

PXRF/WDXRFS INTER-UNIT DATA COMPARISON OF ARIZONA OBSIDIAN SAMPLES

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ABSTRACT

This paper focuses on two separate x-ray fluorescence methods to determine whether or not element readings between them are comparable. Four stable elements from seven varieties of Arizona obsidians are used in this comparison study. The first pXRF method is a non-destructive fluorescence method using the NITON XL3t handheld analyzer, housed in the archaeology laboratory (ARL) at the University of Wisconsin, Milwaukee (UW-M). The second method is the wavelength dispersive x-ray fluorescence spectrometry (WDXRFS), a destructive powder method. The NITON (pXRF) XL3t is a mobile handheld device that can be used in the field, and the other a fixed stationary WDXRFS model. PXRF technology provides an opportunity for scientists to obtain rapid feedback of elemental compositions for raw materials in the field, and the primary importance is that it is non-destructive. However, obsidian researchers are continuously adamant at honing in on which instruments they should use for consistency and reliability, and this paper highlights this issue.

Recently, researchers have expressed interest in understanding the variation in results returned by different x-ray fluorescence instruments. More importantly, the research community has become concerned with the ability to compare results generated by different instruments and to reproduce these results precisely (Shackley 2010). Craig et al. (2007:2016) demonstrated that although the elemental concentration readings produced by both a stationary EDXRF and a portable XRF instrument were able to determine that 66 out of 68 obsidian artifacts could be identified to one particular source, they did not render exactly the same cluster data, which could “be resolved through instrument cross-calibration” (Craig et al. 2007:2012). Drake et al. (2009) and Nazaroff et al. (2010) also showed that there is considerable variation between EDXRF and pXRF instruments.

This study directly addresses the problems inherent to comparing x-ray fluorescence unit data generat-

ed by different types of instruments. I compare elemental concentration measurements that were produced by two different XRF instruments for seven types of obsidian from Arizona (see also Hampel 1984). The first instrument that I use to measure elemental concentrations in the obsidian samples is the pXRF Niton XL3t handheld analyzer. The second XRF instrument I use to analyze the same samples is the Bruker S4 pioneer wavelength dispersive x-ray fluorescence spectrometer (WDXRFS). I test the hypothesis that both the non-destructive pXRF and the destructive WDXRFS methods render very similar patterns of data for each of the obsidian samples.

If analysis results validate the hypothesis, then obsidian researchers may have some confidence in their use of data tables that were generated with different x-ray fluorescent instruments. In addition, researchers may view data produced by pXRF instruments as somewhat reliable in comparison to the consistent results often created by WDXRFS instruments. Validating the reliability of pXRF instruments would be advantageous, as researchers could then trust them to render relatively accurate trace element readings in the field. It would be very beneficial and convenient to examine artifacts or raw materials in the field without collecting objects for lab analysis. Moreover, since pXRF instruments do not require the sample specimen to be crushed into a powder, it would be possible to perform an XRF analysis without destroying archaeological materials. Overall, the expediency of a pXRF device would increase the potential of geochemical artifact analysis.

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APPLICATIONS FOR OBSIDIAN SOURCING

Obsidian is a homogenous, volcanic glass. It is an ideal lithic material for sourcing analyses because the geochemical characteristics of obsidian sources often vary. Therefore, it is often possible to match the geologic signature of an obsidian sample to the signature of its source. In addition, obsidian was a valued lithic resource that was used throughout the prehistoric Southwest. Obsidian has excellent conchoidal fracture properties that are amenable to shaping, and it maintains a very sharp edge for cutting. Thus, people wanted it and traveled great lengths to obtain it (Doyel 2012, Loendorf 2010).

