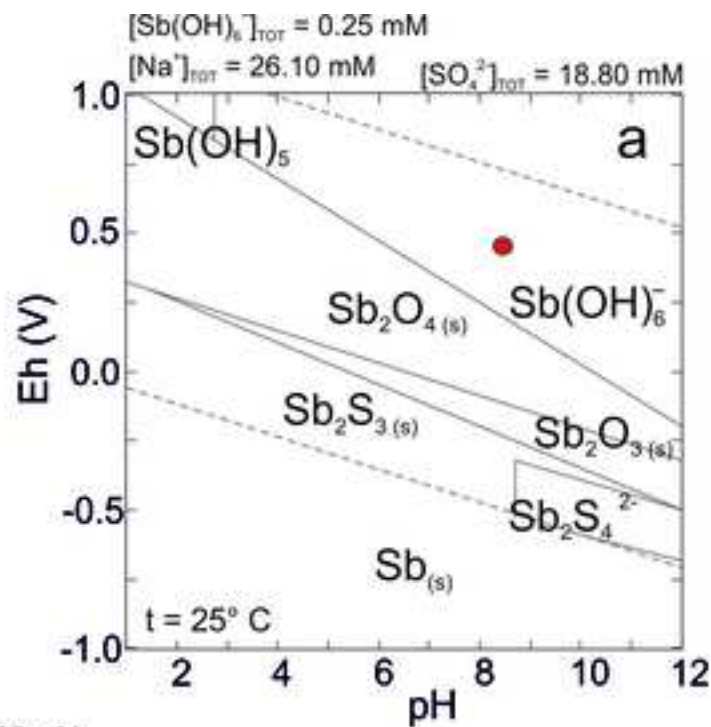Click here to access/download;Figure;Figure_7.jpg ⬇

Supplementary Materials

Antimony contamination sources and alteration pathways of Sb mineral phases in an abandoned mining area: the role of secondary mopungite [NaSb(OH)$_6$]

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Figure S1. XRPD patterns of outcropping rock, mine waste and foundry slags samples. (abbreviations: Cal= calcite; Crs= cristobalite; Dol= dolomite; Gy= gypsum; Hal= halotrichite; Hm= hematite; Hx= hexahydrite; Jar= jarosite; Kal= kalinite; Sb= metallic Sb; Mois= moissanite; Mop= mopungite; Mul= mullite; Pbj= plumbojarosite; Phy= phyllosilicates; Py= pyrite; Qtz= quartz; Sen= senarmontite; Stbn= stibnite; Val= valentinite).
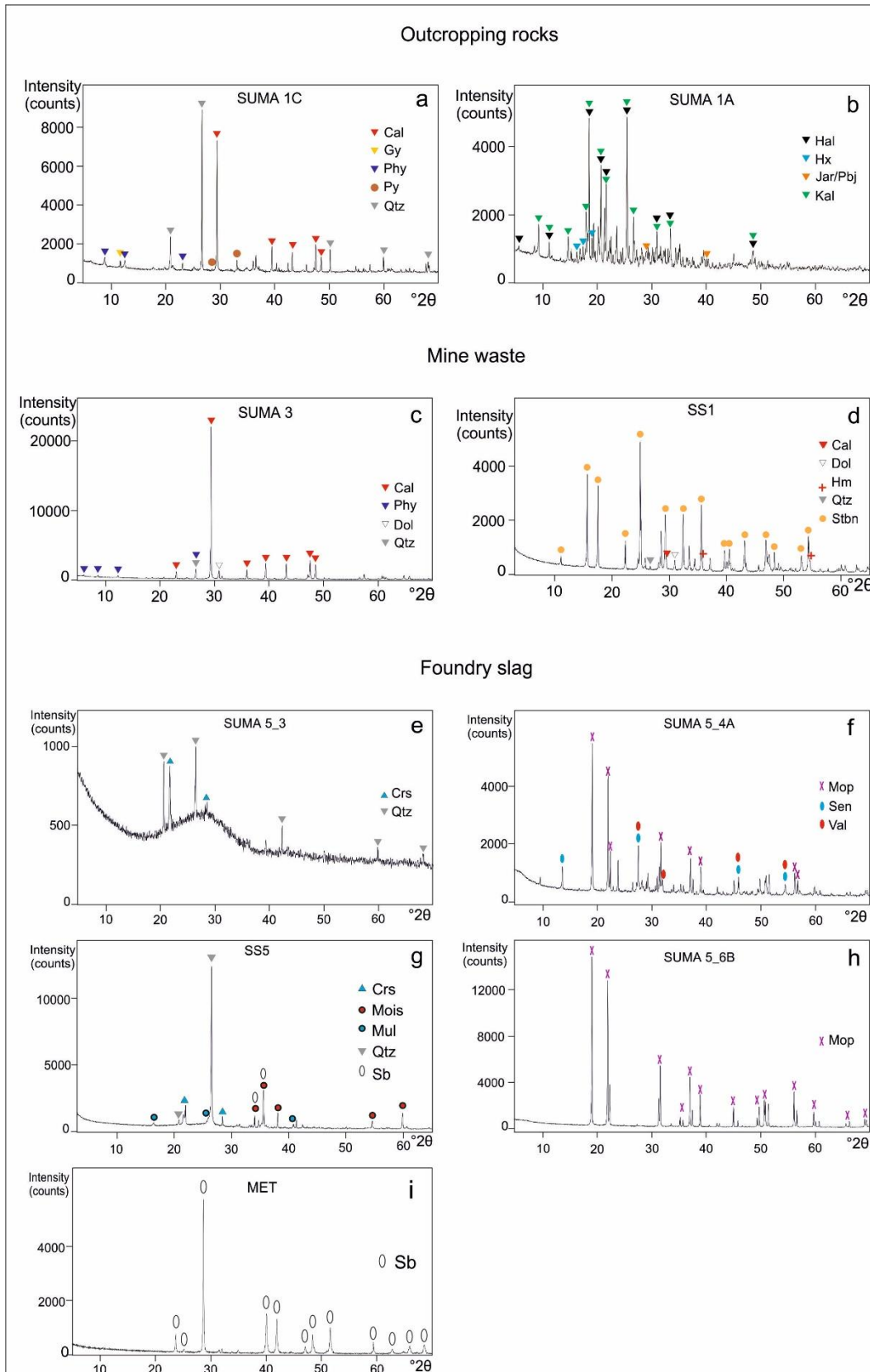
Table S2 List of reflections for the sample SUMA_5_6A (Relative Intensity > 5%).

