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Pre-Columbian metallurgy – Evidence of pyrotechnical ceramics from Rincón Chico, Northwestern Argentina (Andes)

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ABSTRACT

An assemblage of 16 fragments of pyrotechnical ceramics used for metallurgical processing was examined by scanning electron microscopy (SEM). The ceramics came from Rincón Chico in the Andes Region of Northwestern Argentina. They were dated as pre-Hispanic. The examined assemblage comprised seven crucible fragments, five mould fragments, two fragments of so-called perforated crucibles and another two fragments which had not been typologically classified yet. Ten fresh fracture samples were prepared, in order to examine the variation of the degree of vitrification in the ceramics. For comparison subsamples were taken from two fragments and subsequently re-fired under controlled conditions at temperatures between 650 °C and 1150 °C. In this way the micromorphology observed in the archaeological samples could be linked to equivalent firing (or operation) temperatures. Apart from the fresh fractures 14 polished sections were prepared in order to examine elemental composition and microstructure. These provided information concerning the selection of raw materials, the potential addition of pumicite as temper and the application of bone ash mixed with fine clay as lining. Furthermore, the spot analysis of metal residues provided information about the processed metal.

1. Introduction

The present study concerns a small assemblage of Pre-Columbian pyrotechnical ceramics from the Southern Andes Region. The examined material comes from the archaeological site of Rincón Chico (RCh), Yocavil Valley (Catamarca Province), which is located on the eastern range of the Andes (approximately 2000 mamsl) (Fig. 1). Covering an area of 500 ha, Rincón Chico is a good example of the social complexity of the pre-Hispanic period (10th–16th centuries AD), as it is seen in its intricate architectural pattern, its large size and diversity of activities conducted there. The investigation of metallurgical activities in particular is expected to shed light on the level of craftsmanship and material culture.

Primary scope of the present study was to explore the technology of ceramic fabrication and their adaption to pyrotechnical functions. The use of ceramic tools at temperatures, which exceed their common firing temperatures, requires a sufficient level of heat resistance. Even though basic heat resistance was commonly achieved through selection of specific clays and/or addition of non-plastic temper materials (Schneider and Zimmer, 1984; Freestone and Tite, 1986), effectively refractory materials, such as kaolinitic fireclays, were used on a routine basis in Europe only from the Roman period onwards (Freestone, 1989). Only then thin-walled crucibles could be fabricated, which could be heated solely externally (Martinón-Torres and Rehren, 2009). Before, crucibles were heated like furnaces primarily from inside. For internal heating increased porosity has proved to provide advantages in view of reducing heat transfer within the ceramics (Hein et al., 2013). Also the crucibles of the present assemblage indicated a similar functionality, based on their wall thickness and traces of high temperatures mainly at their internal surfaces. Apart from their production technology the ceramics were expected to reveal information about the actual metallurgical process or processes they were involved in. This was of particular interest for the comparison with the results of a recent study of contemporary material from Chile (Plaza and Martinón-Torres, 2015). Even though in the present study it was not possible to directly investigate metallic artefacts, the extant metal or slag residues as well as the metal concentrations in the ceramics allowed for an initial determination of the processed metals.

The analytical approach was focused on the investigation of the ceramics' microstructure. Polished sections as well as fresh fractures of the ceramics were examined under the optical microscope (OM) and under the scanning electron microscope (SEM). The study results will be presented and discussed in terms of technology and function.

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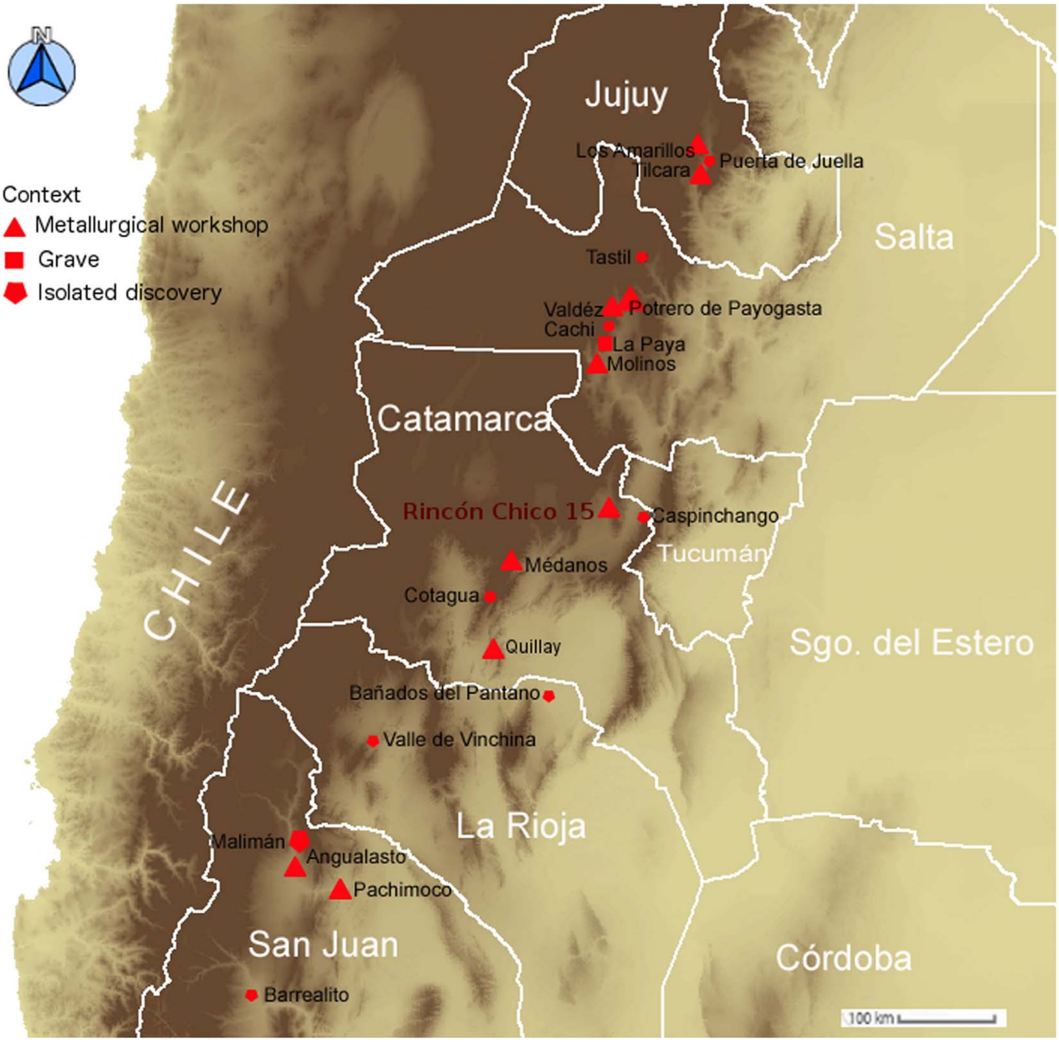