Since obsidians can have different geochemical signatures, archaeologists use various XRF methods to pursue trade and exchange and mobility practices. Because researchers are able to use material science techniques to identify obsidian artifacts to their sources, they are able to address research questions about the movement of people using these items and about the exchange of the items themselves. Archaeologists can examine questions about mobility and about the trade patterns and/or routes that moved obsidian across the landscape. These studies may also involve investigations of human land and resource use, resource procurement strategies, and even large-scale economic strategies (e.g., exchange of raw materials, craft production, exchange of finished crafts, etc),

Obsidian is an ideal material for sourcing studies (Shackley 1988, 1995, 1998, 2005), because researchers have published a great deal of data on individual obsidian samples and sources in the Southwest. Steven Shackley has published¹ EDXRF data from northern Arizona obsidians are a useful referent for comparing trace element readings between all kinds of x-ray fluorescence instruments.

I compare the results of geochemical data that are generated by two different x-ray fluorescence instruments: 1) a pXRF Niton XL3t handheld analyzer and 2) a Bruker S4 pioneer wavelength dispersive x-ray fluorescence spectrometer (WDXRFS). In particular, I test a hypothesis that the results produced by these two instruments produce similar and thus comparable data patterns. To test this hypothesis, I analyze seven obsidian samples, each from a different source, with the two different instruments. First, the pXRF instrument recorded three readings per specimen from a freshly fractured surface that was free of patina, and then the samples were turned into powder with a tungsten-carbide shatter box and prepared for analysis using the WDXRFS instrument. Finally, the two data sets are compared using the geochemical program Iqpet and produced in the form of bi-plots to see if the data are superimposed over one another (i.e. to see if the data

are similar). Such an exercise will draw attention to whether specific part-per-million data rendered using one instrument is either similar or dissimilar to another. This will test the question of whether or not it is reliable to use part-per-million data from data tables generated by one instrument, and assume that it will be the same for another instrument.

GEOLOGICAL SAMPLES

The first group of obsidian samples contains specimens from the Mount Floyd (Round Mountain) volcanic field near Ash Fork, Arizona, on the Colorado Plateau. This volcanic field is Upper Cenozoic (60-15my) in age. Mark Bush (1986) has provided a summary of the geochemical complexity of the Mount Floyd (Round Mountain) volcanic field. I collected samples of three different types of fine-grained volcanics (FGVs) that occur in separate areas of the Mount Floyd fields and that have different geologic and chemical characteristics. I gathered specimens of Round Mountain obsidian (FGV 1), glassy gray rhyolite (FGV6), and black rhyolite (FGV7) for geochemical analysis.

The second sample set is a specimen from the Government Mountain area (FGV 2), near Flagstaff, Arizona. This geographic feature is part of the San Francisco volcanic field. The third sample set is a specimen from Vulture Mountain (FGV 3), which is near the Transition Zone between the Colorado Plateau and the Basin and Range Province of mid-west Arizona. A fourth set of samples are specimens from the Basin and Range Province, which contains older rocks but younger geologic features that are younger (15-0 my) than the Colorado Plateau. I collected a specimen of Saucedo obsidian (FGV 4), which comes from a mountain range located on the Barry M. Goldwater Air Force Range near Gila Bend, Arizona. Both Saucedo and Sand Tank obsidian, two geochemically distinct obsidians, are derived from sources in this area; however, I have only included Saucedo obsidian in this study. The final sample set is a specimen of obsidian from Picketpost Mountain (FGV 5), which is near Superior, Arizona. This source is currently mined for its rich perlite (Reynolds et al. 1986).

