Geochemical Evidence for the Use of Lead in Prehispanic Metallurgy at El Purgatorio, Casma Valley, Peru

REVISED DRAFT MANUSCRIPT

Authors: Melissa Vogel (Clemson University)

Jeremy Fowler (Clemson University)

Lee Drake (University of New Mexico, Bruker Elemental)

William E. Brooks (geologist)

Corresponding Author: Melissa Vogel, mvogel@clemson.edu
Dept. of Sociology & Anthropology
132 Brackett Hall
Clemson, SC 29634

Submitted to *Journal of Archaeological Science: Reports* August 31, 2015

Abstract

Portable X-ray fluorescence analyses of metal artifacts from El Purgatorio, the capital city of the Casma state, show a significant presence of lead in several artifacts. Compositional analysis indicates that late Prehistoric peoples were using either intentional selection of lead-bearing ores, intentional mixing of lead with other metals to form alloys during the manufacturing process, or perhaps using both techniques as part of their metallurgical technology. These findings confirm the use of copper-lead alloys by pre-Inca cultures, an advance that had previously lacked much support, and establish the Casma state as one of the cultures contributing to Andean metallurgical traditions.

Keywords: Peru, metallurgy, lead

1. Introduction

New data from the Peruvian site of El Purgatorio (Figures 1 and 2) is shedding light on Prehispanic metallurgical processes. Until recently, evidence for the use of lead in Prehispanic Andean metallurgy had been sparse. While some artifacts containing lead have been reported in the literature (e.g., Bergsøe 1938; Brooks et al 2012; Burger and Salazar 2004; Howe and Petersen 1992; Petersen 2010 [1970]), far less is known about the role of lead in the metallurgical process and to what extent Prehispanic artisans were practicing intentional selection of lead-rich ores, versus intentional mixing of lead with other metals (such as copper and silver) to create alloys. In this article we argue that the lead-containing artifacts and lead scraps found during excavations at the Casma capital city of El Purgatorio demonstrate intentional selection, at minimum, and most likely also indicate intentional mixing of lead with other minerals in some cases. The data presented here contribute to our knowledge and understanding of late Prehispanic metallurgical techniques and capabilities as well as our growing knowledge of the Casma state and their contributions to Andean prehistory.

2. Site Description

2.1 Environmental and cultural setting

The Casma state was a large coastal polity that occupied approximately 300 km of contiguous valleys on the north-central coast and that endured for at least 600 years (Figure 1). Until recently, the Casma had received relatively little archaeological attention, but knowledge of this culture is growing rapidly and complements the

contributions of previous scholars (e.g., Càrdenas 1976, 1978; Collier 1962; Przadka and Giersz 2003; Silva Vigo 1992; Tello 1956; Thompson 1964, 1974; Vogel 2003, 2011, 2012; Vogel and Pacifico 2011). Using settlement data, several authors have already noted the population explosion in the Casma, Nepeña and Santa Valleys during the late Middle Horizon ca. AD800 (e.g., Mackey and Klymyshyn 1990; Proulx 1973, 1993; Wilson 1988, 1995), attributed to the growth of the Casma state. The Casma were primarily a coastal society, occupying the coastal desert and low-altitude valley habitats. The Casma state appears to have come to power after the collapse of the southern Moche polities, and was contemporaneous with the Lambayeque polities and the Chimú state.

El Purgatorio was an important urban center and served as the Casma capital city, located in the lower Casma Valley, at an altitude of approximately 180masl. Covering 5.32 km², El Purgatorio is the largest site in the valley with a long occupation, from approximately AD700 until they were conquered by the Chimú around 1400AD. The city consists of four contiguous sectors, stretching across the base and up the western and southern slopes of Cerro Mucho Malo (Figure 2). The majority of the monumental architecture, which consists of several large compounds with complex internal layouts and external annexes or associated structures, is located in Sector A. These compounds include the primary temple complex and most elite residences. In Sector B, numerous habitational terraces extend a considerable distance up the slopes of Cerro Mucho Malo, which is crowded with densely packed structures—mostly commoner residences. Pacifico's (2014) dissertation work in Sector B has shown it as the location of a specialized work force that focused primarily on *chicha* (maize beer)

and food production. South of Sector B is Sector C, which consists of three cemeteries, additional compounds, agglutinated room clusters and smaller associated structures. This sector includes administrative structures, production areas, and residences of intermediate elites. Finally, Sector D is located on the hilltop above the southern end of Sector C, filled with smaller stone structures resembling the commoner residences in Sector B and littered with Casma style ceramics. Based on the site's architectural and artifactual variations, El Purgatorio housed a large and socially stratified population consisting of at least three social divisions (e.g., elites, intermediates, commoners).

2.2 Archaeological and Culture Historical Background

Metallurgy played an important role in attaining social prestige and, ultimately, political power in many prehistoric civilizations, including those in the Prehispanic Andes. In fact, the greatest wealth of superbly crafted metal objects found in the New World come from the Moche site of Sipán on the far north coast of Peru (Alva and Donnan 1993). Archaeological sites in northern and central Peru provide some evidence of the metallurgical process (e.g., Lechtman 1991; Lechtman and Klein 1999; Lechtman et al. 1982; Merkel et al. 1992; Shimada and Craig 2013; Shimada et al 1982; Swenson and Warner 2012). Ancient mining relied mainly on following outcrops of ore-bearing veins, first at the surface, and then into the subsurface. (Patterson 1971, p. 291; Shimada et. al. 1982, p.952,). The raw ores were then brought to furnaces/hearths in workshops or homes and the metalworking often took place in the common area as evidenced by metallurgical waste found in the living floors (e.g., Howe and Petersen 1992; Moore 2006; Swenson and Warner 2012).

