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Late Prehistoric copper smelting in the Lao PDR: Experimental reconstruction based on the Vilabouly Complex evidence

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A serie of copper field smelting experiments were carried out in order to test assumptions on the copper production processes involved at the Vilabouly Complex, late prehistoric extraction and production site in Central Laos. First analytical results on the Vilabouly Complex assemblage (ores, crucibles, slags fragments and copper alloys objects) along with geological setting information permit to access first hypotheses on the smelting process. The identification of macroscopic layers of matte associated with copper put in light the introduction of sulfidic ores during the process. The presence of this matte in the Vilabouly Complex assemblages raises several questions: to what extent were sulfidic ores used on site? What type of sulfidic ores could have been added? Was it incidental? An unintentional co-smelting seems to be favored dependent on the mineralization exploited that seems mainly to correspond to carbonates/oxidic ores along with a secondary copper sulfide, chalcocite (Cu₂S). Therefore, The experimental reconstructions were performed to test this co-smelting of carbonates/oxide along with chalcocite in a one step-process using crucibles as reaction vessels, also based on archaeological observation.

1. Introduction

1.1 Context and site

Since 2008, ongoing rescue archaeology in central Laos' Savannakhet Province (Figure 1), has led to the discovery of occupation and industrial sites in the Vilabouly Complex (noted VC, previously known as Sepon or Xepon), thought to date from the regional Late Neolithic (c. 3000 BP) to modern times. With a concentration of Iron Age (for NE Thailand and adjacent central Laos c. 400 BC- c. AD 400) copper production sites with associated occupation and funerary activities, especially *Puen Baolo* (or 'Crucible Terrace') and *Thong Na Nguak* (or 'Dragon Field'; Cadet et al., 2019; Tucci et al., 2014; Pryce et al, 2011). Radiocarbon dating from mining shafts suggest copper mining between about 1000 BC (1071-922 calBC at 95.4%) and AD 700 (650-766 calAD at 95.4%), but the VC's main activity corresponds to the Iron Age of Mainland Southeast Asia, thought to be a period of rapidly rising social complexification, intensification of long-range exchange systems, irrigation-based agriculture, and marked

influences from India and China, where centralised polities were well established (Bellina, 2018, 2007; Ciarla, 2007; Higham et al., 2011; Higham and Rispoli, 2014).

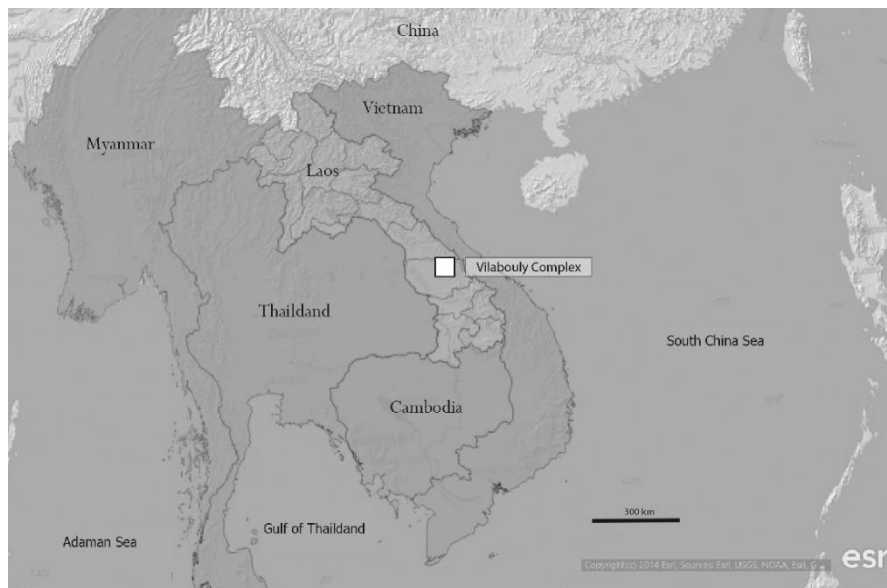


Figure 1: Mainland Southeast Asia with the Vilabouly Complex's location in Savannakhet Province, Lao PDR.

VC mining and high-temperature activity loci brought to light material from the *chaîne opératoire* of copper production: with ore, slag and technical ceramic fragments, as well as different types of copper and copper alloy objects. Despite the VC having been known since the mid-2000s, few artefacts have been submitted to any laboratory study (Pryce et al., 2014, 2011). Therefore, the study of the different artefacts is currently the subject of the lead author's doctoral study which the objectives are first to propose a technological reconstruction of the *chaîne opératoire* of VC copper production and second, to place it in the regional context of Southeast Asia during the crucial transition from the late prehistoric to early historic periods of Mainland Southeast Asia.

The purpose of the present paper was to test through experimental field reconstructions, the feasibility of the first technological hypothesis produced by the macro, micro and compositional analysis of VC metallurgical artefacts, namely, a potential co-smelting of malachite and sulfidic ore in a one-step process using open internally-heated crucibles as reaction vessels. Indeed first investigations have put in light a potential introduction of sulfidic ores during the smelting process at the VC mainly drawn by the identification of 'matte' in some specific objects.

1.2 Type of ore at the Vilabouly Complex

Laboratory analyses of metallurgical materials allowed us to make first iteration hypotheses for the high-temperature processes practiced in the VC, especially on the type of ore(s) used during smelting, which typically determines the complexity of the reduction process (Rostoker et al., 1989). Indeed, at the beginning of the doctoral study of the *chaîne opératoire*, the hypothesis of the use of malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), a copper carbonate, still abundant and occurring close to the surface in the VC geological setting was favored. Furthermore, malachite is one of the easiest ores to smelt in a one-step process (Tylecote, 1962). However, the

identification of 'matte' associated with some types of metal artefacts in the assemblage from Puen Baolo (Figure 2) has led to more probing questions being asked about metallurgical practices in the VC. Matte is an intermediate compound composed of copper, sulfur and sometimes iron, produced in significant quantities when sulfidic ores are present in the smelting charge. Matte is also often recorded as sulfide inclusions in modern and archaeological smelting slags that can also result from relics of sulfidic ore inclusions from a processed oxidic/carbonate ore. As inclusions, matte cannot be associated securely to a sulfidic ore smelting (Rehren et al., 2016). In the case of massive use of sulfidic ore, matte smelting forms part of the process itself (Addis et al., 2016; Doonan et al., 1994; Knapp and Kassianidou, 2008). In these latter case, macroscopic quantities of matte are produced during a stage of the process and can then be reprocessed to obtain copper. Because they correspond to an intermediary stage, matte fragments are rarely recovered in archaeological contexts. In the following when we talk about 'matte' we refer to a real macroscopic layer (Figure 2), not just as inclusions in slags meaning that a bigger amounts of sulfide must have been present during the process. In the VC's case, matte is present as artefacts, initially identified as conical ingots, with a diameter of 4-5 cm and a mass of 32 to 84 g. Conical ingots of near pure copper are indeed plentiful in the VC in, probable, burial contexts, but what to make of the artefacts with two distinct parts: copper and matte? The matte is mainly composed of copper (71 wt%) and sulfur (20.5 wt%) with little iron (1 wt%; Table 1) and overlies a copper button, showing good separation of the two phases. In some other artefacts, the matte layer is absent, replaced by one of fayalitic slag. The presence of this matte in the VC assemblages raises several questions. To what extent were sulfidic ores used in the VC? Was it episodic and/or incidental, or do we have a real matte smelting process? What kind of sulfidic ores could have been added? Was it intentional or 'co-smelting', a hybrid process first identified in nearby late prehistoric central Thailand (Rostoker et al., 1989) and previously tested experimentally for that context (Pryce et al. 2010) and in early Alpine copper production (Burger et al., 2010).



