



Research paper

Clay supply for Aguada ordinary vessels from Piedras Blancas (4th to 12th centuries AC), Ambato Valley (Argentina)

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ABSTRACT

The provenance of the raw materials used to produce ordinary ceramic vessel of the Aguada Culture (4th to 12th c. AC) from the Ambato Valley (Catamarca, Argentina) has been evaluated. Since there are no commercial clay deposits in the area, local clayish sources were selected as possible candidates. Samples were collected from Precambrian to Low Paleozoic metapelites, clays from fault gouges derived from crystalline basement rocks, epiclastic rocks and Quaternary loessic sediments that filled the valley and crop out close to the archaeological sites. The pottery sherds were found at Piedras Blancas highly hierarchical site. Mineralogical and geochemical studies were conducted by XRD and FE-SEM-EDS on both the pot sherds and the possible source materials. The latter were also preliminary evaluated on basic physical and technological properties; test specimens were heated at different temperatures (800, 900 and 1000 °C) to study their thermal behavior and their mineralogical and textural transformations. The physical properties of the metapelites, the clay gouges and the loessic sediments suggest that they are suitable for ceramic production. The epiclastic rocks are mostly bentonitic and could have been used as additives to improve the plasticity and other properties of other clay materials. The mineralogy of the sherds is quite homogeneous with no significant differences between technological classes E and D; most of them bear either phlogopite, hornblende and/or hypersthene and high temperature phases (diopside, spinel, mullite and cristobalite) also found in some clays under natural conditions or after firing at 1000 °C. Commonly used provenance geochemical ratios are relatively similar in all pottery samples and in the selected source rocks and comparable with typical UCC. Hence, according to those values, all samples are related to each other and indistinguishable except for one sample (B30) highly enriched in REE. Nearly all raw materials and ceramics are either enriched in Cs, Bi, Sb or in any of these elements. The trend of using local materials for the pottery is suggested by the mineralogy and the geochemistry.

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1. Introduction

The provenance of the raw materials used for ancient ceramics is an issue of great importance in archaeological studies as it may provide crucial information on the management of natural resources, trading and technology (Rice, 1987). The question of whether raw materials were or not local has been widely discussed in the literature (Druc, 2013). It is not an easy matter to solve since the choices made by ancient potters (Arnold, 2005, 2006, 2011) respond to social, cultural, symbolic and religious or other principles which are not fully understood (Bertolino et al., 2010). Interdisciplinary approaches are needed to characterize the archaeological artifacts and to identify the sources of raw materials. In the last decades there has been a notorious increase on investigations where different measurements techniques are

combined (e.g. Tschegg et al., 2009; Bertolino et al., 2009a, 2009b; Szilágyi et al., 2012; Zimmermann et al., 2015).

This work intends to contribute with mineralogical, geochemical and other geological tools to the archaeological approach on the study of the provenance of clay sources for the ordinary ceramics of the Aguada Culture (Fig. 1) in northern Argentina. The pottery sherds were found in a stratigraphic excavation at Piedras Blancas site (Fig. 3). There are no commercial clay deposits in the valley thus the track of possible clay sources was based on geological and ethnoarchaeological criteria.

The results of such a study will not only contribute to the better understanding of the technological processes and the origin of the used materials but also to assist in establishing a database of Aguada ceramic pastes and raw materials. Moreover, it will help to comprehend the role of the ceramic objects in this new society, the organization of good's production, the consumption, management and selection of commodities and the access to natural resources by this culture active at Ambato Valley. Previous provenance studies of class A1 (black incise) Aguada ceramic from Ambato were based on clay samples selected by

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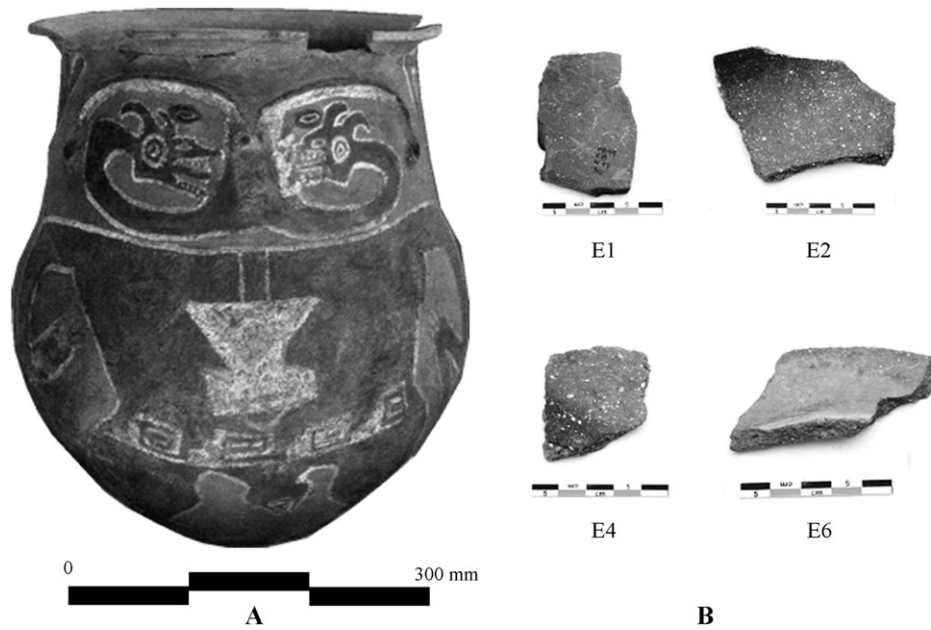


Fig. 1. A. Technological classes of ordinary pottery at PB. Class E vessel (Rosso Collection). B. Examples of classes E1, E2, E4 and E6 sherds, Scale = 5 cm.

ethnoarchaeological criteria (Laguens et al., 2007) but the results were not conclusive. Bertolino and Zimmermann (2013) reported the preliminary results on Piedras Blancas ceramics and pigments suggesting the possible localities of the raw materials. This work continues the archaeometric and methodological research carried out in the last fifteen years on ceramics and pigments from Catamarca province (Bertolino and Fabra, 2003; Bertolino and Zimmermann, 2013; Bertolino et al., 2009a, 2009b, 2011; Galván et al., 2010, Galván Josa, 2012, Galván Josa et al., 2009, 2010a, 2010b, 2013), applying X-ray diffraction (XRD) and scanning electron microscopy (SEM) combined with energy-dispersive spectrometry (EDX) analytical techniques.

2. Archaeological background and sites

In the 4th–5th c. AC, important changes in the way of living occurred at the Ambato valley (Fig. 2) in Northwestern Argentina (NOA) (Laguens, 2006a, 2006b). A new society emerged with a different and unprecedented power configuration.

This new cultural complex is known as the Aguada Culture (González 1961–1964, 1998; Pérez Gollán, 1991) which was the most important in the NOA and contemporary to the central Andean Cultures of Tiwanaku and Wari (González, 1979, 1998). Its influence spread regionally, encompassing most of the NOA. There was a common ideology

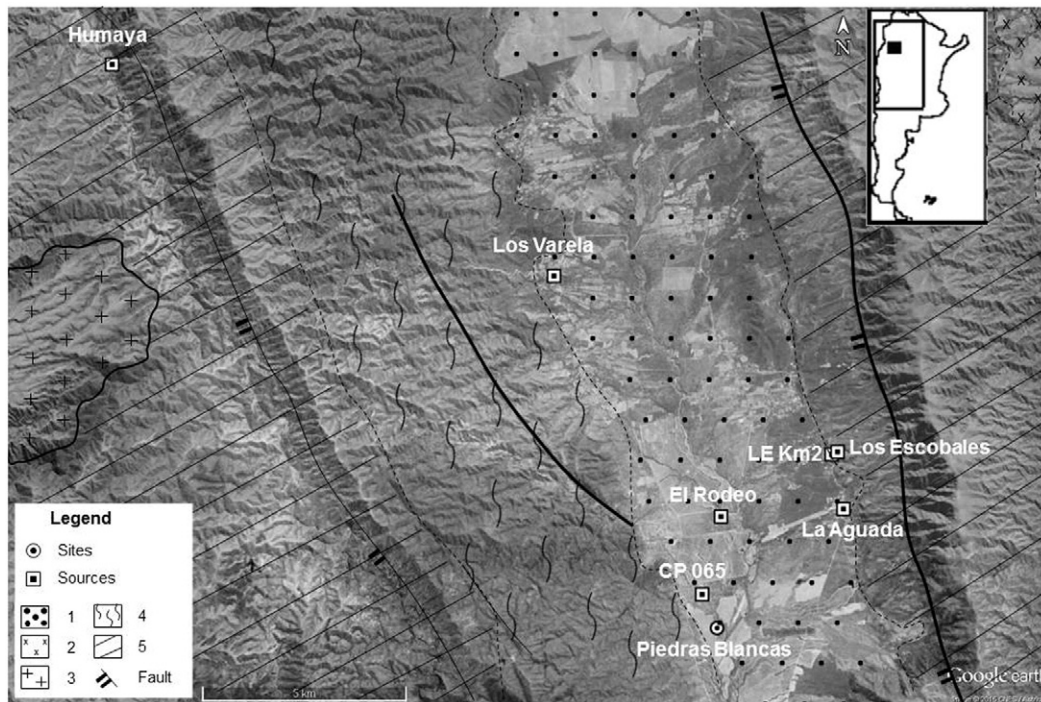


Fig. 2. Location and geologic map of sampled sources (squares) and PB site (circle) at the Ambato Valley. The lithology is as follow: 1) Holocene aeolian to fluvio-aeolian sediments.; 2) Carboniferous San Ignacio-Los Pinos adamellitic granite; 3) Cambrian monzogranites of El Alto Formation; 4) Precambrian to Cambrian quartz-banded phyllites; 5) Precambrian to Cambrian migmatites, syntectonic intrusives and pegmatites (Geology based on Dal Molin et al., 2003).

with the preeminence of a solar cult, long distance exchange of luxury and symbolic goods and the establishment of hereditary social hierarchies (Pérez Gollán, 1991). This culture developed during the Regional Integration Period (300–1000 AC). A precise chronology is still under discussion; based on radiocarbon dating, Marconetto et al. (2014) confirmed that the occupation at Piedras Blancas site lasted from 469–574 AC to 1225–1270 AC. The abandonment of the site is coincident with a series of field fires along the valley which remained unsettled until later times.

Numerous studies focused on the understanding of the degree and extent of these changes at the Ambato Valley where more than 300 sites were identified (Assandri, 2007; Figueroa et al., 2010).

The ceramic technology reflected the most significant changes (Bertolino and Fabra, 2003; Fabra, 2008; Gastaldi, 2010) with craft specialization, development of standardized pottery production (Juez and Laguens, 1999) and the reduction (from 44 to 17) of technological classes used in the previous Formative Period by Ciénaga and Condorhuasi Cultures. Two classes gained wide popularity, Classes E (ordinary) and A1 (black incise). The ceramic objects had new social meanings. Gastaldi (2010) pointed out that the class E pieces (Fig. 1) served for different practices like fermenting beverages (chicha), cooking (including human and camelid meats, associated to anthropophagic practices), storage of food, pigments and paint, etc.

Under this new social context, questions rise like: What kind of choices made the potters regarding the raw material? Were the same choices made to produce different ceramic classes and styles? Were the clay sources local?

The compositional analysis of ceramics combined with the evaluation of technological classes, function, style, etc. as well as the identification and characterization of the possible clay sources are crucial to better understand their meaning. The present work will contribute with significant information to answer these questions.

Piedras Blancas (PB) is located at 100 m from the Los Puestos River, on its second terrace. PB is one of the sites with higher hierarchy and complexity (based on the size, building complexity and other features that reflect the social status of the inhabitants, Assandri, 2007, Fig. 3a). It has been extensively investigated, and the archaeological contexts have been defined in detail (Gastaldi, 2013). PB is a large site (100 m

by 80 m) with two sectors: Sector I -to the west- comprising an elevation called the Dump; a transitional depressed area, and Sector II where several compounds (B, C, E, F, H, I, J) and three open spaces or patios (A, D, G) were identified (Caro, 2002). The architectural features refer to a possible multifunctional place for communal tasks involving several families. Compound H (workroom) was a semi-opened room where several artisanal activities took place (Fig. 3b): metal annealing, handling and firing of pigments, ceramic grounding (to add to the pastes), and objects recycling (plates or other objects made from broken vessels). In a lower stratigraphic level it a pit was found with signs of having had clay-water pulp (Fig. 3c) and two other smaller pits with coarse sand, quartz and micas ground at different sizes probably used to prepare the temper for the ceramic pastes (Gastaldi, 2010). There were also three infant' burials beneath the walls and floor. The Dump is a 3 m high mound resulting from the progressive and continuous accumulation of wastes from rooms and patios of PB, thus represents all actions achieved by their inhabitants. The Dump formation started at the Formative period and continued up to the abandonment of the site. Compound H was built over former rooms from that previous period (Fig. 3b); Since most studied pot sherds come from compound H and the Dump, it is possible that some of them belong to the Formative period (1st c. BC to 4th c. AC).

