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# A new piece of the puzzle: slag and ore analysis to reconstruct the prehispanic smelting technology at the Atacama Desert, Chile

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## Abstract

The Incas appropriated many local metallurgical technologies throughout the Andes, each of which had its unique peculiarities and was based on local ancestral knowledge. The widespread use of tin-bronze during the Inca expansion, the development of mining and smelting sites, as well as ethno-historical records evidence the Incas' interest in copper smelting, a key activity in the Andes since *ca.* 1400 BC. However, little is known about the technical parameters achieved by ancient metallurgists and the changes that occurred during the Inca expansion. In this paper, we address these changes through a case study of Copiapó valley, focusing on the Viña del Cerro site, one of the most famous Inca smelting centres of the southern Andes. Although this place was architectonically restructured by the Incas, its operations began long before the imperial expansion and used wind-powered furnaces. We analysed 19 slag and 11 copper ore samples using OM, SEM–EDS, WD–XRF, and XRD analyses. Results identified heterogeneous and viscous slags, rich in SiO<sub>2</sub> (43 wt%) and poor in FeO (13 wt%). Copper retention was high (up to 60 wt%). Microstructural analyses indicate that slags were formed under unstable oxidising conditions, reaching temperatures that ranged between 1000 to 1100 °C. The copper produced was very pure. High-grade copper ores containing up to 69 wt% CuO were reduced at the site, combining carbonates (malachite, azurite), halides (buttgenschachite, clinoatacamite), and some sulphates (brochantite). We propose that even under the relatively unfavourable conditions for slag formation, the smelting conditions generated at Viña del Cerro were competent enough to extract metal, but not necessarily enough to form liquid slag. These conditions were facilitated by the local metallurgists' thorough knowledge of the wind flow and their ability to select the right ore. This new information contributes to understanding the efficiency of metallurgical technology and the knowledge, skills, and adaptability of the ancient metallurgists from Copiapó valley, a group that was integrated into the economic networks of the Inca Empire.

**Keywords** Copper smelting, Slags, Wind-powered furnaces, WD–XRF, XRD, SEM–EDS, Copper-rich ores, Andean metallurgy, Viña del Cerro, Atacama Desert

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## Introduction

Studying metal production offers both advantages and complexities due to its extensive *chaîne opératoire* that links diverse production systems, activities and people [2, 3]. This allows us to explore and reconstruct different relevant technical and social spheres, starting with the identification of the ore, its extraction, reduction, and the production of a metal object, to its distribution, use, meaning, and disposal. In some cases, all the different pieces in this large technological puzzle can occur within a single society, community or polity; in other cases, such as in the Inca Empire, these diverse processes connected different communities and people across the Andes [4–6].

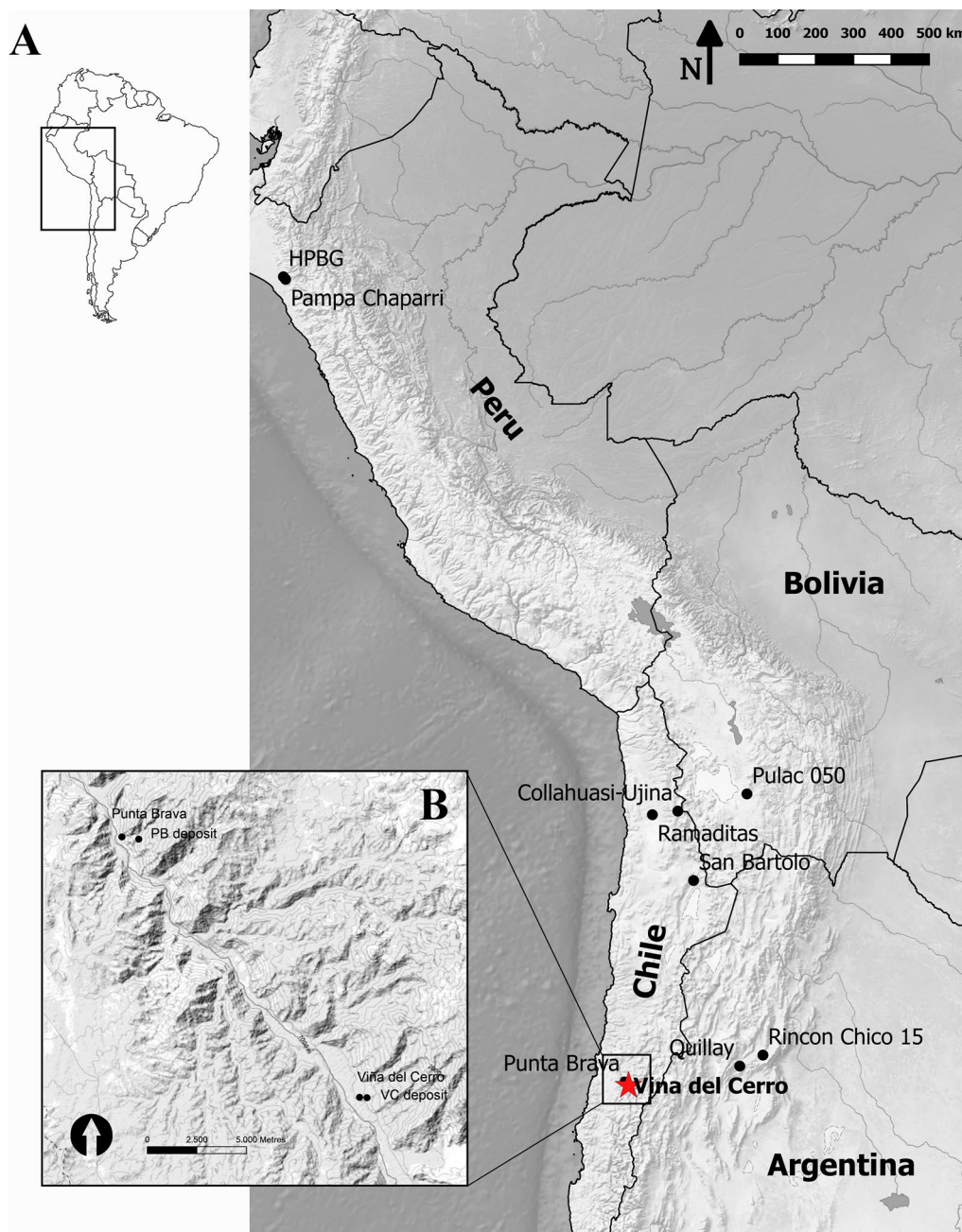
The Incas controlled specific technologies and alloys [7], increased mining labour ([8–10] and many more), and transformed numerous smelting centres and metallurgical workshops [6, 11–13]. In fact, one primary motivation for the Incas to expand towards the *Collasuyu* or southern provinces was the mineral richness of these regions and the presence of expert miners and metallurgists [14]. Even today, the South Central Andes (i.e. south Peru, northern Chile, northwest Argentina and eastern Bolivia) remains one of the world's major sources of copper, tin, silver, gold, and many other minerals [15]. The reason for the imperial interest in these metals is their symbolic meaning, which is linked to the strategic use of metallic artifacts as prestige goods that facilitated a system of wealth finance [7, 16–18]. Metals were offered as gifts to establish political relations with local elites. These ceremonial gifts established a debt relationship with the Incas that had to be repaid through local labour under the *mit'a* system, a form of corvée labour [9, 19].

Since metals were deeply embedded with symbolic meanings within the Andean world, they were an ideal media to spread imperial ideology [4, 7, 19]. For instance, while gold and silver were associated with the Inca elite and deities, copper was predominantly used by commoners. Cosmologically, gold was considered the sweat of the sun, and silver was regarded as the tears of the moon [19]. The Incas extensively adopted tin bronze technology across the empire, building on a technology that had long existed in Bolivia and northwest Argentina [20, 21]. The scarcity and concentrated distribution of tin sources facilitated Inca control over the region's metallurgical centres. To prevent local polities from seizing or disrupting tin bronze production, the Incas employed a decentralised mode of production by geographically separating mining, smelting, and metal artefact crafting locations [5, 6]. In regions like the Copiapó Valley and other imperial provinces, key Inca tin bronze artefacts include *tumi* knives, bracelets, circular plates, and *tupu* pins [19, 22, 23].

However, despite copper's importance in the ancient Andes, there is little information about the strategies on metallurgical technologies practised in the Andes. To successfully extract metal from ore, metallurgists experimented with several “ingredients” such as ore, fluxes, fuel, airflow, and the devices or containers where these raw materials could react and reach the required temperatures and atmospheres. These procedures were, in many cases, accompanied by specific ritual behaviours [24–28]. Under favourable conditions, the right combination of raw materials would lead to successful smelting. This would result in clean metal on the one hand, and a by-product called slag, on the other. The extracted metal is rarely found at the sites, as this final product is usually used and traded. Slag, however, which is generated in larger amounts and does not have other uses,<sup>1</sup> remains in the production sites as a silent witness of the smelting process. Fortunately, we can make slags “talk”. The archaeometric analysis of slag can potentially yield information about the metal produced, the ores and fluxes used, and other process parameters such as redox conditions, temperatures achieved, and length of the process, among other data ([26, 29–39] and many others). Interpreting this information allows archaeologists to understand the cost–benefit dynamics of the metallurgical process, the skills of ancient metallurgists, and a range of social and technical behaviours. These behaviours include knowledge transmission, technological traditions, and how these evolve in response to diverse environmental and cultural constraints [29, 30].

In the Central and South-central Andes, archaeological smelting sites were not very common. Yet, these sites started to appear in increasing numbers when archaeologists began to search in areas such as southern Bolivia, northwest Argentina and northern Chile [12, 40–43] and others] (Fig. 1A). Studies on the smelting process to understand the technical parameters and skill achieved by ancient metallurgists are even more rare. Furthermore, some results of the few known studies are not completely published or publicly available [13, 35, 38, 43–46]. This paper aims to contribute to this topic by characterising a specific technology developed in the Atacama region (northern Chile) at Viña del Cerro (Fig. 1), a renowned complex that produced copper since at least AD 1200, two centuries before the Inca arrival in the region [6, 12]. We use chemical and microstructural analysis on slags and copper ores to provide insights into the composition of the furnace charge, firing temperature, and redox conditions.

<sup>1</sup> Limited secondary uses have been documented, e.g. some crushed slag can be found as temper in ceramics at some places [e.g. 29].

