



Characterization of black paint on Aconcagua Salmon ceramics from the Late Intermediate and Late periods (AD 1000–1540) in Central Chile using LA-ICP-MS and Raman spectroscopy

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ABSTRACT

This paper presents the initial findings of an analysis of black paint on Aconcagua Salmon type vessels of the Aconcagua Culture (Central Chile) using LA-ICP-MS and Raman spectroscopy. Five chemical groups were identified in the process, two composed mainly of copper, iron and clay, two of lead and copper, and one of manganese and iron. Raman spectra confirmed that there were differences among the minerals of these chemical groups and identified those of Cu as copper sulfides, those of Fe as hematite, magnetite and goethite, and those of Mn as jacobsite. The geological information on chemical elements and minerals specific to each metallogenic belt in the study area narrowed down the range of possible colorants found at each archaeological site. We conclude that there was a common recipe for preparing black paints in which copper and clay were always added—the former as a constituent mineral and the latter as a binder—and that these were combined with other minerals in preparing local recipes, according to what was available in each locality.

1. Introduction

Aconcagua Salmon pottery refers to a type of vessel produced by the Aconcagua groups of Central Chile during the Late Intermediate (AD 1000–1450) and Late (AD 1450–1540) periods, and which is characterized by a light orange-toned paste and black painted decorations (Fig. 1). Both the paste and the decorations have been the subject of numerous studies (Massone 1978; Villaseca and Ayala 1997; Falabella 2000; Falabella et al. 2002; Falabella et al. 2003; González 2003; Irrazabal 2020; Falabella et al. 2022), however the black pigment has not been investigated, except for a single XRD characterization of two ceramic sherd conducted more than 45 years ago (Stehberg 1977). The minerals used to make this paint have not been identified to date, and neither has their availability in the region nor the recipes used to

prepare it, despite the fact that analytical techniques exist for this purpose. Such pigment studies are relevant, however, because their composition, the recipes used, and where the raw materials were obtained in the natural world are total social facts (*sensu* Mauss 1924), since they encompass multiple dimensions of social life. To prepare pigments, the maker must have knowledge of the environment in which the minerals can be found, recognize them by their physical attributes (color, luster, shape), extract them, grind them, process them, and mix them with each other and/or with binders, according to a recipe, to obtain a product that properly adheres to the surface of the vessel and delivers the desired shade after firing. Despite being part of the operational chain of ceramic production, the procurement of coloring raw materials does not operate on the same temporal and spatial scale as that of clay and temper, as the former are generally less ubiquitous, required

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in much smaller quantities, and may be obtained from much further away (Rye and Evans 1976; DeBoer and Lathrap 1979; Arnold 1985). For those reasons pigments can offer a different perspective on ceramic production and on relations between the producers and users of these vessels in Central Chile, while enhancing our understanding of the social networks of the Aconcagua people.

The Aconcagua were a non hierarchical polity, based on small and economically self-sufficient co-residential communities, with a dispersed settlement pattern, that integrated themselves with others forming local communities according to spatial and kinship proximity (Falabella et al. 2016; Sanhueza et al. 2019). In our study area, the Maipo River drainage, archaeological data show two major interaction spheres; people from Coastal Plains sites were related to those of the Coastal Range, and people from the Central Valley sites with those of the Andes Mountains (Falabella et al. 2003; Cornejo et al. 2003; Falabella et al. 2007). These four geomorphological units are bisected by distinctive north–south geological features that include metallogenic belts offering a wide variety of minerals that can be used for the preparation of black colorants (Fig. 2). Artifact production was carried out at the community level using mostly local resources, with no evidence of regional production centers or the widespread circulation of artifacts, raw materials, or exotic goods. Pottery production in particular included three types of ceramics with well-differentiated features: Aconcagua Undecorated, used mainly for cooking pots and storage vessels, Aconcagua Red Slipped, and Aconcagua Salmon, the last of these consisting mainly of pitchers and serving bowls. In this work, we analyze Aconcagua Salmon-type vessels, which use a paste recipe in which local reddish-brown clay is blended with white kaolins of very limited availability to achieve the particular light orange-colored tone visible on their surfaces (Falabella et al. 2002). The standardized visual aesthetic, which includes the contrasting black-on-orange color scheme, a limited set of abstract-geometric motifs, and a peculiar design structure, is common across all sites studied. However, it also presents technological differences such as specific tempers, and subtle differences in paste hues, motif combinations, and the execution sequences of strokes, which together suggest that production was organized at the level of residential communities (Falabella 2000; Falabella et al. 2002; Irrazabal 2020). Neutron activation analyses have not been as clear in this regard, because the clay in the mixtures blurs the chemical groupings (Falabella and Andonie 2003). This analysis of the colorants and the recipes used to

produce them therefore constitutes a new line of evidence, initiated by the main author (Saball 2019), that complements our knowledge of ceramic technology and material provenance and links it to socially significant spaces and activities.

The research presented herein pursues two objectives. First, it seeks to identify the minerals used to make the black paint; and second, it strives to understand whether the black paint was produced using a recipe common to all Aconcagua communities, or whether recipes were specific to each local ceramic-producing community. To answer these questions, we conducted a comparative analysis of the black paint found on sherds of Aconcagua Salmon vessels from 12 archaeological sites in the Maipo-Mapocho region using two archaeometric techniques: LA-ICP-MS and Raman spectroscopy. The geological and mineralogical conditions of the study area were also investigated in-depth to aid our interpretation of the data.

2. Materials and methods

2.1. Analytical techniques

2.1.1. LA-ICP-MS

Over the past two decades, laser ablation (LA-ICP-MS) has been used in several studies to analyze the composition of pigments on ceramic surfaces (e.g., Neff 2003, 2012; Speakman and Neff 2002, 2005; Vaughn et al. 2005; Duwe and Neff 2007; Shoval, S. 2018; Dussubieux, L. 2023; Beck et al. 2024). LA-ICP-MS is a multi-elemental analytical method, that can detect most elements of the periodic table in solid samples, with high accuracy and precision, and low detection limits. It is minimally invasive, considering the ablated areas are often indistinguishable with the naked eye. The laser can be targeted at a specific painted area to characterize the paint separately from the underlying paste (Speakman and Neff 2005). This microspatial capability of LA-ICP-MS is one of its greatest advantages. The goal of this pigment analysis is to identify the recipes used to produce different colors and/or identify recipe variations used to yield the same color. LA-ICP-MS analyses were conducted at the CAMAS Lab at Idaho State University using a Thermo Scientific X-series 2 ICP-MS, with New Wave 213 nm laser ablation sample introduction. Instrument sensitivity during the analysis was monitored with simultaneous liquid aspiration of 20 ppb ruthenium, internal standard. The ICP-MS was mass calibrated and tuned for optimal laser ablation sensitivity



Fig. 1. Aconcagua black on salmon serving bowls. A: Exterior surface, with *trinacrium* motif. B and C: Interior surfaces with abstract geometric motifs (photo by National Museum of Natural History, Santiago, Chile).