3. Geological setting

The Ambato Valley (Fig. 2) locates between the Ambato-Humaya (west) and Balcosna (east) mountain belts, which are faulted and tilted blocks related to the continental megastructure of Ambato, one of the northeast-southwest lineament within the Pampean Ranges System (Caminos, 1979; Dal Molin et al., 2003).

The basement rocks (Sosic, 1972; González Bonorino, 1978; Dal Molin et al., 2003) are Proterozoic-Lower Cambrian metamorphic units of: i) quartz-rich banded phyllites on the western flank of the valley; ii) micaschists, mica-garnet schists, quartz-feldspatic gneises, mostly occurring on the eastern flank of the valley but also in the western slope of Humaya Range; iii) syntectonic mylonitic granites (quartz-microcline-oligoclase-white micas); iv) migmatitic tonalites (quartz-oligoclase-micas) on the west and central part of Humaya

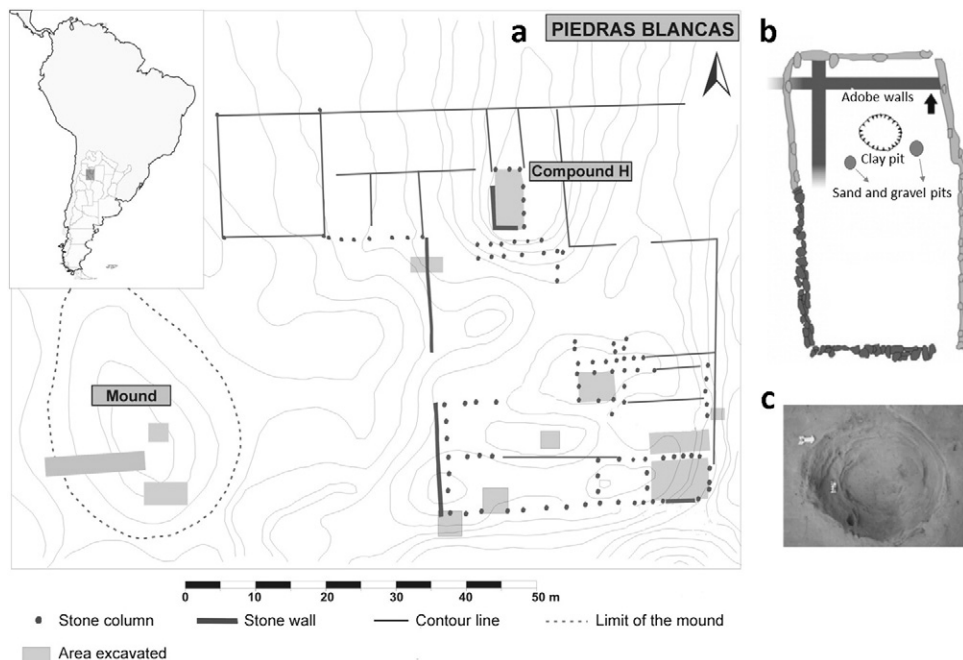


Fig. 3. a) Sketch of Piedras Blancas site; b) sketch of compound H showing the location of clay, sand and gravel pits; c) photograph of the clay pit, the succession of layers of clay pulp deposited on the pit's wall are clearly distinguished.

Range and at the northern part of the valley and v) pegmatites, which affect all the basement rocks but are particularly frequent on the Humaya Range and composed of quartz, microcline (or albite), muscovite and tourmaline. Younger granitoids and granites of Cambrian, Ordovician and Carboniferous, like the San Ignacio-Los Pinos batholith, occur in the eastern and northeastern slope of Balcozana range, they are composed of microcline (kaolinized), quartz, muscovite, biotite and accessory hornblende, apatite and Fe-oxides. There are few low-grade metamorphic metapelite and metasandstone units associated with these basement rocks are, which are possibly equivalent of the Puncoviscana Formation s.s. (Zimmermann, 2008). The Puncoviscana Formation is a widespread sedimentary succession in the region affected by very low grade metamorphism (Zimmermann, 2005). The clastic material had been recycled in several Paleozoic successions in the northwest of Argentina (Zimmermann et al., 2002; Zimmermann and Bahlburg, 2005) and its thickness as well as abundance implicates this formation as the major supplier for clastic material in northwest Argentina (Zimmermann, 2005). Generally, the petrographic data (Qt60–80, F15–35, L5–20, P/F 0.2–0.4, Lv/L = 0) show a composition comparable to foreland-basin successions. Lithoclasts are of metamorphic and metasedimentary origin. Framework clasts are sub-angular to sub-rounded, and the rocks are poorly sorted. The matrix is rich in phyllosilicates, quartz and feldspar, and mainly consists of weathered and dissolved lithoclasts. Alteration affected the feldspars intensely, commonly causing sericitisation and sometimes calcification. In exposures of the region related to this contribution the rocks of the Puncoviscana Formation contain besides polycrystalline and ondulose quartz, mainly alkali-feldspar, few plagioclase, rarely sanidine, albite, muscovite, biotite, zircon, apatite, hematite, ilmenite, chlorite, illite, montmorillonite, rutile, pyrite and epidote. The grains are mostly angular and seldom rounded. The rocks show a moderate to high Chemical Index of Alteration (56–77). Trace element geochemistry is comparable to those of model upper continental crust (UCC). The uniform mineralogical and geochemical composition reflects supra-crustal source(s) for the entire basin, including significant metamorphic rock debris.

Finally, Quaternary (Holocene) fluvio-aolian loessic sediment units, alluvial gravels and sands and eventual landslide deposits fill the intermountain valley. Relicts of Eocene grayish tuffaceous sandstones, with intercalated bentonite clay and tuff banks of the Aconquija Formation are described on the northeast part of the valley, containing plagioclase, hornblende, apatite, biotite, muscovite, clinopyroxene and glass cementing the grains (Dal Molin et al., 2003). They are possibly also exposed between Los Castillos and La Aguada (Los Escobales, Fig. 2). These sedimentary units are not well described in the area.

There are no industrial mineral deposits mentioned in the valley besides muscovite, which was temporary mined in pegmatites (Galliski, 1999). The local inhabitants recall the extraction of clays for different purposes: the bentonitic clays cropping out in Los Escobales area (Fig. 2) to be used on an earth dam, the loessic sediments from La Aguada for adobe preparation and the red clays from Los Escobales used as pigment in wall paint.

4. Materials and methods

This research is based on the mineralogical and chemical analysis of 25 potsherds, and 24 selected local clay sources.

4.1. Local clay sources

All sampled raw materials locate at the Ambato Valley (Fig. 2), except the Andalgá sample. The sampling points are from north to south, as follow (Table 1):

Andalgá (AND, 66 km NW of PB, on the western slope of the Ambato Range): green metapelites; equivalent of the Puncoviscana Formation.

Humaya (HU, 20 km NW of PB): red (HU1 and HU4) and ocher (HU2 and HU5) clay gouge. Cataclastic rocks formed in migmatites, mylonites

and granitoids. They form two parallel sub vertical bands of 1.70 to 2 m thick each (the red and the other sections).

Los Varela (LV1; 9.50 km North of PB): Quaternary sediments of possible fluvio-aolian origin; 0.5–1 m thick dark brown sediments are exposed in the southern entrance of Los Varela village.

Los Escobales (LE, 5 km NE of PB): 1) Dark red clay gouge is a cataclastic rocks formed mainly in granitoids, but also in migmatites and mylonites. It comprises the footwall of a major sub vertical reverse fault. The rock is heterogeneous, with clay-rich bands parallel to the fault; the total thickness of the cataclastic breccia and the clay gouge is about 8 to 10 m. Local people has recently used it for wall painting. Several samples were collected. R3 and R9 reported by Bertolino and Fabra (2003) were also collected from this outcrop. 2) Off-white clay (LE3, LE6, LE2km9): epiclastic rocks and interbedded bentonites (possibly equivalent to the tuffs and tuffaceous sandstone of the Aconquija Formation of Eocene age). These rocks make up the hanging wall in contact with the fault gouge. The total thickness of this section is unknown but it could reach several hundred meters. Bertolino and Fabra (2003) already reported results on sample OW11. 3) Reddish sedimentary clays (LE2 km 1): Quaternary massive sediment are exposed on an 8 to 10 m height wall at Los Escobales ravine.

La Aguada (LAG1; 4.30 km NE of PB): Quaternary sediments of possible fluvio-aolian origin exposed by the road at the La Aguada locality; it is currently used for adobe.

El Rodeo (ER; 2.70 km N of PB): 6 to 7 m of Quaternary sediments of possible fluvio-aolian origin are exposed at the de los Puestos River terrace near the road to Los Castillos. At this locality, both, the sandy levels from the riverbed (ER1: sand and ER3: gravel) and the loessic sediments from the terrace cuts were sampled (ER2).

Cerco de Palos (CP65b1, CP65b2; 900 m North of PB): Quaternary sediments of possible fluvio-aolian origin, which are exposed at the Los Puestos River terrace in the vicinity of sites 065 and 040. The section is about 6 m thick with a faint stratification. Two levels were sampled (composed samples) because of their higher clay content. Similar sediments fill the valley and are exposed few to several hundred meters from the sites.

The selection of Los Escobales 1 and 2, Humaya and Andalgá relied upon ethnoarchaeological criteria based on referrals of local potters and inhabitants. The Ambato Project staff from the Museo de Antropología (Facultad de Filosofía y Humanidades, Universidad Nacional de Córdoba, Argentina) provided samples R3, R9, OW11, HU1, HU2 and AND. The other selection of sources relied upon geological criteria. Field observations suggested that the red and ocher clays at Los Escobales and Humaya were related to the main reverse faults (clay gouges) and both possible affected by hydrothermal alteration.

4.2. Ceramics

The ceramic pieces were found at Compound H and the Dump. Those from Compound H came from stratigraphic units associated to the abandonment of the site (the final occupation phase). The studied ceramic sherds (Table 2) belong to the most popular classes of ordinary vessels: E (ordinary, rough, Fig. 1), and D (light brown/red smoothed).

Class E (Gastaldi, 2010) vessels usually had up to 250 l of capacity depending on the shape. They characterized by thick walls of a coarse-grained paste rich in coarse sand inclusions of quartz and mica with abundant medium to small voids. Several paste mixture types were macroscopically identified by Gastaldi (2010), Mixture 1 (E1, E4): with coarse temper; Mixture 2 (E3) variable sized inclusions; Mixture 4 (E5, E6): small to medium sized inclusions; Mixture 5 (E2): medium to small inclusions; high mica content. Class D (Fabra, 2008) comprised domestic cooking wares and food or liquid containers made of a coarse-grained, brittle paste, with abundant coarse sand inclusions; the external face is polished and painted with Condorhuasi motifs and the inner face is smoothed. Both classes were fired under oxidizing conditions.

Table 1
Compilation of general data for representative samples of the selected local clay sources (Soil Survey Division Staff, 1993). The mineralogy of sample R9 and OW11 is as reported by Bertolino and Fabra (2003). Mineralogical estimation was based on the relative intensities of XRD peak. The main mineralogical changes after firing are listed in the last column: the minerals that disappear are strikethrough and the new phases are in bold.