Fig. 1. Map of the Andes Region: indicated are apart from Rincón Chico other pre-Columbian sites with metallurgical finds.

2. Samples

The examined ceramic assemblage comprised sixteen samples: seven crucible fragments, five mould fragments, two fragments of so-called 'perforated' crucibles and two fragments which had not been typologically classified so far (Table 1). Due to the large typological variation of moulds in the archaeological record, these indeterminate samples are assumedly fragments of moulds whose morphologies have not yet been recognised. With the exception of Sample ARG08, the present samples were found in the metallurgical workshop of Rincón Chico 15 (Yocavil Valley, province of Catamarca, Argentina), one of the most intensely excavated pre-Hispanic metallurgical workshops in Southern Andes (Tarragó, 2007; Gluzman, 2017). In other contexts nearby, all located in the lowest part of the site, metallurgical evidence was registered as well but in a lesser quantity, represented by ARG05. The combination of all evidence indicates a significant level of production. Apart from > 500 fragments of pyrotechnical ceramics the archaeo-metallurgical finds include simple thermally altered structures in the floor, minerals, metal debris, smelting slags and vitrified fuel ash slags (González, 2004). The find assemblage is assigned to the late pre-Hispanic period (10th–16th centuries AD), starting in the pre-Inca period and ranging to the Inca period. According to the data obtained, it is suggested that in the workshop minerals were reduced, metal drops were melted, metals were refined and tin bronze alloys were prepared. The metallurgical processes took place in simple open hearths, in some cases surrounded by medium size clay lumps. The combustion structures would have been used repeatedly but in intermittent ways generating overlapping structures. With the Inca domination the production methods were modified and stone circular furnaces, the so-called *huayras*, with holes on the walls, which allowed the wind to oxygenate the charge, were installed. They co-existed with the open

Table 1
Pyrotechnical ceramic samples included in the present study: the column Sector refers to the sector of the site in which the fragment was discovered. The type of pyrotechnical ceramics could not be determined (n.d.) in two cases.

Sample	Sector	Type
ARG02	801	n.d.
ARG03	638	Mould
ARG04	533	Mould
ARG05	525	Mould
ARG08	RCh 14	Crucible
ARG09	533	Crucible
ARG11	540	Perforated crucible
ARG12	527	Crucible
ARG14	887	Mould
ARG15	951	Mould
ARG16	951	Crucible
ARG20	21	n.d.
ARG24	511	Crucible
ARG26	Rec. Sup.	Crucible
ARG41	Basural	Perforated crucible
ARG43	881	Crucible

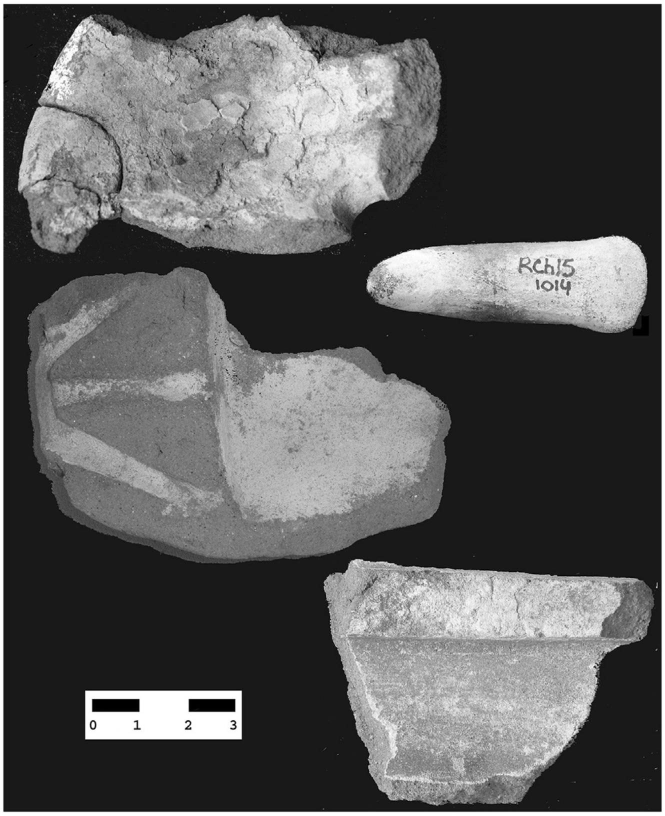

Fig. 2. a) 'Perforated' crucible b) Plug c) Closed mould of small bell, d) Open mould of flat object.

pits, employing them for small-scale metallurgical activities where the use of tuyères was critical to reach the high temperatures needed.

