Experimental study of historical processing of cobalt arsenide ore for colouring glazes (15-16th century Europe)

Judit Molera[(1)], Aurelio Climent-Font[(2)], Gaston Garcia[(2,3)], Trinitat Pradell [(4)], Oriol Vallcorba[(3)], Alessandro Zucchiatti[(5)]*

[1)] MECAMAT. Faculty of Sciences and Technology. University of Vic – Central University of Catalonia. C. de la Laura, 13, 08500 Vic, Catalonia

[2)] Universidad Autónoma de Madrid, Centro de Microanálisis de Materiales, calle de Faraday 3, 28049, Madrid, Spain

[3)] ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain

[4)] Universitat Politècnica de Catalunya, Departament de Física, BRCMSE, campus Diagonal-Besòs, Av. Eduard Maristany 17, 08019, Barcelona, Spain

[5)] University of the Witwatersrand, School of Physics, Private bag 3, WITS 2080, Johannesburg, South Africa

Abstract

Cobalt was used since the early antiquity to tint glass and glazes in blue. The presence of arsenic in blue decorated glazes since ~1500 onwards and absence beforehand, observed in Europe, might be related to the processing of the ore: roasting of the cobalt mineral (*saffre*) and obtaining a glass adding sand and potash (*smalt*) or as by-product of other metallurgical processes, e.g. silver smelting slag. We have replicated the roasting of cobalt arsenide ore ($CoAs_3$) and the processing of silver smelting as described in historical treatises following the transformations by *in situ* variable temperature SR-XRD, PIXE and SEM. Our laboratory tests have proved that roasting cobalt arsenide ore either alone or mixed with fluxes (PbO, CaF_2), $CaCO_3$, SiO_2 and kaolinite was unable to remove the arsenic completely. Roasting cobalt arsenide ore (saffre) alone explains the presence of arsenic in the cobalt blue glasses and glazes after 1520. The product obtained as described by Agricola contains less arsenic forming calcium arsenates, lead arsenates ($Pb_5(AsO_4)_3F$, $Pb_8As_2O_{13}$) and calcium lead arsenates $(Ca,Pb)_5(AsO_4)_3(F,Cl,OH)$ with an hedyphane structure, while cobalt is incorporated into a glassy matrix. As the physical separation of the arsenic free cobalt vitreous phase does not seem possible, these processes can explain the variable content of arsenic shown by the historical blue glazes but not the arsenic free glazes. In this case, the use of an arsenic free cobalt ore such as linnaeite is the most likely source.

Keywords: skutterudite, cobalt pigments, blue glazes, calcium lead arsenate, roasting $CoAs_3$, saffre

** Corresponding author*
Judit Molera

1-INTRODUCTION

Cobalt was used since the early antiquity to tinge glass and glazes in blue. The chemical composition of blue glasses and glazes from various regions and different epochs has been extensively studied. An instrumental study of glass from French archaeological sites (Gratuze et al., 1992; Soulier et al., 1996) and of ceramics form France, Italy, Spain, Maghreb, Uzbekistan, Syria and Egypt (Gratuze et al., 1996) has identified three major groups of cobalt pigments and gave hints on the origin and processing of cobalt ore:

- The first group is characterized by the presence of Co, Zn, Pb and In (min 19 - max 587 ppm), with high concentration of zinc and lead. It includes objects dated from the beginning of 13th to the end of the 15th century. The village of Freiberg in the Erzgebirge, where cobalt minerals are associated with zinc blend and galena, has been suggested by the authors (Gratuze et al., 1992) as the possible source.
- The second group shows only the association of Co and Ni (Co/Ni ~ 4) with very low As content (min 58 - max 687 ppm) and includes objects dated from around the end of the 15th and the beginning of 16th century. The authors suggest that it might be the result of a higher temperature roasting of cobalt arsenates or sulpho-arsenates.
- The third group is characterized by the presence of Co and Ni (Co/Ni ~ 4), a high concentration of As (~20 times those of group 2) and Bi, and includes objects dated from the beginning of 16th century onward. This kind of pigment is associated with the *saffre* discussed below, probably from Schneeberg.

The analysis of ceramics (Gratuze et al., 1996, 2018; Pérez-Arantegui et al., 2008; Porter, 1997; Roldán et al., 2006) confirms so far these three groups. The analysis, by Particle Induced X-ray Emission (PIXE), of the blue glazes in objects of the della Robbia production, accurately dated from 1445 to 1550 (Zucchiatti et al., 2006a), allowed to add precision to the time scale. In the Della Robbia production the compositional change between the second and the third group takes place, sharply, between the years 1515 and 1521 (Pappalardo et al., 2004).

The differences in composition have given rise to several hypotheses about the origin of the cobalt ores and their processing, not all of which could be firmly confirmed. The presence of

arsenic from 1520 until the end of the 17th century suggests the use of the *saffre* produced as described by Kunckel in his *"Ars vitraria experimentalis"* published in 1679 (Kunckel, 1679). Kunckel details the *saffre* fabrication process with *"a metallic stone called cobalt"* which is very poisonous. It has to be roasted in a reverberatory oven, procuring that it emits light and a white smoke (arsenic), collected along a wooden horizontal chimney. The calcined material is milled into a fine powder. Part of the powder is mixed with quartz, moist and pressed inside a barrel to form a compound as hard as a stone. This material, that the miners and other authors call *Zaffera* (the *saffre*), is sent to Holland for the production of plates. Melzer (Melzer, 1684) refers to a specific person, *Peter Weidenhammer* from Schneeberg, as a producer of *Zaffera* and to a year, 1520, in which he had donated a window to the village great church. *Smalt,* invented around 1540–60, is a potassium glass obtained by melting the roasted cobalt ore together with quartz (sand) and potash or added to molten glass (Mühlethaler and Thissen, 1969, Bajnóczi, et al 2014).

The peculiar Co-Ni group, identified by Soulier and coworkers (Soulier et al., 1996), that included objects dated before 1520, i.e. before the *saffre* was introduced, was attributed to roasting of a cobalt ore (like erythrite) at a higher temperature than those obtained in a reverberatory kiln. However, it is not clear if this could explain the drop in arsenic below PIXE detection limits and to the average 93 ppm given by ICP-MS. Looking at an arsenic free cobalt pigment, we cannot exclude, a priori, the possibility that such a material was obtained as a by-product of the silver smelting. In his treatise "*De re Metallica*" (Agricola, Hoover & Hoover, 2011), Georgius Agricola describes meticulously the silver production, from mining to purification of the metal but never mentions explicitly cobalt as a by-product. However, we know that the Erzgebirge silver comes in association with Co, Ni, Fe, As, Bi (Andrews, 1962, Kissin 1992). The exploitation of the Erzgebirge silver mines is documented since 1168 (Freiberg) and has been the major economic activity of the area until the 16th century. Cobalt ores may therefore be present in the smelting. We also know that cobalt has the tendency *"…to remain in the silicate melt until the closing stages of the magmatic differentiation… and this same tendency is manifest in the metallurgical operations when the cobalt is more likely to go into the slag*" (Andrews, 1962). The question is whether the metallurgic operations described by Agricola, would produce a separation of Co and As. For the sake of reproducing in laboratory tests the process he describes, it is worth considering some key sentences of Agricola's text translation (Agricola, Hoover & Hoover, 2011).

"… he [the master smelter] *first throws into the furnace as many cakes melted from pyrites* [the metallurgical matte] *as he requires to smelt the ore; then he puts in two wicker baskets full of ore with litharge and hearth-lead, and stones which fuse easily by fire of the second order, all mixed together; then one wicker basket full of charcoal, and lastly the slags. The furnace now being filled with all the things I have mentioned, the ore is slowly smelted". "… when the lead which the assistant has placed in the forehearth is melted, the master opens the tap-hole of the furnace with a tapping-bar…The slag first flows from the furnace into the forehearth, and in it are stones mixed with metal or with the metal adhering to them partly altered, the slag also containing earth and solidified juices. After this, the material from the melted pyrites flows out, and then the molten lead contained in the forehearth absorbs the gold and silver. When that which has run out has stood for some time in the forehearth, in order to be able to separate one from the other, the master first either skims off the slags with the hooked bar or else lifts them off with an iron fork; the slags, as they are very light, float on the top. He next draws off the cakes of melted pyrites, which as they are of medium weight hold the middle place; he leaves in the forehearth the alloy of gold or silver with the lead, for these being the heaviest, sink to the bottom. As, however, there is a difference in slags, the uppermost containing little metal, the middle more, and the lowest much, he puts these away separately, …".*

Being the cooling of the melt relatively fast in air and driven by sedimentation, we expect the heavy elements, like Bi, to go into the ingot with lead and silver, which would justify the appearance of Bi in the della Robbia glazes only in coincidence with the appearance of As, i.e. when the cobalt mineral is roasted as a whole and not melted and sedimented.

In this study we have thermally processed a cobalt arsenide ore, in order to replicate as close as possible the historical account of roasting (Kunckel, 1679) and we have as well thermally processed mixtures of cobalt arsenide ore and other compounds to reproduce the smelting process described by Agricola (Agricola, 1530)**.** The purpose is to determine the nature of the products obtained from these processing and use the results to assess or deny the various hypotheses found in the literature about the effect that those processes had in the composition of the cobalt pigment, in particular those regarding the partial or complete loss of arsenic.

2- EXPERIMENTAL METHODOLOGY

A cobalt arsenide ore, originating from Ouarzazate mines (Ahmed 2009a) in Morocco (courtesy of the University Moulay Ismail of Meknes), was ground in agate mortar with granulometry below 80 microns: the biggest quartz and calcite grains were removed at an intermediate grinding stage. The mineral composition of the cobalt arsenide ore was determined by X-Ray Diffraction (XRD). The ore is an inhomogeneous aggregate of skutterudite ($CoAs_3$) and a little clinosafflorite ($CoAs_2$) with calcite ($CaCO_3$), quartz (SiO_2) and clinochlore ($(Mg_5Al)(Si,Al)_4)O_{10}(OH)_8$) as gangue minerals. Neither erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$) nor cobaltite (CoAsS) were detected (Table I). The average chemical composition of the cobalt ore was determined by PIXE (Particle Induced X-ray Emission) (Johansson et al., 1995), scanning a few millimetric portions of the grey and visually homogeneous ore areas and averaging the results. The PIXE analysis was performed with a 3 MeV, 30 µm diameter, scanning external proton micro-beam at the AGLAE accelerator of the C2RMF (Calligaro et al., 2000). We collected X-rays with a two detector apparatus described in detail elsewhere (Zucchiatti et al., 2000). The average composition obtained for the mineral is: 63.4 wt% As, 14.3 wt% Co, 3 wt% Ni, 1.6 wt%Fe, 2.4 wt%S, 7.3 wt% Si, 5.3 wt% Ca, 1 wt % Na and 0.5 wt% Al. Magnesium could not be detected since its K line at 1.254 keV cannot be separated by the dominant L line of arsenic at 1.282 keV but SEM-EDS confirmed its presence in the clinochlore particles (**Figure S1**). Based on the elemental composition obtained by PIXE and assuming that all the Co, Ni, As and S and part of the Fe belong to the cobalt arsenide, all the Ca to calcite ($CaCO_3$), all the Al and part of the Fe and Si to clinochlore, taking the composition measured by SEM-EDS (Scanning Electron Microscope-Energy Dispersive Spectroscopy) for the clinochlore, $Mg_3Fe_2Al(Si_3Al)O_{10}(OH)_8$, and the remaining Si to quartz, the mineral composition has been calculated to be about 71% cobalt arsenide, 12% calcite and 12% SiO_2 and 5% clinochlore.

