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Energy Dispersive X-Ray Fluorescence and its Sensitivity to Thermally Induced Changes in Clay Bodies

Elissa Hulit

Abstract: The use of portable X-Ray fluorescence spectrometry in the study of prehistoric ceramics has gained popularity recently due to the many benefits of this technology. Portable Energy Dispersive X-Ray Fluorescence (XRF) is non-destructive, relatively inexpensive, and capable of detecting a range of the elements that commonly distinguish clay bodies. It has been used successfully as a means of differentiating prehistoric pottery from different sources and has provided new insights into pottery manufacture and trade networks. However, when it comes to clay sourcing, the high degree of sensitivity in XRF analysis may present new challenges that must be considered before XRF can be used effectively. Natural clay deposits can be expected to vary in composition as the result of formation or deposition processes. During pottery production, humans introduce new sources of compositional variation at various stages of manufacture. While the compositional variation resulting from the subtraction of natural inclusions and from the addition of tempering materials and decorative slips or paints has received attention, no attempt has been made to determine if XRF alone has the capability to identify compositional variation resulting from different fire temperatures. This paper presents an attempt to identify such differences between a set of control samples. These vessels were made from the same stock clay, but vary in tempering materials and firing temperatures. A principal components analysis of the compositions suggests that chemical changes as a result of firing temperature can be detected by the XRF device. Clay sourcing studies using XRF technology should take this source of variation into account. Furthermore, the interaction between firing temperature and the temper material indicates that while knowledge of the pottery firing temperature may be needed, knowledge of how the tempering material reacts to firing atmosphere may also help refine clay sourcing methodology.

Key words: pottery, compositional analysis, x-ray fluorescence, principal components analysis

Introduction

Over the past several years, the use of portable X-ray fluorescence spectrometry has become more frequent in archaeological analysis. The University of Wisconsin – Milwaukee Archaeological Research Laboratory (UWM ARL) has acquired and used several different models of energy dispersive X-Ray fluorescence (XRF) devices for a range of studies, including ceramic analyses. In addition to being non-destructive and portable, sampling with XRF is relatively cheap and requires no preparation of the item to be sampled (Potts 2008: 12). This makes XRF a good option for studying the chemical composition of artifacts that cannot be loaned to outside institutions or should not be sacrificed in destructive analytical methods. It is also an effective way to study potential source clays within a study area because the low cost and rapid return of results allow the researcher to analyze many more clay samples than through destructive mineralogical or chemical methods, such as petrography and instrumental neutron activation analysis (INAA). However, the use of XRF in clay sourcing is complicated by the

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nature of the final product. The prehistoric potter started with naturally occurring clay of unknown chemical composition. To this was added a variety of foreign materials both passively through the collection processes and actively through manufacturing processes. Finished pottery is a composite material consisting of clay minerals, non-clay minerals, natural organic inclusions, and tempering agents added by the potter during the raw clay preparation stage of construction; all of which affect chemical composition (Rice 1987: 390). The ingredients in this composite clay body undergo numerous physical and chemical changes during the vessel manufacture (Rye 1981: 3). This study is concerned with the chemical changes that take place within the clay body during the firing process.

The firing process cannot be ignored as an important factor in the chemical composition of the pottery vessel under study. During firing the pottery is heated to temperatures above 600 degrees Celsius and begins to undergo chemical changes driven by the interaction of temperature, duration of firing, and atmosphere of the firing (Rice 1987: 88). These changes result in the hardened pottery that can be recovered from the archaeological record. This study focuses on the range of temperatures achieved by open bonfire-type firing atmospheres in prehistoric North American settings. In an open bonfire-type firing the exact settings of temperature, duration, and atmosphere will vary between firing episodes. Vessels constructed of clays from the same source using the same recipes may be fired to very different temperatures depending on fuel, ambient temperature, moisture of the ground, and the firing expertise of the potter (Rice 1987: 80; Rye 1981: 97; Sinopoli 1991: 30). It has been demonstrated that XRF can detect significant differences between prehistoric pottery types on the basis of composition (Shackley 2011: 2; Tagle and Gross 2010: 4). However, firing temperature of the specimen was not taken into account in any of these studies. The next question in XRF study of pottery should be whether or not the readings generated by XRF can differentiate vessels with similar clay bodies on the basis of firing temperature. If the analyzer is sufficiently sensitive to detect chemical changes resulting from the firing process, then it is necessary to determine whether prehistoric firing temperature will prevent useful comparison of the raw source clay sample to prehistoric pottery. In this case, the researcher would need to evaluate the temperature related changes of the sample to determine what chemical changes occur at a variety of firing temperatures before comparing the sample to the prehistoric pottery.

