Journal of Archaeological Science 53 (2015) 626–638

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Portable XRF analysis of archaeological sediments and ceramics

Alice M.W. Hunt*, Robert J. Speakman

Center for Applied Isotope Studies, University of Georgia, United States

ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form
6 November 2014
Accepted 22 November 2014
Available online 2 December 2014

Keywords:
pXRF
Sediments
Ceramics
Phosphorus
Calibration
Analytical protocol

ABSTRACT

Recently, there has been significant interest in the use of portable X-ray fluorescence spectrometers (pXRF) for cultural materials applications, especially ceramics and sediments. Although modern pXRF spectrometers have lower detection limits and better resolution than those of decades past, portable instruments remain subject to the same limitations as bench-top ED-XRF instruments, particularly with respect to sample preparation, instrument calibration, and ability to accurately quantify low-Z elements. In this paper, we evaluate the strengths and limitations of pXRF analysis for the quantitative compositional analysis of archaeological ceramics and sediments and propose an analytical protocol and calibration designed to optimize pXRF performance for these materials.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Bulk chemical characterization of archaeological materials, such as ceramics and sediments, is important for understanding the human past, from determining raw material provenance to understanding economic organization and trade networks to evaluating use of space and assigning activity areas. Compositional analysis by neutron activation (INAA), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF) can be expensive, destructive and/or time consuming. It is not surprising, therefore, that non-destructive compositional analyses by portable XRF (pXRF) have become increasingly popular.

Manufacturers of pXRF spectrometers advertise the ability of these instruments to accurately and precisely quantify the chemical composition of a range of materials, from metals to sediments, 'right out of the box' using any one of a number of factory calibrations and analytical protocols. However, these factory calibrations are generally not appropriate for archaeological materials analysis; the calibrations are not matrix matched for archaeological materials and rarely contain all the elements of interest and/or an adequate elemental dynamic range suitable for archaeological materials characterization.

pXRF studies of archaeological materials using this 'black box' approach rarely generate high quality, accurate compositional data. Partly, this results from the use of pXRF calibrations and analytical protocols developed by manufacturers for non-archaeological materials and partly from a failure by the end-user to recognize or understand the limitations of the instrument and/or material of interest. In this paper, we discuss the optimization of pXRF performance for the compositional characterization of archaeological ceramics and sediment, including a matrix matched calibration and analytical protocol developed by the Center for Applied Isotope Studies (CAIS), University of Georgia.

2. Portable XRF of archaeological sediments and ceramics

2.1. Analytical limitations

ED-XRF analyses of archaeological sediments and ceramics are typically designed to identify activity areas and determine raw material provenance. As such, the elements of interest include low-Z elements, sodium (Na) to titanium (Ti), manganese (Mn) and iron (Fe), often referred to as the major elements, typically reported as oxide wt.%, and minor and trace elements reported in ppm. Not all of the elements of interest can be excited and/or measured by ED-XRF spectrometry; some elements, such as the low-Zs, can only be measured imperfectly and semi-quantitatively on conventional lab-based ED-XRF instruments. Elements typically analyzed by ED-

* Corresponding author. Tel.: +1 706 542 2143; fax: +1 706 542 6106.
E-mail address: ahunt@uga.edu (A.M.W. Hunt).

http://dx.doi.org/10.1016/j.jas.2014.11.031
0305-4403/© 2014 Elsevier Ltd. All rights reserved.

XRF for archaeological sediments and ceramics are highlighted in Fig. 1.

Portable ED-XRF spectrometers are smaller, more compact, and oftentimes, less powerful than conventional lab-based ED-XRF spectrometers. Despite the point-and-shoot nature of handheld pXRF spectrometers, these instruments are subject to the same analytical limitations as bench-top ED-XRF spectrometers. In addition to possessing less powerful X-ray tubes in terms of current and often voltage, decreasing the range of elements which can be optimally excited, pXRF spectrometers cannot generate a full vacuum, further reducing their ability to detect and quantify low-Z elements (see discussion in 2.3). Furthermore, non-destructive pXRF analysis of unprepared archaeological ceramics and sediments not only goes against conventional XRF wisdom but, this analytical short-cutting, introduces matrix effects and chemical contamination, from a variety of processes, which seriously limit pXRF spectrometry for unprepared archaeological specimens.

As discussed in Section 2.4, under the right conditions, a pXRF spectrometer can perform as well as a bench-top ED-XRF for most elements of interest for archaeological ceramic and sediment characterization studies. The notable exceptions and pXRF specific limitations are described below.

2.1.1. Low-Z elements

WD-XRF is the best XRF approach for measuring and quantifying low-Z elements. ED-XRF spectrometers are subject to limitations, such as Bremsstrahlung radiation and escape peaks, which affect detection and quantification of low-Z elements in particular. Although we will demonstrate in Section 2.3 that, under the right conditions, pXRF spectrometers can simulate the performance of bench-top ED-XRF instruments, there are two notable exceptions: P and Na.

Phosphorus, typically reported as phosphorus pentoxide (P_2O_5), is a low-Z element ($Z = 15$) commonly reported in pXRF characterization studies of archaeological ceramics and sediments. In ceramics and non-anthropogenic sediments, P is difficult to detect and quantify even in full vacuum, on a prepared sample, using a bench-top ED-XRF spectrometer (Fig. 2). Several factors contribute to the poor detection of P.

First, archaeological ceramics and non-anthropogenic sediments typically contain relatively low concentrations of P (<1 wt.%). This means that the number of characteristic X-ray generated is correspondingly small. In addition, the characteristic X-rays of P are low energy, with K lines at 2.013 and 2.142 keV, which means that they are readily (re)absorbed into the sample matrix and/or the detector and scattered as Bremsstrahlung radiation. Therefore, fewer P X-rays reach the detector than are excited, reducing the observed intensity of response for P. In combination, these two factors contribute to a P response too low for most detectors to accurately differentiate counts and background (Fig. 3).

A further complication is that the Ca escape peak at 1.950 keV creates a significant shoulder to the left of the P Kα line. In many pXRF spectrometers, a portion of the Ca escape peak X-rays are measured as P due to the inability of the software to deconvolute the two peaks. This inability results in false counts being reported for the P peak where none exist and leads to the calculation of false P concentrations (Fig. 4). In the example in Fig. 4, samples MS15BL-1-19-IVSD and MS15SDO-1-IVSD have similar P concentrations, 0.114 and 0.138 wt.% respectively, but significantly different Ca concentrations, ca. 19 and 0.7 wt.% respectively. Table 1 reports the raw and net counts for these two samples measured using the same pXRF spectrometer and analytical conditions. The Ca escape peak adds almost 24× the number of processed counts recorded as P. These results, in combination with the low concentrations of P in archaeological ceramics and non-anthropogenic sediments, suggest that P cannot be accurately measured by pXRF and that concentrations for P < 1 wt.% reported by pXRF should be treated with extreme caution.

As discussed, pXRF spectrometers cannot measure P at the concentrations typically found in archaeological ceramics and non-anthropogenic sediments. The same is also true for Na. Sodium X-rays are extremely low energy, Kα line at 1.041 keV, and so, to an even greater extent than other low-Z elements, are (re)absorbed into the sample matrix and/or detector and scattered as

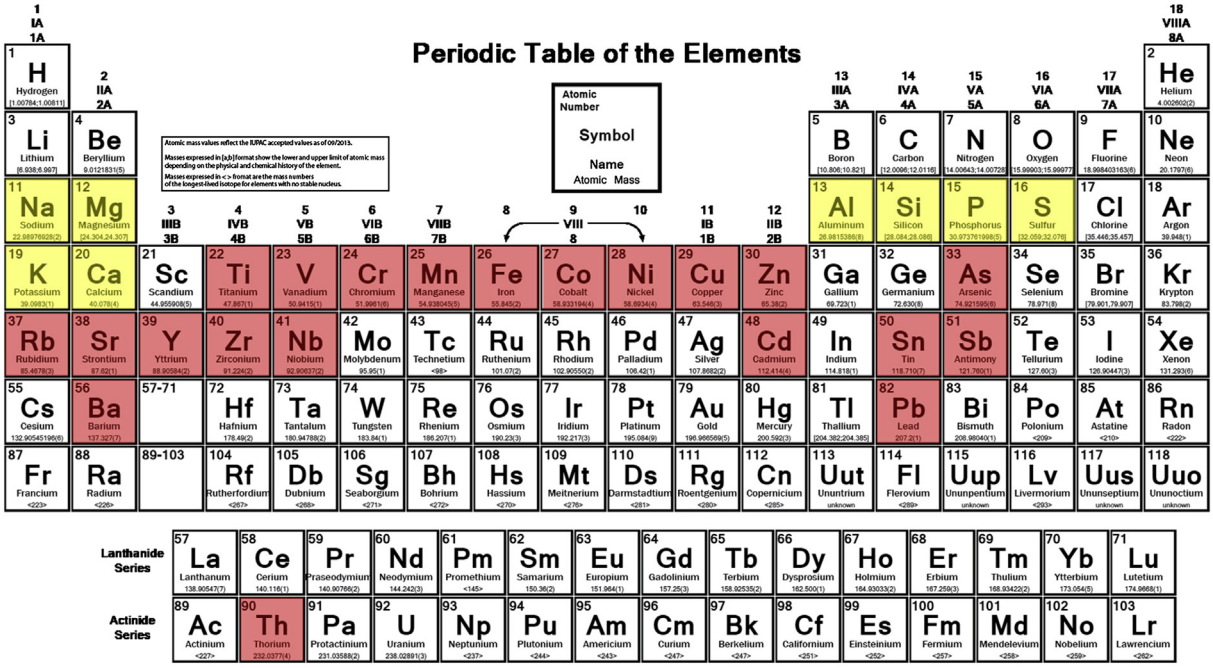

Fig. 1. Elements of interest for the analysis of archaeological ceramics and sediments typically analyzed by XRF.