Location	Lithology	Sample	USD Class	Grit % <44 µm	Clay % <2 µm	Possible use	Mineralogy	Mineralogical changes after firing at 1000 °C
Andalgalá	Metapelite (Puncovicana F.)	AND		n.d.	n.d.	Paste and/or Temper	Bulk: Qz>>>Ms, Chl> Ab <2 µm: I, Chl, Qz	Spl, Mul
	Red fault gouge	HU1		n.d.	n.d.	Paste	Bulk: Qz>>>clays>Cal>Ank, tr. Hem <2 µm: I>Kaol, sc. Hem	
Humaya		HU4	Clay	22.68	44.24	Paste	Bulk: Qz>>Cal, clays, Ank>>Gth, Hem <2 µm: I>Kaol, sc. Hem	Spl, MII, Hem, Mul
	Ocher fault gouge	HU2		n.d.	n.d.	Paste	Bulk: Qz>>Cal, clays tr. Hem <2 µm: I>Kaol, sc. irr. I-Sm	
		HU5	Clay	33.25	40.69	Paste	Bulk: Qz>>>Ank>clays, tr. Gth, Hem, <2 µm: I> Kaol, sc. irr. I-Sm	Spl, MII, Hem
Los Varela	Quaternary loessic sediment	LV1		n.d.	n.d.	Not appropriate	Bulk: Qz>>>Ab>Micas >Kfs, tr. Hem <2 µm: I>>irr. I-Sm, Chl-Sm, Chl, Kaol, Gp	
	1-Red fault gouge	LE2 km7		n.d.	n.d.	Paste	Bulk: Qz>>>Ab>>Crs, Micas, clays, Hem<2 µm: Sm>I, Kaol, sc. Qz	
		LE2 km6b		n.d.	n.d.	Paste	Bulk: Ab>Qz, Kfs, clays>Micas <2 µm: Sm (nontronite), I, Kaol	
		R9	Clay loam	25.90	38.40	Paste	Bulk: Qz>>>Ab>>Kfs, Hem>Micas, clays <2 µm: Sm>I, Kaol, sc. Qz	Micas decrease Spl, Hem, Mul, Crs
Los Escobales	2-Epiclastic rocks & bentonites	LE3		n.d.	n.d.	Additive	Bulk: Qz >>Ab> Fsp>clays>Micas 2 µm: Sm, sc. I, Pl	
		LE6		n.d.	n.d.	Additive	Bulk: Qz>>Fsp>Crs, Micas, Cal, Hbl, clays > Hyp, Ilm <2 µm: Sm, minor I	
		LE2 km9		n.d.	n.d.	Additive	Bulk: Qz>>Fsp>Micas, clays, Cpt-Heu <2 µm: Sm, minor I	
		OW11	Sandy clay loam	66.93	20.65	Additive	Bulk: Qz>Fsp>Micas, clays, Opl-C, Cpt-Hul, Hbl, Hyp 2 µm: Sm, tr. I, Pl	Micas decrease An, Crs, Px, Spl, Hem, Mul, sc.OI, Di
La Aguada	3-Red sedimentary clay	LE2 km1	Silty clay loam	16.70	35.15	Paste	Bulk: Qz>Ab, Kfs>Micas, Anl>>Hyp, Hem 2 µm: Sm >>I, sc. Kaol, I-Sm	OI, Spl, Hem, Crs, Mul
	Quaternary loessic sediment	LAg1	Silty loam	25.41	15.75	Paste, low quality	Bulk: Qz>>>Ab, Kfs, Micas, Cal>Chl, Hem, tr. Hbl, Hyp 2 µm: I, irr. I-Sm, sc. Chl-Sm, Chl, Kaol	Micas decrease Aug, MII, Mul, Hem, Spl, Di
El Rodeo	Riverbed sand	ER1		n.d.	n.d.	Temper	Bulk: Qz >>>Ab>Micas>Kfs	
	Quaternary loessic sediment	ER2		n.d.	n.d.	Paste	Bulk: Qz>>>Ab>Micas>Kfs>Hbl, Kaol, Hem, Hyp <2 µm: I, irr. I-Sm, tr. Kaol	
Cerro de Palos	Riverbed gravel	ER3		n.d.	n.d.	Temper	Bulk: Qz, Micas, Fsp	
	Quaternary loessic sediment	CP65b1	Silty loam	18.62	23.37	Paste, low quality, not appropriate	Bulk: Qz>Ab>Cal, Micas, Hbl, Kaol, Hyp, Ilm, tr. Chl <2 µm: I> irr. I-Sm, Chl-Sm, Kaol	
		CP65b2	Silty clay loam	19.18	28.31	Paste	Bulk: Qz>>>Ab, Micas, Cal, Kaol, Anl, Hbl, Hyp, Cpt-Heu, tr. Chl, <2 µm: I> irr. I-Sm, Chl-Sm, Kaol-Sm, Kaol	Micas decrease Crs, Mul, Aug, Spl, Sa, Hem

Abbreviations (after Whitney and Evans, 2010): Ab: albite, An: anorthite, Anl: analcime, Ank: ankerite, Aug: augite, Cal: calcite, Chl: chlorite, Cpt-Hul: clinoptilolite-heulandite, Crs: cristobalite, Di: diopside, Fsp: feldspars, Gp: gypsum, Gth: goethite, Hem: hematite, Hbl: hornblende, Hyp: hypersthene, I: illite, Ilm: ilmenite, I-Sm: illite/smectite, Kaol: kaolinite, Kfs: potassium feldspars, MII: melilite group, Ms: muscovite, Mul: mullite, Ol: olivine, Opl-C: opal-C, Phyl: phyllosilicates, Pl: plagioclase, Px: pyroxene, Py: pyrite, Qz: quartz, Sa: sanidine, Sm: smectite, Spl: spinel, irr: irregular, n.d.: not determined, sc.: scarce, tr.: traces.

4.3. Experimental techniques

The experimental techniques applied for mineralogical and chemical analyses were: optical methods (using both, petrographic and stereo microscope); X-ray diffraction (XRD) on the bulk (random mounts) and the <2 µm fraction (air dried, glycolated and heated at 375 °C and 550 °C, in oriented mounts) using a Philips X'Pert PRO PW 3040/60 and a PW1710 BASED diffractometers with Cu Kα X-ray radiation at 40 kV and 30 mA, and 36 kV and 20 mA, Si monochromator, 1° divergent slit, 0.2 mm receiving slit, soller slits 0.04 Rad in X'Pert PRO, scan at ~1°/minute and step size of 0.02° 2θ. In most cases, samples were mount on a Si holder of low background were small amounts (few milligrams) can be studied. Mineralogical identification was made with PANalytical High Score Plus® identification software package (Degen et al., 2014)

from Philips. XRD was also applied to identify certain minerals separated by hand under the stereo microscope.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopic (EDS) analyses were performed on natural fragments of samples coated with Au or Pd and analyzed with a FE-SEM Carl Zeiss Sigma scanning microscope coupled with Oxford X-Max 80 energy dispersive spectrometers at the Laboratorio de Microscopía Electrónica y Análisis por Rayos X (LAMARX, UNC, Argentina) and with a Zeiss Supra 35VP field emission SEM coupled with an EDAX Genesis EDS at the University of Stavanger (Norway). Measurements were done in high vacuum mode with an accelerating voltage of 20 to 15 kV and 0.5 mA (Bertolino et al., 2009a).

Whole rock chemical analyses of major, minor, trace and rare earth elements were performed by combined lithium metaborate/tetraborate

Table 2

General description (classification, location and mineralogy) of the ceramic samples. Semi-quantitative mineralogical estimation is based on relative intensities of XRD peaks. Mzn: monacite. Other mineral abbreviations are as in Table 1.

Sample	Class	Location	Fragment	Mineralogy
B38	E1	PB-dump	Body	Qz>>>Ab, Micas>Crs, Mul, tr. Hem
B51*	E1	PB-dump	Body	Ab, Qz>>>>Mul, Micas, Kfs, Hem, Px, Spl, tr. Hbl Mnz, Ilm
B49*	E1	PB-dump	Body	Ab>>>Qz>Kfs>Micas, Mul
B64	E1	PB-compound H	Mouth	Qz>Ab>Micas>Kfs>Hbl, tr. Hem
B2	E2	PB-compound H	Mouth	Qz>Ab>Micas>Kfs, Crs, tr. Hem, Hbl
B5*	E2	PB-compound H	Mouth	Qz>Ab, Kfs> Mul, Crs>>>Micas, tr. Hem, Spl, Px
B30	E2	PB-compound H	Body	Qz>>>Ab>Micas>>>Kfs, Hem, Px
B33	E2	PB-dump	Body	Qz>Ab>>>Kfs, Micas>Mul, Crs, tr. Hem, Hbl
B39	E2	PB-dump	Body	Ab>>>Qz>Micas>Hem
B66	E2	PB-compound H	Body	Qz>Ab>Micas>Kfs, Crs, Px, Chl tr. Hem
B17*	E4	PB-compound H	Body	Qz>>>Ab>>>Kfs, Micas, Px, tr. Hem
B22n*	E4	PB-compound H		Qz>>>Ab>Kfs>>Di>Micas, Px, tr. Hbl, Crs
B27*	E4	PB-compound H		Ab>Qz, Kfs>>>Micas, Spl
B34*	E4	PB-dump	Mouth	Ab>>>Qz>>Mul>>Micas, Di>Gth, Hem
B35*	E4	PB-dump	Body	Ab>>>Qz, Kfs>Mul>Micas, Hem
B37*	E4	PB-dump	Body	Ab>Qz>>>Kfs>Mul
B42	E4	PB-dump	Body	Ab>Qz>>>Kfs> Micas, Hem, Mul
B44*	E4	PB-dump	Body	Qz>>>Ab>>>Mul> Micas, Px
B45*	E4	PB-dump	Body	Qz>Ab, An>Kfs, Crs>>Micas, Hem, Spl, Mul, tr.Hbl
B50*	E4	PB-dump	Body	Qz>>>>Ab>>Micas, Kfs> Hem, Px tr. Hbl,
B67*	E4	PB-compound H		Qz>Ab>Kfs>Micas>Crs, Mul, Hem
B61	E6	PB-compound H		Qz>>>Ab, Kfs, Ol, Micas tr. Hem
B14	D	PB-compound H	Mouth	Qz>>>Ab>Kfs, Micas, tr. Hem
B12	D	PB-compound H		Qz>>>Kfs, Ab, Micas, Crs, Mul, tr. Hbl, Di
B53	D	PB-dump		Qz>Kfs>An>Micas>Crs, tr. Hbl

* Sherds fired at high temperature.

fusion ICP and trace element ICP/MS method (details of the procedures are found in www.actlabs.com) at Activation Laboratories LTD Canada, and at ACME Laboratories (Vancouver, Canada). Samples at the latter were processed and pulverized to very fine mesh (<2 µm) in an ultraclean agate mill and the geochemical data were obtained using ICP-MS and for total C and S analysis by the Leco method. Detection limits are given in Table 3. Details for the analytical method and processing can be found in <http://acmelab.com>.

When sufficient amount of sample was available, basic physical and technological properties of selected clayish materials were preliminary evaluated. This was possible on samples HU4, HU5, R9, OW11, LE2Km1, LAg1, CP65b1, CP65b2; sample ER1 (sand) was taken as a possible temper and added in 10% to CP65b2. Tests consisted on determinations of grain size distribution by wet sieving (ASTM #18, #230 and #325) for the grit (>44 µm) fraction and by sedimentation (Stokes's law) for the <44 µm. Square tiles of 1 cm × 4 cm × 4 cm were prepared as test specimens and fired on a muffle INDEC 134 at 800 °C, 900 °C and 1000 °C, with a heating rate of 2.5 °C/min and a cooling rate of 1.5 °C/min, under oxidizing conditions on air atmosphere to study their thermal behavior. Sample AND from Andalgalá was too small to perform all analyses, only a small fragment has been fired.

5. Results

5.1. Clay resources

5.1.1. Physical properties

Table 1 shows the grit (>44 µm) and clay (<2 µm) percentages and the USDA (Soil Survey Division Staff, 1993) classification determined on selected samples. After the preliminary physical analyses, all test specimens exhibited low (<4%) linear shrinkage after firing at 1000 °C (except OW11); CP65b1 exhibited cracks when drying. This specimen was also too fragile and thus rejected as possible candidate for the ceramic paste. The rest of the samples were hard to very hard after firing.

5.1.2. Mineralogy

Table 1 summarizes the mineralogical composition of the sampled source materials determined on the bulk and the clay fraction

(<2 µm) by X-ray powder diffraction. Figs. 4 and 5 show XRD patterns of the bulk and the <2 µm fractions respectively.

AND is composed of the typical paragenesis of low-grade metamorphic rocks (Fig. 4), with a clay suite of well crystallized illite and chlorite (ferroan clinoclore) (Fig. 5).

Samples from both clay gouge at HU and LE do not have the same mineralogy but kaolinite is present in both cases. At HU, both the red and the ocher clays are composed of quartz, calcite, ankerite, micas (illite), goethite and kaolinite and minor hematite. At LE they contain quartz, albite, potassium feldspars (mostly microcline), micas (muscovite, biotite) smectite, illite and kaolinite. This mineralogy resembles that reported by Bertolino and Fabra (2003) for R9 and R3 (R3 bears more kaolinite than R9).

The epiclastic clays from LE are characterized by quartz, oligoclase-andesine, sanidine, smectite, biotite, amphiboles (hornblende), minor muscovite, opal-C, hyperthene, zeolites (clinoptilolite-heulandite), traces of ilmenite, along with smectite and minor or traces of illite, and plagioclase in the clay fraction (similar to OW11 reported by Bertolino and Fabra, 2003).

The sedimentary clays partially reflect the mineralogy of other clay materials (Table 1, Figs. 4 and 5). LV1 contains quartz, feldspars and micas (muscovite, biotite and phlogopite) with a poorly crystalline clay suite of illite, scarce chlorite and minor irregular I-Sm, Chl-Sm and Kaol-Sm. LE2km1 consist of a mixture of quartz, micas (the same as LV1), feldspars (mainly albite and anorthoclase), minor hyperthene, hematite and smectite, minor illite, I-Sm and traces of kaolinite in the clay fraction. LAg1 is composed of mainly quartz, plagioclase, calcite, micas (the same as LV1), potassium feldspar, minor chlorite and hematite and a clay assemblage of poorly crystalline I-Sm, illite, chlorite and Chl-Sm. At ER, the mineralogy of the loessic sediments ER2 is quartz, albite, micas (the same as LV1), potassium feldspars, minor hornblende, hypersthenite, hematite and a clay suite of illite, I-Sm and scarce kaolinite. The sand and the gravel from ER contain quartz, feldspars and micas (the same as LV1). Finally, at CP65 the sediments are composed of quartz, K-feldspars, plagioclase, micas (the same as LV1), calcite, hornblende, hypersthenite, kaolinite and hematite. CP65b1 in addition contains ilmetite while CP65b2, zeolites and larger proportions of hornblende and hypersthenite.