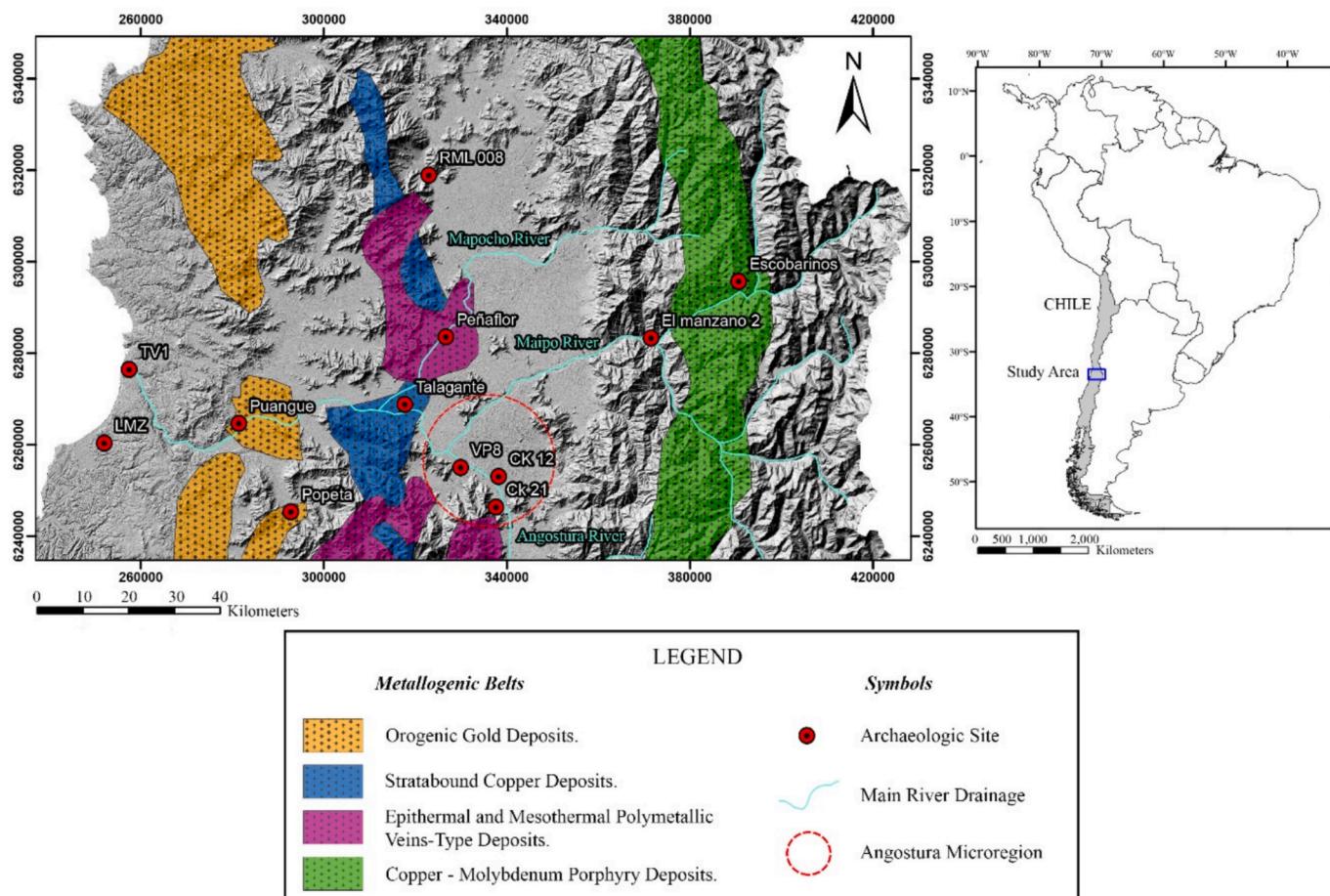


Fig. 2. Map of Central Chile showing the archaeological sites from which samples were taken and the spatial distribution of the different metallogenic belts.

at the beginning of sample analysis each day.

Small painted fragments of each sherd were mounted on disks and ablated in a helium atmosphere. All standards and unknowns were pre-ablated with the laser set to the following parameters: one raster pass at 200 μm spot size, laser power 40 %, raster speed 150 $\mu\text{m}/\text{s}$. Ablation for standard/sample collection was performed with the following parameters: one raster pass at 150 μm spot size, laser power 80 %, raster speed 30 $\mu\text{m}/\text{s}$. All standard and sample runs were preceded by a 120-second washout to reduce background signal and carryover signal from previous acquisitions. Signal intensities were measured by ICP-MS three times each for all 58 chemical elements. Three separate analyses were run on each painted sample, and the results averaged. The LA-ICP-MS data were calibrated to parts per million using NIST glass standards SRM614, SRM612, and SRM610, Little Glass Buttes obsidian, and NIST brick clay SRM679.

2.1.2. Raman spectroscopy

Raman spectroscopy is a well established technology useful for identifying organic and inorganic components used in preparing paint materials (Smith and Clark 2004; Prieto et al. 2005; Bersani and Lottici 2016; Puente et al. 2019; Ratto et al. 2020). Micro-Raman is a non-destructive technique ideal for metal sulfides and oxides (Bell et al. 1997). The analyses described below were conducted at the Sciences Faculty Lab at University of Chile. The Raman spectra of the samples were recorded with a Raman Renishaw InVia Reflex, equipped with a Leica microscope and an electrically cooled CCD detector. The instrument was calibrated using the 520 cm^{-1} line of a Si wafer and a 50 \times objective. Its resolution was set to 4 cm^{-1} , and 1–10 scans of 10–50 s each were performed and averaged. Spectra were recorded in the

200–1800 cm^{-1} region. The laser was used at 785 nm, which reduces the risk of photodecomposition, and a power $\leq 10 \text{ mW}$, a range that minimizes the fluorescence typical in ceramics. This precaution is particularly relevant in compositions with chalcocite, where powers $> 20 \text{ mW}$ induce oxidation phases (Campos and Aguayo 2015). Spectral scanning conditions were chosen to avoid sample degradation and photodecomposition. Data were collected and plotted using the WIRE 3.4, GRAMS 9.0, and OriginLab Pro 2016 programs. The spectra were compared following data published in the online RRUFF database (LaFuente et al. 2015) and other publications (Parker et al. 2008; Goodal et al. 2009; Olivares et al. 2010; Lucas et al. 2018). A spectrum was considered suitable when the signal-to-noise ratio of the main band was ≥ 5 .

2.2. Samples

For the LA-ICP-MS analysis, 122 ceramic sherds were selected from the twelve sites in the study area (Fig. 2). These were recovered from excavations and surface collections in archaeological sites, and were previously analyzed according to shape, paste, and design motifs, ensuring that each sherd belonged to a different vessel (Falabella et al. 2003). Based on the results of this chemical analysis, a subsample of 40 sherds was selected, representing the different chemical groups and sites to be analyzed using Raman spectroscopy.

3. Results

3.1. LA-ICP-MS

Ppm concentrations were obtained for 58 chemical elements, and of

these, the 18 with the highest coloring potential were used for the principal component analysis, namely: Al, Ti, Mn, Fe, V, Cr, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, In, Sn, Sb, and Pb ([Table 1, Supplementary data A](#)). The first five components account for 76 % of the variance in the data. As shown in the plot of the first two principal components ([Fig. 3](#)), the data differentiated five compositional groups (FAL1, FAL1a, FAL2, FAL2a and FAL3),¹ which can be interpreted as distinctive “recipes” used by different potters to manufacture the black paints used on Aconcagua Salmon vessels ([Table 2](#)).