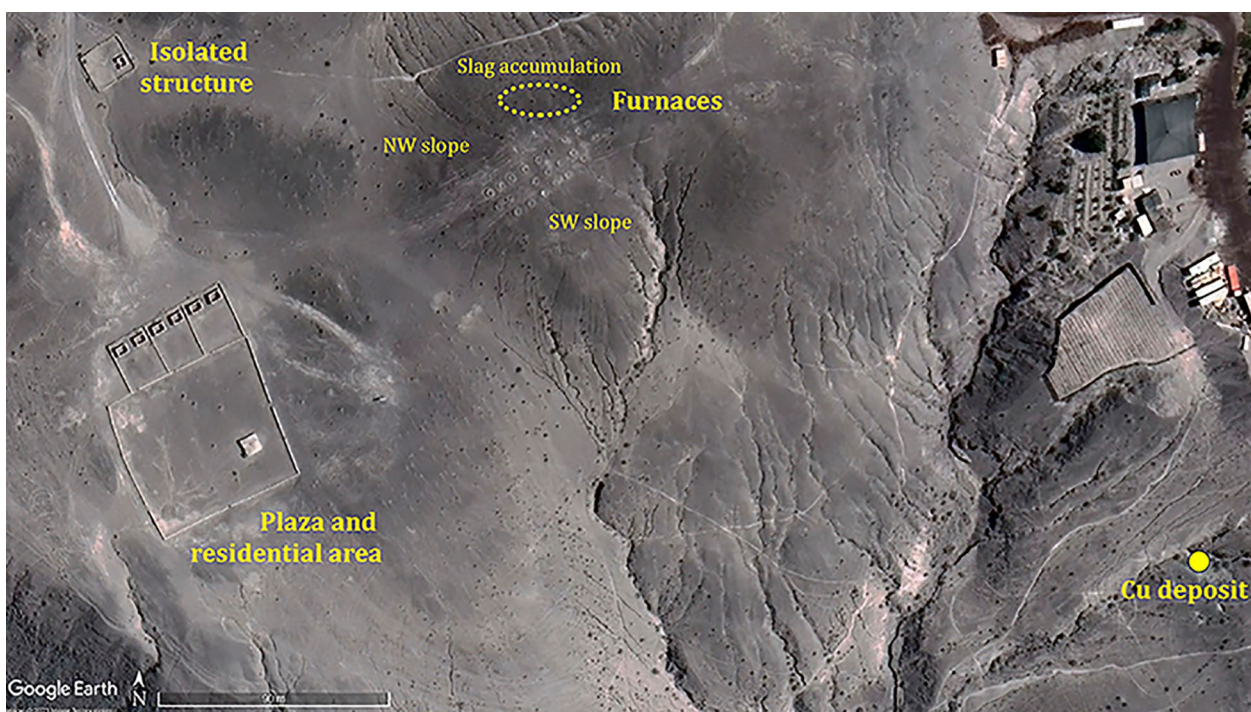


**Fig. 1** A Location of the sites mentioned in this paper. B Copiapó Valley with the location of Punta Brava, Viña del Cerro and nearby copper deposits

We argue that the characteristics of the slag from Viña del Cerro initially point towards a relatively inefficient smelting process. Considering the nature of the ore used and the characteristics of the site, we argue that despite these limitations, the process was efficient enough to successfully extract the required amount of copper from high-grade copper ores. This copper was essential for fulfilling the economic and political needs of both the local society and the Incas.

### Copiapó valley

Copiapó Valley is located at the southern edge of the Atacama Desert (Fig. 1), which is a geographically isolated region with an independent cultural history. Geologically, this valley and its surroundings encompass a vast copper metallogenic province [47]; the area is rich in copper deposits from hypogene and supergene ores. Hypogene Cu-ores are associated with copper-iron sulphides and iron oxides such as chalcopyrite



**Fig. 2** Image of Viña del Cerro (Google Earth 2023)

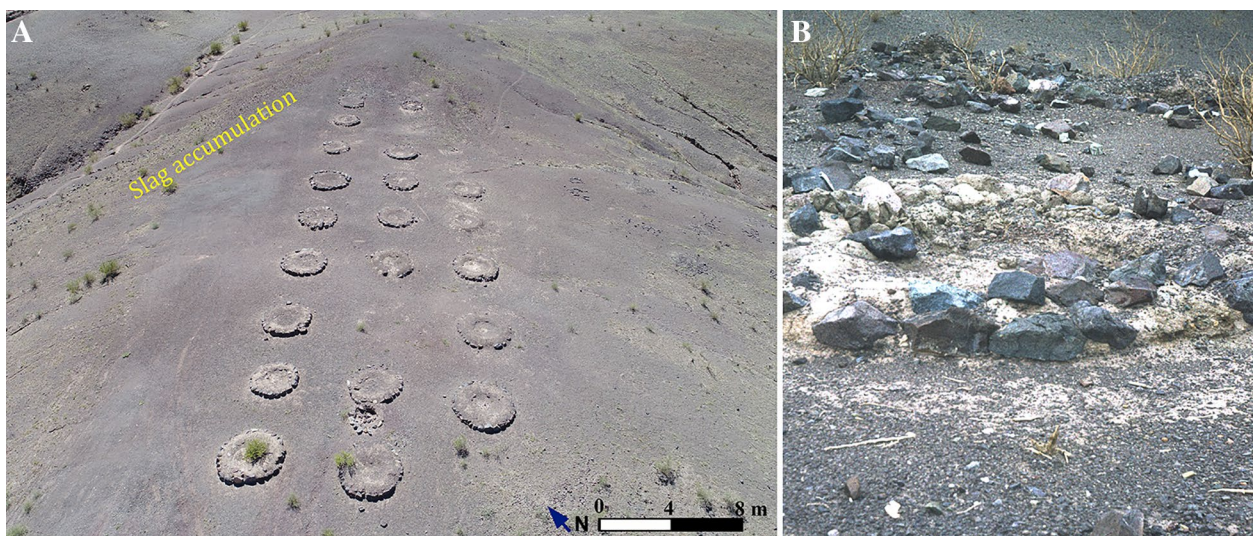
( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), magnetite ( $\text{Fe}_2\text{O}_3$ ), specularite ( $\text{Fe}_2\text{O}_3$ ), pyrite ( $\text{FeS}_2$ ), and marcasite ( $\text{FeS}_2$ ) [47]. Supergene copper deposits are dominated by covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), native copper, malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ), chrysocolla ( $\text{CuH}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), limonite ( $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), and cuprite ( $\text{Cu}_2\text{O}$ ). Quartz ( $\text{SiO}_2$ ), calcite ( $\text{CaCO}_3$ ), barite ( $\text{BaSO}_4$ ) and specularite ( $\text{Fe}_2\text{O}_3$ ); these are the main gangue minerals of these copper ores [47].

Archaeologically, the local population influenced by the Inca Empire is known as the Copiapó Culture. It was a decentralized society with low levels of social complexity and was characterized by a settlement pattern consisting of small scattered agricultural villages comprised of clusters of circular stone structures and a distinctive black-on-red pottery style [48–50]. The presence and impact of the Inca Empire in the valley varied across different areas, depending on the negotiations with individual local chiefs [50]. While some communities remained unaffected, in other places the Incas modified the layout of local villages by incorporating public buildings with a distinctive rectangular style [51, 52]. This might have served as a means to secure political and labour cooperation from the local population.

### Viña del Cerro

One of the primary Inca sites in Copiapó Valley is Viña del Cerro (“VC”), situated in the upper course of the valley (Fig. 1B). This expansive facility spans across 5.5 hectares and exhibits Inca orthogonal architecture, which includes a plaza, a possible ceremonial platform, and 26 round structures believed to be smelting furnaces (Fig. 2) [12, 48, 53, 54].

These 26 structures, with a diameter of approximately 2–3 m, are constructed walls made of rocks that reach a height of 30 cm (Fig. 3). Strategically positioned atop a small hill and located about 100 m from residential structures, they are exposed to strong winds during certain hours of the day. The structures are arranged in three rows consisting of 7–9 units each, following a SW-NE direction (Fig. 3A). The initial excavations conducted at VC in 1974 [48] revealed that some of the foundations were filled with rocks and mortar, while others had plain mud or mud bricks (Fig. 3B) [6, 12, 52, 53]. Minerals, slags, and charcoal fragments used to surround these structures, which have been looted by local miners over time. No clay wall fragments have been found, suggesting the absence of combustion structures resembling the wind-driven *huayras* known in the Potosí area [40, 55]. However, numerous medium and small-sized angular rocks were discovered, which likely formed part of the original pyrometallurgical structures. Nevertheless,



**Fig. 3** **A** Recent view of the smelting furnace bases in Viña del Cerro, after their restoration in 1982 (Image: F. Garrido). **B** Image of one of the furnace bases before restoration. Note the rocks and possible mud blocks in the base (Image: H. Niemeyer)

neither the initial excavations of these structures in 1968 and 1974, nor our own in 2019 provided evidence of direct burning on the ground. Consequently, it is plausible that these round platforms served as furnace bases, and that the actual smelting took place inside smaller devices situated on top of them.<sup>2</sup>

The residential area comprised of six small and highly elaborated square structures (Fig. 2), suggesting that only a few individuals were responsible for managerial functions at the site. Workers and miners likely lived offsite, along the bottom of the valley [6] in nearby local villages such as Punta Brava (“PB”; Fig. 1B), located at about 25 km downstream from VC [52]. Among the activities carried out in VC residential area, people processed red pigment (iron oxides) and larnite ( $\text{Ca}_2\text{SiO}_4$ ), a white calcium silicate mineral [6].

Interestingly, at PB there is no evidence of metallurgical activities. However, a copper ore concentration was present in the courtyard of one of the main residential compounds (unit No. 26), despite the fact that no grinding equipment for mineral beneficiation has been reported in this context. This site is also located relatively near copper deposits that have been exploited in more recent times [52–54]. During our surveys, we identified a potential ore deposit near VC (Fig. 2). However, the lack of archaeological mining and ore processing evidence at VC, alongside the small size of the vein, suggest that most

of the ore used in VC came from elsewhere, most likely from PB [52].

Until recently, VC was considered a good example of wealth finance production in the southern Andes, following the Inca pattern of intensification of production by building infrastructure and centralising the production of copper and metallic artefacts in order to supply the valley and the region [4, 5, 12, 52–54, 56]. However, new <sup>14</sup>C dates enable a re-evaluation of the site to indicate that VC was a local smelting site from the Late Intermediate Period (“LIP”, AD 1000–1400). Subsequently, it was reconstructed and supervised by the Incas during the Late Period (“LP”, AD 1400–1536), while continuing to rely on local labour for its operations [6]. Despite its size, it is likely that it was not intensely occupied, as evidenced by the low density of refuse deposits and metallurgical production remains recovered in previous and recent excavations [6].

At VC, metallurgists were producing pure copper, ruling out for now the probability of co-smelting tin or arsenic-rich ores [6]. In Copiapó Valley, a compositional study of nearly 400 metallic objects from the Late Horizon (AD ~ 1400–1530) determined that 90% of them were made of tin or arsenic bronze [6, 22]. Therefore, these metallic objects were not cast or alloyed at VC, based on the lack of archaeological evidence for such activities [6]. Furthermore, there is no evidence of workshops in the valley that could produce a relatively large supply of metal objects. Considering the destination of the pure copper obtained at VC, it is possible that VC was mainly supplying metallic copper to workshops most likely located in northwest Argentina (“NWA”), participating in

<sup>2</sup> In 1982, Hans Niemeyer restored the residential structures, perimeter walls, and furnace foundations. Specifically, the residential structures were raised by at least one metre through the addition of mud bricks.

a larger productive network controlled and coordinated by the Incas [4, 6]. Thus, instead of evidencing an example of production intensification for the local production and distribution of metallic objects, VC was a key part of a strategy of diversification and decentralization of production, articulated at a regional level by the Inca Empire. This strategy consisted in separating the different steps of the *chaîne opératoire* (i.e. mining, smelting, manufacture) to prevent any single community from controlling all aspects of the production of metal objects, so that the empire could maintain this role [4, 6].