The cobalt ore was roasted alone to replicate the *saffre* production and mixed with other minerals (Table I) to mimic the mixtures that were introduced in the kiln during the silver smelting process as described by Agricola. The materials added were lead oxide (PbO) and minium (Pb_3O_4) (Sigma Aldrich ref. 203610 and ref. 241547, respectively) used as a flux, quartz (SiO_2) (Sigma Aldrich ref. 204358), calcite ($CaCO_3$, Sigma Aldrich ref. 239216), kaolinite ($Al_2Si_2O_5(OH)_4$) (Supelco ref. 1044402500), possibly present in the kiln walls for the silver smelting process. Furthermore,

fluorite (CaF_2) (Sigma-Aldrich ref. 449717) was added since Hoover (Agricola, Hoover & Hoover, 2011) proposed it – with admitted difficulty and uncertainty – as the *stones which fuse easily by fire of the second order*. The mineral content of each mixture is given in Table S1 and the As, Co, Ni, Fe and S composition of each mixture is given in Table S2.

To mimik the roasting and smelting two different procedures have been followed. In a first step a *static process* (SP) was adopted. We roasted/melted about 200 mg of cobalt ore or 1-2 g of the mixtures of Table I, inside alumina vessels, placed into a quartz tube, by means of an electronically controlled oven in a forced air flux. The temperature raised at a rate of 5°C/minute and was maintained at the set maximum value for a period of not less than 8 hours. The maximum temperatures were 460, 650, 850 and 1000 °C. Then the oven cooled down for 10 to 12 hours before the samples were extracted and analyzed by PIXE and SEM-EDS at the Centre de Recherche et Restauration des Musées de France (C2RMF).

Given the results of the SP investigation, we planned a *dynamic process* (DP) for further study by SR-XRD (Synchrotron Radiation powder X-Ray Diffraction). The SR-XRD, time/temperature resolved, was performed at the ALBA synchrotron, in Cerdanyola del Vallès (Barcelona). Mixtures were ground in agate mortar with granulometry below 80 microns and 50 mg were inserted into 500 µm diameter quartz capillaries and heated with an air blower, while performing powder X-ray diffraction. The experiment was carried on at the high-resolution station of the BL04-MSPD (Materials Science and Powder Diffraction) Beamline (Fauth et al., 2013)**.** The diffracted X-rays were collected by the Mythen detector, composed of 6 modules (Dectris/PSI Detectors group) with a strip-pitch of 50 µm and placed at 550 mm of the sample, covering an angular range of 40˚ (2ϑ) with 2ϑ step of $0.6\cdot10^{-2}$˚. Sequential data collection was performed during the heating stage. During the cooling down of the samples, datasets were acquired as fast as compatible with a reasonable level of statistics, in such a way that structural changes during the cooling down could also be explored. In this case, the temperature intervals corresponding to each dataset are very large initially and become progressively smaller as the cooling rate moderates. The energy used for the measurements was 30 keV (wavelength λ=0.4129 Å, determined from a NIST640d silicon standard) which is convenient for the absorption of the samples, including those containing a high percentage of strong absorbing elements such as Pb. The flux on sample was about $4\cdot10^{12}$ photons/s and the beam size 2 x 0.8 mm^2 (WxH). The end station is equipped with a

holder that spins the capillary slightly tilted (5 degrees in our case) with respect to the horizontal plane to avoid powder loss while allowing gas escape from the open end. A FMB Oxford hot air blower controls the temperature growth rate from room temperature (RT) to 90°C at 20°C/min, 90°C to 110°C at 5°C/min, 110°C to 400°C at 20°C/min and 400°C to 900°C at 10°C/min) and data collection time is kept constant (40 seconds/pattern). After reaching a top of 900 °C, the blower returns directly at RT, which is enough to produce a relatively fast cooling of the sample, mimicking the cooling down of the melt once the kiln tap-hole was open and the melt flowed in the fore-heart (Agricola, 1556).

Additional SR-μXRD measurements have been performed after heating at RT along the capillaries, from the area heated by the blower to the edge and which correspond to progressively lower temperatures. The aim of these measurements was to help with the identification of the phases. These measurements were performed at the microdiffraction endstation of the same beamline using a 15x15µm^2 beam (FWHM) at 29.2keV (0.4246 Å wavelength) and a 2D CCD Rayonix SX165 detector. Moreover, a 17th century Catalan blue decorated glaze which contains calcium lead arsenate crystals, similar to those found in the roasted mixtures, were also analysed by SR-μXRD (for more detail on sample preparation see Pradell et al. 2013). Crystals of this sample were also analysed by microprobe (WDS) at Universitat de Barcelona. The experimental conditions for WDS analysis were 15 kV and 15 nA and an electron beam size of 2 mm.

3. THE SAFFRE PRODUCTION PROCESS: LABORATORY TESTS

After roasting the cobalt arsenide ore alone, in the SP process, a white uniform surface layer covered the ore and the quartz tube into which the alumina vessel was placed. The grey ore was transformed into a black compound that was easily broken and showed a complex granular structure (**Figure S2**). The ore in its natural state, the calcined samples and the white patina were analysed by PIXE. The white patina was almost pure arsenic. Despite the As loss, the weight ratio As/Co of the roasted compounds dropped above 460 °C, but it never went below 1, not even at the highest roasting temperature of 1000 °C, as shown in **Figure 1**.

The *DP* of the cobalt ore alone (sample m1 of Table I) was run up to 900 °C. The diffractograms taken during the experiment are shown in **Figure 2**. The diffractogram at the top corresponds to

the raw cobalt ore, the green diffractogram is the one taken at 573 °C (quartz alpha to quartz beta transition) during heating, the red diffractogram is the one taken at the maximum temperature (900 °C) and the diffractogram at the bottom corresponds to the material obtained after firing measured at RT. Following the roasting we could state that skutterudite began to decompose in *DP* at 550ºC, completely disappearing at 851ºC (we should notice that the temperatures indicated are those at which the diffractogram patterns were taken). The presence of clinosafflorite, residual before firing, increases between 717oC and 900oC following the decomposition of skutterudite. Langisite, (Co,Ni)As, is also formed between 809ºC and 900ºC. Cobalt arsenate $Co_3(AsO_4)_2$ is formed during heating at about 575ºC and disappears at 790ºC. The arsenic volatilised diffuses along the capillary and precipitates in the cooler regions as As_2O_3 and also as metallic As (**Figure 3**).

With regard to the other minerals present in the ore, clinochlore decomposes at 650ºC and calcite decomposes quickly between 850ºC and 900ºC and quartz is still detected at the end of the firing. The large peak shifts due to the thermal expansion of the compounds at high temperature makes it difficult to detect CaO. Nevertheless, calcium arsenate $Ca_3(AsO_4)_2$ and possibly a very low presence of calcium cobalt pyroxene, $CaCoSi_2O_6$, are formed at about 775ºC persisting up to 900ºC and after cooling (**Figure 4a**).

In summary, Arsenic is not completely lost and remains in the roasted material after firing. $CoAs_3$ is progressively transformed into an arsenic poorer compound during firing: from $CoAs_3$ to $CoAs_2$ and finally to CoAs in agreement with some studies about decomposition/oxidation of skutterudite (Ertseva & Tsymbulov, 2002; Mikhail et al., 1989; Wilson & Mikhail, 1989). Cobalt arsenate (phase A in **Figure 2**) is formed during heating as soon as skutterudite begins to decompose and is completely decomposed before 800 °C. Some of the cobalt reacts with the gangue and a small amount of a calcium cobalt silicate ($CaCoSi_2O_6$) is formed. Calcium arsenate is formed when calcite decomposes and the CaO reacts with the arsenic oxide (**Figure 2**).

The above results are in good agreement with Mikhail (Mikhail et al., 1989) study on skutterudite roasting which concluded that a complete removal of arsenic is not readily achievable under either oxidizing or inert conditions. Consequently, the presence of arsenic in the cobalt blue

glasses and glazes from the 16th century onwards is consistent with the use of *saffre* obtained by the process described by Kunckel (Kunckel, 1679).

4-COBALT AS A BY-PRODUCT OF SILVER SMELTING: LABORATORY TESTS

The phases determined for the different mixtures of Table I at the *DP* maximum temperature (900ºC) are reported in Table II. The transformations observed during the firing are detailed for each of the mixtures.

4.1 Cobalt arsenide ore, lead oxide, fluorite mixtures

Lead oxide and fluorite are, according to Agricola after interpretation of Hoover (Georg Agricola, Agricola, Hoover & Hoover, 2011), the most important additions to the silver minerals in the smelting. They are the *fluxes of first and second order* respectively. In the smelting, the cobalt arsenides must have been a minor component of the smelt. For this reason, the mixture with the lowest cobalt ore content (m9) is reported with greater detail.

The diffractograms taken during the experiment are shown in **Figure 5**. PbO is in the form of massicot and litharge which are completely decomposed at 785°C and 827°C respectively. Skutterudite is decomposed at about 584°C and the arsenic released reacts with lead and fluorine producing $Pb_5(AsO_4)_3F$ between 535 °C and 835 °C , (letter B in **Figure 5**), $Pb_8As_2O_{13}$ between 560 °C and 835 °C (letter C in **Figure 5**) and Pb_2OF_2 between 567 °C and 785 °C (letter D in **Figure 5**). Calcium lead arsenate with the structure of hedyphane but with fluorine instead of chlorine, $(Ca,Pb)_5(AsO_4)_3F$, is identified between 820 °C and 900°C. We have to mention that cobalt arsenates are not formed. Galena, PbS, (letter E in **Figure 5**) is formed by the reaction of lead with the sulphur released from cobalt ore between 535 °C and 852 °C. At the end of the firing only calcium lead arsenate $(Ca,Pb)_5(AsO_4)_3F$ and fluorite are found (**Figure 4b**). The most representative diffractograms taken along the capillary at RT after firing are also shown in **Figure 6** Elongated crystals of calcium lead arsenate are seen over fluorite cubes by SEM (**Figure 7a**). The data indicates that lead reacts with fluorite and favours the decomposition of skutterudite promoting the formation of calcium lead and lead arsenates with fluorine and lead oxide with fluorine.

Finally, quartz reacts with PbO forming a glassy phase as is observed in the SEM image, **Figure 7b,** and is also evident as a rising background in the diffraction patterns above 840°C **(Figure 5**). The blue particles with various shades seen in the capillaries correspond to a vitreous phase (**Figure S3**). Co is determined in the blue vitreous particles confirming the results of Wood and Hsu (2019).

