**[Supplementary material]**

**Obsidian Procurement and Exchange at the Apogee of Empire: Wari Political Economy in Arequipa, Peru**

David A. Reid1\*, Patrick Ryan Williams2, Augusto Cardona Rosas3, Robin Coleman Goldstein4, Laure Dussubieux5, Cyrus Banikazemi1, and Kurt Rademaker6

1 Department of Anthropology, University of Illinois – Chicago, 1007 West Harrison Street, Chicago, Illinois 60607-7139, USA

2Arizona State University, School of Human Evolution and Social Change, 900 S. Cady Mall, Tempe, AZ 85284, USA

3Centro de Investigaciones Arqueológicas de Arequipa (CIARQ), Arequipa, Peru

4 Department of Anthropology, Northwestern University, 1810 Hinman Avenue, Evanston, IL 60208, USA

5 The Field Museum of Natural History, 1400 S Lake Shore Dr, Chicago, IL 60605, USA

6 Department of Anthropology, Michigan State University, 655 Auditorium Drive, East Lansing, MI 48824, USA

\* Author for correspondence: dreid5@uic.edu

**Supplemental Materials Instrumental Specifications**

**Portable-XRF Instrumentation**

Innov-X Systems™ Alpha pXRF spectrometer

Thirty-five obsidian artifacts from Corralones were analyzed in 2008 using the InnovX spectrometer. For this instrument, samples were run under “Soils” mode for 90s. This mode utilizes a 40 kV voltage and 20 mA beam current using X-rays generated from a Tungsten anode to measure peak intensities for the elements Zn, Rb, Sr, Zr, and Nb. The “light element analysis package” is then utilized using a 15 kV voltage to generate peak intensities for the elements K, Ca, Ti, Mn, and Fe (also see Feinman et al. 2013:63-64).

Thermo Scientific Niton XL3t Goldd+ portable X-ray fluorescence (pXRF) analyzer

A total of 309 obsidian artifacts from the sites Pakaytambo, El Tambo, Santa Rosa II, and La Angostura was analyzed using the Niton Goldd+ instrument. This series utilizes a 50 kV silver anode tube and a geometrically optimized large area drift detector. All samples were analyzed with the “Test All Geo” mode using different filters and parameters corresponding to Main (40 kV and 100 μA), Low (25 kV and 100 μA), Light (15 kV and 200 μA), and High (50 kV and 100 μA). Each filter was set for an acquisition time of 30 seconds totaling 120 s per sample. Comparative studies at the EAF using the Niton XL3t Goldd+ have shown that specimens with rubidium (Rb) concentrations above 150 parts-per-million (ppm) are more accurately detected using the “Soils” mode. Consequently, all samples were additionally run using “Soils” mode with filters set on Main, Low, Light, and High for 30 s each for a total run time of 120 s per sample. Elemental concentrations are reported for a total of 13 elements, including: K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Y, Zr, Nb, Pb, and Th.

Calibration and Limitations of PXRF

Data collected across EAF pXRF instruments are calibrated using a correction developed by Mark Golitko (University of Notre Dame) using 21 in-house and certified standards. Inter-instrumental variation across pXRF devices make it necessary to directly compare artifact elemental concentrations to geologic materials run on the same instrument and settings (see Frahm 2013; Shackley 2010; Speakman and Shackley 2013). Representative Andean geologic obsidians were analyzed using EAF instruments with source samples provided by Kurt Rademaker; Nicholas Tripcevich, and Michael Glascock.

Certain limitations do exist for pXRF specifically pertaining to inadequate sample size, thickness, and surface irregularity (Davis et al. 2011; Reid et al. 2022; Shackley 2010). This is especially of concern for small-sized lithic debitage such as shatter and micro-debitage that may not meet optimal sample requirements. In consideration of these factors, obsidian artifacts were placed along the most planar surface to fully cover the instrument X-Ray beam aperture window (10 mm diameter) at the specimen’s thickest point. As pXRF is only a surficial analysis, areas of cortex, inclusions, or devitrification are avoided.

