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ARCHAEOMETRIC ANALYSIS OF CERAMIC PRODUCTION IN TIWANAKU STATE (*C*.500–1000 CE): AN EXPLORATORY STUDY*

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*The chemical and mineralogical characterization of seven ceramic fragments produced within Tiwanaku state (*c.*500–1000 CE) is reported. The instrumental techniques used included X-ray elemental and mineralogical chemical analysis, Raman spectroscopy, and scanning and light microscopy. The results indicate there are several clay types, although they show similarities, such as the use of a plant-based temper. The red colour of the decoration is hematite, and manganese oxides such as jacobsite are present in the black. The white colour is a mixture of gypsum and clay, and the orange is a mixture of hematite and clay. The use of colours, the quality of the clays and the temperatures reached during pottery firing point to expertise in ceramic production and to complex decision-making processes. The multi-elemental archaeometric approach documented here could become an important tool to shed a light on ancient ceramic technology and the internal variance of Tiwanaku pottery.*

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KEYWORDS: TIWANAKU CERAMICS, MINERALOGY, SEM (EDX), RAMAN SPECTROSCOPY

INTRODUCTION

We present and discuss the archaeometric characterization of seven ceramic fragments of Tiwanaku style. Instrumental techniques used included X-ray elemental and mineralogical chemical analysis, Raman spectroscopy, and scanning and light microscopy. The Tiwanaku state flourished during the so-called Middle Horizon (*c*.500–1000 CE), spreading its influence over large parts of the south-central Andes (Fig. 1, a). The Tiwanaku capital, Tiahuanaco, was located in the southern Lake Titicaca Basin (Bolivia), at an altitude of over 3800 masl. The long history, expansive nature and lavish state rituals of Tiwanaku involved the use of several different styles, types and forms of pottery (Alconini 1995; Bermann 1994; Isbell and Korpisaari 2015; Janusek 2003; Kolata 2003a; Korpisaari 2006; Korpisaari *et al*. 2012; Korpisaari and Pärssinen 2011; Sagárnaga 2007). Many of these ceramic vessels, however, were associated with a rather standardized iconography, which acted as a visual support for the ideological message of the Tiwanaku state (Berenguer 1993, 1998; Cook 1994; Korpisaari and Pärssinen 2011; Llagostera 2006; Torres 1987, 1994, 2001, 2004; Uribe and Agüero 2001; Villanueva and Korpisaari 2013).

This 'state-style' pottery was originally conceived of as a spatially homogeneous group with sequential temporal phases (e.g., Bennett 1934, 1936; Ponce Sanginés 1981; Rydén 1947). However, it has since become clear that in many areas up to three of these 'cultural phases' coexisted, while different subtypes of the Tiwanaku style also selectively emerged and some local pottery types remained independent of state processes (Alconini 1995; Augustyniak 2004;

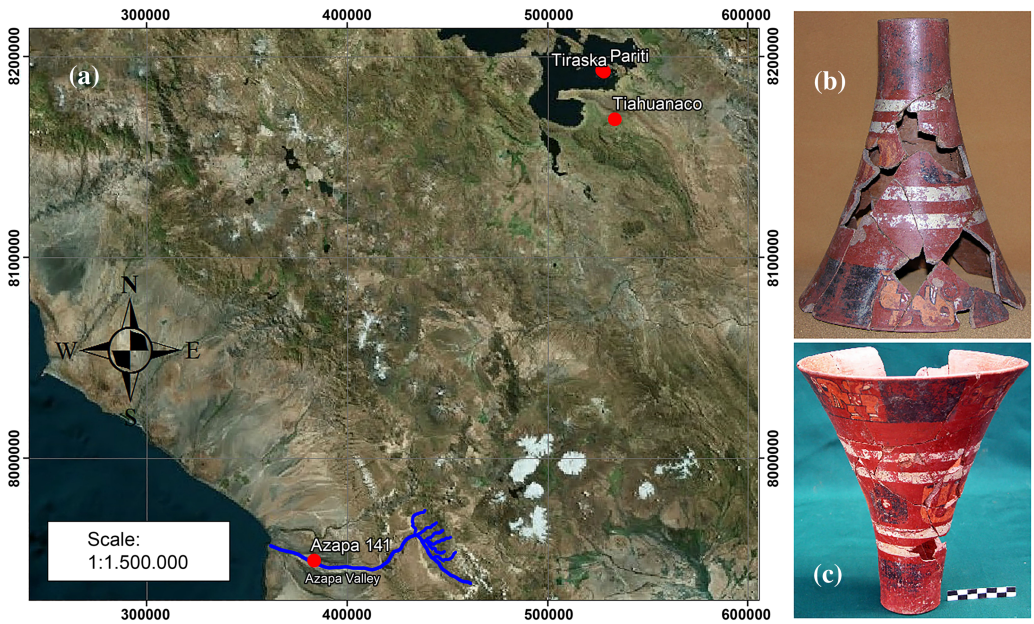


Figure 1 *(a) Map of the general area discussed with the sites mentioned in the text; and (b, c) polychromic ceramics found in the offering wells of Pariti Island of two ch'alladores (b) PRT 00334 and (c) PRT 00335 that show an iconography similar to a sample analysed in the study. [Colour figure can be viewed at wileyonlinelibrary.com]*

Bermann 1994; Burkholder 2001; Korpisaari 2015). Thus, we now recognize that a complex and socially heterogeneous group of peoples produced objects in the Tiwanaku style. We also have a better understanding of the colonial enclave that Tiwanaku established in the Moquegua Valley in southern Peru (Baitzel and Goldstein 2015; Buikstra 1995; Goldstein 2005, 2013; Goldstein and Owen 2001; Goldstein and Palacios 2015; Palacios and Goldstein 2015; Sharratt 2010, 2015, 2016a, 2016b; Williams *et al*. 2015) and of the social groups and pottery styles that emerged after the collapse of Tiwanaku and its Moquegua colony (Korpisaari *et al*. 2014; Ogalde 2015; Owen 2005; Owen and Goldstein 2001; Sharratt 2010, 2015, 2016a, 2016b; Sharratt *et al*. 2009, 2015; Sutter and Sharratt 2010; Williams *et al*. 2015).