The most ubiquitous archaeo-metallurgical debris, however, is the assemblage of pyrotechnical ceramics. Within the site three main categories can be found: (a) open and closed casting moulds, for producing objects as axes, chisels, pins, blades, bells, discs and ingots, i.e. utilitarian and non-utilitarian items, (b) crucibles and (c) 'perforated' crucibles. The latter ones were composed from two parts, a container with a hole in the base and a plug (Fig. 2). It was suggested this type of crucibles was designed to collect the molten metal that was distributed afterwards in different moulds (Niemeyer, 1981). The plug - employed from inside or outside - would block the hole, facilitating the control of the metal poured out (González, 1997). Some of them show very sophisticated fixing systems near their mouth with internal or external perimeter holding channels (González and Gluzman, 2009). González (1997) suggested the 'perforated' crucibles, part of the pre-Inca tradition in the area was a local invention later transferred to other parts of southern Andes, such as North of Chile, by the Incas. By that time they appear to have been a quite common type of metallurgical ceramics (Plaza and Martinón-Torres, 2015).

3. Analytical approach

In order to examine the microstructures of the ceramic fragments scanning electron microscopy (SEM) was used. The SEM analysis was performed using a FEI Quanta Inspect D8334 scanning electron microscope, coupled with an attached energy-dispersive X-ray spectrometer (SEM-EDS) (EDAX PV 7760/68). The EDS measurements were taken at 25 kV with a live time of typically 100 s and the spectra were evaluated using the standardless ZAF quantification method. Sub-samples were cut from ten ceramic fragments using a pair of pincers. The cut pieces were mounted with carbon glue on sample holders so that the fresh cut sections could be examined allowing for an assessment of the degree of vitrification and thus for an estimation of the temperatures or temperature gradients evolving during use or possible pre-firing.

For an adjustment of the temperature estimation two fragments, one mould fragment and one crucible fragment (ARG14 and ARG24), were selected for re-firing. Therefore, from each of the two fragments five small sub-samples were taken from external surfaces, which were assumedly not exposed to extreme temperatures, assuming a primarily internal heat source. In order to investigate the development of the microstructure at specific temperatures the pieces were fired in a laboratory furnace in oxidizing atmosphere at 650 °C, 850 °C, 950 °C, 1050 °C and 1150 °C, respectively. In each case the heating rate was 200 °C/h and the soaking time 1 h. Afterwards also the re-fired ceramic fragments were cut and mounted on sample holders so that fresh fractures could be examined. For the SEM examination all samples were carbon coated.

Apart from the fresh fractured sections fourteen fragments were prepared as polished sections. The sections were cut, mounted in resin, polished and carbon coated. Polished sections provide the essential advantage of more precise EDS results because the sample geometry is better defined. The SEM examination provided information about bulk composition, pore structure, inclusions, metal and slag residues and potential surface treatment or lining. On the other hand the degree of vitrification is not as clearly to examine as in fresh fractured samples. This applies particularly to initial vitrification.

Before the carbon coating all samples, fresh fractures as well as polished sections, were additionally examined with a Leica S6 D optical stereo microscope. This provided basic information about the petrography, colour variations of the fired clay, linings or metal residues and the pore structure.

4. Results and discussion

4.1. Vitrification in fresh fractures

The examination of the re-fired sub-samples taken from ARG14 and ARG24 demonstrated the changes of the microstructure in relation to temperature and allowed at the same time to assess the minimum temperature the ceramics were exposed to in general and the process temperatures at their external surfaces in particular (Table 2). At 650 °C, a firing temperature at which anyway no significant micromorphological changes can be expected, the micromorphology of the mould fragment did not present any clear initial vitrification, resembling basically the micromorphology of the original fragment (Fig. 3). At the same temperature the micromorphology of the crucible sample presented extensive vitrification, again similar as the micromorphology of the original fragment. At a firing temperature of 850 °C initial vitrification was observed in the mould fragment while the micromorphology of the crucible fragment did not change. As for the crucible a significant change of the micromorphology was observed only at a

Table 2
Ten fresh fracture samples examined under the SEM: indicated are the degrees of vitrification observed at the internal surface and in the ceramic body (NV - no vitrification, IV – initial vitrification, EV – extensive vitrification, IMV – intermediate vitrification, TV – total vitrification).

Sample	Type	Vitrification surface	Vitrification body
ARG02	n.d.	IV	NV
ARG04	Mould	IMV	EV
ARG08	Crucible	TV	TV
ARG11	Perforated crucible	IMV-TV	EV-IMV
ARG14	Mould	IV	NV
ARG15	Mould	TV	IMV-TV
ARG20	n.d.	EV	EV
ARG24	Crucible	IMV-TV	EV
ARG26	Crucible	TV	IMV
ARG41	Perforated crucible	IMV-TV	EV-IMV

