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reliability. Reliability is a product of an instrument's *precision* and *accuracy*. Precision pertains to the repeatability and stability of the geochemical source attribution of a sample, while accuracy addresses the extent to which measurements conform to 'correct' values (Hughes 1998).

#### Method

For this study, 56 obsidian artifacts were geochemically analyzed using both laboratory and portable energy dispersive XRF instruments. The artifacts were randomly chosen from the artifact populations of two Classic Period (A.D. 250 - 800) (Coe 2005) Maya sites—Uxbenká and Ek Xux—both located in southern Belize.

The samples were first analyzed by Dr. M. Steven Shackley at the Geoarchaeological XRF Laboratory at the Department of Anthropology, U.C. Berkeley, using a Thermo/ARL *Quant'X* energy dispersive X-ray fluorescence spectrometer. The X-ray tube was operated at 30 kV for 200 live seconds, using a 0.05 mm (medium) Pd primary beam filter in an air path to generate X-ray intensities at the K-alpha<sub>1</sub>-line for elements iron (as Fe<sup>1</sup>), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb). Conversion of raw spectra to trace elemental intensities (reported here in ppm) was achieved at the Berkeley laboratory through a least-squares calibration line for each element from the analysis of international rock standards certified by the National Institute of Standards and Technology (NIST), the US. Geological Survey (USGS), Canadian Centre for Mineral and Energy Technology, and the Centre de Recherches Péetrographiques et Géochimiques in France (Govindaraju 1994).

Following geochemical analysis at Berkeley, the samples were analyzed using a Bruker AXS Tracer 3-V Portable EDXRF analyzer, equipped with a rhodium tube X-ray source and a peltier cooled, silicon PIN diode detector, operating at 40 kV and 9.0 µA from an external power source for 300 live seconds using a filter composed of 6 mil copper (Cu), 1 mil titanium (Ti), and 12 mil aluminum (Al). Samples were positioned with as much contact as possible to the instrument's surface. This was done to ensure that the greatest amount of X-rays would bombard the sample, optimizing the count rate and mitigating the effects of irregular sample surface structure on X-ray scatter. During analysis, the instrument was mounted in a Bruker designed hold, which allowed for fixed positioning during analysis. Energy counts were processed using the Bruker S1PXRf spectra program. Instrument calibration was achieved through comparison of expected and produced elemental concentrations of 17 Mesoamerican obsidian samples of known geochemistry. We used the Bruker S1CalProcess program, which utilizes the Compton's scatter derived from rhodium backscatter. In addition, a single standard sample of known geochemistry was run each day as to ensure the stability of the instrument. Analysis was conducted at the K-alpha<sub>1</sub>-line for tin (Ti), manganese (Mn), iron (Fe), rubidium (Rb), strontium (Sr), zirconium (Zr), niobium (Nb), zinc (Zn), yttrium (Y), and barium (Ba).

### Error Assessment of Portable X-Ray Fluorescence Spectrometry in Geochemical Sourcing

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The availability and use of portable X-ray fluorescence (PXRF) instruments among archaeometrists has increased in recent years. Such proliferation warrants an in depth look at the quality of the instruments and the data they produce. Here we attempt to test one aspect of PXRF instrumentation:



Geochemical source determinations were achieved through utilization of rubidium and zirconium trace elemental concentrations (Figure 1), and by comparison to references provided by the Berkeley standard library. Both instruments determined that the sample population contained seven samples from the Ixtepeque obsidian geochemical group, 47 from the El Chayal group, one from the Pachuca group, and one unknown.

Two-sample t-tests were employed at the 95% confidence level between the El Chayal and Ixtepeque geochemical source clusters for elements Rb, Sr, Zr, and Y derived from portable and laboratory XRF instruments in order to test the accuracy of the PXRF instrument. Previous research (see for instance Davis et al. 1998; Shackley 2005) has demonstrated the validity of laboratory XRF instrumentation for archaeological provenance research. It follows that data produced from the U.C. Berkeley lab make a suitable control for which to test the accuracy of PXRF analysis.

Summary statistics were generated within a single source cluster—El Chayal—and were used to determine the percentage distance between the means of the laboratory and

portable derived El Chayal source clusters. This percentage was then used to generate a treatment for the PXRF data by increasing each datum by that percentage, and re-running the two sample t-tests to determine if systematic (predictable) or random (not predictable) error is present.