Figure 2: Examples of the intermediate metallic products identified with a matte layer (black layer) covering the metallic copper

Malachite, as already mentioned, is abundant in the mineralization in the VC but so is chalcocite (Cu₂S), a secondary copper sulfide, close or sometimes mixed with the malachite (Cromie, 2010; Manini et al., n.d.; Sillitoe, 1998). Primary copper sulfides (chalcopyrite, pyrite and small amount of bornite) are also present, and accessible to ancient metallurgists. Consequently, it remains difficult to clearly identify ancient mined ores extracted and selected for smelting also because of the possibility of archaeology-recovered ores being ancient rejects.

The preferred hypothesis for the technological reconstruction is for now the co-smelting with malachite and other sulfidic copper ores mostly chalcocite maybe 'incidental' (Rostoker et al., 1989), depending on the mineralizations exploited, which lead isotope analysis suggests may have varied in the local area as deposits were exhausted/fell out of use over time (Cadet et al. 2019). Co-smelting, done properly, produces metallic copper but matte production can result from an improperly balanced charge.

SAMPLE	Diameter (cm)	Depth (cm)	Mass (g)	O	S	Fe	Cu	Si	Al
SEALIP/LA/PBL/52	4	1.5	84	7.7	17.1	1.4	71.4	1.2	0.6
SEALIP/LA/PBL/48	4.5	1.7	65	3.7	21.9	0.8	73.4	nd	nd
SEALIP/LA/PBL/51	4.6	1.7	34	3.4	23.5	1.0	72.1	nd	nd
SEALIP/LA/PBL/42	6.7	1.5	129	7.8	23.1	nd	68.5	nd	nd

Table 1: Chemical composition of the two matte layers (SEALIP/LA/PBL/48 and 52) and two matte fragments (SEALIP/LA/PBL/42 et 51) identified in the VC assemblage with the associated diameter, depth and mass of the all ingots. SEM-EDS analyses (wt%)

1.3. Role of crucibles

On the matter of the reaction chamber and air supply, the VC has produced no evidence of hearths or furnaces, or air supply. One feature was identified by excavators as a possible furnace by the Puen Baolo, bearing ashes and showing signs of heating, but in our opinion the dimensions seem far too large for a furnace structure of this period in this part of the world, and with insufficient heat damage for smelting temperatures. We prefer to interpret this feature as a domestic hearth or domestic conflagration.

As the name Puen Baolo ('Crucible Terrace') suggests, technical ceramics identified as crucibles during the study are well-represented in the archaeological record. They are quite homogenous in mineralogical and chemical composition but seems to have variable dimensions. These have a shallow-open form with a round-pointed bottom and an estimated diameter of 5 to 15 cm and a depth of 3 to 6 cm. Twenty examples have been laboratory-studied so far, which are composed of a non-calcareous clay (silica ≈ 65 wt%) rich in alumina (≈20 wt% of Al₂O₃), poor in iron (≈ 3.5 wt% FeO), with a large component of quartz grains and rice chaff temper, usually found in the fabric of Southeast Asian late prehistoric domestic pottery (Carratoni et al., 2018; Tomber et al., 2011; Vincent, 2003) and also identified in crucibles at Ban Chiang, Northeast Thailand, for example (White and Hamilton, 2018). Furthermore, rice chaff is an ideal insulating medium, which is consistent with the identified internally-heating of the crucible (Rehren, 2003). The addition of organic temper may permit to strengthened an unfired/fired ceramic (Freestone, 1989). Various colors can be seen for the ceramics' bodies, some exhibit a thermal gradient from high inside to low outside, with preserved rims also suggesting internal/above heating of the crucible. Different types of slag

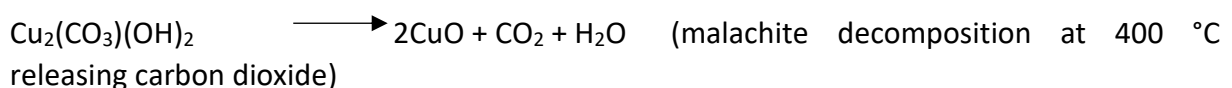
layers can be seen in the inner part of the crucibles, with an half corresponding to fayalitic composition. These observation make us proposed that a part of the crucibles can be in used during the smelting process. Based on visual and textural observations, these crucibles could have been used during the high temperature step without a pre-firing. Furthermore, the use of unfired crucibles is attested for other archaeological sites, like Buto in Egypt (Tereygeol and Mazou, 2019).

The experimental field reconstructions present in the following parts are not aimed to model slags comparable to archaeological evidences but a word can be said about the archaeological slag characteristics. The slags are mostly homogenous in a macroscopic and chemical point of view with a majority of flat fayalitic slags (fragments not exceeding 8 cm in length) mainly composed of ferrous olivine and magnetite in a glassy matrix suggesting temperatures mostly between 1100-1200 °C. The analyses of the slags showed a mastery of the production process leading to homogenous by-products denoting good separation of metallic copper/impurities. Complete results on VC metallurgical materials and their technological reconstruction will be published in an article being prepared concurrently.

1.4. Background to the experimental reconstruction

The archaeometallurgical literature does offer examples of one-step copper co-smelting (Bourgarit and Mille, 2001; Burger, 2008; Burger et al., 2010; Hanning et al., 2010; Hauptmann et al., 2004; Lechtman and Klein, 1999; Rostoker, 1975; Rostoker et al., 1989; Tylecote, 1980; Pryce et al, 2010). This process has been studied through experimental reconstitution and on material from archaeological sites. Indeed, in the early days of archaeometallurgy, developments in copper production were often perceived as an evolutionary sequence, partly geologically-guided and driven by Near Eastern evidence, from the ‘easily’ reduced carbonates/oxides, such as malachite, in one-step lower temperature processes, before progressing to more complex multi-step processes with sulfidic ores, such as chalcocopyrite (CuFe_2S ; Craddock, 1995; Thornton, 2009). It is now largely accepted that this transition is not always the case and many technological pathways were developed, adapted to socio-cultural and socio-economic circumstances, and the local geology. In some documented instances, archaeological sites evidence copper production by co-smelting, whether intentional or not (Hauptmann et al., 2003; Rostoker et al., 1989). Indeed, one has always to consider that these mixes can be naturally present inside the copper deposits and their exploitation can lead, or not, to an adaptation of the process (see, e.g., Rehren et al. 2016). Copper production by co-smelting was first proposed by Rostoker et al. (1989) for the Khao Wong Prachan Valley in Central Thailand, one of the three known prehistoric Southeast Asian copper extraction and production sites, only 600 km from the VC, and this hypothesis was supported by later studies (Pryce et al., 2010).