Principal component 1 (PC1), the major axis of variation, separates groups enriched with the heavy metals Pb, Cd, Ag, and Mo, plus Zn, Mn, and Sb (FAL2 and FAL2a) from groups without lead but with Cr, V, and Fe (FAL1, FAL1a, and FAL3). In the PC2 axis, the contributions of As, Fe, V vs. Al and Ti are differentiated. The FAL1 and FAL1a groupings, for example, can be distinguished from each other by the latter’s V and Fe enrichment. These differences are further illustrated in the bivariate elemental concentration plot Pb vs V ([Fig. 4](#)). FAL2 and FAL2a groups are enriched in Pb. The elemental concentrations of some FAL2 samples contain up to 60 % lead, and the FAL2a group, although less enriched with lead, has a substantially higher concentration of this heavy metal than the other three groups. Most of the samples from the two southernmost sites in Angostura (CK12, CK21) fall within these groups.

The results also show that, with only five exceptions, all sherds analyzed have pigments highly enriched with copper ([Fig. 5](#)), with copper-rich compounds accounting for 6.25–31.25 % of the total amount of copper. However, there may be some remaining inaccuracy in the Cu concentrations, as the values are above even the highest Brill Glass standards (elemental copper correction measure), which have a maximum copper oxide concentration of 2.65 %. Among samples showing low Cu, four belong to the FAL3 group and one to the FAL2 group, with concentrations ranging from 300 ppm to slightly less than 1 % of the elemental concentration.

The FAL3 group contains only four samples, and was only identified at the Puangue ($n = 1$), VP8 ($n = 2$), and CK12 ($n = 1$) sites. In addition to their low copper content, FAL3 samples also have a high manganese and iron content, suggesting that an ore rich in manganese oxide and iron oxide was used instead of copper to achieve the black color. The FAL1a group also shows extreme iron enrichment, about 17 % on average, which probably contributed to the dark color of the pigment in this group’s samples.

Another relevant datum is the high concentration of aluminosilicates in the samples—ranging between 5 % and 11 % of the elemental composition, mainly in the form of aluminum oxide—as it indicates that there is also a clay component in the mixture that must correspond to the binder used to prepare the paint. This concentration of aluminosilicates is lower in the FAL2 group, further differentiating it from the rest as a pigment mixture with less clay.

In summary, the vast majority of the black paints used on Aconcagua Salmon vessels consist of mixtures that include a material rich in copper (in the composition of groups FAL1, FAL1a, FAL2 and FAL2a) and others that also contain Cu but have much more lead minerals (FAL2 and FAL2a). Although FAL1 and FAL1a are similar in composition, the enrichment in iron and vanadium in FAL1a suggests that a different mineral source was used in the preparation of those paints. FAL3 yields the only recipe that presents a different logic, as, instead of copper, it uses minerals rich in manganese as the main coloring material.

In regard to the distribution of these compositional groups by site, most sites studied have only one preferred recipe, which indicates that specific preferences were in play and is consistent with the previous statement that vessels were manufactured at residential sites themselves. Two recipes are found in samples from most sites (FAL1 and FAL1a), while others (FAL2 and FAL2a) are limited to a particular area,

in this case the Angostura micro-region (CK21 and CK12). At some sites (Puangue, VP8 and Escobarinos 1), the recipes identified are heterogeneous, while at others (L. Matanzas, Tejas Verdes 1, Popeta, El Manzano 2, Escobarinos 1) they are more homogeneous ([Table 2, Fig. 6](#)).

3.2. Raman spectroscopy

Forty of the LA-ICP-MS analyzed fragments, representing the five chemical groups and archaeological sites were selected for Raman analysis; 23 provided diagnostic spectra. The remaining 17 showed intense fluorescence that masked the Raman bands, a documented limitation for ceramics ([Centeno et al. 2012](#)). Spectral scanning was performed on different areas of black paint on each sherd, then reviewed under an optical microscope to avoid picking up the clay spectrum from the ceramic paste.

The first relevant finding is that the spectra displayed too little evidence of carbon to consider it a constituent element of the pigmentary mixtures, and no evidence of organic material that could be used as a binder, which corroborates the suggestion arising from the LA-ICP-MS analysis that clay was used for this purpose.

The data obtained from elemental analysis, coupled with geological information, allowed us to narrow down the range of possibilities and discover patterns that enabled the identification of most spectra obtained through Raman spectroscopy. From this, we are proposing that eight minerals were used as constituent elements to manufacture the black paints, the most recurrent of these being copper sulfides (chalcosite and chalcopyrite), ferrous oxides (hematite and magnetite), manganese oxides (jacobsite), and lead sulfides (galena) ([Table 3](#)). Furthermore, the identification of signals associated with Si-O vibrations allows us to identify components of the ceramic paste, such as quartz or kaolinite ([Goodall et al. 2009](#)).

Minerals in the FAL1 and FAL1a recipes

The FAL1 and FAL1a groups have Cu sulfide minerals in common, but differ in their ferrous component, with mainly hematite (Fe_2O_3) used in FAL1 and magnetite (Fe_3O_4) in FAL1a ([Fig. 7](#) and [Fig. 8](#)). Sample F24, from the Escobarinos 1 site in the Andes Mountains and assigned to FAL1, contains magnetite ([Fig. 9](#)), and is one of a few sherds whose composition falls between the two chemical groups ([Fig. 3](#) and [Fig. 4](#)), with the same vanadium levels as those at the lower end of FAL1a, which would explain the presence of magnetite instead of hematite.

Minerals of the FAL2 and FAL2a recipes

In FAL2 and FAL2a samples, copper sulfides, magnetite, and a lead sulfide (PbS), are suggested ([Fig. 10](#)). LA-ICP-MS recorded elevated copper concentrations, allowing us to infer that it did not derive from the extraction of another mineral, but was intentionally included in the mixture. It is worth noting that the only copper available in the polymetallic veins in this zone is in the form of chalcopyrite. Lead concentrations, above 30 % in these samples, point to a massive supply of relatively pure lead-bearing ore. Although Raman isn’t conclusive regarding the presence of galena in the samples, this lead ore constitutes the only primary lead sulfide described in the polymetallic veins in the Angostura zone, and are located within 3 km of the archaeological sites CK12 and CK21 ([Maksaev et al. 2007; Gröpper 2011](#)). These polymetallic veins are also characterized by simultaneous signatures of Pb, Zn, Bi, Mo, Cd, and In, the same geochemical pattern of the lead-enriched fragments in the FAL2 and FAL2a groups ([Table 1](#)). Galena has a relatively low hardness (2.5–3 on the Mohs scale), which makes it possible to obtain a powder that is fine yet sufficiently dense to be used on its own, without the need for mixing with clay or another material. This would explain the low clay component in this recipe.

