

Accurate determination of major and trace elements in nuclear source materials using X-ray fluorescence spectrometry

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ABSTRACT

Reliable characterization of nuclear source materials requires rapid and defensible methods for measuring major oxides and selected trace elements. This study evaluated portable X-ray fluorescence spectrometry (pXRF) and wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) for geochemical analysis of materials relevant to nuclear source material assessment. Twenty-one certified reference materials, including igneous rocks, sedimentary rocks, sediments, and mineralized reference materials, were prepared as pressed powder pellets and analyzed using a Bruker S1 Titan pXRF and a Rigaku Supermini 200 WDXRF. Calibration performance was assessed by comparing measured and certified values using reporting coverage, linear regression, slope, intercept, and coefficient of determination (R^2). For pXRF, manufacturer-provided detection limits and analysis ranges were used as screening references, while WDXRF was evaluated using CRM-based empirical calibration. The pXRF method showed good calibration performance for Cr, Ba, Cu, Ni, Pb, Rb, Sr, Y, Zn, Ca, Fe, K_2O , Ti, and Mn, but had insufficient reporting coverage for Nb, Th, U, and V, and poor performance for S, MgO, and P. WDXRF showed stronger performance for major oxides and good calibration for several selected trace elements, including Cr, Cu, Ni, Rb, S, Sr, V, Y, Zn, and Zr. Overall, WDXRF is preferred for quantitative major-oxide analysis and selected elements such as S, V, and Zr, whereas pXRF is useful for rapid screening of selected trace elements. For U and Th, more sensitive complementary techniques such as ICP-MS/MS are recommended.

INTRODUCTION

In pursuing the goal of nuclear energy development, it is critical to establish the capability to utilize indigenous, conventional nuclear source materials. Naturally occurring nuclear source materials are essentially geological and environmental materials with notable occurrence/concentration of fissile or fertile elements that serve as raw materials for nuclear fuel (i.e., uranium and/or thorium). The growing global interest and demand for nuclear fuel are exemplified by increasing uranium prices and the inclusion of uranium in the 2025 USGS List of Critical Minerals (NEA, 2025; USGS, 2025). In the front end of the nuclear fuel cycle, characterization of nuclear source materials prior to mineral processing not only requires quantification of uranium and thorium abundances but also necessitates the determination of major and trace elements for geochemical rock classification, normative mineralogical determination, and assessment of element mobility due to hydrothermal alteration, among others, which are essential in understanding the origin of uranium and/or thorium mineralization (Dhara and Mishra 2019; Zhang et al. 2019; Fathy et al. 2026). In addition, trace-element concentrations and isotope abundance ratios in uranium-bearing materials are recognized as nuclear forensic signatures for determining the origin, processing history, and potential source of nuclear materials found outside regulatory control (Krachler et al. 2018).

X-ray fluorescence techniques are widely used for rapid geochemical analysis because they provide non-destructive, multi-element measurements with relatively simple sample preparation. Portable energy-dispersive X-ray fluorescence spectrometry (pXRF) is particularly useful for rapid field screening and preliminary geochemical assessment, and can support lithological interpretation where rock units exhibit distinct elemental compositions, whereas wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) provides higher spectral resolution, lower

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detection limits, and better performance for laboratory-based quantitative analysis, especially for light elements and elements with overlapping spectral lines (Lemière 2018; Yamasaki et al. 2023). However, the quantitative reliability of both techniques depends strongly on element-specific calibration, matrix effects, spectral interferences, detection limits, sample heterogeneity, sample preparation, and instrument configuration. Matrix-matched empirical calibrations and validation using certified reference materials are therefore needed to reduce systematic bias and establish whether measured concentrations are fit for purpose for specific rock types and analytes (Steiner et al. 2017; Da Silva et al. 2023). These considerations are especially important for nuclear source material assessment, where rapid screening may be useful for exploration and sample triage, but high-confidence quantification requires clear identification of which elements can be reliably measured by pXRF, which require WDXRF, and which should be referred to more sensitive complementary techniques.

Although pXRF and WDXRF are useful for rapid geochemical analysis, their suitability for nuclear source material assessment must be defined on an element-specific and fit-for-purpose basis. Matrix-matched calibration, certified reference materials, sample homogenization, and cross-method validation are needed because XRF performance is affected by matrix effects, spectral interferences, detection limits, sample heterogeneity, and sample preparation (Da Silva et al. 2023; Steiner et al. 2017). This is particularly important for uranium, thorium, niobium, molybdenum, and other trace elements near detection limits, for which pXRF may provide useful screening information but may be less reliable for low-level quantification. Comparative studies on uranium- and thorium-bearing materials indicate that XRF-based methods require careful validation against more sensitive laboratory techniques, while ICP-MS or ICP-MS/MS remains preferred when ultra-trace concentrations, complex matrices, or high-confidence quantification are involved (Tuovinen et al. 2015; Boulyga et al. 2017). However, for Philippine nuclear source material assessment, it remains necessary to establish which elements can be reliably measured using pXRF, which are better quantified by WDXRF, and which should be referred to more sensitive complementary techniques.