The mechanisms involved in a co-smelting reaction (here of malachite and chalcocopyrite) can be written as follows:



$\text{CuFeS}_2 + 4\text{CuO} \longrightarrow \text{CuO} + \text{FeO} + 2\text{SO}_2$ (partial reduction of iron releasing sulfur dioxide)

$2\text{CuO} + \text{Cu}_2\text{S} \longrightarrow 4\text{Cu} + \text{SO}_2$ (reduction of copper by sulfur, releasing further sulfur dioxide)

If silica is also present in the system, iron is eliminated through a slag formation (fayalite Fe_2SiO_4). A part can also stay trapped inside a 'matte' that can also be produced in the case of an improperly balanced charge.

During the co-smelting of copper carbonates and sulfides, solid oxygen from the carbonates removes the need for a roasting step generally used for desulfurization. Co-smelting can then be performed in a one-step process inside the same reactor. Oxygen allowing sulfur removal with sulfur dioxide as a reduction agent.

These different studies (Bourgarit and Mille, 2001; Burger et al., 2010; Hanning et al., 2010; Rostoker et al., 1989; Tylecote, 1980) have shown that metallic copper can be obtained in a one-step process with a co-smelting of carbonate/oxide and sulfide. However, they are nearly all based on a co-smelting of malachite and chalcopyrite. Yet, in the VC co-smelting with chalcocite is the preferred technological reconstruction. This type of co-smelting has never been tested experimentally, to the best of our knowledge. Burger et al., (2011) did use chalcocite during their laboratory furnace experiments associated to tenorite (CuO), in controlled temperature and redox conditions, but only for the roasting step, in order to test the chalcocite oxidation behavior. Likewise, chalcocite is rarely mentioned as being present in abundance at archaeological metal production sites. A possible reason is that chalcocite is rarely present in large deposits but is usually a minor component associated with other ores, while macroscopic occurrences are rare. Only (Hauptmann et al., 2003; Hauptmann and Weisgerber, 1980) mention it for the Iranian metallurgical site of Shahr i Sokhta. Here they interpreted the use mainly of chalcocite and mostly malachite in an unintentional co-smelting process, in which the products contain metallic copper and matte along with slag. The site also gave intentional discarded cakes of matte with negative impressions of copper regulus underneath, as it was evaluated worthless.

One experimental reconstitution has already been attempted for the VC, made during a master thesis (Griffin, 2017) with the feature mentioned in part 1.3 to be a potential furnace but with the dimensions lowered for these experiments. Malachite was used during the smelting and led to a few metallic copper nodules being recovered along with slags and roasted minerals, not comparable to the archaeological evidence denoting relevant conditions not reached and/or maintained enough. The association of this structure to a potential furnace was then let behind and crucibles are preferred in the present reconstruction.

2. Experimental conditions

2.1 Ores

The raw materials used, minerals and crucible clays do not come from the Vilabouly Complex due to the difficulties and cost of exporting the substantial quantities necessary, and experimentation in Laos was not viable for logistical reasons on a working mine area.

Therefore, we did our field reconstruction at the experimental platform of Melle (Deux-Sèvres) in France using materials sourced from various place around the world to produce morphologically and chemically identical waste to the archaeological examples. In that way, the experiments have more a qualitative purpose than quantitative.

The experimental charges were a mix of different ores in varying proportions: malachite/chalcopyrite, malachite/chalcocite or malachite/chalcopyrite/chalcocite, summarized in Table 2. The malachite used came from the Katanga mines in Congo and was of a high purity, c. 55 wt% copper, with a minor component of zinc, 1 wt% and lead, 0.7 wt%. The chalcopyrite came from the Burc mines in France and was also of a high purity level, c. 33 wt% copper. The chalcocite was obtainable only in small quantities and at considerable expense (300 euros for 2 kg) from a private geological collection and is of unknown origin. The chalcocite was composed mainly composed of copper (75 wt%) and sulfur (20 wt%) with minor components of iron (1 wt%) and zinc (1 wt%). The use of chalcopyrite is, based on the archaeological evidence, not the most likely for the VC but served for familiarization with the experimental set-up and comparison with other charges before using the limited supply of chalcocite.

The total charge mass per smelt was fixed at 150 g, based on the usable volume of the reconstructed crucibles. The effect of grain size was tested by making up crushed and sieved charges in the following grades: 5 mm, between 5 and 3.5 mm, 2 and 3.5 mm, lower than 2 mm and also blocks of uncrushed ores.

2.2 Crucible, hearth and air supply

Based on the laboratory analyses of archaeological crucible fragments (see part 1.3), their use as part of the smelting process, as opposed to or in addition to a hearth or furnace, formed part of the technological reconstruction to be tested with field experimentation. The experimental crucibles were made by a professional potter, using *terre de Langeais*; which is refractory rich in silica (63 wt%) and alumina (25 wt%), and poor in iron (4.5 wt%), containing other minor components such as potash (2 wt%), calcia (1 wt%) and titania (1 wt%) . Rice chaff has been added as tempering agent. The archaeological crucibles have a flat inner part and a rounded bottom but during the experiments, flat bottom crucibles were used in order to facilitate the moving of the vessel and without change on the usable volume remaining the same. Both pre-fired and unfired crucibles were used, to test the behavior of both types (Figure 4).

The crucibles were then placed in a hearth structure (Figure 3), a simple shallow hole in the ground with a clay lining. Features such as this were not detected during excavation in the VC's disturbed and difficult archaeological deposits but would conceivably have left a relatively minor trace due to low heat penetration into the ground, and are necessary experimentally to allow heating from above. In the absence of archaeological data, the experimental hearth was chosen with an open side in order to facilitate removing the crucible from the fire.