Several authors have documented the use of lead in Prehispanic Andean metallurgical smelting (e.g., Howe and Petersen 1992; Schultze 2013 p. 233). However, these authors refer to lead as simply a by-product of the smelting process. At El Purgatorio, the lead-bearing artifacts found indicate that weight of ores was important when smelting and making such tools as spindle whorls. Thus lead was being used deliberately and not just as a tool to refine silver and then discarded as slag. Schultze (2013) interprets lead in the metallurgical process as a waste material, not something that was deliberately used. But Prehispanic lead spoons are known from Colombia, Ecuador, and Perú, and in Mexico, lead may have been used as an intentional alloy with copper (Petersen 2010 [1970], p. 31). A number of Prehispanic lead objects such as club heads, weights, and tiny sculptures are included in collections at the Ethnologisches Museum (Berlin, Germany), the Museo Arqueológico Bruning (Lambayeque, Perú), the Museo Rafael Larco Herrera (Lima, Perú), and the Museo Amano (Miraflores, Perú) (Petersen 2010 [1970]). Biconic lead artifacts earlier described as weights in the Museo Rafael Larco Herrera online collection have now been identified as ancient sling projectiles (Brooks et al. 2012).

Andean mineral occurrences are typically polymetallic and may produce gold, silver, copper, mercury, lead, and other metals. Native lead is more commonly found with galena or other minerals in a variety of mineral occurrences. Petersen (2010 [1970] p. 30) reported millimeter-sized beads of native lead in the gold-platinum sands of Chocó, Colombia. In Perú, lead is found with lead-zinc-silver occurrences and numerous deposits may be found throughout the cordillera from Cajamarca and Lambayeque Departments in the north to Puno, Moquegua, and Tacna Departments in

the south (Ministry of Energy and Mines 1999 p. 15). In 2011, Perú was a world leader in the production of lead (230,200 metric tons), copper (1.1 million metric tons), and other metals (Gurmendi 2011). For example, Quirulvilca, a polymetallic mine in La Libertad Department, produced 2,400 metric tons of Cu; 3,500 metric tons of Pb; 10,000 metric tons of Zn; 55,200 kg of Ag; and 78 kg of Au in 1984 (Mindat 2014). Some of the ore minerals at Quirulvilca include: silver-bearing galena (PbS), bournonite (PbCuSbS_3), hutchinsonite (PbAs_5S_9), and sphalerite (ZnS) (Mindat 2014). Of these minerals, bournonite is especially relevant to this study because: 1) it is known in the region; 2) it is an ore of lead and copper, meaning it is not necessary to smelt a Cu ore and then a Pb ore and add them together; 3) it is widespread; 4) it has a steel-gray to black metallic appearance; and 5) it is heavy owing to its lead content and has a specific gravity of 5.8. Galena also plays an important role as a potential source of lead (Schultze 2013). Due to the nature of some artifacts found at El Purgatorio that contain both silver and lead, this ore could have been a major component in the metallurgical processes.

Alloying different concentrations of different elements can result in large leaps in strength, malleability, and firing temperature need. The classic example is bronze, in which 7-12% tin concentration results in a much stronger metal than pure copper. Another ancient copper alloy was Molybdochalkos, a mixture of copper and lead. One of the earliest forms of copper alloy used in pre-contact Peru was copper-arsenate, in which 0.5% or more of arsenic is used to strengthen copper (Shimada and Craig 1991). In one example, a Moche copper-arsenic alloy likely formed using the lost-wax technique had up to 20.7% As (Shugar et al. 2014).

Prehispanic metallurgical research in the Andes region has focused mainly on the use of gold, copper, and silver. Copper and copper-silver artifacts are found as far south as north-central Chile with the Diaguita culture (Blanco and Mendoza 2012). However, evidence suggests that in some cases metallurgical technology in the Prehispanic Andes region was far more complex than the use of raw metal ores. Analysis of gold, silver, and copper Moche nose rings found in the tomb of the Lady of Cao indicate the use of intentional precious metal alloys (Cesáreo et al. 2014). In addition, PXRF analysis of some gold and silver objects from the elite Moche tombs at Sipán demonstrated the use of gold, silver, and copper alloys as well as gilded copper and *tumbaga* (a poor gold alloy enriched by depletion gilding) (Cesareo et al. 2010). The Moche also used gold sheet plating, though not pure gold but rather a gold-copper mixture (Hörz and Kallfass 2000). And Lechtman et al (1982) argued for depletion gilding and electrochemical replacement plating among the Moche based on artifacts from the Loma Negra site near Cerro Vicús.