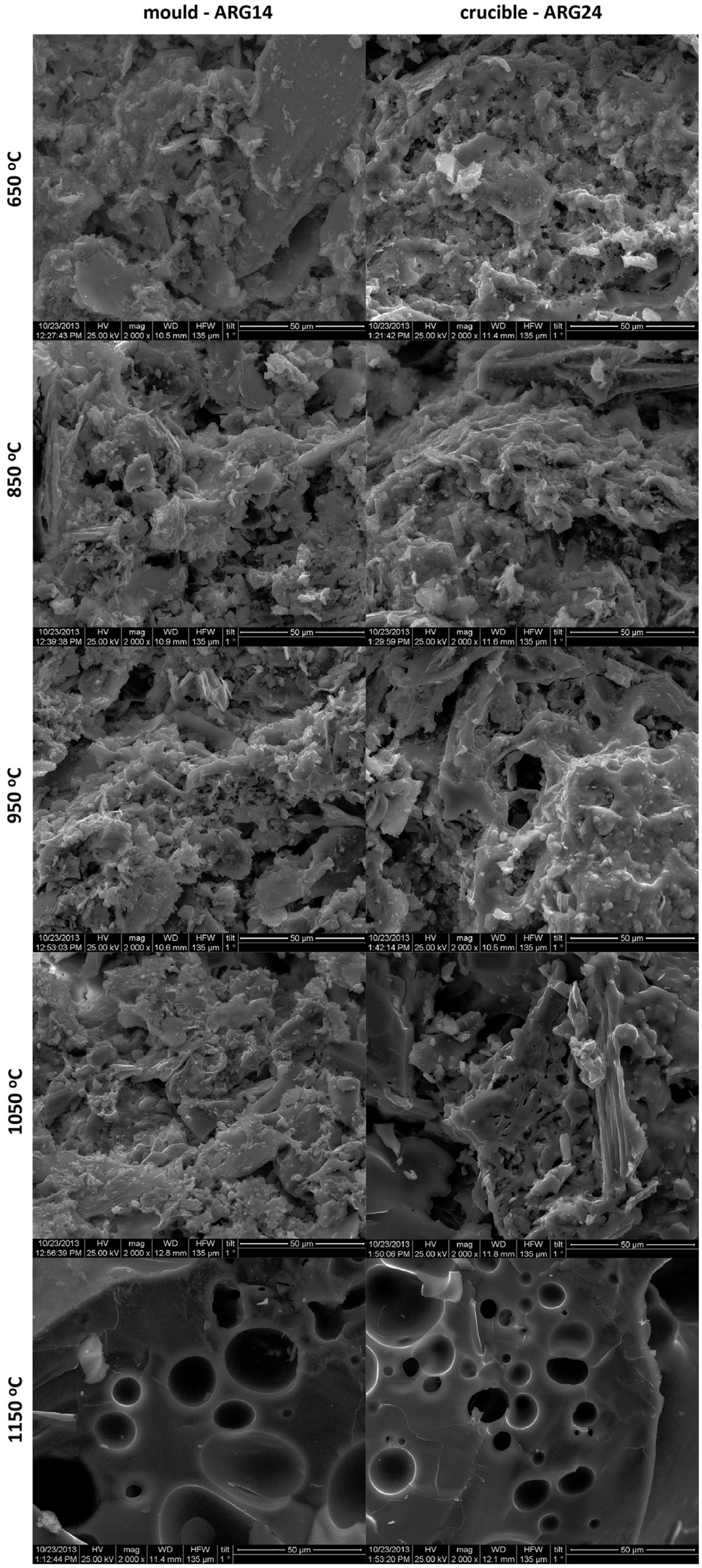

Fig. 3. Microstructure in re-fired sub-samples of a mould fragment (left) and a crucible fragment (right): the sub-samples were fired at 650 °C, 850 °C, 950 °C, 1050 °C and 1150 °C, respectively, with a heating rate of 200 °C/h and a soaking time of 1 h.

Table 3
Chemical composition of the ceramic bodies measured by SEM-EDS: each composition corresponds to the average of several independent measurements of areas typically 0.5 × 0.5 mm^2 to 1 × 1 mm^2, in the polished section of the specific sample. Each measurement was normalized to 100% and the number of measurements is indicated in parentheses after the sample code.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO
ARG03 (2)	2.0	2.0	13.1	67.6	0.2	0.1	0.5	4.5	4.2	0.8	0.3	4.8	n.d.
ARG05 (4)	2.3	1.5	14.0	68.6	0.4	0.2	0.5	5.2	2.1	0.6	0.3	4.0	0.3
ARG08 (4)	3.0	1.5	14.9	67.5	0.2	0.3	0.3	4.8	2.9	0.6	0.2	3.5	0.3
ARG09 (5)	2.4	1.4	14.4	69.8	n.d.	n.d.	n.d.	5.2	2.2	0.5	0.1	3.9	0.1
ARG11 (3)	2.3	1.3	13.1	70.3	0.4	0.3	0.5	5.0	2.8	0.4	0.3	3.0	0.3
ARG12 (5)	2.1	1.7	14.4	67.2	0.4	0.2	0.7	5.1	2.5	0.6	0.3	3.9	0.3
ARG14 (7)	2.0	1.9	14.6	65.7	0.2	0.2	0.4	4.8	5.1	0.5	0.1	4.5	n.d.
ARG15 (4)	3.9	1.4	14.3	68.9	0.1	0.1	0.1	4.2	1.8	0.6	0.2	3.6	0.4
ARG16 (3)	2.9	1.5	14.5	66.2	0.2	0.1	0.2	5.9	3.6	0.6	0.2	3.8	0.3
ARG20 (4)	2.1	1.9	15.1	68.2	0.2	0.2	0.5	4.6	2.1	0.6	0.3	4.1	n.d.
ARG24 (6)	2.9	1.4	14.9	67.6	0.3	0.1	0.6	5.6	1.6	0.6	0.3	3.8	0.3
ARG26 (4)	3.1	1.5	13.8	67.0	0.2	0.2	0.2	4.7	4.2	0.5	0.2	3.3	0.9
ARG41 (3)	2.5	1.6	14.3	69.0	n.d.	n.d.	0.3	3.8	4.0	0.5	0.2	3.7	n.d.
ARG43 (4)	2.9	1.6	14.4	67.4	0.2	0.1	0.2	4.7	3.3	0.6	0.2	4.2	0.2