	Ore(s) mix	Rapport masse	Charge	Malachite (g)	Chalcopyrite (g)	Chalcocite (g)	Grain size	Time	Crucible	Pouring contenant	Total produce
Smelting 1	Ma/chalp	4:1	150	120	30	-	+ 5 mm	41 min	Fired	"casting sand"	20 g
Smelting 2	Ma/chalp	4:1	150	120	30	-	5-3,5 mm	30 min	Fired	"casting sand"	30 g
Smelting 3	Ma/chalp	4:1	150	120	30	-	3,5 2,5 mm	30 min	Reused of smelt 2 crucible	"casting sand"	23 g
Smelting 4	Ma/chalp	4:1	151	120	30	-	mm	45 min	Unfired	"casting sand"	22 g
Smelting 5	Ma/chalp	1:1	150	75	75	-	+ 5 mm	76 min	Unfired	"casting sand"	43 g
Smelting 6	Ma/chalp	1:1	150	75	75	-	5-3,5 mm	84 min	Unfired	Ashes	36 g
Smelting 7	Ma/chalp	1:2,5	150	110	40	-	+ 5 mm	47 min	Reused of smelt 7 crucible	Ashes	77 g
Smelting 8	Malachite	-	160	160	-	-	Blocs	69 min	Unfired	Ashes	83 g
Smelting 9	Ma/chalc	1:1	150	75	-	75	+ 5 mm	69 min	Unfired	Ashes	83 g
Smelting 10	Ma/chalc	1:1	150	75	-	75	5-3,5 mm	70 min	Reused of smelt 10 crucible	"casting sand"	40 g
Smelting 11	Ma/chalc/chalp	1:1:1	150	50	50	50	+ 5 mm	62 min	Reused of smelt 11 crucible	"casting sand"	108 g
Smelting 12	Ma/chalc/chalp	1:1:1	150	50	50	50	5-3,5 mm	70 min	Unfired	"casting sand"	106 g
Smelting 13	Ma/chalc	1:1	150	75	-	75	- 2,5 mm	75 min	Unfired	Ashes	76 g
Smelting 14	Ma/chalp	1:1	150	75	75	-	+ 5 mm	84 min	Unfired	"casting sand"	79 g
Smelting 15	Ma/chalc/chalp	1:1:1	180	60	60	60	Blocs	62 min	Unfired	"casting sand"	132 g
Smelting 16	Ma/chalc	4:1	150	120	-	30	Mix	120 min	Unfired	"casting sand"	49 g
Smelting 17	Ma/chalc	9:1	150	135	-	15	Mix	90 min	Unfired	"casting sand"	62 g

Table 2: Experimental conditions for the different smelting. Ma = malachite, Chalc = chalcocite and Chalp = chalcopyrite.

No tuyères or fragments thereof have been excavated in the VC. This was also the case for the Khao Wong Prachan Valley, where similar experimentation suggested that a natural draft or wind-powered operation was unlikely and that an “archaeologically-invisible” forced blast must have been present (Pryce 2009; Pryce et al. 2010). Our experimental air supply is likewise forced, using a leather hand-operated bellows and a 90°-angled tuyère, as per Burger et al. (2010). The crucible was placed under the tuyère and covered with large fragments of charcoal (up to 150 mm in length) with holes filled with lower sized charcoal (‘qualité restaurant’), of a European species (beech) obviously different to that available in the VC.

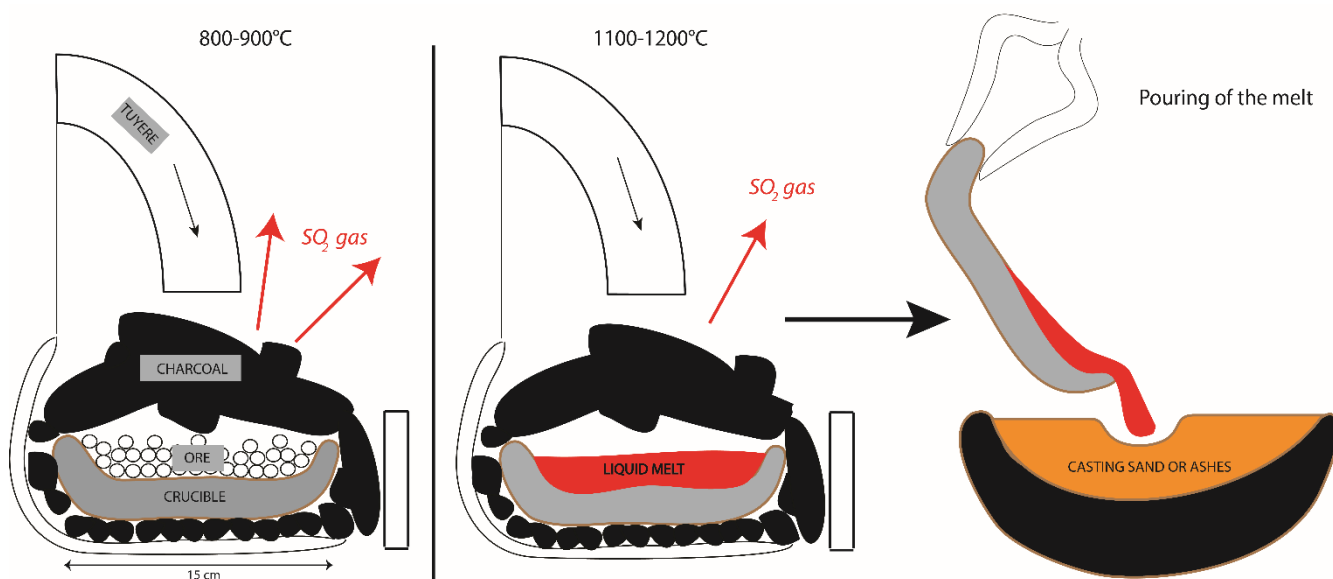


Figure 3: Schematic representation of the experimental reconstructions

The temperature was then raised to 800-900 °C and maintained for thirty minutes, based on observations made by Burger (2008) who noted that beyond this limit the charge tended to agglomerate and prevent the escape of SO₂ gas from the melt. Once most of the SO₂ gas was assumed to have been eliminated, the temperature was increased. The temperature was monitored using a 1200 °C-rated thermocouple (type K simple class 1), which served to record the rate of temperature change until its limits were exceeded. The thermocouple only has an indicative purpose because the temperature is highly variable inside the crucible and more than one will be necessary in order to get access to precise temperature information. The temperature was also controlled by the operator based on color changes inside the fire. Furthermore, once the crucible contents reached a fully liquid state, the crucible was removed from the fire using an iron tongue and the melt immediately poured into another vessel filled with ‘casting sand’ or ashes where an hemispherical rounded print was applied (Figure 3). The use of more than one thermocouple could also have slowed the action of pouring. ‘Casting sand’ and ashes were chosen in the absence of precise archaeological evidence for pouring receptacles, also because archaeological products exhibit smooth surfaces without gas holes or any inclusions showing that the receptacle did not react with the melt, which is the case for ‘casting sand’ and ashes.