Although VC offers a better understanding of the broader picture of how metallurgical production was being articulated at a regional level during the LP, there remain several research challenges. We know that the smelting technology used at VC had local roots, but there is no specific information regarding the smelting process; i.e. we do not know the technical parameters used by ancient metallurgists nor their variation through time. Thus, in this paper, we explore in depth the smelting technology used at VC. Following an archaeometric approach, we have analysed 19 slags and 11 ore samples from VC to determine the technical parameters used in the smelting process, such as temperatures, redox conditions, type of ores, fluxes, and metal produced, in order to reconstruct the particularities and metal recovery efficiency of the smelting technology employed. This information will create a basis for comparison between this particular technology and earlier smelting sites, to understand the development of metallurgical technology in Copiapó valley and the Atacama region, alongside the technological changes experienced during the times of the Inca expansion.

## Materials and methods

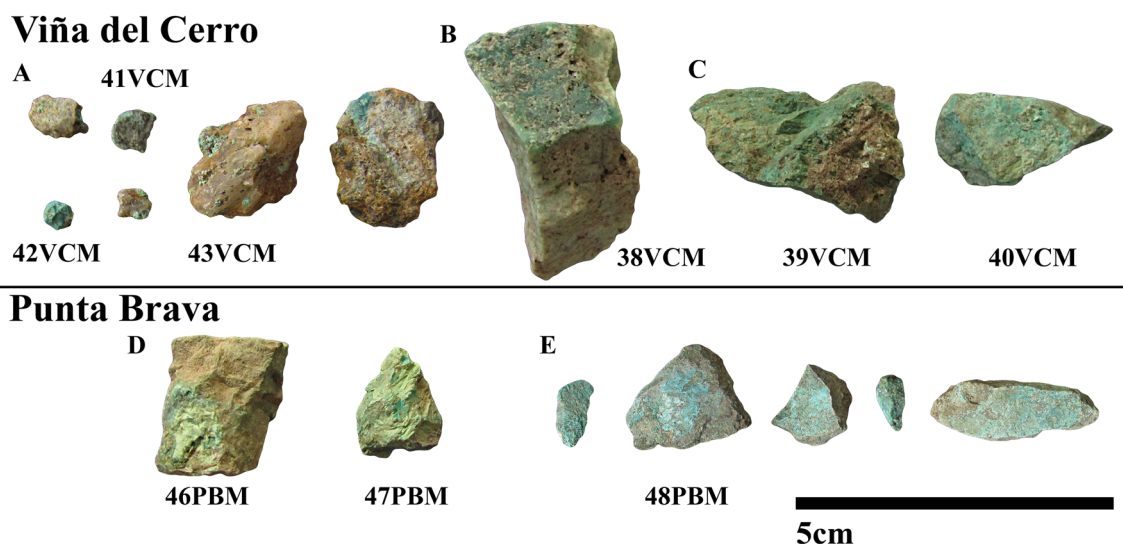
Slags both recovered in excavation and surface collection were included in this research. Slags were found within and near the 26 pyrometallurgical structures, but most of them are spread on the NW slope of the hill (Fig. 3). They present a dispersed distribution amongst middle-sized angular rocks of between 5 and 15 cm in length. Overall, slags are not very abundant, and they do not form a dense deposit. For their sampling, we considered their spatial distribution (i.e. different parts of the hill and pyrometallurgical structures excavated) and their morphological characteristics in order to represent different types of slags. The macroscopic features considered in the slags were their porosity, size, presence and absence of flow texture, visible inclusions and green staining on their surface. Around 230 slag samples were selected for this study, from which 19 were chosen for further analysis (Additional file 1).

Samples of ore were collected from VC, the PB site, and from mineral deposits near both of them (Fig. 1B). At VC, small green mineral fragments were collected around the furnace bases, the residential area and plaza (Fig. 2). In the initial survey of the site conducted between 1956 and 1958, archaeologist Jorge Iribarren noted the presence of green ore accumulations near the pyrometallurgical structures (no accumulations were mentioned in the residential area or plaza) [65]. However, when archaeologist Hans Niemeyer resumed the research of VC in 1968, the few ore fragments that survived the looting of contemporary small-scale miners were identified as chrysocolla<sup>3</sup> [38]. During our field visits, no piles of ore were seen at VC, and minerals were scant and scattered on the surface. Three samples were analysed (41–43VCM). Additionally, we found relatively large blocks of a green-whitish mineral dispersed on the SE slope of the hill, which were also analysed (Fig. 2; sample 38VCM) together with samples of a potential ore deposit identified at 400 m from the furnaces<sup>4</sup> (Fig. 2; samples 39–40VCM). As for PB, in 2019 we excavated a test pit in the residential compound No. 26 and collected surface ore samples for analysis. For this research, we selected four ore samples from the site (44–47PBM) and one sample from a potential ore deposit near PB (48PBM; Fig. 1B). In total, 11 ore samples were selected for detailed analyses.

We applied Optical Microscopy (“OM”) and Scanning Electron Microscopy (“SEM–EDS”) to describe and analyse mineral phases and internal microstructures in slags. We applied X-ray Fluorescence (“WD–XRF”) to obtain the chemical composition of slags and ore, and X-ray-Diffraction (“XRD”) to determine the mineralogy of the ores. The 19 slag samples were first documented at the macroscopic scale, and then we proceeded to obtain polished sections to be observed by OM and SEM microscopy following the standard procedure of mounting the samples in epoxy resin and preparing them by grinding on successively finer abrasive paper. Finally, they were polished with 1 µm diamond paste. OM was performed with a ZEISS Primotech MAT equipped with both polariser and analyser. Bulk elemental composition was estimated by a FEI Quanta 600 SEM fitted with energy-dispersive spectrometer (“EDS”), and Oxford Instruments INCA software to interface with the analyser. Operating conditions were typically 11 mm working distance, 25 kv and 4.0 of spot size. Samples were not coated, since the SEM was operated in Low Vacuum mode.

<sup>3</sup> There is no mention of the type of analysis employed to identify the minerals as chrysocolla.

<sup>4</sup> It is important to consider that samples from potential mining deposits are leftovers; they probably contain part of the main ore, but its grade is likely not as high as it was, and is probably richer in gangue minerals.



**Fig. 4** Examples of green minerals recovered at Viña del Cerro (VC) and Punta Brava (PB). Minerals from **A** VC site, **B** VC SE slope; **C** VC ore deposit; **D** PB site; **E** PB ore deposit. Note that the mineral 38VCM contains little copper, despite its green colour

Eighteen pieces of the 19 slags and the 11 ore samples were powdered for WD-XRF and XRD analyses. The samples were first crumbled in a Retsch BB51 jaw crusher and then milled to a grain size of approximately 50  $\mu\text{m}$ , using a Retsch RS200 vibratory disc mill equipped with a tungsten carbide container. The powder was dried to remove moisture; mixed with an alkali flux ( $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ , 34/66% wt.) and fused at 1150  $^\circ\text{C}$  in a Pt-Au crucible using a PANalytical Per'X3 fluxer to obtain a glass disk. The bulk chemical analyses were carried out using an Axios PANalytical WD-XRF spectrometer (calibration details in Additional file 2). For XRD analysis, we used a X'Pert PRO MPD PANalytical diffractometer. A small quantity of milled sample ( $\sim 1$  g) was placed on a back-load sample holder, and the interpretation of the resulting diffraction pattern was performed with the PANalytical Highscore Plus v4.7 software and the ICSD database. Semiquantitative analysis was carried out according to the Chung method by using High Score Plus software, based on the Reference Intensity Ratios (RIR) of the existing phases [57]. All analyses were undertaken at the Microscopy and Micro-computed tomography, and Archaeometry laboratories at the Centro Nacional de Investigación sobre la Evolución Humana (CENIEH, Burgos, Spain).

## Results

### Ore

XRD results indicate that ores found at the sites VC (41–43VCM) and PB (44–47PBM) are combinations of copper carbonates such as malachite and azurite; copper halides such as buttgenschite (or possibly connellite)

and clinocamite; and brochantite, a copper sulphate (Fig. 4; Table 1). The  $\text{CuO}$  content in these samples is high, between 22.2 and 68.8 wt%, except sample 46PBM with 9.8 wt% (Table 2; Fig. 5). Samples are also rich in silicates such as quartz and phyllosilicates (between 10.7 and 76.0 wt%  $\text{SiO}_2$ ), which aligns with the high amount of  $\text{SiO}_2$  identified in VC slags (Fig. 5), and the gangue expected in these minerals (see "Copiapó valley"). Iron contents are low, between 1.4 and 7.4 wt%  $\text{FeO}$ , except in sample 42VCM, where hematite was detected (18.5 wt%  $\text{FeO}$ ). The samples taken from a copper deposit near VC (39–40VCM) contain between 8.2 and 16.2 wt%  $\text{CuO}$ , possibly derived from malachite and clinocamite. In the case of the deposit near PB (48PBM), samples contain malachite and brochantite, together with quartz and phyllosilicates. Both potential ore deposits contain copper minerals that are consistent with the findings at the archaeological sites. Likewise, the ores found at PB are similar to the ones found at VC. Thus, as proposed before [53], it is quite likely that mineral used at VC came in part from PB. Interestingly, the sample of green and whitish mineral (38VCM) found in big blocks at the SE slope of the hill at VC is mainly composed of silicates and calcite, with scant copper content (1.2 wt%  $\text{CuO}$ ) in comparison with the rest of the ore assemblage. Its composition rules out for now its use as copper ore, and explains its presence as unused large blocks.

### Slags

The slags from Viña del Cerro are fragmented porous pieces of  $\sim 2$ –6 cm long showing black to dark grey colours in surface, frequently showing reddish and

**Table 1** Mineralogy of 11 samples expressed by relative presence of different minerals, by XRD

Mineral type	Mineral	Formula*	Viña del Cerro (VC)										Punta Brava (PB)			
			Site					SE slope					Site			
			41VCM	42VCM	43VCM	38VCM	39VCM	40VCM	44PBM	45PBM	46PBM	47PBM	48PBM	Mine		
Copper carbonate	Malachite	$Cu_2CO_3(OH)_2$	xxx	-	-	-	-	xx	-	-	xxx	-	-	-	xx	
	Azurite	$Cu_3(CO_3)_2(OH)_2$	-	-	-	-	-	-	-	-	-	-	-	xx	-	
Copper sulfate	Brochantite	$Cu_4SO_4(OH)_6$	-	xxx	xxx	-	-	-	-	-	xx	-	xx	-	x	
Copper halide	Buttgenbachite**	$Cu_{19}Cl_4(NO_3)_2(OH)_{32} \cdot 2H_2O$	-	-	xx	-	-	-	-	-	-	-	-	-	-	
	Clinoatacamite	$Cu_2(OH)_3Cl$	-	-	-	-	-	xx	x	-	-	-	-	-	-	
Silicate	Quartz	$SiO_2$	x	xx	-	xx	xx	xx	xx	xx	xxx	-	xxx	xx	xxx	
	Plagioclase	$(Na,Ca)(Si,Al)_4O_8$	-	-	-	-	-	-	xx	xx	-	-	-	-	-	
	Phyllosilicates	-	xx	xx	xx	xxx	xx	xx	xx	xx	xx	xx	xx	xx	xx	
Iron oxide	Hematite	$Fe_2O_3$	-	xx	-	-	-	-	-	-	-	-	-	-	-	
Calcium carbonate	Calcite	$CaCO_3$	-	-	-	x	-	-	-	-	-	-	-	-	-	
Phosphate	Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	-	-	-	-	-	-	-	-	-	-	-	-	(?)	

