

Evaluating pXRF instrument performance using reference materials

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Introduction and objectives

The portable X-Ray fluorescence (pXRF) lab at the Wisconsin Geological and Natural History Survey (WGNHS) has recently focused its efforts on understanding instrument error and improving data quality. Building on work by Zambito and others (2016), this study provides a more in-depth assessment of instrument performance. We use the same reference material used by Zambito and others (2016), but apply a different method of analysis in order to document and define instrument error (accuracy and precision). This work will address current gaps in our suite of reference materials, which limit the understanding and applicability of our instrument. This is the first step in a comprehensive quantification of measurement uncertainty and development of standardized data correction methodology.

Reference materials, also known as 'standards' or 'controls', are geologic materials that have been analyzed with several high-quality analytical methods (e.g., ICP-MS, DCP, WD-XRF) to statistically determine their elemental concentrations. Because the reference materials have known elemental concentrations and uncertainties, they are an efficient and widely used tool to assess instrument performance and data quality (Bourke and Ross, 2016; Fisher and others, 2014; Hall and others, 2013; Potts and West, 2008; Rowe and others, 2012).

The pXRF provides fast, real-time, non-destructive, multi-element data at a relatively low cost with minimal sample preparation (Bourke and Ross, 2016; Durance and others, 2014; Gazley and others, 2014; Haas and others, 2017; Hall and others, 2013; Marsala and others, 2012; Stewart and Mauk, 2017; Zambito and others, 2017). The WGNHS uses geochemical data from the pXRF to characterize the composition of geologic materials such as bedrock drill core, water-well cuttings, and rock samples collected from outcrop. The data are primarily used qualitatively or semi-quantitatively to aid in stratigraphic correlation (e.g., Zambito and others, 2017; 2018). We define semi-quantitative as data that yields an approximation (or estimate) of the quantity; therefore, we currently use the pXRF data to provide an estimate of elemental concentrations on lithologic samples.

The WGNHS uses a Thermo Fisher Niton XL3t GOLDD+ hand-held energy dispersive (ED)-XRF instrument with a 50 kV X-ray tube source. The instrument is mounted on a stand beneath a lead-lined box with the beam pointing upwards though a port in the box. The X-rays emitted by the pXRF cover an area of approximately 10 mm² at the port. The instrument is equipped with four excitation filters that optimize the analyzers' sensitivity to various elements: (1) High range, used to optimize sensitivity for Ba through Ag, (2) Main range, used to optimize sensitivity for Mn through Bi, (3) Low Range, used to optimize sensitivity for Ti through Cr, and (4) Light range, used to optimize sensitivity for Mg through Sc (Thermo Fisher Scientific Niton Analyzers, 2010). Our pXRF instrument reports measurements on 43 elements, however, for this study we focus on 13 major rock-forming elements: aluminum (AI), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), phosphorus (P), sulfur (S), silicon (Si), strontium (Sr), titanium (Ti), zinc (Zn), and zirconium (Zr).

In this study we statistically compare how accurately and precisely our instrument measures elemental concentrations compared to reported reference values. The goal is to characterize

solely the error inherent to the instrument itself and not error introduced by external factors (e.g. sample preparation).

Methods

The data set used to quantify instrument performance includes all measurements collected between September 10, 2018, and February 28, 2020, on four pressed-powder reference materials using Niton's Test All Geo calibration mode. The Test All Geo mode is a calibration algorithm designed to optimize analysis of major, minor, and trace elements when analyzing a variety of lithologies (Thermo Fisher Scientific Niton Analyzers, 2010). It uses proprietary software that combines the Mining Mode algorithm, which uses fundamental parameters, and the Soils Mode algorithm, which uses Compton normalization (Potts and West, 2008; Thermo Fisher Scientific Niton Analyzers, 2010; Willis and Lachance, 2004).The reference materials include: NIST argillaceous limestone (**SRM-1d**), USGS Brush Creek Shale (**SBC-1**), USGS Devonian Ohio Shale (**SDO-1**), and USGS Carbonatite (**COQ-1**). All analyses in the data set were run for a total of 75 seconds (15 seconds on the Main, Low, and High filters, and 30 seconds on the Light filter) using the Test All Geo mode. Measurements were captured using the Thermo Scientific Niton Data Transfer software suite and downloaded to a .csv file format.

Preliminary data processing

The first step in the data processing workflow is data cleanup in order to remove data that are unrepresentative of the typical performance of our pXRF. The data are processed in Microsoft Excel to remove all timed-out runs, analyses with bad balances, drifted analyses, and anomalous outlying analyses. These data can result from incomplete analyses, poor quality analyses, internal issues (e.g. internal algorithms, which are factory-installed calibrations that convert elemental peak intensities, measured by the instrument, to concentrations of various elements), and external issues with the instrument or reference materials (e.g. contamination, poor placement on analyses port).

Timed-out runs and bad balances are two ways that bad data are generated. They are influenced by the instrument make and model, easy to identify, and removed from the data set prior to data manipulation. Analyses were programmed to run for 75 seconds. Based on previous published and unpublished studies by the WGNHS and others (e.g. Newlander and others, 2015) a 75-second run time is optimal for our current use of the pXRF data. Extending the run time to 90 or 120 seconds does not increase the precision to a degree that justifies the reduced number of samples we can analyze in a given session. If the run-time was reported to be less than 75 seconds, it is considered a timed-out run. Timed-out runs can occur for several reasons and often indicate an issue with the analysis The pXRF at the WGNHS cannot distinguish elements lighter than magnesium (Mg) from the background scatter due to severe attenuation of the low-energy fluorescence X-rays when the sample is measured in air (Potts and West, 2008; Thermo Fisher Scientific Niton Analyzers, 2010). Elements lighter than Mg are grouped together and reported as the 'balance'. The instrument balance is included with every analysis, reported in ppm, and represents the indistinguishable light elements. The balance is

considered acceptable if it is between 450,000-700,000 ppm. A balance outside this range indicates a problem with the analysis.

Anomalous outlying analyses, referred to as outliers, and drift, a subset of outliers, can indicate contamination or other issues with the instrument. The generation of these outliers could be related to either the reference material that was used or the sample preparation process, both of which are heavily user-influenced and are more difficult to quantify. This study provides the baseline instrument performance information needed to statistically define and identify drift and outliers. We define drift as analyses showing a continual and steady increase or decrease in measured value over time. We define outliers (with respect to each element on each reference material) as analyses having a percent difference from the median at least four-times that of the overall instrument precision. For example, if the instrument precision for phosphorus is 9%, as determined from equation 1 below, any individual measurement for phosphorus with a percent difference of 36% (4*9%) or higher, from the median of all measurements, is considered an outlier. We do not use a certain number of standard deviations from the mean to define outliers because most of our data is not normally distributed. Our definition of outliers for this study is meant to be generous because it is essential that we are confident our data represents baseline instrument performance and does not over-or under-represent its accuracy and precision. For this reason, we perform a visual inspection of the data plotted over time prior to identifying outliers by statistical calculations.

Additionally, for any given analysis, the instrument can output '<LOD', indicating less than the limit of detection, as defined by the built-in algorithms. This result can indicate: (1) The element is present, but in a concentration too small for the instrument to pick up and distinguish from the background scatter, (2) The element is not present, or (3) There were interference issues detected in the built-in correction algorithms (Hall and others, 2012; Rousseau, 2001). Analyses that were reported as '<LOD' are excluded from the statistical calculations.

Quantifying accuracy and precision

To assess instrument performance, we determine uncertainty in the instrument measurements by quantifying accuracy and precision of each element for each individual reference material.

Precision is defined as the degree of agreement between replicate measurements and provides an estimate of random error (Potts and West, 2008). Precision is determined by calculating the coefficient of variation, or the relative standard deviation (RSD). The RSD is equal to the standard deviation in parts per million (ppm) divided by the median value in ppm multiplied by 100 (Bourke and Ross, 2016; Hall and others, 2013; Newlander and others, 2015; Potts and West, 2008), as illustrated by equation 1:

$$RSD = \left(\frac{\text{standard deviation (ppm)}}{\text{median (ppm)}}\right) * 100$$

Eq. 1

Accuracy, or instrument bias, is defined as the difference between a measured value and the reference or true value and provides an estimate of systemic error (Potts and West, 2008). Accuracy is determined by calculating the percent (or relative) difference (%Diff) between the median of all measurements and the reported reference value. As illustrated in equation 2, %Diff equals the median in ppm minus the known reference value in ppm divided by the known reference value in ppm multiplied by 100 (equation 2):

%Diff=
$$\left(\frac{\text{median (ppm)-known reference value (ppm)}}{\text{known reference value (ppm)}}\right)$$
*100

Eq. 2

In both equations 1 and 2 the median was used rather than the average. This was done to avoid skewing the results with erroneous, non-typical, analyses, and because most data sets, for each element, are not normally distributed.

Results

Preliminary data processing

Table 1 presents results from the preliminary data processing. After removing the timed-out runs and analyses with bad balances, the initial visual check identified both drift and outliers, and the statistical check identified additional outliers.