K-means cluster analysis was employed to identify a central point of variation in the El Chayal, Ixtepeque source groups. This was done using the Lloyd algorithm and partitioning the data into three clusters based on the sources confirmed through laboratory XRF analysis, i.e. the laboratory XRF data sets a hypothesis by which to judge the PXRF instrument. The standard error in each cluster was used to generate confidence levels about the centroid, allowing comparison of the overlap between laboratory and portable XRF data both graphically and statistically (Figure 2). These data were then run through a two sample t-test to assess accuracy.

### Results

*P-values* between laboratory XRF and both untreated and treated PXRF data are seen in Table 1. With the exception of yttrium, all trace elements showed significant differences at

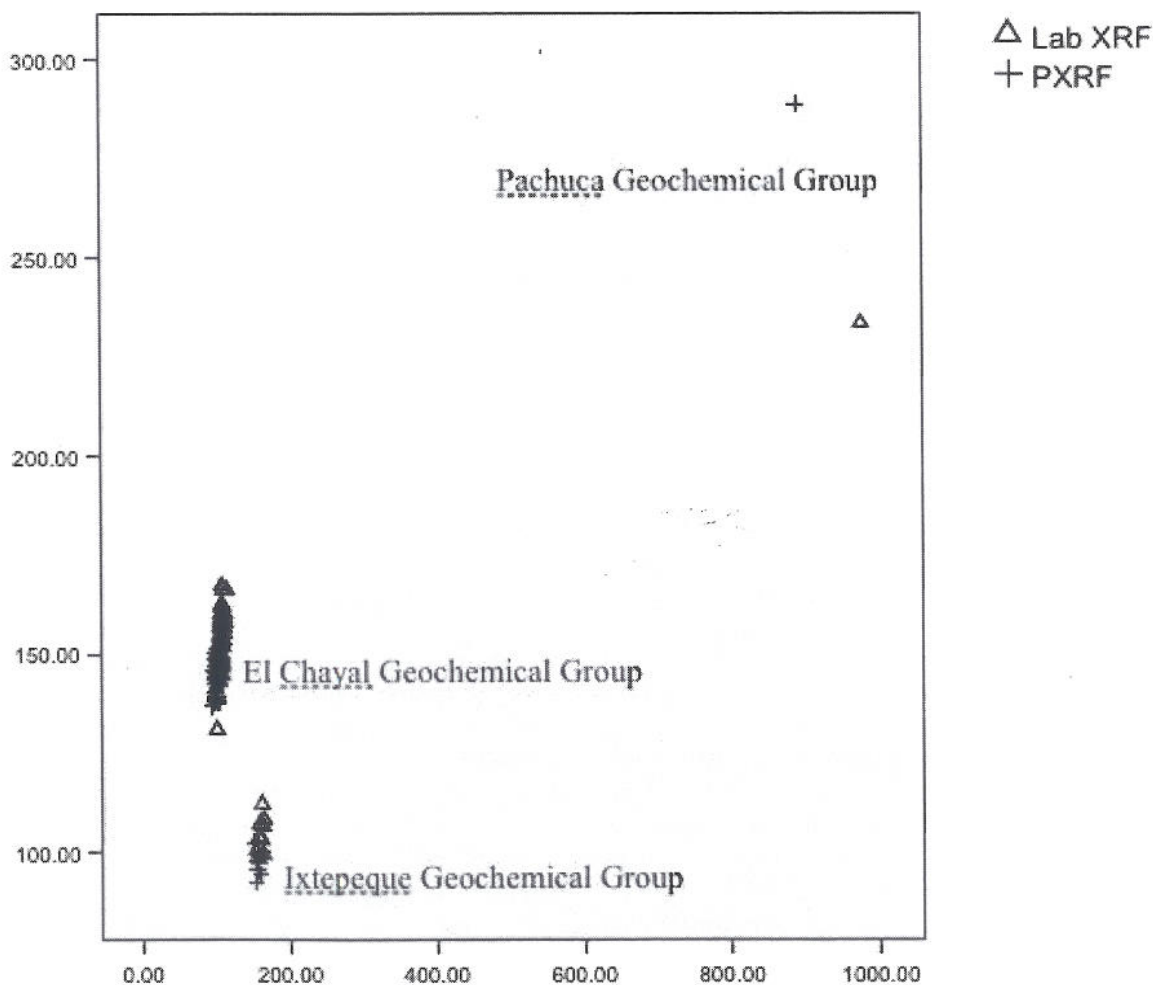


Figure 1. Bivariate plot of rubidium (Rb) (y-axis) and zirconium (Zr) (x-axis) trace element concentrations, utilized in source assignment, acquired via laboratory EDXRF (triangles) and Portable EDXRF (crosses) instruments.