METHODS

To examine any differences in the measurements returned by different x-ray fluorescence instruments, I subjected the seven obsidian samples to xrf analysis with two different devices. The samples served as experimental controls in the study. The geochemical composition of each of the seven samples was measured first with a Niton pXRF instrument, and then with a WDXRFS one. Each specimen's compositional read-

ings from the Niton pXRF and the WDXRFS were then compared using the program Igpct. The seven obsidian samples were analyzed both with a Niton XL3t pXRF analyzer and a Bruker S4 pioneer wavelength dispersive x-ray fluorescence spectrometer (WDXRFS). The Niton pXRF is intended for use in the metal alloy industry, but the instrument has a soil function that can be used specifically for obsidian studies. It is equipped with a Rhodium (Rh) anode target. The Niton bombards the specimen with high-energy photons dispersed from a 50 keV 40 μ A maximum miniature x-ray vacuum tube with multiple primary filters (Thermo Scientific NITON 2007). This causes the sample to fluoresce, and to produce characteristic x-rays for each of the elements present. The x-ray detector then receives the secondary x-rays from the sample specimen and determines its unique geochemical composition.

The WDXRFS instrument² is a Bruker S4 pioneer wavelength dispersive x-ray fluorescence spectrometer has analyzer crystals and collimators for higher quality elemental resolution. It is a stationary device that requires the samples to be prepared into flat glass beads (circular discs) using a Claisse M4 fusion system.

Sample Preparation

Some obsidian trace element studies involve many sample specimens to seek regional patterns of results (sensu Shackley 2005). In the current study, this is unnecessary because it is focused on whether the two instrumental methods render similar patterns of results using only a small number of selected obsidian samples.

The preparation of samples for pXRF analysis and the actual pXRF analysis itself are relatively simple. An obsidian sample is laid over the instrument's aperture within a lead-lined containment box. Then the trigger, controlled by an attached computer, is depressed for 180 seconds. Preparation of samples for a WDXRFS analysis and the subsequent analysis (which used a 10 to 1 dilution glass bead fusion method) are much more complex than for the pXRF analysis. After each sample specimen was powdered in a tungsten-carbide (WC) shatter box for four minutes, the powdered sample was dehydrated overnight in a 105° C oven. Then, 1.0000 \pm 0.0003 g of the powdered sample was combined with 10.0000 \pm 0.0003 g of Claisse 50:50 LiT:TiM flux with an integrated LiBr non-wetting agent and mixed with 1 g of ammonium nitrate-oxidizer. The mixture was then heated in a platinum crucible to a maximum temperature near 1050° C, and fused into a glass bead with a Claisse M4 fluxer. The x-ray beam was centered on either a fresh fracture plane of an obsidian specimen, or a fresh surface of a flake of a specimen.

Data Collection and Processing

The data that I have collected represent three readings of each specimen from the pXRF analysis, and one reading from the WDXRFS analysis. I took three readings of each sample with the Niton pXRF in order to test and ultimately improve the accuracy of measurements from this instrument. In general, the data returned by the Niton pXRF instrument were more inconsistent than data returned by the WDXRFS instrument. Elemental concentrations for the Niton pXRF and the WDXRFS raw data were calculated with a calibration curve based on 11 USGS rock standards (Table 1) using the program F-Quant. After calculation (calibration) of elemental concentrations, only 4 trace elements were chosen from the XRF analysis of obsidian samples using the Niton pXRF instrument. The 4 elements that were chosen were based on a consistently rendered amount of the elements shared between both instruments to facilitate data comparison.

The WDXRFS produced 9 major elements and 24 trace elements. In total, the calibrated elemental concentration data sets from both the Niton pXRF and the WDXRFS analyses included only four specific elements that were rendered consistently by both instruments: major elements CaO, TiO₂, and Fe₂O₃, and trace element Sr. Many of the other elements that were recorded by the two instruments were rendered inconsistently, and were not useful for comparing the results produced by the two different instruments. Thus,

Table 1. Weight percent oxides (major elements) and trace element data.