Reason for exclusion With brief description	Number of analyses (out of 1,001 total analyses) and elements affected	Comment
Timed-out run The run time of the analysis was less than 75 seconds.	7 total: 3 from COQ-1 (all) 1 from SDO-1(all) 2 from SBC-1(all) 1 from SRM-1d (all)	All analyses (except for 1 analysis on SDO-1) also had bad balances Reasons for time-outs unknown
Bad balance The balance should fall within 450,000 and 700,000 ppm and represents light elements that cannot be analyzed. Bad balance falls outside of this range.	19 total: 9 from SDO (all) 9 from SBC (all) 1 from SRM-1d (all)	All SDO and SBC due to bad thin film used from 1/29/20 through 1/31/20 Reason unknown for SRM-1d (analysis from 10/17/18)
Outliers Analyses having a percent difference from the median at least four-times that of the overall instrument precision	20 total: <u>16 identified visually</u> : 9 from COQ-1 (all) 7 from SRM-1d (all) <u>4 identified statistically</u> : 1 from SRM-1d (Zn) 1 from SBC-1 (Fe) 1 from SDO-1 (Ti) 1 from COQ-1 (K)	All COQ-1 and SRM-1d due to bad thin film used from 1/29/20 through 1/31/20 Reasons unknown for additional 4 outliers
Drift Analyses showing a continual and steady increase or decrease in measured value over time.	401 total: all identified visually ¹ 201 SBC-1 (Ca) 200 SDO-1 (Ca)	Possibly a contamination issues, but reason for elemental drift is unknown

Table 1. Analyses removed from the data set during preliminary data processing.

¹Also observed in SiO₂ instrument blank.

Drift, identified visually, was the greatest source of outlying analyses, with approximately 200 analyses removed from the calcium results for two of the reference materials. Four outliers were identified statistically using the WGNHS definition of analyses having a percent difference from the median at least four times greater than the overall instrument precision included: 1 for zinc in SRM-1d, 1 for iron in SBC-1, 1 for titanium in SDO-1, and 1 for potassium in COQ-1. These outliers are shown in the plots presented in appendix 1 where the datasets for the thirteen focus elements are listed alphabetically and plotted by date of measurement. The causes of these outliers are unknown. These outliers are shown in figures A1.12D, A1.3B, A1.11C, and A1.4A, respectively. Sixteen outliers were also identified visually.

All analyses collected between January 29 and February 3, 2020 (7 for SRM-1d and 9 for COQ-1) were visually identified as outliers and removed from the data set (figure 1). Analyses for reference materials SBC-1 and SDO-1 during this period all have bad balances and were excluded from the data set prior to plotting the data (figure 1). Figure 2A shows an example for silicon (Si) in SRM-1d. Review of data collection notes shows that between January 29 and February 3, 2020, a different type of X-ray window film (thin film) than normally used was applied to the instrument. We attribute the outliers to the use of this thin film, thus affecting all elements in SRM-1d and COQ-1 during the period it was used. All analyses collected during these dates were removed from the SRM-1d and COQ-1 data sets.

Positive drift was visually observed for calcium in SBC-1 and SDO-1 on measurements collected prior to February 2020. The SiO₂ instrument blank, which the WGNHS routinely uses to identify contamination, also showed increasing calcium concentrations over this same period indicating a possible contamination issue with the instrument or the reference materials. In February 2020, the drifting data was flagged by the pXRF lab technicians and all reference materials were thoroughly cleaned with compressed air, which stopped the drift. Figure 2B shows an example of the observed drift for SDO-1 prior to February 2020, and the effect of the compressed air cleaning. The cause of the drift is still unknown. Visual and statistical inspection of elemental concentrations for other elements collected during this time did not show evidence for contamination significant enough to skew the accuracy and precision calculations. Additionally, we assume SRM-1d and COQ-1 were also affected by this issue. However, the effect was negligible due to the high concentrations of calcium in the reference materials. All calcium analyses from SBC-1 and SDO-1 prior to February 2020 were removed from the data set.



Figure 1. Examples of outliers and drift identified during the preliminary data processing. The measured values are plotted in parts per million (ppm) against analysis date. The reference value (Ref Value) is plotted as a solid black line and the standard deviation (Ref 2SD) is plotted below and above the solid line as dashed lines. Measurements are plotted as blue circles (panel A) and orange circles (panel B), with two standard deviation uncertainty bars in grey. Panel A, Outliers are circled in red and observed for silicon (Si) in SRM-1d on all analyses collected between January 29 and February 3, 2020. Similar outliers were also observed for Ca and Sr in SRM-1d and Ca, Si, P, S, and Sr in COQ-1. Analyses on reference materials SBC-1 and SDO-1 during this period all have bad balances and were excluded from the data set prior to plotting the data. The outliers are attributed to the use of a bad window thin film and all analyses for all elements were removed from the data sets for SBC-1 and SDO-1 on analyses collected prior to February 2020 when the reference materials were cleaned with compressed air. These data were removed from the data set. The data from February 2020 are shown in a red rectangle. A similar drift was also observed for Ca in SBC-1.COQ-1 and SRM-1d were negligibly affected due to their inherently high calcium concentrations.

Precision and Accuracy

In this section, we present the results for instrument precision and accuracy for the thirteen focus elements in figures 2 through 17.

Overview

All precision and accuracy results are presented in figure 2, while figures 3 and 4 present the precision and accuracy results separately for the different lithologies: the carbonates, COQ-1 and SRM-1d, and the shales, SBC-1 and SDO-1.



* Phosphorus was not detected by the pXRF on reference material SRM-1d

** Sulfur was not reported on the certificate of analysis for the reference material COQ-1; zirconium was not reported on the certificate of analysis for the reference material SRM-1d

Figure 2. Precision and accuracy results for the thirteen focus elements. Panel A, precision is presented as relative standard deviation. Panel B, accuracy is presented as the percent difference from the known reference value.



* Phosphorus was not detected by the pXRF on reference material SRM-1d

Figure 3. Precision (RSD) results for the thirteen focus elements by reference material lithology. Panel A, Carbonates COQ-1 carbonatite and SRM-1d argillaceous limestone. All elements were detected by the pXRF for reference material COQ-1; phosphorus was not detected by the pXRF on reference material SRM-1d. All elements are reported on the certificate of analysis for reference material COQ-1 and SRM-1d Panel B, Shales SDO-1 and SBC-1. All elements were detected by the pXRF and are reported on the certificate of analysis for reference material SDO-1 and SBC-1. Grey shaded areas are the US EPA recommended acceptable value (United States Environmental Protection Agency, 2007), between 0%-20%, and are included for visual comparison across other figures.



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****** Sulfur was not reported on the certificate of analysis for the reference material COQ-1; zirconium was not reported on the certificate of analysis for the reference material SRM-1d

Figure 4. Accuracy (percent difference) results for the thirteen focus elements by reference material lithology. Panel A, Carbonates COQ-1 carbonatite and SRM-1d argillaceous limestone. Panel B, Shales SDO-1 and SBC-1. All elements were detected by the pXRF and are reported on the certificate of analysis for reference material SBC-1 and SDO-1. Grey shaded areas are the US EPA recommended acceptable value (United States Environmental Protection Agency, 2007), between -20%-20%, and included for visual comparison across panels.

Precision shows less variability than accuracy (fig. 2). Elements commonly have a relative standard deviation (RSD) of 10% or less, but the majority are within 20% RSD (fig. 2). Precision for all elements in the shale reference materials (SBC-1 and SDO-1), except for magnesium, have an RSD of 20% or less (fig. 3). Aluminum, potassium, magnesium, titanium, zinc, and zirconium have an RSD greater than 20% in one or both carbonate reference materials (COQ-1 and SRM-1d), with the highest RSD values being those for potassium (41%) and titanium (72%) in SRM-1d.

Accuracy is commonly within \pm 20% of the known values, with the majority between \pm 30% difference (fig. 2). All but potassium, magnesium, manganese, and sulfur show % difference values outside the \pm 20% range in one or both shale reference materials, and of those, only magnesium has a percent difference greater than 30 (fig. 4). In the carbonate reference materials, one or both show % difference values greater than \pm 30% for aluminum, iron, magnesium, manganese, silicon, titanium, and zinc. Additionally, the range of results for the carbonates is -44 to 527 % difference, while the range for the shales is -41% to 26% difference.

Cross plots: pXRF-measured values versus known values

Below, we present cross plots of pXRF-measured values versus known reference values alphabetically by element for the 13 focus elements (figs. 5-17A). Cross plots for the remaining non-focus elements are presented in appendix 2, alphabetically, by element (figs. A2.1-A2.16A). The instrument accuracy and precision results for each element are presented in tables 2-14. The tables also show the reference material certified concentrations (listed in the column with header 'known'), and the number of analyses reported above the instruments factorydetermined limit of detection ('N>LOD') compared to the number of analyses collected ('N').