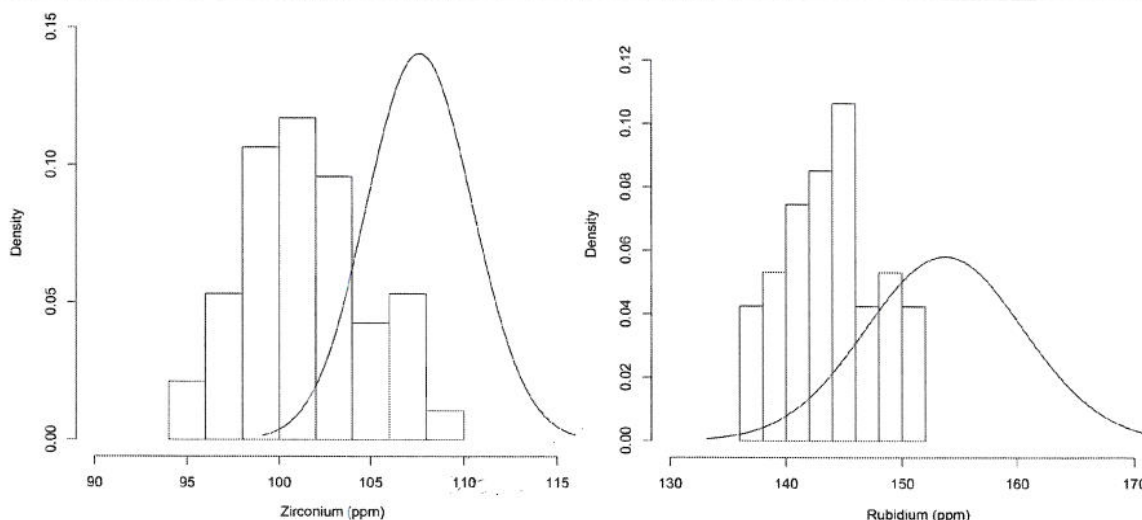


Figure 2. Histograms of Zirconium and Rubidium comparing PXRF data (bars) to laboratory XRF (solid line curve).

Table 1. Average trace element concentrations detected in the El Chayal cluster by laboratory XRF and PXRF with the percent error between the two instruments.

Instrument	Zr (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)
LXRF	107.5957	153.7021	151.9787	19.44681
PXRF	101.2867	143.90896	144.8979	20.81104
% Error	5.86%	6.37%	4.66%	-7.02%

the 95% confidence level for untreated PXRF data. This supports the argument that our PXRF instrument is inaccurate when compared with data derived via laboratory XRF analysis.

By contrast, treated PXRF data showed non-significant differences at the 95% confidence level with varying degrees of strength. This suggests that while inaccurate, PXRF data are precise.

Measurement between data from laboratory XRF and untreated PXRF show that Bruker PXRF tends to produce geochemical readings for Rb, Sr, Zr and Y which consistently differ from the laboratory XRF data by 6%. The results of these analyses can be seen for each element in Table 2 and Figure 2.

K-means cluster analysis mirrored the two sample t-test results. Untreated PXRF results showed statistically significant differences with a *p*-value of < 0.001, while treated PXRF results had a *p*-value of 0.500.

An additional strength of k-means cluster analysis was generating an automated sourcing technique; the identification of clusters was done directly through computer calculation.

Both treated and untreated PXRF data was automatically and properly sourced despite inaccuracy when compared with laboratory XRF data (Figure 2).

Table 2. Table of *p*-values from two-sample t tests between laboratory XRF and both raw and treated PXRF data.

Test	Zr	Rb	Sr	Y
LXRF - Untreated PXRF	0	0	0	0.406
LXRF- Treated PXRF	0.343	0.824	0.706	0.969

## Discussion

Consistent with past research (Craig et al. 2007), while statistical analysis demonstrates that geochemical data acquired from the PXRF instrument are not equivalent to that acquired via laboratory XRF, it can successfully distinguish geochemical source clusters.

Of central importance to this discussion is the nature of this inter-instrument error. By creating a treatment for the PXRF data, a large amount of error (roughly 6% in trace elements Rb, Sr, Zr, Y) can be identified and potentially corrected; this is depicted in Figures 1 and 2.