3 Weight Percent Oxides and one Trace Element				
USGS rock standards	CaO(%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	Sr(%)
RGM-1	1.15	0.267	1.86	0.011
STM-1	1.09	0.135	5.22	0.07
AGV-1	4.94	1.05	6.77	0.066
BCR-2	7.12	2.26	13.8	0.035
BHVO-2	11.4	2.73	12.3	0.039
BIR-1	13.24	0.96	11.26	0.011
DNC-1	11.27	0.48	9.93	0.015
DTS-2B	0.12	0	7.76	0
GSP-2	2.1	0.66	4.9	0.024
SGR-1	8.38	0.264	3.03	0.042
G-2	1.96	0.48	2.66	0.048
mean	5.706364	0.844182	7.226364	0.032818
std dev	4.797719	0.88324	4.119756	0.022947

Table 2. Elemental data after using the multipliers. The multipliers to obtain this data table are (Ca=0.7143, Ti=0.5995, Fe=0.6994).

Percents after Multipliers			
USGS rock standards	Ca%	Ti%	Fe%
RGM-1	0.82	0.16	1.30
STM-1	0.78	0.08	3.65
AGV-1	3.53	0.63	4.73
BCR-2	5.09	1.35	9.65
BHVO-2	8.14	1.64	8.60
BIR-1	9.46	0.58	7.88
DNC-1	8.05	0.29	6.95
DTS-2B	0.09	0	5.43
GSP-2	1.50	0.40	3.43
SGR-1	5.99	0.16	2.12
G-2	1.40	0.29	1.86

I was limited to the elements Ca, Ti, Fe, and Sr for the data comparison between both instruments.

Typically, in obsidian studies, researchers use specific "transition metals" (Rb, Sr, Y, Zr, and Nb) to compare two or more obsidian data sets. The relative concentration of these metals reflects the geochemical variation among different obsidian sources. However, in this study, I am not comparing two different obsidian data sets. Rather, I am comparing two versions of the same samples: one version that contains readings from a Niton pXRF instrument, and a second version that contains readings from a WDXRFS instrument. In this case, it is not imperative to follow the protocol of comparing "transition metals." Researchers, including Shackley, often include Ti, Fe, and Sr elements in their analytical work to identify obsidian from different sources. Since the elements of Ti, Fe, and Sr have been utilized by others elsewhere in many of analyses of obsidian, it is appropriate for me to use them, as well as the element Ca, for use in my comparative analysis between instruments.

In order to compare the instrument data, I had to convert the weight percent oxides that were obtained using the WDXRFS to make the data from both instruments comparable in parts per million. I chose the three major elements (CaO, TiO₂, and Fe₂O₃) rendered from the WDXRFS, which were converted (Table 2) to percents using the following multipliers (Ca=0.7143, Ti=0.5995, Fe=0.6994) in order to compare the data to the pXRF results in parts per million

(ppm). Once the new data table (from Table 2) was generated after using the multipliers, each of the numbers were then multiplied by 10,000, because the conversion from weight percent oxides to ppm involves multiplication by 104 (Tables 3 and 4).

When the three elements plus the trace element Sr were chosen for correlation to the United States Geologic Survey (USGS) rock standard samples, a calibration curve showed that all four elements had high correlation coefficients (R²= 0.99). Therefore, only four biplots of these four elements were necessary to compare both the Niton and the WDXRFS instruments. Once the weight percent oxides (CaO, TiO₂, and Fe₂O₃) were converted to trace elements in ppm, the combination of the four total elements (Fe, Ti, Ca, and Sr) became easier to compare the data between the Niton and the WDXRFS instruments.

RESULTS

The geochemical data that the pXRF and the WDXRFS instruments returned for each of the samples is presented in Table 5. To compare the similarity of these two data sets, I created two scatter plots with Igpert, a software package developed by Dr. Michael Carr at Rutgers University for analyzing lithic geochemical data (Figures 1 and 2). Each of the scatter plots displays the amount (in parts per million [ppm]) of one element in an obsidian sample against the amount of a second element in that element. One scatter graph plots the amount (in ppm) of Fe against the amount of Ti in the analyzed obsidian samples, while the second plots the amount of Ca versus the amount of Sr. Since only four elements were isolated to work with there was no particular reason for conducting bi-plots of these particular elements. For each of the seven samples in the study, I plot both the WDXRFS measurements and the pXRF measurements. Thus, I plot two placements on the graph for each sample. I can then visually compare the measurements that were recorded by each instrument by inspecting the placement of the two sample runs on the scatter plot.