In addition to this, studies of lake-bed sediments in the Andes region suggest the use of other metals besides copper, gold, and silver. A sediment core taken from Laguna Lobato, near the base of former silver mines in Potosí, Bolivia, shows large deposits of silver, tin, lead, antimony and bismuth between A.D. 1500-1600 and A.D. 1000 - 1200 (Abbott and Wolfe 2003). While the later spike corresponds to Spanish use of the mines, the earlier period of metallurgy corresponds to the collapse of the Tiwanaku Empire. A sediment core from Laguna Pirhuacocha in central Peru shows increases in the same elements plus zinc from A.D. 1100-1300 (Cooke et al. 2007).

There is no evidence to suggest that elements such as zinc and antimony were used or recognized - they are likely bi-products of mining ores such as copper.

It is clear that metallurgical technology was considerably advanced among Andean cultures prior to contact with the Spanish; there is evidence of electrochemical plating and alloying of precious metals. Herein, we present evidence for lead-copper alloys present within the Casma state (ca. AD700-1400).

Description of Sample

From 2007 through 2010, a number of metal artifacts were excavated at the site of El Purgatorio, Peru. Seventeen of these artifacts were later found to contain traces of lead, a metal that was previously thought to have been virtually absent in the metallurgical processes of prehistoric Peru (but see Petersen 2010 [1970]). Of these 17 artifacts containing lead, 11 were spindle whorls and two other artifacts were most likely spindle whorls, but are too degraded to be certain. The other lead-bearing artifacts include a copper pendant, two pieces of scrap metal, and a tiny metal ball made mostly of silver. All but one of these artifacts was recovered from burials in Cemetery 1 of Sector C (Figure 3). The other, a piece of lead scrap, was found in Room 13 of Compound 6 in Sector A.

Several different materials were used to make the spindle whorls discovered at El Purgatorio, Peru: stone, ceramic, and metal. Some metal spindle whorls were originally considered beads until the discovery of one such bead with string and spindle still attached, which allowed for the reclassification of the beads as spindle whorls. These whorls are made mostly of copper; however, they also contain various amounts

of lead which affects their weight. A heavier whorl would be used to produce finer yarn. By using portable x-ray fluorescence, each of the 26 metal spindle whorls was analyzed. Eleven of these whorls showed the presence of lead. The photon count of every element in these whorls was then analyzed (Table 1).

In Sector C there are two important burials containing artifacts with a lead presence. Cemetery 1, Unit 2, Feature 2 contained a burial which included seven spindle whorls and a pendant. In most of these whorls and the pendant (CCM1U2F2-M1BEAD1-4 and 7, and CCM1U2F2-M1PENDANT), the main compositional metal is copper. However, in one whorl (CCM1U2F2-M1BEAD5) the main compositional metal is lead. This is interesting to note because the spindle whorl is in good condition with only some degradation from the conditions of the burial. Another whorl (CCM1U2F2-M1BEAD6) contains unequal amounts of lead and copper throughout the object. The photon count and spectra of each side of the artifact show the heterogeneity of the whorl composition.

In Cemetery 1, Unit 2, Feature 6, a tiny metal ball was discovered (Table 1). This ball is composed mostly of silver. However in addition to the large photon count of silver, there is also a significant amount of lead in the artifact. Lead seems to represent about 91% of the artifact's elemental composition by mass (Table 1).

In Unit 8 of the same cemetery, the burial described as Feature 1 contained another set of spindle whorls. There were four complete whorls and these were labeled as CCM1U8F1-M1BEAD2-4 and CCM1U8F1-M1PIRURO. Upon PXRF analysis, copper was found to be the main compositional metal of these whorls. However, there

was also a lead presence in each of these artifacts (Table 1). Two more artifacts were recovered from this burial that contained lead. They were found in the same area as the spindle whorls, however they were broken and greatly degraded. These artifacts are believed to be spindle whorls, but due to the degraded nature of CCM1U8F1-M1BEAD5-6 this identification is not completely certain.

3. Materials and Methods

3.1 Fieldwork and Laboratory Analyses

Fieldwork at the site of El Purgatorio was conducted over the course of seven seasons from 2004-2011. A total of 82 units were excavated across Sectors A, B and C, from which metal artifacts were extracted via dry sifting. Additional data for the analysis presented here came from the artifact assemblage, especially the ceramic data, and the analysis of architecture and spatial patterns by Melissa Vogel and David Pacifico. For the purposes of spatial analysis, excavation units were classified as to their function and status. All units in Sectors A (36 units) and B (22 units) were within the architecture, but only five units in Sector C were within the architecture, while the remaining 19 units were located in the cemeteries. These contexts are important to consider for interpreting the reasons behind the deposition of cultural material in each area. For example, most remains in the cemetery were found directly in association with a burial feature and therefore are considered personal belongings of the deceased individual.

Radiocarbon assays indicate that although Sectors A and C were occupied as early as the 8th and 9th centuries respectively (Vogel 2011, Table 3), Sector B was a

single-occupation settlement that lasted from about AD 1277-1405 (Pacífico 2014).

Excavations in 2010 revealed that this part of El Purgatorio was a commoner residential district with ritual, administrative, and productive functions.