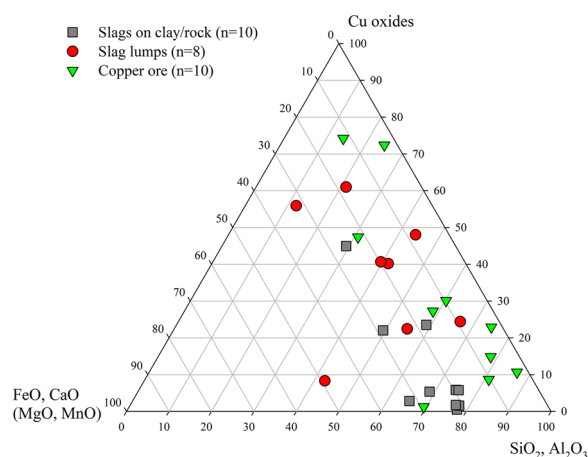
Samples were recovered from VC and PB. xxx = > 40% (major phase); xx = 10–40% (minor phase); x = < 10% (traces); ? = uncertain; — = not detected. (\*) From <http://webmineral.com>. (\*\*) Or connellite ( $Cu_{19}Cl_4(SO_4)(OH)_3 \cdot 3(H_2O)$ )



**Table 2** Elemental composition of 10 mineral samples, by WD-XRF (mayor compounds)

Sample	SiO2	CuO	Al2O3	As2O5	FeO	SO3	Na2O	K2O	MgO	CaO	Sb2O3	TiO2	P2O5	MnO	Analytical total*
Viña del Cerro (VC)	41VCM	17.6	68.8	5.7	bdl	2.2	1.2	1.9	1.6	bdl	bdl	bdl	0.1	bdl	81.7
	42VCM	21.7	41.8	5.6	bdl	18.5	7.7	1.9	1.9	0.1	bdl	bdl	0.1	bdl	93.1
	43VCM	10.7	57.9	0.2	15.1	5.3	4.9	1.8	bdl	2.4	bdl	bdl	0.2	bdl	93.6
SE slope Deposit	38VCM	46.7	1.2	21.2	bdl	1.9	0.3	1.6	bdl	bdl	bdl	bdl	0.1	bdl	97.7
	39VCM	46.5	26.2	9.7	bdl	9.2	0.4	1.3	1.1	3.3	bdl	1.0	0.2	0.3	88.2
Punta Brava (PB)	40VCM	60.2	8.2	16.0	bdl	5.5	0.2	2.6	1.5	2.2	bdl	1.2	0.5	0.2	88.7
	44PB	48.6	28.2	7.8	0.9	7.4	2.4	1.8	bdl	0.7	1.3	bdl	bdl	bdl	91.4
	45PB	na	na	na	na	na	na	na	na	na	na	na	na	na	na
VC site+PB Site	46PB	76.0	9.8	3.7	3.5	1.5	0.9	1.1	0.3	0.1	1.0	0.9	0.3	bdl	95.3
	47PB	65.1	22.2	7.0	bdl	1.4	0.3	0.7	1.3	bdl	bdl	0.9	bdl	bdl	88.1
	48PB	62.6	13.9	10.9	1.6	4.4	0.7	1.5	0.6	0.0	bdl	0.7	1.0	bdl	90.2
Average	<b>39.9</b>	<b>38.1</b>	<b>5.0</b>	<b>6.5</b>	<b>6.0</b>	<b>2.9</b>	<b>1.5</b>	<b>1.3</b>	<b>0.8</b>	<b>1.0</b>	<b>1.1</b>	<b>0.9</b>	<b>0.2</b>	-	-
SD	27.2	22.4	2.7	7.6	6.5	2.9	0.5	0.7	1.1	0.3	0.2	0.0	0.1	-	-
Min	10.7	9.8	0.2	0.9	1.4	0.3	0.7	0.3	0.1	0.7	1.0	0.9	0.1	-	-
Max	76.0	68.8	7.8	15.1	18.5	7.7	1.9	1.9	2.4	1.5	1.3	0.9	0.3	-	-

na = not analysed; bdl = below detection limits. Data are normalised at 100 wt% with oxygen added by stoichiometry, reporting the analytical totals (\*). CuO wt% is highlighted, sample 45PB had enough material for WD-XRF



**Fig. 5** Ternary diagram CuO-(SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>)-(FeO, CaO, MgO, MnO) showing the bulk chemical composition of 10 ore samples and 18 slag fragments and from VC, by WD-XRF. Note the similar compositions between copper ores and slags

green spots, typical of copper oxidation. The texture is generally smooth with thick flow signals, many presenting drop-shaped bumps (Fig. 6). Characteristically, many of them are found adhered to an orange clay layer (possibly soil) or a piece of rock that assumed a tablet-like shape in these cases (Fig. 6A–E). When the clay layer is absent, the fragments tend to be smaller, bulkier and of bulbous appearance, presenting more evident signals of flowing (Fig. 6H–O). Significantly, the 110 specimens adhered to clay or rocks tend to be less fragmented, and can form cakes up to 10 cm long; only 15% of them reacted to the magnet (moderate–strong). In contrast, the 119 specimens not attached to clay or rocks rarely reached 4 cm long, and 59% of them showed moderate to strong magnetism. It is relevant to note that the fractures in both cases are natural, ruling out the possibility of intentional crushing activities at the site, as reported at other Inca sites from northern Chile [13, 58].

In polish section, their texture is quite heterogeneous, showing abundance of large vacuoles (up to ~1 cm) and porosity left by gas bubbles (Fig. 6E, J, L). Equally abundant are partially or unreacted inclusions of relatively large size minerals (up to ~5 mm width) largely white in colour. Both unreacted inclusions and mineral fragments are joined by a very irregular molten matrix, more ceramic than glassy in appearance (Fig. 6D–E, I, J, L). Occasionally, small round brownish prills are visible on the fresh section or distinguishable on the surface (Fig. 6F–G, M–O). Charcoal imprints are noticeable in a couple of specimens (Fig. 6P).

### Microstructure and mineralogy

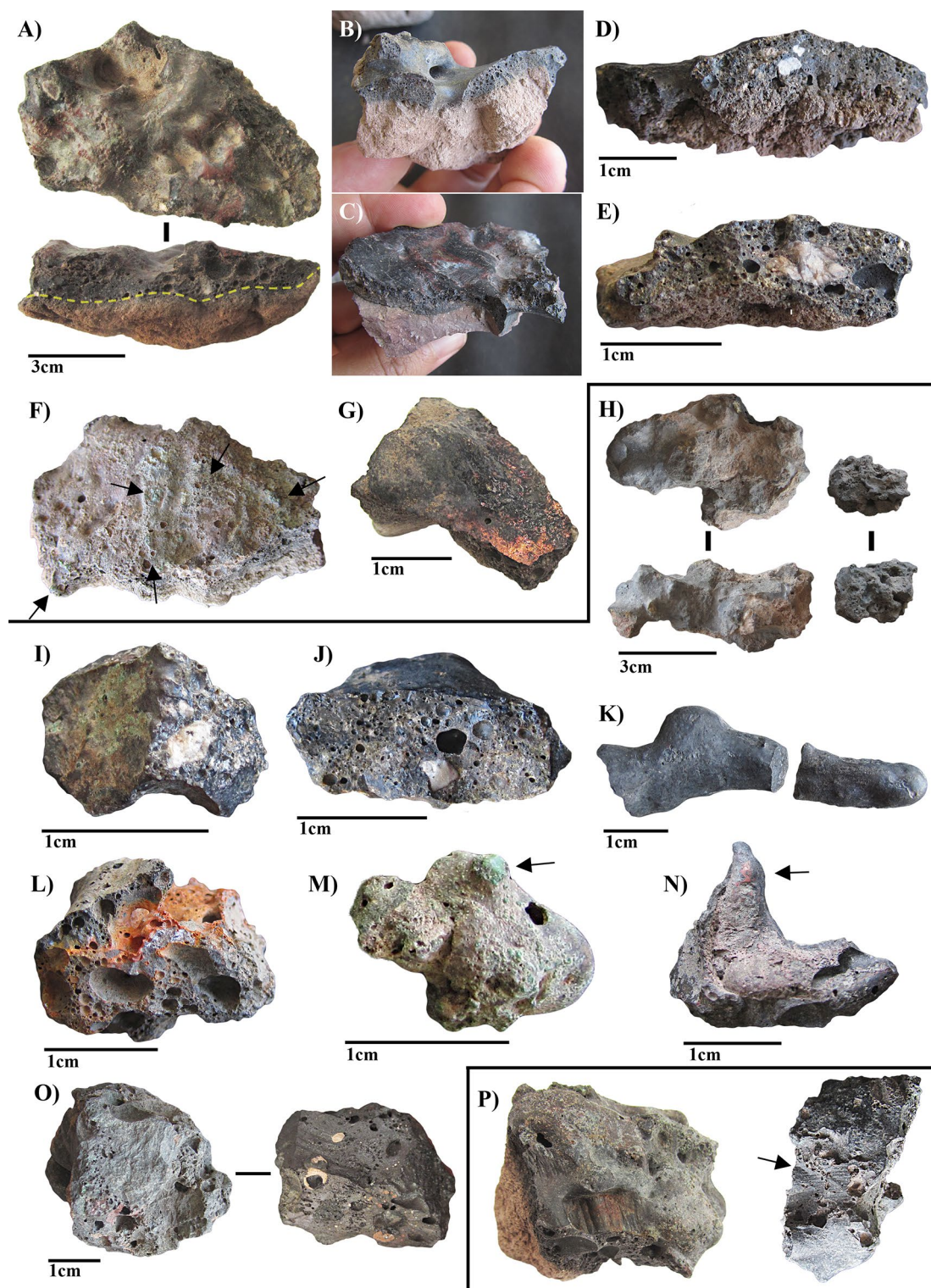
The microstructure of the slag is quite similar in all the specimens, more similar in appearance to technical ceramics than to slag, showing abundant porosity and sporadic glassier areas. Overall, they typically present a silicate or ceramic-like matrix, characterised by high porosity, plenty of bubble gas cavities, and very abundant partially reacted or sometimes barely reacted inclusions (Fig. 7A, B). Unreacted and cracked quartz grains are present in almost all samples (Fig. 7A, B, E). Although iron oxides are common, they are less frequent in the silicate matrix, typically forming masses (Fig. 7H) or bands of intermediate phases of hematite (Fe<sub>3</sub>O<sub>4</sub>) and magnetite (Fe<sub>2</sub>O<sub>3</sub>). Well-formed skeletons crystals or flakes of tiny size are much more rare (~20 μm; Fig. 7F, G) (Additional file 3).