Table 3
 Geochemical data for all samples used in this study. In grey, samples measured at ACME-lab with ICP-MS. Detection limits are given Abbreviations: UCC: typical unrecycled Upper Continental Crust after Taylor and McLennan (1985) and McLennan et al. (2006); PAS (post-Archean average shale) includes PAMS (post-Archean Australian average shale) for rare earth elements and are here taken from McLennan (2001); McLennan et al. (2006) combined with Rudnick and Gao (2003) marked with **; % = weight percent; ppm = parts per million; n.d. = not determined; b.l. = below detection limit; LOI = loss on ignition; 'N' = annotates normalization to chondritic values after Taylor and McLennan (1985); TOC = total carbon; TOS = total sulfur.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	TOC	TOS	Si	Al	Fe	Mg	Ca	Na	K	P	LOI	TOC	TOS	
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LE2km6b	60.1	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	60.1	0.04	0.01	0.01	0.01	0.01						

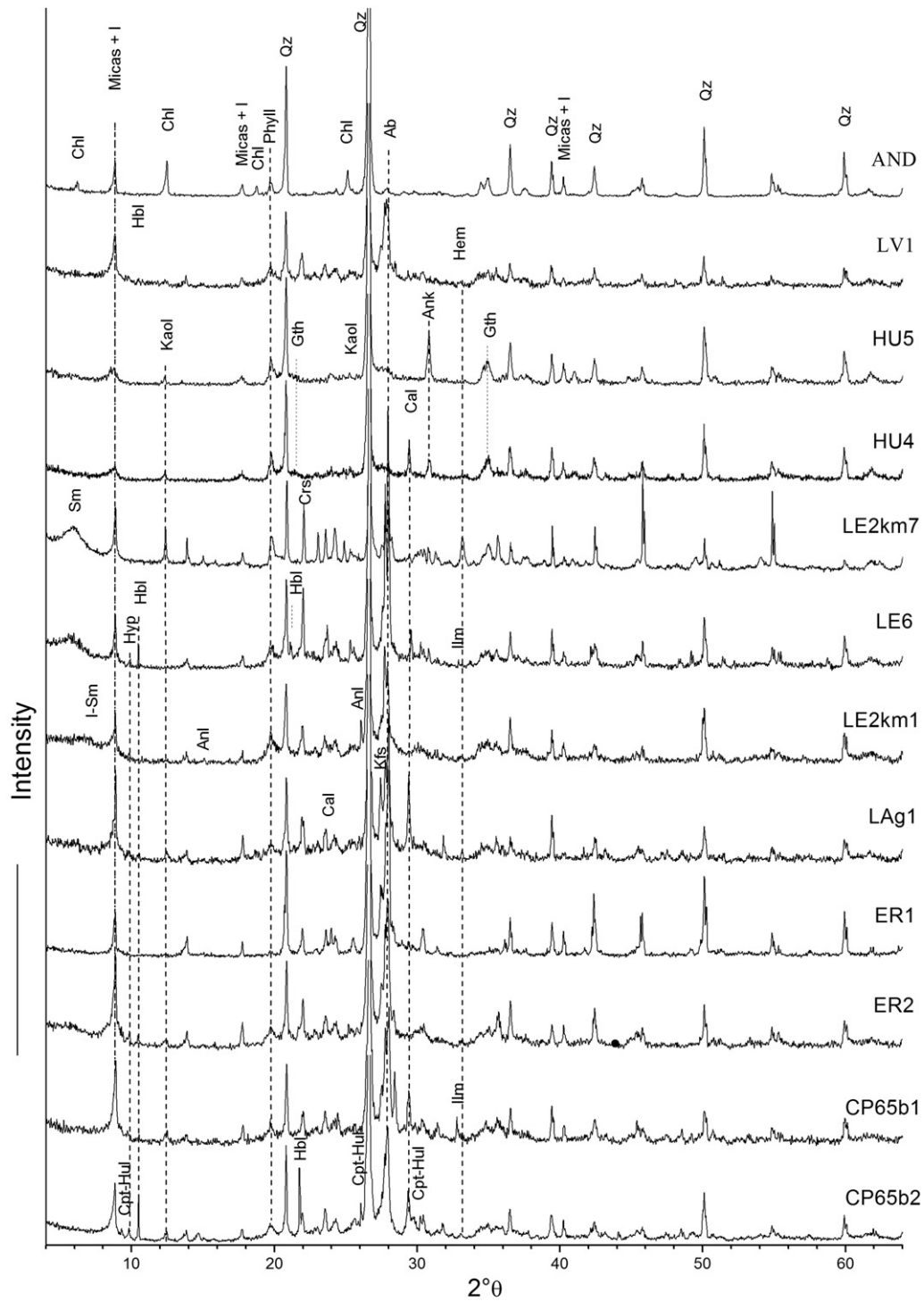


Fig. 4. XRD patterns of bulk samples of local clays. Mineral abbreviations are as in Tables 1 and 2.

only a short distance, hence the rocks are comparable to low recycled typical upper continental crust, which is typical for large foreland basins (see Zimmermann, 2005). The samples do not show any remarkable enrichment or depletion in commonly used compatible trace elements for petrogenetic modeling (like Ti, Nb, Ta, Cr, V, Ni, Co, Sc; Table 3). Using different trace element ratios often applied to discriminate the geochemical composition of sediments, it is not possible to expose any significant differences among the sampled source materials (Fig. 8). Only four samples (OW11, LEkm9, LAg1, LV1) differ with slightly higher Nb/Y ratios than all other samples, but not in Zr/Ti abundances

(Table 3). The two former samples are tuffaceous sediments and therefore, rather similar in their geochemical compositions and slightly more alkaline than all other samples, pointing to the nature of the volcanic component. Using Th/Sc and Zr/Sc ratios, they do not differ (Fig. 8a), neither when using La/Sc and Ti/Zr ratios (Table 3).

Rare earth element (REE) abundances (Table 3; Fig. 8b) are again very homogeneous throughout nearly all samples. The two alkaline tuffaceous sediments (OW11 and LE2km9) have lower abundances ($\Sigma\text{REE} < 120$ ppm) than all other samples besides ER1, which is depleted in nearly all trace elements because of its silica-rich nature (Table 3).

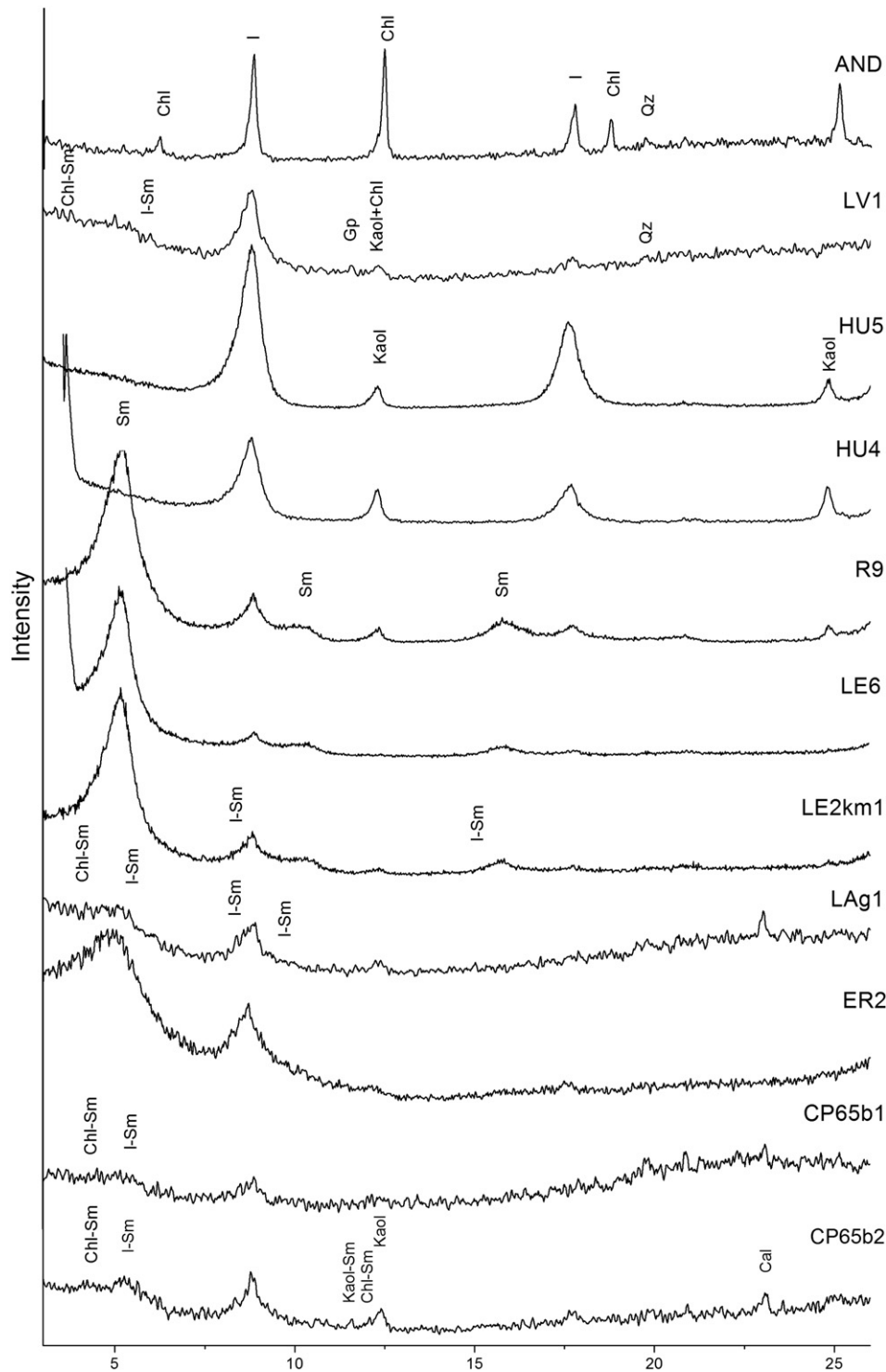


Fig. 5. XRD patterns of the clay fraction (<2 μm) of local clays, glicolated. Mineral abbreviations are as in Tables 1 and 2.

The REE patterns are typical for UCC with $La/Yb_{(N)}$ values reflecting a typical fractionation between light and heavy REE. The same accounts for Eu/Eu^* values (Table 3).

Three major and interesting exceptions are the element distributions of Cs, Sb and Bi. Nearly all samples are either enriched in the three or in two of them (except LE2km9 and ER1), which is peculiar and outstanding (Table 3, Fig. 8c). Cs is extremely enriched in samples R9, HU1, HU2 and AND and only slightly in LE2km7, compared to UCC but not to PAS (post-Archean average shale after McLennan, 2001; McLennan et al., 2006; Rudnick and Gao, 2003, see Table 3). This has

also been observed in the rocks of the Puncoviscana Complex of that region (Zimmermann, 2005). Sb is enriched in the samples HU1, HU2 and AND, while Bi is abundant in R9 and OW11. The samples R9, HU1, HU2 and AND, are also slightly enriched in Cu and Pb in comparison to all other samples. One sample is definitely different from all others (ER1), it is depleted in nearly all trace elements and enriched in SiO_2 , which dilutes the trace element composition. This is also reflected in the total sum of REE with only 76 ppm.