A portable energy-dispersive X-Ray Florescence (pXRF) unit was used at the site of El Purgatorio in 2010 and 2011 to analyze the elemental composition of the artifacts found. Data were obtained using a Tracer IIIIV+ with a pin-diode detector and a Rhodium-anode tube. Data were collected using a 1 mil Titanium, 12 mil Aluminum filter at 40 keV with a current of 3.5 μ A under dry air conditions for 120 seconds in 2010. Each artifact was assayed on opposite sides. Data from 2011 fieldwork was taken for 180 seconds. This increase in the timed assay was based on the manufacturer's recommendation. The XRF instrument was connected to a laptop and each reading was recorded and analyzed using Bruker S1XRF software (2.2.35) to obtain spectra. Each artifact had readings taken on both the top and bottom sides in order to gather more precise measurements for the overall composition of the artifact. The artifacts are not of homogeneous mixture and thus the readings vary between the sides.

Data were processed using a Bayesian deconvolution routine used in Spectra software 7.4.0.0 created by Bruker Nano. This was used to generate net photon counts after a background subtraction and basic inter-elemental corrections (Table 1). These data were then used to generate semi-quantitative weight % data based on depth (using the mass attenuation coefficients), atomic weight, and fluorescence efficiency (Table 1, Table 2). This method of quantification assumes a) all elements present are visible in the spectrum (e.g. no oxidization), b) filter effects are minimal between elements, and c) isotopes are similar to crustal abundance, as significant deviances of isotopic ratios will

affect the mass contribution of the element to a given gram of material. This same quantification protocol was applied to a standard alloy (C31400-72B) 5 times, which mean, standard deviation, and the coefficient of variation (CoV) reported (Table 2). In addition to this, complex inter-elemental effects, including the secondary excitation of copper K-lines by lead L-lines were not incorporated. Perhaps most importantly, data were assumed to be homogenous, when even qualitative data (Figure 4) show that data is highly heterogeneous. For these reasons, particularly the last, it is impossible to characterize these metals as a traditional alloy by current definitions. However, heterogeneity is common in prehistoric Andean alloys. It is however possible to understand the variance of their composition both within and between objects.

3.2 Results

High variability in lead net counts per second suggests that lead differentiation occurred within the artifacts present (Table 1). While these data are only semi-quantitative, they illustrate the high level of heterogeneity in the artifacts. This effect is common in copper alloys as lead (atomic mass 207.20 g/mol) is significantly denser than copper (atomic mass 63.55 g/mol). As a copper-lead alloy cools, lead will sink down due to gravitational acceleration. This effect varies due a number of factors, including the amount of lead initially present and the length of cooling time after the alloy is cast.

XRF analysis on its own cannot determine whether the artifacts were products of melt casting or hammer casting. It can, however, show that these alloys were very

rough and nascent in design. The presence of a lead scrap (2009A6R13U1L1) and lead spindle whorls (2007CCM1U2F6, 2009CCM1U8F1) shows that lead was either obtained in its pure form or secondarily extracted from ore (Figure 5). The variability of lead in copper within the same object may suggest that lead was added intentionally - most likely to improve malleability and lower melting temperature. The very high variability in some artifacts (namely 2009CCM1U8F1) suggests that the hammering of two metal sources was a major component of the process, as the sharp increase in lead (from 42.96% to 83.54%) is not easily explained by liquid alloying. Another possibility is that the multi-mineral component input resulted in variable smelting.

Discussion

El Purgatorio and its immediate hinterlands have yielded evidence for at least three stages of metallurgy: Prehispanic mining and initial ore processing, as well as by-products and finished products of metallurgical activity. Unfortunately as of this writing we have not yet located a metallurgical workshop so as to have examples of the complete *chaîne opératoire*—several steps in the process are still undocumented. However, a brief survey in 2009 of the area within an approximately 20km radius of El Purgatorio revealed at least four mines (Montegrando, Tajo Abierto, Señor de la Soledad and Adán) that had not only been recently exploited, but also showed clear evidence of Casma usage (Brooks 2010, Sanchez et al 1995). This usage was evidenced by the presence of Casma style ceramics at all mines visited, as well as grinding stones (*batanes* and *chungas*) and surface evidence for hearths. At Montegrando the hillside had been terraced and there were looted human skeletal

remains visible on the surface. These mines yielded copper and perhaps gold; however, due to the extensive mining of every available copper source in recent years our ore samples were meager. Thus sourcing the copper in the artifacts from El Purgatorio to one of the mines surveyed was not feasible. However, given the Casma presence at nearby mines and the presence of metallurgical waste at El Purgatorio it seems likely that at least some of the copper artifacts were produced locally.

The data described above demonstrate that Casma metallurgical workers likely utilized both intentional selection of lead-bearing ores and intentional mixing of lead to produce copper-lead alloys, advanced metallurgical techniques for Andean cultures during this time period. The evidence from El Purgatorio comes primarily in the form of metal spindle whorls and beads (Figure 6). A detailed functional and iconographic analysis of the spindle whorls will be published elsewhere (Vogel et al, n.d.), but analyses have shown that these artifacts were used for both utilitarian purposes (to spin yarn) and perhaps to demonstrate status or as a form of wealth, since they were found strung together in burial contexts. Thus they may have been worn around the interred individuals' neck in life as in death, for personal adornment and display. The whorls may also be an expression of gender identity, since they were found almost exclusively in female burials. Ethnographic and ethnohistoric documentation (e.g., Costin 1993, 1995, 1998; Silverblatt 1987) show that textile production tended to be a female task in the Prehispanic Andes, although men did participate in some cases as well. Children also learned to spin, although the presence of whorls in the burials of infants who were clearly too young to spin indicates that one could possess spindle whorls before one could actually use them, again suggesting that whorls may have been an indicator of

status, wealth, or perhaps even femininity (if these children were indeed female—they are too young to be sexed). These artifacts also reflect varying degrees of standardization, and may have been manufactured by specialists (Vogel et al., n.d), given the technological skills necessary to produce both the metal whorls and the fancy stone whorls. As our investigation of Casma sites in the rest of the Casma Valley (and beyond) continues, these whorls may prove to be indicators of intrapolity exchange patterns, especially if workshops can be located.