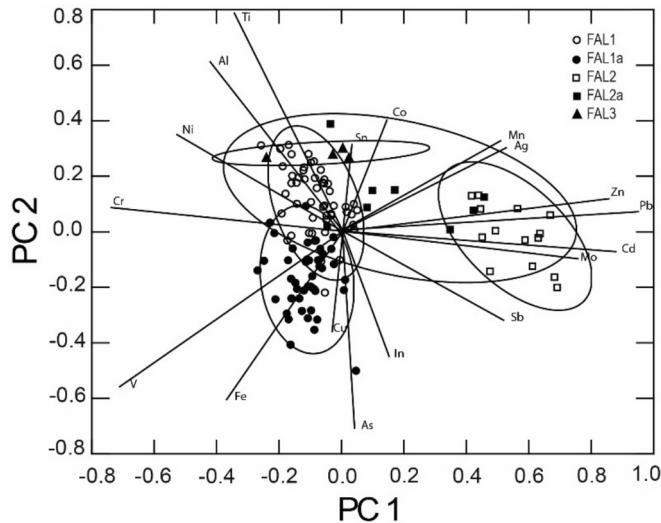
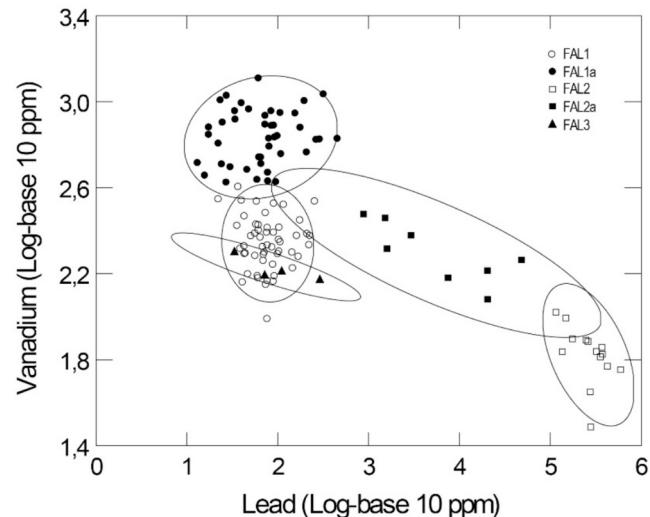
The hypothesis that recipe FAL2a may fall between recipes FAL1 and FAL2 is strengthened by the identification of magnetite minerals in a sample from this compositional group for which a mineral colorant was identified (sample F64 from Puangue site, [Table 3](#)). As the LA-ICP-MS analysis highlighted, that sample is elementally rich in lead and various sulfides. It is similar to the FAL2 recipe in composition, but with

¹ FAL is the laboratory designation for our samples and is used to designate the chemical groups.

Table 1

Mean and SD of ppm concentration values per chemical group.

Chemical Element	FAL1		FAL1a		FAL2		FAL2a		FAL3			
	n = 53	Mean	SD	n = 43	Mean	SD	n = 14	Mean	SD	n = 4	Mean	SD
Al	88.768,70	16.773		71.189,75	16.385		57.235,03	12.986	85.827,60	8.936	85.042,29	16.678
Ti	3.659,10	1.491		2.067,48	813		1.582,07	497	3.655,43	1.255	4.393,96	1.665
V	228,54	64		712,58	210		69,27	19	206,96	65	168,28	23
Cr	51,59	32		48,26	17		14,06	7	47,84	10	52,64	46
Mn	1.408,55	650		1.735,69	2.084		7.306,92	5.580	18.908,20	36.084	52.766,26	26.576
Fe	109.536,82	39.717		178.835,46	41.275		91.729,48	44.689	90.389,97	28.223	214.621,02	32.025
Co	25,94	13		25,36	15		33,10	12	45,31	36	163,99	87
Ni	30,60	14		24,73	10		13,51	6	26,86	8	65,62	52
Cu	102.174,00	44.035		109.531,38	36.881		91.386,89	58.012	94.973,62	39.392	2.667,17	3.949
Zn	515,30	498		390,17	245		6.503,09	6.674	4.142,05	5.947	591,35	172
As	55,07	64		181,88	176		62,34	55	180,24	338	84,81	116
Mo	21,37	87		10,42	22		157,62	139	27,52	52	4,63	2
Ag	48,84	57		13,88	20		187,68	346	172,16	203	1,50	1
Cd	2,17	2		3,31	6		132,44	134	70,49	139	1,24	1
In	2,79	14		1,07	1		1,39	1	1,06	2	0,90	0
Sn	4,39	3		3,00	1		5,33	9	4,21	2	7,27	3
Sb	7,22	14		12,72	17		34,25	48	207,04	313	5,10	2
Pb	89,67	53		94,94	93		291.239,81	130.296	12.929,95	16.421	126,75	114
Bi	21,79	129		4,01	4		161,47	143	85,84	149	2,53	3

**Fig. 3.** Biplot of principal components 1 and 2 showing the five chemical groups and the weight of chemical elements in them. The ellipses represent 90% confidence intervals for assignation to each of the groups.**Fig. 4.** Bivariate plot of lead and vanadium (log base 10 ppm): the ellipses represent a 90 % confidence interval.

minerals associated with FAL1 recipes. The other FAL2a sample from the Talagante site (F20) contains Ti oxide, which is not part of the colorant itself.

Minerals of the FAL3 recipe.

It was previously noted that recipe FAL3 appeared to have a different composition from the other recipes described, being low in Cu and high in Mn (**Table 1**). Raman analysis confirmed this inference, identifying jacobsite (MnFe_2O_4) in FAL3 samples (**Fig. 11**). No deposits of this mineral have been described in Central Chile, but other types of manganese oxides are frequent, including pyrolusite, which thermoalteration converts into jacobsite at temperatures above 900°C ([Schweizer and Rinay 1982](#); [Molera et al. 2013](#)). The coexistence of jacobsite and hematite shows that the FAL3 recipe has a technological pattern consistent with the black pigments from Northwest Argentina during the Late and Inca periods ([De La Fuente et al. 2024a](#)). The genesis of jacobsite from pyrolusite above 900°C ([Molera et al. 2013](#)) implies higher firing temperatures, suggesting a differentiated technology, possibly introduced in the context of *trans*-Andean interaction during the Inca expansion ([De La Fuente et al. 2024b](#); [Dinator and Morales 1990](#)). These fragments do not differ in shape, macroscopic

Table 2
Number of samples assigned to each chemical group in each site.