If a larger amount of cobalt ore is added to the mixture (m2), langisite and clinosafflorite are formed at intermediate temperatures (langisite appears in larger amounts than in m1) remaining in the final fired product. Consequently, cobalt arsenides are still present when lower amounts of lead oxide and fluorite are added. The colour of this mixture is dark blue (**Figure S3**).

The presence of arsenate acicular crystals is often found in blue ceramic glazes after 1520 aD (among other: Hancock et al, 2000; Capelli, et al., 2002; Viti et al., 2003; Zucchiatti et al., 2006b; Tite 2009; Pradell et al., 2013; Van Pevenage et al., 2014; Colomban et al., 2017, 2018, 2020; de Viguerie et al., 2019). In particular the presence of lead rich KNaPb arsenates ($NaKPb_8(AsO_4)_6$) with apatite structure have been determined by SR-XRD (Pradell et al., 2013). Van Pevenage et al. (2014) found a lead arsenate similar to mimetite ($Pb_5(AsO4)_3Cl$) in the pigments of the ruan-cai blue colour Chinese porcelain dating from the 18th century. Colomban et al. (2018) detected lead arsenates by Raman of blue-decorated early soft-paste porcelain after 1750 and lead arsenate apatite phase of the type $Na_{1-x-y}K_xCaPb_4(AsO_4)_3$ in 17th–18th century enamelled French watches. Although the presence of acicular arsenate crystals is often described, the phases have been rarely unambiguously identified.

In this study, crystalites of $(Ca,Pb)_5(AsO_4)_3F$ have been detected for the first time. We added fluorite, and the phase formed is equivalent to hedyphane ($Ca_2Pb_3(AsO_4)_3Cl$ but with F instead of Cl. Hedyphane has an apatite like structure and contains Cl but it may also contain OH (hydroxilhedyphane) and F (fluorhedyphane) (Pesaro, et al. 2010).

In fact similar calcium lead arsenate crystallites were also found in Catalan Blue wares with the following composition ($Ca_{2.74}Pb_{2.26}P_{0.39}As_{2.61}O_{12}Cl_{0.19}$) determined by microprobe (**Figure 8a and 8b**). The Rietveld refinement of this structure with Fullprof software (Rodríguez-Carvajal, 1993)

using as starting model the described structure for hedyphane (Rouse et al., 1984) shows an excellent match (**Figure 8c**) with cell parameters a=b=9.9320(3) Å and c=7.1001(2) Å, V=606.56(3) $Å^3$. This verifies the formation of this type of calcium lead arsenates also in historical glazes.

Although the amount of arsenic present in the glazes is normally very low, the precipitation of lead arsenates and in particular the arsenates with hedyphane structure is expected to happen and their presence is a marker of the use of cobalt arsenide ore.

When the mixture m9 is fired at 1200°C in *SP* mode (definitely out of reach for 15^{th} and 16^{th} century smelters and also for SR-XRD air blower used) only calcium arsenate crystals are found (hexagonal prismatic and acicular) (**Figure 7c**) together with aggregates of tiny crystals rich in cobalt, iron and nickel (**Figure 7d**). Flat, approximately rectangular, calcium aluminosilicate crystallites (anorthite type) resulting from the reaction with the alumina crucible were also formed at this high temperature.

4.2 Cobalt arsenide ore, lead oxide, fluorite, quartz Mixtures

From the *DP* analysis of mixture m4 we observe that the addition of quartz favours the development of the liquid phase producing a more vitrified product (lead silicate vitreous phase). After firing at 900°C only very little langisite, (Co,Ni)As, lead fluoride arsenate $Pb_5(AsO_4)_3F$ and fluorhedyphane $(Ca,Pb)_5(AsO_4)_3F$ are present, along with quartz, cristobalite and fluorite. With a lower amount of the cobalt ore (m11) the material obtained is even more vitrified and the cobalt arsenides are residual (**Figure 4b and Figure 9**). The vitreous phase appears blue in the capillaries (**Figure S3**) which are related to the vitreous phase which incorporates the cobalt (**Figure S4**).

4.*3 Cobalt arsenide ore, lead oxide, calcite, kaolinite*

Fluorite was added in the previous mixtures as a flux in silver smelting because it was mentioned in the Agricola text as *stones which fuse easily by fire of the second order*. But, fluor is not normally determined in the analyses of glazes and glass. For this reason, calcite has been added instead of fluorite. A mixture incorporating calcite and Pb_3O_4 instead of PbO (m16, Table I) have been produced to explore the effect that different sources of Pb and Ca had in the final product. Moreover, some kaolinite, which was present in the kiln walls, was also added to check its effect in the final slag obtained.

The SR-XRD patterns (**Figure 10** and **Figure 4c**) show that Pb_3O_4 and kaolinite disappear at 591°C and 676°C respectively, while skutterudite and calcite decompose completely at 692°C and 900°C. Kaolinite ($Al_2Si_2O_5(OH)_4$) promotes the formation of lead feldspars ($PbAl_2Si_2O_8$). Both the stable monoclinic and the metastable hexagonal lead feldspar are formed during the firing at about 700°C, and the monoclinic phase increases from 845°C to 900°C. Finally, calcium lead arsenates with hedyphane structure but incorporating OH, $(Ca,Pb)_5(AsO_4)_3OH$ (Hydroxylhedyphane) are formed at about 700°C increasing at 845°C. A glassy phase is also formed (**Figure S4b**) but in lower amounts than in the mixtures m4 and m11. The SEM observation indicates that the cobalt is concentrated in the glassy particles, as in the previous cases.

5- DISCUSSION

Our laboratory tests have proved that roasting a rich cobalt arsenide ore at high temperature or even for a long time is unable to remove completely the arsenic from the ore. The typical composition of historical blue glazes after 1520 is perfectly compatible with the material obtained roasting of minerals from the cobalt arsenides deposits of the Erzgebirge area (Weber, 1986), to produce *saffre*, as described by Kunckel (Kunckel, 1679).

Our replication of the processes described by Agricola gave rise to the formation of a lead rich silica glassy phase which incorporates cobalt in variable amounts together with calcium and lead arsenates of various compositions. We have also found that the amount and composition of the glassy phase depends on the amount of quartz and lead oxide and fluorite added. Adding a larger amount of quartz and fluxes a most extensive glassy phase is obtained and less crystalline compounds (calcium lead arsenates) are produced. As the physical separation of the different phases does not appear possible, the question is then reduced to the possible commercialization and use of the material obtained by this process in the production of cobalt blue glazes. Considering that the glassy phase would integrate into the glaze, part of the arsenic still present would be removed in the glaze firing and the remaining arsenic would either dissolve or recrystallise into calcium lead arsenate, the use of the subproduct obtained to tinge lead glazes could not be discarded. This could account for the variable content of arsenic shown by the historical glazes. However, as fluor has not been reported in the historical glazes, either fluorite

was added in low amounts or another flux was added instead. We should mention that the presence of fluorite has been reported in the white but also blue Chinese cloissonné enamels (Colomban et al., 2020). The use of fluorite is not clear in Agricola's description of the process and other fluxes could have been added instead. In fact, the processing described by Agricola and replicated in this study produces, among other compounds, a cobalt blue glassy product not very different from *smalt*, as *smalt* is also a cobalt blue glass obtained adding quartz and a flux, in this case potash.

The study has also provided direct evidence of the crystallisation of an hedyphane type of calcium lead arsenates, incorporating Cl, F or OH. A phase which has been found in historical glazes, but never properly identified until now.

Our results indicate that an arsenic free cobalt compound could not have been produced by a higher temperature treatment of skutterudite or during the smelting of silver as described by Agricola (Agricola, Hoover & Hoover, 2011). Therefore, other sources of cobalt must be considered to explain the appearance, between the beginning of the 15th century and the third decade of the 16th century of the CoNi with trace amounts of As pigment used to colour blue glasses and glazes.

Since the coeval literature describes blue pigments as coming from *la Magna* (Cennini, 1400) the minerals of the Erzgebirge must again be considered. Agricola (Agricola, 1530) gives account of the existence of different cobalt minerals but with the same *properties*, saying, in particular, that all were corrosive because of their As content. Andrews (Andrews, 1962) reports that "*the principal deposits of the Erzgebirge, consisting of smaltite, erythrite, linnaeite and asbolane in association with barites, silver and bismuth, occur in contact-metamorphosed slates underlain by granites…*".

An As free Co from *la Magna* could have come from the processing of linnaeite ($Co^{2+}Co^{3+}{}_2S_4$) or asbolane ($(Co,Ni)_{1-y}(Mn^{4+}O_2)_{2-x}(OH)_{2-2y+2x}\cdot n(H_2O)$ a mixture of hydrated Co and Mn oxides). The PIXE analysis of blue glazes of the *della Robbia* production, whenever As is below PIXE detection limits, do not show sufficient Mn content to support the origin of the *saffre* from asbolane that contains more Mn (65-96%) than Co (35-4%) (Andrews R.W, 1962). In the group of *della Robbia* sculptures dated before 1520, we found a MnO/CoO ratio always below 0.20 except when

417 manganese was deliberately added to make the blue turn violet or when a black coloured glaze
418 diffused into the blue glaze during firing.
419
420 As concerns linnaeite, there are significant coincidences between what is reported above for
421 the *della Robbia* glazes (Zucchiatti et al., 2006a) and for the 9th century Islamic Samarra faiences
422 (Kleinman, 1990). Kleinmann's morphological analysis reveals the presence of pigment remnants
423 in three phases aggregates: a granulated nucleus, surrounded by silicate crystals in a vitreous
424 matrix. The granulated nuclei were identified as Co-Fe-Ni spinels with an extremely variable
425 composition (Co 13.90-47.69%; Fe 9.51-82.13%; Ni 1.01-59.15%). The same kind of structure will
426 reappear (Kleinmann, 1986; Kleinmann, 1987) in medieval Persian faiences. Linnaeite would fit,
427 according to Kleinmann, with the description (Allan, 1973) of a stone "… *like white silver shining*
428 *in a sheath of hard black stone".* Will fit also with the morphology observed in the *della Robbia*
429 blue glazes prior to 1520 and, finally, with the quite variable relation between the characterizing
430 elements Co-Fe-Ni, detected by PIXE in the As free glazes. Roasted linnaeite would fit much better
431 than arsenates or sulpho-arsenates as the origin of the specific Co-Ni group. It might be that the
432 *della Robbia* used, before the advent of the *saffre*, the same pigment that was utilized in the blue
433 and white Chinese porcelain of the early Ming period (1368-1424). This was characterized by a
434 very high Fe/Mn ratio (Wen et al., 2007) that we find as well in the analyses of the *della Robbia*
435 glazes (Fe_2O_3/MnO >15). The pigment is very similar to the one found in Middle Eastern ceramics
436 from the 9th century onwards and could correspond to the so-called *Sumali* blue probably
437 exported, from Iran, both to the Far East and Europe.