Figure 4: On the left, the smelting hearth with the bent tuyère above the charcoal-covered crucible. Bottom right, exterior of the unfired experimental crucibles and top right, interior of the fired experimental crucibles

3. Analytical methods

The products and debris from the different smelting experiments were studied at the *Laboratoire Archéomatériaux et Prévision de l'Altération* (LAPA-IRAMAT) in Saclay, France, using the same techniques and procedures as per the VC archaeological artefacts. Cut samples were mounted in epoxy resins and ground using silicon carbide wet-dry paper (80-4000 grit) before final polishing with diamond pastes (3, 1 and 0.25 μm). The microstructures were studied using a Zeiss reflected-light optical microscope (OM). In order to assess the chemical composition of different phases, the OM samples were carbon coated and studied using an Energy Dispersive Spectrometer (EDS) coupled with a Scanning Electron Microscope (SEM, JEOL-7001F) operated in both secondary (SE) and back-scattered electron (BSE) mode, using a 20 kV accelerating voltage, a 10 mm working distance and an Oxford Instruments Silicon Drift Detector. Resulting spectra were processed using Oxford Instruments Aztec software. Global compositions for each sample were calculated by a mean of 3-4 area scans per sample avoiding inclusions when possible.

4. Results

The temperatures and redox conditions expected for crucible-pouring smelt, with gravity-based separation of the metallic copper, were reached for most of our crucible-based experiments. Except for the first smelts, 1 to 5, with malachite/chalcopyrite mixes that often led to agglomerated melts that were difficult to pour, where the product therefore were agglomerates of copper nodules with matte and roasted minerals.

Complete oxidation of the sulfide was never reached, leading to the formation of matte with all charge variations. Four types of product and by-product could be differentiated after the smelts: metallic copper, matte, partially reacted minerals and some slag. The main

components consisted of metallic copper and matte recovered after the melt was poured. The copper and matte formed as small hemispherical ingots, with masses of 40 to 132 g, diameters of between 2.8 and 4.3 cm, and thicknesses of 1 to 1.4 cm. In most cases the denser copper formed at the bottom of the ingot and was covered with a layer of matte, as per the VC originals (Figure 5). In some cases, only the copper (smelts 8 and 17) or matte layers (smelts 7 and 12) were present. Metallic copper can also be recovered as small independent prills. It was not possible to assess the masses of the different products and by-products independently because it would imply a crushing and the products have been analyzed in order to have the transition zones between the different phases.

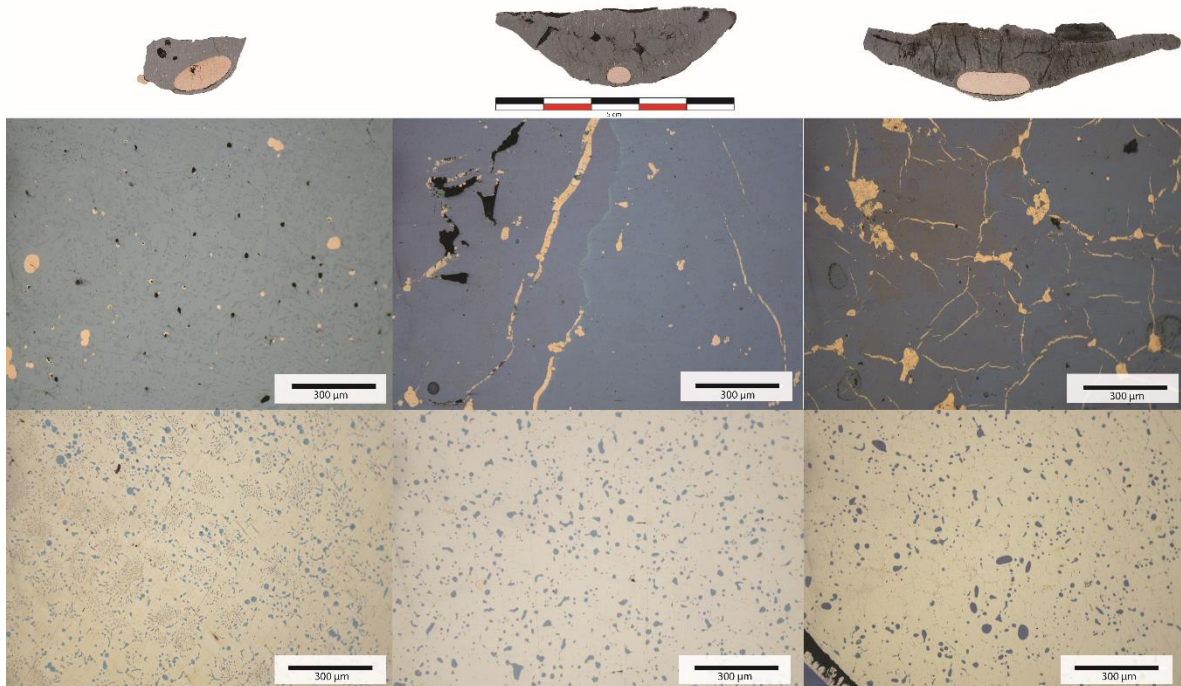


Figure 5: Products of Smelts 10, 11 and 14 (left to right) with associated OM observation for the matte and metallic copper layers.

4.1 Metallic copper

Copper metal was recovered from all the experiments, notwithstanding the differing ore charge ratios. This copper was present as macroscopic layer and sometimes present as small prills or veins trapped in the matte layer. The copper contained up to 2.5 wt% sulfur, present mostly as round inclusions (Figure 5). The copper also contained up to 2 wt% zinc and iron in solid solution (Table 3), both elements being present in the original ores used. Lead inclusions are also visible and are mostly likely derived from the original ores as well. The mean composition of the metallic copper does not seem to be affected by the charge ratio. However, sulfide inclusions can contain iron up to 10 wt% when chalcopyrite is present in the charge.

4.2 Matte

As expected, the matte layers' elemental composition appears to vary depending on the charge used, and is summarized in Table 3. Different type of microstructure can be seen for the matte: nodular and lamellar. For some smelts, a dissolution of the matte in different phases can be identified (smelts 4, 5, 7, 10, 14). To take representative examples of the three

main charge mixes used we focus on smelts 10, 11 and 14 (Figure 5). Smelt 10 was a mix of malachite and chalcocite in equal proportion (75g/75g). This charge produced a matte with 78 wt% of copper and 19 wt% of sulfur (Table 3).

Smelt 11 used a mix of all three ores, malachite, chalcocite and chalcopyrite in equal proportion (Table 3). The resulting matte contains 67 wt% of copper, 21.6 wt% of sulfur and 8.8 wt% of iron. The iron would have mostly been derived from the chalcopyrite ore.

When the charge is composed only of malachite and chalcopyrite in equal proportions, as per smelt 14, the amount of iron in the final matte increases to 15 wt% (Table 3) with 60 wt% of copper and 22 wt% of sulfur.