Site/Recipe	Chemical Group					Total
	FAL1	FAL1a	FAL2	FAL2a	FAL3	
L. Matanzas	9	1	0	0	0	10
Tejas Verdes 1	1	10	0	0	0	11
Puangue	8	4	0	2	1	15
Popeta	9	1	0	0	0	10
RML-008	3	7	0	0	0	10
Peñaflor	4	6	0	0	0	10
Talagante	1	7	1	1	0	10
VP8	4	3	0	1	2	10
CK21	1	0	6	3	0	10
CK12	0	1	7	1	1	10
El Manzano 2	5	1	0	0	0	6
Escobarinos 1	8	2	0	0	0	10
Total	53	43	14	8	4	122

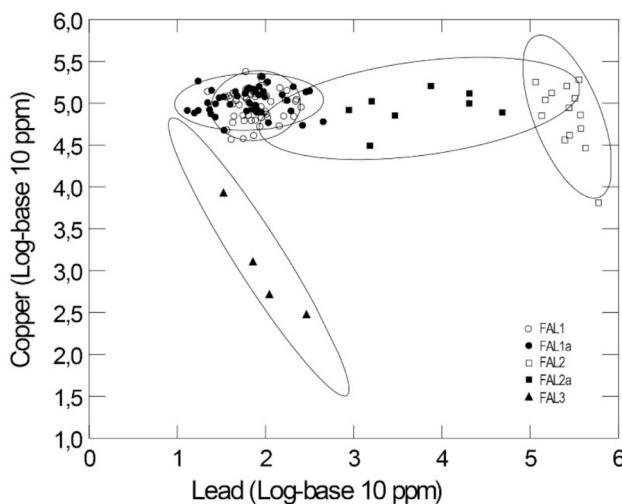


Fig. 5. Bivariate plot of lead and copper (log base 10 ppm): the ellipses represent a 90 % confidence interval.

characteristics of the pastes or painted designs compared to the larger sample of ceramics analyzed in this work (Sanhueza et al. 2023). So this leads us to consider that this novel painting recipe was used by some Aconcagua potters for their pots during Inca times.

4. Discussion

4.1. Provenance of mineral pigments

Having geological information available for Central Chile, in particular the characterization and location of metallogenic belts with different correlations of major, minor and trace elements in their mineralogies (Maksaev et al. 2007; Gröpper 2011) is helpful for associating the mineral pigments identified in the analyses with particular locations (Fig. 2, Table 4). This understanding is essential, as a given chemical group does not necessarily correspond to a single recipe or origin. By associating the chemical elements and minerals in a given paint mixture with particular belts, we can address the provenance of the raw materials and determine the potential access that potters at each site had to these sources.

Resources from the Jurassic orogenic gold belt, characterized by gold, silver, and iron ores (magnetites and hematite), with a chemical signature of arsenic and antimony in association, are the nearest sources with access from coastal sites. The most remarkable feature of this metallogenic belt is the absence of copper veins. This contrasts with the elements and minerals identified in samples from the coastal sites Tejas Verdes 1 and L. Matanzas, all of which are rich in copper, which accounts for more than 20 % of the elemental concentration in some cases. This indicates that the Cu mineral used to prepare black paint at these sites is not local and must have been obtained from further inland. On the other hand, the ferric raw materials, namely magnetite at the Tejas Verdes 1 site and hematite (iron low in vanadium) at L. Matanzas, are both locally available, but potters at each site procured them from different sources.

Sites in the Coastal Range are situated along the Jurassic orogenic

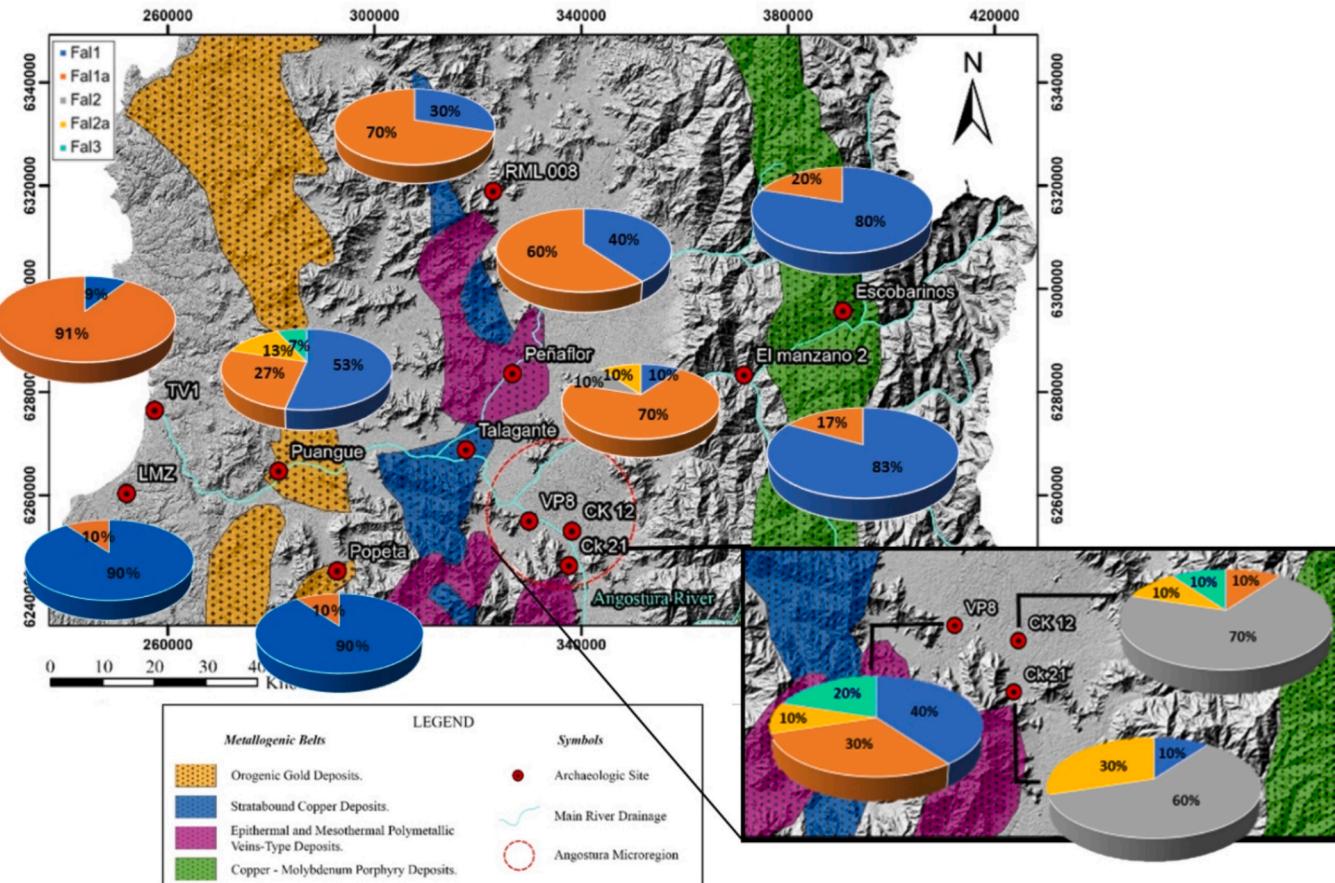


Fig. 6. Frequency of chemical groups in the archaeological sites studied.

Table 3

Minerals inferred from elemental analysis, geological information and Raman spectra for each chemical group.

Chemical Group	Site	Sample	N° spectra	Minerals	Cu	Pb	Mn	Fe	Other
FAL1	L.Matanzas	F36	3	chalcocite				hematite	
	L.Matanzas	F38	1	chalcocite				hematite, magnetite	
	L.Matanzas	F39	2					hematite	
	Talagante	F18	1			Mn oxide*		hematite	
	Manzano	F42	3	chalcocite				magnetite	
	Escobarinos 1	F24	3	Cu sulfide				hematite, magnetite	
	VP8	F84	3	chalcocite					
FAL1a	Tejas Verdes 1	F103	2	Cu n.id.				magnetite	
	Tejas Verdes 1	F109	1					magnetite	
	Puangue	F57	4	chalcocite				magnetite	
	Popeta	F48	2					magnetite	
	Popeta	F54	5	chalcocite				magnetite	
	Peñaflor	F8	3	chalcocite				magnetite	
	Talagante	F13	2					magnetite	
FAL2	Talagante	F15	3						Ti oxide*
	CK12	F98	2			galena*			
	CK12	F100	2	chalcopyrite*					
FAL2a	CK21	F79	3						
	Puangue	F64	1	chalcocite				magnetite	
	Talagante	F20	3					magnetite	kaolinite
FAL3	Puangue	F58	1						Ti oxide*
	CK12	F96	4					jacobsite	
	VP8	F90	1					hematite	
								goethite, hematite, magnetite	
								hematite	

* Raman signals were not conclusive. These inferences must be validated by other methods (XRD).