Conclusion

The data presented here demonstrate several important facts about Prehispanic metallurgy. First, the lead objects recovered at El Purgatorio support Howe and Petersen's (1994) assertion that Prehispanic cultures were extracting lead for use in metallurgy. In other words, Casma artisans were practicing both intentional selection of lead-bearing ores and intentional mixing of lead with other minerals to create alloys. In fact, this may be the first published example of lead alloy use in a Pre-Inca Andean culture. Second, the Casma state appears to have participated in the Andean metallurgical tradition, at least in the vicinity of their capital city, El Purgatorio. Nearby mines show clear evidence of use during the Casma occupation of the valley. Third, the presence of various metal artifacts in intermediate class graves suggests that small metal objects such as spindle whorls and pendants were commodities to be distributed amongst Casma citizens, rather than closely guarded by the uppermost elites. They may have been symbols of individual wealth and considered very personal items, since they were buried with their owners rather than passed down to living relatives. Finally,

as research on the Casma state continues at hinterland sites in the Casma Valley, it may be possible to trace the circulation of some metal objects with the larger state political economy.

Acknowledgments

Funding for Project El Purgatorio was provided by the Brennan Foundation, the National Science Foundation (grants #BCS-0814338 and #1049318), Fulbright-Hays, Clemson University and the University of Chicago. We thank Pat Jenkins for his generous matching donation that allowed for the purchase of the PXRF instrument used in this analysis. We also wish to thank the anonymous reviewers for their invaluable suggestions for revision of this article.

References Cited

- Abbott, M.B. and Wolfe, A.P. 2003, 'Intensive Pre-Incan Metallurgy Recorded by Lake Sediments from the Bolivian Andes', *Science*, 301(5641), pp.1893-1895.
- Alva, W. and Donnan, C. 1993. *Royal Tombs of Sipán*. Los Angeles: Fowler Cultural History Museum, p. 229
- Bergsøe, Paul, 1938. *The Metallurgy and Technology of Gold and Platinum among the Pre-Columbian Indians*, Copenhagen: Danmarks naturvidenskabelige samfund, i kommission hos G.E.C.
- Blanco, E.L., Mendoza, P.L. 2012. Los metales en la cultura Diaguita chilena (ca. 900-1536 DC): una aproximación metadológica e interpretiva. *Intercersiones en Antropología* 12: 319-322.
- Brooks, W. E. 2010. Geologic Reconnaissance of El Purgatorio, Casma, Peru, 12-17 July 2009. Technical report submitted to Project Director Melissa Vogel.
- Brooks, W. E. and Parodi, L. 2012, 'Antigua fundición de plomo en el sitio inca de Curamba, departamento de Apurímac, Perú,' *Bulletin de l'Institut Français d'Études Andines*, 41 (2): 197-208.
- Brooks, W. E., Parodi, L., Farfán, A., and Dykstra, D. 2012, 'Lead in Ancient Peru: the Curamba Smelter and Lead Sling Bullets', *Journal of Metals*, 64(11), pp.1356-1364.
- Brooks, W, Parodi L., Farfan A., and Lopez D. 2013, 'Proyectiles de plomo en el antiguo Peru,' *Bulletin de l'Institut Français d'Études Andines*, 42 (1).
- Bustamante, A., Cesareo, R., Brunetti, A., Rizzutto, M., Calza, C., Pereira de Freitas, R., Holmsquit, U. and Diestra, D. 2013, 'Analysis of Pre-Columbian objects from Cupisnique, one of the oldest culture from Perú, using a portable X-ray fluorescence equipment,' *Appl. Phys. A*, 113(4), pp.1065-1067.
- Burger, R. and Salazar. 2004. *Machu Picchu*, New Haven: Yale University Press.
- Cárdenas, M. 1976. *Informe Preliminar del Trabajo de Campo en el Valle de Chao*. National Institute of Culture, Lima.
- Cárdenas, M. 1978. *Columna Cronológica del Valle de Chao*. Pontificia Universidad Católica del Perú, Lima.
- Cesareo, R. 2014, 'Thickness and composition of gold and silver alloys determined by combining EDXRF-analysis and transmission measurements', *X-Ray Spectrom.*, 43(6), pp.312-315.