As noted in Table 2, smelt 16 and 17 had the purpose to lower the chalcocite ore content inside the mix in order to test the limit of matte layer formation. Smelt 16 contained 20% of chalcocite (30g) and smelt 17 only 10% (15g). With 20% of chalcocite, adding to the charge the matte layer is still present in the final product but when the amount added is lowered to 10% the matte layer is no longer produced. Thus, the amount of sulfidic ore in the charge must be higher than 10% in order to produce a matte layer. The matte composition of smelt 16 is also composed of copper at 80 wt% and sulfur 18.6 wt% as per smelt 11 meaning that only the layer thickness is affected by this change.

4.3 Slag

The purpose of these experiments was not to produce slag and, as no flux was added to the smelting charge, very little slag was produced.

The small quantities of slag recovered are usually heterogeneous and coarse, containing unreacted minerals, copper prills and matte inclusions in significant proportions (Figure 6). Crystalline phases can be observed: mainly fayalite and iron oxide (magnetite, little wüstite) in a glassy matrix. The presence of these crystalline phases is indicative that sufficient temperatures of 1100-1200 °C (higher when wüstite is present) were reached for their formation but not maintained or exceeded for sufficiently good slag/matte/copper separation (Bachmann, 1982; Donaldson, 1976). As no flux was added to model an optimum Fe/Si ratio for the formation of fully molten slags of fayalitic composition (Rehren et al., 2007), it is not surprising to have such heterogeneous experimental slags.

Cu	Smelt N°	Ore(s) mix	Ratio	O	Si	S	Fe	Cu	Zn	Pb
	1	Ma/chalp	4:1	0.5		1.2	0.2	98.1		
	3	Ma/chalp	4:1	0.6		1.2		98.2		
	4	Ma/chalp	4:1	0.6		2.5		96.8		
	5	Ma/chalp	4:1	0.5		1.6	0.3	97.5		
	8	Malachite		4.1			0.4	93.2	1.4	1.9
	10	Ma/chalc	1:1	0.7	0.1	1.7		97.6		
	11	Ma/chalp/chalc	1:1:1	0.9		1.2	0.9	95.8	1.1	
	13	Ma/chalc	1:1	0.6		1.2		96.7	0.7	0.7
	14	Ma/chalp	1:1	0.8	0.1	1.8	2.0	94.0	1.3	
	15	Ma/chalp/chalc	1:1:1	0.6	0.2	1.5	0.5	95.5	0.9	1.0

	16	Ma/chalc	4:1	0.6	1.1	98.3												
	17	Ma/chalc	9:1	0.6	1.0	98.4												
Matte				O	Si	S	Fe	Cu	Zn									
	1	Ma/chalp	4:1	0.9		19.7	2.3	77.1										
	2	Ma/chalp	4:1	1.4	0.1	20.3	2.0	76.3										
	3	Ma/chalp	4:1	0.9		19.3	0.7	78.9										
	4	Ma/chalp	4:1	1.4		17.6	0.3	80.7										
	5	Ma/chalp	4:1	1.9		23.3	13.6	61.2										
	6	Ma/chalp	1:1	2.0	0.2	20.7	6.3	71.0	0.2									
	7	Ma/chalp	1:2.5	2.5	0.2	21.5	15.2	60.6										
	10	Ma/chalc	1:1	1.0	0.2	19.6	0.6	78.7										
	11	Ma/chalp/chalc	1:1:1	1.8	0.2	21.6	8.8	67.0	0.6									
	12	Ma/chalp/chalc	1:1:1	2.1	0.2	21.5	9.1	66.8	0.2									
	13	Ma/chalc	1:1	1.4	0.2	19.1	1.3	77.6	0.3									
	14	Ma/chalp	1:1	2.4	0.2	22.3	14.8	59.9	0.6									
	15	Ma/chalp/chalc	1:1:1	1.4	0.2	20.4	3.7	73.8	0.4									
	16	Ma/chalc	4:1	1.1		18.6	0.1	80.1	0.2									
Slag				O	Mg	Al	Si	P	S	K	Ca	Mn	Fe	Cu	Pb	Zn	U	
	1	Ma/chalp	4:1	25.3	0.5	1.4	12.5	0.1	0.2	0.2	2.7		49.9	2.1	1.0	4.5		
	4	Ma/chalp	4:1	31.8	0.9	1.7	16.6	0.5	0.1	0.6	2.9	0.2	35.0	2.6	2.7	4.2		
	7	Ma/chalp	1:2.5	30.9	0.9	1.6	14.4	0.4	0.3	0.4	2.2	0.2	42.4	1.5	4.1	2.2	0.9	
	11	Ma/chalp/chalc	1:1:1	33.8	0.8	1.3	15.8	0.5	0.3	0.4	3.0	0.2	39.4	1.0		1.9		

Table 3: Compositional results by SEM-EDS means (wt%) of the different phases recovered after the experimental smelting: matte, copper and slag. Ma = malachite, Chalc = chalcocite and Chalp = chalcopyrite.

4.4 Partially reacted minerals

Partially reacted minerals were present at the end of smelts 1, 2, 3, 4, 5 and 7 when required conditions were not reached or maintained long enough for a complete reaction and gravity separation of phases. They are agglomerates of roasted ores along with matte and copper prills.

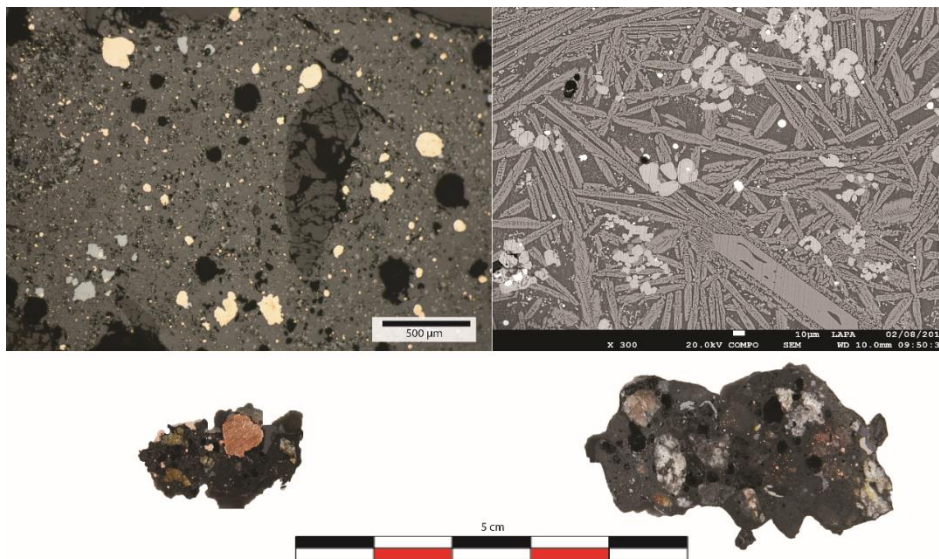


Figure 6: Two polished sections of small coarse slags obtained from smelts 4 (bottom left) and 11 (bottom right) along with a micrograph x5 PPL (top left) showing quartz inclusions and metallic copper/matte prills. The SEM BSE image (top right) shows the presence of crystalline phases, fayalite and magnetite, as well as interstitial glass.