To sum up, in the Andean high plateau and in several valley settings, pottery studies have been fundamental in establishing the chronology and investigating the cultural development and complexity of Tiwanaku. Little by little, these investigations have changed our understanding of Tiwanaku, from that of a centralized state to an entity of growing social complexity using several ceramic styles to express its internal variety. Furthermore, it is now clear that in the former enclaves or colonies of the Tiwanaku state, several derived, post-Tiwanaku styles (such as Tumilaca and Ilo-Cabuza), earlier interpreted as manifestations of centralized state rule, were developed and could live on for some centuries after state collapse. We feel that an increasing precision and depth of pottery studies on a transversal scale (referred to the notion of 'state-style pottery') and/or regional scale (referred to the notion of 'internal variety') are necessary to gain an even better understanding on these topics, which are fundamental for interpretations of Tiwanaku and its internal social complexity. Both approaches (regional and/or transversal) in Tiwanaku pottery studies would call for extensive, long-term investigations. As a necessary first step toward such more extensive archaeometric research projects, we selected seven ceramic samples from different Tiwanaku contexts (Table 1). We present our samples, methods and results below, and discuss the technological processes and necessary know-how related to the raw materials identified. We hope to show that, when applied to a larger sample, the analytical approach documented here could provide solid empirical grounds on which to characterize and differentiate between ceramic substyles, while also opening up new ways in which to study particular aspects of ceramic manufacture, including the agency of individual potters, workshops and/or groups. As far as we know, these are the first published results using this kind of approach to study and characterize Tiwanaku-style pottery.

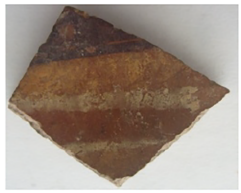
ARCHAEOLOGICAL SITES AND SAMPLES

For this exploratory study of the applicability of detailed archaeometric analyses to study ceramic production in the Tiwanaku state, we chose to analyse ceramic fragments from four different sites. These sites and samples are briefly characterized below.

Tiahuanaco

The archaeological remains of the type site of the Tiwanaku culture, located in the Department of La Paz in Bolivia, 16 km south-west of Lake Titicaca, cover an area of about 6 km^2 (Kolata 2003b). The sample includes two polychrome fragments, TWTIA001-IAI485 and TWTIA003-IAI487, recovered during surface collections made in Tiahuanaco.

Table 1 *Samples analysed, with details of the fragments used to study all the colours and the clay matrix*

Sample	*Site*	*Fragments*	
TWTIA001-IAI485	Tiahuanaco		
TWTIA003-IAI487			
TWPRT001-IAI488	Isla de Pariti		
TWPRT00286-IAI490			
TWTIR001a-IAI492	Tiraska		
TWTIR001b-IAI493			
TWAZ141-IAI495	Valle de Azapa		

Pariti Island

Pariti is located in the Bolivian part of the Lago Menor of Titicaca, 20–30 km north-west of Tiahuanaco. Archaeological excavations carried out in 2004–06 uncovered two deep pits containing the remains of at least 435 intentionally broken ceramic vessels, buried near the foundations of a possible ceremonial structure (Korpisaari *et al*. 2012; Korpisaari and Pärssinen 2011; Sagárnaga 2007; Villanueva and Korpisaari 2013). One of the samples (TWPRT00286-IAI490) came from Offering Pit 1. It is from a *quero* beaker in the so-called blackware style. The other sample, TWPRT001-IAI488, was surface-collected in the present-day village of Pariti. As for its iconography, this latter fragment is very similar to two *ch'alladores* (PRT 00334 and 00335) (Fig. 1, b, c) found in the scientifically excavated offerings pits of Pariti.

Tiraska

This habitation and cemetery site is located a few kilometres north-east of Pariti. In 1998–2003, 32 tombs of (post-)Tiwanaku affiliation were excavated (Korpisaari 2006). Both Tiraska samples we studied, TWTIR001a-IAI492 and TWTIR001b-IAI493, were surface-collected in the present-day village and are very similar to one another.

AZ-141

This cemetery site is located in the Azapa Valley, in the extreme north of Chile. A total of 55 funeral contexts have been excavated, and several of these tombs contained Tiwanaku-style ceramics and/or other objects indicative of high plateau influence (Korpisaari *et al*. 2014). The final ceramic sample included in the study, fragment TWAZ141-IAI495 recovered at AZ-141, came from a Tiwanaku-style polychrome *quero*.

METHODS

Mineralogical analysis

We cut pieces of 30 × 30 mm or less to be preserved in Epofix resin blocks, which were cut and polished with alcohol-based lubricants and emulsions to avoid humidifying the fragment. Finally, the bricks were covered with an approximate 200–250 Å carbon layer for analysis. The mineralogical analysis was performed with a quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) model E430 based on a ZEISS EVO 50 scanning electron microscope (SEM) combined with a Bruker Series 4 energy-dispersive spectroscopy (EDS) detectors and processed with iDiscover v5.3.2 software. The composition map was built with the Fieldscan operation, with a separation of 10 µm between measurements. These analyses were performed in the Scientific Equipment Unit (MAINI) of the Universidad Católica del Norte, Chile.

Scanning and optical microscopy

We took microphotographs of the ceramic fragments analysed using an Olympus SZX-7 stereo microscope. The ceramic fragments (approximately 1 cm^2) were then mounted on the stubs of an EVO LS SEM for chemical analysis with an energy-dispersive X-ray (EDX) Oxford detector (8.5 WD, 450 kV, detection limit of 0.1% by weight). The SEM images were captured at 100× and 600× with the secondary electron and retrodispersed electron detectors. The analysis was

performed in the Laboratorio de Bioarqueología of the Instituto de Alta Investigación de la Universidad de Tarapacá, Arica, Chile.

Raman analysis

The ceramic samples were mounted on coverslips to obtain the Raman spectrum of the different coloured surface areas using a Renishaw Raman Microscope System RM1000 (laser diode at 785 nm), a Leica microscope, a charge-coupled display (CCD) detector cooled electrically, and a notch filter to eliminate elastic scattering. The spectra were obtained using a 50× object, with the laser out at 2.0 mW and a spectral resolution of 2 cm^{-1}. This analysis was performed in the Facultad de Ciencias of the Universidad de Chile, Santiago, Chile.

Statistical tools

The results for the elements detected by EDX were analysed by principal components analysis (PCA) to select those that contributed most to the variability. The normality of the reduced set of elements was examined with the Shapiro and Wilk tests. Analysis of variance (ANOVA) was used to compare pigments and clay matrixes when their distributions were normal, and a non-parametric test was used when these were not. When the null hypothesis of equal means or medians was rejected, significant differences were detected using Tukey's post-hoc tests.