Although the four elements in this analysis were chosen as a result of the high coefficient of determination of comparability using 11 USGS rock standards, each of the seven obsidians measured by both instruments in the graphs should hypothetically be centered over one another, but they are not. A scatterplot of Fe concentrations against Ti concentrations in the obsidian samples reveals that the results generated by the pXRF and the WDXRFS are not identical for many of the samples (Figure 1). Contrary to expectations, none of the pairs of measurements for the same samples measured by each instrument matched. The difference in the Fe measurements between the two sample runs ranges from 0-5000 ppm, while the difference in Ti

Table 3. Calcium and titanium percents converted to ppm data. The multiplier here is 10⁴.

Percent Conversions to ppm					
Ca(%)			Ti(%)		
USGS rock standards	Ca ppm standard	Ca ppm Niton	USGS rock standards	Ti ppm Niton	Ti ppm rock standards
RGM-1	8214.45	1299.11	RGM-1	493.79	1600.665
STM-1	7785.87	1205.62	STM-1	0	809.325
AGV-1	35286.42	9751.95	AGV-1	2109.15	6294.75
BCR-2	50858.16	14583.65	BCR-2	4759.87	13548.7
BHVO-2	81430.2	24397.87	BHVO-2	5477.26	16366.35
BIR-1	94573.32	28786.13	BIR-1	1858.77	5755.2
DNC-1	80501.61	24223.08	DNC-1	864.73	2877.6
DTS-2B	857.16	0	DTS-2B	0	0
GSP-2	15000.3	3128.61	GSP-2	1220.18	3956.7
SGR-1	59858.34	19212.33	SGR-1	498.36	1582.68
G-2	14000.28	2968.48	G-2	980.66	2877.6

Table 4. Iron and strontium percents converted to ppm data. The multiplier here is 10⁴.

Percent Conversions to ppm					
Fe(%)			Sr(%)		
USGS rock standards	Fe ppm Niton	Fe ppm standards	USGS rock standards	Sr ppm Niton	Sr ppm standards
RGM-1	817.34	13008.84	RGM-1	4.58	110
STM-1	2533.15	36508.68	STM-1	53.4	700
AGV-1	3349.9	47349.38	AGV-1	52.9	660
BCR-2	7310.32	96517.2	BCR-2	23.67	350
BHVO-2	6363.49	86026.2	BHVO-2	30.16	390
BIR-1	5738.5	78752.44	BIR-1	4.85	110
DNC-1	5068.09	69450.42	DNC-1	7.7	150
DTS-2B	3993.28	54273.44	DTS-2B	1	0.00
GSP-2	2364.61	34270.6	GSP-2	17.45	240
SGR-1	1545.63	21191.82	SGR-1	27.95	420
G-2	1244.63	18604.04	G-2	34.7	480

Table 5. The WDXRFS data used in this analysis is on top, while the pXRF Niton data used in this analysis is on the bottom. Be advised that a "1" had to be used for strontium, because the Niton did not register the element. This was done in order to include the Sr symbol in the biplot in the program Iqpet.