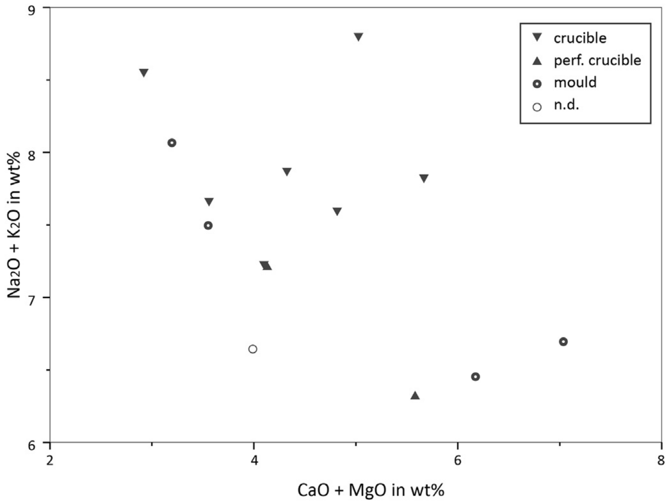

Fig. 4. Sums of the Na2O and K2O concentrations versus the sums of the CaO and MgO concentrations: each symbol corresponds to the average concentrations measured in a specific polished section.

firing temperature of 950 °C, presenting still extensive vitrification, though. The mould fragment re-fired at this temperature presented a similar micromorphology. Therefore, the crucible body was presumably exposed to an equivalent firing temperature of 850 °C to 950 °C, either through pre-firing before use or through external heating in the open hearth during the metallurgical process. On the other hand, in the case that the mould was pre-fired before use the firing temperature must have been clearly below 850 °C. The sub-samples re-fired at 1050 °C presented extensive to intermediate vitrification while sub-samples of both fragments were totally vitrified when re-fired at 1150 °C (Fig. 3). This allowed for adjusting the following observations in different layers of the original samples to equivalent firing temperatures and for estimating the operation conditions of the metallurgical processes (Hein et al., 2007).

All investigated ceramic fragments presented clear vitrification, which confirmed not only their assumed use in high temperature processes but indicated also pre-firing before use. Particularly the crucibles showed extensive to intermediate vitrification of the ceramic body, indicating an original pre-firing at equivalent firing temperatures probably of above 950 °C. It has to be considered, though, that they were assumedly also heated during their use. However, in an open hearth temperatures of above 950 °C are difficult to maintain and the firing process of the ceramics would have consumed energy, which would have not been available for the actual metallurgical process. Their internal surfaces presented generally a higher degree of vitrification, intermediate to total, supposedly due to the contact with the load of molten metal and fuel during their operation (Table 2). This confirmed that the crucibles were primarily heated internally. The metallurgical process must have reached temperatures of clearly above 1100 °C. Crucible ARG08 was totally vitrified over the whole section, assumedly as a result of additional external heating during the metallurgical process, reaching in this specific case a temperature of 1100 °C. Also the two perforated crucibles presented extensive to intermediate vitrification of the body and intermediate to total vitrification at the internal surface. The moulds and the un-classified fragments, on the other hand, presented generally a lower degree of vitrification of the ceramic body. Pre-firing can be assumed but apparently at lower equivalent firing temperatures, compared to the crucibles, and also the degree of vitrification of their internal surfaces was lower. But this could also be related to the smaller duration of their operation because the metal was cooling immediately after casting. The mould ARG15 was an exception because it presented intermediate to total vitrification. Whether this was related to pre-firing at a higher temperature or whether this mould had been used under different operation conditions could not be clarified yet.

4.2. Bulk composition and inclusions

The bulk analysis of the ceramic bodies by SEM-EDS indicated the use of quite similar raw materials for all types of ceramics. The ceramic body of each polished section was analyzed in at least three different areas of typically 1 × 1 mm^2. The ceramics presented relatively high SiO_2 concentrations of c. 65 to 70 wt%. They were comparably low calcareous, with CaO concentrations of c. 2 to 5 wt%, and on the other hand rich in alkalines, with Na_2O concentrations of c. 2 to 3 wt% and K_2O concentrations of c. 4 to 6 wt% (Table 3). The crucibles apparently tended to present a slightly higher alkaline content, which was assumedly caused by contamination with fuel ash (Fig. 4). Apart from the used clays the high alkaline concentrations were probably related also to pumicite and phyllite inclusions, which could be frequently observed in the ceramic body (Fig. 5) (Table 4). Pumicite inclusions in this abundance are not observed in common pottery from the area (Palamarczuk, 2008, 2011) while on the other hand prevalent pumicite inclusions have been observed also in material from the metallurgical workshop of Quillay, in Catamarca province and attributed to Inca times (Spina and Gluzman, 2017). Even though it cannot be clarified at this stage, whether the clays were additionally tempered with pumicite, the presence of these porous materials in the ceramic body was technologically of advantage because the heat transfer through the ceramic walls was suppressed which increased at least in the case of the