The sample AND does not match exactly any other primary substance but stands out with high silica, Cs and Sb (Table 3). Samples

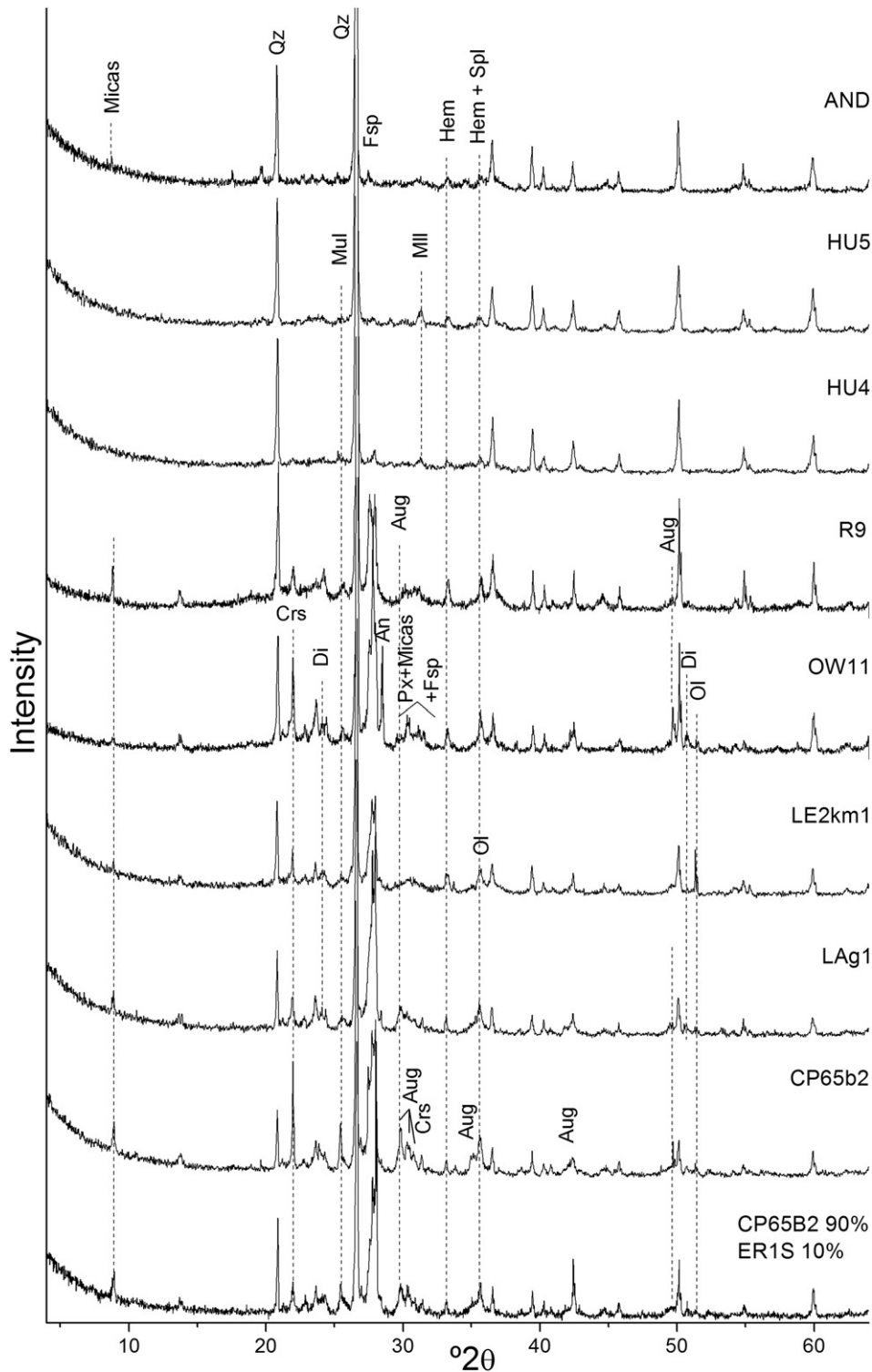


Fig. 6. XRD patterns of local clays fired at 1000 °C. Mineral abbreviations are as in Tables 1 and 2.

from the fault gouge at Los Escobales (Table 3) are similar to each other, R9 and LE2km7 are strongly enriched in Cs but the latter is depleted in Bi. Sample OW11 (a reworked tuff) is strongly enriched in Bi, moreover, it contains less REE and silica. The samples from Humaya (fault gouge) are partly similar to those from Los Escobales being both slightly enriched in Sb and extremely enriched in Cs. However, compared to PAAS HU1 has lower Σ REE, with c. 30% less REE (184 ppm; Taylor and McLennan, 1985) and HU2 is slightly enriched. Hence, although the

XRD did not show significant differences, HU2 is somewhat differently composed of phases that affect the REE budget. Samples from the silty sediments of Cerco de Palos match typical UCC but do have lower Cs concentration than samples above discussed (Table 3). The other two single samples from La Aguada and Los Varela match as well UCC values (Fig. 8; Table 3) and are, therefore comparable and geochemically indistinguishable from those of Cerco de Palos. Sample ER2 is depleted in Cs compared to typical UCC and contains low Bi and Sb concentrations.

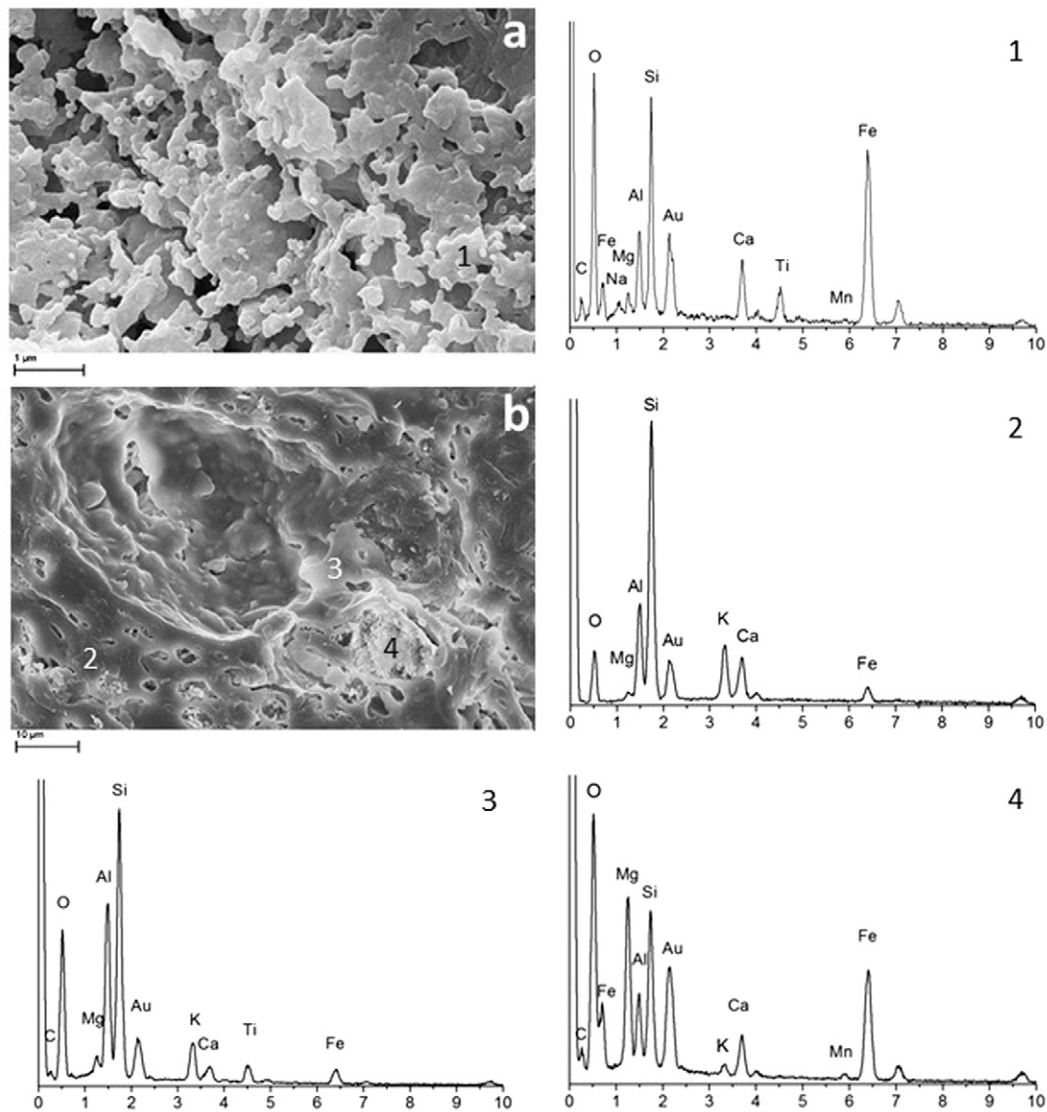


Fig. 7. FE-SEM images and EDS spectra of the clay matrix of local clays after firing at 1000 °C: a: CP65b2, detail of microgranular new phases (augite), EDS 1 shows their composition. b: HU4. The matrix was extensively vitrified and new phases formed in voids. EDS 2 and 3 show the compositional variability of the resulting vitrified matrix. EDS 4 shows the composition of the new phases dominated by the melilite group; the high Fe content suggests that some hematite is also present in that area.

5.2. Ceramics

5.2.1. Mineralogy

The mineralogical composition of pastes is quite homogeneous mostly differing on proportions of phases (Table 2, Fig. 9). Quartz, micas, plagioclases (mostly a calcian albite but anorthite may also occur), microcline (occasionally sanidine) and hematite are always present along with lithoclasts of mostly metamorphic, igneous and possibly volcanoclastic rocks (observed under optical microscope). Phlogopite was typically found in most pieces, this mineral occurred on a wide size range (seen with naked eye) on ceramics' surfaces and in the paste; it is usually the dominant mica, accompanied by muscovite and biotite. It is thus presumed that the golden mica identified in the paste is not only the fired biotite but also phlogopite as suggested by the XRD patterns. XRD peaks of mica have lower intensities in samples B22n, B27, B34, B35, B42, B44, B45, B50, B51. Accessory hornblende (magnesium rich) occur in class E samples B2, B22n, B33, B45 (observed under polarizing microscope), B50, B51, B64 and class D B12 and B53, and mullite in samples B5, B33, B35, B37, B38, B34, B42, B44, B45, B49, B51, B67 and in class D sample B12; mullite concentrates in the clay

fraction. Other minerals occasionally found by XRD are cristobalite, Mg, Al (e.g. B27) and Mn, Fe, Ti (e.g. B5 and B45) spinels, and diopside (B22n, B34 and traces in B12). Monazite and ilmenite are minor accessory minerals identified in B51 on thin section by EDS analysis. Bertolino et al. (2009a) reported the mineralogical composition of B53.

The observations under the polarizing microscope revealed that lithoclasts (mostly metamorphic), quartz, micas and feldspars are the dominant inclusions of the paste of B5, B17, B22n, B27, B38, B39, B45 and B51 sherds. B5 and B51 also contained scarce grog. The inclusions are angular to subangular with a polymodal size distribution, they have all features of intentionally added temper.

Textures observed under the SEM in most cases showed highly vesicular areas (Fig. 10a and b) on the matrix. This phenomenon appeared usually in patches (B38, B53) but sometimes (e.g. B44, B50, B51) in the whole paste. Those are all vitrification features suggesting high firing temperatures. On the contrary, samples B30, B39 (Fig. 10c) do not exhibit those features and the clay flakes could still be distinguished in the fine matrix. The clay flakes occasionally even show crenulated edges as having some expandable layers.

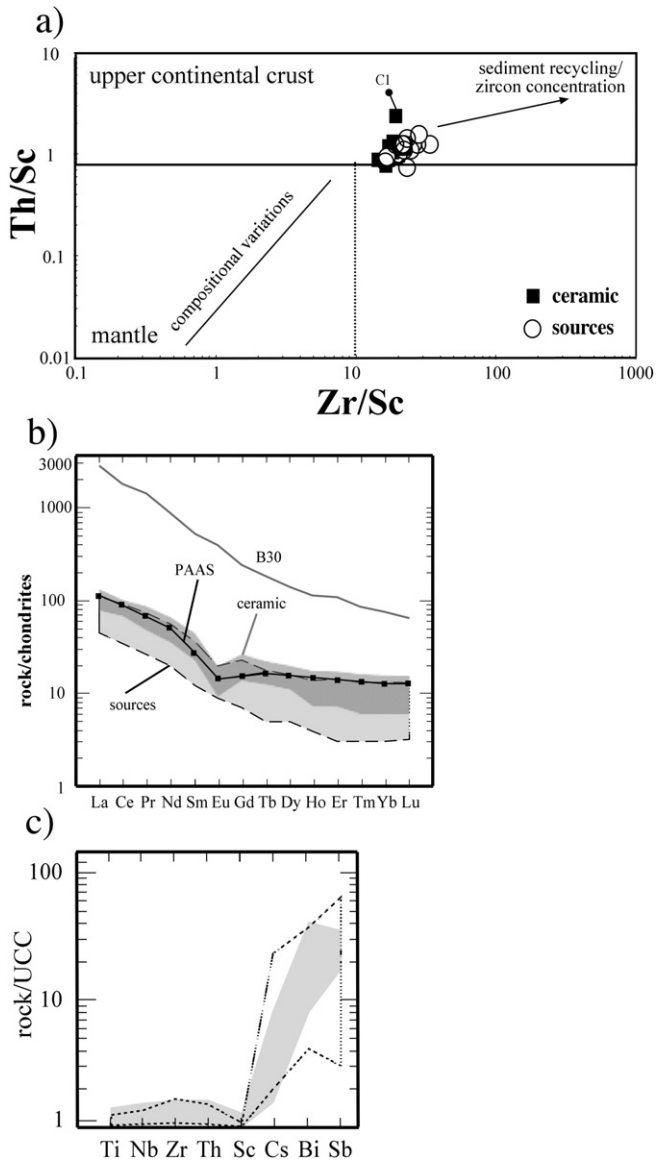


Fig. 8. a) Zr/Sc versus Th/Sc diagram for further details on the chemical composition of the samples (after McLennan et al., 1990). All samples are relatively similar and comparable to typical UCC (Table 3). b) Chondritic normalized rare earth element patterns for all samples. The shaded areas frame the entire variation in the group of ceramics and sampled proposed materials. Both match typical average shale (PAAS, post-Archean Australian average shale after Taylor and McLennan, 1985). Chondritic normalization is after Taylor and McLennan (1985). c) Selected trace elements are normalized to typical UCC (Table 3) to show the extreme enrichment in Bi and Sb and moderate concentrations in Cs. Only those samples have been used with increased values (compare Table 3 and see text). Grey field enveloped the ceramic samples; the field surrounded by the stippled line is for the raw materials. Note the logarithmic scale.

In all cases, the matrix either vitrified or not, has a similar composition of high Si, Al and minor Fe, K, Mg, Ca and Ti content as detected by EDS (Fig. 10a, EDS 1).