WDXRFS Data	Ca(ppm)	Ti(ppm)	Fe(ppm)	Sr(ppm)
FGV1a	3000.06	239.8	7384.35	0.03
FGV2a	5928.69	659.45	7695.27	78.15
FGV3a	3214.35	719.4	6218.4	56.74
FGV4a	3357.21	599.5	11737.23	16.18
FGV5a	5071.53	839.3	9560.79	109.22
FGV6a	11285.94	1618.65	15779.19	182.39
FGV7a	11357.37	1618.65	15701.46	181.54
pXRF Data				
Case#				
FGV1b 1	1974.64	262.86	5592.97	1
2	1920.76	230.61	5625.22	1
3	2054.68	209.48	5257.3	1
FGV2b 1	5939.82	636.31	4440.63	71.22
2	5854.56	705.08	4248.68	67.45
3	6027.62	631.52	4536.38	66.86
FGV3b 1	2562.5	702.19	4056.9	43.28
2	2355.37	642.72	4013.46	40.13
3	2552.26	601.34	4154.47	35.66
FGV4b 1	2754.99	426.18	7174.22	6.02
2	2871.39	492.27	7263.7	6.05
3	3108.35	515.43	7309.97	7.43
FGV5b 1	2779.24	600.38	3264.29	15.8
2	2841.4	627.54	3453.71	17.03
3	2950.16	618.37	3362.1	14.37
FGV6b 1	8784.99	1449.11	10328.32	185.57
2	8410.18	1428.28	10158.12	188.56
3	8679.13	1371.91	10315.47	186.54
FGV7b 1	17826.91	2984.26	16336.06	240.04
2	17750.33	3209.44	16842.02	231.33
3	18103.71	3102.37	16717.45	233.45

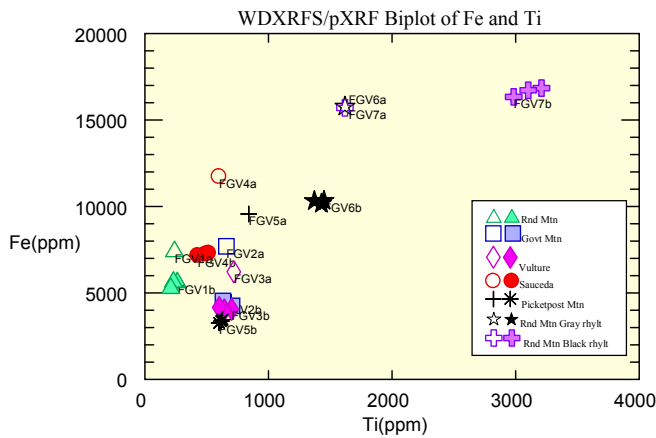
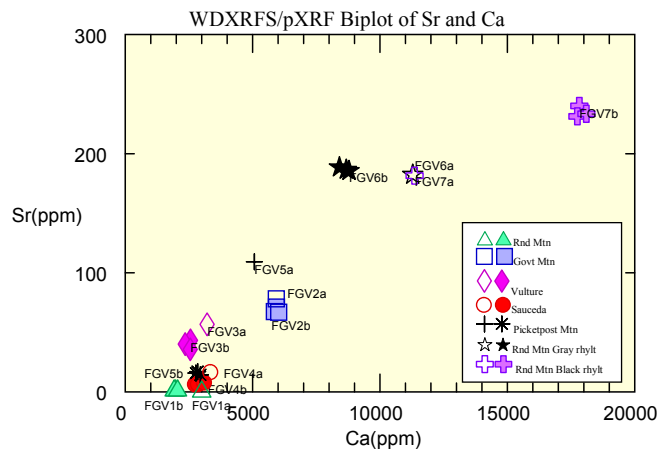


Figure 1. WDXRFS data (FGV 'a') and Niton (pXRF) data (FGV 'b') are compared here viewing seven obsidians, comparing both Fe and Ti. Empty symbols are WDXRFS, and the corresponding solid symbols are pXRF.



(Fig. 2) WDXRFS data (FGV 'a') and Niton (pXRF) data (FGV 'b') are compared here viewing seven obsidians, comparing both Sr and Ca. Empty symbols are WDXRFS, and the corresponding solid symbols are pXRF.

measurements ranges between 0 – 1000 ppm. However, the WDXRFS Round Mtn. gray rhyolite was similar to Round Mtn. black rhyolite, while the pXRF readings for the same samples were off by more than 1000 ppms in this plot. This begs the question by how many ppms creates a difference in XRF studies?