Here, we describe an analytical calibration program for robust, rapid quantitative analyses of major, minor, and trace elements in nuclear source materials using conventional WDXRF and pXRF. The study uses 21 certified reference materials prepared as pressed powder pellets to evaluate reporting coverage, CRM-based calibration performance, and element-specific suitability of pXRF and WDXRF for geochemical analysis. This work is designed as a calibration-development and performance-assessment study. As such, all 21 CRMs were used to maximize the range of geological matrices and analyte concentrations represented, rather than partitioning the dataset into calibration and validation subsets. The use of pressed powder pellets of certified reference materials is

intended to circumvent the potential occurrence of sulfide minerals in Philippine nuclear source materials, which may degrade or alloy with platinum crucibles used in glass bead preparation. Pressed powder pellets also offer an advantage for determining certain trace elements associated with refractory minerals (e.g., Zr in zircon, $ZrSiO_4$), which may be difficult to dissolve in fused beads for XRF and in acid-digested solutions for solution ICP-MS. Hence, the calibrated method may also provide complementary rapid screening of Zr-rich samples for subsequent zircon-focused U-Pb geochronology and related geochemical studies. The calibration approach is therefore intended to support rapid screening and laboratory-based assessment of geological materials relevant to nuclear source material exploration, while also defining the analytical limitations of each XRF technique and identifying cases where more sensitive complementary methods may be required.

MATERIALS AND METHODS

Geochemical reference materials

A set of twenty-one (21) certified reference materials primarily from the Geological Survey of Japan consisting of igneous and sedimentary rocks (JP-1, JB-1b, JB-2, JB-3, JA-2, JA-3, JGb-1, JGb-2, JR-3, JSy-1, JH-1, JG-1a, JG-2, JG-3, JSI-1), and stream and lake sediments (JLk-1, JSd-1) were considered in this study (Table 1a). Mineralized reference materials, including a Pb-Zn ore (JZn-1), a porphyry Cu mill head (USGS GXR-4), a Au-U ore (African Mineral Standards AMIS0429), and a U-bearing pegmatite (African Mineral Standards AMIS0408), were also considered (Table 1). The reference materials were prepared as 32 mm pressed powder pellets set in polyvinyl chloride (PVC) rings using a Maekawa BRE-33 briquetting press set at a pressure of 20 MPa for 60 seconds with no binding material used. The choice of reference materials was considered to cover the expected range of major oxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, Na_2O , K_2O , P_2O_5) and selected trace elements (Ba, Cr, Cu, Mo, Nb, Ni, Pb, Rb, S, Sr, Th, U, V, Y, Zn, Zr) in Philippine nuclear source materials. JG-1a, JG-2, and JG-3 (granite and granodiorites) were selected to represent potential granite-related nuclear source materials such as those in the northern Palawan terrane of continental origin. Likewise, JSy-1 (syenite) was chosen as the corresponding rock type for the high-K alkalic porphyry Cu intrusives in northeastern Luzon. JSI-1 (clay slate) was selected to represent skarn-hosted uranium mineralization in Camarines Norte, whereas JP-1 (Horoman peridotite) was included to extend the calibration to high magnesium lithologies (e.g., ophiolitic samples). The inclusion of JSd-1 and JLk-1 (stream and lake sediments) makes the calibration suitable to environmental samples as well. The reference values adopted in this study, reported by Imai et al. 1995, 1996, 1999, USGS and AMIS, are listed in Table 1.

Table 1a: Certified major elemental concentration of reference materials used for calibration method development

Component			SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
ELline			Si K α	Ti K α	Al K α	Fe K α	Mn K α	Mg K α	Ca K α	Na K α	K K α	P K α
Sample	Locality & lithology	Reference	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
JP-1	Horoman peridotite	Imai et al. 1995	42.38	0.006	0.66	8.37	0.121	44.6	0.55	0.021	0.003	0.002
JB-1b	Kitamatsuura basalt	Terashima et al. 1995	51.11	1.26	14.38	9.02	0.147	8.14	9.60	2.63	1.32	0.256
JB-2	Oshima volcano basalt	Imai et al. 1995	53.25	1.19	14.64	14.25	0.218	4.62	9.82	2.04	0.42	0.101

JB-3	Fuji volcano basalt	Imai et al. 1995	51.96	1.44	17.2	11.82	0.177	5.19	9.79	2.73	0.78	0.294
JA-2	Goshikidai sanukitoid	Imai et al. 1995	56.42	0.66	15.41	6.21	0.108	7.6	6.29	3.11	1.81	0.146
JA-3	Asama volcano andesite	Imai et al. 1995	62.37	0.7	15.56	6.6	0.104	3.72	6.24	3.19	1.41	0.116
JGb-1	Utsushigatake gabbro	Imai et al. 1995	43.66	1.6	17.49	15.06	0.189	7.85	11.9	1.2	0.24	0.056
JGb-2	Mt. Tsukuba leucogabbro	Imai et al. 1999	46.47	0.56	23.48	6.69	0.13	6.18	14.10	0.92	0.059	0.017
JR-3	Ashizuri peralkaline rhyolite	Imai et al. 1999	72.76	0.21	11.90	4.72	0.083	0.050	0.093	4.69	4.29	0.017
JSy-1	Nephton syenite, Ontario, Canada	Imai et al. 1999	60.02	0.0015	23.17	0.084	0.0024	0.016	0.25	10.74	4.82	0.014
JH-1	Nishi-Dohira pyroxene hornblendite	Imai et al. 1999	48.18	0.67	5.66	10.27	0.19	16.73	15.02	0.71	0.53	0.099
JG-1a	Sori granodiorite	Imai et al. 1995	72.3	0.25	14.24	2.0	0.057	0.69	2.13	3.39	3.96	0.083
JG-2	Naegi granite	Imai et al. 1995	76.83	0.044	12.47	0.97	0.016	0.037	0.7	3.54	4.71	0.002
JG-3	Mitoya granodiorite	Imai et al. 1995	67.29	0.48	15.48	3.69	0.071	1.79	3.69	3.96	2.64	0.083
JLk-1	Lake Biwa sediment	Imai et al. 1996	57.16	0.668	16.73	6.929	0.266	1.736	0.686	1.051	2.805	0.208
JSl-1	Toyoma clay slate	Imai et al. 1996	59.47	0.725	17.6	6.764	0.0599	2.413	1.479	2.184	2.845	0.202
JZn-1	Kamioka mine Pb-Zn ore	Okai et al. 2002	43.95	0.20	6.32	11.8	1.49	1.94	18.1	0.45	0.83	<0.005
JSd-1	Ibaraki stream sediment	Imai et al. 1996	66.55	0.643	14.65	5.059	0.0924	1.813	3.034	2.727	2.183	0.122
GXR 4	Porphyry Cu ore	USGS	66.2	0.5	13.6	4.4	0.0	2.8	1.4	0.8	4.8	0.3
AMIS 0429			87.7			5.0	0.0		0.5		0.5	
AMIS 0408			48.2	0.3	17.4	7.3	3.3	0.5	3.9	1.4	0.8	2.8