Results

Fragment TWPRT00286-IAI490 from Pariti Island (Fig. 2, a) has a very fine, uniform, dark brown paste with a porosity of 8%. The matrix is 60% clay, considering all the grains < 15 µm as matrix (Courtois 1976); micas (muscovite > chlorite > biotite) and quartz are less common. The

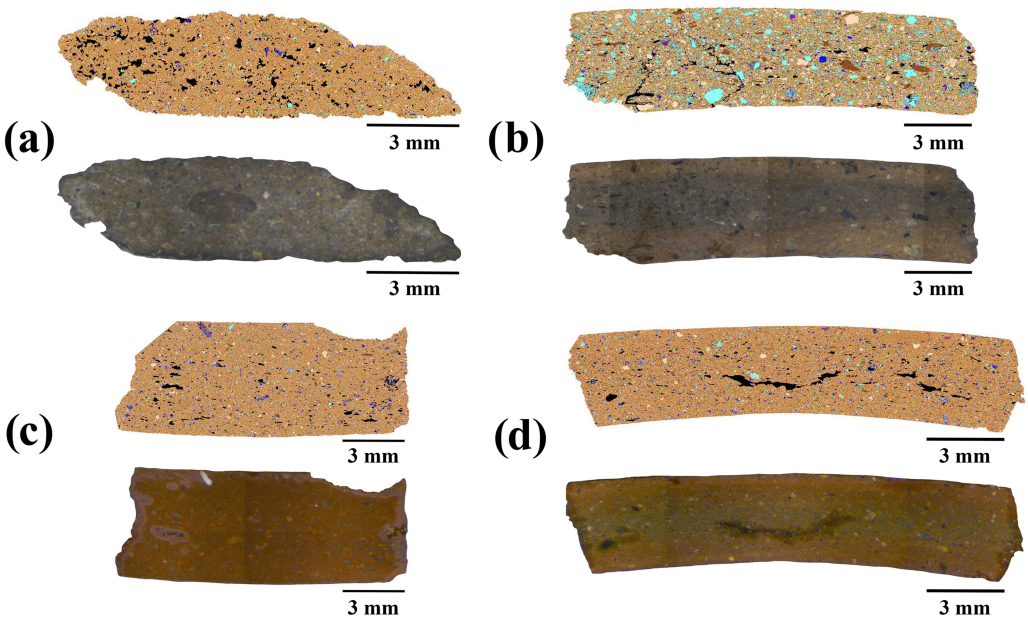


Figure 2 *Mineralogical maps provided by iDiscover (upper row) and photograph of fresh paste (lower row) of samples (a) TWPRT00286-IAI490, (b) TWPRT001-IAI488, (c) TWTIR001a-IAI492 and (d) TWTIR001b-IAI493. [Colour figure can be viewed at wileyonlinelibrary.com]*

non-plastic inclusions are of the size of medium to fine sand, subangular to subrounded, with good selection and distribution. The inclusions are composed of quartz crystaloclasts, biotite (rich in Fe-Mg), K feldspar (orthoclase) and plagioclace (oligoclase > albite). The sample also has 15% of rounded clay lithoclasts, which are differentiated from the matrix by their dark brown colour and the scarcity of muscovite. The accessory minerals are crystaloclasts of Ti oxide.

The second sample from Pariti Island (TWPRT00-IAI488) (Fig. 2, b) has a grey-brown centre (reducing area) and brown, slightly reddish borders (oxidizing area). The paste is medium, moderately compact, with a porosity of 5%. The clay matrix has an abundance of 58%, mostly clays, and in lower proportion muscovite, chlorite, quartz and feldspars. The 37% of non-plastic inclusions are from coarse sand to medium silt (1000–15 μm) in size, angular to subrounded, with moderate selection and distribution. Some inclusions are plagioclase crystaloclasts (oligoclase > albite), quartz, biotite and K feldspar; others are lithoclasts of probable volcanic origin, while the accessory minerals are crystaloclasts of Ti oxide and Fe.

Samples TWTIR001a-IAI492 and TWTIR001b-IAI493 from Tiraska (Fig. 2, c, d) have 72% and 70% of their matrix of clay, respectively. The porosity is well distributed, 4% and 6%, respectively. The clay matrix of TWTIR001a-IAI492 is composed of clay minerals and, in lower proportions, of micas (muscovite > biotite > chlorite) and quartz. The matrix of TWTIR001b-IAI493 has clay minerals, with little micas, quartz or feldspars. Both samples have 24% of non-plastic inclusions, with sizes from fine sand to medium silt (250–15 μm), subrounded to rounded, with a good selection and distribution. The inclusions of TWTIR001a-IAI492 are composed of crystals of K feldspar, quartz, plagioclases and biotite. The most important accessory minerals are oxides of Ti and Fe and amphiboles. In sample TWTIR001b-IAI493 the important accessory minerals are crystals of plagioclase, quartz, K feldspar and, in lower proportion, a felsic lithoclast and others, probably of volcanic origin.

Sample TWAZ141-IAI495 from the Azapa Valley has a uniformly brown paste from the borders to the centre. The paste is fine and highly compacted, with a porosity of 3% and good distribution. The abundance of clay in the matrix is 64%, with clay minerals and micas in lower proportion. The 33% of non-plastic inclusions are from medium to very fine sand in size (500–63 μm), angular-elongated to subrounded, with a moderate selection and good distribution. They have quartz crystaloclasts, plagioclase, K feldspar and biotite, while the accessory minerals have crystaloclasts of Ti and Fe oxides, as well as pores filled with evaporitic minerals.

The chemical compositions determined by SEM-EDX (Table 2) were analysed by PCA, indicating a maximum of 14 elements important in the first three components. The first component explained 62% of the total variance. It included eight elements: those with the highest weights were Mg, C, Ti, Al and Si, while Ca, P and Fe (had low weights. ANOVA showed significant differences among the elements; Tukey tests showed that Al and Si appeared in significantly greater proportions in the clay matrix and the white and orange colours than in the black. The Kruskal–Wallis test on Ca, P and Fe found significant differences in their medians; the Tukey tests showed that Fe appears in higher proportion in the black colour than in the red (Fig. 3, a). The orange colour has the highest concentration of Fe, and white the lowest; this latter colour is rich in Ca.

The topographical analysis in the white areas of the polychrome fragments showed that they have heterogeneous Ca and S contents in some cases, while in others Si and Al are also increased (Fig. 3, b). The colour orange also appears associated with an increase of Fe and with clay and/or increases of Ca and S. The Raman spectra (Fig. 4) showed peaks at 220, 290, 408, 492, 608 and 1320 cm^{-1} for red, which correspond to hematite (α-Fe_2O_3). For the black colour in sample TWTIA003-IAI487, the spectrum shows the hematite peaks and an additional peak at

Table 2 *Results of the analysis of the chemical composition of the clay matrix and the coloured surface using scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX)*