A scatterplot of Ca concentrations against Sr concentrations in the obsidian samples reveals a similar result as the previous plot. The measurements taken by the pXRF are not identical to those recorded by the WDXRFS (Figure 2). The difference in the Ca measurements between the two sample runs ranges from 0-7000 ppm, while the difference in Ti measurements ranges from 0-100 ppm. The two samples whose pXRF and WDXRFS readings deviated the most widely are

the Picketpost Mountain and black Round Mountain rhyolite specimens.

DISCUSSION

This paper follows a suite of recent publications highlighting instrument commensurability. As a result, it highlights some benefits of comparing two different XRF techniques, which becomes especially relevant when a newer technique is less well known, such as the pXRF (Niton). Until now, there have been few studies that compare portable-EDXRF (pXRF) techniques with other more reliable and peer-tested and reviewed XRF ones like the WDXRFS. The results of this analysis suggest that the readings from a Niton pXRF instrument are not directly comparable to the results produced by a WDXRFS instrument when using the same samples.

However, in any comparative analysis of measurements generated by different XRF instruments, we must establish that systematic differences are not due to differences or errors in sample preparation and data collection. A variety of errors can be introduced into XRF analysis results from the following sources: specimen contamination, equipment contamination, background effects, "the statistical nature of the emission and detection of x-rays" (Willis 2006: Section 10), matrix effects, apparatus stability. There are also some other kinds of problems that every scientist must take into consideration in XRF studies: reproducibility, reliability, random errors, systematic errors, and the variability between inter-observer error and the interpretation of data. I tested whether a certain piece of technical equipment would render comparable results as another, and in this analysis, I made every effort to eliminate these sources of error under the close supervision of Dr. Lindsay McHenry in the controlled laboratories of the Geosciences Department, and the Anthropology Department in Sabin Hall at the University of Wisconsin-Milwaukee.

After controlling for analytical differences between the instruments and most major sources of analytical error, I conclude that there is only one plausible explanation for the differences in the pXRF and the WDXRFS measurements, which is that errors exist within the Niton pXRF software. Thus, I am suspicious of the Niton and its continued use in XRF studies for archaeological applications. I recommend that researchers conduct additional comparative tests, like the one conducted in this paper, to identify appropriate instruments for archaeologically-related analyses. These studies should focus on issues of measurement consistency, accuracy, and replicability. In addition, researchers should also discuss the issue of instrument standardization to ensure that published data are comparable.

Finally, as material scientists continue to evaluate different x-ray instruments, it is important to consider the benefits of non-destructive methods over destructive ones. It is of course desirable to preserve all archaeological materials in an analysis. It is also convenient to collect data in the field with such a portable XRF instrument, and (if possible) leave specimens in situ. At present, though, the reliability and consistency of the Niton (pXRF) data remains to be demonstrated.

CONCLUSIONS

This analysis indicates that elemental concentration data generated by a Niton pXRF instrument are not comparable to elemental data produced by a WDXRF instrument, even after calibration with curves of 11 USGS rock standards. Until more studies can ameliorate the deficiencies between inter-instrumental x-ray fluorescence methods, I suggest that researchers use considerable caution when aggregating ppm data from different studies that may have used different x-ray fluorescence instruments. Future investigations should focus on detailed comparison of results produced by different instruments. More specifically, these investigations should concentrate on evaluating each of the sources of error that I have discussed in order to identify the source of incomparable measurements.

Notes

See Shackley's websites here:

<http://www.swxrflab.net/swobsrscs.htm>,
<http://www.sourcecatalog.com/index.html>

2. See booklet:

http://www.bruker-axs.com/uploads/tx_linkselector/forpdfpool/01954_BR_S4_Pioneer_E_Internet.pdf

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