438 **7-CONCLUSIONS**

439
440 We performed laboratory tests to investigate the production of cobalt materials in blue glazed
441 ceramics from the Renaissance. The previous analyses of ancient glass and glaze put in evidence
442 a change of the cobalt material at the edge between the 15th and 16th century. The replication of
443 the roasting process of a natural cobalt arsenide ore has shown that a complete removal of arsenic
444 is not obtained, which explains the presence of arsenic in the cobalt blue glasses and glazes from
445 the 16th century onwards. Our results fit very closely with the description of the process done in
446 historical texts and with the beginning of trade of a new commercial material, called *saffre,* from
447 the rich cobalt arsenides deposits of the Erzgebirge area.
448

Assuming that cobalt could have been a slag of the massive silver smelting in the Erzgebirge area and following the description that Agricola gives of the silver mining and smelting, we have produced various mineral mixtures and followed their transformation, mimicking the smelting process. Our replication of the processes described by Agricola gave rise to the formation of a lead rich glassy phase which incorporates cobalt in variable amounts together with lead arsenates ($Pb_5(AsO_4)_3F$, $Pb_8As_2O_{13}$) and calcium lead arsenates $(Ca,Pb)_5(AsO_4)_3(F,Cl,OH)$ with an hedyphane structure, while cobalt is incorporated into a glassy matrix. When kaolinite is added, lead feldspars are also formed. Therefore, the separation of the cobalt from arsenic is accomplished. However, as the physical separation of the cobalt glassy phase from the other crystalline compounds does not appear possible, the question is then reduced to the possible commercialization and use of the material obtained by this process in the production of cobalt blue glazes. Although the use of this slag as a cobalt pigment to tinge lead glazes cannot be discarded, the material obtained is not arsenic free and therefore, it can hardly account for the arsenic free material like the one used by the *della Robbia* and other before 1515-1520.

In addition, it is not straightforward to justify a consistent production of cobalt materials with the much lower abundance of linnaeite in the Erzgebirge (Seifert & Sandmann, 2006). It is worth observing that the revision of available data puts in evidence some compositional similarity between the *della Robbia* sculptures, the Near East pottery and the Chinese blue and white porcelain. The similarity might be explained by the common use of arsenic free cobalt materials produced, for example, from linnaeite in the Qamsar mines in Iran and traded towards the Mediterranean basin and China before the massive introduction on the market of the German *saffre*. The processing of linnaeite definitely deserves specific studies, both dynamical and microscopic, as we did so far for the cobalt arsenide ore.

ACKNOWLEDGMENTS

One of us (A.Z.) is pleased to acknowledge the support of Istituto Nazionale di Fisica Nucleare of Italy and Universidad Autónoma de Madrid at the time he performed part of this work being a member of their respective staff. We are indebted to the Centre de Recherche et Restauration des Musées de France. Experiments were performed at BL04 MSPD Beamline at ALBA synchrotron Facility with the collaboration of Alba Staff (Ref. 2018092994, 2018022748, 2015091398) for financial support during part of this work. We are indebted to professors Badra and Haddad of

481 the Moulay Ismail University of Meknes (Morocco) for providing us with the cobalt ore. J.M. and
482 T.P. are grateful to the project PID2019-105823RB-I00 funded by the Ministerio de Ciencia e
483 Innovación (Spain) and TP is grateful to Generalitat de Catalunya grant 2017SGR-0042.

484

References

Agricola, G. (1530). *Bermannus Sive De Re Metallica Dialogus*. available at the Biblioteca Nazionale Braidense, Milano, Italy.

Agricola, Georg, Agricola, G., Hoover, H. & Hoover, L. H. (2011). Georgius Agricola De re metallica, tr. from the 1st Latin ed. of 1556, with biographical introduction, annotations and appendices upon the development of mining methods, metallurgical processes, geology, mineralogy & mining law, from t. In *Georgius Agricola De re metallica, tr. from the 1st Latin ed. of 1556, with biographical introduction, annotations and appendices upon the development of mining methods, metallurgical processes, geology, mineralogy & mining law, from the earliest times to the 16th century*. https://doi.org/10.5962/bhl.title.30118

Ahmed AH, Arai S, Ikenne M (2009a) Mineralogy and paragenesis of the Co-Ni arsenide ores of Bou Azzer, Anti-Atlas, Morocco. Econ Geol 104:249–266

Allan, J. W. (1973). Abū'l-Qāsim's Treatise on Ceramics. *Iran*. https://doi.org/10.2307/4300488

Andrews R.W. (1962). Cobalt. In *Overseas Geological Surveys. Minerals resources Division. Her Majesty's stationery office*.

Bajnóczi, B., Nagy, G., Tóth, M., Ringer, I. & Ridovics, A. (2014): Archaeometric characterization of 17th-century tin-glazed Anabaptist (Hutterite) faience artefacts from North-East-Hungary. *Journal of Archaeological Science,* 45, 1-14. https://doi.org/10.1016/j.jas.2014.01.030

Calligaro, T., Dran, J. C., Ioannidou, E., Moignard, B., Pichon, L., & Salomon, J. (2000). Development of an external beam nuclear microprobe on the aglae facility of the Louvre museum. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, *161*, 328–333. https://doi.org/10.1016/S0168-583X(99)00899-X

Capelli, C. & Riccardi, M. P. (2002): Il contributo delle analisi petrografiche allo studio dei rivestimenti di ceramiche in blu: alcuni esempi. Atti XXXV convegno internazionale della ceramica. Ceramica in blu, diffusione e utilizzazione del blu nella ceramica. Savona, 31 maggio – 1 giugno. Centro Ligure per la storia della ceramica, Albisola, 19-28.

Cennini, C. (1400). *Il libro dell'arte, o Trattato della pittura* (1859 a cura di Gaetano e Carlo Milanesi, Le Monnier, Firenze (ed.)).

Colomban, P., Arberet, L., & Kırmızı, B. (2017). On-site Raman analysis of 17th and 18th century Limoges enamels: Implications on the European cobalt sources and the technological relationship between Limoges and Chinese enamels. *Ceramics International*. https://doi.org/10.1016/j.ceramint.2017.05.040

Colomban, P., Maggetti, M., & d'Albis, A. (2018). Non-invasive Raman identification of crystalline and glassy phases in a 1781 Sèvres Royal Factory soft paste porcelain plate.

Journal of the European Ceramic Society. https://doi.org/10.1016/j.jeurceramsoc.2018.07.001

Colomban, P., Kırmızı, B., Gougeon, C., Gironda, M. & Cardinal, C. (2020). Pigments and glassy matrix of the 17th-18th century enamelled French watches: a non invasive on-site Raman and pXRF study. Journal of Cultural Heritage, 44[1-14]. https://doi.org/10.1016/j.culher.2020.02.001

de Viguerie, L., Robador, M. D., Castaing, J., Perez-Rodriguez, J. L., Walter, P., & Bouquillon, A. (2019). Technological evolution of ceramic glazes in the renaissance: In situ analysis of tiles in the Alcazar (Seville, Spain). *Journal of the American Ceramic Society*. https://doi.org/10.1111/jace.15955

Ertseva, L. N. & Tsymbulov, L. B. (2002). On transformations of iron, nickel, and cobalt arsenides and sulfoarsenides under thermal treatment in various media. In *Russian Journal of Applied Chemistry*. https://doi.org/10.1023/A:1022290609934

Fauth, F., Peral, I., Popescu, C., & Knapp, M. (2013). The new material science powder diffraction beamline at ALBA synchrotron. *Powder Diffraction*. https://doi.org/10.1017/S0885715613000900

Gratuze, B., Pactat, I., & Schibille, N. (2018). Changes in the signature of cobalt colorants in late antique and early Islamic glass production. *Minerals*. https://doi.org/10.3390/min8060225

Gratuze, B., Soulier, I., Barrandon, J. N., & Roy, D. (1992). De l'origine du cobalt dans les verres. *Revue d'Archéométrie*. https://doi.org/10.3406/arsci.1992.895

Gratuze, B., Soulier, I., Blet, M., & Vallauri, L. (1996). De l'origine du cobalt : du verre à la céramique. *Revue d'Archéométrie*. https://doi.org/10.3406/arsci.1996.939

Hancock., R.G.V., McKenzie, J., Aufretier, S.; Karklins, K., Kapches, M., Sempowski. M., Moreau, J.J., Kenyon, I. (2000). Non-destructive analysis of European cobalt blue trade beds. Radioanal. Nucl. Chemistry, 244 [3], 567-573.

Johansson, S. A. E., Campbell, J. L., Malmqvist, K., & Winefordner, J. (1995). Particle-Induced X-Ray Emission Spectrometry (PIXE) Edited by Sven A. E. Johansson (Sweden), John L. Campbell (Canada), and Klas G. Malmqvist (Sweden). Wiley & Sons: New York. 1995. xxiii + 451 pp. $79.95. ISBN 0-471-58944-6. In *Journal of the American Chemical Society*. https://doi.org/10.1021/ja955314e

Kleinman, B. (1990). Cobalt-pigments in the Early Islamic blue glazes and the reconstruction of the way of their manufacture. In *Archaeometry 90: Proceedings of the 27th International Symposium on Archaeometry*.

Kleinmann, B. (1986). History and development of early Islamic pottery glazes. In *Proceedings of the twenty-fourth International Archaeometry Symposium*.

559 Kleinmann, Barbara. (1987). Technological studies of Medieval and later Persian faience:
560 possible successors to the faience of antiquity. In *Early vitreous materials*.

561 Kunckel, J. (1679). *Ars vitraria experimentalis*, *Oder Vollkommene Glasmacher-Kunſt*
562 *Lehrende*, Franckfurt und Leipzig

563 Matin, M., & Pollard, M. (2015). Historical accounts of cobalt ore processing from the Kashan
564 Mine, Iran. In *Iran*. https://doi.org/10.1080/05786967.2015.11834755

565 Melzer, C. (1684). *Berglauftige Beschreibung der Stadt Schneeberg*.

566 Mikhail, S. A., Turcotte, A. M., & Bowman, W. S. (1989). A study of the decomposition of
567 higher cobalt arsenides by thermal analysis. *Thermochimica Acta*.
568 https://doi.org/10.1016/0040-6031(89)85442-5

569 Mühlethaler, B., Thissen, J. (1969). Smalt. Stud. Conserv., 14, 47-61

570 Pappalardo, G., Costa, E., Marchetta, C., Pappalardo, L., Romano, F. P., Zucchiatti, A., Prati, P.,
571 Mandò, P. A., Migliori, A., Palombo, L., & Vaccari, M. G. (2004). Non-destructive
572 characterization of Della Robbia sculptures at the Bargello museum in Florence by the
573 combined use of PIXE and XRF portable systems. *Journal of Cultural Heritage*.
574 https://doi.org/10.1016/j.culher.2003.08.002

575 Pérez-Arantegui, J., Resano, M., García-Ruiz, E., Vanhaecke, F., Roldán, C., Ferrero, J., & Coll,
576 J. (2008). Characterization of cobalt pigments found in traditional Valencian ceramics by
577 means of laser ablation-inductively coupled plasma mass spectrometry and portable X-
578 ray fluorescence spectrometry. *Talanta*, *74*(5), 1271–1280.
579 https://doi.org/10.1016/j.talanta.2007.08.044

580 Pesaro, M., Kampf, A.R., Ferrari, C., Pekov, I.V., Rakovans, J., White, T.J. (2010). Nomenclature
581 of the apatite supergroup minerals. Eur. J. Mineral., 22, 163–179

582 Porter, Y. (1997). Origines et diffusion du cobalt utilisé en céramique à l'époque médiévale.
583 Etude préliminaire. In *La céramique médiévale en Méditerranée. Actes du VIè congrés*
584 *international.* (pp. 505–512).