Method

Testing whether the current portable XRF spectrometer at the UWM ARL can reliably detect chemical differences in pottery fired to different temperatures requires studying a sample of homogenous pottery fired to known temperatures. This study uses a collection of nine bowls and three tiles created from commercially available White Raku clay. As part of an earlier experiment, this clay was chosen to create bowls for testing the heating efficiency of vessels with varying types of temper and firing temperature. The clay was purchased from a commercial clay retailer and was chosen for the coarse texture, high porosity and low firing temperatures similar to that expected from naturally occurring clays in Wisconsin. At the time of purchase, this clay also contained a small amount of crushed fired clay inclusions, or grog, a common inclusion in prehistoric pottery sherds. Because of the homogeneity of commercial clay, both the chemical

content of the grog and the proportion of grog per unit of clay should be consistent in all vessels made from this clay.

The author created three sets of three bowls each, one group containing no added temper (group A), one group containing sand temper (group B), and one group containing crushed burned shell temper (group C). Both the sand and the shell had been sifted through #10 wire mesh screens to remove large pieces. After selecting the raw material, the clay was mixed with temper using a 1:5 ratio of temper to clay by volume following experimental work by Carter (2002: 22). The clay was then formed into bowls by rolling the clay out in a slab, approximately one centimeter thick, and forming it over a mold. Once constructed, the bowls were divided into three groups with one bowl of each temper type placed into each group. The first group was fired to 600C (1,112° F), the second group was fired to about 717C (1,322° F), and the third group was fired to 999C (1,830° F). These temperature ranges span the temperatures that could reasonably be obtained in an open-air bonfire- or pit fire-type setting (Carter 2002: 21-22; Rice 1987: 156). Bowls were labeled according to their temper group and firing temperature group (designations 1-3 indicating increasing firing temperature). For example, the shell tempered bowl fired to 600C was designated 'C1'.

The author originally designed and used these bowls in a series of heating experiments designed to simulate cooking (Hulit 2006). The results of this first experiment will not be detailed here, but it is important to remember that these bowls were not in pristine condition at the start of the XRF analysis detailed below. The shell tempered bowl fired to the highest temperature range, C3, was never used in that earlier experiment due to catastrophic failure shortly after firing. At around 900C the calcium carbonate (CaCO_3) in shell loses carbon dioxide (CO_2) molecules. After the vessel returns to ambient temperatures the shell begins to rehydrate and expand (Rye 1976: 120). In the case of vessel C3 this expansion caused the vessel to fall to pieces before the cooking experiment began. After completion of that experiment the bowls were put into storage and all but forgotten until this project was conceived. Still missing were the unfired samples, however, as the author had also retained remnants of the prepared clays from the original production process, it was a simple matter to create one tile for each temper group; untempered (A0), sand tempered (B0), and shell tempered (C0). The number in these tile designations reflects the fact that they remain unfired. The remnants were rehydrated and formed into tiles approximately 5cm x 5cm square that were then air dried.

The XRF analysis was conducted using the Bruker Tracer III-V handheld analyzer. The analyzer was set using the filter composed of 12mil Al + 1mil Ti + 6mil Cu. This filter allows the researcher to target Potassium (K), Calcium (Ca), Titanium (Ti), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Rubidium (Rb), Strontium (Sr), Yttrium (Y), Zirconium (Zr), and Niobium (Nb). These elements are important in chemical compositional analysis of ceramics because of the way these elements become bound into clay mineral forms, the inter-element correlation of these elements in geochemical data, and the presence of iron oxides and hydroxides in weathering soil profiles typical of clay deposits (Glasscock 1992: 16; Velde and Meunier 2008: 71). For each vessel tested, these elements can be exported as net intensities that can be used in Principal Component Analysis (PCA).

Each sample was scanned at five locations, three readings per location, for 180 seconds. A multi-location/multi-reading approach was adopted because taking readings at multiple locations would allow the author to verify that the readings are internally consistent and provide an adequate sample size for statistical analysis. The XRF analyzer is connected to a Dell laptop computer with SP1XRF and ARTAX software which allow the computer to remotely control the analyzer and to export the data into a format compatible with statistical analysis programs.