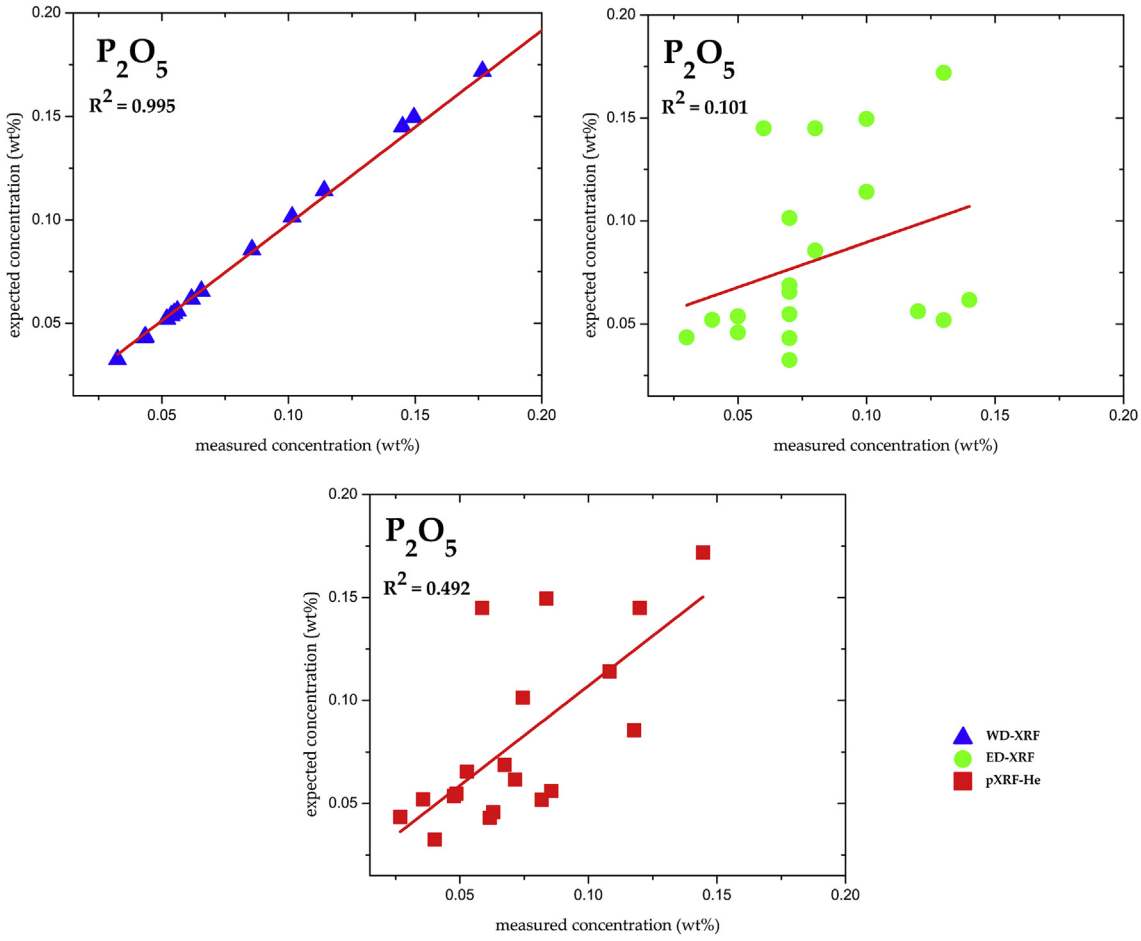

Fig. 2. Biplots of measured vs expected concentrations of phosphorus for 20 CRMs analyzed by WD-XRF (blue triangle), ED-XRF (green circle), and pXRF (red square). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

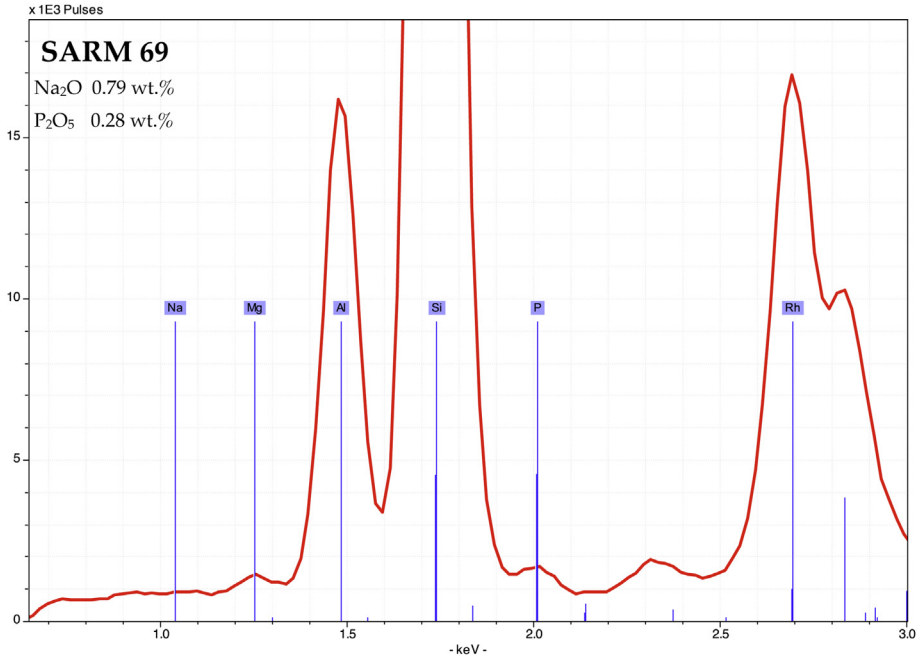

Fig. 3. pXRF spectrum illustrating the lack of response (recorded counts) for sodium and minimal response for P even under optimal analytical conditions.

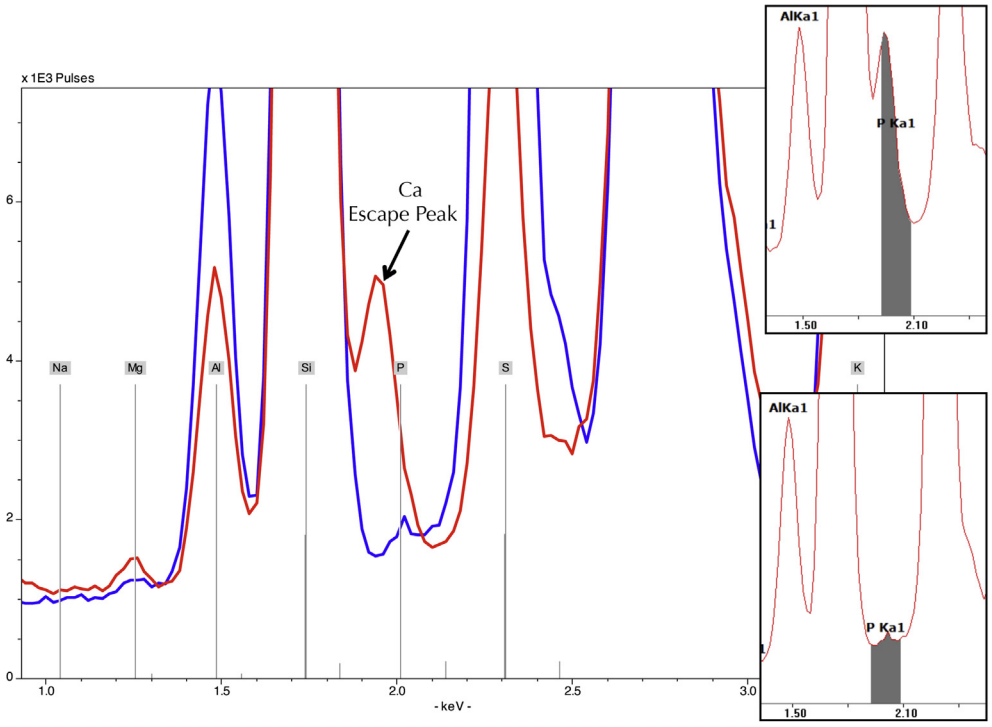

Fig. 4. pXRF spectrum illustrating the spectral overlay interference created by the escape peak of Ca onto the Kα line of P.

Bremsstrahlung radiation. Even at relatively high concentrations, ca. 3.5 wt.%, few Na X-rays reach and are counted by the detector; at the low concentrations typical of archaeological ceramics and sediments (≤3 wt.%), the response for Na is virtually invisible by pXRF. For example, in Fig. 3, the pXRF spectrum for SARM 69, with a recommended Na_2O concentration of 0.79 wt.%, has no visible peak at 1.041 keV. Therefore, like P, Na cannot be measured by pXRF at the concentrations typically found in archaeological ceramics and sediments.