Table 1b: Certified Trace Elemental Concentrations of Reference Materials Used for Calibration Method Development

Component	Ba	Cr	Cu	Mo	Nb	Ni	Pb	Rb	S	Sr	Th	U	V	Y	Zn	Zr
El.line	Ba L α	Cr K α	Cu K α	Mo K α	Nb K α	A Ni K α	Pb L α	Rb K α	S K α	Sr K α	Th L α	U - LA	V - KA	Y - KA	Zn-KA	Zr-KA
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
JP-1	19.5	2807.0	6.7	0.1	1.5	2460.0	0.1	0.8	26.9	3.3	0.2	0.0	27.6	1.5	41.8	5.9
JB-1b		439.0	55.5			148.0	6.8	39.1	10.0	439.0			214.0		80.0	
JB-2	222.0	28.1	225.0	1.1	1.6	16.6	5.4	7.4	17.9	178.0	0.3	0.2	575.0	24.9	108.0	51.2
JB-3	245.0	58.1	194.0	1.1	2.5	36.2	5.6	15.1	9.9	403.0	1.3	0.5	372.0	26.9	100.0	97.8
JA-2	321.0	436.0	29.7	0.6	9.5	130.0	19.2	72.9	8.0	248.0	5.0	2.2	126.0	18.3	64.7	116.0
JA-3	323.0	66.2	43.4	1.9	3.4	32.2	7.7	36.7	214.0	287.0	3.3	1.2	169.0	21.2	67.7	118.0
JGb-1	64.3	57.8	85.7	0.6	3.3	25.4	1.9	6.9	1910.0	327.0	0.5	0.1	635.0	10.4	109.0	32.8
JGb-2	36.5	125.0	11.4	0.4	1.9	13.6	1.5	2.9	599.0	438.0	0.2	0.0	174.0	4.5	48.5	11.6
JR-3	65.8	3.5	2.9	0.5	510.0	1.6	32.8	453.0	39.0	10.4	112.0	21.1	4.2	166.0	209.0	1494.0
JSy-1	15.7	2.0	1.3	0.0	0.5	1.1	4.9	66.3	13.0	19.3	0.2	0.2	2.1	2.6	3.2	70.2
JH-1	106.0	616.0	8.6	0.8	4.2	58.2	2.6	14.4	567.0	153.0	1.4	0.6	228.0	13.7	61.8	48.3
JG-1a	470.0	17.6	1.7	0.5	11.4	6.9	26.4	178.0	11.0	187.0	12.8	4.7	22.7	32.1	36.5	118.0
JG-2	81.0	6.4	0.5	0.4	14.7	4.3	31.5	301.0	7.0	17.9	31.6	11.3	3.8	86.5	13.6	97.6

JG-3	466.0	22.4	6.8	0.5	5.9	14.3	11.7	67.3	54.7	379.0	8.3	2.2	70.1	17.3	46.5	144.0
JLk-1	574.0	69.0	62.9	2.2	15.8	35.0	43.7	147.0	1052.0	67.5	19.5	3.8	117.0	40.0	152.0	137.0
JSI-1	305.0	60.9	40.8	0.8	9.5	37.6	17.4	117.0	1467.0	193.0	10.0	2.6	131.0	30.0	108.0	174.0
JZn-1	208.0	21.0	29.0			6.0	1610.0	42.0		358.0			24.0		22200.0	
JSd-1	520.0	21.5	22.0	0.7	11.1	7.0	12.9	67.4	68.0	340.0	4.4	1.0	76.0	14.8	96.5	132.0
USGS GXR 4	1640.0	64.0	6520.0	310.0		42.0	52.0	160.0	17700.0	221.0	22.5	6.2	87.0	14.0	73.0	186.0
AMIS 0429		751.0			15200.0				15700.0			722.0				
AMIS 0408		1641.6									113.0	406.0				

Portable X-ray fluorescence analysis

The pelletized samples were analyzed using a portable X-ray fluorescence spectrometer or pXRF (Bruker S1 Titan, Bruker Corporation, USA). The instrument is equipped with a 4 W rhodium thin-window X-ray tube operated over a 5–50 kV range with a maximum current of 200 μ A, a large-area silicon drift detector with a graphene window for improved light-element sensitivity, an automated five-position primary beam filter changer, and an 8 mm analysis spot size. The instrument is capable of detecting elements from Mg to U. Measurements were performed using the GeoExploration Oxide3phase method, a manufacturer-prebuilt calibration based on 97 reference materials and optimized for mining, exploration, grade control, drilling, and soil screening applications. A certified reference material, Bruker CS-M2, was analyzed at the start of each measurement batch to ensure instrument stability and consistency of the reported results. During analysis, the pXRF was mounted upright on a custom stand, with the beam directed toward the resting, pelletized samples. Each sample was analyzed in triplicate with a 90-s acquisition time per measurement. The results of the triplicate analysis are reported as the mean ($\bar{x}$) $\pm$ standard deviation.