All statistical analysis for this study was performed in the R Statistical Analysis program, version 2.14.1 (R Development Core Team 2011). The statistical analysis used several additional data packages within the R program including the *compositions*, *StatDA*, and *robustbase* packages (Filzmoser and Steiger 2012; Rousseeuw, et al. 2011; van den Boogaart, et al. 2011). The fifteen readings for each vessel were examined for outliers. This process reduces the risk that a larger than average temper inclusion dominates the reading and skews the results of the analysis. The Mahalanobis distance measure is a statistically robust method of calculating the distances of each shot from the average composition of the readings (De Maesschalek, et al. 2000: 5; Glasscock 1992: 18). The distances are calculated for each reading and if all the readings reflect an acceptable amount of difference from the centroid of the group there should be no pattern in the distances of each reading. However, if all three shots from any one location have the three highest distances, that location may be considered anomalous and the values removed one at a time until there is no discernible structure in the readings. As discussed above, these vessels are internally homogenous and inclusions should not exert undue influence on these readings. After examination of the outliers, it was determined that no reading locations were compromised and no readings were removed from this dataset.

These net intensities can then be examined using Principal Components Analysis (PCA) of the Isometric Logratio Transformation (ILR). PCA of back-transformed ILR data provides a robust method for analyzing variation in compositional data (Filzmoser, et al. 2012: 79; Reimann, et al. 2008: 203). This process reduces the amount of variation present among 12 elements to 11 principal components that express variation in terms of the relationship between the elements. The principal components are arranged in order of diminishing explanatory power. The analysis here will focus on the first principal component. Within R, there are a set of commands to control the ILR transform process, however, there is overlap in the command names used in the *StatDA* package that conflict with other packages used in the analysis. The analysis in this paper utilized a set of ILR source code created by Dr. J.P. Gray of the Anthropology Department of University of Wisconsin-Milwaukee. The results of this analysis will be discussed in more detail below.

Discussion

The first step in exploring firing temperature was to determine if there was any significant difference between the compositions of the full sample. A first step was to look the first and second components of PCA of the compositions. These describe 47.32% of the chemical compositional variation in the vessels sampled. The results of the PCA can be visualized in a biplot that depicts the readings as points around a set of rays indicating the relations between elements. Using the vessel designation as the point label allows the biplot to

depict both the temper categories and the firing range in relation to the chemical composition. The angle between element rays indicates strength of correlation with the strongest positive correlation being represented by an angle close to zero and opposition represented by angles approaching 180 degrees. Longer rays indicate stronger influence in the PCA than shorter rays. Figure 1 highlights the relationship of the data points to the PCA.