Sample	*Colour*	*C*	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*K*	*Ca*	*Ti*	*Mn*	*Fe*	*O*
TWTIA001-IAI485	Black	7.2	0.5	0.6	3.6	18.1	0.5	0.3	0.3	2.3	1.7	0.2	2.2	12.3	50.1
	Red	5.3	1.1	0.9	6.3	21	0.7	0.4	0.5	4.2	1.7	0.5	0	7.3	50.1
	White	7.6	0.5	0.7	6.2	20.9	0.7	0.3	0.5	3.7	2.0	0.4	0	2.5	54.1
	Orange	5.9	0.5	0.7	6.3	22.4	0.5	0.4	0.5	3.4	1.8	0.3	0	5.1	51.8
	Matrix	8.7	0.9	1.1	7.9	19.5	0.1	0	0	2.2	0.7	0.4	0	3.2	55.4
TWTIA003-IAI487	Black	7.4	0.7	1.4	5.3	14.6	0.5	1.0	0.2	3.6	2.3	0.3	1.5	11.3	49.9
	Red	7.7	1.0	1.0	5.4	16.7	1.1	1.0	0.1	4.3	3.8	0.4	0	5.2	52.4
	White	6.8	0.8	1.1	8.3	18.1	0.8	1.0	0.1	4.4	3.3	0.4	0.1	2.4	52.7
	Matrix	7.4	1.1	1.0	7.0	21.1	0	0	0	2.6	1.2	0.4	0	4.7	53.6
TWPRT001-IAI488	Black	6.5	0.3	0.7	6.8	15.4	0.8	0.3	0	2.6	1.5	0.4	1.3	14.8	48.9
	Red	6.8	0.3	0.8	7.2	18.7	0.4	0.2	0	3.0	1.1	0.4	0	9.8	51.3
	White	6.2	0.3	0.7	9.4	21.3	0.3	0.2	0	4.0	0.9	0.4	0	3.6	52.8
	Orange	5.7	0.2	0.5	8.9	20	0.4	0.4	0	3.4	1.1	0.4	0	8	51.0
	Matrix	6.4	0.4	0.8	8.2	20.3	1.8	0	0	2.3	1.5	0.5	0	4.6	53.2
TWPRT00286-IAI490	Black	7.4	0.5	0.9	8.3	21.3	0	0	0	2.5	0.8	0.4	0	3.7	54.2
	Red	7.5	0.5	0.9	9.1	20.3	0.1	0	0	2.5	0.7	0.3	0	3.9	54.2
TWTIR001a-IAI492	Black	7.5	0.6	0.9	5.9	15.4	0.2	2.5	0.1	4.0	3.5	0.3	2.7	4.5	52.1
	Matrix	4.1	0.4	1.2	9.5	24.6	0	0	0	3.0	1.4	0.4	0	4.5	51.0
TWTIR001b-IAI493	Black	8.5	0.8	0.7	4.4	13.3	0.3	0.2	0	2.6	1.4	0.3	3.2	14.7	49.7
	Blanco	8.2	0.9	1.7	6.2	19.0	0.3	0.2	0	5.3	1.4	0.3	0	3.0	53.7
	Matrix	5.5	1.0	1.3	8.1	23.8	0	0	0	2.7	0.8	0.4	0	4.0	52.4
TWAZ141-IAI495	Black	6.4	1.1	0.9	5.4	16.5	0.1	2.8	0.4	1.9	4.6	0.2	0.8	7.8	50.7
	Red	7.0	1.1	1.1	6.1	15.2	0	1.3	0.4	1.7	3.4	0.3	0.7	10.7	49.8
	White	5.5	1.3	1.2	7.2	18.9	0	2.7	0.7	2.9	4.2	0.4	0	3.8	51.3
	Orange	3.9	1.2	0.9	5.4	16.8	0	5.8	0.6	2.1	7.4	0.2	0.4	6.1	49.3
	Matrix	7.6	0.9	1.0	7.6	20.0	0	0.3	0.3	2.7	1.4	0.3	0	4.3	53.8

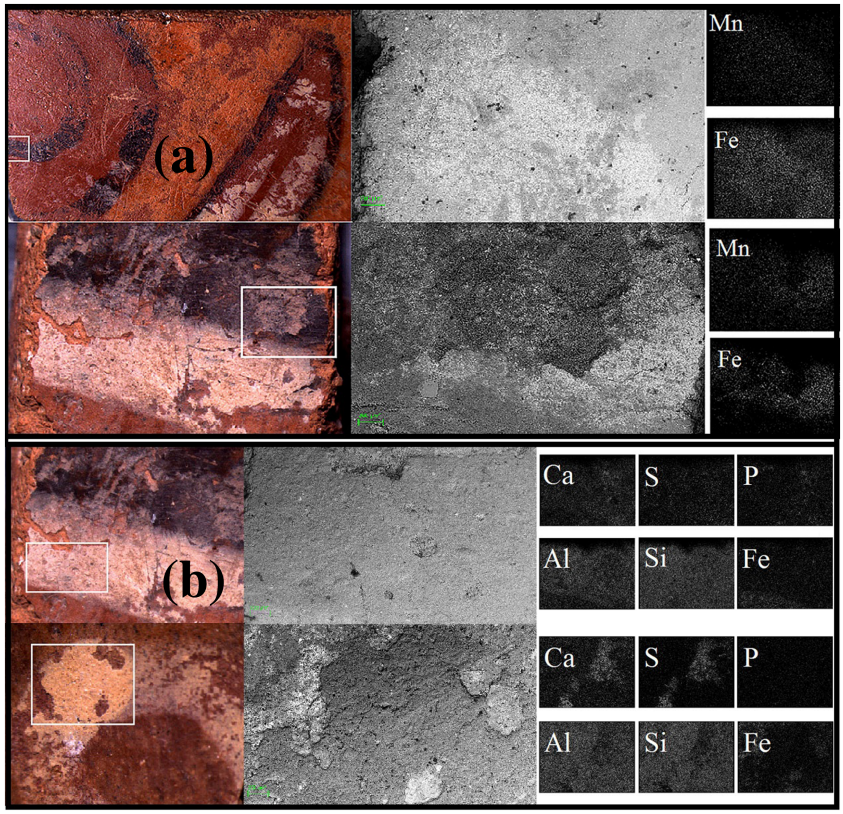


Figure 3 *(a) Optical and scanning electron microscopy (SEM) (×100) photographs of samples TWPRT001-IAI488 (upper row) and TWTIA003-IAI487 (lower row), indicating the area of black colour mapped along with the respective contents of Mn and Fe. (b) Optical microscope and SEM (×100) photographs of the white colour of samples TWTIA003-IAI487 (upper row), with an increase of Ca, S, Al and Si, and TWAZ141-IAI495 (lower row), which only showed an increase of Ca and S. [Colour figure can be viewed at wileyonlinelibrary.com]*

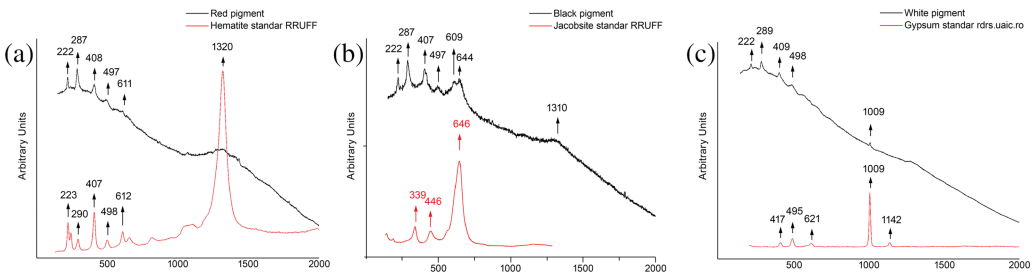


Figure 4 *Raman spectra of sample TWAZ141-IAI495 for (a) red, (b) black and (c) white pigments. [Colour figure can be viewed at wileyonlinelibrary.com]*

645 cm^{-1}, which corresponds to jacobsite ($Mn^{2+}(Fe^{3+})_2O_4$). The spectrum for the white in sample TWAZ141-IAI495 shows a peak at 1009 cm^{-1} characteristic of gypsum ($CaSO_4 \cdot 2H_2O$), as well as hematite peaks at 220, 290, 408, 492, 608 and 1320 cm^{-1}.