The cross plots of pXRF-measured values versus known reference values are visual representations of the accuracy and precision results. All measurements for each reference material (N) are plotted (smaller colored dots) along with the median (larger black dots). The spread in the plotted analyses represents the precision for each reference material; if the spread is large, the precision is also large (or less precise), and vice-versa. However, it should be noted that some data appear to have a smaller spread (better precision) due to the low number of analyses reported above the instrument limit of detection and the tabulated results (tables 2-4) should be reviewed.

The dotted line shown on each plot is a 1:1 line representing perfect accuracy. The distance between the pXRF-measured values and the dashed line visually represents instrument accuracy. The accuracy values presented in tables 2–14 are calculated using the medians for each individual element dataset. The farther the median point is from the 1:1 dashed line, the less accurate, and vise-versa. If the median point is above the dashed line, the pXRF overestimated the concentration, if the point is below the dashed line, the pXRF underestimated the concentration.

We also present cross plots of precision versus the reference material certified values (figs. 5-17B) and accuracy versus the reference material certified values (figs. 5-17C). In doing this, we can better understand if and how (e.g., linear relationship or not) concentration of an element affects accuracy and precision. As an estimate of this relationship, the data are fit with a least squares line, R², which is shown on each cross plot. Given the inherent nature of the pXRF instrument, it is expected that, to a certain degree, both accuracy and precision will improve with increasing concentration, as there is a certain amount of analytical noise associated with XRF analysis that can obscure the signature of elements at low concentrations. If this is not the case, lithology and/or certain characteristics of the element itself (e.g. atomic weight, spectral interference) may play a large role in the instrument accuracy and precision capabilities. Additionally, it is important to understand if error changes with concentration, as this will affect which technique is used to determine correction factors. For example, a least square linear fit should not be used if the magnitude of measurement error changes with concentration (Ripley and Thompson, 1987). Therefore, these cross plots also help improve our understanding of the pXRF limit of detection.

Aluminum (Al)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SBC-1 (shale)	4%	-12%	240/240	97273 ± 8634	111,144 ± 423
SDO-1 (shale)	4%	-14%	239/239	56145 ± 5022	64,940 ± 2434
SRM-1d (argillaceous limestone)	23%	6%	207/238	2951 ± 1360	2,784 ± 69
COQ-1 (carbonatite)	23%	42%	156/242	2779 ± 1251	1,958 ± 423

Table 2. Results summary for aluminum.



Aluminum (Al)

Figure 5. Cross plots for aluminum. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per fit; the associated R² value is also shown.

The known concentration of aluminum (Al) in the WGNHS suite of reference materials ranges from 1,958 to 111,144 ppm. The shales (SDO-1 and SBC-1) have the highest concentration of aluminum (69,940 \pm 2434 and 111,144 \pm 423 ppm) and the carbonates (COQ-1 and SRM-1d) have the lowest (1958 \pm 423 and 2784 \pm 69 ppm). There is a large gap in the range of concentrations represented, between 2,784 and 64,940, as well as between 64,940 and 111,144 ppm (fig. 5A).

Precision ranges from 4% to 23% and is best for the shales SDO-1 and SBC-1 (both with an RSD of 4%) and worst for the carbonates (both with an RSD of 23%). Precision versus concentration has a positive trend and an R^2 value of 0.87 (fig. 5B).

Accuracy ranges from -14% to 42% and is best for argillaceous limestone SRM-1d (6% difference), which has a relatively low concentration of aluminum (2,784 \pm 69 ppm). Accuracy is worst for carbonatite COQ-1 (42% difference), which has the lowest concentration of aluminum (1,958 \pm 423 ppm). Additionally, only 156 of 242 analyses detected aluminum above the instrument-defined limit of detection in COQ-1. SRM-1d also showed a lower detection rate, with 207 of 238 analyses above the limit of detection. Accuracy versus concentration (fig. 5C) has a positive trend and an R² value of 0.15.

In summary, the pXRF overestimates the concentration of Al in the carbonates, by 42% for carbonatite and by 5% for the argillaceous limestone (SRM-1d). The pXRF underestimates the concentration for the shales by 12 to 14% (-12 and -14% difference). In summary, precision is best for shales with higher concentrations of aluminum.

Calcium (Ca)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SRM-1d (argillaceous limestone)	1%	15%	238/238	433,755 ±7,962	377,717 ± 1,144
COQ-1 (carbonatite)	1%	22%	242/242	419,570 ±9,361	345,198 ± 5,432
SBC-1 (shale)	3%	-6%	39/39	19,873 ±1059	21,084 ± 143
SDO-1 (shale)	2%	-4%	39/39	7,216 ±322	7,500 ± 940

Table 3. Results summary for calcium.



Calcium (Ca)

Figure 6. Cross plots for calcium. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses, note the small number of analyses for SDO-1 and SBC-1 due to an instrument drift issue prior to February 2020; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed R2 value is also shown.

The known concentration of calcium (Ca) in the WGNHS suite of reference materials ranges from 7,500 to 377,717 ppm. The carbonates (COQ-1 and SRM-1d) have the highest concentration of calcium (345,198 \pm 5,432 and 377,717 \pm 1,144 ppm) and the shales (SBC-1 and SDO-1) have the lowest (21,084 \pm 143 and 7,500 \pm 940 ppm). There is a large gap in the range of concentrations represented, between approximately 21,000 and 345,000 ppm (fig. 6A).

Precision ranges from 1% to 3% and is best for the carbonates (both with and RSD of 1%) and worst for SBC-1 (3% RSD). Precision versus concentration (fig. 6B) has a positive trend and an R^2 value of 0.94.

Accuracy ranges from -6% to 22% and is best for the SDO-1 shale (-4% difference), which has the lowest concentration of calcium (7,500 ± 940 ppm) and worst for carbonatite COQ-1 (22% difference), which has the second greatest concentration (345,198 ± 198ppm). Accuracy versus concentration (fig. 6C) has a negative trend and an R² value of 0.84.

In summary, the pXRF overestimates the concentration of Ca in the carbonates, by 22% for carbonatite and by 15% for the argillaceous limestone (SRM-1d). The pXRF underestimates the concentration for the shales by 4 to 6%. Precision is good across the reference materials. However, it should be noted again that only 39 analyses were used for SBC-1 and SDO-1 due to the calcium drift issue noted during preliminary data processing (fig. 1).

Iron (Fe)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SBC-1 (shale)	1%	1%	240/240	68,893 ±1,059	67,915 ± 143
SDO-1 (shale)	1%	-5%	239/239	61,826 ± 1,176	65,327 ± 2,938
COQ-1 (carbonatite)	4%	-12%	242/242	18,085 ± 1 416	20,563 ± 1,259
SRM-1d (argillaceous limestone)	4%	-32%	238/238	1,512 ± 107	2,232 ± 48





Iron(Fe)

Figure 7. Cross plots for iron. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). The apparent small number of analyses for SRM-1d is due to the high precision of 4% at very low concentration. Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is also shown.

The known concentration of iron (Fe) in the WGNHS suite of reference materials ranges from 2,232 to 67,915 ppm. The shale reference materials (SBC-1 and SDO-1) have the highest concentration of iron (67,915 +-/ 143 and 65,327 \pm 1,176) and the carbonates (COQ-1 and SRM-1d) have the lowest (20,563 \pm 1,259 and 2,232 \pm 48). There are two large gaps in the range of concentrations represented, between approximately 2,200 and 20,500 ppm and between 20,500 and 65,000 ppm (fig. 7A).

Precision ranges from 1% to 4% and is best for the shales (both with an RSD of 1%). Both carbonates have an RSD of 4%. Precision versus concentration (fig. 1B) has a positive trend and an R² value of 0.90.

Accuracy ranges from -32% to 1% and is best SBC-1 (1% difference), which has the highest concentration of iron (67,915 \pm 143 ppm). Accuracy is worst for argillaceous limestone SRM-1d (-32% difference), which has the lowest concentration of iron (2,232 \pm 48 ppm). Accuracy versus concentration (fig. 7C) has a positive trend and an R² value of 0.83.

In summary, the pXRF overestimates the concentration of Fe in SBC-1 by 1% and underestimates the concentration for SDO-1, COQ-1, and SRM-1d (-5, -12, -32% differences respectively). Precision is best for the shales with higher concentrations of iron.

Potassium (K)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SBC-1 (shale)	1%	-24%	240/240	21,791 ± 565	28,640 ± 166
SDO-1 (shale)	2%	-26%	239/239	20,585 ± 338	27,810 ±1,013
COQ-1 (carbonatite)	11%	2%	242/242	1 358 ± 299	1,328 ± 332
SRM-1d (argillaceous limestone)	41%	23%	238/238	1,389 ± 1 145	1,127 ± 38





Potassium (K)

Figure 8. Cross plots for potassium. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Arrows are highlighting the binary analysis results for SRM-1d, discussed in the main text of this report. Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed R² value is also shown.

The known concentration of potassium (K) in the WGNHS suite of reference materials ranges from 1,127 to 28,640 ppm. The shale reference materials (SBC-1 and SDO-1) have the highest concentration of potassium (28,640 \pm 166 and 27,810 \pm 1,013) and the carbonates have the least (1,328 \pm 332 and 1,127 \pm 38). There is a large gap in the range of concentrations represented, between approximately 1,300 and 27,800 ppm (fig. 8A).