Wavelength-dispersive X-ray fluorescence analysis

Elemental quantification of the pelletized samples was performed using a Rigaku Supermini 200 wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. The instrument was operated at 50 kV, 4 mA, utilizing a 200 W X-ray tube with a Pd

target for primary X-ray generation. Primary beam conditioning was achieved using either Zr200 or Al40 filters, selected according to sample matrix requirements. Diffracted X-rays were analyzed using an automatic crystal changer equipped with three analyzing crystals: LiF(200), PET, and RX25, selected based on the characteristic wavelengths of the target elements. Detection was performed using a scintillation counter for wavelengths below 0.275 nm and a proportional counter for wavelengths above 0.275 nm.

The twenty-one pressed powdered certified rock reference materials were analyzed to determine calibration intensities for major and trace element quantification. The instrumental analytical conditions employed are summarized in Table 2. An analytical runtime of 19 minutes per measurement was established for each sample.

Matrix correction was applied to compensate for inter-element absorption and secondary fluorescence effects within the sample matrix. Correction factors derived from coexisting elemental signals were iteratively applied to the analyte intensities to minimize matrix-induced spectral interference and maximize analytical accuracy. The obtained calibration constants and matrix correction factors for each analyte are summarized in Tables S1 and S2.

Table 2: Measurement conditions Employed for Major and Trace Element Determination of the 21 Certified Reference Material Samples. BG Coefficients are all zero

El.line	Crystal	Detector	PHA1	Peak/B	Angle (deg)	Time(sec)
Si-KA	PET	PC	100- 300	Peak	108.902	40
				BG1	106.350	10
				BG2	110.900	10
Ti-KA	LiF(200)	SC	100- 400	Peak	86.102	20
				BG1	85.300	10
				BG2	86.860	10
Al-KA	PET	PC	100- 300	Peak	144.582	40
				BG1	147.050	10
Mn-KA	LiF(200)	SC	100- 400	Peak	62.940	20
				BG1	62.180	10
				BG2	63.640	10
Mg-KA	RX25	PC	100- 300	Peak	38.548	40
				BG1	36.200	10
				BG2	40.350	10
Ca-KA	PET	PC	100- 300	Peak	45.100	40
				BG1	43.350	10
				BG2	46.900	10
Na-KA	RX25	PC	100- 300	Peak	46.852	40
				BG1	44.400	10
				BG2	48.900	10
K -KA	PET	PC	100- 300	Peak	50.562	40

				BG1	52.150	10
P -KA	PET	PC	100- 300	Peak	89.306	40
				BG1	86.800	10
				BG2	90.950	10
Fe-KA	LiF(200)	SC	100- 400	Peak	57.488	20
				BG1	58.220	10
Ba-LA	LiF(200)	SC	100- 300	Peak	87.124	20
				BG1	86.640	10
				BG2	88.020	10
Cr-KA	LiF(200)	SC	100- 400	Peak	69.320	20
				BG1	68.380	10
				BG2	70.260	10
Cu-KA	LiF(200)	SC	100- 375	Peak	45.006	20
				BG1	45.760	10
Mo-KA	LiF(200)	SC	100- 300	Peak	20.332	20
				BG1	19.620	10
				BG2	20.980	10
Nb-KA	LiF(200)	SC	100- 300	Peak	21.390	20
				BG1	21.460	10
				BG2	21.120	10
Ni-KA	LiF(200)	SC	100- 400	Peak	48.646	20
				BG1	47.720	10
				BG2	49.540	10
Pb-LA	LiF(200)	SC	100- 300	Peak	33.934	20
				BG1	33.100	10
				BG2	34.840	10
Rb-KA	LiF(200)	SC	100- 300	Peak	26.620	20
				BG1	27.380	10
S -KA	PET	PC	100- 300	Peak	75.680	40
				BG1	73.500	10
				BG2	77.450	10
Sr-KA	LiF(200)	SC	100- 300	Peak	25.150	20
				BG1	24.460	10
				BG2	26.000	10
Th-LA	LiF(200)	SC	100- 300	Peak	27.374	20
				BG1	26.940	10
				BG2	27.920	10
U -LA	LiF(200)	SC	100- 300	Peak	26.160	20
				BG1	25.520	10
				BG2	26.740	10
V -KA	LiF(200)	SC	100- 400	Peak	76.868	20
				BG1	76.940	10
				BG2	76.240	10
Y -KA	LiF(200)	SC	100- 300	Peak	23.796	20
				BG1	23.200	10
				BG2	24.460	10
Zn-KA	LiF(200)	SC	100- 350	Peak	41.786	20
				BG1	42.540	10
Zr-KA	LiF(200)	SC	100- 300	Peak	22.554	20
				BG1	21.920	10
				BG2	23.260	10