Discussion

The mineralogical analysis indicated that sample TWPRT00286-IAI490 had the finest paste, although it was also the most brittle of all the seven fragments analysed (probably due to extensive use). The other fragment from Pariti Island, TWPRT001-IAI488, had coarser raw materials (medium sand). The samples from Tiraska were very similar to one another, but had a few differences. The matrix of sample TWPRT00286-IAI490 was rich in clays, while the *quero* TWAZ141-IAI495 from the Azapa Valley has a fine paste, but is different from the previous samples in having proportionally more inclusions that were not very rounded (perhaps not sieved). In spite of these differences, all seven samples had common characteristics, such as the regular micropores that are homogeneously distributed on all the external and internal surfaces, oriented towards this axis. The EDX analysis of samples near these micropores found high C and N content. This may be evidence of the incorporation of organic material, such as finely powdered and homogeneously distributed ash, which was carbonized and evaporated as CO_2 during firing.

The dark colour of sample TWPRT00286-IAI490 is mainly due to firing in reducing conditions, which chemically reduced the Fe minerals to dark chromophores. This kind of pottery is called blackware. It has a hard paste with well-polished surfaces and modelled decoration depicting birds, camelids and human features, as well as other decoration such as incisions or post-firing colouring (Alconini 1995; Burkholder 2001; Korpisaari *et al*. 2012; Korpisaari and Pärssinen 2011). Blackware is also present in the Tiwanaku colony of Moquegua, in cemetery M10P the of Omo 10 site and in cemeteries M43A and M70B of the Río Muerto site (Goldstein 2005; Goldstein and Palacios 2015; Palacios and Goldstein 2015). However, Tiwanaku blackwares are scarce in the Azapa Valley and are exclusively associated with cemeteries such as AZ-143 (Acori 2017), which has yielded the most numerous and finest Tiwanaku ceramics of this valley (Goldstein 1996, 2005). Blackware allowed the manufacture and diffusion of a pottery type in which the black colour was part of the clay matrix itself —not only a layer of painted slip covering this matrix—and, therefore, more permanent and resistant to wear than any slip could ever be.

Sample TWPRT001-IAI488 has polychrome iconography, applied on a red slip, in which only hematite was identified. Thermogravimetric analysis (TGA) has shown that between 30 and 60°C there is complete transformation of limonite into goethite by evaporation of the chemically retained water. The goethite is dehydroxylated at 210–300°C, forming the respective oxides. The retention of residual OH groups at 900–1000°C has led to the idea of phase transitions in the sequence goethite-protohematites-hematite, where the protohematites are formed only by thermal decomposition of crystalline goethite at 900–1000°C (López *et al*. 2006; Rendon *et al*. 1983; Romero-Gómez *et al*. 2013). Finding only hematite by Raman spectroscopy (see the example of TWAZ141-IAI495 in Fig. 4, a) suggests that 900–1000°C was reached in the consolidation of this chromophore as slip.

Numerous studies in the south-central Andes corroborate the use of hematite in very diverse pictorial supports, areas and chronological periods (Brooks *et al*. 2008; Eerkens *et al*. 2009, 2014; Petersen 2010; Vaughn *et al*. 2005). Hematite is a common chromophore with a strong colour and good adherence and opacity, and it is easily powdered (Harben and Kužvart 1996). The extraction of hematite is also among the first evidences of mining processes in South America (Petersen 2010; Salazar *et al*. 2011; Vaughn *et al*. 2005, 2007, 2013).

Over the hematite slip, black bidimensional designs were painted using Mn chromophores. Jacobsite was identified in the black chromophore based on the Mn in sample TWAZ141-

IAI495. The TGA curves of Mn show that at 300°C the decomposition of the hydrated phases such as todorokite and danusite occurs. The decomposition of MnO_2 oxides (i.e., pyrolusite and cryptomelane) begins at 600°C and is complete at 850°C. At 900°C the oxides of Mn_2O_3 type are transformed into Mn_3O_4-type oxides, and minerals such as hausmannite appear. Jacobsite (the least common mineral) may be formed from hematite and pyrolusite (the most common mineral) at $>$ 1200°C (Faria *et al*. 2012; Ortega *et al*. 1995). Thus, the colour of the Mn oxide identified in sample TWAZ141-IAI495 could be fixed without problems during the ceramic firing process.

The use of gypsum ($CaSO_4{\cdot}2H_2O$) to obtain the white colour of sample TWAZ141-IAI495 from the Azapa Valley is suggested by the increases in Ca and S, and the decreases in Si and Al. The application of a white colour of a dihydrated gypsum base would have had to have taken place post-firing, since this could not withstand heats $>$ 300°C. Gypsum is a sedimentary mineral of Ca sulfate that is part of the evaporates, common due to its geological origin related to the drying of salt lakes or seas without spillways to the ocean; it is found in compact masses, soft rocks, earthy masses and, in some cases, dissolved into certain waters (Sánchez 2003). This mineral is generally present in two forms, one anhydrous and crystallized ($CaSO_4$), which is called anhydrous, and the other a hydrated form, with two molecules of water ($CaSO_4{\cdot}2H_2O$), which is called gypsum rock. The expulsion of water from the dihydrate happens in two phases at low temperatures. The first evaporation to produce the mono-hydrate is at 120–180°C ($CaSO_4{\cdot}H_2O$), while at 180–300°C it is completely dehydrated ($CaSO_4$) as soluble anhydrate. In the range of 400–800°C, the anhydrate becomes insoluble, and at 900–1000°C, hydraulic gypsum is generated (Sánchez 2003).