Less abundant but equally quite recurrent in all the specimens is the appearance of relatively short areas of a glassier matrix. These areas are, to some extent, randomly interspersed within the silicate matrix (Fig. 7C, F). Preferentially within the glassier areas, the microstructure is usually dominated by dendritic cuprite (Cu<sub>2</sub>O) and crystals (lattice) of delafossite (CuFeO<sub>2</sub>) of variable size which typically range 100–200 μm, although it is not rare to find these crystals appearing intermittently within the more silicate matrix areas (Fig. 7D, J). Another frequently observed texture is a transitional phase between the partially or barely reacted inclusions and reduced Cu-prills. These consist of undetermined phases of oxides, often Cu-rich silicates, which are occasionally iron-rich. These tend to be tiny pseudomorphs or globules that also tend to form dendrites (Fig. 7E, H, K, L). More rarely, they contain areas of reduced metal, and they may also correspond to partially reacted oxidic or carbonate copper ore relicts (see previous section). As may be expected, slags attached to clay or rocks show fewer glassier areas, a more silicate matrix, and plenty of semi-reacted inclusions. In contrast, the smaller slag lumps of smooth bulky appearance are richer in glassier areas.

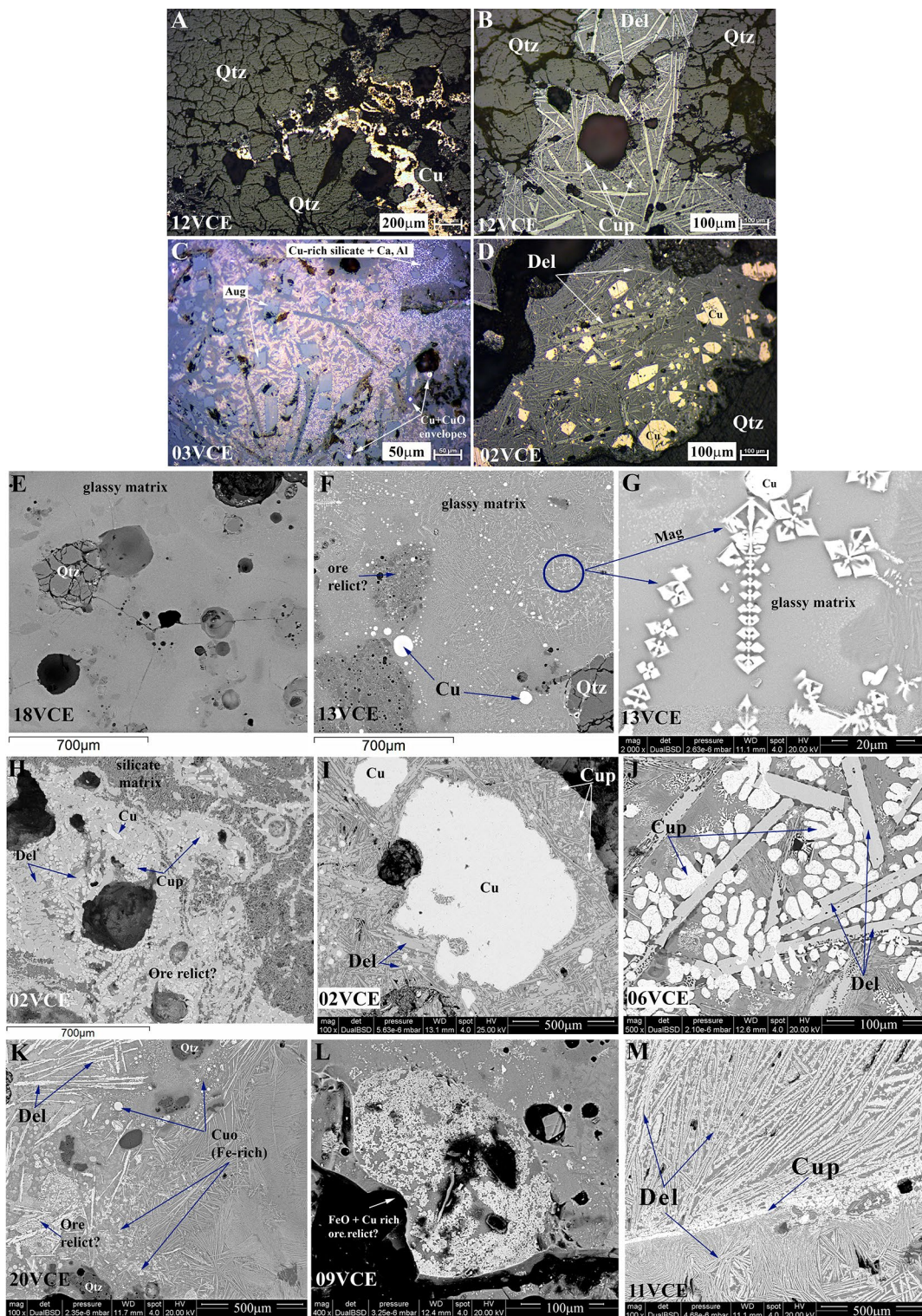
In general, the VC slag texture is similar to what Hauptmann [23, 52] describes as phases formed by reactions in the solid state, where solid elements interact with partially liquefied parts over short periods of time (Fig. 7A, B). Overall, VC slags are viscous, trapping large copper prills and showing partially reacted and unreacted areas (Figs. 6O, 7D).

### Copper prills

Other very frequent phenomena are Cu-prills and droplets. These typically present an outer envelope of oxides (cuprite (Cu<sub>2</sub>O) or tenorite (CuO)). If the droplets are large, they show β phases (dendrites) of cuprite, or



**Fig. 6** Slags from Viña del Cerro. **A–G** Examples of platy slag adhered to clay or rocks. **H–O** Examples of slag lumps. **D, E** Detail of unreacted minerals. **F** Detail of green mineralization and possible copper prills. **G** Metallic lustre (18VCE). **I, J** Detail of unreacted minerals within the slag. **L** Detail of reddish areas, **M, N** Visible copper prills, **O** Surface and interior of a lumpy slag 11VCE, note the amount of copper visible to the naked eye. **P** Fragments with charcoal imprints



**Fig. 7** Microstructure of slag samples from Viña del Cerro. **A–D** Under plain and cross polarised light (OM). **E–M** Backscattered electron image (SEM). Legend: Cu: metallic copper, Cup: cuprite, Del: delafossite, Qtz: quartz fragments, Aug: augite, Mag: magnetite

**Table 3** Averages of point analyses on copper prills and copper masses within 15 slags samples, by SEM–EDS

Slag id (#Cu prills)	O	S	Fe	Cu	As	Ag	Refs.
5 (1)	–	–	–	100.0	–	–	
6 (3)	–	–	–	100.0	–	–	
15 (1)	–	–	–	100.0	–	–	
20 (1)	–	–	–	100.0	–	–	
19 (5)	0.6	–	–	99.7	–	–	Garrido and Plaza [6]
17 (1)	0.3	–	–	99.7	–	–	Garrido and Plaza [6]
8 (3)	0.3	–	1.9	99.0	–	–	Garrido and Plaza [6]
11 (2)	–	–	1.5	98.5	–	–	
10 (3)	3.6	–	–	98.2	–	–	Garrido and Plaza [6]
14 (1)	–	–	–	98.0	–	–	
13 (5)	1.3	–	1.8	97.7	–	–	Garrido and Plaza [6]
7 (13)	0.8	–	2.1	97.0	–	–	Garrido and Plaza [6]
3 (3)	3.5	–	–	96.2	–	0.4	Garrido and Plaza [6]
2 (4)	–	2.8	0.7	89.6	–	6.8	
16 (5)	–	–	1.0	89.3	9.7	–	

Values are normalised to a 100, expressed in wt% and organised by copper content. The numbers in parentheses show the number of prills analysed, from which the averages were calculated. Legend: (–) Not detected

intermediate unstable phases. The metal rich phases are of very variable size ~5–2500  $\mu\text{m}$  albeit the bulk of them range between ~200 and 600  $\mu\text{m}$ , often visible in section to the naked eye (Fig. 71). The roundness of most prills suggests that they were solidified from a completely liquid state. SEM–EDS analysis indicate that the copper produced at VC was relatively pure, mostly 96–100 wt%Cu, with the occasional appearance of up to ~2% Fe and ~3% O (Table 3). In only three slag samples, the copper contained other impurities such as sulphur, arsenic, and silver, but these are extremely rare, in alignment with their anecdotal levels detected in the bulk chemical composition (see below).

#### Chemical composition

The bulk chemical composition of 18 samples was obtained by WD–XRF (Table 4). The results show that on average, the VC slags comprised mainly of silicates (~43 wt%), iron oxides (~13 wt%), alumina (~9 wt%), lime (~7 wt%), and an extremely high and variable copper oxide content (~22 wt%; Fig. 5). The chemical composition is supplemented by small amounts of MgO, Na<sub>2</sub>O, K<sub>2</sub>O (~1.4–1.9 wt% each), whereas other transition metals such as titanium, manganese, and zinc are typically present in concentrations below 0.6 wt%. The levels of sulphur and arsenic detected are very low (<0.5 wt%), and the striking variation among the principal oxides is notable: SiO<sub>2</sub> 11–60 wt%, FeO 7–26 wt% or CuO 0.5–59 w% (Fig. 8).

Table 4 shows the compositional difference between the slags attached to clay cakes or rocks, and the single

lumps observed macroscopically (Fig. 5). Overall, the group attached to clay or rocks shows a higher content in ceramic compounds: more than ~10 wt% in SiO<sub>2</sub>, ~6 wt% in Al<sub>2</sub>O<sub>3</sub> and ~3 wt% in CaO than the single lumps. In this case, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are positively correlated, suggesting that both oxides have common origins. Correspondingly, their values are higher in rocks and clay than in slags (Additional file 4), indicating that the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> enrichment in these slags reflects the interaction with the clay and rocks during the smelting process [59]. In contrast, slag lumps are ~5 wt% richer in iron oxides and remarkably higher in copper oxides (~26 wt% more).

Based on the chemical composition, it is possible to assess the viscosity of the slags calculating the K-index, as proposed by Bachmann [36] and Addis et al. [60]. The K-index is the ratio of the viscosity-reducing oxides (CaO + FeO + MgO + MnO + K<sub>2</sub>O + Na<sub>2</sub>O), against viscosity increasing-oxides (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>). The higher the K-index, more fluid the slag. In the case of VC slags, the K-index values are between 0.2 and 0.9, most of them under 0.5 (Table 4), with two exceptions, 1.2 (16VCE) and 2.7 (02VCE). These values show that most slags were highly viscous, and even in the case of sample 02VCE with a K-index of 2.7, copper retention was high (54.9 wt%). The most liquid slag is sample 16VCE, with high FeO (23.1 wt%) and CaO (24.4 wt%).