All other low-Z elements have the potential to be measured and quantified as well by pXRF as by a bench-top ED-XRF (Fig. 8).

2.1.2. Low/mid-Z trace elements

Of the low/mid-Z trace elements (Z = 21–30), vanadium (V), chromium (Cr), cobalt (Co) and nickel (Ni) can only be measured semiquantitatively by pXRF due to spectral overlay interference and the low concentrations of these elements typical in archaeological ceramics and sediments. As illustrated in Fig. 5, detection and quantification of Ti, V, and Cr is complicated by spectral overlapping of the Kβ line of the lower Z element and the Kα line of the next higher Z element, for example V Kβ line overlays the Kα line of Cr. Additionally, in high iron (Fe) samples the escape peak of Fe (4.660 keV) overlaps the Kα line of Ti (4.508 keV). However, Ti can be present in archaeological ceramics and sediments at concentrations up to 3 wt.% TiO_2, whereas V and Cr are typically present only in the low 100 s ppm. The combined effect of the low concentration/small number of counts for V and Cr and interference from spectral overlay radiation is that these two elements can only be semiquantitatively measured by pXRF (Fig. 6), whereas Ti can be detected as well by pXRF as by a bench-top ED-XRF spectrometer (Fig. 8).

Detection and quantification of Co also is affected by spectral overlap interference, in this case the Kβ line of Fe, and typically low elemental concentrations in the sample material. However, for Co, it is the latter which most dramatically limits its detection and quantification. Although Co can occur naturally in archaeological ceramics and sediments in concentrations as high as 200–250 ppm, it more commonly is found at concentrations <100 ppm. At these lower concentrations (<150 ppm), the detector is unable to differentiate Co X-rays from background radiation (limit of detection or LOD)[1] and/or the Fe Kβ line, and so the element is not measured. As illustrated in Fig. 8, at concentrations ≥150 ppm pXRF instrument response to Co is both linear and accurate. However, these high Co concentrations are the exception rather than the rule in archaeological ceramics and sediments.

Detection and quantification of Ni in archaeological ceramics and sediments by pXRF is complicated. Nickel, typically present in archaeological ceramics and sediments at concentrations <70 ppm in North and South America and at concentrations as high as 150 ppm in other parts of the world, can be affected by spectral overlap radiation of the Cu Kα line onto its Kβ line. However, filters also appear to be a factor in Ni detection and quantification. As we discuss in Section 2.4, on our pXRF the best filter for measuring and quantifying trace elements in a clay/sediment matrix is composed of Al, Ti and Cu. Filters of other compositions, for example in Fig. 6 the bench-top ED-XRF uses a palladium (Pd) filter and the

Table 1
Concentrations of P and Ca for the two samples in Fig. 6. Notice how the Ca escape peak is measured as P counts.

Sample	P_2O_5			CaO
	Concentration	Raw counts	Net counts	Concentration
MS15BL-1-19-IVSD	0.114 wt.%	27,040	12,000	19.037 wt.%
MS15SDO-1-IVSD	0.138 wt.%	13,824	521	0.709 wt.%

[1] Limit of Detection (LOD) is defined by the International Union of Pure and Applied Chemistry (IUPAC) as the elemental concentration at which an instrument in no longer able to differentiate between signal and noise (i.e. the element and background).

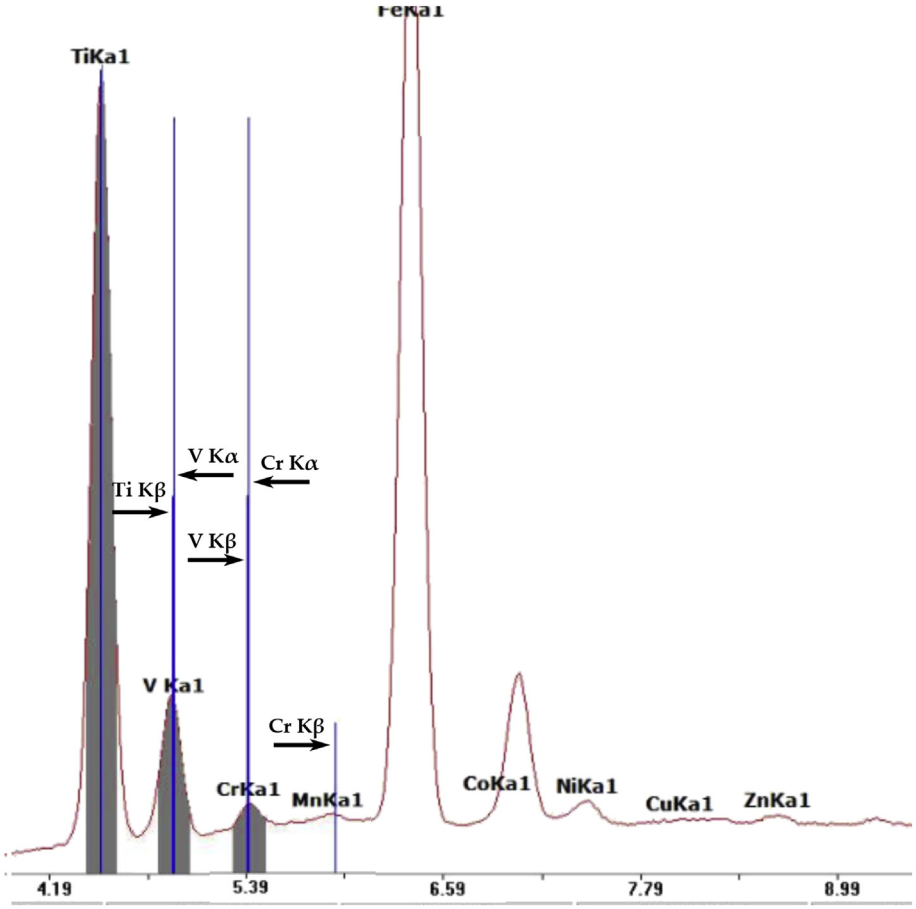

Fig. 5. pXRF spectrum illustrating overlapping K line radiation.

'mudrock' pXRF protocol (discussed below) uses an Al:Ti filter, do not appear to affect the quality of Ni measurement significantly. Although we cannot explain this phenomenon to our satisfaction, we believe it is a filter effect and, as a result, that low concentration Ni measurements, like Co measurements, should be considered semiquantitative in a ceramic or sediment matrix.

Most other low/mid-Z trace elements of interest for compositional analysis of archaeological ceramics and sediments and elements with L line energies measured in the low/mid-Z range (e.g., Cu, Zn, Rb, Sr, Y, Zr, Nb, Th, and Pb) can be measured as accurately and precisely by pXRF as by bench-top ED-XRF instruments (Fig. 9), under appropriate analytical conditions.

2.1.3. High-Z trace elements

There are many higher energy elements of potential interest for compositional analysis of archaeological ceramics and sediments, including barium and a few lanthanide group elements. However, barium (Ba) is really the only higher energy element that can be measured well by ED-XRF. The K lines of Ba are 32.065 and 36.553 keV, placing their optimal excitation energies >50 kV: out of range for many pXRF spectrometers. Ba L lines, on the other hand, at 4.467 and 4.828 keV, are easily excited by pXRF. However, Ba L lines overlap with the K lines of Ti and V (Fig. 7). Likewise, for the few lanthanide group elements that it might be possible to measure by pXRF, assuming they are present at higher concentrations, their L lines overlap the K lines generated by many of the first row transition metals, and/or their K lines are barely visible above background and cannot be measured or quantified with accuracy or precision.

2.2. Calibration and matrix matching

Laboratory based XRF spectrometers typically do not come calibrated. Scientists operating these instruments are responsible for developing calibrations appropriate for the sample material of interest. Conversely, most pXRF instruments are calibrated by the manufacturer and it is oftentimes not possible for the user to create a matrix matched empirical calibration. Some software packages allow users to adjust preset elemental correction factors/calibration coefficients based on the manufacturer's measured and expected concentrations. While modifying correction factors might improve the accuracy of reported concentrations within a specific dynamic range, they may or may not improve the accuracy of reported concentrations outside that range. Alternatively, users can correct their data offline by developing regressions based on the measurement of multiple CRMs and applying these equations to their unknown samples. However, we underscore that the adjustment of correction factors and/or calibration coefficients is not in any way comparable to calibrating an instrument and/or creating a true empirical matrix-matched calibration.