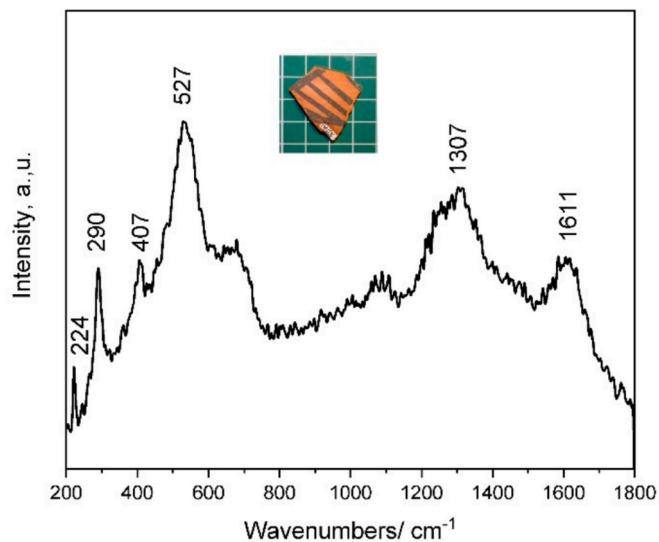


Fig. 7. Sample F18 (FAL1) from Talagante site. Raman peaks at 224, 290, 407 cm^{-1} corresponding to hematite, and from 1307 and 1611 cm^{-1} to amorphous carbon.

gold belt and near an area where copper (chalcocite) is abundant, both in the belt of stratabound deposits near the Puangue site and in the belt of polymetallic veins near the Popeta site. At Puangue, although copper and iron are also core components, most samples display a more heterogeneous mix of elements, as suggested by the distribution of samples in the four chemical groups (Table 2). Samples from the geographically more isolated Popeta site are more elementally homogeneous, similar to those of the L.Matanzas site, but with a much more variable copper content that ranges from 3 % to a maximum of 24 %. These findings confirm that Puangue and Popeta pigmentary mixtures display different elemental compositions. Despite sharing the FAL1 group with Popeta, the Puangue site mixture is low in arsenic and enriched in silver, which associates its recipes with the stratabound deposits and the orogenic gold belt (Table 1). Popeta FAL1 samples, in contrast, have higher phosphorus levels, along with a considerable level of sulfides in some

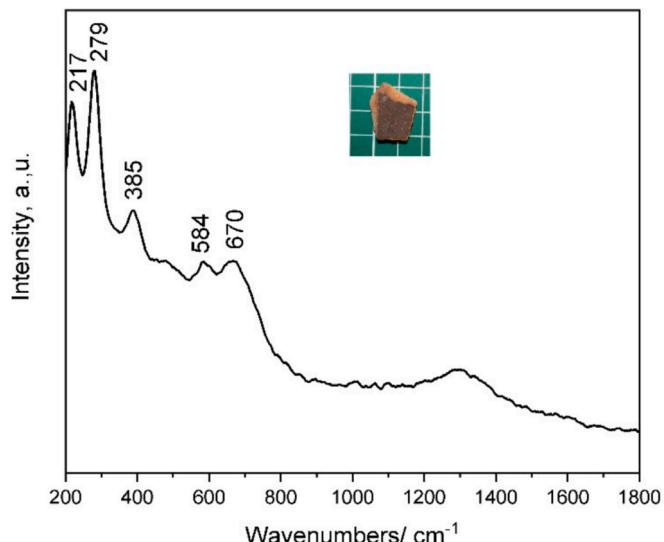


Fig. 8. Sample F8 (FAL1a) from the Peñaflor site. Raman peaks at 217, 279, 385 cm^{-1} corresponding to chalcocite, 670 cm^{-1} to magnetite.

samples that associates them with the belt of polymetallic veins (Table 4).

Central Valley sites are situated along the N-S axis of the stratabound copper belts and polymetallic veins-type belt. Two of them, RML-008 and Peñaflor, present no substantial variation in their respective recipes, with copper and iron being the most important components in the mixtures. Copper is in the same range for both, but iron is more variable; this is expressed in the two chemical groupings present at the sites, with FAL1a containing more iron than FAL1 (70 % and 30 %, respectively). While the copper, being similar, must come from more circumscribed veins associated with the metallogenic province of stratabound deposits, there are no elements that allow us to infer the use of the polymetallic veins, given the low level of sulfides present in these samples. Talagante, located further south in the broad Maipo River Valley, is different from RML-008 in two ways: a) it has hematite and manganese oxide minerals enriched with indium and molybdenum, suggesting a different

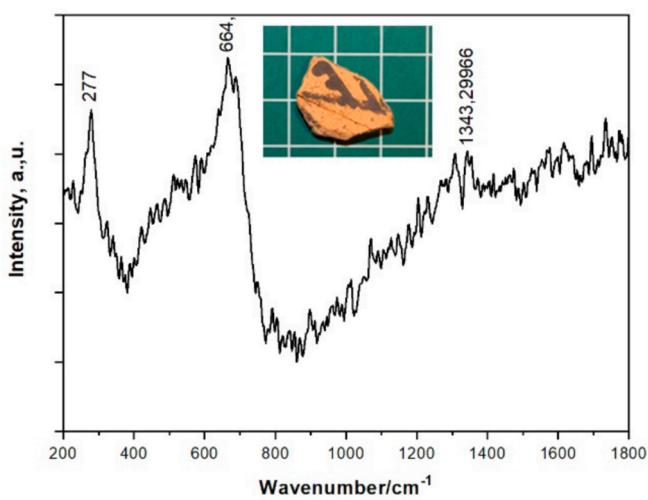


Fig. 9. Sample F24 (FAL1) from the Escobarinos 1 site. Peak at 277 cm^{-1} corresponding to copper sulfide, and 665 cm^{-1} to magnetite.

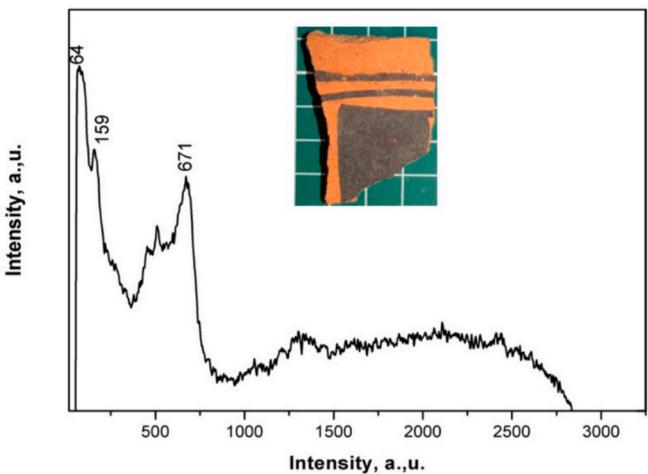


Fig. 10. Sample F79 (FAL2) from the CK21 site. Raman peaks at 159 cm^{-1} corresponding to kaolinite, and 671 cm^{-1} to magnetite.