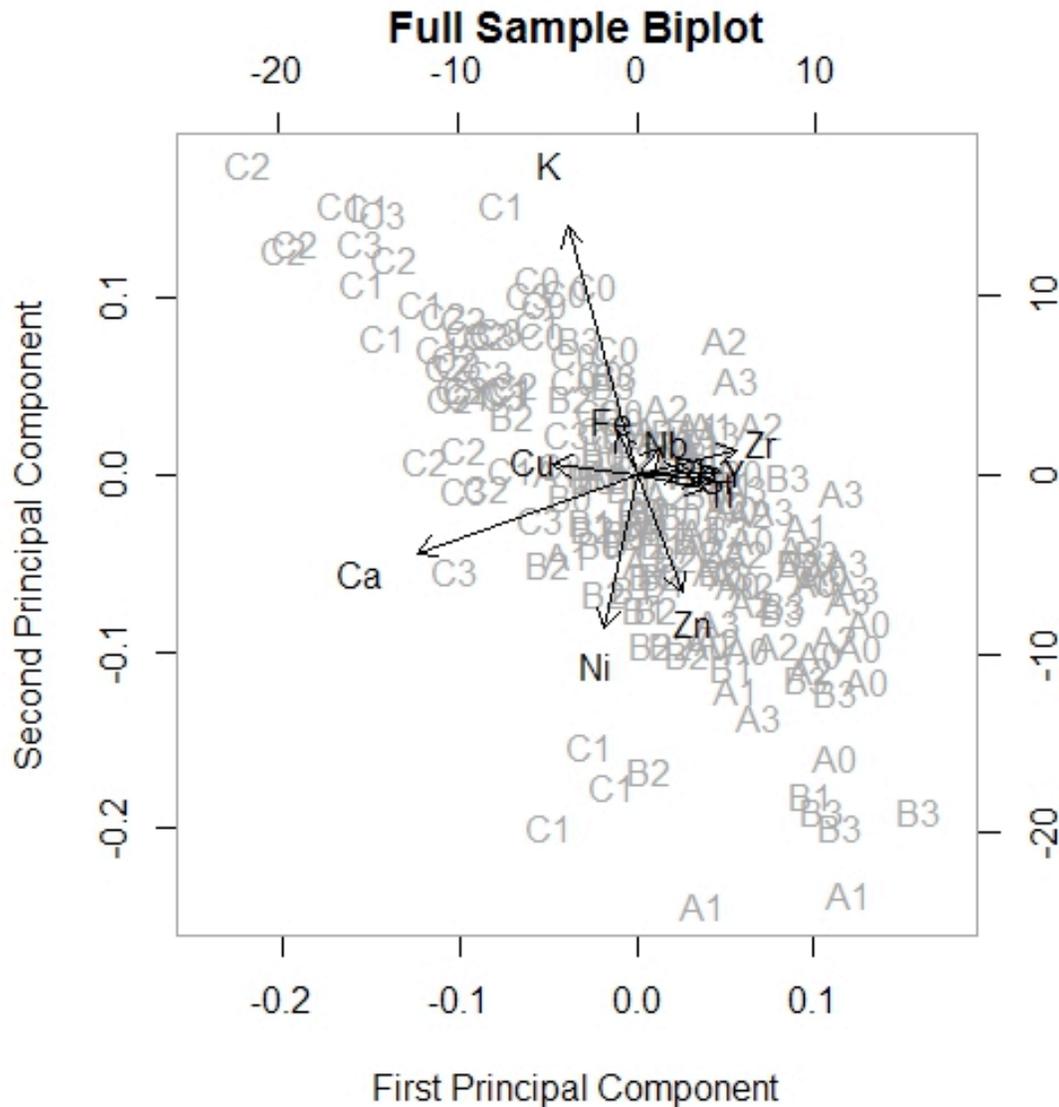


Figure 1. Biplot of First and Second Principal Components. The main distinction seems to be the isolation of shell tempered vessels (designated by C) from the other two temper types. Approximately 42.37% of the variation in the total sample is depicted in this plot.

In the first principal component it appears that as vessels are differentiated by higher amounts of Ca and Cu, they exhibit lower amounts of Y and Zr and vice versa. On the second principal component, higher amounts of Zn and Ni are opposed to lower amounts of Fe and K. The largest distinction appears to be between the shell tempered vessels, which are strongly

associated with calcium, and the other two temper types. There is no apparent patterning by firing temperature. However, appearances can be deceiving and further exploration of the data was necessary.

First, the compositions were analyzed to determine if the temper groups were significantly different. Analysis of Variance (ANOVA) of the first principal component as modeled by the three temper groups demonstrates that the temper groups are significantly different (F value= 150, $df=2$, p -value $<2.2e-16$). Tukey post-hoc tests indicate that each group is significantly different from each other temper group (all adjusted p -values $<1.85e-05$). Examination of the compositions by temper group indicates that the shell tempered vessels are distinguished primarily by higher proportions of calcium than the other temper types. The untempered vessels are distinguished by higher proportions of Zr and Y and lower amounts of Ca and Cu. Proportions of these four elements within the sand tempered vessels appear to fall between the amounts noted in other two temper categories. The addition of large amounts of calcium in the form of calcium carbonate in shell temper has been shown to produce a dilution of the other elemental components within samples (Glasscock 1992: 16). The addition of sand temper appears to produce a similar dilution effect by significantly increasing the concentration of Ca and Cu relative to the Zr and Y.

Next, the compositions were analyzed to determine whether compositions differ significantly when divided by the firing temperatures. ANOVA of the first principal component modeled by the four different firing temperatures was significant (F value= 4.221, $df=3$, p -value=0.0065). Tukey post-hoc tests show that the temperature group fired to 717°C is significantly different from both the non-fired group and the 999°C firing group (adjusted p -values 0.0264 and 0.0385, respectively). The compositions show that the non- and highest fired groups have more Ca and Cu and less Y and Zr when compared to the middle firing ranges. Reasons for this difference are not immediately apparent. Intuitively, if there is significant differentiation on the basis of firing temperature, the non-fired group should not be the most similar to the highest fired group. The possibility of an interaction between the temper group and the firing temperature must be explored next.