4.5 Crucibles

The experimental crucibles proved up to the task of successful high-temperature operations. One of them was used three times and could have served again (smelt 9 to 11). All smelting operations resulted in some matte and copper staying trapped at the bottom of the crucible, even when the melt was liquid enough for pouring. This layer was predominantly matte and up to 4 mm thick. The amount of trapped material in the crucibles was difficult to estimate. Vitrification was observed in the interior rim but mostly for the crucibles used several times, while the exteriors remained preserved. Even if both pre-fired and fired crucibles gave successful smelts, differences can be seen. The pre-fired crucibles are compact and have a less evident thermal gradient in section, and seem to have been less altered by the heat, whereas the unfired crucible show more porosity and color changes, as these were never fired (Figure 7). Based on these visual observation unfired crucibles seems to be possible for the VC.

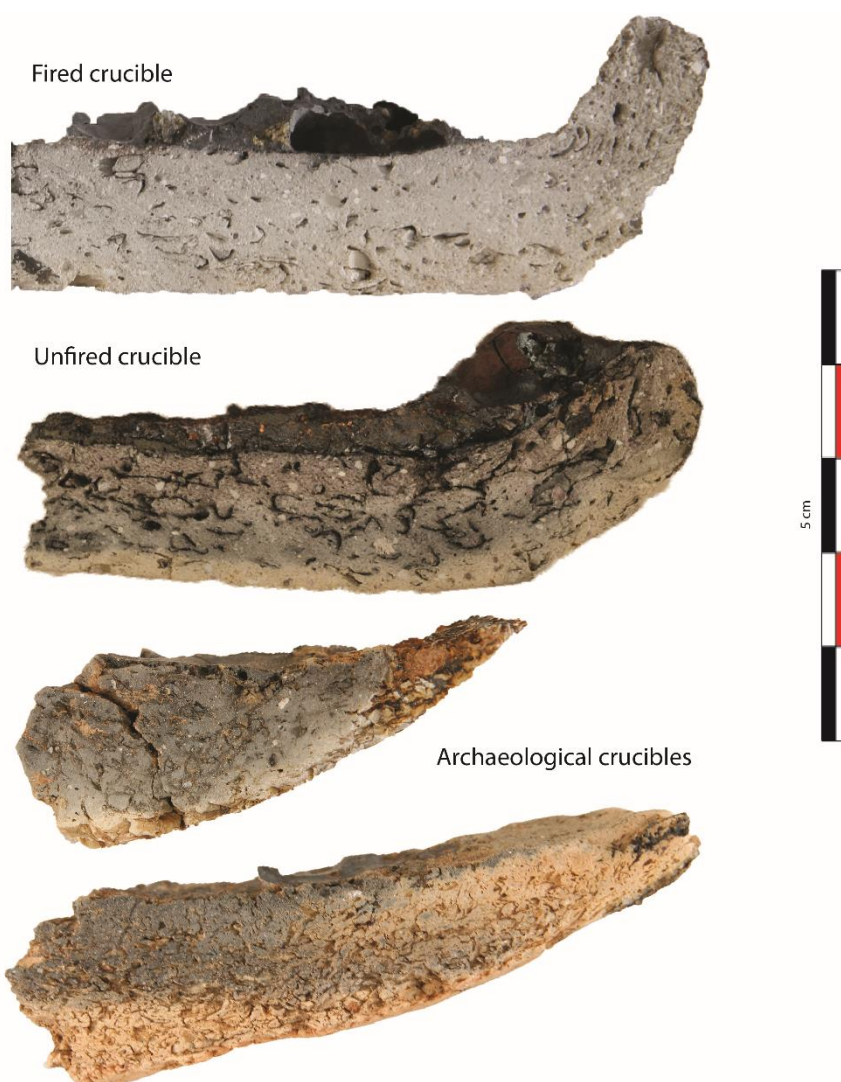


Figure 7: At the top, cut sections of two experimental crucibles, fired (smelt 2) and unfired (smelt 7) compared to two archaeological crucibles at the bottom

5. Discussion: Comparison with the archaeological remains

The experimental products were compared to the archaeological evidence. The form and mass of experimental products was close to the VC artefacts (see Figure 2 and Figure 5). Indeed, most of the experimental products were composed of two layers, copper overlain by matte, just as seen for some of the archaeological 'ingots' thought to be intermediate smelting products. In addition, their mass ranges from 21 to 132 g for the smelts resulting in small hemispherical ingots whereas archaeological examples are of 32-84 g. This comparison suggest the calculated usable volume of the archaeological crucibles is broadly correct.

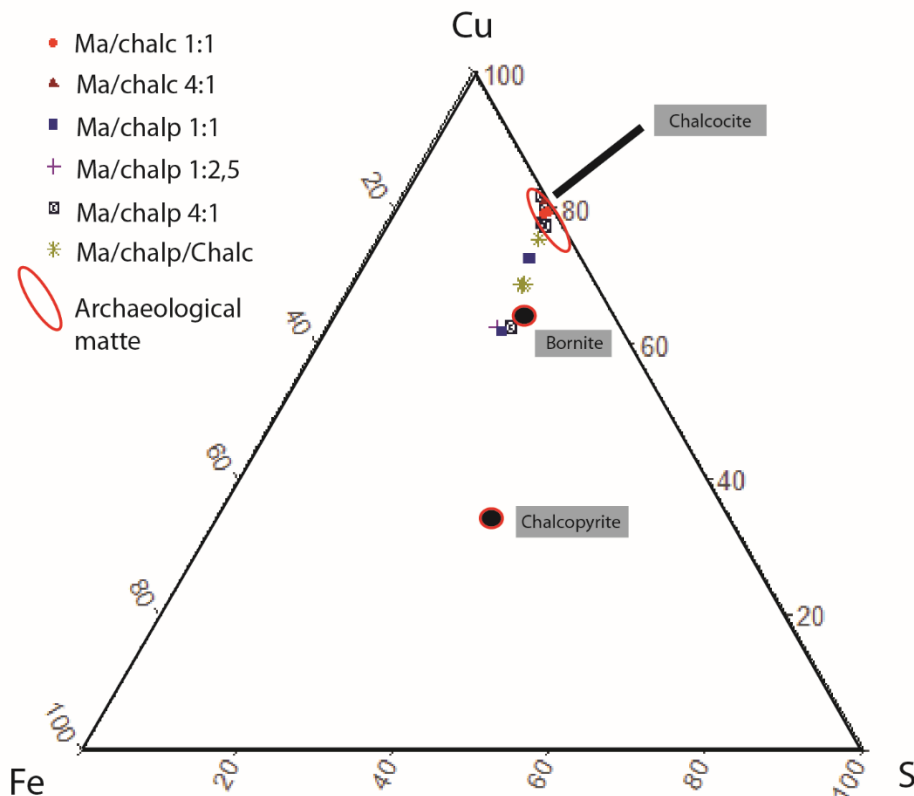


Figure 8: Ternary diagram Fe-Cu-S showing the chemical composition of the matte layers obtained from the different charge ratios, along with the standard composition of chalcocopyrite, bornite and chalcocite, the three main sulfidic minerals.