585 Pradell, T., Molina, G., Molera, J., Pla, J., & Labrador, A. (2013). The use of micro-XRD for the
586 study of glaze color decorations. *Applied Physics A: Materials Science and Processing*,
587 *111*(1), 121–127. https://doi.org/10.1007/s00339-012-7445-x

588 Prati P. and Massabò D. (2019). *private communication*.

589 Rodríguez-Carvajal, J. (1993). Recent advances in magnetic structure determination by
590 neutron powder diffraction. *Physica B: Physics of Condensed Matter*.
591 https://doi.org/10.1016/0921-4526(93)90108-I

592

Roldán, Clodoaldo, Coll, J., & Ferrero, J. (2006). EDXRF analysis of blue pigments used in Valencian ceramics from the 14th century to modern times. *Journal of Cultural Heritage*. https://doi.org/10.1016/j.culher.2006.02.003

Rouse, R. C., Dunn, P. J., & Peacor, D. R. (1984). Hedyphane from Franklin, New Jersey and Langban, Sweden: cation ordering in an arsenate apatite. *American Mineralogist*.

Seifert, T., & Sandmann, D. (2006). Mineralogy and geochemistry of indium-bearing polymetallic vein-type deposits: Implications for host minerals from the Freiberg district Eastern Erzgebirge, Germany. *Ore Geology Reviews*. https://doi.org/10.1016/j.oregeorev.2005.04.005

Soulier, I., Gratuze, B., & Barrandon, J.-N. (1996). The origin of cobalt blue pigments in French glass. In *Archaeometry 94: Proceedings of the 29th International Symposium on Archaeometry*.

Tite (2009) The production technology of Italian maiolica: a reassessment. Journal of Archaeological Science, 36, 2065-2080. https://doi.org/10.1016/j.jas.2009.07.006

Van Pevenage, J., Lauwers, D., Herremans, D., Verhaeven, E., Vekemans, B, De Clercq, W., Vincze, L., Moensa L. and Vandenabeele, P. (2014). A combined spectroscopic study on Chinese porcelain containing ruan-cai colours. Anal. Methods, 2014, 6, 387

Viti, C., Borgia, I., Brunetti, B., Sgamellotti, A., & Mellini, M. (2003). Microtexture and microchemistry of glaze and pigments in Italian Renaissance pottery from Gubbio and Deruta. *Journal of Cultural Heritage*. https://doi.org/10.1016/S1296-2074(03)00046-3

Weber W. (1986). Der Freiberger Bergbau. *Lapis Mineralien Magazin*, *11*, 13–27.

Wen, R., Wang, C. S., Mao, Z. W., Huang, Y. Y., & Pollard, A. M. (2007). The chemical composition of blue pigment on Chinese blue-and-white porcelain of the Yuan and Ming dynasties (AD 1271-1644). *Archaeometry*. https://doi.org/10.1111/j.1475-4754.2007.00290.x

Wilson, L. J., & Mikhail, S. A. (1989). Investigation of the oxidation by thermal analysis of skutterudite. *Thermochimica Acta*, *156*(1), 107–115.

Wood, J.R. and Hsu, Y.T. 2019 An Archaeometallurgical Explanation for the Disappearance of Egyptian and Near Eastern Cobalt-Blue Glass at the end of the Late Bronze Age, *Internet Archaeology 52.* https://doi.org/10.11141/ia.52.3

Zucchiatti, A., Bouquillon, A., Katona, I., & D'Alessandro, A. (2006a). The "della Robbia blue": A case study for the use of cobalt pigments in ceramics during the Italian Renaissance. *Archaeometry*. https://doi.org/10.1111/j.1475-4754.2006.00247.x

Zucchiatti, A., Bouquillon, A., Katona, I., & D'Alessandro, A. (2006b). The "della Robbia blue": A case study for the use of cobalt pigments in ceramics during the Italian Renaissance. *Archaeometry*, *48*(1), 131–152. https://doi.org/10.1111/j.1475-4754.2006.00247.x

Zucchiatti, A., Bouquillon, A., Moignard, B., Salomon, J., & Gaborit, J. R. (2000). Study of Italian Renaissance sculptures using an external beam nuclear microprobe. *Nuclear Instruments and Methods in Physics Research*, Section B: Beam Interactions with Materials and Atoms. https://doi.org/10.1016/S0168-583X(99)00905-2

FIGURE CAPTIONS

Figure 1 . The As and Co weight percent in the cobalt arsenide ore (mixture m1 in Table I) and at different roasting temperatures determined by PIXE. Quantitative analysis was performed on millimetric scanned areas. The percent errors are around 2% and do not exceed the marker size.

Figure 2. Diffractogram evolution of cobalt arsenide ore (mixture m1 in Table I) from room temperature (top pattern) to the maximum temperature of 900 °C (red pattern) and cooling to room temperature (bottom pattern). The green diffractogram corresponds to 573 °C (α-quartz to β-quartz transition).

Figure 3. SR-XRD patterns corresponding to the cobalt arsenide ore (mixture m1 in Table I). (a) before heating, (b) white zone of capillary (c) dark zone of capillary, (d) zone of maximum heating collected at RT after cooling.

Figure 4. Thermal stability ranges of phases of m1, m9 and m16.

Figure 5. Diffractogram evolution of mixture m9 (Table I) from room temperature (top pattern) to the maximum temperature of 900 °C (red pattern) and cooling to room temperature (bottom pattern). The mixture components at RT, are identified by the symbols in the legend. The phases formed during the thermal treatment are indicated by the letter B to E.

Figure 6. SR-XRD patterns corresponding to the mixture m9 (Table I). (a) before heating, (b) external zone of capillary (c) middle zone of capillary, (d) near maximum temperature of capillary (e) zone of maximum heating collected at RT after cooling.

Figure 7. SEM images of mixture m9 fired at 900°C (DP) (a) and (b) and 1200°C (c) and (d) (SP).
(a) Lead arsenate tiny crystals (2) grown over cubes of fluorite (1).
(b) Fluorite crystals (1) surrounded by lead rich vitreous phase (2).
(c) Calcium arsenate crystals (1) and calcium aluminosilicate crystallites (anorthite type) (2).
(d) Calcium arsenates crystals (1) and aggregates of tiny crystals rich in cobalt, iron and nickel (2)

667
668 **Figure 8**. Blue decorated Catalan glaze from 18th century (SBG17). (a) Thin section of glaze. The
669 blue decoration was applied overglaze. The Ca-Pb arsenates acicular crystals ($(Ca,Pb)_5(AsO_4)_3Cl$)
670 are formed in the contact between tin lead glaze and blue decoration layer. B) SEM BSE image of
671 Ca-Pb arsenates (white colour) and lead feldspars (grey colour). C) Rietveld refinement of the Ca-
672 Pb arsenate apatite-like structure.
673
674 **Figure 9.** Diffractogram evolution of mixture m11 (Table I) from room temperature (top pattern)
675 to the maximum temperature of 900 °C (red pattern). The green diffractogram corresponds to
676 573 °C (quartz alpha to quartz beta transition).
677
678 **Figure 10.** Diffractogram evolution of mixture m16 (Table I) from room temperature (top
679 pattern) to the maximum temperature of 900 °C (red pattern). The green diffractogram
680 corresponds to 573 °C (quartz alpha to quartz beta transition).
681

Figures

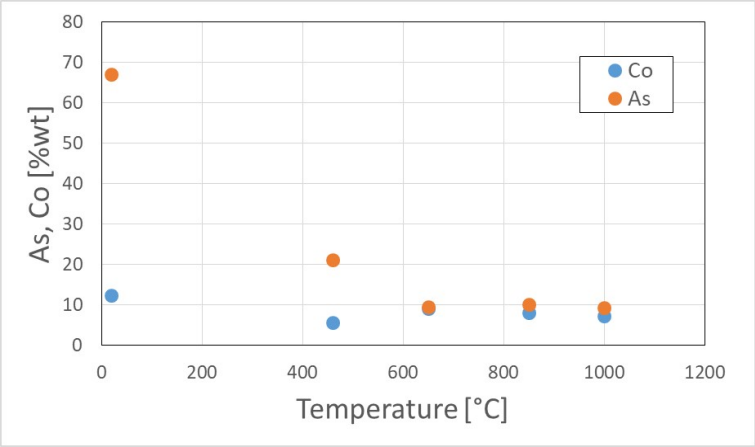


Fig.1. Co and As content (wt%) in the raw cobalt ore and at different roasting temperatures determined by PIXE.

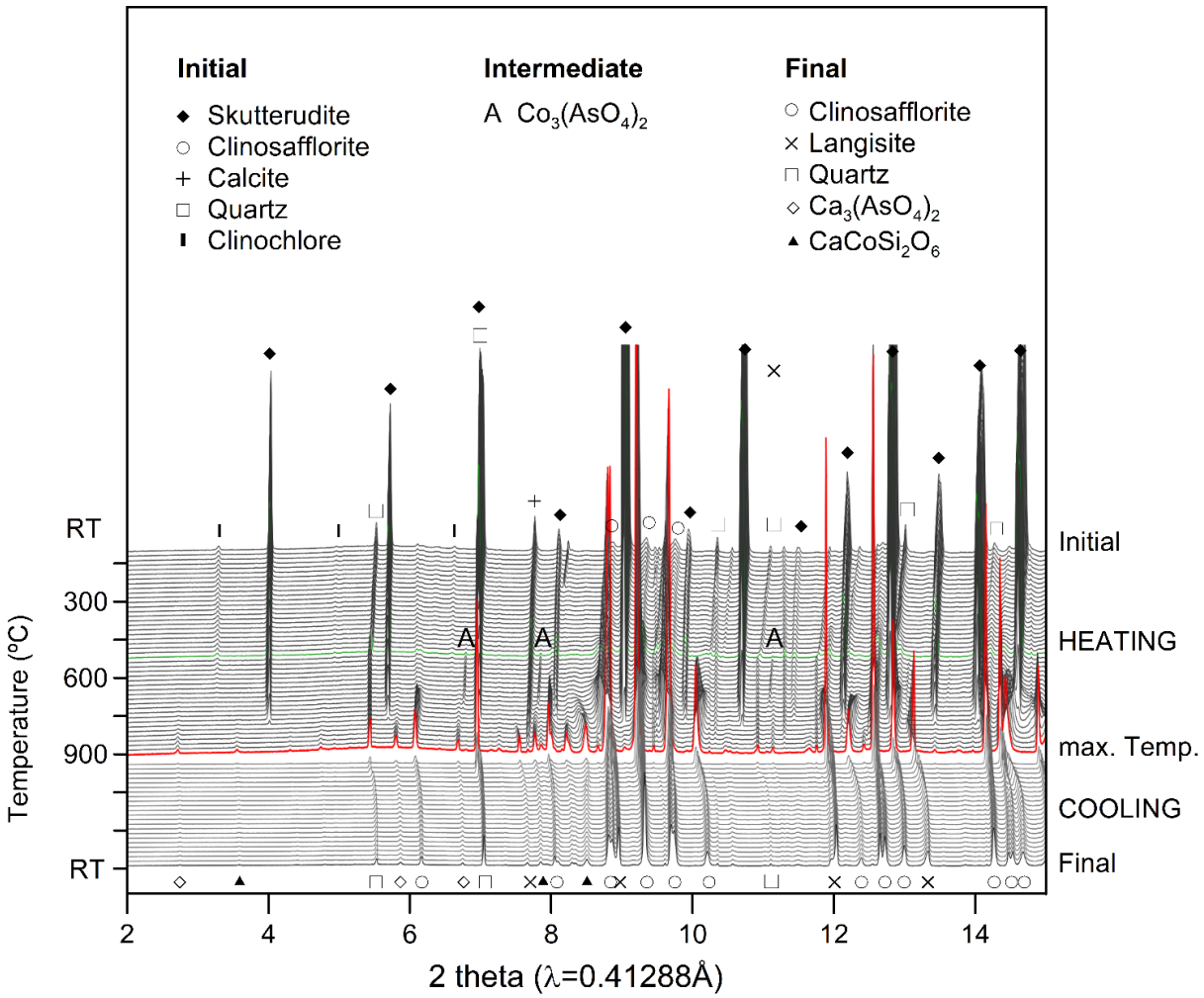


Figure 2. Diffractogram evolution of cobalt arsenide ore (mixture m1 in table I) from room temperature (top pattern) to the maximum temperature of 900 °C (red pattern) and cooling to room