#### Discussion

##### Technical parameters and raw materials at Viña del Cerro

As introduced above, the VC slag fits well as a heterogeneous by-product of partially reacted materials, mineral

**Table 4** Bulk chemical composition of 18 slag samples from VC, by WD-XRF, organised by slag type (attached to rocks, clay or lumps) and id number

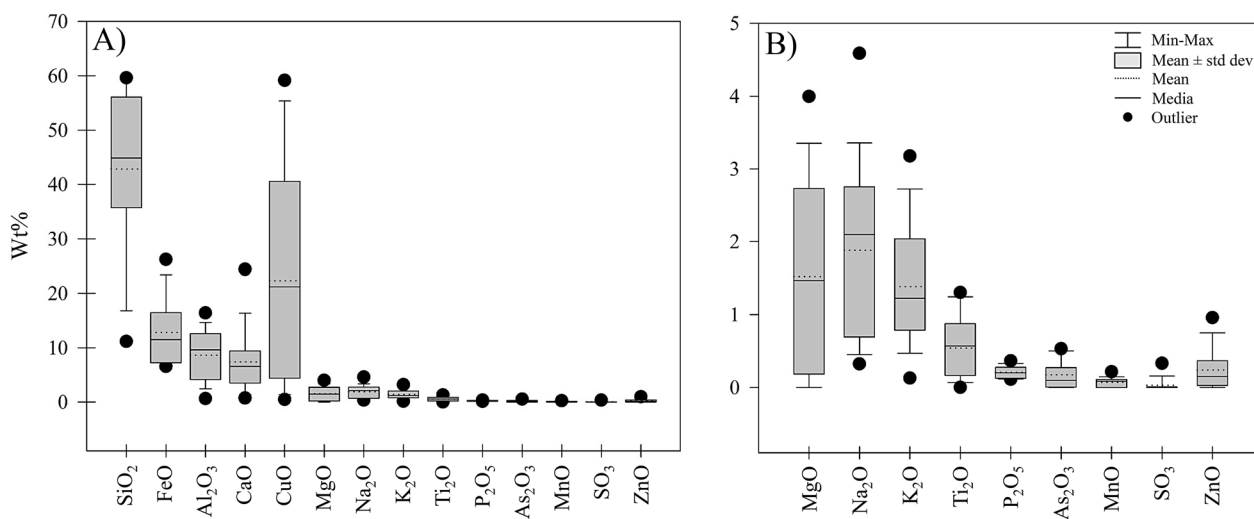
Samples	Slag	SiO <sub>2</sub>	CuO	FeO	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	ZnO	P <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>3</sub>	MnO	SO <sub>3</sub>	Analytical total*	K-index
03VCE	Rock	37.9	20.9	8.6	9.0	15.4	2.9	2.7	0.9	0.8	0.1	0.2	0.5	0.1	bdl	101.0	0.7
04VCE	Rock	43.8	22.1	7.3	11.5	6.7	2.5	3.0	1.1	1.3	0.2	0.3	0.1	0.1	bdl	100.9	0.4
05VCE	Clay	55.9	0.5	7.9	16.4	9.2	3.3	3.2	2.0	1.2	bdl	0.3	0.01	0.1	bdl	99.5	0.4
07VCE	Clay	51.3	2.7	18.4	10.7	9.9	1.9	1.8	2.2	0.6	0.0	0.3	bdl	0.1	bdl	100.0	0.6
08VCE	Clay	59.5	5.6	8.5	11.3	7.9	2.0	2.4	1.6	0.7	0.2	0.3	bdl	0.1	bdl	100.1	0.3
09VCE	Clay	58.2	1.5	6.5	14.4	10.2	2.7	2.7	2.4	0.9	0.0	0.4	bdl	0.1	0.02	98.6	0.3
14VCE	Clay	51.3	5.0	14.9	12.5	6.9	2.2	2.6	3.2	0.7	0.4	0.2	0.1	0.1	bdl	100.1	0.5
15VCE	Clay	24.1	43.7	19.5	4.3	4.4	1.0	1.1	0.9	0.3	0.1	0.2	0.3	0.1	bdl	102.1	0.9
17VCE	Clay	56.4	5.4	8.0	14.4	6.5	3.2	3.0	1.7	0.9	bdl	0.2	bdl	0.1	0.1	100.0	0.3
18VCE	Clay	59.6	1.6	7.1	12.8	9.2	4.0	2.7	1.6	1.0	bdl	0.3	0.03	0.1	bdl	99.8	0.3
	Average	<b>49.8</b>	<b>10.9</b>	<b>10.7</b>	<b>11.7</b>	<b>8.6</b>	<b>2.6</b>	<b>2.5</b>	<b>1.7</b>	<b>0.8</b>	<b>0.2</b>	<b>0.3</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>		
	SD	11.5	13.9	5.0	3.4	3.0	0.8	0.6	0.7	0.3	0.1	0.1	0.2	0.0	0.1		
	Min	24.1	0.5	6.5	4.3	4.4	1.0	1.1	0.9	0.3	bdl	0.2	bdl	0.1	bdl		
	Max	59.6	43.7	19.5	16.4	15.4	4.0	3.2	3.2	1.3	0.4	0.4	0.5	0.1	0.1		
02VCE	Lumps	11.2	54.9	26.2	0.6	5.3	bdl	0.5	0.1	bdl	0.2	0.1	0.5	0.02	0.3	102.3	2.7
06VCE	Lumps	36.4	46.7	7.0	6.5	0.7	bdl	0.8	0.9	0.1	0.6	0.1	0.3	bdl	bdl	102.5	0.2
11VCE	Lumps	17.4	59.1	15.4	3.1	1.9	bdl	0.8	0.6	0.1	1.0	0.1	0.5	bdl	bdl	103.0	0.9
12VCE	Lumps	38.2	39.5	14.3	2.6	3.6	bdl	0.3	0.5	0.1	0.3	0.1	0.3	bdl	0.04	102.0	0.5
13VCE	Lumps	45.9	21.5	14.8	6.8	6.2	0.8	0.7	2.7	0.2	0.0	0.2	0.2	0.03	bdl	100.0	0.5
16VCE	Lumps	38.2	8.1	23.1	3.5	24.4	0.5	0.5	0.5	0.2	0.7	0.1	0.1	0.2	bdl	100.3	1.2
19VCE	Lumps	52.1	22.9	6.9	10.1	1.4	0.3	4.6	0.9	0.5	bdl	0.1	0.1	bdl	bdl	101.0	0.2
20VCE	Lumps	33.6	39.4	15.8	4.9	3.2	0.2	0.7	1.3	0.2	0.3	0.1	0.3	bdl	bdl	101.9	0.6
	Average	<b>34.1</b>	<b>36.5</b>	<b>15.4</b>	<b>4.8</b>	<b>5.8</b>	<b>0.5</b>	<b>1.1</b>	<b>0.9</b>	<b>0.2</b>	<b>0.5</b>	<b>0.1</b>	<b>0.3</b>	<b>0.1</b>	<b>0.2</b>		
	SD	13.7	17.7	6.8	3.0	7.7	0.2	1.4	0.8	0.2	0.3	0.0	0.2	0.1	0.2		
	Min	11.2	8.1	6.9	0.6	0.7	bdl	0.3	0.1	bdl	bdl	0.1	0.1	bdl	bdl		
	Max	52.1	59.1	26.2	10.1	24.4	0.8	4.6	2.7	0.5	1.0	0.2	0.5	0.2	0.3		
	Total Av	<b>42.8</b>	<b>22.3</b>	<b>12.8</b>	<b>8.6</b>	<b>7.4</b>	<b>2.0</b>	<b>1.9</b>	<b>1.4</b>	<b>0.6</b>	<b>0.3</b>	<b>0.2</b>	<b>0.2</b>	<b>0.1</b>	<b>0.1</b>		
	SD	14.5	20.1	6.1	4.7	5.6	1.2	1.2	0.8	0.4	0.3	0.1	0.2	0.0	0.1		
	Min	11.2	0.5	6.5	0.6	0.7	bdl	0.3	0.1	bdl	bdl	0.1	0.0	bdl	bdl		
	Max	59.6	59.1	26.2	16.4	24.4	4.0	4.6	3.2	1.3	1.0	0.4	0.5	0.2	0.3		

Data is normalised in wt% with oxygen added by stoichiometry, (\*) analytical totals are given. Legend: bdl: below detection limit of the WD-XRF instrument ( $\leq 0.01$  wt%); K-index: viscosity index. Sample 10VCE lacked enough material for WD-XRF analysis

formations, glassy slag, metal and occasionally charcoal. All these characteristics are typical of early metallurgical traditions, i.e. the Chalcolithic period in Europe and the Middle East [31, 33, 61]. This type of slag is frequently labelled as “immature” as they are generated when the metallurgical process is still not well-developed [62–65].

The Cu–Fe–O equilibrium diagram in Fig. 9 shows the appropriate atmosphere and temperature necessary to form the principal minerals present in VC slags: delafossite, copper, and copper oxides (typically tenorite and cuprite), and iron oxides (hematite, magnetite). Experiments applied to the cuprite–delafossite–tridymite–pyroxene quaternary system [66] have shown that when heated, cuprite crystallises around 1075 °C and melts

over 1080 °C [61, 66]. Similarly, delafossite crystallises at 1075 °C, but transforms into spinels around 1090 °C [61, 66]. Additionally, delafossite and magnetite may form during cooling, just under 980 °C [33]. According to Hauptmann [33], under the right redox conditions, delafossite, cuprite, magnetite, and some clinopyroxenes such as augite (03VCE, 04VCE) could begin to crystallise just below 1000 °C; whereas the intergrowth of delafossite and cuprite in extensive areas, seen in seven samples, may suggest temperatures just below 1100 °C (cnf. [67]). These temperatures are in line with the presence of round copper prills in 15 slag samples, indicating that the copper melting point at 1084 °C was achieved in the majority of the slag. The combination of crystal needles



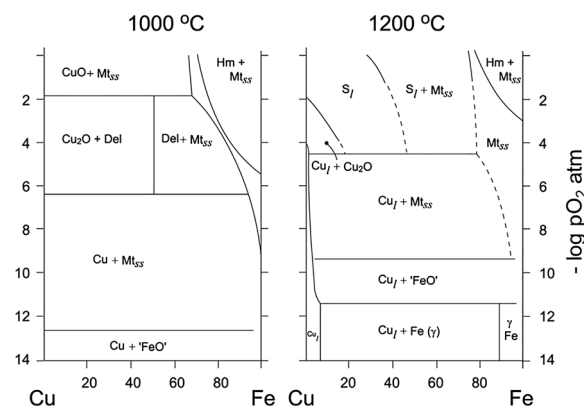
**Fig. 8** **A** Box and whisker plot summarising the bulk chemical composition of 18 slag samples, by WD-XRF. Note that SiO<sub>2</sub> and CuO are the two major components, followed by FeO, Al<sub>2</sub>O<sub>3</sub> and CaO. **B** Detail of the oxides present under 5 wt%

of different thickness and sizes within and between samples points to rapid changes in temperature during the smelting process (Fig. 7M).

Considering the partial pressure, most of the minerals may form at relatively high pressures ranging  $\sim 10^{-2}$ – $10^{-6}$  pO<sub>2</sub>, even though a lower pressure would be necessary to extract copper at 1000 °C (Fig. 9). However, since most of the newly formed crystals are closer to 1100 °C than to 1000 °C, it is reasonable to propose that the reactions likely occurred at approximately  $\sim 1000$  °C and occasionally reaching up to  $\sim 1100$  °C. The redox conditions were not reducing, probably reaching at atmosphere of  $10^{-8}$  pO<sub>2</sub> maximum, but more likely operating within an oxygen-rich atmosphere. The relatively high redox conditions are also reflected in the low iron content of the copper prills trapped in the slag<sup>5</sup> [31, 68]. Point analysis on metallic prills detected copper containing up to 2.1 wt% iron in six slag samples (Table 3). This composition is similar to Chalcolithic slags (up to 3 wt% iron), which were also generated under oxidising and unstable redox conditions [31]. At the same time, this avoids undesirable—and not easily removable—iron amounts going into the copper [62, 64, 65].