5.1 Matte and copper

The main objective of these experiments was to test the co-smelting of malachite and chalcocite, in order to see whether it worked and what type of products can be obtained. Some experimental matte samples had a composition similar to those of archaeological matte with copper at 79 wt% and sulfur at 19 wt% (Figure 8). These matte samples were obtained with a malachite and chalcocite charge, and therefore support the hypothesis of this process having been used in the VC.

The malachite/chalcocopyrite charge ratio of 4:1 (smelts 1, 3 and 4) also produced a matte of this elemental composition. However, the products were not small two-phase ingots, with metallic copper overlain by matte, but agglomerates of roasted minerals along with matte and metallic copper nodules resulting from an incomplete melt.

The experimental copper, in terms of microstructure and elemental composition, was also comparable to archaeological copper ingots (Cadet et al., 2019), with abundant sulfide inclusions and mean sulfur content of 1-2 wt%.

5.2 Slag

The few experimental slags produced are not comparable to Vilabouly Complex examples, as the former are coarse, very heterogeneous and with abundant copper and matte inclusions showing sub-optimal conditions and potentially operator skill. The VC samples are mostly flat and homogenous fayalitic slags, showing good separation of metallic copper/impurities; comparable to Bachmann's (1982) *plattenschlacke*. Cuprite (CuO) is frequently identified in the experimental slag, whereas it is absent from archaeological examples, possibly indicating excessively oxidizing conditions due to the absence of a protective slag bath.

The main purpose of the reported experiments was not to produce slag but one might still question whether it is possible to obtain flat fayalitic slags with the current experimental procedure? Can sufficient temperature and redox conditions be maintained during crucible smelting with more realistic charges with lower ore quality? Sites where this kind of slag have been identified, mostly in Alpine contexts, usually have scarce evidence for furnaces (Addis et al., 2016; Bourgarit et al., 2010; Burger, 2008), with the exception of the Mitterberg area in the Austrian Alps (Herdits, 2003). In their study of copper slag from Transacqua and Segonzano in the Italian Alps, Addis, et al (2017) proposed that flat slags pertained to the last step of a chalcopryrite smelting process and could have been obtained using either crucibles or small furnaces, left to cool outside the heating structure. This question can be also asked of the VC, and as no definitive furnace structure has been discovered so far, and the huge scale of the mining area, it remains open to discussion. The very beginnings of copper metallurgy are often associated with crucible smelting, being portable, low-capital reaction vessels offering better control of small-scale copper production (Martín-Torres and Rehren, 2014; Rehren, 2003) which are later replaced by furnace smelting for copper mass production, but for later periods either mode of production can be present, as adapted to local socio-economic conditions and skill levels.

5.3 Crucibles

The reported experiments permit us to infer that their volume/form and raw materials used during the experiments based on archaeological evidence is consistent with successful one-step smelting, as desired and proven by previous studies (Hanning et al., 2010; Rostoker et al., 1989; Rovira and Ambert, 2002; Tylecote, 1975). Results also demonstrated that heating from above produces interior slag/matte, occasionally vitrified rims and non-vitrified exteriors, as per the archaeological crucibles. It seems possible that unfired crucibles more accurately model the VC examples, by their appearance and porosity, even if we assumed that the raw materials are not from local sources. The current evidence for VC technical ceramics and domestic pottery (Katherine Cameron, personal. comm) suggests that the same raw materials were probably used for all purposes with no special adaptation. The rice chaff identified in pottery and crucibles was sufficiently insulating and anti-crack propagating for copper smelting.

5.4 Pouring of the melt

Assuming crucibles to be the reaction vessels, the archaeological flat fayalitic slags with flow signs and small ingots are thought to be the direct product of pouring the melt into a conical mould/depression. Indeed, the thin slag layer present at the rim of archaeological crucibles suggests pouring took place immediately after smelting like in the Khao Wong Prachan Valley. This usage would also permit re-use of crucibles, as noted with the experimental one. Furthermore, results from the experiments support out original hypothesis, with similar results to the intermediate archaeological products, with the exception of the slag, which must be modelled in future experiments.

Puen Baolo (the main extraction/production place at the VC) has little evidence for foundry activities, just one fragment of a potential sandstone mold and one for seemingly conical-shaped objects (surface find). Two types of container have been used during the experiments to pour the melt: 'casting sand' and ashes. It is unlikely that casting sand was used at the VC but observations on VC objects permit to show that the pouring receptacle must have been made with a material that did not react, as VC slag/copper/matte ingots generally show smooth surfaces with no sign of reaction. The pouring of the melt may also have had the advantage of homogenizing it, which can be sought after to obtain a better metallic copper/impurities separation (Hauptmann et al., 2003).

The pouring hypothesis is also reinforced by the on-site discovery at Puen Baolo of complete crucibles with a pouring spout, even if these crucibles are surface finds with no associated context and must be interpreted with caution.

6. Conclusion

Despite no local raw materials (from VC) have been used, the experimental reconstruction was largely successful, resulting in intermediate products of metallic copper and matte using a simple internally-heated crucible. The results allow us to strengthen a major part of the field observation and laboratory-derived hypothesis, that the crucibles' form and composition are adapted to a high temperature process and have a practical usable volume.

With one exception, all charge ratios tested produced metallic copper in varying amounts. Different types of matte (matte containing only copper and sulfur, matte with copper, sulfur and iron and a matte with copper, sulfur and an increased amount of iron) were produced, dependent on the original charge. The products from the malachite/chalcocite charges have shown good correspondence to the archaeological examples, which supports their having been co-smelting in a one-step process in the VC. The VC process did not, perhaps, have the purpose of treating sulfidic ores but to directly obtain metallic copper, their process was therefore not necessarily adapted to the near-complete removal of sulfur. Experiments have also shown that a matte layer only formed if the charge contained at least 20% of sulfidic ore. We can also ask what happened in the following steps of the *chaîne opératoire*? Were the VC smelters aware of the potential re-processing of matte? Was it of economic and/or cultural pertinence for them to do so, if aware? Re-use of the matte produced during these experiments could be also tested in order to collect further information in the future. This

gives various possible outcomes to the VC technological reconstruction but we view the reported experiments as a step forward.

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