The white colour in the ceramic sample from the Azapa Valley was produced by post-firing thermal processes at low temperatures, which leads to differentiated thermal aspects in the production of this colour. By contrast, the white colour in sample TWTIA003-IAI487 shows an increase in the Si and Al content, as well as in Ca and S, which suggests the mixture of gypsum with white caolinite-type clays. This means that at least two different technological processes were used to achieve the white colour. Preliminary observations suggest that the mixture of clay and gypsum gives a white that is more resistant but with less shine. This was preferentially used when there were large areas to be covered with the white colour. For lines painted in white, only gypsum was used in order to produce a white colour more labile, but with greater shine. It follows that these technological decisions about the white colour were made with respect to the pictorial role it would fulfil.

Analogously, the orange colour was produced by combining hematite and white clays. This mixture is resistant and capable of consolidating the desired colour at high temperatures. The orange colour of sample TWAZ141-IAI495 shows low Si and Al content, as well as increases of Ca and S. This could be due to the use of gypsum to generate the orange colour. In summary, in the polychrome fragments we studied, the complex technological production of the white and orange colours necessarily implied different thermal processes and mixtures of substances.

The small differences in the mineralogy of the two Tiraska samples, and the fact that only one has the black colour rich in Fe, suggest that there were different sources of provisions and/or technical treatment in this regional ceramic style (Korpisaari 2006). Given the great outward similarity of the Tiraska fragments, we see detailed archaeometric analysis as a very promising way to advance in the characterization of this substyle of Tiwanaku pottery. Furthermore, we are certain that such fine-grained analysis of larger datasets pertaining to different substyles of Tiwanaku ceramics would help us to understand the technological choices and identities of individual potters, workshops and groups of people within the larger Tiwanaku phenomenon.

CONCLUSIONS

The main results of the exploratory analysis of a sample of seven Tiwanaku ceramic fragments are:

- Tiwanaku potters had a general tendency to work with (different) fine raw materials, which undoubtedly increased the difficulty of pottery production at the modeling stage.
- This technological expertise is most notable in the ceramic fragments found in the ritual context of Pariti Island and in the Tiwanaku capital Tiahuanaco.
- Some general patterns imply the use of a plant-based temper (perhaps ash) in Tiwanaku pottery production.
- There were slight differences in the raw materials used by different potters, workshops and/or groups, and these differences seem to distinguish the regional ceramic styles preliminarily sampled here.

In America and in the area of interest, the archaeometric approach is highly useful for evaluating the material and technological characteristics and knowhow of ancient populations (e.g., Giesso *et al*. 2011; Scott and Meyers 1994). Furthermore, to the extent that an archaeometric focus provides detailed information about ceramic traditions (e.g., Martínez and Santos Valero 2020; Weber *et al*. 2020), it will be possible to analyse the technological decisions of the potters, workshops and/or groups that manufactured particular styles of ceramics. Particularly useful are the archaeometric studies of regional ceramics from the Tiwanaku and Wari period and/or post-state moments (e.g., Knudson 2007; Montoya *et al*. 2009; Sharratt *et al*. 2009, 2015; Stovel *et al*. 2013). Thus, we feel that an archaeometric approach of the kind preliminarily tested and documented here would be highly suitable for a future large-scale, systematic study of Tiwanaku pottery, taking into account and further clarifying the regional diversity and chronological depth within the Tiwanaku cultural and political phenomenon.

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REFERENCES

Acori, A., 2017, *Caracterización cerámica del sitio AZ-143: Periodo Medio en el Valle de Azapa, Norte Grande de Chile*, Universidad de Tarapacá, Facultad de Ciencias Sociales y Jurídicas, Departamento de Antropología, Arica, Chile.

Alconini, S., 1995, *Rito, símbolo e historia en la pirámide de Akapana, Tiwanaku: Un análisis de cerámica ceremonial prehispánica*, Editorial Acción, La Paz, Bolivia.

Augustyniak, S., 2004, Dating the Tiwanaku state, *Chungará*, **36**(1), 19–35.

Baitzel, S., and Goldstein, P. S., 2015, Variabilidad mortuoria en Río Muerto: Asentamientos de colonias Tiwanaku en Moquegua, Perú, in *El Horizonte Medio: Nuevos aportes Para el Sur del Perú, norte de Chile y Bolivia* (eds. A. Korpisaari and J. Chacama), 163–76, Instituto Francés de Estudios Andinos, Lima and Universidad de Tarapacá, Arica.

Bennett, W. C., 1934, *Excavations at Tiahuanaco*, Anthropological papers 34(3), American Museum of Natural History, New York.

Bennett, W. C., 1936, Excavations in Bolivia, in , Anthropological papers 35(4), American Museum of Natural History, New York.

Berenguer, J. R., 1993, Gorros, identidad e interacción en el desierto antes y después del colapso de Tiwanaku, in *Identidad y prestigio en los Andes: Gorros, turbantes y diademas* (ed. J. Berenguer), 41–64, Museo Chileno de Arte Precolombino, Santiago, Chile.

Berenguer, J. R., 1998, La iconografía del poder en Tiwanaku y su rol en la integración de zonas de Frontera, *Boletín del Museo Chileno de Arte Precolombino*, **7**, 19–37.

Bermann, M., 1994, *Lukurmata: Household archaeology in Prehispanic Bolivia*, Princeton University Press, Princeton.

Brooks, W., Piminchumo, V., Suárez, H., Jackson, J. C., and McGeehin, J. P., 2008, Mineral pigments at Huaca Tacaynamo (Chan Chan, Peru), *Bulletin del'Institut Français d'Études Andines*, **37**(3), 441–50.

Buikstra, J. E., 1995, Tombs for the living … or … for the dead: The Osmore ancestors, in *Tombs for the living: Andean mortuary practices* (ed. T. D. Dillehay), 229–80, Dumbarton Oaks Library and Research Collections, Washington, D.C.

Burkholder, J. E., 2001, La cerámica de Tiwanaku: ¿Qué indica su variabilidad? *Boletín de Arqueología PUCP*, **5**, 217–49.

Cook, A. G., 1994, *Wari y Tiwanaku: Entre el estilo y la imagen*, Fondo Editorial de la Pontificia Universidad Católica del Perú, Lima.

Courtois, L., 1976, *Examen au microscope pétrographique des céramiques archéologiques*, Notes et Monographies Techniques 8, CNRS, Paris.

Eerkens, J. W., Vaughn, K., and Linares, M., 2009, Pre-Inca Mining in the Southern Nasca Region, Peru, *Antiquity*, **83**, 738–50.

Eerkens, J. W., Barfod, G., Vaughn, K., Williams, R., and Lesher, C., 2014, Iron isotope analysis of red and black pigments on Pottery in Nasca, Peru, *Archaeological and Anthropological Sciences*, **6**(3), 241–54.

Faria, G., Reis, E., Janotti, N., and Araújo, F., 2012, Caracterização química, física e mineralógica do produto granulado de manganês proveniente da Mina do Azul, *Revista Matéria*, **17**(1), 901–8.