695 temperature (bottom pattern). Green diffractogram corresponds to 573 °C (α-quartz to β-quartz
696 transition).
697

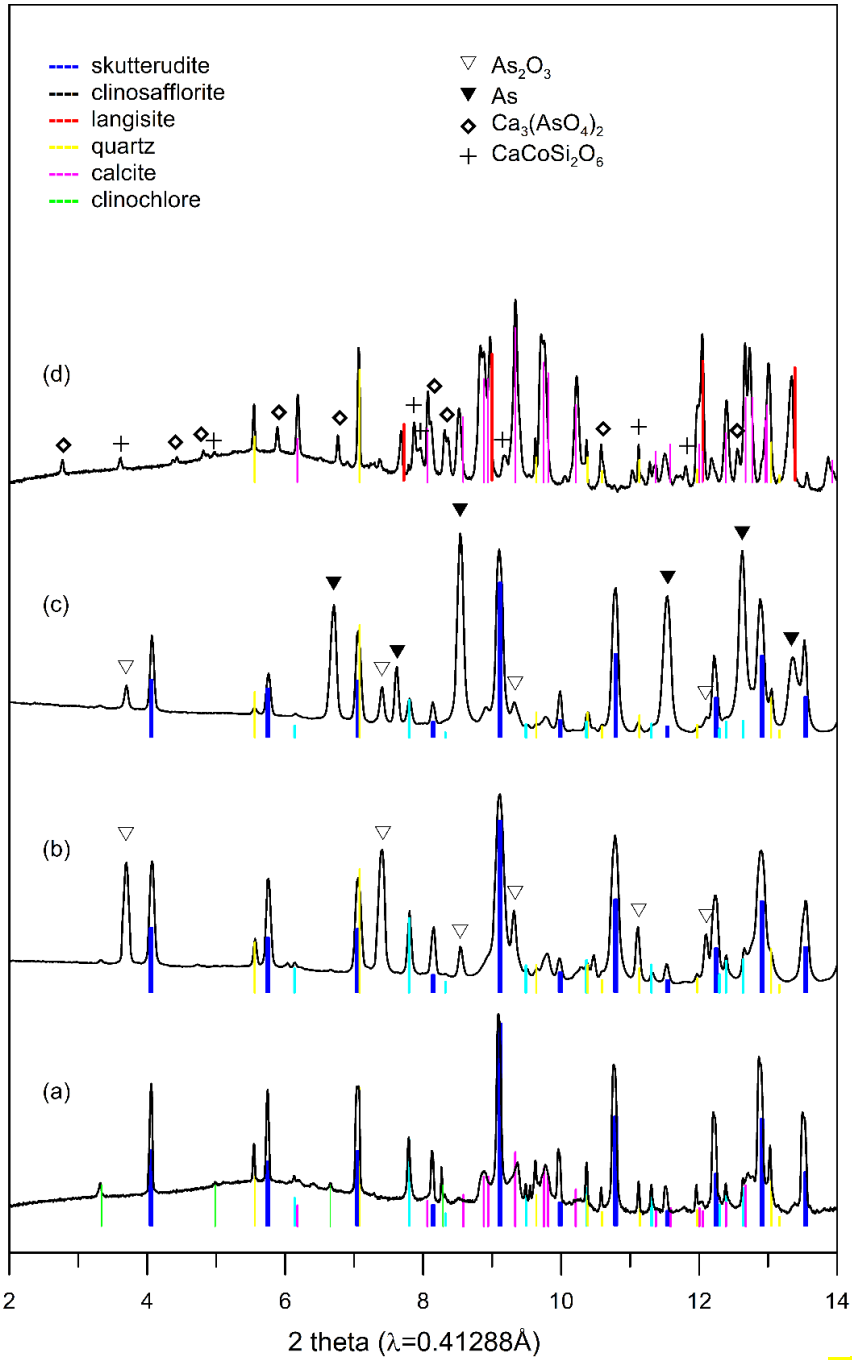


Figure 3. SR-XRD patterns corresponding to the cobalt arsenide ore (mixture m1 in table I). (a) before heating, (b) white zone of capillary (c) dark zone of capillary, (d) zone of maximum heating collected at RT after cooling.

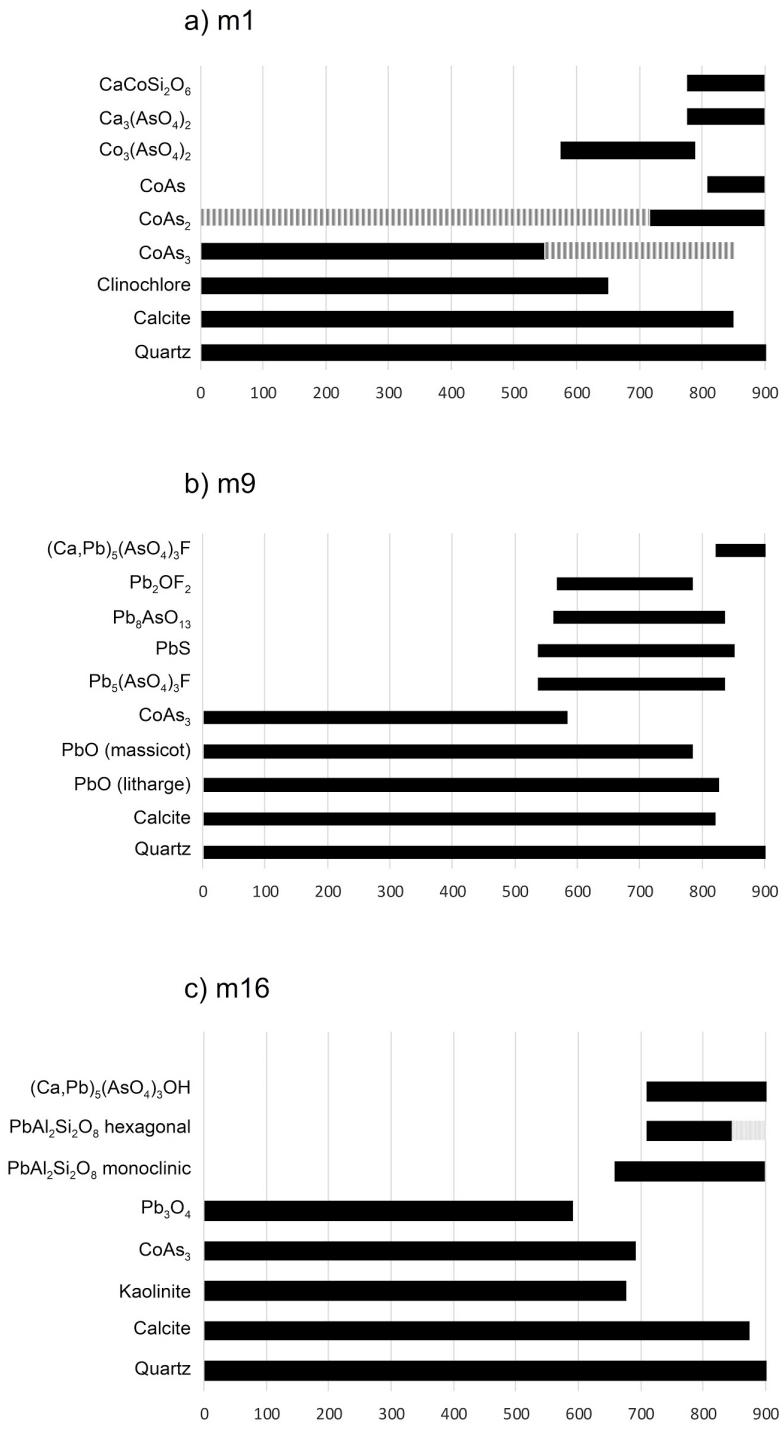


Figure 4. Thermal stability ranges of phases of m1, m9 and m16.