RESULTS AND DISCUSSION

CRM-based calibration performance of portable X-ray fluorescence

Portable X-ray fluorescence analysis of the 21 igneous and sedimentary rock certified reference materials showed element-specific differences in reporting coverage and calibration performance (Table 3). Because not all CRMs have certified values for all elements, the calibration assessment was first limited to CRMs with available certified concentrations. Manufacturer-provided limits of detection (LODs) and analysis ranges for the GeoExploration Oxide 3 phase method were used as screening references to evaluate whether pXRF reported concentrations above LOD. The proportion of CRMs with certified values that yielded pXRF concentrations above LOD was defined as the CRM reporting coverage. As an operational screening criterion, elements with less than 50% >LOD coverage were considered to have insufficient coverage for robust CRM-based calibration assessment in this dataset. Most elements showed >LOD coverage above this threshold. However, Nb, Th, U, and V yielded >LOD pXRF values for only 47.1%, 27.8%, 21.1%, and 36.8% of their corresponding certified CRMs, respectively. These elements were therefore classified as having insufficient coverage, even when their regression statistics showed high R^2 values. This distinction is important because high apparent linearity based on only a small number of above-LOD CRMs may not represent reliable calibration performance across the concentration range of the CRM suite.

For elements with sufficient >LOD coverage, CRM-based linear regression was performed by plotting certified CRM concentrations against pXRF-reported concentrations. The resulting slope and intercept define the element-specific correction equation recommended in this study:

$$C_{corrected} = mC_{pXRF} + b$$

where C_{pXRF} is the concentration reported by the manufacturer-prebuilt pXRF calibration, and $C_{corrected}$ is the corrected concentration estimated from the CRM-based regression. These correction equations are intended for pXRF measurements of igneous and sedimentary rock matrices comparable to those in the CRM suite, analyzed under similar measurement conditions. Calibration performance was classified as Good for $R^2 \geq 0.90$, Moderate for $0.80 \leq R^2 < 0.90$, and Poor for $R^2 < 0.80$.

Among the elements with sufficient >LOD coverage, 14 showed Good calibration performance: Cr, Ba, Cu, Ni, Pb, Rb, Sr, Y, Zn, Ca, Fe, K_2O , Ti, and Mn. These elements had R^2 values ranging from 0.9579 for Sr to 0.9990 for Rb, indicating strong linear relationships between pXRF-reported concentrations and certified CRM values. Several of these elements also had regression slopes close to unity, including Cu, Ni, Sr, Ti, Cr, and Mn, indicating that the manufacturer-prebuilt calibration yielded values that were broadly proportional to certified concentrations. However, the slopes and intercepts were not always ideal, indicating residual element-specific bias that can be addressed through the CRM-derived correction equations.

Three elements were classified as Moderate: Zr, SiO_2 , and Al_2O_3 , with R^2 values of 0.8270, 0.8197, and 0.8704, respectively. These results indicate usable but less robust linearity compared with the elements in the Good category. Three elements were classified as Poor despite sufficient >LOD coverage: S, MgO, and P. These had R^2 values of 0.6759, 0.7976, and 0.2857, respectively, indicating weak CRM-based calibration performance under the present measurement conditions.

For selected elements, one or two high-concentration CRMs were excluded from the linear regression because they exerted disproportionate leverage on the calibration line relative to the remaining CRM concentration range, forcing the R^2 closer to 1. These cases were explicitly identified in Table 3 and involved S, Zn, Zr, and MgO. The exclusions were applied only to the regression statistics and correction equations, and the affected elements were still interpreted according to the same >LOD coverage and R^2 classification criteria.

Overall, the pXRF results show that the manufacturer-prebuilt GeoExploration calibration produced strong CRM-based linearity for several major oxides and selected minor-to-trace elements, particularly, Cr, Ba, Cu, Ni, Pb, Rb, Sr, Y, Zn, Ca, Fe, K_2O , Ti, and Mn. The CRM-derived slopes and intercepts provide an additional element-specific correction layer that may improve the accuracy of pXRF measurements for igneous and sedimentary rock matrices similar to those represented by the 21 CRMs. However, the calibration utility remained element-specific and was limited by insufficient >LOD coverage for Nb, Th, U, and V, and by poor linearity for S, MgO, and P.

Table 3: Reporting coverage and CRM-based calibration performance of pXRF measurements using 21 igneous and sedimentary rock certified reference materials. Calibration plots are available in the supplementary material.

Element	Certified CRMs, n	CRMs measured above LOD, n	^a >LOD coverage, %	^b Manufacturer LOD on pure SiO_2 (ppm)	^b Manufacturer Analysis Range (%)	Slope	Intercept	R^2	Calibration Class	Notes
Cr	21	18	85.7%	45	0.014-2.4	1.122	-6.860	0.9913	Good	
Ba	18	16	88.9%	45	0.015-2.7	1.201	-84.558	0.9825	Good	
Cu	19	13	68.4%	3	0.003-6.8	1.022	-2.470	0.9910	Good	
Nb	17	8	47.1%	4	0.002-42.4	1.243	-0.051	0.9259	Insufficient coverage	≤50% of certified CRMs above LOD
Ni	19	18	94.7%	4	0.002-1.4	1.002	-6.729	0.9817	Good	
Pb	19	13	68.4%	5	0.002-1.4	1.185	-3.312	0.9880	Good	
Rb	19	17	89.5%	2	0.001-0.07	1.142	1.436	0.9990	Good	
S	19	17	89.5%	85	0.03-3.7	1.356	-579.698	0.6759	Poor	Two high-concentration CRMs excluded