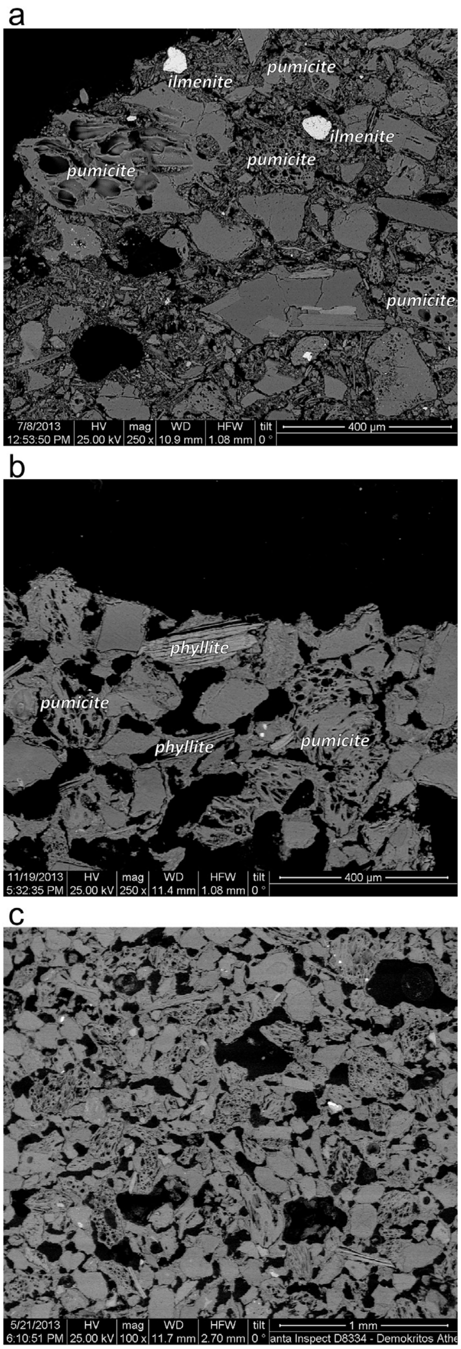

Fig. 5. SEM micrographs in backscattering mode of mould sample ARG14 (top) and crucible sample ARG24 (centre and bottom): typical inclusions such as pumicite and ilmenite (top) or phyllite (centre) can be observed. Particularly the pumicite appears to be quite abundant and well sorted in the ceramic matrix (bottom).

crucibles their heating efficiency (Hein et al., 2013). Another common strategy to increase the porosity of pyrotechnical ceramics, tempering with organic fibres, which was common for example in the Mediterranean region (Evely et al., 2012), could not be observed in the present ceramic assemblage.

Further typical inclusions, observed in the ceramics, were heavy minerals like ilmenite $FeTiO_3$ and monazite $(Ce,La,Nd)PO_4$. Their presence was most probably related to the geological environment of the used raw materials and their paragenesis in the supposedly igneous parent rock (Table 4).

4.3. Lining

A conspicuous technological feature was a calcium and phosphorus rich lining, which could be observed on most of the internal surfaces of the examined ceramic fragments, crucibles as well as moulds. The lining presented a thickness of typically 100–200 µm but it reached in some cases up to 500 µm (Table 4). The major component of the lining was assumedly hydroxyapatite $Ca_5(PO_4)_3(OH)$ which was mixed as bone ash with fine clay slurry and applied on the ceramic body (Table 5). A similar lining technology has been observed in the study of pyrotechnical ceramics from Inca sites in the Aconcagua Valley, Central Chile (Plaza and Martinón-Torres, 2015). In this case, however, apparently also the ceramics were additionally tempered with bone fragments increasing the calcium and phosphorus content in the ceramic body. This was not observed in Rincón Chico. It has to be further examined, whether the apatite rich lining had a solely protecting function for the ceramic body or whether it was actually reacting with the metal and supporting the process. However, because the lining was applied to both crucibles and moulds their primary function was probably the protection of the ceramic body. A particularly interesting case was the crucible ARG43, in which two separate layers of lining could be observed evidencing presumably the repair and reuse of this specific crucible (Fig. 6).

4.4. Metal residues

In the analyzed bodies of moulds and crucibles copper was in general present with concentrations of up to c. 1 wt% particularly in a layer of 0.5 to 1 mm below the internal surface (Table 3). The apatite lining presented higher copper concentrations of up to c. 3.5 wt% (Table 5). The measured concentrations were assumedly the result of intrusion of metals into the matrix of either crucibles or moulds during the metallurgical process. The resulting metal content depends to a large extent on the vapour pressure of the specific elements with copper as well as tin presenting comparably small vapour pressures (Kearns et al., 2010). Apparently the apatite lining protected the ceramic matrix from metal intrusion, indicated by its higher copper concentrations.

Apart from the copper content, observed in ceramic body and lining, occasionally also small metal prills could be determined in the fragments commonly close to their internal surfaces (Fig. 7). These observations allowed for conclusions concerning the metallurgical process. The metal residues were detected in five of the crucibles and in one mould (Table 6). Apart from copper also tin could be verified with concentrations of up to 15 to 20 wt%, indicating the processing of tin bronzes, coinciding with studies on bronze objects from the site (González, 2004; Lechtman, 2014). In the metal residues on the surface of the mould fragment ARG15 also a small arsenic concentration was measured (c. 5–6 wt%), while the presence of arsenic could not be verified in metal residues of other fragments. Finally, some of the metal residues presented increased chlorine content probably related to post-depositional corrosion of the metallic copper residues within a chlorine rich environment.

5. Conclusions

The success of the metallurgical work was strongly linked to the functionality of the pyrotechnical ceramics. These had to withstand temperatures of up to 1200 °C during different processes, such as melting, refining or casting. The degree of vitrification observed in the surfaces of the analysed ceramics indicated that temperatures like this were indeed reached. Particularly the crucibles were exposed to these temperatures assumedly for a considerable time during which, failure such as distortion or fracture, had to be avoided. The moulds, on the other hand, had to withstand the extreme temperatures only for a comparably smaller time because after the casting the metal was left for cooling. During the actual casting, however, thermal shock and thermal

Table 4
Characterization of the microstructure and lining observed in the examined polished sections.