5.2.2. Geochemistry

In regard of their major element composition, pottery samples are relatively homogeneous besides TiO_2 and Al_2O_3 , which have the widest scattering. Sample B39 with high Fe_2O_{3T} concentrations (7.07 %) alike B34 (8.61 %) (both with high hematite content), or some sherds have low Na_2O content (B38, B30, B44, B53, Table 3). Silica concentrations vary slightly as do CaO and K_2O possibly depending on slightly more felsic material used. CaO correlates with Sr and TOC.

For trace element compositions there is no significant trend between all the different sample groups beside E1 and one extraordinary sample of class E2 (B30, strongly enriched in REE). The ratios of Nb/Y and Zr/Ti show that nearly all samples are similar and similar to the here sampled source material samples (Table 3). Th/Sc and Zr/Sc ratios (Fig. 8a) are likely to show any extraordinary input of material (detritus) into a sediment (McLennan et al., 1990). However, again nearly all ceramic samples are extremely close to each other and similar to the proposed source material (Fig. 8a). As these ratios do not include REE, sample B30 is remarkable as it contains several % (!) of REE (Table 3). When using La/Sc and Ti/Zr ratios the trend is the same, nearly all samples have similar values (except B30 with extremely high La concentration) including the source material samples and match typical UCC (Table 3).

REE patterns are shown together with those of the proposed source materials in Fig. 8c. It is visible that all ceramic samples (except B30) match the source materials and typical average shale (PAAS, after Taylor and McLennan, 1985). Sample B30 is spectacular as it contains > 4% (!) REE. This is absolutely outstanding and the pattern is as well different from other samples as $La/Yb_{(N)}$ is very high and the sample does not show a Eu anomaly (Table 3; Fig. 8b).

However, like in the source materials, Cs, Bi and Sb seem to be the most indicative.

In class E1, both samples are strongly enriched in Bi and Sb but not in Cs and possibly slightly enriched ΣREE compared to UCC. The three samples of class E2 are different from E1, only one sample has higher concentrations of Sb (B30). Cs concentrations are slightly elevated for UCC but typical for PAS. In class E4 some samples are enriched in Cs and Sb (B44) or Sb and Bi (B50) or in Bi (B17, B45). B53 represents class D and extremely enriched in Sb and Bi but not in Cs. The sample is also slightly enriched in Cu, Pb, Zn as well as As.

The unusual composition in some ceramic samples for Cs, Bi and Sb is demonstrated in Fig. 8b where the values are normalized to typical upper crustal.

6. Discussion

When selecting the possible clay sources for the common ceramics, it was considered not only deposits highly enriched in clay minerals such as the clays of Andalgalá, Humaya, Los Escobales or the epiclastic rocks, but also the clayish loessic sediments that filled the valley (such as CP65b1 and 2, LAg1 and LE2km1 or LV1). Those sediments looked like common materials usually used to produce structural clay products; they are wide spread within the valley and exposed at the river terraces close to the production sites having many and easy accesses along the valley.

Arnold (2005, 2006, 2011) proposed a model for threshold walking distances from production sites to the clay sources at 7 km, but commonly at 1 km, which could be larger with other means of transportation (e.g. animals). Based on this, the author defines the “resource area” (“the area in which the potters obtain their resources to make pottery”, Arnold, 2005, p.17) represented by a circle around the potter’s community that has for radius the threshold walking distance. Except for Andalgalá (66 km), Humaya (20 km) and Los Varela (9.50 km) all other deposits fall within a resource area centered in Piedras Blancas of 5 to 5.5 km radius, being the CP65 sampling point at <1 km. They match Arnold’s model so those are good candidates as clay sources; if Humaya or Andalgalá clays were used, it is likely that the artisans prioritized other reasons for the use of these sources.

The finding of the pits with clay pulp (Fig. 3c), sand and crushed quartz, feldspars and micas in Compound H reduces the speculations regarding the manufacturing of these vessels regarding the use of temper. The features of the inclusions observed under the polarizing microscope also confirmed that the inclusions were intentionally added to the clay pulp. Still, we do not know if the used temper was compositionally or

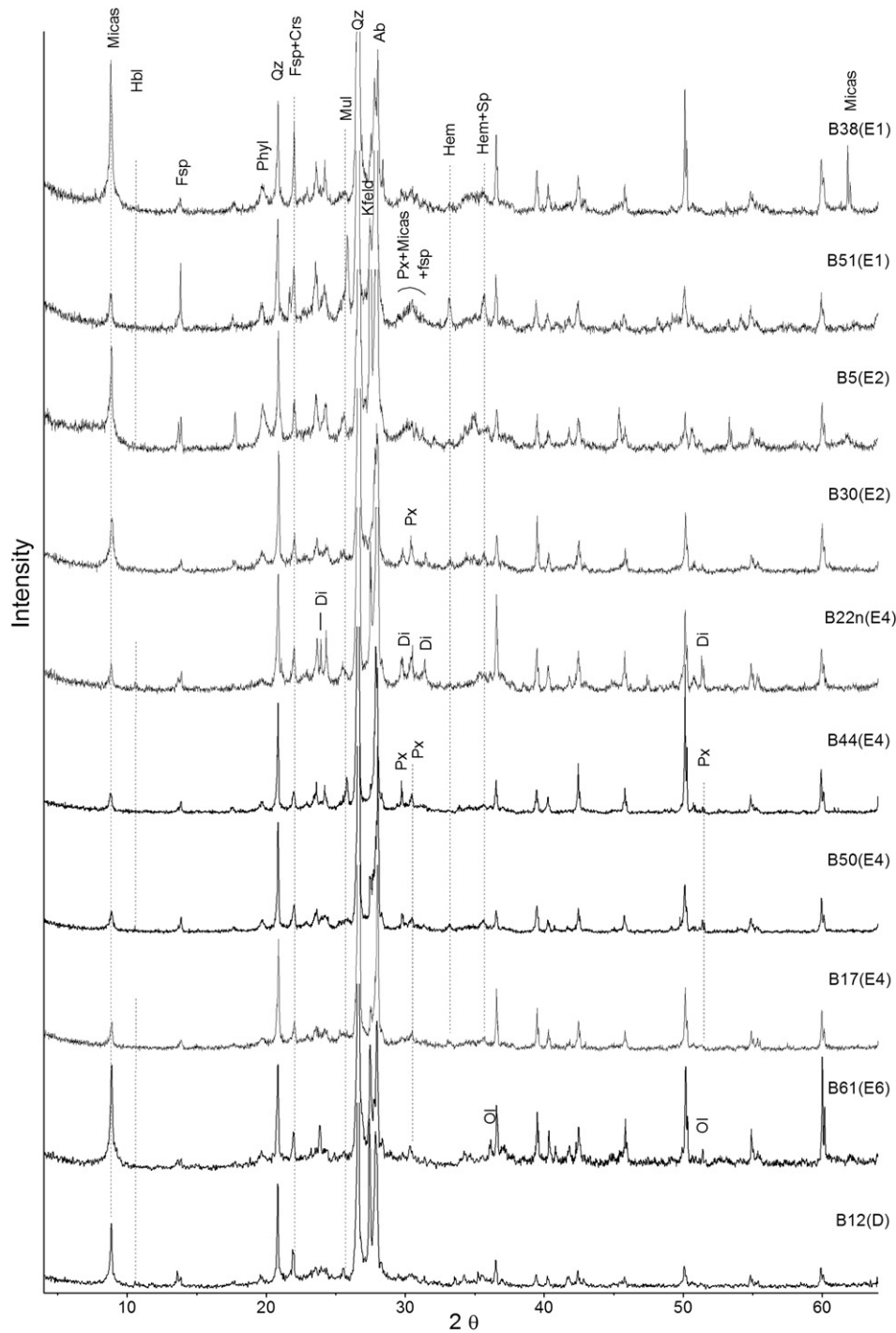


Fig. 9. XRD patterns of representative sherds; mineral abbreviations are as in Table 2.

lithologically associated with the clay material (since they could use a material naturally tempered).

The physical, mineralogical (Table 1) and geochemical (Table 3) results suggest that, with the exception of LV1 or the epiclastic bentonitic clays (OW11, LE2km9), all here discussed samples have suitable properties to be used in the ceramic production. LV1 is mostly silty and not plastic enough while the epiclastic clays since they are mostly smectitic (montmorillonite) have excessive shrinkage and dry too slow among other negative features for this purpose. Still, the epiclastic clays could be added in minor proportions to improve the plasticity of some of other materials with lower clay content like those from Cerco de Palos or La Aguada.

Test specimens were fired at various temperatures to evaluate the phase transformations and compare them with the phases found in the sherds. It is not possible to reproduce the firing conditions used by artisans and not only the mineralogical composition but also the processing techniques (shaping, firing time) and grain size greatly affect the resulting microstructure (Riccardi et al., 1999; Carretero et al., 2002). Nevertheless, XRD patterns and SEM-EDS showed clear phase changes (Figs. 4, 6 and 7) and the development of microgranular phases with compositions close to those found in the sherds. In general, phyllosilicates (small mica flakes and clay minerals), hornblende and hypersthene tend to disappear over 1000 °C. Hematite, cristobalite and mullite usually formed as well as Ca and/or Fe, Mg oxides and/or

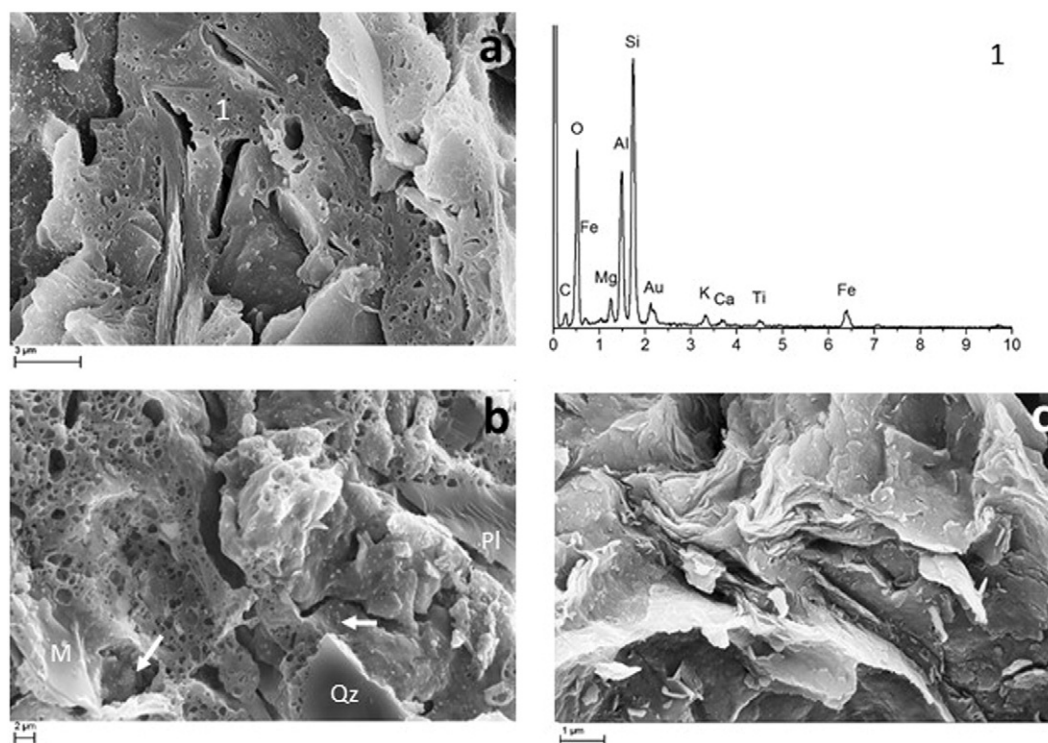


Fig. 10. FE-SEM images of sherds. a: B50, vitrified paste, EDS 1 shows its composition; b: B51, detail of the highly vesicular and vitrified paste, temper grains of plagioclase, quartz and mica are distinguished, as well as microgranular new phases (white arrow); c: B30, detail of the matrix, with no evidence of vitrification, clay flakes are clearly identified.

silicates of Ca, Fe and/or Mg, Al and Ti. Spinel formed at 900–1000 °C along with other new phases, undetermined because of their incipient development. Diopside was formed in OW11 and LAg1 and olivine in OW11 and LE2km1. When calcite and/or ankerite were present in the raw clay, like in HU4, melilite is formed (Figs. 6 and 7 EDS 4).