Precision ranges from 1% to 41% and is best for the shales SBC-1 and SDO-1 (RSD of 1% and 2%, respectively). Precision is worst for the carbonates, COQ-1 (RSD of 11%) and SRM-1d (RSD of 41%). Precision versus concentration (fig. 8B) has a positive trend and an R² value of 0.58.

Accuracy ranges from -26% to 23% and is best for carbonatite COQ-1 (2% difference), which has a relatively low concentration of potassium (1,358 \pm 299 ppm). Accuracy is worst for shale SDO-1 (-26% difference), which has the second highest concentration of potassium (27,810 \pm 1,013 ppm). Accuracy versus concentration (fig. 8C) has a negative trend and an R² value of 0.39.

In summary, the pXRF overestimates the concentration of K in the carbonates, by 2% for COQ-1 and 23% for the argillaceous limestone (SRM-1d). The pXRF underestimates the concentration for the shales by 2426%. Precision is best for shales with higher concentrations of potassium.

Magnesium (Mg)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SBC-1 (shale)	23%	-41%	240/240	9,173 ± 4 272	15,679 ± 121
SDO-1 (shale)	27%	-35%	209/239	6,015 ± 3,215	9,287 ± 458
COQ-1 (carbonatite)	23%	78%	59/242	13,411 ±6,059	7,538 ± 362
SRM-1d (argillaceous limestone)	17%	527%	28/238	11,386 ±3,931	1,815 ± 60

Table 6. Results summary for magnesium



Magnesium (Mg)

Figure 9. Cross plots for magnesium. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million Reference material concentrations in parts per material certain as the reported reference material concentrations in parts per material certain precision. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is also shown.

The known concentration of magnesium (Mg) in the WGNHS suite of reference materials ranges from 1,815 to 15,679 ppm. The shale reference materials (SBC-1 and SDO-1) have the highest concentration of magnesium (15,679 \pm 121 and 9,287 \pm 458). The carbonates have the lowest (7,538 \pm 632 and 1,815 \pm 60) There are no large gaps in the range of concentrations represented (fig. 9A); however, the range represented is relatively small.

Precision ranges from 17% to 27% and is best for argillaceous limestone SRM-1d (RSD of 17%) and worst for the shale SDO-1 (RSD of 27%). Precision versus concentration (fig. 9B) has a small negative trend and an R² value of 0.43.

Accuracy ranges from -41% to 527% and is best for shale SDO-1 (-35% difference), which has a concentration of 9,287 \pm 458 ppm. Accuracy is worst for argillaceous limestone SRM-1d (527% difference), which has the lowest concentration of aluminum (1,815 \pm 60 ppm). The carbonates COQ-1 and SRM-1d had low detection rates (59/242 and 28/238, respectively). Accuracy versus concentration (fig. 9C) has a positive trend and an R² value of 0.66.

In summary, the pXRF overestimates the concentration of Mg in the carbonates by 78% for carbonatite and by 527% for the argillaceous limestone (SRM-1d). The pXRF underestimates the concentration for the shales by 35% in SDO-1 and 41% in SBC-1. Precision is relatively poor for the suite of reference materials.

Manganese (Mn)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
COQ-1 (carbonatite)	4%	8%	242/242	3,583 ± 291	3,330 ± 31
SBC-1 (shale)	5%	-2%	240/240	1,145 ± 114	1,162 ± 15
SDO-1 (shale)	11%	19%	239/239	387 ± 88	325 ±77
SRM-1d (argillaceous limestone)	11%	69%	238/238	354 ± 78	209 ± 5

Table 7. Results summary for manganese.



Manganese (Mn)

Figure 10. Cross plots for manganese. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per fit; the associated R2 value is also shown.

The known concentration of manganese (Mn) in the WGNHS suite of reference materials ranges from 209 to 3,330 ppm. COQ-1 and SBC-1 have the highest concentration of manganese (3,330 \pm 31 and 1,162 \pm 15). There is one large gap in the range of concentrations represented, between 1,160 and 3,300 ppm (fig. 10A).

Precision ranges from 4% to 11% and is best for the carbonates COQ-1 (4% RSD) and SRM-1d (5% RSD). Precision is worst for the shales SDO-1 and SBC-1 (both with an RSD of 11%). Precision versus concentration (fig. 10B) has a positive trend and an R² value of 0.71.

Accuracy ranges from -2% to 69% and is best for shale SBC-1 (-2% difference), which has a relatively low concentration of manganese (1,162 \pm 15 ppm). Accuracy is worst for argillaceous limestone SRM-1d (69% difference), which has the lowest concentration of manganese (209 \pm 5 ppm). Accuracy versus concentration (fig. 10C) has a positive trend and an R² value of 0.31.

In summary, the pXRF overestimates the concentration of Mn by 8% for COQ-1, 19% for SDO-1, and 69% for SRM-1d. SBC-1 is the only reference material where the concentration is underestimated (-2% difference). Precision is fairly good for the suite of reference materials.

Phosphorus (P)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
COQ-1 (carbonatite)	5%	-16%	242/242	9,488 ± 882	11,347 ±1,047
SBC-1 (shale)	12%	-12%	240/240	1 416 ± 347	1,615 ± 17
SDO-1 (shale)	20%	-1%	174/239	474 ± 194	480 ± 61
SRM-1d (argillaceous limestone)	N/A	N/A	0/238	N/A	180 ± 11





Phosphorus (P)

Figure 11. Cross plots for phosphorus. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow. The pXRF did not detect any phosphorus in SRM-1d. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is a least squares linear fit; the associated R2 value is also shown.

The known concentration of phosphorus (P) in the WGNHS suite of reference materials ranges from 180 to 11,347ppm, although the pXRF did not detect any phosphorus in reference material with the lowest concentration. COQ-1 and SBC-1 have the highest concentration of phosphorus (11,347 \pm 1,047 and 1,615 \pm 17 ppm). There is one large gap in the range of concentrations represented, between 1,600 and 11,300 ppm (fig. 11A).

Precision ranges from 5% to 20% and is best for COQ-1(5% RSD) and worst for SDO-1 (20% RSD). Precision versus concentration (fig. 11B) has a positive trend and an R^2 value of 0.81.

Accuracy ranges from -16% to -1% and is best for SDO-1 (-1% difference), which has a relatively low concentration of phosphorus (480 \pm 61 ppm). Accuracy is worst for carbonatite COQ-1 (- 16% difference), which has the greatest concentration of phosphorus (11,347 \pm 1,047 ppm). Accuracy versus concentration (fig. 11C) has a negative trend and an R² value of 0.60.

In summary, the pXRF underestimates the concentration of P in all the reference materials and despite having a reported value, the pXRF did not detect phosphorus in the argillaceous limestone SRM-1d with a concentration of 180 ± 11 ppm. Precision is best for the reference material with the highest concentration of phosphorus.

Sulfur (S)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SDO-1 (shale)	2%	26%	239/239	67,204 ± 2,459	53,500 ± 8,800
SBC-1 (shale)	3%	-17%	240/240	5,900 ± 364	7,150 ± 160
SRM-1d (argillaceous limestone)	9%	-1%	229/238	1,019 ± 186	1,028 ± 62
COQ-1 (carbonatite)	7%	N/A	242/242	1,940 ± 263	Unknown







Figure 12. Cross plots for sulfur. Colors are consistent across all plots: reference material SBC-1 is red, SDO-1 is yellow, SRM-1d is green. COQ-1 does not have a reported concentration. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRFmeasured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown.

The known concentration of sulfur (S) in the WGNHS suite of reference materials ranges from 1,028 to 53,500 ppm. The shale reference materials (SBC-1 and SDO-1) have the highest concentration of sulfur (53,500 \pm 8,800 and 7,150 \pm 160 ppm). There is a small gap in the range of concentrations represented between 1,000 and 7,000 ppm and a large gap between 7,200 and 53,500 ppm (fig. 12A).

Precision ranges from 2% to 9% and is best for the shales SDO-1 (2% RSD) and SBC-1 (3% RSD). Precision is worst for argillaceous limestone SRM-1d (9% RSD). Precision versus concentration (fig. 12B) has a positive trend and an R² value of 0.51.

Accuracy ranges from -17% to 26% and is best for argillaceous limestone SRM-1d (-1% difference), which has a relatively low concentration of sulfur (1,019 \pm 186 ppm). Accuracy is worst for shale SDO-1 (26% difference), which has the greatest concentration of sulfur. Accuracy could not be determined for COQ-1 as it has no reported value on the certificate of analysis; the pXRF measured the concentration at 1,940 \pm 263 ppm. Accuracy versus concentration (fig. 12C) has a negative trend and an R² value of 0.67.

In summary, the pXRF overestimates the concentration of S for SDO-1 by 26% and underestimates the concentration for SBC-1 (-17% difference) and SRM-1d (-1% difference). Precision is best for the shales with higher concentrations of sulfur but remains adequate for the carbonates.