										from linear equation
Sr	19	18	94.7%	2	0.001-1.1	0.973	7.783	0.9579	Good	
Th	18	5	27.8%	7	0.002-0.7	0.849	3.006	0.9971	Insufficient coverage	≤50% of certified CRMs above LOD
U	19	4	21.1%	1	0.001-0.2	1.189	-34.034	0.9718	Insufficient coverage	≤50% of certified CRMs above LOD
V	19	7	36.8%	25	0.008-10.7	1.564	-41.447	0.9535	Insufficient coverage	≤50% of certified CRMs above LOD
Y	17	16	94.1%	2	0.001-0.22	0.803	1.616	0.9907	Good	
Zn	19	18	94.7%	3	0.001-1.5	1.346	-3.004	0.9928	Good	One high-concentration CRM excluded from linear equation
Zr	17	16	94.1%	2	0.001-1.6	0.553	23.205	0.8270	Moderate	One high-concentration CRM excluded from linear equation
SiO ₂	21	21	100.0%	N/A	N/A	0.837	175480.770	0.8197	Moderate	
Al ₂ O ₃	20	20	100.0%	350	0.12-69	1.444	15096.603	0.8704	Moderate	
Ca	21	21	100.0%	30	0.01-31.1	1.555	-1446.375	0.9989	Good	
Fe	21	20	95.2%	16	0.005-34.5	1.465	897.886	0.9853	Good	
MgO	20	15	75.0%	1400	0.5-70	1.866	9380.114	0.7976	Poor	One high-concentration CRM excluded from linear equation
K ₂ O	21	20	95.2%	50	0.016-15.4	1.202	613.048	0.9880	Good	
Ti	20	18	90.0%	30	0.01-19.4	1.116	21.001	0.9818	Good	
Mn	21	21	100.0%	16	0.005-16	0.947	21.866	0.9745	Good	
P	20	20	100.0%	45	0.015-13.2	0.577	-120.198	0.2857	Poor	

a. LOD coverage was calculated as the proportion of CRMs with certified values for which pXRF reported concentrations above LOD.

b. Manufacturer LODs and analysis ranges were used as screening references and were not experimentally determined in this study.

c. Calibration classes were assigned as Good ($R^2 \geq 0.90$), Moderate ($0.80 \leq R^2 < 0.90$), and Poor ($R^2 < 0.80$), after excluding elements with insufficient >LOD coverage.

Table 4: Reporting coverage and CRM-based calibration performance of WDXRF measurements using 21 igneous and sedimentary rock certified reference materials. Calibration plots are available in the supplementary material.

Element	Certified CRMs, n	CRMs measured above zero, n	^a Positive reporting coverage, %	^b Analysis Range (%)	Slope	Intercept	R ²	^c Calibration Class	Notes
Cr	21	19	90.5%	0.0002-0.2800	1.000	0.009	0.9992	Good	
Ba	18	17	94.4%	0.0016-0.0574	1.023	17.592	0.8325	Moderate	One high-concentration CRM excluded from linear equation
Cu	19	17	89.5%	0.0001-0.0225	0.981	2.761	0.9919	Good	One high-concentration CRM excluded from linear equation

Nb	17	16	94.1%		-0.227	234.530	0.7744	Poor	One high-concentration CRM excluded from linear equation
Ni	19	19	100.0%	0.0001-0.0148	1.072	0.929	0.9734	Good	One high-concentration CRM excluded from linear equation
Pb	19	15	78.9%		0.626	10.625	0.5361	Poor	One high-concentration CRM excluded from linear equation
Rb	19	19	100.0%	0.0001-0.0453	1.001	0.206	0.9915	Good	
S	19	19	100.0%	0.0007-1.7700	1.000	0.494	0.9979	Good	
Sr	19	18	94.7%	0.0003-0.0439	0.985	1.944	0.9899	Good	
Th	18	18	100.0%		0.941	6.601	0.4403	Poor	
U	19	16	84.2%		-0.049	4.151	0.0232	Poor	
Mo	17	12	70.6%		0.065	0.690	0.1684	Poor	
V	19	17	89.5%	0.0002-0.0635	1.000	0.000	0.9193	Good	
Y	17	17	100.0%	0.0002-0.0166	1.004	0.326	0.9889	Good	
Zn	19	16	84.2%	0.0014-0.0166	0.879	8.578	0.9244	Good	One high-concentration CRM excluded from linear equation
Zr	17	17	100.0%	0.0006-0.0186	1.004	0.354	0.9738	Good	One high-concentration CRM excluded from linear equation
SiO ₂	21	21	100.0%	42.000-87.700	0.942	2.913	0.9635	Good	
Al ₂ O ₃	20	20	100.0%	0.6600-23.480	1.032	0.249	0.9818	Good	
CaO	21	20	95.2%	0.0001-0.0020	1.001	0.014	0.9994	Good	
Fe ₂ O ₃	21	21	100.0%	0.0000-0.0015	0.976	0.242	0.9661	Good	
MgO	20	20	100.0%	0.0001-0.0045	1.001	0.024	0.9966	Good	
K ₂ O	21	20	95.2%	0.0030-4.8300	1.000	0.000	0.9985	Good	
TiO ₂	20	19	95.0%	0.0020-1.6000	0.986	0.000	0.9901	Good	
MnO	21	21	100.0%	0.0020-3.3000	1.000	0.000	0.9998	Good	
P ₂ O ₅	20	20	100.0%	0.0020-2.7600	1.009	0.007	0.9969	Good	
Na ₂ O	20	20	100.0%	0.0210-10.740	0.989	0.074	0.9898	Good	