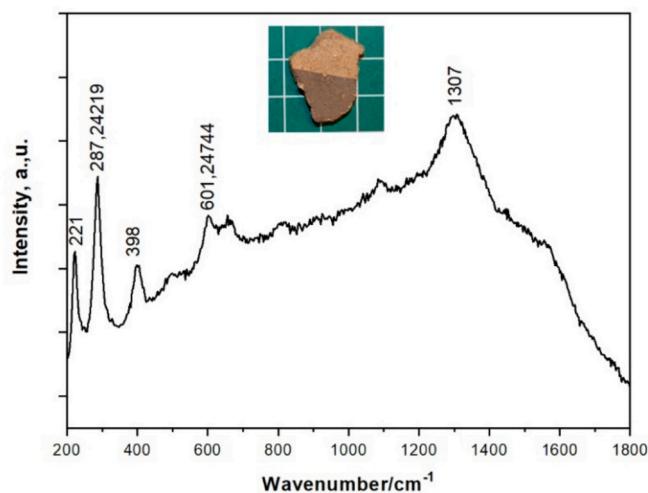


Fig. 11. Sample F96 (FAL3) from site CK12. From the peaks of 221, 287 and 1307 cm^{-1} , goethite is inferred. From the peak of 601 cm^{-1} and the valley shape, jacobsite ore is inferred.

provenance linked to the belt of polymetallic veins, which is consistent with the location of the site where these deposits proliferate; and b) it has one sample in the FAL2 chemical group and another in FAL2a that were probably non-local or painted with non-local resources.

The Andes Mountain sites of El Manzano 2 and Escobarinos 1 are associated with the Miocene-Pliocene Copper-Molybdenum porphyry belt, the youngest described for the Central Zone. This belt contains the Cu minerals chalcopyrite and chalcocite. Despite some minor differences, there is no significant variability in the paint recipes used at these Cordillera sites. The predominance of FAL1 with low vanadium content, and the geological conditions described for the sector, are both consistent with the magnetite found in the Raman spectra. The samples from these sites are the least enriched in silver and phosphorus, unlike those from the coastal sector and the interior of the Coastal Range, which suggests that we can hypothesize different origins for the FAL1 recipe in each sector (Coast vs. Andean Range).

The Angostura sites (CK12, CK21 and VP8), in the southern part of the basin have ready access to the metallogenic belt of Upper Cretaceous polymetallic veins, which is characterized by the presence of massive faulted veins and polymetallic hydrothermal breccias. In this belt, one can find a wide variety of sulfides such as chalcopyrite (iron and copper sulfide) and pyrite (iron sulfide), as well as sphalerite (zinc sulfide), galena (lead sulfide), and tennantite (copper sulfide), along with iron oxides such as magnetite-hematite and native silver metals. Manganese veins and lead-zinc deposits have also been documented nearby. The particularity of these veins is that, as they are abundant in this metallogenic province, they are enriched with multiple minerals in mutual association, leaving a very identifiable chemical signature. Thus, while in the coastal gold-orogenic belt arsenic is associated with antimony, in the polymetallic belt, its relationship with bismuth and other sulfides is more prominent. In turn, associations among lead, zinc, cadmium and molybdenum, which are not present in the other belts, are common here. Coincidentally, samples from sites CK12 and CK21 have an elemental composition that differs from those of all the above-described sites, with lead being the most important element in the recipe of the FAL2 chemical groups, and somewhat less important in FAL2a. The associations of lead with zinc, bismuth, molybdenum, cadmium, and indium, in the elemental composition of the samples analyzed (Table 1), replicates the mineralogy of the Late Cretaceous polymetallic veins, and, together with the coexistence of chalcopyrite as the only copper ore, point to the potters' use of locally sourced raw materials. A unique feature of the samples from these sites is that, despite the very evident use of lead, copper still appears in the mixture, leading us to believe that lead and copper minerals were indeed being intentionally mixed, as they still are today by local potters who add Cu to create a deeper hue of black (Max Enuel Robles, personal communication, 2022). Within this same area, the VP8 site, although near the CK sites, has other compositional features, with a predominance of the FAL1 and FAL1a groups, along with two samples that fall into the FAL3 group.

Lastly, the recipes based on jacobsite (FAL3) seem to correspond to a different preparation that is rare in our set of samples (4 cases). Silver content is also lower in these recipes than in the rest of the mixtures, and they are the only ones with very low metal content. The relative lack of cadmium, bismuth, molybdenum, and antimony indicates that these are not sulfide-based recipes, but use oxides as their main component (Table 1). In addition, their high iron content and low copper concentration yield an elemental composition that is different from all other recipes. Thus, by using iron and manganese oxides, FAL3 represents a distinct compositional logic. The use of iron and manganese as the main mineral pigments for black paint has been reported as a common feature in Northwest Argentina, in both pre-Inca and Inca ceramic samples, especially from Catamarca Province (Puente et al. 2017; Puente et al. 2019; Tomasini et al. 2020; Palamarcuk et al. 2021; Ratto et al. 2021; De la Fuente et al. 2024a). In our case, all the sherds were of Aconcagua style, and the sites where we found this recipe have either Inca contact dates or Inca components. Furthermore, one of them, site VP8, is located

Table 4

Summary of the mineralogical and chemical characteristics of the metallogenic belts of Central Chile (Maksaev et al. 2007; Gröpper 2011).

Location	Metallogenic Belt	Type of Deposit	Mineralization	Primary mineral association	Secondary mineral association	Chemical elements
Coastal plains/ Western Coastal Range	Jurassic Orogenic Gold Deposits	Intrusive Jurassic, Felsic dykes, quartz veins and veinlets	Disseminated, in veins and veinlets	Quartz – gold – magnetite – (pyrite)	Cinnabar, orpiment, arsenopyrite and realgar	Au, Fe (+2, +3), S, + Hg, + As, Sb
Eastern Coastal Range	Lower Cretaceous Stratabound Copper Deposits	Rhyodacite and basalt rocks of the Lo Prado Formation and Inferior Member of the Veta Negra Formation	Disseminated, hydrothermal breccias, in veinlets and infilling primary and secondary spaces	Chalcocite – bornite, bornite-chalcopyrite, chalcopyrite-pyrite and pyrite	Hematite, calcite, quartz, albite and rare sphalerite, galena, arsenopyrite and bitumen	Cu, Fe, S, Ca, Na, Zn, Pb, As, C
Eastern Coastal Range	Upper Cretaceous Epithermal and Mesozonal Polymetallic Veins-type Deposits	Intrusive rocks from the Late Early – Early Late Cretaceous, but also volcanic rocks with intercalations of Jurassic and Cretaceous sedimentary rock	Massive faulted veins, stockwork, disseminated and hydrothermal polymetallic breccias	Sphalerite, chalcopyrite, pyrite, arsenopyrite, silica, baryte, carbonates, gold, argentite, silver, electrum	Magnetite, hematite, magnesium oxides, galena, tetrahedrite, tennantite, bornite	Au, Ag, Cu, Zn, Fe, Pb, S, Ba, Ca, Mn, As, P
Andes Mountains	Miocene-Early Pliocene Cu-Mo Porphyry Deposits	Volcanic rock (Abanico and Farellones formations), intrusive granodiorites, and porphyry bodies	Cement in “magmatic” breccias, stockwork, wallrock, breccia clasts and veinlets	Chalcocite, bornite, chalcopyrite, covellite, molybdenite, pyrite	magnetite, actinolite, anhydrite, specularite, turmaline, gypsum, siderite, rare galena, and tennantite	Cu, Fe, Mo, S, Ca, As