Artifacts are sourced to geochemical character groups using Ward’s hierarchical cluster analysis and compared to reference geologic materials. Prior investigations have shown that the Niton XL3t Goldd+ portable XRF series exaggerate ppm values for small-sized samples (Frahm 2016; Reid et al. 2022b). Ternary graphs and ratios of elemental concentrations are thus used to mitigate these effects including Sr/Rb, the two elements best known to discriminate Andean obsidians using XRF (Glascock et al. 2007) (see Supplemental Materials Figures 1). For an extensive review of pXRF methods utilized by the Field Museum’s Elemental Analysis Facility (EAF) to source small-sized debitage, including artifacts reported in this publication from Pakaytambo, El Tambo, Santa Rosa II, and La Angostura, see Reid et al. (2022).

**LA-ICP-MS Instrumentation**

LA-ICP-MS analyses were supervised by Dussubieux and included geologic samples provided by Rademaker in 2005, Chuquibamba artifact samples by Goldstein in 2008, and geologic and Majes artifact samples by Reid in 2019. Analyses were conducted at the Field Museum of Natural History in Chicago, USA, with a Varian Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) in 2005 and 2008 and a Thermo ICAP Q ICP-MS in 2019. Both ICP-MS were connected to a New Wave UP213 laser for direct introduction of solid samples. The parameters of the ICP-MS are optimized to ensure a stable signal with a maximum intensity over the full range of masses of the elements and to minimize oxides and double ionized species formation (XO+/X+ and X++/X+ < 1 to 2%). For that purpose, the argon flows, the RF power, the torch position, the lenses, the mirror and the detector voltages are adjusted using an auto-optimization procedure.

For better sensitivity, helium is used as a gas carrier in the laser. The choice of the parameters of the laser ablation not only will have an effect on the sensitivity of the method and the reproducibility of the measurements but also on the damage to the sample. To be able to determine elements with concentrations in the range of ppm and below while leaving a trace on the surface of the sample invisible to the naked eye, we use the single point analysis mode with a laser beam diameter of 55 to 100 mm, operating at 80% of the laser energy (0.1 mJ) and at a pulse frequency of 20 Hz. A pre-ablation time of 20 s is set in order, first, to eliminate the transient part of the signal and, second, to be sure that a possible surface contamination or corrosion does not affect the results of the analysis. For each sample, the average of four measurements corrected from the blank is considered for the calculation of concentrations.

To improve reproducibility of measurements, the use of an internal standard is required to correct possible instrumental drifts or changes in the ablation efficiency. The element chosen as internal standard has to be present in relatively high concentration so its measurement is as accurate as possible. In order to obtain absolute concentrations for the analyzed elements, the concentration of the internal standard has to be known. The isotope Si29 was used for internal standardization. Concentrations for major elements, including silica, are calculated assuming that the sum of their concentrations in weight percent in glass is equal to 100% (Gratuze 1999).

 Fully quantitative analyses are possible by using external standards. To prevent matrix effects, the composition of standards has to be as close as possible to that of the samples. Over time, two approaches were subsequently adopted. Initially, two different series of standards were used to measure major, minor and trace elements. The first series of external standards are standard reference materials (SRM) manufactured by NIST: SRM 610 and SRM 612. Both of these standards are soda-lime-silica glass doped with trace elements in the range of 500 ppm (SRM 610) and 50 ppm (SRM 612). Certified values are available for a very limited number of elements. Concentrations from Pearce et al. (1997) will be used for the other elements. The second series of standards were Glass Buttes and Sierra Pachuca obsidians (see Glascock 1999). For the most recent measurements of this study (conducted in 2019), these two obsidian samples were replaced by two glass samples manufactured by Corning. Glass B and D are glasses that match compositions of ancient glass (Brill 1999:544).

In some cases, overlap occurs between artifact groups and more than one geologic source depending on elemental comparisons. In these cases, various scatterplots are generated to accurately assign artifacts to obsidian source groups. For example, in Figure 7 of the manuscript, there is overlap between Alca-1 and Anillo and Alca-4 and Lisahuacho. Here we provide example scatterplots that separate the respective groups (see Supplemental Materials Figures 2 and 3).

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