a. Positive reporting coverage was calculated as the proportion of CRMs with certified values for which pXRF reported concentrations above zero.
b. Analysis ranges were the lowest and highest values analyzed in this CRM suite. Those with a classified calibration class of " Poor " are not reported here.
c. Calibration classes were assigned as Good ($R^2 \geq 0.90$), Moderate ($0.80 \leq R^2 < 0.90$), and Poor ($R^2 < 0.80$), after excluding elements with insufficient coverage.

CRM-based calibration performance of wavelength-dispersive X-ray fluorescence

Wavelength-dispersive X-ray fluorescence analysis of the 21 igneous and sedimentary rock certified reference materials showed generally strong CRM-based calibration performance across most measured elements and oxides (Table 4). Unlike pXRF, which used

a manufacturer-prebuilt calibration, the WDXRF calibration was constructed using the CRM suite. Elemental analysis was performed using the empirical method, wherein CRM-based calibration curves were established for the known elemental concentrations of the CRMs. The analysis ranges reported in Table

4, therefore, represent the lowest and highest measured values within the present CRM suite.

Because experimental LODs were not determined for the constructed WDXRF calibration, reporting coverage was assessed based on the number of CRMs with certified values that yielded positive measured concentrations. In cases where WDXRF returned negative values, these were not counted as reportable measurements. This metric is therefore referred to as positive reporting coverage and should not be interpreted as formal >LOD coverage. All WDXRF analytes showed positive reporting coverage above 50%, with the lowest coverage observed for Mo at 70.6%, followed by Pb at 78.9%, U and Zn at 84.2%, and Cu and V at 89.5%. Thus, no WDXRF analyte was excluded from calibration assessment on the basis of insufficient positive reporting coverage.

For elements and oxides with sufficient positive reporting coverage, CRM-based linear regression was performed by plotting certified CRM concentrations against WDXRF-measured concentrations to assess their calibration performance. The slope and intercept define the CRM-derived certified/measured relationship:

$$C_{\text{certified}} = mC_{\text{WDXRF}} + b$$

where C_{WDXRF} is the concentration measured by the WDXRF using the empirical method, and $C_{\text{certified}}$ is the certified elemental concentrations of CRMs. Similar to the pXRF results, calibration performance was classified as Good for $R^2 \geq 0.90$, Moderate for $0.80 \leq R^2 < 0.90$, and Poor for $R^2 < 0.80$.

Most WDXRF analytes showed Good calibration performance. These included Cr, Cu, Ni, Rb, S, Sr, V, Y, Zn, Zr, SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , MgO , K_2O , TiO_2 , MnO , P_2O_5 , and Na_2O . Their R^2 values ranged from 0.9193 for V to 0.9998 for MnO, indicating strong linear relationships between WDXRF-measured concentrations and certified CRM values. Many of these analytes also showed slopes close to unity, particularly Cr, Rb, S, V, Zr, CaO , MgO , K_2O , and MnO , suggesting that the constructed WDXRF calibration yielded measurements that were closely proportional to the certified values for these elements and oxides.

Ba was classified as Moderate, with an R^2 value of 0.8325 after exclusion of one high-concentration CRM from the linear equation. Although the slope for Ba was close to unity, the lower R^2 indicates that the calibration relationship was less robust than those of the Good-performing analytes. Five analytes were classified as Poor: Nb, Pb, Th, U, and Mo, with R^2 values of 0.7744, 0.5361, 0.4403, 0.0232, and 0.1684, respectively. Although WDXRF produced positive measured values for these analytes in several CRMs, the weak linear relationships suggest that many of these measurements were likely near or below the practical detection or reporting capability of the constructed WDXRF calibration. Because experimental LODs were not determined in this study, this interpretation should be treated as a working explanation rather than a confirmed LOD-based classification.

For selected elements, one high-concentration CRM was excluded from the linear regression because it exerted disproportionate leverage relative to the remaining CRM concentration range, forcing the R^2 towards 1. These cases involved Ba, Cu, Nb, Ni, Pb, Zn, and Zr, and are identified in Table 4. These exclusions were applied only to the regression statistics and calibration/correction relationships, while the analytes were still interpreted according to the same positive reporting coverage and R^2 classification criteria. Overall, the WDXRF results show that the CRM-constructed calibration produced strong linearity for most major oxides and

several selected minor elements in the 21 CRMs. WDXRF yielded broad positive reporting coverage across the CRM suite and particularly strong calibration performance for major oxides, including SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , MgO , K_2O , TiO_2 , MnO , P_2O_5 , and Na_2O . However, calibration performance remained element-specific, with weak linearity observed for Nb, Pb, Th, U, and Mo, most likely because several measured values for these elements were close to the practical reporting limits of the constructed calibration. Future work should include matrix-matched LOD determination for the WDXRF calibration to better distinguish low-level reportable measurements from values that are positive but analytically unreliable.