Silicon (Si)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SDO-1 (shale)	2%	2%	239/239	234,383 ± 10,633	230,353 ± 5,890
SBC-1 (shale)	2%	8%	240/240	240,602 ± 11,514	222,687 ± 813
SRM-1d (argillaceous limestone)	5%	3%	238/238	19,710 ± 1,784	19,071 ± 332
COQ-1 (carbonatite)	4%	44%	242/242	23,347 ± 1,939	16,220 ± 1,028







Figure 13. Cross plots for silicon. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed line is allows shown.

The known concentration of silicon (Si) in the WGNHS suite of reference materials ranges from 16,220 to 230,353 ppm. The shale reference materials (SBC-1 and SDO-1) have the highest concentration of silicon (230,353 \pm 5,890 and 222,687 \pm 813 ppm). There is a large gap in the range of concentrations represented, between 19,000 and 222,600 ppm (fig. 13A).

Precision ranges from 2% to 5% and is best for the shales SDO-1 and SBC-1 (both with an RSD of 2%). Precision versus concentration (fig. 13B) has a positive trend and an R^2 value of 0.98.

Accuracy ranges from 2% to 44% and is best for SDO-1 (2% difference) and argillaceous limestone SRM-1d (3% difference), which very differing concentrations of silicon (230,353 \pm 5,890 and 19,071 \pm 332 ppm, respectively). Accuracy is worst for carbonatite COQ-1 (44% difference), which has the lowest concentration of silicon (16,220 \pm 1,028 ppm). Accuracy versus concentration (fig. 13C) has a positive trend and an R² value of 0.31.

In summary, the pXRF overestimates the concentration of Si in all the reference materials. Precision is good across the suite of reference materials.

Strontium (Sr)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
COQ-1 (carbonatite)	1%	-7%	242/242	11,125 ± 185	12,000 ± <200
SRM-1d (argillaceous limestone)	2%	-10%	238/238	231 ± 9	256 ± 9
SBC-1 (shale)	2%	-7%	240/240	166 ± 7	178 ± 3
SDO-1 (shale)	3%	-13%	239/239	66 ± 4	75 ± 22





Strontium (Sr)

Figure 14. Cross plots for strontium. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per fit; the associated R2 value is also shown.

The known concentration of strontium (Sr) in the WGNHS suite of reference materials ranges from 75 to 12,000 ppm. The carbonate reference materials (COQ-1 and SRM-1d) have the highest concentration of strontium (12,000 \pm <200 and 256 \pm 9 ppm). There is a large gap in the range of concentrations represented between 250 and 12,000 ppm (fig. 14A).

Precision ranges from 1% to 3% and is best for COQ-1 (1% RSD) and worst for SDO-1 (3% RSD). Precision versus concentration (fig. 14B) has a positive trend and an R² value of 0.64.

Accuracy ranges from -13% to -7% and is best for COQ-1 and SBC-1 (both with a percent difference of -7%). Accuracy is worst for SDO-1 (-13% difference), which has the lowest concentration of strontium (75 ± 22 ppm). Accuracy versus concentration (fig. 5C) has a positive trend and an R² value of 0.19.

In summary, the pXRF underestimates the concentration of Sr in all the reference materials. Precision is good for all the reference materials.

Titanium (Ti)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SBC-1 (shale)	2%	0%	240/240	5,136 ± 213	5,124 ± 36
SDO-1 (shale)	2%	-2%	239/239	4,176 ± 174	4,255 ± 372
COQ-1 (carbonatite)	2%	-44%	2/242	502 ± 20	899 ± 24
SRM-1d (argillaceous limestone)	72%	7%	220/238	197 ± 281	183 ± 4





Titanium (Ti)
Figure 15. Cross plots for titanium. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Note that only two analyses were above the detection limit for COQ-1. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is also shown. Panel C, Instrument reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares linear fit; the associated R² value is a least squares

The known concentration of titanium (Ti) in the WGNHS suite of reference materials ranges from 183 to 5,124 ppm. The carbonate reference materials (COQ-1 and SRM-1d) have the highest concentration of titanium (5,124 \pm 36 and 4,255 \pm 372 ppm). There are small gaps in the concentrations represented between the carbonates and between the shales as well as a large gap between 900 and 4,200 ppm (fig. 15A).

Precision is worst for argillaceous limestone SRM-1d (72% RSD); the other three reference materials all had an RSD of 2%. Precision versus concentration (fig. 15B) has a positive trend and an R² value of 0.44.

Accuracy ranges from -44% to 7% and is best for SBC-1 (0% difference), which has the highest concentration of titanium (5,124 \pm 36 ppm). Accuracy is worst for carbonatite COQ-1 (-44% difference), which has the second lowest concentration of titanium (899 \pm 24 ppm). Additionally, only 2 of 242 analyses detected titanium above the instrument-defined limit of detection in COQ-1. Accuracy versus concentration (fig. 15C) has a positive trend and an R² value of 0.35.

In summary, the pXRF overestimates the concentration of Ti in SRM-1d by 7% and underestimates the concentration for SDO-1 and COQ-1 (-2 and -44 % difference) Precision is good for all reference materials, except SRM-1d.

Zinc (Zn)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SBC-1 (shale)	7%	-8%	240/240	171 ± 23	186 ± 3
COQ-1 (carbonatite)	20%	-14%	235/242	75 ± 29	87 ± 3
SDO-1 (shale)	12%	-12%	239/239	57 ± 13	64 ± 14
SRM-1d (argillaceous limestone)	24%	55%	227/238	28 ± 13	18 ± 2







Figure 16. Cross plots for zinc. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow, SRM-1d is green. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per fit; the associated R² value is also shown.

The known concentration of zinc (Zn) in the WGNHS suite of reference materials ranges from 18 to 186 ppm. Reference materials COQ-1 and SBC-1 have the highest concentration of zinc (87 \pm 3 and 186 \pm 3 ppm). There is one gap in the range of concentrations represented between 90 and 180 ppm (fig. 16A).

Precision ranges from 7% to 24% and is best for SBC-1 (7% RSD) and worst for COQ-1 (27% RSD). Precision versus concentration (fig. 16B) has a positive trend and an R² value of 0.70.

Accuracy ranges from -14% to 55% and is best for SBC-1 (-8% difference), which has the greatest concentration of zinc (186 \pm 3 ppm). Accuracy is worst for argillaceous limestone SRM-1d (55% difference), which has the lowest concentration of aluminum (18 \pm 2 ppm). Accuracy versus concentration (fig. 16C) has a positive trend and an R² value of 0.53.

In summary, the pXRF overestimates the concentration of Zn inSRM-1d by 55% and underestimates the concentration for the remaining reference materials by 814%. Precision is best for the shales.

Zirconium (Zr)

Ref. Material	Precision	Accuracy	N >LOD / N	Median ± 2SD (ppm)	Known ± 2SD (ppm)
SDO-1 (shale)	2%	-8%	239/239	152 ± 7	165 ± 48
SBC-1 (shale)	3%	2%	240/240	136 ± 7	134 ± 3
SRM-1d (argillaceous limestone)	21%	N/A	231/238	11±5	Unknown
COQ-1 (carbonatite)	28%	17%	235/242	76 ± 43	65 ± 6







Figure 17. Cross plots for zirconium. Colors are consistent across all plots: reference material COQ-1 is purple, SBC-1 is red, SDO-1 is yellow. SRM-1d does not have a reported concentration. Panel A, Cross plot of pXRF-measured values versus known values from the reference material certificates (reference values). Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Panel B, Instrument precision, presented as relative standard deviation (RSD) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown. Panel C, Instrument accuracy, presented as the absolute value of percent difference (abs(%Diff)) versus the reported reference material concentrations in parts per million (ppm). Dashed line is a least squares in parts per million (ppm). Dashed line is a least squares linear fit; the associated R2 value is also shown.

The known concentration of zirconium (Zr) in the WGNHS suite of reference materials ranges from 65 to 165 ppm. The shale reference materials (SBC-1 and SDO-1) have the greatest concentration of zirconium (165 \pm 48 and 134 \pm 3 ppm). There are no large gaps in the range of concentrations represented; however, the range represented is small (fig. 17A).

Precision ranges from 2% to 28% and is best for the shales SDO-1 (2% RSD) and SBC-1 (3% RSD). Precision is worst for the carbonates SRM-1d (21% RSD) and COQ-1(28% RSD). Precision versus concentration (fig. 17B) has a positive trend and an R² value of 0.82.

Accuracy ranges from -8% to 17% and is best for SBC-1 (2% difference) and worst for COQ-1 (17% RSD). Accuracy could not be determined for SRM-1d as it has no reported value on the certificate of analysis; the pXRF measured the concentration at 11 ± 5 ppm. Accuracy versus concentration (fig. 17C) has a positive trend and an R² value of 0.56.

In summary, the pXRF overestimates the concentration of Zr in SBC-1 by 2% and COQ-1 by 17%. The pXRF underestimates the concentration SDO-1 by 8%. Precision is best for the shales with higher concentrations of zirconium.