Sample	Type	Lining	Metal remains	Inclusions
ARG03	Mould	Ca&P (apatite) c. 100–200 µm		Pumicite, phyllite, monazite, ilmenite
ARG05	Mould	Ca&P (apatite) c. 50 µm		Monazite, phyllite, pumicite, ilmenite
ARG08	Crucible	Ca&P (apatite) c. 100–200 µm	Cu&Sn	Monazite, phyllite, pumicite, ilmenite
ARG09	Crucible	Ca&P (apatite) c. 100–200 µm		Pumicite, monazite
ARG11	Perforated crucible	Ca&P (apatite) c. 100 µm		Monazite, phyllite, pumicite, ilmenite
ARG12	Crucible	Ca&P (apatite) c. 100–200 µm		Monazite, phyllite, pumicite, ilmenite
ARG14	Mould	n.d.		Phyllite, pumicite, ilmenite
ARG15	Mould	Ca&P (apatite) c. 500 µm	Cu, As&Sn, CuCl	Pumicite
ARG16	Crucible	Ca&P (apatite) > 500 µm	Cu&Sn, CuCl	Pumicite
ARG20	n.d.	Ca&P (apatite) c. 100 µm		Pumicite, phyllite, monazite
ARG24	Crucible	n.d.	Cu&Sn	Pumicite, phyllite
ARG26	Crucible	Ca&P (apatite) c. 100–200 µm	Cu&Sn, Cu	Pumicite
ARG41	Perforated crucible	Ca&P (apatite) c. 100 µm		Pumicite, phyllite, monazite
ARG43	Crucible	Ca&P (apatite) c. 500 µm	Cu&Sn	Monazite, phyllite, pumicite, ilmenite

Table 5
Bulk compositions of hydroxyapatite rich linings, supposedly bone ash mixed with clay slurry, measured with SEM-EDS: Each composition corresponds to the average of several independent measurements of areas typically $0.1 \times 0.1\ \mathrm{mm}^2$ to $0.5 \times 0.5\ \mathrm{mm}^2$, in the polished section of the specific sample. Each measurement was normalized to 100% and the number of measurements is indicated in parentheses after the sample code. The last column indicates the average ratio of CaO to P_2O_5.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	CaO/P_2O_5
ARG03 (2)	0.4	0.9	1.1	4.5	40.2	0.1	2.3	0.3	49.4	0.0	0.1	0.5	n.d.	1.2
ARG05 (1)	1.1	1.2	5.3	29.2	24.5	0.0	1.8	2.3	30.3	0.8	0.2	2.8	0.5	1.2
ARG08 (4)	2.0	1.9	5.2	18.4	27.8	0.4	1.4	1.7	37.1	0.6	0.3	2.8	0.4	1.3
ARG11 (3)	1.2	1.8	1.9	5.4	35.6	1.6	2.9	0.4	48.0	0.2	0.2	0.7	0.2	1.3
ARG12 (1)	1.5	4.5	9.5	41.0	13.9	0.3	2.6	4.1	15.1	0.6	0.2	4.3	0.4	1.1
ARG15 (2)	4.1	1.9	4.6	18.8	25.0	0.8	3.1	0.9	35.1	0.3	0.2	1.9	3.4	1.4
ARG16 (1)	1.7	1.8	3.3	10.4	33.6	0.6	2.5	1.0	41.6	0.4	0.3	1.7	1.2	1.2
ARG26 (1)	3.1	1.3	5.5	32.2	18.5	0.0	2.2	3.4	27.2	0.4	0.1	2.8	3.5	1.5
ARG41 (1)	0.5	1.7	1.4	7.7	37.6	0.3	1.4	0.3	47.6	0.4	0.2	1.2	n.d	1.3
ARG43 (7)	0.9	1.2	1.6	5.0	38.5	0.6	2.7	0.4	47.6	0.1	0.1	0.8	0.5	1.2

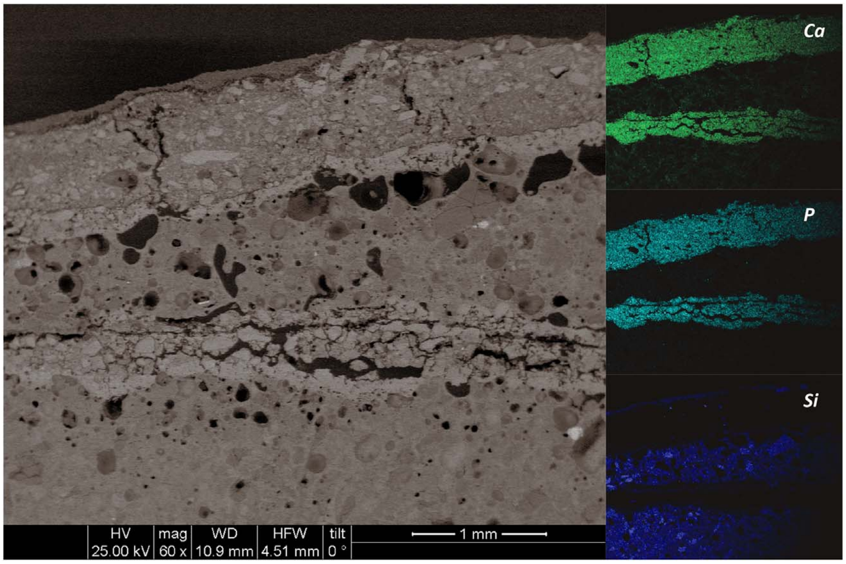

Fig. 6. SEM micrograph in backscattering mode and element maps of calcium, phosphorus and silicon of the internal surface of crucible fragment ARG43: the surface had been apparently repaired because two separate linings are visible one applied above the other.

stress had to be controlled in order to avoid fracture and eventual failure of the mould.