at the foot of Cerro Collipeumo, an Inca fortification (Sanhueza et al. 2023). It therefore seems reasonable to assign this recipe to a particular “way of doing” from Inca times, either because the potters had access to a new firing technology to reach higher temperatures, as would have been required for jacobsite, or because the potters were adopting new recipes, maybe through contact with *trans*-Andean populations, which are well documented in the literature during Inca times (De La Fuente et al., 2024b).

4.2. Implications for networks of social relations

The recipes used to create the black paint of Aconcagua Salmon vessels are diverse, yet they have one element in common: copper ores. This particular use of Cu in Central Chile to achieve the color black was described in the only previous XRD paint analysis of a sherd of Aconcagua Salmon pottery found at the María Pinto site that contained abundant copper, and an Inca-style sherd from the Quilicura site that contained very little copper (Stehberg 1977). The use of Cu in preparing the black paint is also common in Diaguita ceramics from sites in the neighboring region of Chile’s semi-arid north that are contemporaneous with Aconcagua Salmon ceramics (Dinator and Morales 1990; Seguel et al. 2005; Osorio et al. 2014; Campos and Aguayo 2015). While only a limited number of Diaguita samples have been analyzed, they appear to have used tenorite, a copper oxide not found in Central Chile. This suggests that the Aconcagua and Diaguita groups of Chile used locally available copper minerals in their black paint recipes.

In regard to the implications of our findings for relational networks among Aconcagua groups, the sharing of core ideas and their local application, as described above for black paint recipes, and for Aconcagua ceramic production in general, is consistent with the proposal made by some authors, that Aconcagua groups were socially integrated, and that Aconcagua Salmon type vessels played a particular role in this dynamic (Falabella et al. 2016). However, the diversity of the recipes, clearly based on the local availability of resources, reaffirms the territorial anchorage of Aconcagua groups and their ceramic production, which relied largely upon local resources. The same also holds for the pigment of Aconcagua Salmon type vessels. This is true for sites in the mountains and Central Valley and is especially clear in sites in the southern part of the basin (Angostura), where the Pb signal and its chemical associations are linked directly to nearby metallogenic belts.

For sites on the coast and in the valleys of the Coastal Range, the copper component of recipes determined from sherds found there

suggests that the pigments were obtained from sources located inland. This seems to reaffirm the notion that the groups inhabiting these territories interacted with each other in a spatially integrated pattern that lasted until at least the 16th century (Contreras 2009). Stable isotope studies of individuals buried at Tejas Verdes 1, L. Matanzas, and Puangue have shown, through analyses of drinking water and diet, that both males and females circulated between the Coast and the Coastal Range (Falabella et al. 2020). Studies of pottery, on the other hand, have highlighted stylistic relationships and the presence of vessels produced with Puangue clays at coastal sites (Falabella and Andonie, 2011; Falabella et al. 2021). However, the coast is not a homogeneous area, as coastal sites do not share clay sources or the same pigment recipe, and do not appear to have had links with the same inland zones.

Having copper as a common factor among the black pigments of Aconcagua Salmon ceramics is another quality of this type of vessels, representing a complex synthesis of homogenization with an integrating effect and local and even personal decisions. In this regard, investigators have emphasized the particular unifying effect of these vessels, based on three characteristics: their color, stylistic pattern, and the three-armed *trinacrium* motif. These findings therefore seem to suggest that the visible physical qualities of the vessels (salmon color, black paint, decorative style, and *trinacrium* motif), as well as non-visible ones such as mixing clays and the use of copper as pigment, seem to be equally important in fulfilling their integrative function.

5. Conclusion

The compositional characterization of 122 Aconcagua Salmon type ceramic sherds from twelve sites in the Central Zone of Chile was carried out with LA-ICP-MS and 40 of them with Raman. The results identified five chemical groups, two of which are composed mainly of copper, iron, and clay, two enriched with lead, and one of manganese and iron with very low copper content. The minerals detected by Raman are in line with the chemical groupings. The composition of the most abundant groups, FAL1 and FAL1a, is based on Cu and Fe ores mixed with clay. This composition is typical of sites along the Maipo River Valley from the Pacific coast to the Andes Mountains and—with the exception of Cu minerals at coastal sites—we were able to establish that the raw materials used were available in the vicinity of the sites, by cross-referencing information obtained in this study with the particular elemental characteristics of metallogenic belts nearby. For its part, the FAL2 group is essentially composed of a Pb ore, probably galena, a mineral with

distribution limited to the southern part of the Maipo River basin, which is also the location of two of the sites (CK12 and CK21) that exclusively use this recipe—a mixture that also includes Cu minerals, magnetite, and a small amount of clay. FAL2a, which also incorporates Pb ores and is present at these sites, appears too in some samples further north. However, this principle of using local resources to prepare the paints, does not rule out the possibility that groups obtained materials from other zones or communities. Pigments, or the minerals used to prepare paints, have a much wider radius of procurement than clays used to prepare paste, and so we do not rule out the possibility that these materials were in circulation and served as a mechanism to strengthen ties between communities. The FAL3 chemical group, in contrast, has an entirely different composition that is based on jacobsite—a manganese mineral—along with Fe minerals, but in contrast to all previous groups, FAL3 samples showed a very low Cu content in chemical analysis and no Cu minerals were suggested in the Raman spectra. This composition appears in sites that remained in use during the Inca period and coincides with the recipe described for sites from the same period in Argentina (De La Fuente et al. 2024a; Prieto et al. 2010), which is why we have assigned it to a new modality introduced or adopted by potters through contact with *trans*-Andean people in Inca times.

We conclude that paint production at the regional level involved shared knowledge and a shared way of doing (recipe) in which the inclusion of copper ore played a central role. This was put into practice by potters in different communities using local raw materials and formed part of the integrative principle underlying Aconcagua Salmon ceramics.

CRediT authorship contribution statement

Amapola Saball: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Fernanda Falabella:** Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation. **Lorena Sanhueza:** Writing – review & editing, Validation, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **Hector Neff:** Methodology, Investigation, Formal analysis. **John V. Dudgeon:** Methodology, Formal analysis. **Álvaro Aliaga:** Methodology, Formal analysis. **José Cárcamo Vega:** Methodology, Formal analysis. **Carlo Divasto:** Visualization, Methodology, Investigation.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jasrep.2025.105386>.

Data availability

Data will be made available on request.

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