Giesso, M., Durán, V., Neme, G., Glascock, M. D., Cortegoso, V., Gil, A., and Sanhueza, L., 2011, A study of obsidian source usage in the Central Andes of Argentina and Chile, *Archaeometry*, **53**(1), 1–21.

Goldstein, P. S., 1996, Tiwanaku settlement patterns of the Azapa Valley, Chile: New data, and the legacy of Percy Dauelsberg, *Diálogo Andino*, **14**(15), 57–73.

Goldstein, P. S., 2005, *Andean diaspora: The Tiwanaku colonies and the origins of south American empire*, University of Florida Press, Gainesville.

Goldstein, P. S., 2013, Tiwanaku and Wari state expansion: Demographic and outpost colonization compared, in *Visions of Tiwanaku* (eds. A. Vranich and C. Stanish), 41–63, Cotsen Institute of Archaeology Press, University of California, Los Angeles.

Goldstein, P. S., and Owen, B., 2001, Tiwanaku en Moquegua: Las colonias altiplánicas, *Boletín de Arqueología PUCP*, **5**, 139–68.

Goldstein, P. S., and Palacios, P., 2015, Excavaciones en el templete Tiwanaku de Omo, Moquegua, Perú, in *El Horizonte Medio: Nuevos aportes Para el Sur del Perú, norte de Chile y Bolivia* (eds. A. Korpisaari and J. Chacama), 117–44, Instituto Francés de Estudios Andinos, Lima and Universidad de Tarapacá, Arica.

Harben, P., and Kužvart, M., 1996, *Industrial minerals: A global geology*, Industrial Minerals Information Ltd, London.

Isbell, W. H., and Korpisaari, A., 2015, Bodies of evidence: Mortuary archaeology and the Wari-Tiwanaku paradox, in *Funerary practices and models in the ancient Andes: The return of the living dead* (eds. P. Eeckhout and L. S. Owens), 137–57, Cambridge University Press, Cambridge and New York.

Janusek, J. W., 2003, Vessels, time, and society: Toward a ceramic chronology in the Tiwanaku heartland, in *Tiwanaku and its hinterland: Archaeology and paleoecology of an Andean civilization. Vol 2. Urban and rural archaeology* (ed. A. L. Kolata), 30–91, Smithsonian Institution press, Washington, D.C. and London.

Knudson, K., 2007, La influencia de Tiwanaku en San Pedro de Atacama: Una investigación utilizando el análisis de isótopos del estroncio, *Estudios Atacameños*, **33**, 7–24.

Kolata, A. L., 2003a, Tiwanaku ceremonial architecture and Urban Organization, in *Tiwanaku and its hinterland: Archaeology and paleoecology of an Andean civilization. Vol 2. Urban and rural archaeology* (ed. A. L. Kolata), 175–201, Smithsonian Institution press, Washington, D.C. and London.

Kolata, A. L., 2003b, The Proyecto Wila Jawira research program, in *Tiwanaku and its hinterland: Archaeology and paleoecology of an Andean civilization. Vol 2. Urban and rural archaeology* (ed. A. L. Kolata), 3–17, Smithsonian Institution press, Washington, D.C. and London.

Korpisaari, A., 2006, Death in the Bolivian high plateau: Burials and Tiwanaku society, in *BAR international series 1536*, Archaeopress, Oxford.

Korpisaari, A., 2015, Carlos Ponce-Sanginés y la cronología absoluta de la cultura Tiwanaku, *Chachapuma: Revista de Arqueología Boliviana*, **8**, 44–7.

Korpisaari, A., and Pärssinen, M., 2011, *Pariti: The ceremonial Tiwanaku Pottery of an Island in Lake Titicaca*, Academia Scientiarum Fennica, Helsinki.

Korpisaari, A., Sagárnaga, J., Villanueva, J., and Patiño, T., 2012, Los depósitos de ofrendas tiwanakotas de la isla Pariti, Lago Titicaca, Bolivia, *Chungará*, **44**(2), 247–67.

Korpisaari, A., Oinonen, M., and Chacama, J., 2014, A reevaluation of the absolute chronology of Cabuza and related ceramic styles of the Azapa Valley, northern Chile, *Latin American Antiquity*, **25**(4), 409–26.

Llagostera, A., 2006, Contextualización e iconografía de las tabletas psicotrópicas Tiwanaku de San Pedro de Atacama, *Chungará*, **38**, 83–111.

López, F., Ramírez, M., López-Delgado, A., Alguacil, F., Alonso, M., and Pons, J., 2006, Estudio cinético de la descomposición térmica de escombros lateríticos, in *Actas del IX Congreso Iberoamericano de Metalurgia y Materiales*, 282–90, Havana, Cuba.

Martínez, G., and Santos Valero, F., 2020, Petrographic thin sections and exotic rocks provenience among hunter–gatherer societies in the eastern Pampa–Patagonia transition (lower basin of the Colorado River, Argentina), *Archaeometry*, **62**(3), 493–505.

Montoya, E., Glowacki, M., Zapata, J., and Mendoza, P., 2009, Caracterización de cerámicos Wari mediante análisis por activación neutrónica, *Rev Soc Quím Perú.*, **75**(4), 473–8.

Ogalde, J. P., 2015, Análisis químico y problematización técnica de los pigmentos en la tradición alfarera Cabuza del Valle de Azapa, norte de Chile, in *El Horizonte Medio: Nuevos aportes Para el Sur del Perú, norte de Chile y Bolivia* (eds. A. Korpisaari and J. Chacama), 227–46, Instituto Francés de Estudios Andinos, Lima and Universidad de Tarapacá, Arica.

Ortega, P., Del Barrio, S., and Valle, F., 1995, Caracterización mineralógica y química de un material pirolusítico Para su utilización en cerámica, *Bol. Soc. Esp. Cerám. Vidrio*, **34**(2), 71–5.

Owen, B. D., 2005, Distant colonies and explosive collapse: The two stages of the Tiwanaku diaspora in the Osmore drainage, *Latin American Antiquity*, **16**, 45–80.

Owen, B. D., and Goldstein, P., 2001, Tiwanaku en Moquegua: Interacciones regionales y colapso, *Boletín de Arqueología PUCP*, **5**, 169–88.

Palacios, P., and Goldstein, P., 2015, Variabilidad mortuoria en Río Muerto: Asentamientos de colonias Tiwanaku en Moquegua, Perú, in *El Horizonte Medio: Nuevos aportes Para el Sur del Perú, norte de Chile y Bolivia* (eds. A. Korpisaari and J. Chacama), 163–75, Instituto Francés de Estudios Andinos, Lima and Universidad de Tarapacá, Arica.

Petersen, G., 2010, *Mining and metallurgy in ancient Peru*, Special Paper 467, The Geological Society of America Press, Boulder.