Discussion and conclusions

This study provided a detailed analysis of instrument performance for 13 major rock-forming elements using a suite of reference materials, minimizing, to the best of our ability, external sources of error. The statistical analyses we employed allowed us to define the accuracy and precision of each element by reference material and assess our suite of reference materials for gaps. In doing so, this work helps to identify necessary changes in our methodology in order to improve data quality. Additionally, these results improve our understanding of the roles of lithology and elemental concentration has on measurement uncertainty. This is an important first step in being able to develop a much more comprehensive understanding of measurement uncertainty and developing data correction methodology.

Accuracy and precision

For the thirteen focus elements analyzed on our pressed-powder reference materials, results show that both accuracy and precision vary by reference material and by element: accuracy being more variable than precision, indicating that our instrument is more precise than accurate. Results also show that precision and accuracy are independent of each other. Additionally, lithology (matrix) and elemental concentration show varying degrees of control on instrument error and that our pXRF algorithms may be best suited for fine-grained siliciclastics.

Precision, although variable (1% to 72% RSD), particularly for the carbonate reference materials, is adequate (</= 20% RSD) for most of the elements. Longer run-times may be needed for carbonates, mixed lithology samples (e.g., argillaceous limestone SRM-1d) and samples with low concentrations of elements of interest in order to improve precision (Newlander and others, 2015). On cross plots of precision versus concentration (figs. 5-17B), all elements except Mg (fig. 9B) have positive slopes to their linear trend lines and most of the data have an R² less than or equal to 0.8; the exceptions being Al, Ca, Fe, Si, P, and Zr (figs. 5B, 6B, 7B, 11B, 13B, and 17B). These results suggest that, in general, precision appears to improve with concentration for all elements except magnesium. However, the low R² values, for most elements, may indicate that precision and concentration do not have a linear relationship. It is likely that lithology plays a significant role in precision... This is further indicated by the results for the mixed lithology reference material, argillaceous limestone SRM-1d, which shows the highest variability and the two results with the lowest precision (41% and 72% RSD).

Accuracy shows much more variability than precision, both among the reference materials and for each element. And, like precision, results are generally better for the shales than the carbonates, and three of the four results with the lowest accuracy (55, 69, and 527% difference) come from the mixed lithology reference materials SRM-1d. There is high variability in slope and R² values for the accuracy versus concentration plots (figs. 5-17C). For some elements, such as Ca, K, P, and S, accuracy gets worse with increasing concentration of the elements (figs. 6C, 8C, 11C, and 12C). For many elements, the data are, again, poorly fit by a linear trend line as accuracy can be quite variable for similar concentrations (Al, K, Mn, Si, Sr) (figs. 5C, 8C, 10C, 13C, and 14C). Only Ca and Fe have R² values greater than 0.80. These results suggest concentration and lithology also affect accuracy, and perhaps more so than for precision. This is

an unsurprising result; several others have noted that lithology (matrix) can play a significant role in accuracy due to the calibration algorithms used in pXRF instruments (Al-Musawi and Kaczmarek, 2020; Potts and West, 2008; Rowe and others, 2012). Al-Musawi and Kaczmarek (2020) recognized the need for carbonate-specific instrument calibration.

Magnesium and potassium warrant a separate discussion as both show unusual results relative to the other elements. For magnesium, it is likely that our reference materials do not have an adequate range of Mg concentration to appropriately characterize instrument error for this element. The negative slope and poor accuracy (-41-527% difference) may be a characteristic of concentrations near the detection limit and/or interference with other elements in higher abundance, coupled with the fact that Mg is the lightest element that the pXRF can detect. These results could also be a product of a lithologic control on the precision for magnesium.

Potassium for reference material SRM-1d is the only element that displays a binary clustering phenomenon of the data (figs. 8A and A1.4D). As discussed in the methods section, the algorithm we use on our instrument is Test All Geo, which combines the Mining and Soils Mode algorithms, and is optimal when analyzing a variety of lithologies (Thermo Fisher Scientific Niton Analyzers, 2010). Results from a previous, unpublished study at WGNHS, which analyzed the reference materials using the Mining and Soils Modes independently showed that the two algorithms can produce varying results for concentration of a single element. Potassium was one such element, showing two different results, which align well with the binary concentration results of this study. Further data is needed to understand why this is occurring for potassium in SRM-1d, but the mixed lithology of the argillaceous limestone could be part of the answer.

It is important to keep in mind that this assessment of instrument accuracy and precision is limited to the elemental concentrations and lithologies of our current pressed-powder reference materials. Instrument accuracy and precision was not assessed for concentrations outside the represented values. It is also important to note that these results cannot be interpreted as total analytical uncertainty of our pXRF on unknown samples. Analyses of unknowns introduces additional sources of error (Potts and West, 2008) beyond the focus of this study.

Reference materials

The small number of reference materials used in this study limits our ability to fully assess instrument performance for several reasons including: (a) instrument accuracy and precision may not be well constrained where there are large gaps in reference material concentrations (e.g. Ca and K) (figs. 6A and 8A), (b) the range of concentrations represented by our reference materials may not represent element concentrations present in the Wisconsin lithologies we analyze, (c) we cannot assess instrument performance over a large range of concentrations for a single lithology, and (d) lithologies such as sandstones, limestones, and dolostones, common in Wisconsin, are not represented in our reference materials

A preliminary look at the adequacy of our elemental concentration ranges is shown in figure 20, where we compare a suite of mud rock reference materials from Rowe and others (2012), and a

suite of carbonate reference materials from Al-Musawi and Kaczmarek (2020) to our current reference material suite. The study by Rowe and others (2012) includes 90 diverse mudrock reference materials. The study by Al-Musawi and Kaczmarek (2020) uses 57 carbonate reference materials that represent a range of lithologies (limestone, dolostone, mixed), carbonate textures, depositional environments, burial depths, and ages.

In this comparison, ranges for a few elements (Ca, Fe, Mn, P, S, Sr, Ti, and Zn) seem well represented by our reference materials. However, others (Al, K, Mg, P, Si, and Zr) likely do not span the range of concentrations expected in Wisconsin stratigraphy. However, further review of representative elemental concentrations in siliciclastics and carbonates is needed, along with an assessment of concentrations expected in Wisconsin lithologies so that we can obtain a broad range of elemental concentrations in our suite of reference materials. This is particularly important if data correction coefficients will be applied (Potts and West, 2008; Rowe and others, 2012). Additionally, broadening our reference material lithologies (matrices and submatrices) to include sandstones, dolostones, and limestones is important as matrix effects significantly impact sample analysis results (Rowe and others, 2012).





Figure 18. Comparison of elemental concentration ranges for the WGNHS suite of reference materials (n=4), a suite of mud rock reference materials from Rowe and others (2012) (n=90), and a suite of carbonate reference materials from Al-Musawi and Kaczmarek (2020) (n=57). Note the use of three different x-axis scales. Green dots represent the actual values for the WGNHS reference material.

Improving data quality - lessons learned from this study

As a result of this work, the WGNHS has incorporated several new steps into both the data collection and data processing workflow to improve data quality. For example, we routinely blow-off the reference materials with compressed air prior to analysis and we now keep the reference materials in separate containers. To the best of our knowledge, the calcium drift issue was caused by the reference materials being stored loosely together in a shared container. Blowing the reference materials off with compressed air stopped the observed drift in the data. It should also be noted that once the reference materials were cleaned with compressed air, some of the elements showed improved data quality (more precise and or more accurate), for example, Al in SRM-1d (fig. A1.1D).

We also now download and process all data monthly, at a minimum, so that data processing occurs regularly. This includes inspection of the data plotted over time to flag outliers, drift, and any other data anomalies. We are also using the quantitative definition of outliers, developed in this study, automatically flag outliers in the data set during processing. Furthermore, we can use this definition to track instrument performance in real-time during data collection, without having to download the data. This is discussed in more detail below.

Real-time instrument performance check

The results of this study highlight the necessity for routine instrument performance and data quality assessments to identify issues with the data as soon as possible. Although monthly data processing is a step forward, and will continue, monitoring data in real-time will take us even further in better tracking instrument performance and improving data quality.

We have incorporated the results of this study into a real-time instrument performance and data quality check during the data collection process. To do this, we first selected several elements from each reference material that have the greatest reported precision. We then determined maximum and minimum acceptable values in both ppm and percent for each of these elements using our quantified definition of outliers. However, for this purpose of real-time monitoring, we have used 3-times the instrument precision (RSD) (equations 3 and 4) rather than 4, as is used to flag outliers.

minimum=[(-RSD*3)*median]+median

Eq. 3

Eq. 4

The elements, instrument precision, and the maximum and minimum acceptable values are presented in table 15.

After each reference material is analyzed, the pXRF user checks that the measured values are within the acceptable range for several elements. Should the results fall outside of the acceptable range, the pXRF user will be alerted to issues with the instrument in real-time.