The interaction of temper group and firing temperature is significant (F value= 6.6929, $df=6$, $Pr(>f)=3.029e-08$) and Tukey post-hoc tests indicate that there is a significant interaction between the firing temperature at the 717C group and the sand temper group ($Pr(>|t|)=0.0184$), between the non-fired temperature group and the sand temper group ($Pr(>|t|)=0.0073$), and between the 717C group and the shell tempered group ($Pr(>|t|)=0.0065$). This indicates that the interaction between temper and temperature cannot be ruled out in XRF analysis of pottery. However, each temper group appears to react differently and these temper related differences must be explored next.

In order to examine the different interactions noted here, the sample is subdivided by temper group and the PCA process is repeated. First, the untempered group is studied as a control sample. If there is no difference, then it can be concluded that the clay minerals in the paste do not undergo significant chemical changes during firing. Examination of the first principal component indicates that most of the variation in the untempered group is described by the relationship between Ca and K relative to Y and Z. However, ANOVA indicates that there is

no significant difference between the firing temperature groups within the untempered subsample (F value= 0.323, df=3, p-value=0.809). If this result is extended to practice of clay sourcing, samples containing a minimum of non-clay minerals or inclusions should display no significant differences regardless of firing temperature.

This is not the case among the other tempered groups. PCA of the sand tempered sample identifies variation based on the relationship of Cu and Ca relative to Zr, Zn, and Y. ANOVA of the sand tempered subsample was significant (F value= 3.946, df=3, p-value=0.0127) and post-hoc tests indicate that the 717C firing group is significantly different from the 999C firing group (adj. p-value=0.0318) and the 999C firing group is significantly different from the non-fired group (adj. p-value=0.0152). As with the entire sample, there is no clear pattern in the scores that would indicate gradual trends in the composition over increasing firing temperature. Instead, there appears to be a gradual trend of reducing amounts of Ca and Cu and increasing amounts of Zr and Y with increase in temperature, and a sudden reaction taking place between 717C and 999C that suddenly increases the amount of Ca and Cu present relative to the Zr and Y. Without knowing the mineral components of the sand used in this temper, it is difficult to make an educated guess about the specific mineral conversions taking place between the 717C and 999C firing temperatures. However, I would suggest that there are several minerals slowly losing Ca and Cu or gaining Zr, Zn, or Y from their mineral structure in the early firing stages, and that if the firing process is allowed to continue to the highest firing temperature range, this trend alters such that the chemical composition moves back into the compositional range of the lower fired groups, but remains outside of the range of the non-fired group. Furthermore, the range of variation within a single vessel increases with increasing firing temperature (as measured by the standard deviation of the case scores on the first principal component) suggesting that as firing temperature increases, the minerals in the temper become less stable and begin forming altered minerals.

Examination of the shell tempered vessels indicates that the variation in the first principal component is largely affected by the relationship between Ca and K relative to Y and Zn. ANOVA of the shell tempered group by firing temperature was significant (F value= 4.832, df=3, p-value=0.0046). Tukey post-hoc tests reveal only one significant difference between temperature ranges; the non-fired group is significantly different from the 717C group (adj. p-value=0.0025). However, the difference between the non-fired group and the 600C group approaches significance (adj. p-value=0.0685). The proportion of Ca in the unfired sample is relatively low compared to the fired samples. Among the fired samples, the proportion of Ca per sample decreases relative to the other elements as the firing temperature increases. This may be caused by the structural decomposition of calcium carbonate (CaCO_3) between 650 and 900C releasing CO_2 into the firing atmosphere. As was discussed above, the highest fired shell tempered vessel fell apart due to the rehydration of the CaO remaining in the vessel body. However, at high firing temperatures, new calcium compounds can also form within the clay body using adjoining minerals or elements present in the firing atmosphere (Rice 1987: 98). It seems that this could be the case here. If elements, such as Cu, Zr, and Y, are driven off in the low firing stages, but absolute amounts of Ca remains constant, it would increase the relative proportion of Ca in the composition. Samples that reach high firing temperatures might trap certain elements in new mineral structures diluting the Ca measured by the XRF enough to prevent the highest fired group from being distinguished from the non-fired group.