Phlogopite, hornblende and pyroxenes (diopside, occasionally hypersthene) were identified in the selected sources (both the raw and the fired samples, Table 1, Figs. 4 and 6) and in some sherds (Table 2, Fig. 9) Hornblende is present in B51 and B64 of class E1, B2, and B33 of class E2, in B22n, B45 and B50 of class E4 of class E6, and B12 and B53 of class D. Diopside and other pyroxenes were found in B51 of class E1, B5, B30 and B66 of class E2, B17, B22n, B34, B44 and B50 of class E4 and B12 of class D. Hornblende and pyroxenes (hypersthene and diopside) were also found in some sherds of class A from PB (Bertolino et al., 2014) and in 8 out of 9 adobes from PB and CP065 sites (Bertolino and Gastaldi, 2014). Phlogopite occurs in all sherds. These minerals are usual components in all the quaternary sediments that filled the valley and crop out close to the sites like Cerco de Palos (CP65b1 and CP65b2), La Aguada (LAg1), Los Escobales (LE2km1) and Los Varela (LV1). Some sherds exhibited high vitrification and the development of new phases (Fig. 10a and b) with compositions very close to those resulting from the firing experiment on test specimens of raw materials (Fig. 7b). Evaluation of firing temperatures are still under discussion but in some cases typical features of having reached or even overpassed 900–1000 °C were observed by XRD as previously reported by Bertolino et al. (2008). It is supported by the here presented XRD measurements (Fig. 9) by the occurrence of spinel, mullite, anorthite, diopside, very low intensities of micas diffraction peaks (i.e. class E4 B22n, B27, B34, B44 and B50 and class E1 B51 in Fig. 9). In addition, SEM studies (Fig. 10) also prove this temperature range based on the occurrence of vitrified areas and of Fe-rich and Ca-Si-rich micro-granular phases in voids. The matrix of both the sherds and the fired specimens of source clays with high Si, Al and minor Fe, K, Mg, Ca and Ti content (Fig. 10a, EDS 1) are also similar to the compositions reported by Bertolino and Fabra (2003) on sherds from other classes and styles. Most of those sherds (B49, B5, B17, B27, B32, B35, B37, B44, B45, B50

and B67, Table 2) did not have hornblende but contained mullite, diopside and spinel (Table 2). Because hornblende and hypersthene decreased or even disappeared in the test specimens after firing at 1000 °C, it is suspected that the ceramics with features of having been fired at high temperatures do not have or have little hornblende because of the firing temperature and that those minerals could have been present in the unfired pastes.

There are no mineralogical or chemical compositional correlation when considering the technological classes (E or D) suggesting that the choices of raw materials to manufacture these wares were in terms of the temper rather than in the clay. The use of the local red clays has been suggested also by Bertolino et al. (2014) after identifying similar minerals (kaolinite, calcite, phlogopite and hematite) in some red pigments from PB like in the red clays found in the valley at Los Escobales and Humaya.

In comparison with other studies (Zimmermann et al., 2015) typical provenance diagrams for pottery are not even capable to identify differences among samples or to identify typical source compositions. As Table 3 and Fig. 8 show, most of the robust provenance ratios are relatively similar in all pottery samples and in the here selected raw materials. Variations are only small and cannot be used for a systematic differentiation. Few samples do show a different character but they do not point to a trend rather an individual variation like sample B30 with its high REE concentrations, which would be extraordinary in a provenance diagram using La/Sc ratios (Table 3). Expectedly, some ceramic and some sampled potential materials do not show any other characteristic than unrecycled typical UCC (Table 3) because of the supracrustal nature of the raw materials. Some sherds are slightly enriched in clays and therefore in Σ REE but these differences are so small that heterogeneity of the sampled materials cannot be excluded. Hence, conventional trace element values cannot be used here as distinguishing criteria.

However, both ceramic and source materials show partly unusual enrichments in Sb, Bi and Cs. Almost all the pottery and source samples have moderately high Cs concentrations, which matches often PAAS values or are even higher (Table 3). The source materials found at Los

Escobales (R9), Humaya (HU1 and HU2) and the sample AND do contain high concentrations in Cs only matched by the ceramic sample B44 (Table 3). Interestingly, there is only one well-studied rock succession in the regional geology with such high Cs concentrations, which is the metasedimentary Puncoviscana Complex (Zimmermann and Bahlburg, 2003; Zimmermann, 2005, 2008; unpublished data Zimmermann). Anomalies of Bi and Sb are extremely rare in supracrustal rocks and unknown in conventional provenance publications or sediment-geochemical studies in northwest of Argentina. However, in the area locations of Cs, Bi, Sb and polymetallic mineralizations were identified (Márquez and Galliski, 2007). In class E1 samples B51 and B38 are both enriched in Bi and Sb with Cs concentrations above typical UCC but similar to typical PAS (Table 3). There is no sample among the collected raw materials which enriched similarly in these two trace elements. If the sampled material is the source for the pottery mixing is required. To match the values of the ceramic of class E1 only AND would supply sufficient Sb and OW11 and R9 the necessary amount of Bi, but then the ceramic should be higher enriched in Cs. Samples of class E2 are moderately enriched in Cs compared to UCC and comparable to PAS (Table 3) and only sample B30 is enriched in Sb. Nearly all raw materials (R9, OW11, HU1, HU2, AND and ER1s, the latter because of its depletion in Cs) would then be candidates for the ceramic, besides B30. In class E4, two samples are only enriched in Sb (B22e, B44), one in Bi and Sb (B50) and two in Bi only (B17, B45), with Cs compositions comparable to PAS for all ceramic samples (Table 3). Similarly to B30, AND is the only raw material with sufficiently high Sb concentrations for B44 and B22e. B50 falls in the same category as those samples from E1 and requires a mixing of two different raw materials (Table 3). The three samples without any enrichment for the two base metals Bi and Sb (B22n, B27, B34) can be related to the raw material for class E2. This implies that the sampled raw materials do have partly similarly unusual enrichments in Cs, Bi and Sb, as some ceramic samples and reflect therefore a very unusual anomaly in their chemical compositions. This alone allow in speculating that major source for most of the ceramic is local. Ceramic samples without a significant anomaly in these elements are also covered by the sampled raw materials, as their composition is comparable to typical unrecycled UCC or PAS, which is not surprising as the raw materials are composed of supracrustal geological materials. Some ceramic samples are only enriched in Bi (B17, B45). Only OW11 would match this characteristic, but because of the physical properties of this clay it is unlikely that it was used alone, but added as a plasticity corrector material. B45 contains lithoclasts with hornblende crystals and significant proportions of anorthite, spinel, hematite, cristobalite and mullite, like the fired piece of OW11 (see Fig. 6 and Table 2). B17 has minor olivine but not anorthite. B5 is slightly enriched in Bi (0.4 ppm) and has minor mullite, cristobalite and traces of spinel and pyroxenes. B30 is solely enriched in Sb (Table 3).

Finally, a last group of ceramic is enriched in Bi and Sb (B51, B38, B50, B53) and show also moderated to elevated Cs concentrations. None of the sampled source materials have similar characteristic (Table 3). However, since the source materials enriched in Sb and Bi have very high Cs (HU, AND), to match these ceramics from the source materials requires the dilution of Cs. This could be done by adding silica-rich material to dilute the clays in the sample, for example by using ER1 or a similar material.

B30 is spectacular with more than 4% REE, but otherwise the sample is as typical as all other samples with enrichment in Sb (Table 3). Monazite contains very high concentrations in REE (Taylor and McLennan, 1985) as well as high Th. However, the concentration of the latter is comparable to all other samples (Table 3) thus, monazite can be excluded as the REE bearing mineral (McLennan, 1989). The extremely high La/Yb(N) (where 'N' denotes normalization to chondritic values after McLennan, 1989) value of 36.9 combined with La_N (2918) points to the possibility of an extreme enrichment of fluorapatite or allanite (epidote) in the range of far more than 100% (according to McLennan, 1989). None of these minerals has been identified by XRD, but c. 1–2 % of allanite (beyond the detection limit of XRD)

would be sufficient to reach the REE concentrations. It is well established that fluorapatite is quite common in local granites and water drained through these geological formations (Zimmermann et al., 2005). Besides the high REE, B30 is totally similar to all source materials in terms of trace element ratios and can be easily modeled with the given source materials.

7. Conclusions

This study tracked down the clay resources used by ancient Aguada Culture artisans to manufacture ordinary vessels (classes E and D) at Piedras Blancas's site. The preliminary evaluation of the physical properties on selected clay materials suggests that they are suitable for pottery making either used alone like those from Andalgalá, Humaya, Los Escobales red clays and the sedimentary units from Los Escobales and Cerco de Palos, or as additives to improve the quality and plasticity like the epiclastic clays from Los Escobales. Though nowadays there is no record of clay deposits, it appears to be a wide availability of raw material resources in the valley for the production of ceramics. Restrictions that may have existed could have been more linked to the quality of raw material than to the limitations of the clay supply.

The mineralogy and the geochemistry supported this idea of using local materials for the pottery. Fingerprinting minerals (phlogopite, hornblende and hypersthene) were found in many ceramics and in the quaternary sediments that filled the valley. Hornblende and hypersthene are in the epiclastic rocks. Several new phases (mullite, hematite, pyroxenes, diopside and/or cristobalite) which formed in the test specimens of raw materials after firing at 1000 °C were also identified in the sherds with features of having been fired at high temperatures. Most of the ceramic and source materials show similar geochemical characteristics (major and incompatible trace element distributions) close to typical unrecycled UCC and are indistinguishable one from another except for B30 (with >4% of REE).

Some raw material and ceramic samples are enriched in the very rare trace elements Bi and Sb. These elements can be associated with local mineralizations (Márquez and Galliski, 2007). This allows to speculate about a common origin and would point to local sources of raw materials for some of the ceramic. Cs is enriched in some local sedimentary formations as in some samples raw materials too. All ceramic samples have enriched values compared to typical UCC and are comparable to PAS or even higher. This trend in some ceramic samples might also be a local characteristic of the geochemical composition, but further studies are needed to establish a possible systematic relationship.

The geochemical study is not conclusive enough to differentiate among the sampled local clayey materials and to interpret fully the provenance of the ceramics. The results obtained by combining the geochemistry with the evaluation of the mineralogy suggest that the use of the local clays was possible although the individual source could not be identified. It can also be confirmed that the inclusions found in the pastes were intentionally added. No significant differences were found among the technological classes.