The abundance of copper oxidic phases (e.g. delafossite, cuprite) suggests an inefficient process in terms of metal extraction, whereas the chemical composition indicates that a substantial amount of the copper contained in the ore was never liberated as metallic copper. Copper losses

are essentially affected by both oxidation and viscosity [59, 67]. Oxidising atmospheres will prevent the reduction of metallic copper and would facilitate the formation of spinels (Fe<sup>3+</sup>), such as magnetite or cuprospinel; in turn, spinels increase slag viscosity by trapping copper prills inside [59]. As shown by the low K-index values obtained at VC ( $\sim 0.2$ – $0.5$ ; Table 4), this effect would be intensified if the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content is high, as both are considered viscosity-increasing oxides [36, 60, 67]. Additionally, viscosity is largely dependent on the temperature conditions, so the low temperatures reached at



**Fig. 9** pO<sub>2</sub>/T-diagram of the systems Cu–Fe–O at 1000 °C and 1200 °C. At 1000°C the association of delafossite (Del), cuprite (Cu<sub>2</sub>O) and magnetite (Mt<sub>ss</sub>) show high oxygen partial pressures between  $10^{-6}$  and  $10^{-2}$ . As mentioned, delafossite transforms into spinel around 1090 °C, and is therefore not present at 1200 °C. Note that fayalite (as 'FeO' here) needs strong reducing conditions to crystallise. Hm: hematite [31, 33]

<sup>5</sup> In contrast to copper with high iron content, which is a sign of a smelting process of high temperatures and strong reducing conditions [33].

VC would explain why some slags with better K-index that would be more liquid ( $>0.9$ ) are still retaining so much copper (up to 26 wt% CuO).

As evidenced by the chemical composition and microstructural analyses, these are not fayalitic slags. Olivines are absent in all specimens, whereas the bulk chemical composition points out that the formation of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) is quite improbable, since the iron oxide content is by far insufficient. Moreover, the low levels of FeO (~13 wt%) and MnO (~0.1 wt%), compared to  $\text{SiO}_2$  (~43 wt%), suggest that no flux was added to the charge. Therefore, it appears that the ore was beneficiated and was introduced into the furnace in an enriched state, using only charcoal.

Overall, the main difference in composition between slags and the analysed copper ores is the high content of FeO and CaO in slags (Tables 2, 4). The average of FeO in slags is 12.8 wt%; whereas in the ore analysed, it is 6.0 wt%, with a maximum of 18.5 wt% (42VCM). Even though some enrichment could derive from the 7.6 wt% FeO contained in the clay/rock adhered to slags (Additional file 4), these percentages do not explain the relatively high amount of FeO in slags, with some reaching up to 26 wt% (Table 4). The most probable option is an unintentional enrichment where FeO is coming from the copper ore used. Therefore, increasing the analysis of ore samples to detect samples with higher FeO would provide a better comparative base. Nevertheless, there is another—more speculative—option. Considering the evidence of iron oxide processing as pigment at VC, it cannot be ruled out that some intentional addition of FeO to the charge occurred as a ritualistic step in the process, aiming to ensure a successful production. Similar behaviours have been reported elsewhere [28]. In this case, it is clear that FeO was not used as iron-rich flux to generate fayalitic liquid slag, although small amounts could help to lower to some extent the melting temperature of the gangue [69]. In the case of the CaO, its average in slags is 7.4 wt%, compared to 1.1 wt% in the ore. The high percentage of CaO is partially explained by the rock/clay enrichment (5.4 wt% CaO, Additional file 4). Still, the main difference may derive from charcoal [38] or, perhaps, by the addition of larnite ( $\text{Ca}_2\text{SiO}_4$ ), a calcium silicate that was ground at the VC site.

Similarly, slags contain low levels of MnO and ZnO (~0.1–0.3 wt%), but these oxides were not present in the analysed Cu-ore samples. In the case of MnO, up to 0.2 wt% could be derived from charcoal ashes [70]. While the ZnO levels are too low to indicate an intentional addition, it is likely that they originated from ores that were not analysed in this study. Conversely,  $\text{As}_2\text{O}_3$  and  $\text{SO}_3$  are higher in the ores, with very varied compositions ranging from below detection limits to 15 wt%  $\text{As}_2\text{O}_3$  and 7.7

wt%  $\text{SO}_3$ . In slags, both oxides are present between 0.1 and 0.2 wt%. These low percentages are not uncommon if we consider that both elements are volatile and evaporate during smelting. Over all, the comparable composition between the potential original ore and the slag (Fig. 5), especially in the specimens adhered to clay materials, lends support to the proposition of using highly graded copper ores. Furthermore, the variations observed in the main elements align with the transformation and enrichment of minerals subjected to low temperatures and oxidising redox conditions.

Considering the overall absence of glassy matrices, the varying degree of reactions observed within and between different slag samples, the prevalence of mineral relicts in most of the slag fragments, the high levels of potentially reducible Cu trapped in the slag, and the absence of fluxes, it can be inferred that the smelting conditions within VC furnaces were not optimal. The smelting system at VC exhibits characteristics of non-equilibrium reactions, unstable temperatures, a variable atmosphere that appears to be relatively oxygen-rich, and insufficient reaction times. These features are consistent with those of early metallurgical systems in the world [30, 31, 33, 58, 59, 61, 62, 71]. However, in the following section, we will argue that this process, while imperfect in terms of metal recovery, was not driven by the lack of the smelters' technological skills, but was possibly intentionally implemented.

#### Smelting technology at Viña del Cerro: cost–benefit analysis and metal recovery

As Hauptmann points out, slags with high copper content are not necessarily produced by technologically immature smelting processes. In fact, rich ores with 33–66 wt% of copper can be directly smelted without any addition of fluxing agents. If such rich ores are available, more complex techniques could appear as “*obsolete and unnecessary*” according to the author [33]. Regardless of the expected variation in microstructure and mineralogy, all the samples from VC are coherent as by-products of a similar procedure to extract copper from oxidic ores; whereas XRD and WD-XRF analyses on three ore samples have enabled the identification of malachite and buttenbachite, both copper-rich minerals that are relatively easy to reduce. The ore also contains some brochantite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ ), a cupric sulphate usually found in association with malachite, and formed in the oxidised zones of copper deposits, mainly in arid regions [72]. The scant amounts of arsenic and sulphur contained in the slag, both present in less than 0.5 wt%, are likely the outcome of reducing minerals containing these elements during the smelting process. Given the low temperatures and oxygen-rich atmospheres, the conditions



would be similar to a roasting process to evaporate the sulphur. Therefore, people in VC were almost certainly smelting very Cu-rich oxidic ores.

On the other hand, the heterogeneous textures and high viscosity observed in the slag evidence an irregular exposure to high temperatures and unstable, oxygen-rich atmospheres. These conditions align with and support the notion that wind-driven furnaces were used. As air-flow controls both temperature and atmosphere, sudden, intense changes to the air supply would produce rapid variations that would affect the length and nature of the reactions within the smelting furnaces [27, 73]. There is evidence that smelting at VC started during de LIP (~1185 AD) and that the site was selected and rebuilt by the Incas. Thus, it can be assumed that its location, technology and productivity were considered good enough that the Incas wanted to control and expand it without introducing major technological changes. The location of the furnaces was also strategic, because the terrain topography favours an important increase in wind speed. When wind encounters gentle hillslopes as obstacles, such as the case of VC, it increases the speed at the top up to 200% to maintain its flow. We tested the wind speed at VC obtaining 2.4 m per second (“m/s”) at the plaza (11:18 am), and 4.3 m/s (11:33 am) on top of the hill, i.e. twice the speed. Our preliminary wind measurements at VC indicates that around 1 pm, wind speed increases between 5.8 and 9.5 m/s, and official records indicate that higher speeds are reached between 12 and 4 pm, especially between November to February (Additional file 5). Experimental wind-powered furnaces or *huayras* have operated successfully with wind speeds between 6 and 9 m/s, reducing metal in three hours [27], indicating that VC has the conditions to properly reduce metal. Likewise, experiments conducted in prehispanic bench-type furnaces were able to reach 800–900 °C with winds below 1 m/s, and 1200 °C with winds of ~3 m/s [74], a range of temperatures that fits within the range proposed for VC. Finally, people at VC used high-grade ores, containing up to 68.8 wt% CuO (or ~55 wt% Cu). Additionally, we cannot rule out the possibility that this rich copper ore contained some native copper, as some chroniclers have pointed out [75]. In fact, the use of high-grade ores is usually reported when using the wind-powered furnaces in the Andes [27, 76], which would explain, for instance, the relatively small amount of slag found at VC [68].

How can this new evidence help us better understand the smelting process developed at VC? We propose that even if the slag was rather of “low quality” in terms of formation and metal recovery, the ores used at VC were rich enough to render satisfactory amounts of metallic copper. It is clear that the smelting conditions generated at VC were insufficient to produce liquid slag, which

would have required mineral equilibrium, more reducing conditions, higher and more stable temperatures, and longer reaction times [30]. However, these conditions still allowed for the separation of a good deal of liquid metal from imperfect slags, despite the amount of copper retained in them. This was possible, as Hauptmann suggests, because the reduction of ore to liquid metal is much faster than the formation of liquid slag [33]. Slags from VC were probably formed by reactions in the solid state, described as the interaction between solid constituents and liquid, or partially liquid parts under unstable conditions. Considering the presence of reduced metal among large quartz grains, as in sample 12VCE (Fig. 7A), it is possible that some reduction occurred as solid state melting [33]. Moreover, as seen in Fig. 6, the copper content of slags is visible to the naked eye, which suggests that if metallurgists needed more metal, they could easily crush or re-smelt these remains, although this apparently did not occur. There is no evidence or early report of slag crushing either to retrieve part of the trapped copper, or to grind the debris to use it again as charge. Overall, slags do not appear to be mechanically crushed, and there are no areas of slag concentration associated with crushing tools, as reported in other sites of the Atacama Desert such as Collahuasi [13]. All the grinding equipment was recovered at the domestic area of the site, and this was used to process red pigment and larnite [6, 53]. In this vein, another possible scenario would be that these slags are intermediate products, i.e., that these are the product of a first reduction stage waiting for a second stage in the furnace (e.g. [13, 60]). However, if this were the case, we would expect to find material evidence of such purportedly more “efficient” slag type. This was not found anywhere within the archaeological site. Therefore, the most plausible scenario is that the imperfect Cu-rich slag was the result of an intentional one-step smelting process.

In this last scenario, the metallurgists at VC were quite skillful given their constraints. They had enough but variable wind for only a few hours during the day, and this occurred only within the right annual season. At VC, the fact that strong winds are achieved only during some months of the year suggests that metallurgy was most likely a seasonal activity (see also [26]), which would explain the low occupation density and the small amount of production remains at the site [6]. The skills of the local metallurgists were most likely based on a thorough knowledge of the wind flow and the selection of the right ore, given that fuel would not have been an issue in a valley rich in firewood [12, 53].