- Cesareo, R., A.D. Bustamante, J. S. Fabian, S. Del Pilar Zambrano, W. Alva, L.Z. Chero, M.C. Del Carmen Espinoza, R.R. Rodriguez, M.F. Seclen, F.V. Gutierrez, E.B. Levano, J.A. Gonzales, M.A. Rizzutto, E. Poli, C. Calza, M. Dos Anjos, R. Pereira De Freitas, R.T. Lopes, C. Elera, I. Shimada, V. Curay, M.G. Castillo, G.E. Gigante, G.M. Ingo, F. Lopes, U. Holmquist and D. Diestra. 2013. Multilayered Artifacts in the pre-Columbian metallurgy from the North of Peru. *Applied Physics A* 113: 889-903
- Cesareo, R., Calza, C., Dos Anjos, M., Lopes, R., Bustamante, A., Fabian S., J., Alva, W. and Chero Z., L. 2010. 'Pre-Columbian alloys from the royal tombs of Sipán; energy dispersive X-ray fluorescence analysis with a portable equipment,' *Applied Radiation and Isotopes*, 68(4-5), pp.525-528.
- Cesareo, R., Gigante, G., Fabían, J., Zambrano, S., Franco, R., Fernández, A., Bustamante, A. 2014. Composition and thickness of gold and silver nose decorations from the tomb of the Lady of Cao determined by combined EDXRF-analysis and X-ray transmission measurements. *Revista de Investigación de Física* 17: 1-6.
- Collier, D. 1962. 'Archaeological Investigations in the Casma Valley, Peru.' *Akten des 34. Internationalen Amerikanistenkongress*, Wien 1960: 411-417. Vienna: Verlag Ferdinand Berger, Horn.
- Cooke, C.A., Abbott, M.B., Wolfe, A.P., Kittleson, J.L. 2007. 'A millenium of metallurgy recorded recorded by lake sediments from Morococha, Peruvian Andes.' *Environ. Sci. Technol.* 41: 3469-3474
- Cooke, C., Wolfe, A. and Hobbs, W. 2009, 'Lake-sediment geochemistry reveals 1400 years of evolving extractive metallurgy at Cerro de Pasco, Peruvian Andes, *Geology*, 37(11), pp.1019-1022.
- Costin, Cathy L.
 1993 Textiles, Women and Political Economy in Late Prehispanic Peru. *Research in Economic Anthropology* 14:3-28.
 1995 Cloth Production and Gender Relations in the Inka Empire. *In Research Frontiers in Anthropology- Advances in Archaeology and Physical Anthropology*, Peter Peregrine, C. Ember and E. Ember, eds. Pagination Varies. Englewood Cliffs: Prentice Hall.
 1998 Housewives, Chosen Women, Skilled Men: Cloth Production and Social Identity in the Late Prehispanic Andes. *In Craft and Social Identity*, Cathy Lynne Costin and Rita P. Wright, eds. Pp. 123–144. Archeological Papers of the American Archaeological Association Vol. 8. Arlington, VA: American Anthropological Association.

- Forster, N., Grave, P., Vickery, N. and Kealhofer, L. 2011, 'Non-destructive analysis using PXRF: methodology and application to archaeological ceramics', *X-Ray Spectrom.*, 40(5), pp.389-398.
- Gurmendi, A.C., 2011, 'Minerals Yearbook: Peru: U.S. Geological Survey Minerals Yearbook', pp. 17.1-17.14, <<http://minerals.usgs.gov>>. [June 13, 2014].
- Hörz, G. and Kallfass, M. 2000. The treasure of gold and silver artifacts from the Royal Tombs of Sipán, Peru — a study on the Moche metalworking techniques. *Materials Characterization* 45(4-5): 391-420.
- Howe, E. and Petersen, U. 1994, 'Silver and lead in the Late Prehistory of the Mantaro Valley, Peru,' In: *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* (D. Scott & P. Meyers, eds.): 183-198; Los Angeles: The Getty Conservation Institute.
- Lechtman, H. 1991, 'The Production of Copper-Arsenic Alloys in the Central Andes: Highland Ores and Coastal Smelters?', *Journal of Field Archaeology*, 18(1), p.43.
- Lechtman, H., Erlij, A. and Barry, E. 1982. New perspectives on Moche metallurgy: techniques of gilding copper at Loma Negra, Northern Peru. *American Antiquity* 47(1): 3-30.
- Lechtman, H. and Klein, S. 1999, 'The Production of Copper–Arsenic Alloys (Arsenic Bronze) by Cosmelting: Modern Experiment, Ancient Practice,' *Journal of Archaeological Science*, 26(5), pp.497-526.
- Mackey, C. J., and A. U. Klymyshyn 1990. "The Southern Frontier of the Chimú Empire." In *The Northern Dynasties: Kingship and Statecraft in Chimor*, eds. M. E. Moseley and A. Cordy-Collins, Washington, D.C.: Dumbarton Oaks , pp. 195-226.
- Merkel, J. F., Shimada, I., Swann, C. P., and Doonan, R. 1992. 'Pre-Hispanic Copper Alloy Production at Batán Grande, Peru: Interpretation of the Analytical Data for Ore Samples, In *Archaeometry of Pre-Columbian Sites and Artifacts*, edited by David A Scott and Pieter Meyers, Getty Conservation Institute: Los Angeles
- Mindat, 2014, Quirulvilca Mine, La Libertad Department, Perú: <http://www.mindat.org/loc-2558.html>. [June 13, 2014].
- Ministry of Energy and Mines, 1999, Mining and energy in Perú: Ministry of Energy and Mines, Lima, Perú, pp. 1-111.