The trends noted here have several limitations. The sample size used is very small, the clay was homogenous commercial clay that may not react to firing changes in the same ways as natural clays, and hypotheses about mineralogical changes are made without having any actual knowledge about the minerals present in the samples. Despite these drawbacks, this experiment has made a contribution to what is known about the sensitivity of the XRF device. The methods discussed here show that while relatively pure clay does not undergo detectable changes during firing, tempering agents do. This exposes one of the issues with using XRF to study naturally occurring clay bodies. Very few natural clay deposits are as 'pure' as the commercial clay used here. While the main clay minerals of the deposit may not change during firing, any mineralogical impurities such as sand, organic detritus, and weathered minerals present in the natural deposits should change in response to the firing conditions. In clay sourcing studies, studying the natural inclusions and the ways the clays react to the firing process is necessary to understand whether the temperature changes will mask similar clay bodies. The raw clay sources should not be compared directly to the prehistoric pottery until this question is addressed.

Conclusions

This study has provided evidence that XRF is sensitive enough to detect chemical changes in homogenous clay bodies caused by differing firing temperatures. The major implication of these results is that researchers cannot ignore the potential effects of firing temperature in chemical compositional studies of prehistoric ceramics. This is especially important in the context of clay sourcing, but it also has implications for comparison of prehistoric pottery using the XRF compositional analysis.

As discussed above, raw source clays can only be compared directly to prehistoric pottery if two conditions are met. First, it must be demonstrated that the hypothetical source clay is free from impurities that undergo compositional changes during firing. Second, the prehistoric pottery must be shown to be compositionally similar to its original non-fired state. Meeting the first condition is possible, though even if the clay deposit is relatively pure, a certain amount of contamination can be expected to take place during collection and transport to the processing location, especially if the clay is accessed by digging through non-clay sediment layers. This clay can then be analyzed with the XRF for raw state chemical composition. The samples should be fired and reanalyzed to verify that firing has no significant effect on the composition of the clay sample.

However, the second condition is more problematic. As shown above, temper was the major factor in firing temperature related compositional changes. Even in cases where no firing temperature changes had taken place, the temper itself caused the PCA to separate each temper group from its untempered counterpart. However, it should be noted that only one type of clay was used in this experiment. It is possible that a duplicate experiment using two or more similar clays and identical tempering agents might still be able to differentiate between raw clay sources, despite the addition of temper. Until such duplicate experiments are carried out, there is no reason to abandon all hope that XRF can be used successfully for clay sourcing studies.

Lastly, this study provides a cautionary guideline in the use of XRF for study of prehistoric pottery. In open bonfire-type settings there is a wide variety of potential combinations of firing temperature, atmosphere, and firing duration. When the chemical changes brought about by these fluctuations are detected by the XRF readings, a large collection of pottery made from the same clay source and according to the same traditional paste recipe could be expected to vary significantly in chemical composition. The degree to which this range of variation for one vessel tradition could be expected to overlap with that of another tradition has not been demonstrated. For example, if potters from village A and village B both use burned mussel shell as a tempering agent, and each collect their clays from the same outcrop along a hypothetical river, the raw clay vessels would be expected to have very similar chemical compositions. Since both villages have capable potters and access to resources, there is almost no trade of finished vessels between sites. The potters in village A tend to fire their pottery to between 600-800C, while the potters of village B tend to fire their pottery to temperatures ranging from 700C to 900C, the resulting fired vessels might produce two significantly different compositional groups. This would mimic the effect of two different pottery production techniques. Village A would produce more low fired pottery while village B would produce more high fired pottery, however, high and low fired pottery would be found at both sites. A casual XRF analysis of the discarded pottery from the two villages might conclude that there is a significant difference between potting traditions, but that because both are found in each site, the villages must have been trading vessels on a regular basis. The researcher would reach a spurious result because of the effect of firing temperature.

While this hypothetical example is surely an over simplification, it illustrates why understanding the ability of the XRF device to detect firing temperature based changes is important in the application of XRF to study of prehistoric pottery collections. This issue could become even more important when studying pottery from prehistoric groups that used kilns or other complicated firing techniques. Kilns allow for greater control over firing conditions, thus potentially narrowing the range of compositional variation. With a large sample of vessels made from the same clay source using the same recipe fired in two different contemporaneous kilns that consistently reach different temperature ranges, the risk of overemphasizing differences in clay compositions could increase.

This study has demonstrated that there are certain pitfalls in the use of XRF in addition to its many benefits. A larger study of the effect of firing temperature using a variety of natural clays is needed in order to establish an acceptable range of variation produced by firing atmosphere for a given type of clay. This would allow researchers to better identify significant differences between groups of pottery. If portable XRF technology has the potential to detect chemical changes dependent on temperature benchmarks, as demonstrated above, the effect of firing temperature must be addressed in chemical compositional studies of pottery.

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