The result of this process would be a satisfactory extraction of copper through employing a low-cost strategy: the mechanic beneficiation of widely available rich ores, which saved infrastructure and considerable human

**Table 5** Main technical parameters of nine Andean metallurgical sites, including Viña del Cerro

Site	Chronology	Metal produced	Redox conditions	Temperatures (°C)	Cu-ore	CuO wt%	Use of fluxes	References
Viña del Cerro	1185–1609 AD	Copper	Oxidising	1000–1100	Oxidic/carbonates	1–64	–	Garrido and Plaza [6]
Collahuasi	1000–1536 AD	Copper	–	~1200	Oxidic	<20	–	Figueroa et al. [13]
San Bartolo	1400–1536 AD	Copper	Oxidising	>1125	Oxidic, sulphidic, native copper	2 and 28	MnO	Alunni [79]
Ramaditas	50 BC	Copper	–	1100–1250(?)	Sulphidic	1–9	–	Graffam et al. [44–46]
Rincón Chico 15	900–1536 AD	Copper, bronze, silver, gold	Reducing	1150	Oxidic/carbonates	–	FeO, MnO	González [11]
Quillay	1400–1536 AD	Copper	Oxidising-slightly reducing	1100–1300(?)	Sulphidic	No CuO	SiO <sub>2</sub> (?)	Spina [43]
Pulac-050	674–874 AD	Copper, silver-rich lead	Oxidising	>1128	Oxidic, sulphidic, complex polymetallic ores	–	–	Lechtman et al. [35]
Huaca del Pueblo Batán Grande	900–1532 AD	Arsenical copper	–	1100–1200	Oxidic + arsenic-rich ores	2–10	FeO	Merkel and Shimada [82]
Pampa Chaparrí (site 256A01)	1031–1270 AD	Copper	Reducing	1250–1300	Oxidic/carbonates	2–3	FeO	Killick and Hayashida [38]

For more details, see Additional file 6. Legend: “–” = without information; (?) = uncertain results or information

resources by using wind to supply air into the furnace. The process would have likely required a low to moderate fuel consumption, based on the expenses described for other wind-driven devices [77]. Thus, the final balance in the cost–benefit analysis would lean towards the positive side.

Andean ethnographic examples suggest that achieving an optimal metal recovery was not always the main goal of the metallurgists. The case of Carlos Cuiza in the Bolivian Altiplano is particularly enlightening because each time he smelted lead, he invested minimal effort to only produce enough metal to extract the desired amount of silver, just enough to cover his immediate necessities, with no intention to generate surplus [26, 77]. He used the *huayrachina* furnace, a wind-driven device that is particularly efficient for low fuel consumption, but at the cost of sacrificing a good deal of potential metal that gets trapped in the slag. From the strict perspective of metal recovery, this would be a very “inefficient” process that generates slags with high lead and silver retention [26]. Nonetheless, the advantage of the *huayrachina* is that it solves the main issue in the Bolivian Altiplano, which is to procure enough fuel in a context of scarce firewood and an abundance of high-grade lead–silver ores [26, 77, 78]. Thus, sacrificing ore appears to be the best strategy to obtain a benefit while saving on fuel, equipment, and

human labour. The hypothesis that we propose for copper smelting at VC aligns with this concept of technological adaptation and cost–benefit analysis.

#### Viña del Cerro technology within the Andean region

In conclusion, how does VC technology compare with the broader Andean context? Metallurgical centres where slags have been studied to reconstruct ancient technological parameters are not common in the Andes. Despite the little published evidence, it is clear that there was a wide variation in the Andean metallurgical technology. Whereas there are similarities, each system is unique, showing the knowledge, skills, and adaptability of ancient metallurgists. Additional file 6 presents a summary of the smelting parameters published for eight smelting sites that we will discuss here (Table 5; Fig. 1A): Collahuasi-Ujina [13], San Bartolo [79], Ramaditas [44–46], Rincón Chico-15 [11], Quillay [43, 80, 81], Pulac-050 [35], Huaca del Pueblo Batán Grande (“HPBG”) [82] and Pampa Chaparrí-25601 [38].

All the reviewed Andean smelting technologies are more or less similar, in the sense that in one case only they reached the maximum metal recovery efficiency, i.e. very fluid slags with limited copper retention [38]. In the case of temperatures, reaching high temperatures was not a problem for ancient Andean metallurgists. Except

for VC, temperatures reported in other smelting sites are usually over 1100 °C, and up to 1150–1200 °C (Table 5). Pampa Chaparrí and Quillay reached the highest temperature, up to 1300 °C, although the range given for Quillay is only a general estimate. Conversely, it appears that the most difficult parameter to control was the redox conditions to obtain strong reducing atmospheres. In seven sites, including VC, redox conditions were most likely variable and mainly oxidising. Rincón Chico-15 and Pampa Chaparrí are the only sites that report fayalitic-type slags, suggesting the use of more reduced atmospheres [11, 38]. Slags from Pampa Chaparrí also contain wüstite, which is formed under reduced atmospheres; it is so far the only site where liquid slags were formed [38]. At both sites, copper retention is low (e.g. 2–3 wt% in Pampa Chaparrí). To evade the redox condition issue, metallurgists achieved high temperatures (>1100 °C) and held them for long time, as in the case of Collahuasi and San Bartolo. Another alternative was the use of fluxes, as identified in San Bartolo, Rincón Chico-15 and HPBG, which were able to reduce the melting point in spite of the oxidising conditions [11, 42, 79, 82].

Both temperature and atmosphere are intimately connected and directly controlled through the air supply [33]. Diverse experiments have shown that furnaces powered either by wind (most Andean cases) or blow pipes (e.g. in HPBG and Pampa Chaparrí) can easily reach temperatures of around 1200 °C. However, temperatures can quickly drop too, when adding a new charge, or when the wind flow changes [26, 27, 82]. We are confident that ancient metallurgists noted those effects and tried to manage them, especially by using very high-grade copper ores.

The smelting structure used is also key in keeping and controlling temperatures and atmospheres, and probably played an important role at VC, where temperatures did not go over 1100 °C. However, we do not have enough evidence to reconstruct the shape of the furnaces for now. At the site, there is no evidence of ceramic walls, but there are several middle-size angular rocks dispersed, usually splashed with slag. Studying the photos and reports from 1968 to 1980, several of these rocks were dispersed near the furnace bases (Fig. 3). It is likely that these rocks formed the walls of the furnaces and the spaces in between were blocked with mud, similar to what González describes for Rincón Chico-15 [11]. Nevertheless, experimental archaeology has shown that rock-wall furnaces are unable to smelt lead because of the high heat losses due to the cracks and spaces in the walls [27]. Further experimentation is needed to better clarify this issue.

The metallurgists at VC probably experienced similar problems, along with potential changes in wind flow

during the smelting process. These factors could explain the low temperatures and oxidising conditions. What is interesting is that even with these complications, metallurgists from VC were able to produce sufficient copper for their needs. The local Copiapó society had low population and was not highly stratified, which might explain why there was not a pressing necessity to increase their metallurgical production to manufacture a larger amount of prestige goods. The Incas changed the architecture of VC and the labour relations involved in the metallurgical process, but they did not change the local smelting technology. The Inca reliance on this last aspect, and the use of the scant skilled labour force under a seasonal scheme, possibly determined that despite imperial interests, VC might have not radically increased its previous output potential.

## Conclusions

This article has provided a comprehensive and scientific study of a group of slags and copper ore from Copiapó Valley to contribute valuable insights into the local and regional smelting technology. Our results reveal that slags at VC are heterogeneous and viscous, due to unstable firing conditions that reached up to 1100 °C, with variable and relatively oxidizing atmospheres. These slags were briefly exposed to maximum firing temperatures, which was insufficient to achieve a fully liquid state, and smelters did not use fluxes to lower the melting point. Consequently, slags retained relatively high amounts of copper. These conditions align with the use of wind-driven furnaces. As the airflow regulates both temperature and atmosphere, sudden changes in the intensity of the air supply would result in rapid variations that affected the duration and characteristics of the reactions within the smelting furnaces.

Compared to other smelting sites in the Andes, smelters at VC were not able to reach and maintain high temperatures, but redox conditions were similar. Despite these unstable conditions, smelters at VC were skillful at producing metallic copper by using a low-cost strategy. They employed widely available copper-rich ores, which were well beneficiated. They saved in infrastructure by using the available rocks and mortar to build the furnaces. They also saved in considerable human resources that would have provided air supply, by instead harnessing their thorough knowledge of the wind flow. This smelting system most likely relied on a relatively low fuel consumption, although fuel would not have been an issue in a valley. Overall, the final balance in a cost–benefit analysis of copper production leaned towards the positive side, even if important amounts of copper were retained in the slag. These benefits were clearly understood by the Incas, who introduced VC into their larger productive

## network to fund their imperial expansion in the southern Collasuyu.

### Abbreviations

VC	Site of Viña del Cerro
LIP	Late Intermediate Period (AD 1000–1400)
LP	Late Period (AD 1400–1536)
XRD	X-ray diffraction
WD-XRF	X-ray fluorescence
SEM-EDS	Scanning electron microscopy with energy dispersive spectroscopy
OM	Optical microscopy
PB	Site of Punta Brava
m/s	Meters per second
na	Not analysed
bdl	Below detection limits
HPBG	Huaca del Pueblo Batán Grande

### Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-023-01017-z>.

**Additional file 1:** Summary of the analyses made on each slag and ore sample. Slag samples were divided in two parts for SEM-EDS and WD-XRF. Samples 10VCE and 45PBM were too small to apply WD-XRF. All analyses were undertaken at the Microscopy and Microtomography, and Archaeometry laboratories at the Centro Nacional de Investigación sobre la Evolución Humana (CENIEH, Burgos, Spain), between 2021 and 2022.

**Additional file 2:** Calibration of the WD-XRF equipment.

**Additional file 3:** Table summarising the main microstructures identified under SEM-EDS in 19 slag samples from Viña del Cerro. ??: Not sure. L: lumpy; R: platy slag on rock; S: platy slag on clay.

**Additional file 4:** Scatter plot showing the positive correlation between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> wt% using XRF data. We added rock and clay values obtained by SEM-EDS of five samples (03VCE, 04VCE, 05VCE, 14VCE and 17VCE). Note that rocks and clay show much higher SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> values than slag samples. Numbers in the plot indicate the number of the sample compared (see Table S1).

**Additional file 5:** Daily (1) and annual (2–3) wind speed at the area of Viña del Cerro. Note that a) these measures are made over 5 m from the surface, and b) the shape of the hill where furnaces are placed, favour a particular increment of wind speed, that is most likely not considered in these measurements. Source: “Explorador eólico”, Ministry of Energy, Chilean Government (<https://eolico.minenergia.cl/inicio>).

**Additional file 6:** Brief description of smelting sites from the Andes mentioned in the paper. The location of the sites are mapped in Figure 1 (see paper). LIP: Late Intermediate Period, AD 1000–1400; LP: Late or Inca Period AD 1400–1536.

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### Author contributions

MTP designed the project, conducted field research, processed the samples, analysed the data, and wrote the drafts of this paper. FG conducted field research and worked on the drafts of this paper. DL analysed the samples, interpreted the data and worked on the drafts of this paper. All authors read and approved the final manuscript.

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### Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

### Declarations

#### Competing interests

The authors declare no competing interests.

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