Most, if not all, pXRF manufacturers offer a 'soils' or sediments mode/calibration. These 'soils' calibrations tend to focus on heavy metals related to environmental issues and often do not include either the elements of interest for archaeological ceramics and sediments and/or the dynamic range necessary for their accurate quantification. In addition, the details of these calibrations, such as analytical range, matrix of the standards/reference materials used to develop it, and even the composition of the filters, are oftentimes considered proprietary and are not readily available to

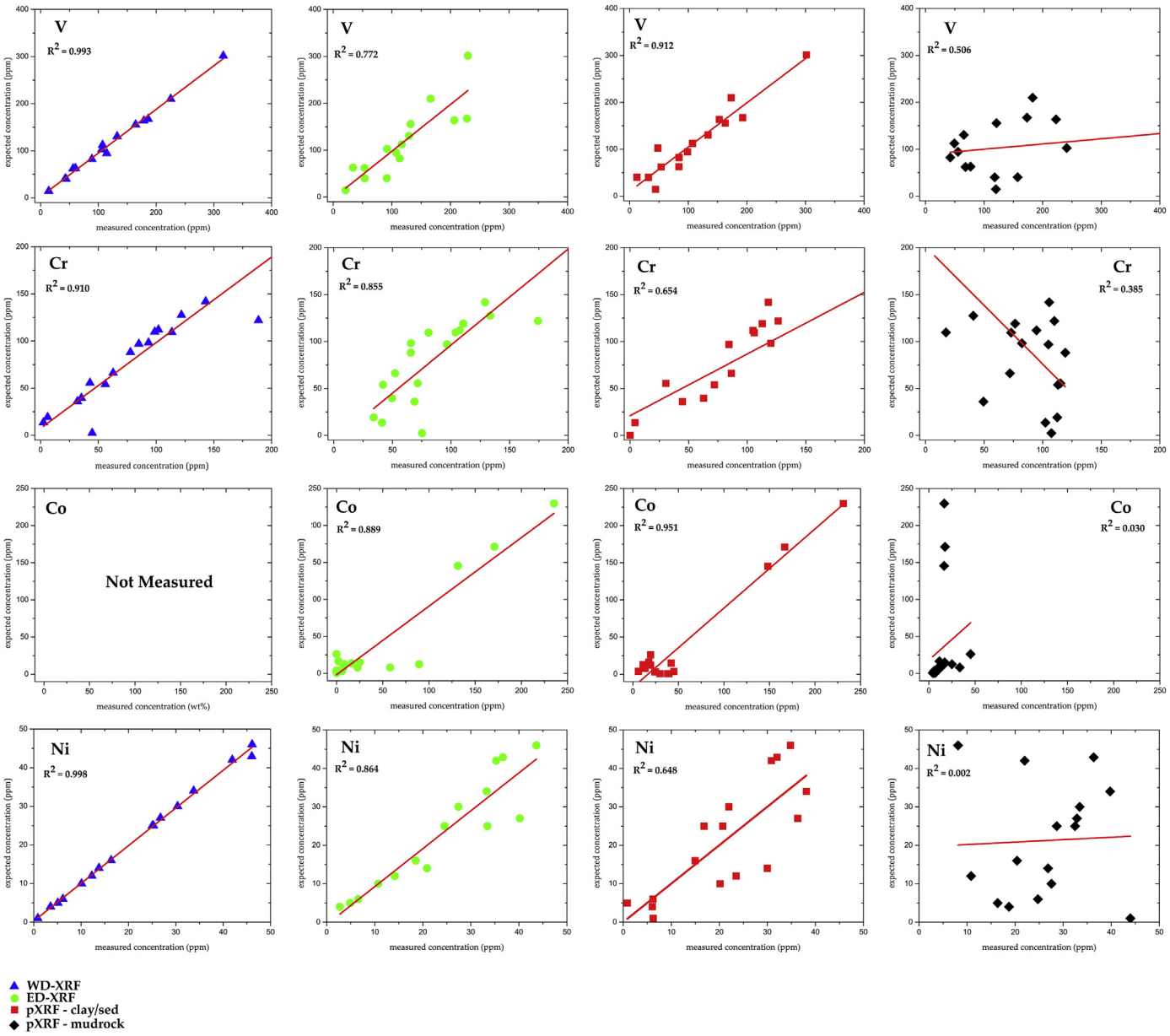

Fig. 6. Biplots of measured vs expected concentrations of V, Cr, Co and Ni for 20 CRMs analyzed by WD-XRF (blue triangle), ED-XRF (green circle), pXRF clay/sediment calibration (red square), and pXRF 'mudrock' calibration (black diamond). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the user (e.g., Frahm et al., 2014). Issues with this 'black box' approach are myriad. In a future paper, we address in detail issues of pXRF instrument response and the accuracy and precision of these factory calibrations for compositional analysis of archaeological materials (Hunt and Speakman, in preparation). For the purposes of this exercise, however, we are concerned with the optimization of pXRF performance for archaeological ceramics and sediments.

The three critical aspects of a calibration are: (a) that it include all the elements of interest in the sample material; (b) that is has a dynamic range appropriate for the elemental concentrations typical or expected in the sample material; and (c) that the certified reference materials (CRMs) or standards used to build the calibration have a similar matrix to the samples. The importance of each of these factors should be self-evident and are discussed here only briefly.

Not including fundamental parameters algorithms, an element can only be quantified, that is concentrations calculated from spectral counts or pulses, if there is a reference database of counts/concentrations for that element. Although an XRF spectrum records all the fluorescence energy emitted by a sample, without a reference calibration the analytical software cannot associate that energy with the characteristic emission of a particular element and/or calculate the elemental concentration from the measured fluorescence. Therefore, a calibration must contain all the potential elements of interest for a given material. For archaeological ceramics and sediments, elements of interest 'visible' by pXRF include Mg–Si, K–Ca, Ti–Zn, Rb–Nb, and Th. Other potential elements of interest, such as P, S and Cl, are oftentimes not visible due to their low concentrations in archaeological ceramics and sediments, spectral overlap, and/or because of peaks resulting from the anode material in the X-ray tube.

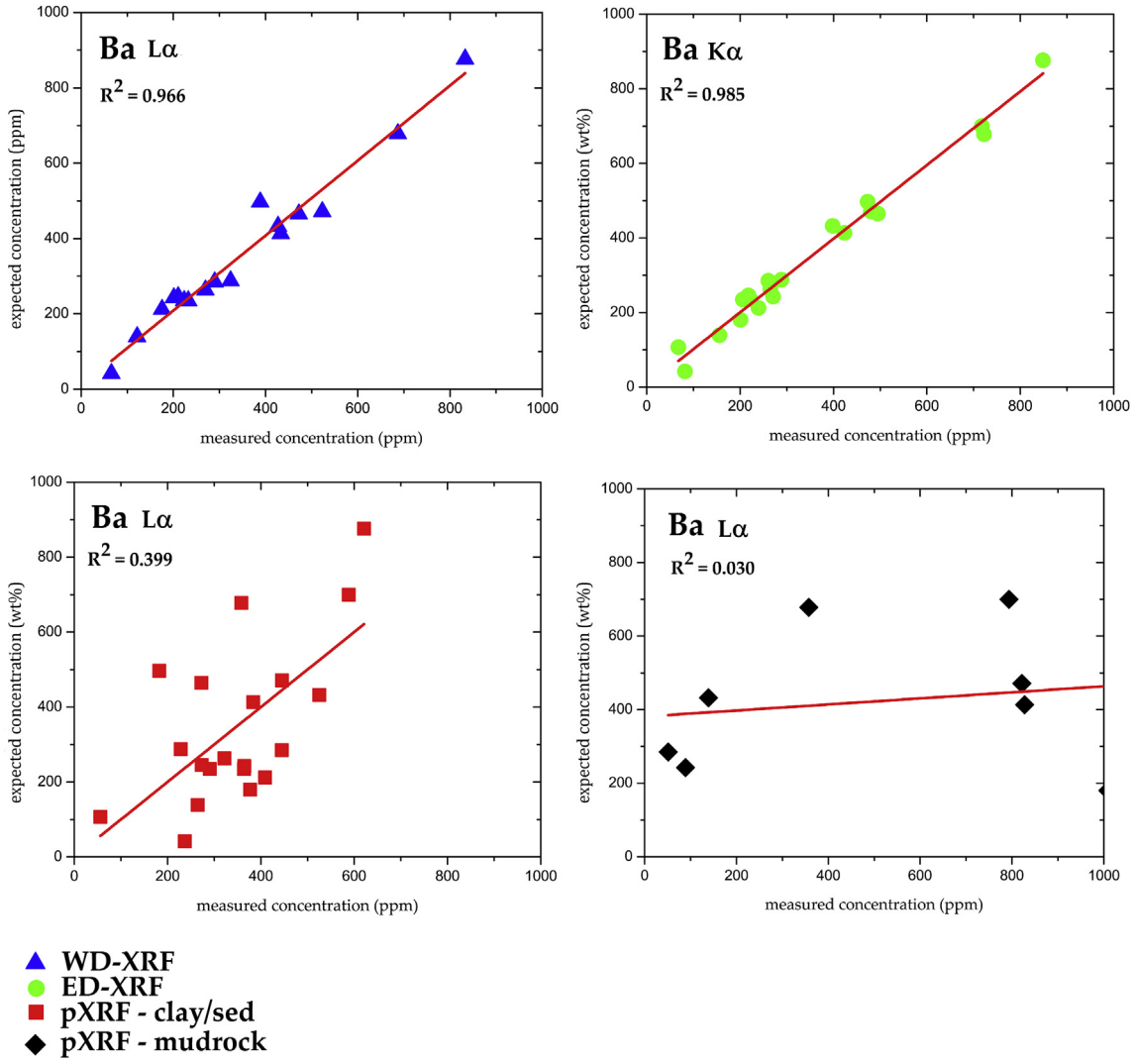

Fig. 7. Biplots of measured vs expected concentrations of Ba for 20 CRMs analyzed by WD-XRF (blue triangle), ED-XRF (green circle), pXRF clay/sediment calibration (red square), and pXRF 'mudrock' calibration (black diamond). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

One of the factors affecting the accuracy of reported elemental concentrations is the dynamic or analytical range of the calibration for that element. Each CRM/standard in an elemental calibration provides the analytical software with a reference point consisting of the number of measured or normalized counts and the elemental concentration associated with these counts. Most analytical software assumes a directly proportional relationship between counts and concentration, i.e., as the number of counts increases so does concentration. This relationship is used by the software to create a model, usually linear, of measured counts and concentration. When the software is presented with measured counts for an element of unknown concentration, it uses this model to predict where those counts are located within the parameters of the model, between the high and low reference concentrations, and calculates the elemental concentration associated with that number of counts. Although calibrations can calculate concentrations outside of the high-low reference range, calculated concentrations are less accurate the farther away the model moves from a reference standard. Therefore, it is important when building a calibration that the dynamic range of each elemental simulates the expected compositional range of the sample material.