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References

- Arnold, D.E., 2005. Linking society with the compositional analyses of pottery: a model from comparative ethnography. In: Livingstone Smith, A., Bosquet, D., Martineau, R. (Eds.), *Pottery manufacturing processes: reconstruction and interpretation* International Series 1349. British Archaeological Reports, Oxford, pp. 15–21.
- Arnold, D.E., 2006. The threshold model for ceramic resources: a refinement. In: Gheorghiu, D. (Ed.), *Ceramic Studies: Papers on the Social and Cultural Significance of Ceramics in Europe and Eurasia from Prehistoric to Historic Times*. BAR International Series 1553, pp. 3–9 (Oxford).
- Arnold, D.E., 2011. Classics reviews: ceramic theory and cultural process after 25 years. *Ethnoarchaeology* 3 (1), 63–98.
- Assandri, S.B., 2007. Procesos de complejización social y organización espacial en el Valle de Ambato, Catamarca. Master Thesis. Publicaciones Tesis. Digital Format. Universidad Internacional de Andalucía, España.
- Bertolino, S.R., Fabra, M., 2003. Provenance and technology of pot sherds from ancient Andean cultures at the Ambato Valley, Argentina. *Appl. Clay Sci.* 24, 21–34.
- Bertolino, S.R., Gastaldi, M.R., 2014. Adobes y materias primas de elementos arquitectónicos en dos sitios Aguada (600–1000d.c.): Piedras Blancas (600–900d.c.) y Cerco de Palo, valle de Ambato, Catamarca, Argentina. Simposio de Arcillas, XIX Congreso Geológico Argentino, Córdoba, pp. S1–17.
- Bertolino, S.R., Zimmermann, U., 2013. Before the Pot: Tracking the Possible Clay Source of Aguada Culture (300–1000AC) Ceramics and Pigments, Catamarca, Argentina. XV Intern. Clay Conference, Brasil, p. 706.
- Bertolino, S., Barrionuevo, E., de la Fuente, G., Carreras, A., Laguens, A., Riveros, J.A., 2008. Caracterización de piezas cerámica de la cultura aguada (Catamarca, Argentina) mediante técnicas de rayos X. Avances en Análisis por Técnicas de Rayos X, XIV, Arica, Chile, pp. 240–245.
- Bertolino, S., Galván Josa, V., de la Fuente, G., Carreras, A., Laguens, A., Riveros, J.A., 2009a. Caracterización de pastas cerámicas de la cultura Aguada (Catamarca, Argentina) mediante técnicas de rayos X. In: O., Palacios, Vázquez, C., Palacios, T., Cabanillas, E. (Eds.), *Arqueología Latinoamericana*. 2do. Congr. Argentino y 1ro. Latinoamericano de Arqueometría, Talleres Gráficos Centro Atómico Constituyentes, Buenos Aires, pp. 35–39.
- Bertolino, S., Galván Josa, V., Carreras, A., Laguens, A., de la Fuente, G., Riveros, J.A., 2009b. X-ray techniques applied to surface paintings of ceramic pottery pieces from Aguada culture (Catamarca, Argentina). *X-Ray Spectrom.* 38, 95–102.
- Bertolino, S.R.A., Zimmermann, U., Galván, V., Laguens, A., 2010. Composición mineralógica y química y posible proveniencia de cerámica pre y post-hispánica del valle del río Copacabana, NO de Córdoba. In: Bertolino, S., Cattáneo, R., Izeta, A. (Eds.), *La arqueometría en Argentina y Latinoamérica*, Editorial de la Facultad de Filosofía y Humanidades, Universidad Nacional de Córdoba, Córdoba, pp. 35–42.
- Bertolino, S.R., Zimmermann, U., Gastaldi, M.R., Laguens, A., 2014. The ceramics and pigments from Piedras Blancas (600–1000 AC), Aguada Culture: clay provision, technology, and social change at the Ambato Valley (Argentina). Symposium on Characterization of Andean Ceramics, p. 65 Society for American Archaeology 79th annual meeting, Austin.
- Caminos, R., 1979. Sierras Pampeanas Noroccidentales: Salta, Tucumán, Catamarca, La Rioja y San Juan. In: J.M.C. Turner (Ed.), *Geología Regional Argentina*, 1 Academia Nacional de Ciencias, Córdoba, pp. 225–291.
- Caro, M., 2002. Desigualdad social y su registro arquitectónico en el sitio arqueológico Piedras Blancas. Publicación digital. Marginalidad social y vulnerabilidad: diversidad, desigualdad y pobreza <http://www.flyh.unc.edu.ar/secretarias/cyt/jor2002/lljor.htm>.
- Carretero, M.I., Dondi, M., Fabbri, B., Raimondo, M., 2002. The influence of shaping and firing technology on ceramic properties of calcareous and non-calcareous illitic-chloritic clays. *Appl. Clay Sci.* 20, 301–306.
- Dal Molin, C.N., Fernández, D., Escosteguy, L., 2003. Hoja Geológica 2766-IV, Concepción, provincias de Tucumán, Catamarca y Santiago del Estero. Instituto de Geología y Recursos Minerales, Servicio Geológico Minero Argentino. Boletín N°342, Buenos Aires, p. 41.
- Degen, T., Sadki, M., Bron, E., König, U., Nénert, G., 2014. The HighScore Suite. Powder Diffraction, 29, Supplement S2, S13–S18.
- Druc, I., 2013. What is local? Looking at ceramic production in the Peruvian highlands and beyond. *J. Anthropol. Res.* 69, 485–513.
- Fabra, M., 2008. Producción tecnológica y cambio social en sociedades agrícolas prehispánicas (Valle de Ambato, Catamarca). BAR International Series (Oxford).
- Figuerola, G., Dantas, M., Laguens, A., 2010. Prácticas agropastoriles e innovaciones en la producción de plantas y animales en los Andes sur. El Valle de Ambato, Argentina, Primer Milenio d.C. *Int. J. S. Am. Archaeol.* 7, 6–13.
- Galliski, M., 1999. Distritos pegmatíticos Ambato y Quilmes, Catamarca y Tucumán. In: E.O., Zappetini (Ed.), *Recursos Minerales de la República Argentina*, Instituto de Geología y Recursos Minerales SEGEMAR, Anales 35, Buenos Aires, pp. 389–392.
- Galván Josa, V., 2012. Caracterización de materiales inhomogéneos mediante microscopía electrónica de barrido y técnicas de rayos x. Doctoral Thesis. Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Córdoba.
- Bertolino, S.R., Galván Josa, V., Castellano, G., 2011. Ceramic surface paintings and pigments from the Aguada culture (Argentina): XRD and SEM-EDX archaeometric studies. Chapter 10. In: Sarrica, S.M. (Ed.), *Paints: Types, Components and Applications*, Serie Chemistry Research and Applications. Nova Science Publishers, New York, pp. 169–211.
- Galván Josa, V., Bertolino, S.R., Riveros, J.A., Castellano, G., 2009. Methodology for processing backscattered electron images. Application to Aguada archaeological paints. *Micron* 40, 793–799.
- Galván Josa, V., Bertolino, S.R., Laguens, A., Riveros, J.A., Castellano, G., 2010a. X-ray and scanning electron microscopy archaeometric studies of pigments from the Aguada culture, Argentina. *Microchem. J.* 96, 259–268.
- Galván Josa, V.M., Bertolino, S.R., Riveros, J.A., Castellano, G.E., 2010b. Procesamiento de imágenes de rayos X y de electrones retrodispersados para la caracterización de pinturas en cerámicas arqueológicas. In: Bárcena, J.R., Chiavazza, H. (Eds.), *Arqueología Argentina en el Bicentenario de la Revolución de Mayo*, XVII Congreso Nacional de Arqueología Argentina, Mendoza, II, pp. 907–911.
- Galván Josa, V., Castellano, G., Bertolino, S.R., 2013. Quantification by SEM-EDS in uncoated non-conducting samples. *Radiat. Phys. Chem.* 88, 32–37.
- Galván, V., Bertolino, S., Castellano, G., Laguens, A., Riveros, A., 2010. Cuantificación mineralógica de pigmentos pertenecientes a la cultura Aguada mediante refinamiento Rietveld. In: Bertolino, S., Cattáneo, R., Izeta, A. (Eds.), *La arqueometría en Argentina y Latinoamérica*, Editorial de la Facultad de Filosofía y Humanidades, Universidad Nacional de Córdoba, Córdoba, pp. 331–337.
- Gastaldi, M.R., 2010. Cultura Material, Construcción de Identidades y Transformaciones sociales en el Valle de Ambato durante el Primer milenio d. C. Doctoral Thesis. Facultad de Ciencias Naturales y Museo, Universidad Nacional de la Plata, La Plata, Argentina.
- Gastaldi, M.R., 2013. Métodos de Excavación, Estratigrafía y Sig: Reconstrucción de Contextos Deposicionales en el Sitio Piedras Blancas, Valle De Ambato, Provincia de Catamarca, Argentina. In: Figuerero Torres, M.J., Izeta, A.D. (Eds.), "El uso de Sistemas de Información Geográfica (SIG) en la arqueología sudamericana. BAR International Series, Oxford, pp. 186–200.
- González, A.R., 1961–1964. La Cultura de La Aguada del Noroeste argentino. *Rev. Inst. Antropológico* 205–252 II–III, Córdoba.
- González, A.R., 1979. Dinámica cultural del N.O. Argentino. Evolución histórica en las culturas del N.O. Argentino. *Antiquitas*, Universidad del Salvador, Buenos Aires, pp. 28–29.
- González, A.R., 1998. Cultura La Aguada. *Arqueología y Diseños*, Filmediciones Valero, Buenos Aires.
- González Bonorino, F.G., 1978. Descripción Geológica de la Hoja 14 f. San Fernando del Valle de Catamarca. 1: 200000. Servicio Nacional Minero Geológico, Buenos Aires, Boletín N° 160.
- Juez, S., Laguens, A., 1999. Especialización en la manufactura cerámica de pucos Aguada. XIII Congreso Nacional de Arqueología Argentina, Córdoba, Actas, Tomo I, pp. 489–504.
- Laguens, A., 2006a. Continuidad y ruptura en procesos de diferenciación social en comunidades aldeanas del valle de Ambato, Catamarca, Argentina. *Chungara* 38 (2), Arica, Chile, pp. 211–222.
- Laguens, A., 2006b. Campo y espacio social en el estudio arqueológico de la desigualdad. In: Gnecco, C., Langebaek, C. H. (Eds.), *Contra la tiranía tipológica en arqueología: Una visión desde suramérica*. Facultad de Ciencias Sociales, CESO, Universidad de los Andes, Chile. (Ediciones Uniandes).
- Laguens, A., Giesso, M., Bonnin, M., Speakman, J., Glascock, M., Manasse, B., Kriscautzky, N., 2007. Estudio de producción y distribución de la cerámica gris-negra grabada del Valle de Ambato (ca. 300–1000 d.C.). In: Cremonese, B., Ratto, N. (Eds.), *Cerámicas arqueológicas. Perspectivas arqueométricas para su análisis e interpretación*, San Salvador de Jujuy, pp. 147–167.
- Marconetto, M.B., Gastaldi, M., Lindsoug, H., Laguens, A., 2014. Merging the matrix: stratigraphy, radiocarbon dates, and fire regimens in the Ambato Valley (Catamarca, NW Argentina). *Radiocarbon* 56 (1), 1–19.
- Márquez, M.F., Galliski, M.A., 2007. Chatkalita, nekrasovita y otros minerales del grupo de la estannita de veta María Eugenia, Cerro Atajo, Catamarca. *Rev. Asoc. Geol. Argent.* 62, 289–298.
- McLennan, S.M., 1989. Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary process. In: Lipin, B.R., McKay, G.A. (Eds.), *Geochemistry and Mineralogy of Rare Earth Elements*, Mineralogical Soc. Amer., *Reviews in Mineralogy*. 21, pp. 69–200.
- McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem. Geophys. Geosys.* 2 (2000GC00109).
- McLennan, S.M., Taylor, S.R., McCulloch, M.T., Maynard, J.B., 1990. Geochemical and Nd-Sr isotopic composition of deep-sea turbidites: Crustal evolution and plate tectonic associations. *Geochim. Cosmochim. Acta* 54, 2015–2050.
- McLennan, S.M., Taylor, S.R., Hemming, S.R., 2006. Composition, differentiation, and evolution of continental crust: constrains from sedimentary rocks and heat flow. In: Brown, M., Rushmer, T. (Eds.), *Evolution and Differentiation of the Continental Crust*, pp. 92–134.
- Pérez Gollán, J.A., 1991. La Cultura de la Aguada vista desde el Valle de Ambato. *Publicaciones CIFYH*, Arqueología 46, Córdoba, pp. 157–173.
- Riccardi, M.P., Messiga, B., Duminuco, P., 1999. An approach to the dynamics of clay firing. *Appl. Clay Sci.* 15, 393–409.
- Rice, P., 1987. *Pottery Analysis. A Sourcebook*. The University of Chicago Press., Chicago (559 pp).
- Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. In: Holland, H.D., Turekian, K.K., Rudnick, R.L. (Eds.), (Ex.Eds.), *Treatise on Geochemistry* 3. Elsevier, pp. 1–64.
- Sosic, M.J.V., 1972. Descripción Geológica de la Hoja 14 d, Tinogasta. Servicio Nacional Minero Geológico, Buenos Aires. 1: 200000. Boletín N°129.
- Soil Survey Division Staff, 1993. *Soil Survey Manual*. Soil Conservation Service. U.S. Department of Agriculture Handbook 18.
- Szilágyi, V., Gyarmati, J., Tóth, M., Taubald, H., Balla, M., Kasztovszky, Zs., Szakmány, Gy., 2012. Petro-mineralogy and geochemistry as tools of provenance analysis on archaeological pottery: study of Inka period ceramics from Paria, Bolivia. *J. South Amer. Earth Sci.* 36, 1–17.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific, Oxford (312 p).
- Tschegg, C., Taflos, T.N., Hein, I., 2009. Integrated geological, petrologic and geochemical approach to establish source materials and technology of Late Cypriot Bronze age plain white ware ceramics. *J. Archaeol. Sci.* 36, 1103–1114.

- Whitney, D.L., Evans, B.W., 2010. Abbreviations for names of rock-forming minerals. *Am. Mineral.* 95, 185–187.
- Zimmermann, U., 2005. Provenance studies of very low- to low-grade metasedimentary rocks of the Puncoviscana complex, northwest Argentina. In: Vaughan, A., Leat, P., Pankhurst, R. (Eds.), *Terrane Processes at the Margins of Gondwana*, Geological Society London. Special Pub 246, pp. 381–416.
- Zimmermann, U., 2008. Provenance studies of metasedimentary rocks in northwest Argentina: Deeper crustal equivalents of the Puncoviscana Formation? 33th International Geological Congress, Oslo (Abstract volume).
- Zimmermann, U., Bahlburg, H., 2003. Provenance analysis and tectonic setting of Ordovician volcanic sedimentary successions in NW Argentina. *Sedimentology* 50 (6), 1079–1114.
- Zimmermann, U., Bahlburg, H., 2005. The crustal evolution of the Central Andes during the Neoproterozoic to the Silurian. *Geochim. Cosmochim. Acta* 69 (10S), A877.
- Zimmermann, U., Luna Tula, G., Marchioli, A., Narváez, G., Olima, H., Ramírez, A., 2002. Análisis petrográfico, geoquímico e isotópico geoquímicos de las arenitas de la Formación Falda Ciénaga (Ordovícico Medio) y sus implicaciones para la evolución de la cuenca ordovícica en la Puna (NO Argentina). *Asoc. Argentina de Sedimentología* 9 (2), 165–188.
- Zimmermann, U., Huizenga, J.-M., Fischer, J., Mubenga, S.B., Russell, J., van Niekerk, H., 2005. Water analysis in Andalgalá and San Fernando Del Valle (Catamarca, NW Argentina): insights in the water quality of the Sierras Ambato and Aconquija. XVI Congreso Geológico Argentina, La Plata, Actas 4, 315–421.
- Zimmermann, U., Kristoffersen, E.S., Fredriksen, P.D., Bertolino, S.R., Andò, S., Bersani, D., 2015. Provenance and composition of unusually chrome and nickel-rich bucket-shape pottery from Rogaland (southwestern Norway). *Sedimentary Geology* (in press), doi: <http://dx.doi.org/10.1016/j.sedgeo.2015.09.001>.