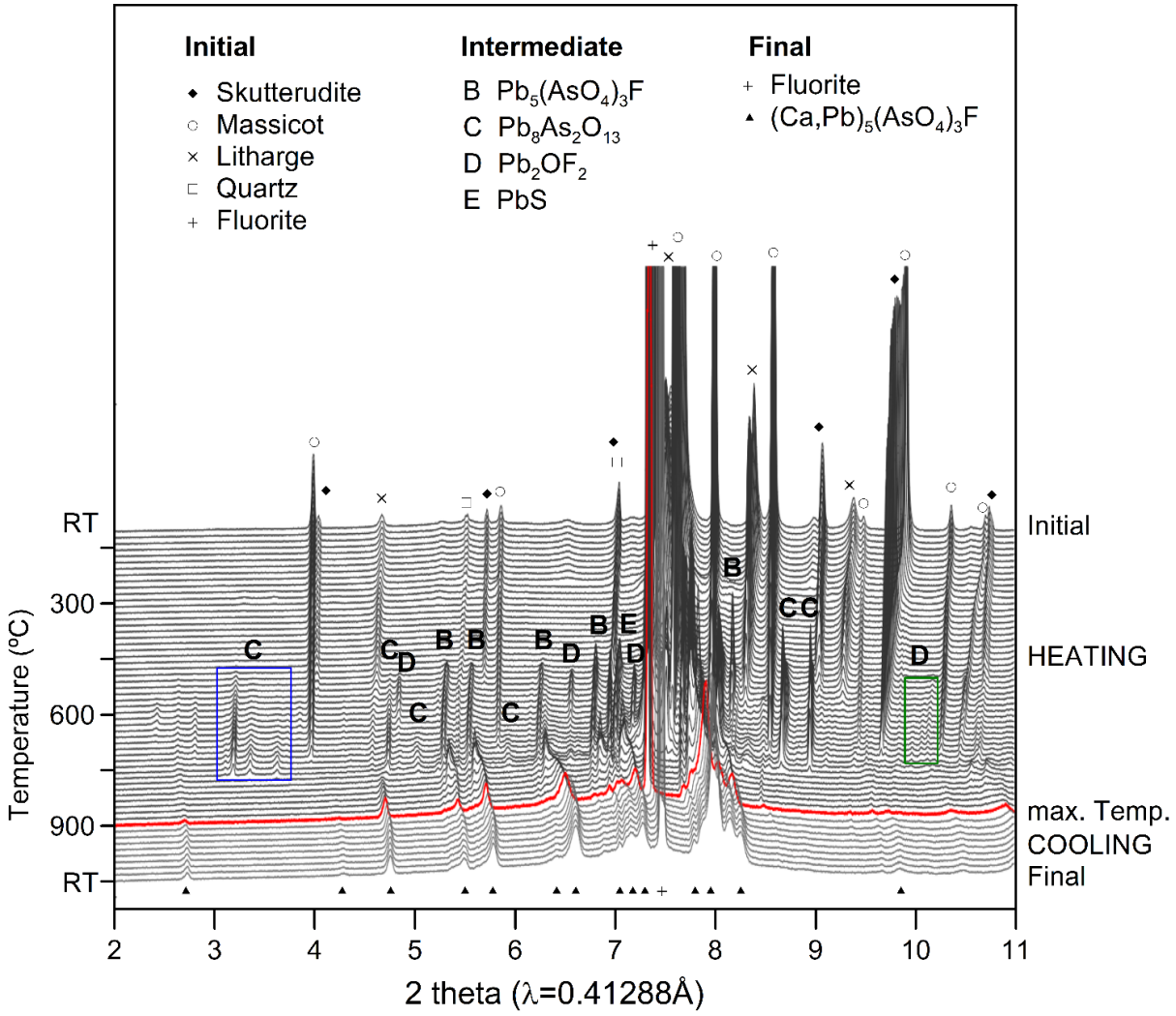


Figure 5. Diffractogram evolution of mixture m9 (Table I) from room temperature (top pattern) to the maximum temperature of 900 °C (red pattern) and cooling to room temperature (bottom pattern). The mixture components at RT, are identified by the symbols in the legend. The phases formed during the thermal treatment are indicated by the letter B to E.

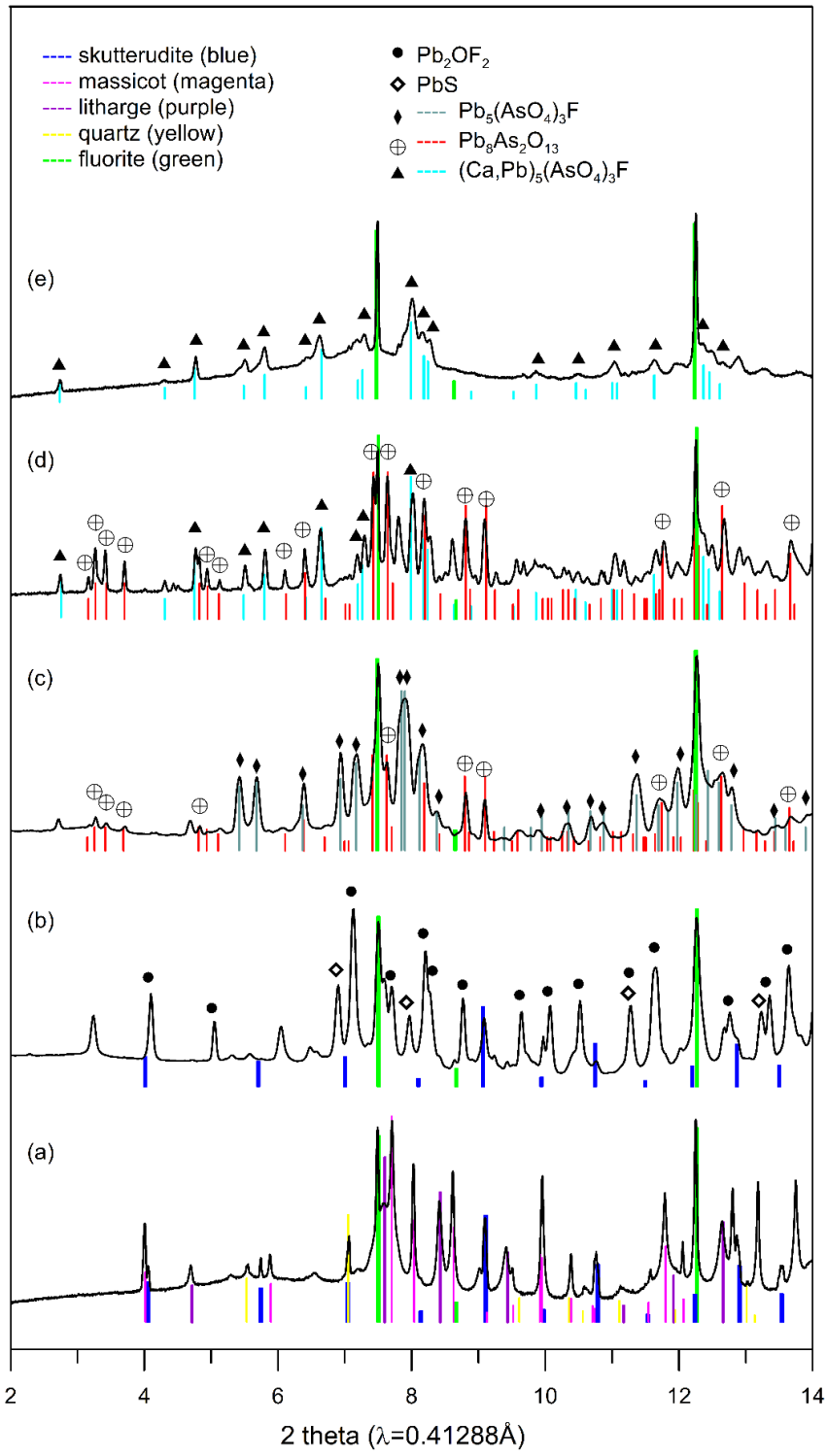


Figure 6. SR-XRD patterns corresponding to the mixture m9 (table I). (a) before heating, (b) external zone of capillary (c) middle zone of capillary, (d) near maximum temperature of capillary (e) zone of maximum heating collected at RT after cooling.

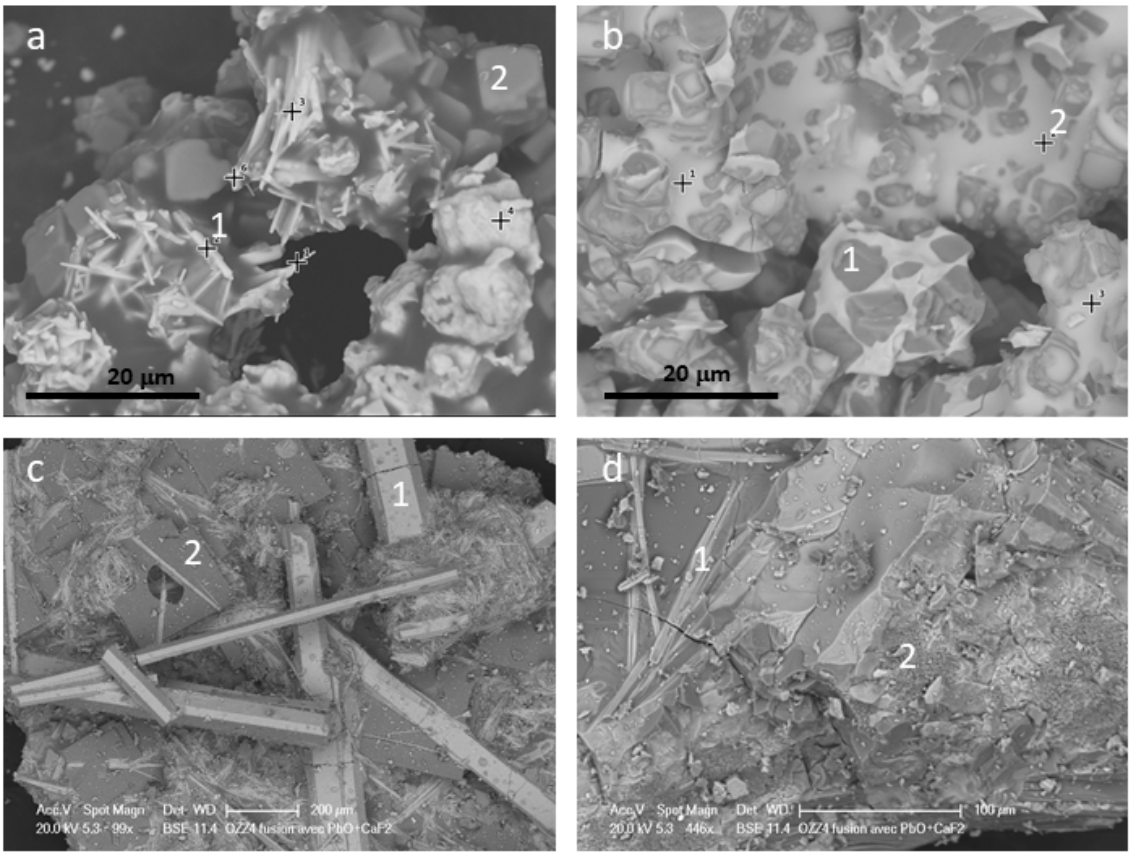


Fig. 7. SEM images of mixture m9 fired at 900°C (DP) (a) and (b) and 1200°C (c) and (d) (SP).
a) Lead arsenate tiny crystals (1) grown over cubes of fluorite (2).
b) Fluorite crystals (1) surrounded by lead rich vitreous phase (2).
c) Calcium arsenate crystals (1) and calcium aluminosilicate crystallites (anorthite type) (2).
d) Calcium arsenates crystals (1) and aggregates of tiny crystals rich in cobalt, iron and nickel (2)