No.	Pos. [°2Th.]	FWHM [°2Th.]	h	k	l	Mult.	d-spacing [Å]	Rel. Int. [%]
1	11.88363	0.05019	1	1	1	8	4.60380	100
2	13.65477	0.05185	0	2	0	4	4.00924	67.7
3	19.52234	0.05802	0	2	2	8	2.81147	36.2
4	13.88228	0.05207	0	0	2	2	3.94360	27.8
5	22.77805	0.06185	1	3	1	8	2.41398	23.6
6	23.90358	0.06323	2	2	2	8	2.30190	20.1
7	30.94527	0.07253	0	4	2	8	1.78700	18.2
8	31.26120	0.07297	0	2	4	8	1.76939	16.5
9	33.96565	0.07684	2	4	2	8	1.63221	15.5
10	19.35891	0.05784	2	2	0	4	2.83496	14.6
11	34.25668	0.07726	2	2	4	8	1.61875	14.2
12	27.51452	0.06786	0	4	0	4	2.00462	11.6
13	33.96565	0.07684	4	2	2	8	1.63221	10.3
14	30.83931	0.07238	2	4	0	4	1.79299	10.3
15	23.05743	0.06219	1	1	3	8	2.38513	9.7
16	30.28320	0.07161	1	3	3	8	1.82511	6.8
17	30.83931	0.07238	4	2	0	4	1.79299	6.8
18	30.06673	0.07131	3	3	1	8	1.83794	6.7
19	36.01436	0.07986	1	5	1	8	1.54220	6.7
20	30.28320	0.07161	3	1	3	8	1.82511	6.6
21	42.12682	0.08939	4	2	4	8	1.32656	5.6
22	41.21045	0.08792	5	3	1	8	1.35472	5.4
23	44.25653	0.09288	0	6	2	8	1.26571	5.2
24	39.65062	0.08544	0	4	4	8	1.40573	5.2

Table S3 List of reflections for the sample SUMA_5_6B (Relative Intensity > 5%)

No.	Pos. [°2Th.]	FWHM [°2Th.]	h	k	l	Mult.	d-spacing [Å]	Rel. Int. [%]
1	11.87996	0.04753	1	1	1	8	4.60534	100
2	13.64945	0.04860	0	2	0	4	4.01092	69.3
3	19.51808	0.05296	0	2	2	8	2.81231	36.6
4	13.88115	0.04874	0	0	2	2	3.94432	29.6
5	22.77068	0.05587	1	3	1	8	2.41494	23.7
6	23.89720	0.05696	2	2	2	8	2.30267	20.0
7	30.93570	0.06448	0	4	2	8	1.78766	18.4
8	31.25603	0.06485	0	2	4	8	1.76979	16.9
9	33.95476	0.06805	2	4	2	8	1.63282	16.4
10	19.35237	0.05282	2	2	0	4	2.83615	15.2
11	34.24984	0.06841	2	2	4	8	1.61917	14.4
12	27.50478	0.06066	0	4	0	4	2.00546	12.3
13	33.95476	0.06805	4	2	2	8	1.63282	11.0
14	23.05395	0.05614	1	1	3	8	2.38567	10.6
15	30.82826	0.06436	2	4	0	4	1.79374	10.2
16	30.27587	0.06372	3	1	3	8	1.82567	7.2
17	30.27587	0.06372	1	3	3	8	1.82567	7.1
18	36.00156	0.07058	1	5	1	8	1.54283	6.6
19	30.82826	0.06436	4	2	0	4	1.79374	6.4
20	30.05638	0.06348	3	3	1	8	1.83869	6.2
21	42.11586	0.07858	4	2	4	8	1.32697	5.5
22	41.19549	0.07733	5	3	1	8	1.35528	5.4
23	39.64093	0.07526	0	4	4	8	1.40615	5.2
24	44.24112	0.08150	0	6	2	8	1.26621	5.1