- Moore, J. 2006. Copper metallurgy in a prehistoric household, Casma Valley, Peru. *Nawpa Pacha: Journal of Andean Archaeology*, (28), pp.141-149.
- Pacifico, D. 2014. *Neighborhood Politics: Diversity, Community, and Authority at El Purgatorio, Peru*. Unpublished Doctoral Dissertation. Department of Anthropology, University of Chicago.
- Patterson, Clair C. 1971, 'Native Copper, Silver, and Gold Accessible to Early Metallurgists,' *American Antiquity* 36(3): 286-321.
- Petersen, G., 1970/2010, Mining and metallurgy in ancient Perú [translated by William E Brooks]: Geological Society of America Special Paper 467, 90 p.
- Proulx, D.A. 1973. *Archaeological Investigations in the Nepeña Valley, Peru*. Department of Anthropology, University of Massachusetts.
- Proulx, D.A. 1993. "The Nepeña Valley Survey: A Retrospective View." *Ela'qua: Essays in honor of Richard B. Woodbury*, pp. 225-236.
- Przadka, P., and M. Giersz 2003. *Sitios arqueológicos de la zona del valle de Culebras, Vol. I: Valle bajo*. Polish Society for Latin American Studies. Andean Archaeological Mission of the Institute of Archaeology, University of Warsaw, Warsaw.
- Sanchez, A., Molina, O., And Guitierrez, R., 1995. Geologia de los cuadrangulos de Chimbote, Casma y Culebras, hojas 19f, 19g, 20g: Instituto Geologico Minero y Metalurgico Boletin 59, 223 p.
- Schultze, C. 2013. Silver Mines of the Northern Lake Titicaca Basin. In *Mining and Quarrying in the Ancient Andes: Sociopolitical, Economic, and Symbolic Dimensions*, eds. N. Tripcevich and K. Vaughn, 1st ed. New York: Springer Science+Business, pp.231-251.
- Shimada, I. and Craig, A.K. 2013. The style, technology, and organization of Sicán mining and metallurgy, northern Peru: insights from holistic study. *Chungara, Revisita de Antropología Chilena* 45(1): 3-31
- Shimada, I., S.M. Epstein and A.K. Craig 1982, 'Batan Grande: a prehistoric metallurgical center in Peru', *Science*, 216: 952-9.
- Shimada, I. and Merkel, J. 1991, 'Copper-Alloy Metallurgy in Ancient Peru,' *Scientific American*, 265(1), pp.80-86.
- Shimada, I. and J.A. Griffin. 1994, 'Precious metal objects of the Middle Sican,' *Scientific American*, 265(1): 80-6.

- Shugar, A., Notis, M., Newbury, D. and Ritchie, N. 2014, 'Investigating a Moche Cast copper artifact for its manufacturing technology. *Mater. Res. Soc. Symp. Proc.* 1656
- Silva Vigo, E. 1992. "Cerro la Cruz: Asentamiento Chimú en el Sector Medio del Valle de Chao." *Gaceta Arqueológica Andina* VI(22):35-49.
- Silverblatt, Irene
1987 *Moon, Sun and Witches: Gender Ideologies and Class in Inca and Colonial Peru*. Princeton: Princeton University Press.
- Swenson, E. and Warner, J. 2012, 'Crucibles of power: Forging copper and forging subjects at the Moche Ceremonial Center of Huaca Colorada, Peru,' *Journal of Anthropological Archaeology*, 31(3), pp.314-333.
- Tello, Julio C. 1956. *Arqueología Del Valle De Casma: Culturas: Chavín, Santa o Huaylas Yunga y Sub-Chimú*. Editorial San Marcos Lima.
- Thompson, D. E., 1964, "Postclassic Innovations in Architecture and Settlement Patterns in the Casma Valley, Peru," *Southwestern Journal of Anthropology* 20(1): 91-105.
- Thompson, D.E. 1974. Arquitectura y Patrones De Establecimiento En El Valle De Casma. *Revista del Museo Nacional* 40:9-29.
- Wilson, D. J., 1988, *Prehispanic Settlement Patterns in the Lower Santa Valley, Peru: A Regional Perspective on the Origins and Development of Complex North Coast Society*. Smithsonian Institution Press, Washington, D.C.
- Wilson, D. 1995. 'Prehispanic Settlement Patterns in the Casma Valley, North Coast of Peru: Preliminary Results to Date.' *Journal of the Steward Anthropological Society* 23:189-227.
- Vogel, M.A. 2003. *Life on the Frontier: Identity and Sociopolitical Change at Cerro la Cruz, Peru*. Unpublished PhD dissertation, Department of Anthropology, University of Pennsylvania, Philadelphia. University Microfilm International, Ann Arbor.
- Vogel, M.A. 2011. 'Style and Interregional Interaction: Ceramics from the Casma Capital of El Purgatorio', *Ñawpa Pacha: a Journal of Andean Archaeology*, 31(2): 201-224.
- Vogel, M.A. 2012, *Frontier Life in Ancient Peru*, University Press Florida, Gainesville.
- Vogel, M.A., Buhrow, K., and Cornish, C. n.d. Gender, Class and Textile Production at El Purgatorio, Peru. Article under review at *Latin American Antiquity*.