Ponce Sanginés, C., 1981, *Tiwanaku: Espacio, tiempo y cultura: Ensayo de síntesis arqueológica*, Editorial Los Amigos del Libro, La Paz, Bolivia.

Rendon, J., Cornejo, J., De Arambarri, P., and Serna, C., 1983, Pore structure of thermally treated goethite (α-FeOOH), *Journal of Colloid and Interface Science*, **92**(2), 1–9.

Romero-Gómez, P., González, J., Bustamante, A., Ruiz-Conde, A., and Sánchez-Soto, P., 2013, Estudio *in-situ* de la transformación térmica de limonita utilizada Como pigmento procedente de Perú, *Bol. Soc. Esp. Cerám. Vidrio*, **52** (3), 127–31.

Rydén, S., 1947, *Archaeological researches in the highlands of Bolivia*, Erlanders Boktryckeri, Gothenburg.

Sagárnaga, J. A., 2007, Cerámica vidriada en Pariti, *Chachapuma: Revista de Arqueología Boliviana*, **1**, 65–9.

Salazar, D., Jackson, D., Guendon, J. L., Salinas, H., Morata, D., Figueroa, V., Manríquez, G., and Castro, V., 2011, Early evidence (ca. 12,000 BP) for iron oxide mining on the Pacific coast of South America, *Current Anthropology*, **52**, 463–75.

Sánchez, J., 2003, *Materiales fibrosos de base conglomerada*, Universidad de Colombia, Medellín.

Scott, D., and Meyers, P. (eds.), 1994, *Archaeometry of pre-Columbian sites and artifacts: Proceedings of a symposium organized by the UCLA Institute of Archaeology and the Getty conservation institute Los Angeles, California march 23–27, 1992*, The Getty Conservation Institute, USA.

Sharratt, N., 2010, Identity negotiation during Tiwanaku state collapse, in *Identity crisis: Archaeological perspectives on social identity* (eds. L. Amundsen-Meyer, N. Engel, and S. Pickering), 167–77, Chacmool Archaeological Association, Calgary.

Sharratt, N., 2015, Viviendo y muriendo en medio de la efervescencia política: Excavaciones en una aldea Tiwanaku terminal (950–1150 d. C.) del Valle de Moquegua, Perú, in *El Horizonte Medio: Nuevos aportes Para el Sur del Perú, norte de Chile y Bolivia* (eds. A. Korpisaari and J. Chacama), 201–23, Instituto Francés de Estudios Andinos, Lima and Universidad de Tarapacá, Arica.

Sharratt, N., 2016a, Crafting a response to collapse: Ceramic and textile production in the wake of Tiwanaku state breakdown, in *Beyond collapse* (ed. R. K. Faulseit), 407–30, CAI Occasional Papers. CAI Press, Carbondale, IL.

Sharratt, N., 2016b, Collapse and cohesion: Building Community in the Aftermath of Tiwanaku state breakdown, *World Archaeology*, **48**(1), 144–63.

Sharratt, N., Golitko, M., Williams, P. R., and Dussubieux, I., 2009, Ceramic production during the middle horizon: Wari and Tiwanaku clay procurement in the Moquegua Valley, Peru, *Geoarchaeology*, **24**(6), 792–820.

Sharratt, N., Golitko, M., and Williams, P. R., 2015, Pottery production, regional exchange and state collapse during the middle horizon (a.D. 500–1000): LA-ICP-MS analyses of Tiwanaku Pottery in the Moquegua Valley, Peru, *Journal of Field Archaeology*, **40**(4), 397–412.

Stovel, E., Whitehead, W., Deibel, M., and Uribe, M., 2013, Relaciones cerámicas y sociales entre San Pedro de Atacama y el Loa Superior durante el período Intermedio Tardío a través del análisis de fluorescencia de rayos X portátil, *Estudios Atacameños*, **46**, 47–60.

Sutter, R. C., and Sharratt, N., 2010, Continuity and transformation during the terminal middle horizon (AD 950–1150): A bioarchaeological assessment of Tumilaca origins within the middle Moquegua Valley, Peru, *Latin American Antiquity*, **21**(1), 67–86.

Torres, C., 1987, *The iconography of south American snuff trays and related paraphernalia*, Etnografiska Museet, Gothenburg.

Torres, C., 1994, Iconografía Tiwanaku y alucinógenos en San Pedro de Atacama: Sus implicaciones Para el estudio del Horizonte Medio andino, in *En Plantas, chamanismo y estados alterados de conciencia* (ed. J. Fericgla), 151–73, Los Libros de la Liebre de Marzo, Barcelona.

Torres, C., 2001, Iconografía Tiwanaku en la parafernalia inhalatoria de los Andes, *Boletín de Arqueología PUCP*, **5**, 427–54.

Torres, C., 2004, Imágenes legibles: La iconografía Tiwanaku Como significante, *Boletín del Museo Chileno de Arte Precolombino*, **9**, 55–73.

Uribe, M., and Agüero, C., 2001, Alfarería, textiles y la integración del Norte Grande de Chile a Tiwanaku, *Boletín de Arqueología PUCP*, **5**, 397–426.

Vaughn, K. J., Conlee, C., Neff, H., and Schreiber, K., 2005, A compositional analysis of Nasca polychrome pigments: Implications for craft production on the Prehispanic south coast of Peru, in *Laser ablation ICP-MS: A new frontier in archaeological characterization studies* (eds. R. J. Speakman and H. Neff), 138–54, University of New Mexico Press, Albuquerque.

Vaughn, K. J., Linares, M., Eerkens, J., and Edwards, M., 2007, Hematite Mining in the Ancient Americas: Mina primavera, a 2,000 year old Peruvian mine, *JOM: Journal of Minerals, Metals & Materials Society*, **59**(12), 16–20.

Vaughn, K. J., Van Gijseghem, H., Linares, M., and Eerkens, J., 2013, Minería de hematita en la costa Sur del Perú: Investigaciones arqueológicas en Mina primavera, *Chungará*, **45**(1), 131–42.

Villanueva, J., and Korpisaari, A., 2013, La cerámica Tiwanaku de la isla Pariti Como recipiente: Performances y narrativas, *Estudios Atacameños*, **46**, 83–108.

Weber, M., Valencia, V., Caballero, J., Villada, B., Cardona, A., and Lizuka, F., 2020, U-Pb dating of zircon: A sourcing method for pottery from La Morena archaeological site, north-west Colombia, *Archaeometry*, **62**(3), 439–68.

Williams, P. R., Janusek, J. W., and Lémuz, C., 2015, Monumentalidad e identidad en la producción monumental lítica de Tiwanaku, in *El Horizonte Medio: Nuevos aportes Para el Sur del Perú, norte de Chile y Bolivia* (eds. A. Korpisaari and J. Chacama), 31–56, Instituto Francés de Estudios Andinos, Lima and Universidad de Tarapacá, Arica.