Matrix matching the standards and sample material is, perhaps, the most important consideration when building a calibration. X-rays attenuate, refract, and are absorbed differently by different materials in accordance with their density, chemical composition, and crystal structure. The interaction between a material and excitation/emission X-ray radiation affects its fluorescence response and the detection of that response as much as, if not more than, the accelerating voltage and current of the excitation energy and/or detector resolution. Matrix effect(s) is the blanket term used to explain these interactions. The three most important interactions for pXRF analysis of archaeological ceramics and sediments are: grain size effects, heterogeneity, and mineralogical effects. Grain size effects result in the differential penetration of the X-rays into the sample: X-rays are able to pass through smaller grains, exciting deeper into the sample and generating a more representative fluorescence response; larger grains may exceed the penetration depth of the X-ray so that only a single phase in the sample is excited. Heterogeneity of the material is one of the most commonly discussed issues in compositional analysis and results from the inhomogeneous mixing of phases in a materials so that compositional analysis of the material is not 'representative' of its total chemical content and/or composition of the sample varies

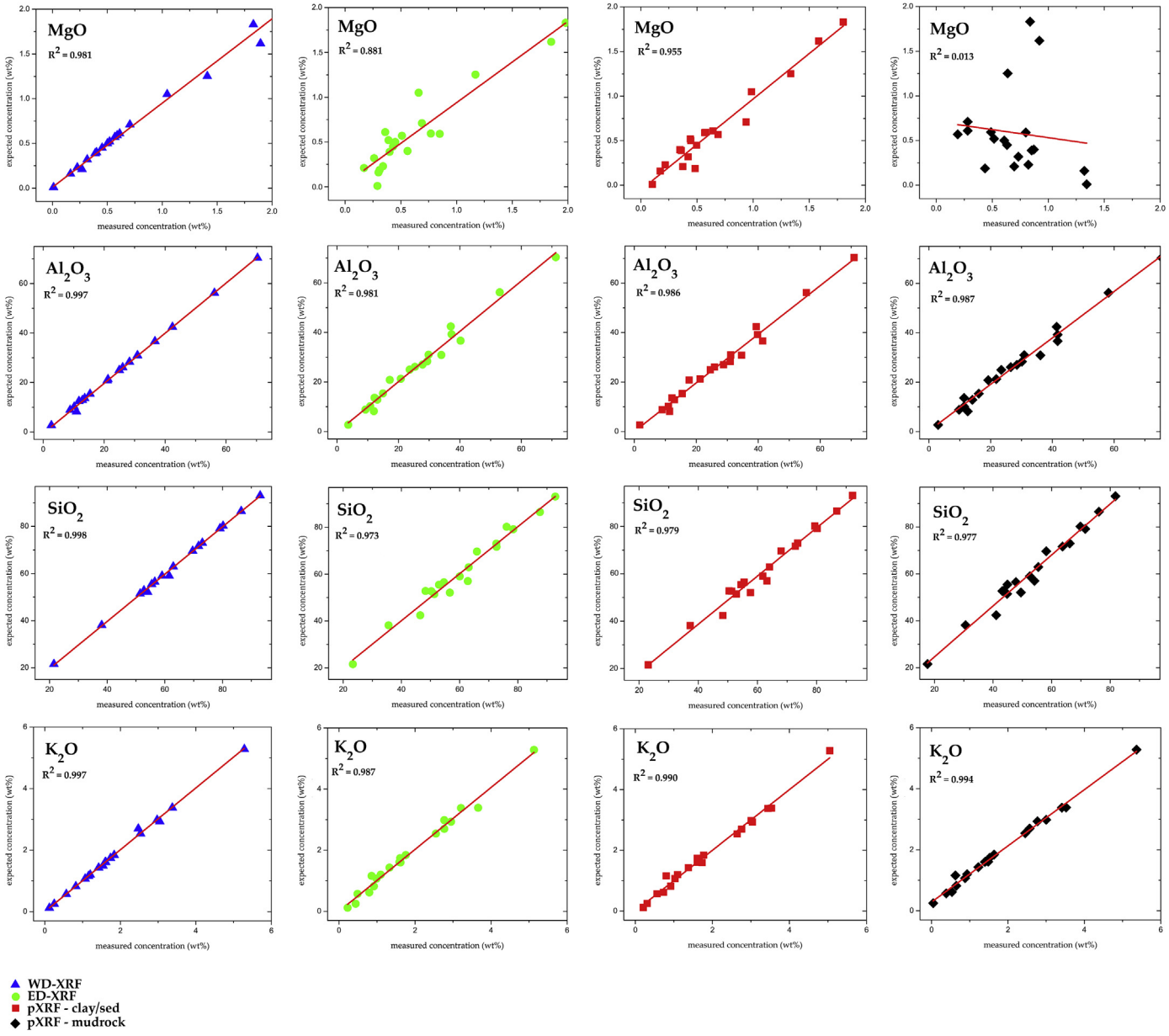

Fig. 8. Biplots of measured vs expected concentrations of the low-Z elements for 20 CRMs analyzed by WD-XRF (blue triangle), ED-XRF (green circle), pXRF clay/sediment calibration (red square), and pXRF 'mudrock' calibration (black diamond). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

across the sample area (see Fig. 3 in Speakman et al., 2011). Mineralogical effects result from differences in crystal structure, composition, and density of different mineral phases which lead to the differential attenuation of excitation and emission X-rays and they pass through these phases; a highly attenuating phase may prevent excitation X-rays from exciting other phases due to loss of energy and/or prevent lower energy emission X-rays from exiting the sample.

Grain size and mineralogical effects and heterogeneity are significantly reduced when the analyte is prepared as a pressed powder pellet or fused bead. Therefore, a calibration built using CRMs prepared as pressed pellets is only appropriate for sample material prepared the same way: 'matrix matched' to reduce matrix effects. For this reason, we believe that fully quantitative analysis of archaeological ceramics and sediments by ED-XRF can only be conducted using pressed pellets and/or fused beads; data resulting from the analysis of whole sherds and loose sediments cannot be considered fully quantitative.

The procedure for making pressed pellets is simple and inexpensive: at CAIS 10 g of powdered sample (ground to approximately 10 μm or the consistency of talcum powder) is homogenized in an agate mortar with a binding agent (we use 2 mL of Elvacite dissolved in acetone) and pressed into a 40 mm aluminum sample cup at 23–25 PSI for 3 min. Another benefit of pressed pellets is that the die press ensures a uniformly flat analytical surface eliminating matrix effects related to surface topography (which are admittedly minor in ED-XRF). All of the CRMs used in this study were prepared as pressed pellets according to this protocol.

An important consideration for matrix matching a calibration to the sample material is the matrix or material itself. Reliable analysis of copper alloys requires a calibration built using copper alloy CRMs, reliable analysis of obsidian requires a calibration built using