Figure S4 BSE images of samples analysed by EMP with the exact position of selected spot analyses reported in Tables 3, 4 and 5. Each image is labelled with the name of the sample it belongs to.
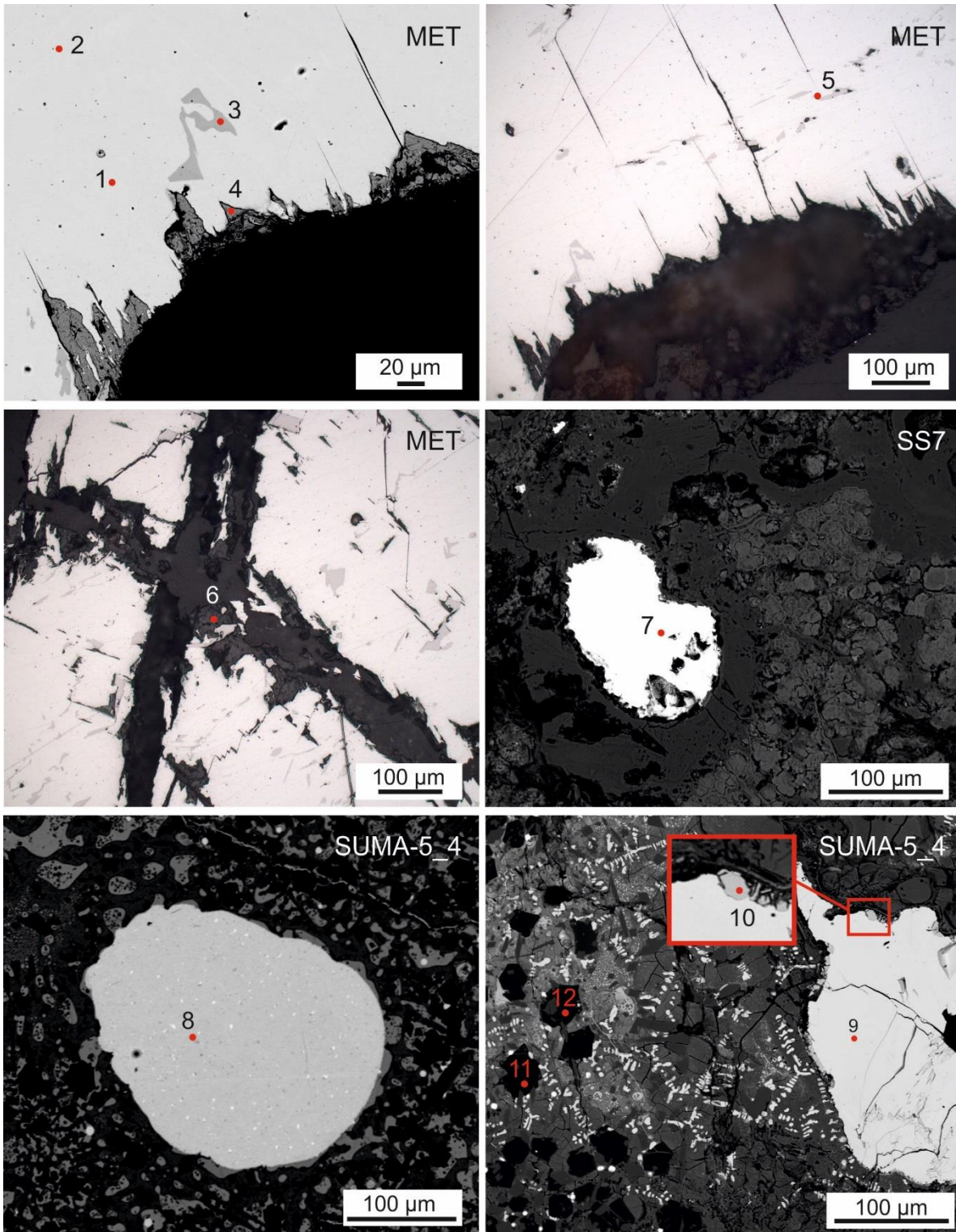
Figure S5 BSE images of samples analysed by EMP with the exact position of selected spot analyses reported in Tables 3, 4 and 5. Each image is labelled with the name of the sample it belongs to.