Reference Material	Element	Median (ppm)	Precision (RSD)	Min (pp	om, %)	Max (p	pm, %)
COQ-1	Si	23,347	4%	20,439	2.04	26,255	2.63
	Р	9,488	5%	8,165	0.82	10,811	1.08
	S	1,940	7%	1,546	0.15	2,335	0.23
	Са	419,570	1%	405,528	40.55	43,3611	43.36
SBC-1	Si	240,602	2%	223,330	22.33	257,873	25.79
	S	5,900	3%	5,355	0.54	6,446	0.64
	к	21,791	1%	20,662	2.07	22,921	2.29
SDO-1	Si	234,383	2%	218,434	21.84	250,332	25.03
	S	67,204	2%	63,515	6.35	70,893	7.09
	К	20,585	2%	19,572	1.96	21,598	2.16
	Ti	4,175	2%	3,915	0.39	4,437	0.44
SRM-1d	Si	1,9710	5%	17,035	1.70	22,385	2.24
	S	1,019	9%	739	0.07	1,298	0.13
	Са	433,755	1%	421,813	42.18	445,698	44.57

Table 15: Accepted ranges of pXRF measured concentration to be used for real	-time
monitoring.	

Future work

Future work will include assessing instrument accuracy and precision using additional reference materials that represent a broader range of lithologies and elemental concentrations. Recently, WGNHS has acquired six additional reference materials: basalt BCR-2, granodiorite GSP-2, rhyolite RGM-2, mica schist SDC-1, syenite STM-2, and diabase W-2a.

In addition to using the same method applied in this study, the WGNHS plans to incorporate a maximum likelihood fitting of a functional relationship (MLFR) (Ripley and Thompson, 1987) method to complete a more comprehensive assessment of instrument uncertainty across the suite of reference material, moving towards our goal of developing standardized data correction methodology. Additionally, the WGNHS plans to model uncertainty of our instrument across gaps in our reference materials data using confidence and prediction bounds.

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Appendix 1

In this appendix, we present plots of pXRF-measured values versus analysis date for the thirteen focus elements, presented alphabetically: Al, Ca, Fe, K, Mg, Mn, P, S, Si, Sr, Ti, Zn, and Zr (figs. A1.1- A1.13). These plots are meant to complement the results section of this report because it is difficult to fully describe how the instrument performs over time using just mean values, 2 standard deviations, accuracy, and precision. Additionally, we would like to visually present the four statistically determined outliers, which were left in the data set for figures A1.3B, A1.4A, A1.11C, and A1.12D.

Aluminum (Al)



Figure A1.1. Analysis date versus pXRF-measured concentration of aluminum (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for aluminum. X Ref = reference material; SD = standard deviation.

Calcium (Ca)



Figure A1.2. Analysis date versus pXRF-measured concentration of calcium (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for calcium. Note that for SBC-1 and SDO-1 the data sets are significantly smaller due to the data drift issue; see text in main report for more information. Ref = reference material; SD = standard deviation.

Iron (Fe)



Figure A1.3. Analysis date versus pXRF-measured concentration of iron (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for iron except for one outlier (red box in panel B for SBC-1). This analysis was statistically determined as outliers and removed from the data set prior to quantifying accuracy and precision. Ref = reference material; SD = standard deviation.

Potassium (K)



Figure A1.4. Analysis date versus pXRF-measured concentration of potassium (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d; note the binary nature of the data. These data represent the full data set that was used to determine accuracy and precision of our instrument for potassium except for two outliers (red box in panel A for COQ-1). This analysis was statistically determined as outliers and removed from the data set prior to quantifying accuracy and precision. Ref = reference material; SD = standard deviation.

Magnesium (Mg)



Figure A1.5. Analysis date versus pXRF-measured concentration of magnesium (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for magnesium. Note the small size of the data sets for COQ-1 and SRM-1d due to many analyses being reported as <LOD. Ref = reference material; SD = standard deviation.

Manganese (Mn)



Figure A1.6. Analysis date versus pXRF-measured concentration of manganese (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for manganese. Ref = reference material; SD = standard deviation.

Phosphorus (P)



Figure A1.7. Analysis date versus pXRF-measured concentration of phosphorus (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. Phosphorus was not detected by the pXRF in SRM-1d. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for phosphorus. Ref = reference material; SD = standard deviation.

Sulfur (S)



Figure A1.8. Analysis date versus pXRF-measured concentration of sulfur (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for sulfur. Ref = reference material; SD = standard deviation.

Silicon (Si)



Figure A1.9. Analysis date versus pXRF-measured concentration of silicon (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for silicon. Ref = reference material; SD = standard deviation.

Strontium (Sr)



Figure A1.10. Analysis date versus pXRF-measured concentration of strontium (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for strontium. Ref = reference material; SD = standard deviation.

Titanium (Ti)



Figure A1.11. Analysis date versus pXRF-measured concentration of titanium (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for titanium except for one outlier (red box in panel C for SDO-1). This analysis was statistically determined as an outlier and removed from the data set prior to quantifying accuracy and precision. Note the small data set for COQ-1 due to most of the analyses (240 of 242) being reported as <LOD. Ref = reference material; SD = standard deviation.

Zinc (Zn)



Figure A1.12. Analysis date versus pXRF-measured concentration of zinc (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for zinc except for one outlier (red box in panel D for SRM-1d). This analysis was statistically determined as an outlier and removed from the data set prior to quantifying accuracy and precision. Ref = reference material; SD = standard deviation.

Zirconium (Zr)



Figure A1.13. Analysis date versus pXRF-measured concentration of zirconium (circles) and 2SD, as reported by the instrument (grey error bars) for WGNHS reference materials. X-axes are only titled for the bottom two plots. Solid and dashed black horizontal lines in each plot represent the reported reference material concentration and 2 standard deviations, respectively, from the certificates of analysis. Panel A, COQ-1, Panel B, SBC-1, Panel C, SDO-1, and Panel D, SRM-1d. These data represent the full data set that was used to determine accuracy and precision of our instrument for zirconium. Ref = reference material; SD = standard deviation.

Appendix 2

Although this study focuses on major rock-forming elements, here we present cross plots of pXRF-measured values versus reference material values reported on the certificates of analyses for minor and trace elements, which are: As, Ba, Cd, Co, Cr, Cs, Cu, Mo, Nb, Ni, Pb, Rb, Sn, Th, U, and V (figs. A2.1 – A2.16).Only timed-out runs and bad balances have been removed from the data sets; the data are not assessed for outliers. Plots also include a 1:1 dotted line representing perfect accuracy. Although the accuracy and precision of our instrument on most of these elements cannot be adequately evaluated at this time due to current data limitations. These include:

- (1) No detection by our instrument (e.g., lead in SRM-1d) (fig. A2.11, table A2.11).
- (2) Limited detection by our instrument (more than half the analyses are reported as "<LOD") therefor the data set is not robust enough for statistical analysis (e.g., cobalt in SRM-1d) (fig. A2.4, table A2.4).
- (3) Element concentration not reported on reference materials certificate of analysis (e.g., molybdenum in COQ-1) (fig. A2.8, table A2.8).
- (4) A range of concentration is reported on the certificate of analysis (e.g. cadmium in SDO-1) (fig. A2.3, table A2.3).

Tables A2.1 through A2.16 are provided to summarize the number of analyses reported above the instrument's factory-determined limit of detection (N>LOD) compared to the number of analyses run (N), the median and two standard deviations of the pXRF-measured values, and the certificate of analysis reported concentration, if any.

Arsenic (As)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	30 ± 9 ppm	Yes – 25.7 ± ppm
SDO-1 (shale)	239/239	64 ± 10 ppm	Yes – 68.5 ppm
SRM-1d (argillaceous limestone)	6/238	9 ± 2 ppm	no
COQ-1 (carbonatite)	14/242	16 ± 3 ppm	no

Table A2.1. Arsenic

¹ Number of analyses reported above the instrument's factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.1. Cross plot of pXRF-measured values versus known values from the reference material certificates for arsenic. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Only two reference materials (SBC-1 and SDO-1) have reported concentrations on their certificates of analysis and can be plotted.

Barium (Ba)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	1003 ± 74 ppm	Yes – 788 ± 15.4 ppm
SDO-1 (shale)	239/239	659 + /- 68 ppm	Yes – 397 ± 76 ppm
SRM-1d (argillaceous limestone)	238/238	639 ± 68 ppm	Yes – 29.6 ± 9.9 ppm
COQ-1 (carbonatite)	0/242	N/A	Yes – 1000 ± <200 ppm

Table A2.2. Barium

¹Number of analyses reported above the instrument's factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.2. Cross plot of pXRF-measured values versus known values from the reference material certificates for barium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. All four reference materials have reported concentrations on their certificates of analysis, but COQ-1 was not detected by the pXRF.

Cadmium (Cd)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	161/240	22 ± 8 ppm	Yes – 0.4 ± 0.04 ppm
SDO-1 (shale)	200/239	23 ± 10 ppm	Yes – 2 to <10 ppm
SRM-1d (argillaceous limestone)	127/238	24 ± 8 ppm	Yes – 0.3 ppm
COQ-1 (carbonatite)	0/242	N/A	no

Table A2.3. Cadmium

¹ Number of analyses reported above the instrument's factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.3. Cross plot of pXRF-measured values versus known values from the reference material certificates for cadmium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Only two reference materials (SBC-1 and SRM-1d) have reported concentrations on their certificates of analysis and can be plotted. The pXRF did not detect cadmium in COQ-1, and the certificate of analysis for SDO-1 reports a range instead of a single value.