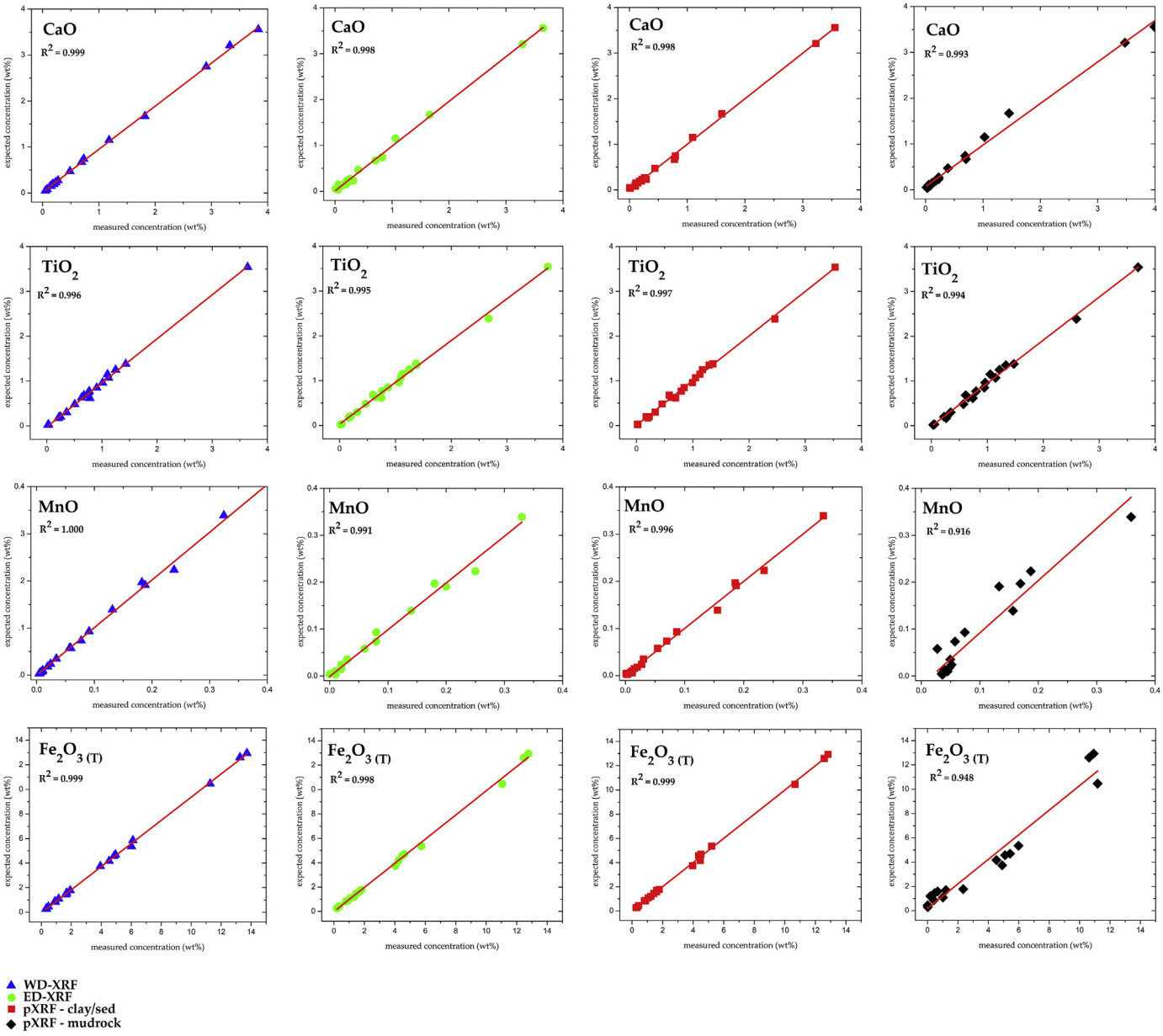

Fig. 8. (*continued*).

obsidian CRMs, and reliable analysis of ceramic and sediments requires a calibration built using clay and sediment CRMs. Archaeological ceramics and sediments are often considered comparable to rocks: both are formed by geologic processes, composed of discrete mineral phases, and have similar geochemistry. However, sediments and rocks differ in several significant ways which prevent rocks, even sedimentary rocks such as mudstones, from being a 'matrix match' for archaeological ceramics and sediments.

Rock is substantially denser and contains significantly less structural water than sediments and clays. Preparing sample material as pressed pellets eliminates matrix issues related to density; however, there remains the issue of structural water and hydrous mineral phases. During the lithification process, sediments are compacted, pore space is reduced, and some of the structural water contained in the mineral phases is released. This water may carry mineral components and/or soluble phases in solution, often precipitating as new mineral phases in the remaining pore space cementing the sediments into rock. Sediments and clays, on the other hand, have not been through the lithification process and contain their original water content both as structural water and hydrous phases. Drying sediment samples prior to pressing them into pellets removes water absorbed by the sediments/clay minerals but is typically at temperatures too low to drive off the structural water. Fired clay or ceramic has typically reached temperatures high enough for long enough to cause dehydration and dehydroxylation. However, during the subsequent cooling of the vessel, its use and/or deposition, ceramics absorb water into their void space and minerals rehydroxylate. Thus, archaeological ceramics and sediments have a higher structural water content than sedimentary rocks.

Twenty CRMs (Table 2), 6 sediments and 14 clays, were prepared as pressed pellets and analyzed using a Bruker Tracer IIIV pXRF spectrometer and elemental concentrations were calculated using a clay/sediment calibration developed by CAIS and a manufacturer's

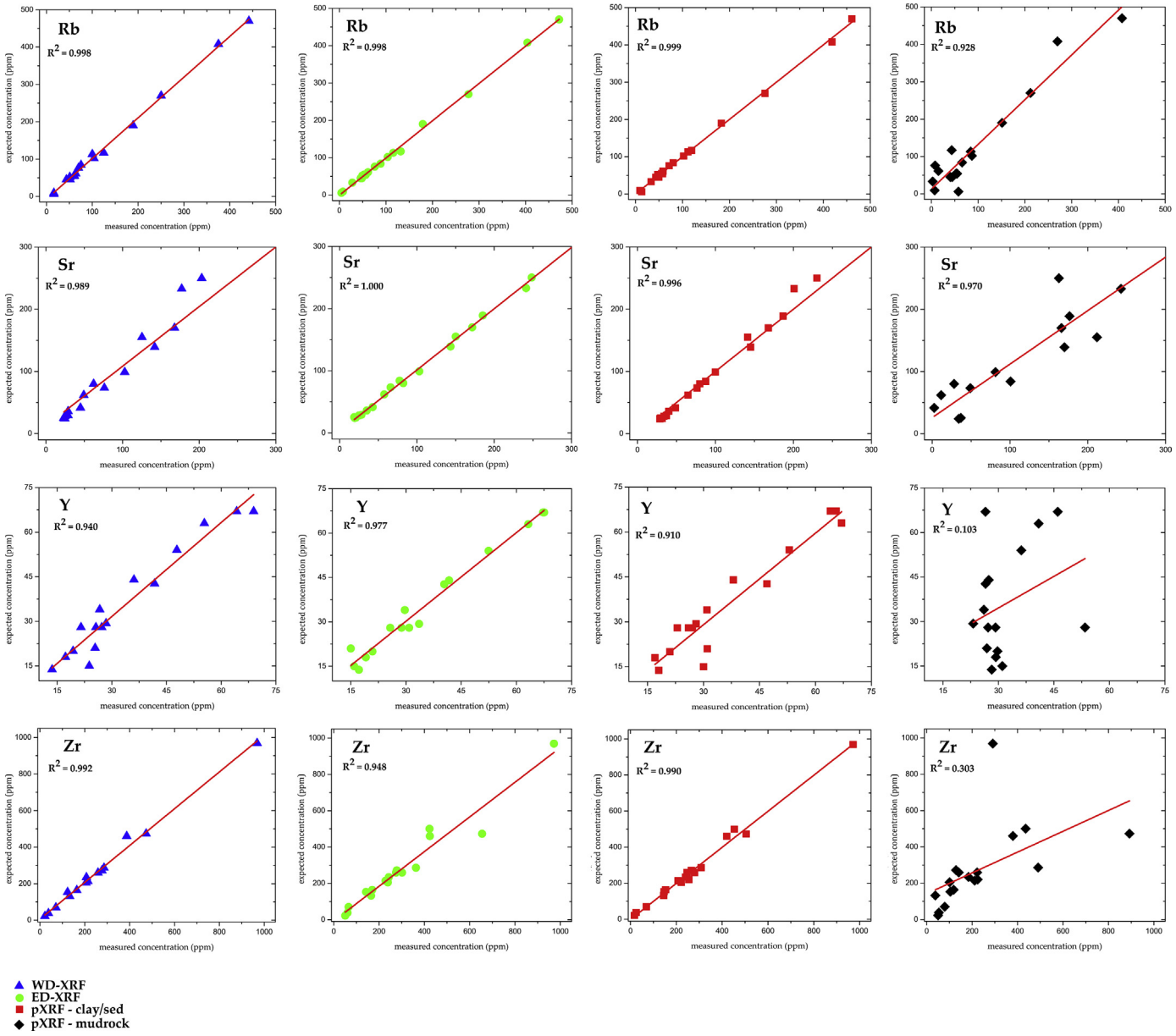

Fig. 9. Biplots of measured vs expected concentrations of the mid-Z elements for 20 CRMs analyzed by WD-XRF (blue triangle), ED-XRF (green circle), pXRF clay/sediment calibration (red square), and pXRF 'mudrock' calibration (black diamond). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

recommended factory calibration for ceramics and soils, hereafter referred to as the 'mudrock' calibration (Table 3). The 'mudrock' calibration appears to be the equivalent of what is oftentimes referred to as the 'soils' mode by other manufacturers and is Bruker's recommended method for quantitative compositional analysis of archaeological ceramics and sediments. Therefore, all 20 CRMs were analyzed according to the manufacturer's protocol for the 'mudrock' calibration and the protocol developed by CAIS for the clay/sediment calibration (Table 4).

As illustrated in Fig. 8, the 'mudrock' calibration is unable to measure magnesium (Mg), manganese (Mn), and Fe as well as the clay/sediment calibration. We believe that for Mg this is a result of analytical protocol: Mg is best detected in the presence of helium (He) or full vacuum (Section 2.3). Fig. 6 demonstrates that, although neither pXRF calibration analyses V, Cr, Co or Ni adequately, the clay/sediment calibration generates a linear response to changes in concentration whereas the 'mudrock' calibration appears to 'collapse'. The non-linear response of the 'mudrock' calibration for V, Cr, Co and Ni may result from an inadequate dynamic range for these elements in the calibration or be caused by matrix effects. The latter appears to be the cause of the poor performance of the 'mudrock' calibration for the mid-Z trace elements Rb, Sr, Y, Zr, Nb and Th: elements typically quantified easily by pXRF.