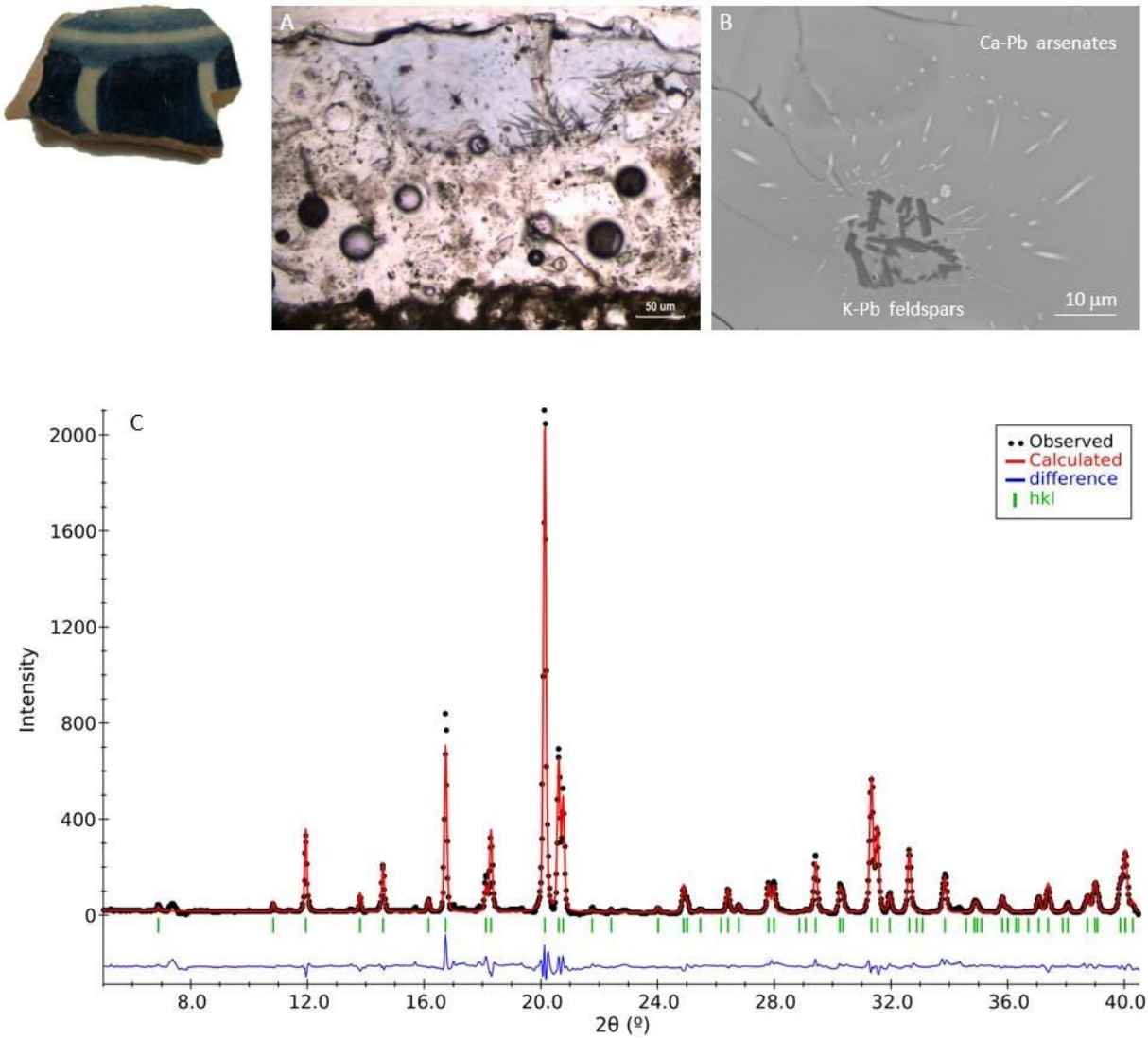
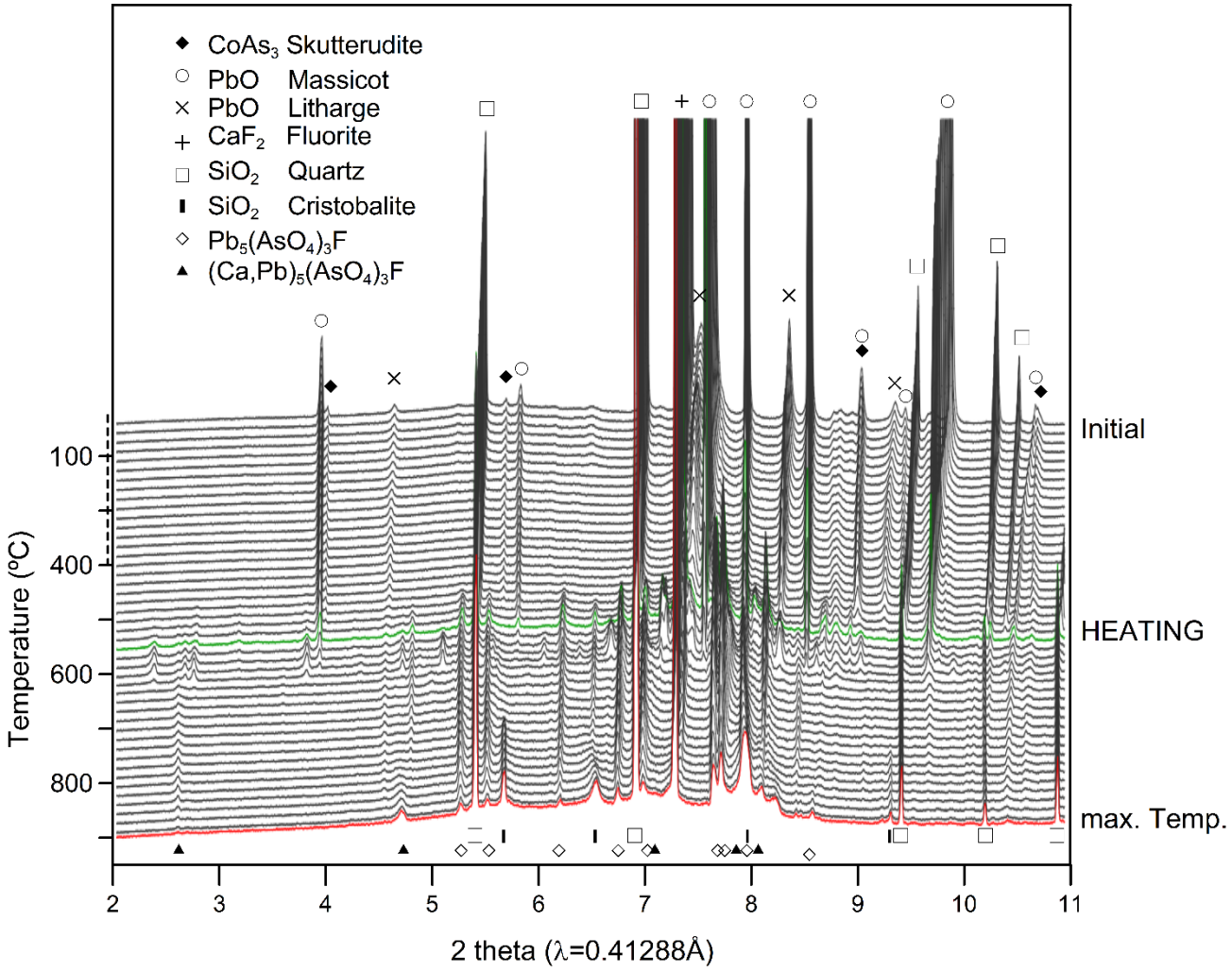


Figure 8. A) Thin section of blue decorated Catalan glaze from 18th century (SBG17). The blue decoration was applied overglaze. The Ca-Pb arsenates acicular crystals are formed in the contact between tin lead glaze and blue decoration layer. B) SEM BSE image of Ca-Pb arsenates (white colour) and lead feldspars (grey colour). C) Rietveld refinement of the Ca-Pb arsenate apatite-like structure.

734 .



735
736 **Figure 9.** Diffractogram evolution of mixture m11 (table I) from room temperature (top pattern) to
737 the maximum temperature of 900 °C (red pattern). Green diffractogram corresponds to 573 °C
738 (quartz alpha to quartz beta transition).
739

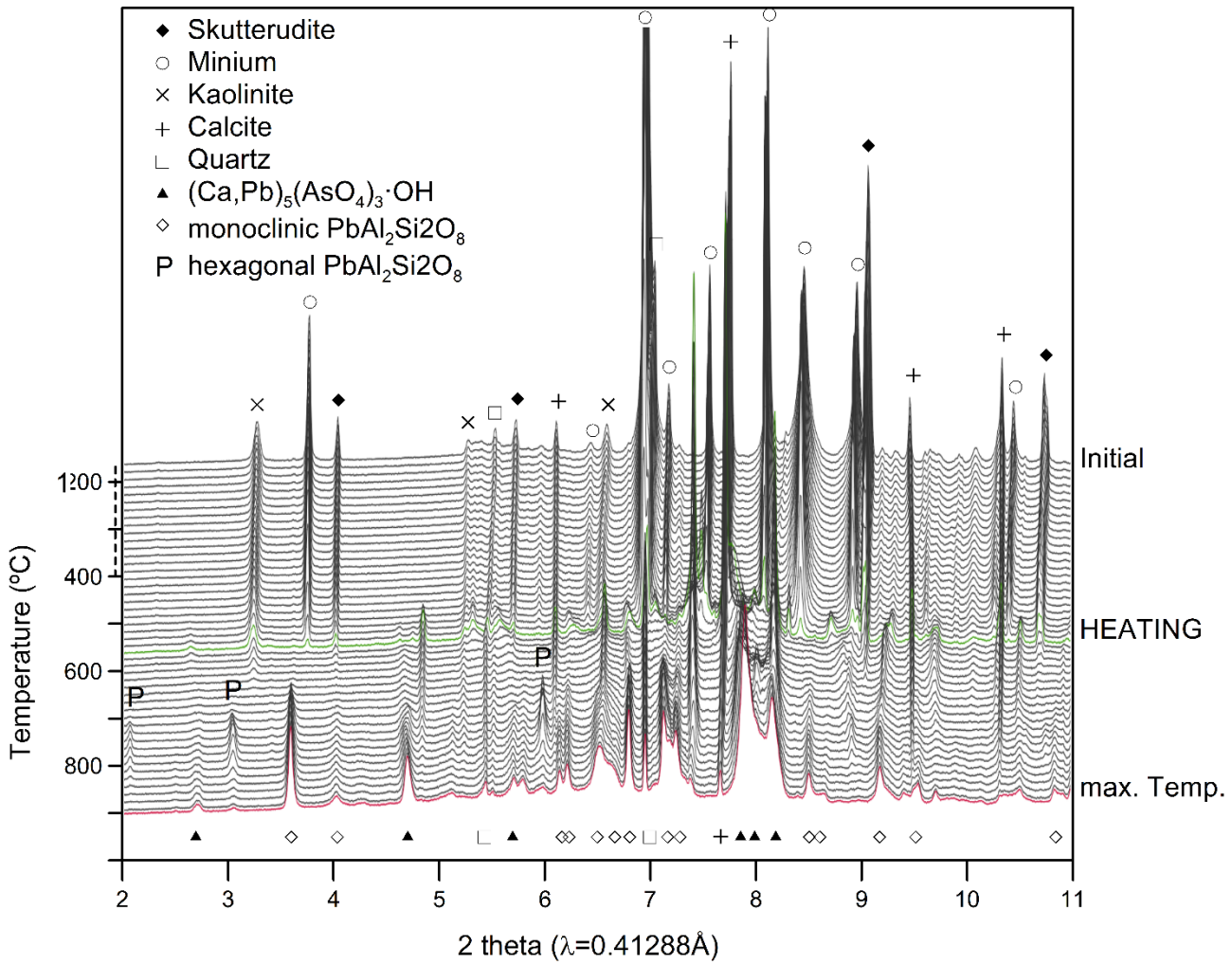


Figure 10. Diffractogram evolution of mixture m16 (table I) from room temperature (top pattern) to the maximum temperature of 900 °C (red pattern). Green diffractogram corresponds to 573 °C (quartz alpha to quartz beta transition).