Cobalt (Co)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	12/240	306 ± 91 ppm	Yes – 22.7 ± 0.6 ppm
SDO-1 (shale)	42/239	299 ± 105 ppm	Yes – 46.8 ± 13 ppm
SRM-1d (argillaceous limestone)	125/238	83 ± 26 ppm	no
COQ-1 (carbonatite)	0/242	N/A	Yes - <5ppm

Table A2.4. Cobalt

¹Number of analyses reported above the instrument's factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.4. Cross plot of pXRF-measured values versus known values from the reference material certificates for cobalt. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Only two reference materials (SBC-1 and SDO-1) are plotted. Cobalt was not detected by the pXRF in COQ-1 and the certificate of analysis has no reported cobalt value for SRM-1d.

Chromium (Cr)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	248 ± 93 ppm	Yes – 109 ± 2 ppm
SDO-1 (shale)	239/239	170 ± 54 ppm	Yes – 66.4 ± 15 ppm
SRM-1d (argillaceous limestone)	15/238	90 ± 39 ppm	Yes – 8.2 ± 1.37 ppm
COQ-1 (carbonatite)	0/242	N/A	Yes <10 ppm

Table A2.5. Chromium

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.5. Cross plot of pXRF-measured values versus known values from the reference material certificates for chromium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. COQ-1 is not plotted as the pXRF did not detect chromium in this reference material.

Caesium (Cs)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	137 ± 15 ppm	Yes – 8.2 ± 0.2 ppm
SDO-1 (shale)	239/239	124 ± 14 ppm	Yes – 6.9 ± 2.4 ppm
SRM-1d (argillaceous limestone)	238/238	154 ± 18 ppm	Yes – 0.4 ppm
COQ-1 (carbonatite)	0/242	N/A	Yes – 0.2 ± 0.02 ppm

Table A2.6. Caesium

¹ Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.6. Cross plot of pXRF-measured values versus known values from the reference material certificates for caesium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. COQ-1 is not plotted as the pXRF did not detect caesium in this reference material.

Copper (Cu)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	227/240	48 ± 20 ppm	Yes – 31 ± 1.2 ppm
SDO-1 (shale)	239/239	63 ± 19 ppm	Yes – 60.2 ± 19 ppm
SRM-1d (argillaceous limestone)	57/238	38 ± 13 ppm	no
COQ-1 (carbonatite)	8/242	69 ± 7 ppm	Yes - <10

Table A2.7. Copper

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.7. Cross plot of pXRF-measured values versus known values from the reference material certificates for copper. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Only two reference materials (SBC-1 and SDO-1) are plotted. There is no reported value on the certificate of analysis for SRM-1d and the reported value for COQ-1 is a range rather than a single value.
Molybdenum (Mo)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	18/240	6 ± 2 ppm	Yes – 2.4 ± 0.14 ppm
SDO-1 (shale)	239/239	119 ± 29 ppm	Yes – 134 ± 42 ppm
SRM-1d (argillaceous limestone)	2/238	5 ± 1 ppm	no
COQ-1 (carbonatite)	234/242	13 ± 5 ppm	no

Table A2.8. Molybdenum

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Molybdenum (Mo)

Figure A2.8. Cross plot of pXRF-measured values versus known values from the reference material certificates for molybdenum. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). Only two reference materials (SBC-1 and SDO-1) have reported concentrations on their certificates of analysis and can be plotted.

Niobium (Nb)

Table A2.9. Niobium

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	20 ± 4 ppm	Yes – 15.3 ± 0.4 ppm
SDO-1 (shale)	239/239	19 ± 3 ppm	Yes – 11.4 ± 2.4 ppm
SRM-1d (argillaceous limestone)	3/238	5 ± 1 ppm	Yes – 0.7 ppm
COQ-1 (carbonatite)	242/242	3931 ± 306 ppm	Yes – 3900 ± 200 ppm

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Niobium (Nb)

Figure A2.9. Cross plot of pXRF-measured values versus known values from the reference material certificates for niobium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). All reference materials are plotted.

Nickel (Ni)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	147 ± 29 ppm	Yes – 82.8 ± 1.6 ppm
SDO-1 (shale)	239/239	126 ± 30 ppm	Yes – 99.5 ± 20 ppm
SRM-1d (argillaceous limestone)	238/238	114 ± 30 ppm	Yes – 4 ppm
COQ-1 (carbonatite)	48/242	137 ± 30 ppm	Yes – 13 ± 2 ppm

Table A2.10. Nickel

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.10. Cross plot of pXRF-measured values versus known values from the reference material certificates for nickel. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. All reference materials are plotted.

Lead (Pb)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	29 ± 8 ppm	Yes – 35 ± 0.6 ppm
SDO-1 (shale)	239/239	23 ± 7 ppm	Yes – 27.9 ± 10 ppm
SRM-1d (argillaceous limestone)	0/238	N/A	no
COQ-1 (carbonatite)	0/242	N/A	no

Table A2.11. Lead

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.11. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Only two reference materials (SBC-1 and SDO-1) have reported concentrations on their certificates of analysis and can be plotted.

Rubidium (Rb)

Reference Material	N>LOD/N ⁺	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	92 ± 5 ppm	Yes – 147 ± 2 ppm
SDO-1 (shale)	239/239	77 ± 4 ppm	Yes – 126 ± 7.8 ppm
SRM-1d (argillaceous limestone)	232/238	4 ± 2 ppm	Yes – 6 ppm
COQ-1 (carbonatite)	222/242	10 ± 4 ppm	no

Table A2.12. Rubidium

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Rubidium (Rb)

Figure A2.12. Cross plot of pXRF-measured values versus known values from the reference material certificates for rubidium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Dashed box shows the location of inset (plot shown to the right). COQ-1 is not plotted because there is no reported value for rubidium on the certificate of analysis.

Tin (Sn)

Table A2.13. Tin

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	36 ± 11 ppm	Yes – 3.3 ± 0.2 ppm
SDO-1 (shale)	239/239	35 ± 11 ppm	Yes – 3.7 ± 2.4ppm
SRM-1d (argillaceous limestone)	238/238	34 ± 12 ppm	Yes – 1 ppm
COQ-1 (carbonatite)	0/242	N/A	no

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.13. Cross plot of pXRF-measured values versus known values from the reference material certificates for tin. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. COQ-1 is not plotted because there is no reported value for tin on the certificate of analysis.

Thorium (Th)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	236/240	13 ± 6 ppm	Yes – 15.8 ± 0.4 ppm
SDO-1 (shale)	92/239	9 ± 3 ppm	Yes – 10.5 ± 1.1 ppm
SRM-1d (argillaceous limestone)	27/238	7 ± 2 ppm	Yes – 0.5 ppm
COQ-1 (carbonatite)	0/242	N/A	Yes – 10 ± 2 ppm

Table A2.14. Thorium

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.14. Cross plot of pXRF-measured values versus known values from the reference material certificates for thorium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. COQ-1 is not plotted because the pXRF did not detect any thorium.

Uranium (U)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	0/240	N/A	Yes – 5.76 ± 0.22 ppm
SDO-1 (shale)	239/239	42 ± 11 ppm	Yes – 48.8 ± 13 ppm
SRM-1d (argillaceous limestone)	5/238	10 ± 2 ppm	Yes – 1 ppm
COQ-1 (carbonatite)	0/242	N/A	Yes – 11 ± 1.2 ppm

Table A2.15. Uranium

¹Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.15. Cross plot of pXRF-measured values versus known values from the reference material certificates for uranium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. Only two reference materials are plotted (SRM-1d and SDO-1); the pXRF did not detect uranium in SBC-1 or COQ-1.

Vanadium (V)

Reference Material	N>LOD/N ¹	Median ± 2SD	Reported on certificate of analysis?
SBC-1 (shale)	240/240	271 ± 85 ppm	Yes – 220 ± 2.8 ppm
SDO-1 (shale)	239/239	212 ± 63 ppm	Yes – 160 ± 42 ppm
SRM-1d (argillaceous limestone)	17/238	114 ± 49 ppm	Yes – 10 ppm
COQ-1 (carbonatite)	217/242	237 ± 134 ppm	Yes – 110 ± 12 ppm

Table A2.16. Vanadium

¹ Number of analyses reported above the instruments factory-determined limit of detection (N>LOD) compared to the number of analyses run (N)



Figure A2.16. Cross plot of pXRF-measured values versus known values from the reference material certificates for vanadium. Smaller colored points are individual pXRF analyses; larger black points are the median of all the analyses; 2 standard deviations (2SD) are also shown about the median point for both the pXRF-measured values (as calculated for the median) and reference values (reported on the certificate of analyses). The dotted 1:1 line represents perfect accuracy. All reference materials are plotted.