Linearity of instrument response is an indication of how accurately the analytical software is able to calculate elemental concentrations using a particular calibration. Table 5 presents the results of the compositional analysis of CRM SARM 69 using the 'mudrock' and clay/sediment calibrations. SARM 69 was selected

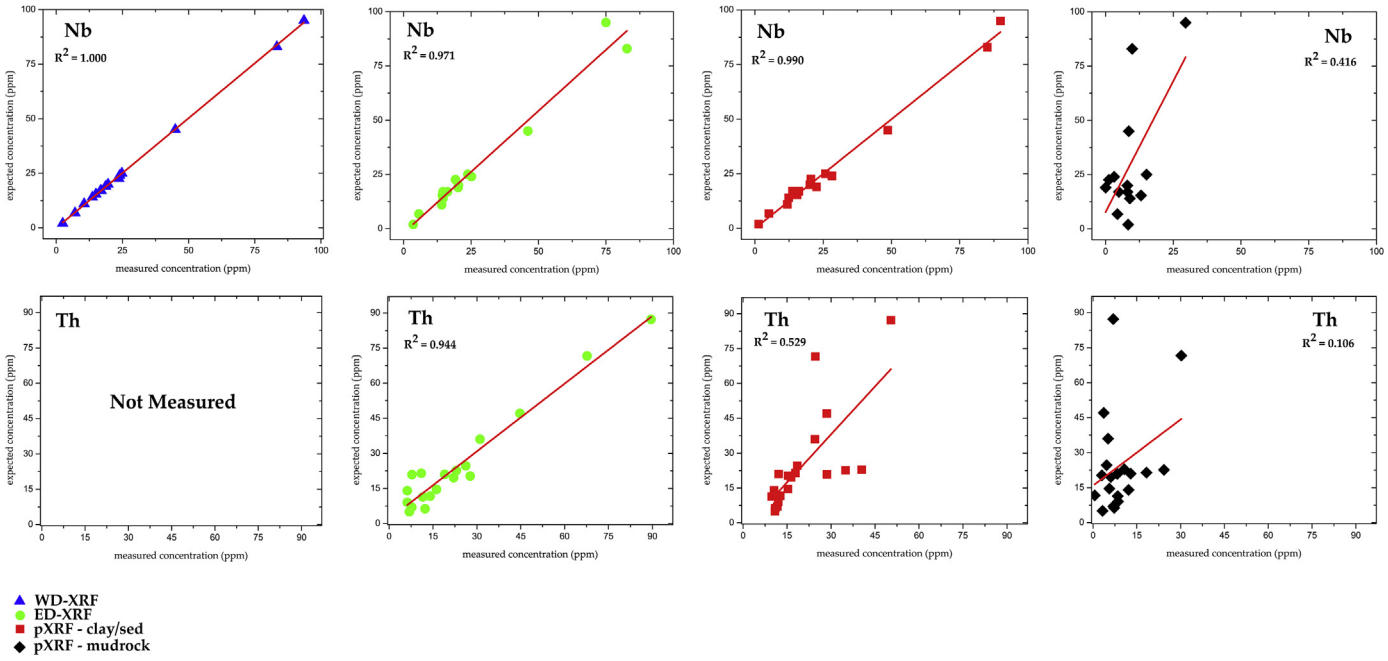

Fig. 9. (*continued*).

because it is composed of fired potsherds and was not used to build the clay/sediment calibration. Analyses were run in triplicate and measurement precision for each element is reported as percent relative standard deviation (% RSD). The 'mudrock' and clay/sediment calibrations have similar precision for the low-Z elements, however, the 'mudrock' calibration calculates inaccurate concentrations for most elements except Mn. Performance of the two calibrations for V, Cr, Co, and Ni is variable. The 'mudrock' calibration grossly underreports the Cr content of SARM 69; the clay/sediment calibration also underreports Cr but it is an entire order of magnitude closer to the certified value. Both calibrations underreport Ni and under/overreport V by the similar amounts. The clay/sediment calibration calculates highly accurate concentrations for the mid-Z trace elements performing almost identical to the benchtop ED-XRF. The 'mudrock' calibration also calculates accurate concentrations for these elements, however, they are not as close to the certified or ED-XRF values as those generated by the clay/sediment calibration.

Table 2
The 20 CRMs used to evaluate performance of clay/sediment and 'mudrock' pXRF calibrations.

Clay/ceramic	Sediment
NIST 679	NIST 8704
NIST 97b	GBW 07310
NIST 98b	GBW 07311
NCS DC 60102	GBW 07312
NCS DC 60103	GBW 07302
NCS DC 60104	GBW 07405
NCS DC 60105	
NCS DC 61101	
Č-137	
Č-138	
Č-139	
NCS HC 14807	
NCS HC 14808	
NCS HC 14809	

2.3. Helium vs. vacuum

X-rays, particularly low energy X-rays, attenuate and are absorbed by air. Bench-top XRF spectrometers operate under full vacuum to eliminate the interference of air with the detection of low-Z elements. Some pXRF spectrometers have the ability to generate partial vacuum: the space between the window and the detector is evacuated. However, during this process, the window is pulled into the chamber creating a slight concavity between the window and sample surface into which air is (re)introduced to the system.

Air is composed primarily of nitrogen (78%) and oxygen (20%) but also contains water vapor (1%) and argon, carbon dioxide, dust and pollen (<1%). Most of these components are 'invisible' by pXRF; argon is not. In Fig. 10, the argon peak is clearly visible in the

Table 3
Clay and sediments CRMs used to build the clay/sediment pXRF calibration at CAIS.

Clay/ceramic	Sediment
NIST 679	NIST 2710
NIST 97b	NIST 8604
NIST 98b	GBW 07310
NCS DC 60102	GBW 07311
NCS DC 60103	GBW 07312
NCS DC 60104	GBW 07302
NCS DC 60105	GBW 07405
NCS DC 61101	LKSD-1
Č-137	LKSD-2
Č-138	LKSD-3
Č-139	LKSD-4
NCS HC 14807	STSD-1
NCS HC 14808	STSD-2
NCS HC 14809	STSD-3
MURR New Ohio Red	STSD-4
MURR Ohio Gold	MESS-2
MURR Talc-free	PACS-2
MURR Terra Cotta	SARM 46
	SARM 52

Table 4
Analytical protocols used to evaluated performance of clay/sediment and 'mudrock' PXRF calibrations.

	CAIS Clay/Sediment calibration	Bruker mudrock calibration
Low Z elements	200 s count time	180 s count time
	15 kV/20 μA	15 kV/20 μA
	He flow	Vacuum
	No filter	No filter
Mid Z elements	200 s count time	60 s count time
	40 kV/30 μA	40 kV/30 μA
	'green' filter:	'yellow' filter:
	300 μm Al/20 μm Ti/150 μm Cu	300 μm Al/20 μm Ti

spectrum collected in air/no vacuum. This spectrum also illustrates that in air, with the exception of the two low-Z elements present in high concentration (Al and Si), no counts are recorded for elements below the Rh Compton peak, Z < 19. Under partial vacuum, the argon peak is no longer visible, however X-rays for elements Z < 13 are not recorded (Fig. 10). The spectrum collected with helium (He) flowing through the chamber/window, displacing all the air between the detector and sample surface, enables the detector to record counts for Mg (Z = 12) (Fig. 10). Notice that Na is not visible by pXRF using any of these analytical conditions.

From this, we conclude that the presence of air between the sample surface and window under partial vacuum, while not enough to generate a visible argon peak, is enough to interfere with the detection of Mg Therefore, Mg concentrations calculated by pXRF under partial vacuum should be considered suspect.

Table 5
Expected and measured concentrations for SARM 69 using INAA, WD-XRF, ED-XRF, pXRF clay/sediment calibration and pXRF 'mudrock' calibration. Major elements are reported as wt%; minor and trace elements reported as ppm unless otherwise stated. Uncertified concentrations reported in brackets. Concentrations reported in shaded cells are informational only. Expected and measured concentrations for major elements reported as elements were converted to oxides using the conversion factors in Glascock (2006). These values are marked with an asterisk (*).