Vogel, M.A. and D. Pacifico. 2011. Arquitectura de El Purgatorio: Capital de la Cultura Casma. In *Andes 8: Boletín del Centro de Estudios Precolombinos de la Universidad de Varsovia; Arqueología de la Costa Ancash*, eds.M. Giersz and I. Ghezzi, University of Warsaw, pp. 357-397.

Table and Figure Captions:

Table 1: Elemental net counts per second (ncps) determined via Bayesian deconvolution and semi-quantitative data calculated based on atomic parameters.

Table 2: Quantification of standard alloy (C31400-72B) with the same methods employed on Casma alloys.

Figure 1: Map of Peru's north coast showing El Purgatorio and Cerro La Cruz

Figure 2: Aerial photograph of El Purgatorio showing all 4 sectors of the site

Figure 3: Site map of El Purgatorio showing locations where lead-bearing artifacts were found

Figure 4: Example of heterogeneity in artifacts; lead is concentrated on one side of the spindle whorl

Figure 5: Spectrum of a spindle whorl with high lead content

Figure 6: Metal spindle whorls and pendant found in a grave at El Purgatorio

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1

Data	Ag ncps	Ag %	As ncps	As %	Cu ncps	Cu %	Fe ncps	Fe %	Pb ncps	Pb %	Pb/Cu Ratio
2007CCM1U2F2-M1BEAD1a	13	0%	35	0%	4130	85%	6	0%	121	15%	0.03
2007CCM1U2F2-M1BEAD1b	7	0%	39	1%	3636	94%	2	0%	34	5%	0.01
2007CCM1U2F2-M1BEAD2a	7	0%	29	0%	3232	58%	1	0%	403	42%	0.12
2007CCM1U2F2-M1BEAD2b	14	0%	89	1%	3253	82%	3	0%	114	17%	0.04
2007CCM1U2F2-M1BEAD3a	7	0%	47	1%	2940	97%	4	0%	11	2%	0.00
2007CCM1U2F2-M1BEAD4a	6	0%	167	2%	2828	79%	3	0%	115	19%	0.04
2007CCM1U2F2-M1BEAD5a	2	0%	29	0%	104	1%	3	0%	1257	98%	12.09
2007CCM1U2F2-M1BEAD5b	1	0%	17	0%	110	3%	2	0%	680	97%	6.18
2007CCM1U2F2-M1BEAD6a	1	0%	7	0%	507	22%	1	0%	315	78%	0.62
2007CCM1U2F2-M1BEAD6b	1	0%	7	0%	884	36%	2	0%	265	63%	0.30
2007CCM1U2F2-M1BEAD7a	19	0%	59	1%	2577	82%	3	0%	93	17%	0.04
2007CCM1U2F2-M1BEAD7b	18	0%	60	1%	2801	62%	6	0%	287	37%	0.10
2007CCM1U2F2-M1PENDANTa	5	0%	72	1%	4224	88%	2	0%	92	11%	0.02
2007CCM1U2F2-M1PENDANTb	14	0%	15	0%	3420	98%	3	0%	10	2%	0.00
2007CCM1U2F6-M1tinyBALLa	2059	6%	42	1%	16	1%	15	1%	333	91%	20.81
2007CCM1U2F6-M1tinyBALLb	2293	7%	5	0%	24	1%	3	0%	319	92%	13.29
2009A6R13U1L1-M1LEADa	641	1%	23	0%	266	4%	20	1%	1060	95%	3.98
2009A6R13U1L1-M1LEADb	839	1%	23	0%	264	7%	27	2%	567	90%	2.15
2009CCM1U8F1-M1BEAD1a	3	0%	148	4%	1860	93%	2	0%	12	3%	0.01
2009CCM1U8F1-M1BEAD1b	3	0%	118	2%	3233	97%	4	0%	7	1%	0.00
2009CCM1U8F1-M1BEAD2a	1	0%	2	0%	705	71%	8	2%	46	27%	0.07
2009CCM1U8F1-M1BEAD2b	2	0%	3	0%	451	77%	2	1%	22	22%	0.05
2009CCM1U8F1-M1BEAD3a	4	0%	58	1%	1590	32%	8	0%	579	67%	0.36
2009CCM1U8F1-M1BEAD3b	5	0%	20	0%	1832	60%	3	0%	210	40%	0.11
2009CCM1U8F1-M1BEAD4a	3	0%	32	0%	1498	38%	3	0%	416	62%	0.28
2009CCM1U8F1-M1BEAD4b	5	0%	15	0%	1486	43%	7	0%	327	56%	0.22
2009CCM1U8F1-M1BEAD5	1	0%	5	0%	11	1%	1	0%	198	99%	18.00
2009CCM1U8F1-M1BEAD6	1	0%	14	0%	76	2%	2	0%	538	97%	7.08
2009CCM1U8F1-M1PIRUOa	2	0%	63	1%	747	15%	7	0%	691	84%	0.93
2009CCM1U8F1-M1PIRUOb	3	0%	38	0%	2409	56%	2	0%	314	43%	0.13

Table 2

	Cu %	Zn %	Pb %
Certified Value	90.08%	7.81%	1.99%
Mean	91.17%	9.23%	1.12%
StDev	0.11%	0.09%	0.04%
CoV	0.12%	0.94%	3.58%