This systematic error, once identified and removed, results in non-significant differences at the 95% confidence level between data acquired by portable and laboratory XRF instruments.

This method of dual-analysis using two instruments may be of use in determining the error rates of other PXRF instruments.

The inaccuracy demonstrated here is not intended to dismiss the use of PXRF instrumentation in archaeological provenance research. Indeed, the Bruker instrument was found to have sufficient intra-instrument consistency for geochemical source determination.



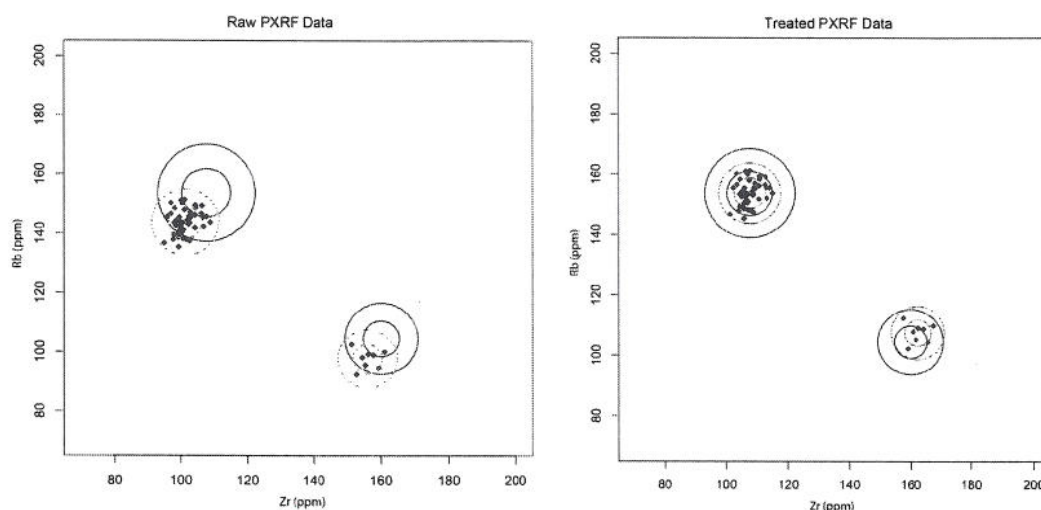


Figure 3. K-means cluster analysis centroids centered around El Chayal (upper left) and Ixtepeque (lower right). Data in the left diagram reflect raw PXRF data, while in the right diagram treated PXRF data are used. Solid line circles represent laboratory XRF data at the first and second standard deviations; dotted lines show the same standard deviations for PXRF data.

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#### Archaeometallurgy

Thomas R. Fenn, Guest Associate Editor

The column in this issue includes the following categories of information on archaeometallurgy: 1) New Books; 2) Ph.D. Theses; 3) Previous Meetings; 4) Forthcoming Meetings; and 5) Online Resources.

#### New Books

*Iron and Steel in Art: Corrosion, Colorants, Conservation*, David A. Scott and Gerhard Eggert, 2009, 196 pp., 138 illus., ISBN: 1904982050, £55.00/\$90.00 (Hardback). Contents: 1. Iron and steel in art: an introduction, 2. Iron oxides and hydroxides, 3. Iron carbonates, 4. Iron chlorides, 5. Iron sulphides and sulphates, 6. Iron phosphates, 7. Iron silicates, 8. Iron organometallic compounds and cyanides, 9. Iron corrosion in the soil and burial, 10. Iron corrosion in the atmosphere, 11. Iron corrosion in marine environments, 12. The conservation of iron: an overview, 13. The conservation of iron from soil burial, 14. The conservation of iron in the atmosphere, 15. The conservation of iron from marine sites, 16. Conservation decisions, 17. Appendix 1, 18. Bibliography, 19. Glossary of Some Technical Terms. This book will be of interest to all who seek to further their understanding of iron artefacts, their corrosion, conservation and pigments based on iron compounds, which mankind has used for millennia. The authors take the reader through some of the latest observations on the occurrence and role of compounds of iron – from the hot water undersea vents where the presence of iron pyrites is thought to be vital to the emergence of life on Earth to the discovery of jarosite on the surface of Mars, possibly indicating the occurrence of water; from the pyrophoric surprises one can have when dealing with iron artefacts taken from beneath the sea to the use of a blue oxide of iron as a pigment in mediaeval wall paintings; from rusticles on the Titanic to the analysis of colouring matter on the Turin shroud. The great variety of iron