Element	Cert	INAA ($n = 5$)	WD-XRF ($n = 10$)	ED-XRF ($n = 10$)	pXRF Clay/Sed ($n = 3$)	pXRF mudrock ($n = 3$)
MgO	1.85		1.88	1.46	1.16	11.84*
			0.27 %RSD	6.43 %RSD	3.32 %RSD	2.60 %RSD
Al_2O_3	14.4	14.26	14.39	13.89	14.22	14.94*
		1.80 %RSD	0.14 %RSD	0.21 %RSD	0.29 %RSD	0.38 %RSD
SiO_2	66.6		65.88	65.18	67.50	55.04*
			0.09 %RSD	0.05 %RSD	0.19 %RSD	0.36 %RSD
K_2O	1.96	1.89	1.97	2.04	2.07	3.69*
		10.40 %RSD	0.21 %RSD	0.80 %RSD	0.40 %RSD	0.33 %RSD
CaO	2.37	2.40	2.41	2.29	2.22	4.04*
		7.80 %RSD	0.28 %RSD	0.45 %RSD	0.39 %RSD	0.19 %RSD
TiO_2	0.777	0.77	0.776	0.77	0.71	1.10*
		8.30 %RSD	0.36 %RSD	0.59 %RSD	0.73 %RSD	0.77 %RSD
MnO	0.13	0.14	0.129	0.13	0.12	0.13*
		4.40 %RSD	0.63 %RSD	3.62 %RSD	1.36 %RSD	1.66 %RSD
Fe_2O_3 (T)	7.18	7.01	7.33	6.78	6.48	8.69*
		0.90 %RSD	0.14 %RSD	0.26 %RSD	0.47 %RSD	0.20 %RSD
Ba	518	504	521	505	426	2216
		8.60 %RSD	2.04 %RSD	2.24 %RSD	3.11 %RSD	27.58 %RSD
Co	28	26	n. m.	9	<16	22
		0.90 %RSD		111.65 %RSD		8.98 %RSD
Cr	223	213	199	164	167	81
		1.60 %RSD	0.68 %RSD	1.81 %RSD	1.61 %RSD	1.85 %RSD
Nb	(9)		9	8	9	7
			2.94 %RSD	6.90 %RSD	4.28 %RSD	3.28 %RSD
Ni	53	66	50	39	36	41
		143.50 %RSD	1.20 %RSD	7.32 %RSD	12.47 %RSD	1.85 %RSD
Rb	(66)	68	72	62	61	57
		3.90 %RSD	0.53 %RSD	3.30 %RSD	3.06 %RSD	4.07 %RSD
Sr	(109)	85	109	102	102	107
		137.00 %RSD	0.33 %RSD	2.30 %RSD	1.22 %RSD	2.81 %RSD
Th	(9)	9	n. m.	7	8	6
		3.60 %RSD		0.01 %RSD	8.74 %RSD	2.09 %RSD
V	(157)	160	154	137	120	190
		4.20 %RSD	2.08 %RSD	12.83 %RSD	0.98 %RSD	2.44 %RSD
Y	(29)		29	29	30	31
			1.50 %RSD	2.77 %RSD	1.53 %RSD	3.60 %RSD
Zr	(271)	208	260	254	268	248
		12.00 %RSD	0.27 %RSD	3.26 %RSD	0.16 %RSD	0.82 %RSD

2.4. pXRF optimization for archaeological sediments and ceramics

The ability to generate accurate and reliable compositional data for archaeological ceramics and sediments by pXRF requires a matrix matched calibration and a material specific analytical protocol. A matrix matched calibration requires, not only that the calibration standards and sample material be of the same type, i.e., both clay/sediments, but that the calibration standards and sample material be prepared the same way, i.e., as pressed pellets. Analysis of unprepared samples is not fully quantitative using a pXRF spectrometer because of the heterogenous nature of ceramic and sediment samples and matrix effects which prevent X-rays from interacting with the unprepared sample in the same way as the prepared calibration standards. This differential interaction or response to the X-rays causes the analytical software to over or undercalculate elemental concentrations in the sample material. Archaeologists sometimes abrade the surface of ceramic sherds to remove surface corrosion and treatments, such as slips, paints and glazes. These 'prepared' surfaces are, perhaps, more representative of the body/matrix material of the ceramic, however, they do not necessarily result in improved analytical accuracy because they do not address the matrix effects preventing accurate quantification of unprepared sherds by pXRF.

Optimal performance of pXRF spectrometers for archaeological ceramics and sediments also requires using appropriate analytical protocol. Given the low concentrations and energies of many of the elements of interest for archaeological ceramics and sediments, we optimized our performance using a count time of 200 s at 15 kV/20 μA in He to quantify low-Z elements and 200 s at 40 kV/30 μA using an Al:Ti:Cu filter to quantify mid-Z elements. Even using a matrix matched calibration and the above analytical protocol it is important to remember that Na, P and Ba L lines do not provide reliable numbers by pXRF and the analysis of V, Cr, Co and Ni appears to be semi-quantitative at best.

To summarize, optimization of pXRF spectrometers for the quantitative analysis of archaeological ceramics and sediments requires:

- a matrix matched calibration
- samples prepared as pressed pellets
- He flow for low-Z element detection
- an appropriate filter for mid-Z element quantification

A pXRF cannot accurately quantify Na, P, V, Cr, Co, Ni and Ba (using L lines) in archaeological ceramics and sediments at typical concentrations.

3. Conclusions

Commercially pXRF spectrometers, which have been around since the 1960's, were never really designed to be replacements for fully quantitative laboratory-based systems. Instead these instruments were designed to aid both scientists and non-scientists in the identification of hazardous materials and heavy metals in ground water and sediments, for quality control applications in industrial metals, mining, and recycling settings, and/or to

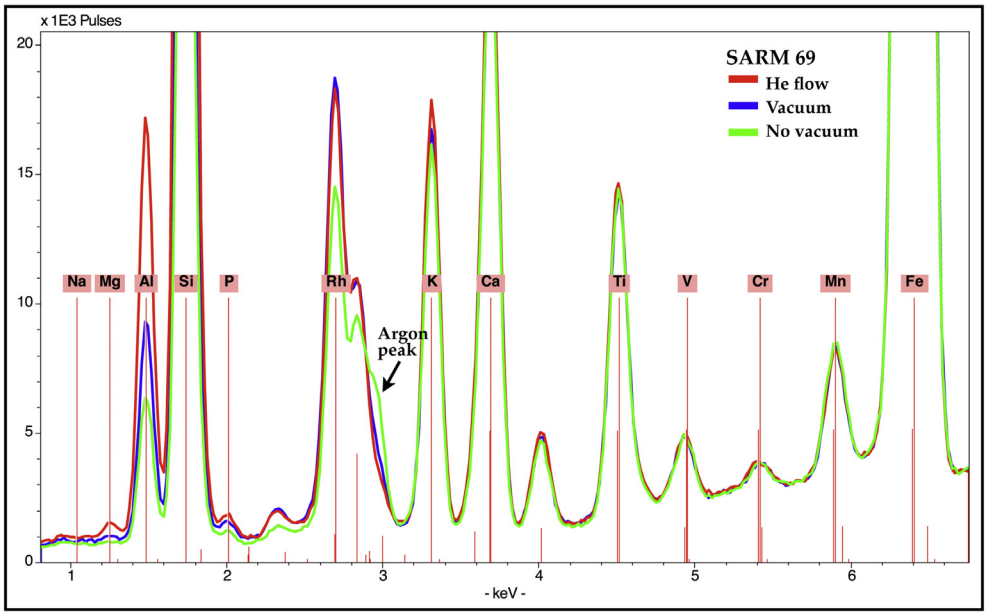

Fig. 10. pXRF spectrum comparing the detection of low-Z elements in air (green), under partial vacuum (blue) and with a helium flow (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

conducted specialized studies where sampling and/or export of samples was prohibitive. In contrast to earlier instruments which required specialized scientific knowledge, modern pXRF instruments have become little more than point-and-shoot devices requiring little-to-no specialized knowledge. The desire to use these instruments as an inexpensive short cut to quantitative bulk chemical analysis of archaeological materials, such as ceramics and sediments, is understandable and has resulted in numerous studies that would not have been possible otherwise. However, as discussed elsewhere (Speakman and Shackley, 2013), these analyses must be undertaken with caution and some degree of understanding of the physics involved. Unlike obsidian, for which it is relatively easy to determine a geologic/geographic source, provenance studies of ceramics are inherently challenging under the best of circumstances, using some of the more powerful analytical techniques (Hunt, 2012). It is primarily for this reason that archaeologists historically have not used XRF for provenance studies of ceramics; despite the large number of laboratory based ED- and WD-XRF spectrometers available at virtually every major institution, in most cases, XRF is insufficient for provenance determination of archaeological ceramics.

As demonstrated here, pXRF spectrometers, under the right conditions, such as a matrix matched calibration, He-flow and prepared samples, can perform similar, if not identical, to bench-top ED-XRF spectrometers for certain elements. However, a pXRF spectrometer cannot accurately quantify Na, P, V, Cr, Co, Ni and the L lines of Ba in an archaeological ceramic or sediment matrix at the concentrations in which they are typically present. As a result of these limitations, compositional analysis of archaeological ceramics and sediments by pXRF cannot and should not be considered a substitute for fully quantitative analysis by WD-XRF, INAA and/or ICP-MS.

References

Frahm, E., Schmidt, B., Gasparyan, B., Yeritsyan, B., Karapetian, S., Meliksetian, Kh, Adler, D.S., 2014. Ten seconds in the field: rapid Armenian obsidian sourcing with portable XRF to inform excavations and surveys. J. Archaeol. Sci. 41, 333–348.

Glascock, M., 2006. Tables for Neutron Activation Analysis, sixth ed. University of Missouri, Columbia, MO.

Hunt, A.M.W., 2012. On the origin of ceramics: moving toward a common understanding of 'provenance'. Archaeol. Rev. Camb. 27, 85–97.

Hunt, A.M.W., Speakman, R.J., Comparison of five portable X-ray Fluorescence (pXRF) spectrometers for archaeological and culture history applications: ceramics and sediments (in preparation)

Speakman, R.J., Little, N.C., Creel, D., Miller, M.R., Iñañez, J.G., 2011. Sourcing ceramics with portable XRF spectrometers? a comparison with INAA using Mimbres Pottery from the American Southwest. J. Archaeol. Sci. 38, 3483–3496.

Speakman, R.J., Shackley, M.S., 2013. Silo science and portable XRF in archaeology: a response to Frahm. J. Archaeol. Sci. 40, 1435–1443.