The present study indicated sufficient material properties of the ceramics, which were achieved for example by a high content of pumicite. The pumicite, which was assumedly intentionally added as temper to the clay paste, increased the porosity of the ceramics. Thus, the heat transfer in the ceramics was suppressed, which effectively increased the heating efficiency of the crucibles. A similar effect was possibly achieved by the addition of phyllite. The addition of organic temper, on the other hand, could not be discovered. This was a common strategy for example in the Mediterranean region to increase the porosity of pyrotechnical ceramics.

Another technical feature, which has been observed also at other metallurgical sites in the Andes, was the coating of crucibles and moulds with a lining consisting assumedly of bone ash mixed with clay slurry. The layer had most probably a protecting function for the ceramic body suppressing for example the intrusion of metal in the ceramic body. Furthermore, the lining provided an effective heat insulation reducing thermal impact on the ceramic body.

According to the excavated metal objects the metallurgical

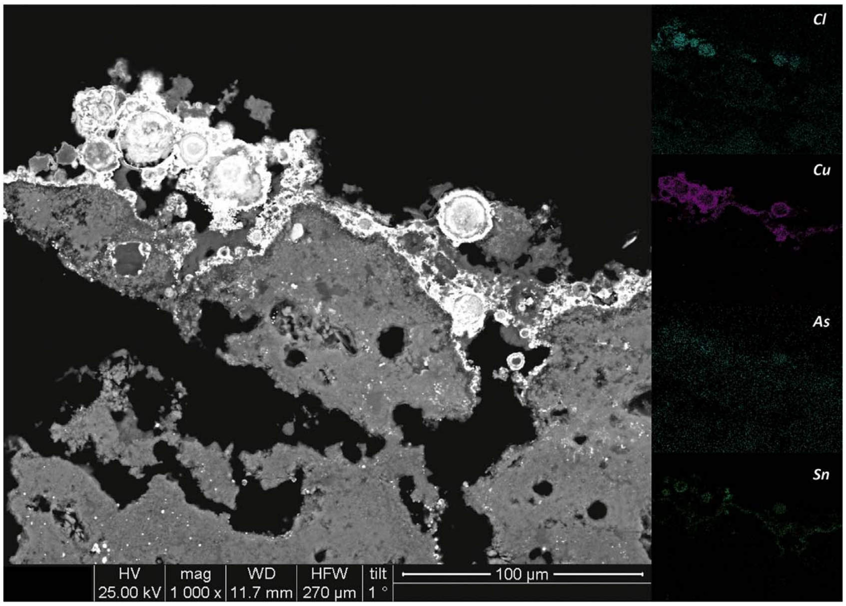

Fig. 7. SEM micrograph in backscattering mode and element maps of chlorine, copper, arsenic and tin of the internal surface of mould fragment ARG15: the metal residues on the surface present an inhomogeneous distribution of the elements belonging assumedly to the processed alloy.

Table 6

Elemental composition of metal residues determined in some of the fragments: the composition is normalized to 100%: the concentrations are semi-quantitative as oxygene is not considered in the normalization. Furthermore, post-depositional alterations have to be considered.

Sample	Shape	Cl	Cu	As	Sn
ARG08	Metal particle (5 × 20 μm^2)	0.2	71.6	n.d.	28.2
ARG15	Spherical prill (∅: 20 μm)	12.3	56.2	5.4	26.1
	Spherical prill (∅: 20 μm)	12.5	53.8	5.8	27.9
	Spherical prill (∅: 30 μm)	5.7	88.8	4.9	9.2
ARG16	Spherical prill (∅: 30 μm)	5.7	85.1	n.d.	9.2
ARG24	Metal particle (5 × 5 μm^2)	1.1	91.5	n.d.	7.4
	Metal particle (5 × 5 μm^2)	0.6	81.8	n.d.	17.6
	Metal particle (5 × 5 μm^2)	0.4	82.8	n.d.	16.8
ARG26	Spherical prill (∅: 20 μm)	0.5	97.0	n.d.	2.5
	Spherical prill (∅: 20 μm)	0.4	98.4	n.d.	1.2
	Metal particle (30 × 20 μm^2)	0.3	99.0	n.d.	0.7
	Metal particle (30 × 30 μm^2)	0.5	99.0	n.d.	0.5
	Spherical prill (∅: 20 μm)	0.3	99.3	n.d.	0.4
	Spherical prill (∅: 60 μm)	0.7	98.5	n.d.	0.8
	Spherical prill (∅: 50 μm)	0.2	99.5	n.d.	0.3
	Spherical prill (∅: 10 μm)	0.3	99.7	n.d.	0.0
ARG43	Metal particle (20 × 10 μm^2)	0.8	71.6	n.d.	27.6
	Metal particle (5 × 5 μm^2)	8.1	64.2	n.d.	27.7
	Metal particle (10 × 5 μm^2)	0.8	7.3	n.d.	92.0
	Metal particle (5 × 5 μm^2)	2.8	68.8	n.d.	28.4

workshops, using this kind of pyrotechnical ceramics, were able to produce decorated bronze objects such as axes, plaques and big bells of oval section, sometimes of several kilograms. At the present site no diachronic change in terms of the morphology of the different types of pyrotechnical ceramic tools was observed. On the other hand also on a regional scale recurrence of shapes and application of the apatite rich lining can be observed. The perforated crucible is one example which can be found in several sites along Northwestern Argentina as well as in the North of Chile.

The presence of several layers of lining observed in some samples from the area suggested the repair and reuse of these ceramics. At a site scale, the sum of the evidence allows to consider the existence of a successful and conserving ceramic technology employed in the production of bronze objects that did not change with time. At a regional scale, and taking into consideration other research conducted in Southern Andes, the evidence allows for arguing that a particular metallurgical tradition was shared in the area, reflected both in the formal characteristics of the goods produced and the technology evolved.

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