Element-specific comparison of pXRF and WDXRF performance

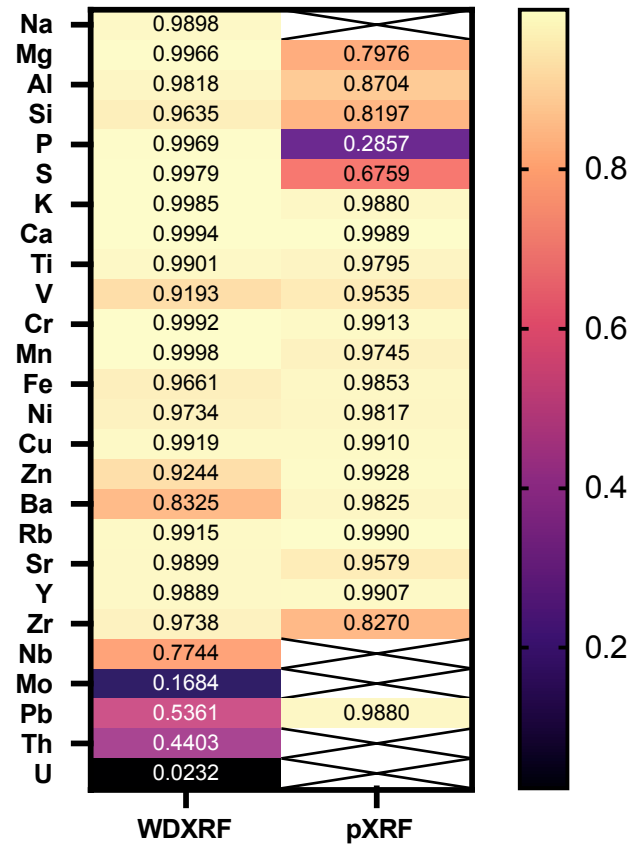


Figure 1: CRM-based calibration performance of pXRF and WDXRF. R^2 values compare measured concentrations against certified CRM values. For pXRF, elements with <50% reporting coverage above the manufacturer-provided LOD are not reported and denoted with "X".

The element-specific comparison of pXRF and WDXRF shows that the two XRF techniques have complementary strengths for geochemical analysis (Figure 1). Although both methods produced CRM-based calibration relationships for several elements, their performance differed depending on elemental mass, concentration range, reporting coverage, and instrument configuration. For this reason, the comparison was interpreted using both calibration linearity and reporting coverage, rather than R^2 values alone.

For major oxides and lighter elements, WDXRF showed a clear advantage over pXRF. WDXRF produced Good calibration performance for Na_2O ($R^2 = 0.9898$), MgO ($R^2 = 0.9966$), Al_2O_3 ($R^2 = 0.9818$), SiO_2 ($R^2 = 0.9635$), P_2O_5 ($R^2 = 0.9969$), K_2O ($R^2 = 0.9985$), CaO ($R^2 = 0.9994$), TiO_2 ($R^2 = 0.9901$), MnO ($R^2 = 0.9998$), and Fe_2O_3 ($R^2 = 0.9661$). In contrast, pXRF showed Good calibration performance for K_2O ($R^2 = 0.9880$), Ca ($R^2 = 0.9989$),

Ti ($R^2 = 0.9818$), Mn ($R^2 = 0.9745$), and Fe ($R^2 = 0.9853$), but only Moderate performance for SiO₂ ($R^2 = 0.8197$) and Al₂O₃ ($R^2 = 0.8704$), and Poor performance for MgO ($R^2 = 0.7976$) and P ($R^2 = 0.2857$). These results indicate that WDXRF is the more appropriate method for quantitative major-element analysis of igneous and sedimentary rock materials, particularly for light elements and major oxides.

The stronger WDXRF performance for these analytes is consistent with the differences in instrument configuration. The pXRF system used in this study is a handheld instrument equipped with a 4 W Rh thin-window X-ray tube and operated in air, with an 8 mm analysis spot size. In contrast, the WDXRF system is a laboratory instrument equipped with a 200 W Pd-target X-ray tube operated at 50 kV and 4 mA. The WDXRF system also uses wavelength-dispersive optics, including LiF(200), PET, and RX25 analyzing crystals, together with scintillation and proportional counters selected according to the wavelength region of the analyte. In addition, WDXRF analysis was performed under vacuum, which reduces air absorption of low-energy X-rays. These features provide stronger excitation, better spectral resolution, and improved sensitivity for light elements compared with pXRF analysis in air.

Sulfur also showed a clear method-specific difference. WDXRF produced Good calibration performance for S ($R^2 = 0.9979$), whereas pXRF produced Poor calibration performance for S ($R^2 = 0.6759$), despite sufficient >LOD coverage. This indicates that, under the present measurement conditions, WDXRF is more suitable for sulfur determination in the CRM concentration range evaluated in this study. Similarly, WDXRF is preferred for Na₂O ($R^2 = 0.9898$) because Na was included in the WDXRF calibration but was not reported in the pXRF output used in this study.

For selected trace elements, both pXRF and WDXRF showed strong CRM-based linearity. Cr, Cu, Ni, Rb, Sr, Y, and Zn showed Good calibration performance using both techniques: Cr (pXRF $R^2 = 0.9913$; WDXRF $R^2 = 0.9992$), Cu (pXRF $R^2 = 0.9910$; WDXRF $R^2 = 0.9919$), Ni (pXRF $R^2 = 0.9817$; WDXRF $R^2 = 0.9734$), Rb (pXRF $R^2 = 0.9990$; WDXRF $R^2 = 0.9915$), Sr (pXRF $R^2 = 0.9579$; WDXRF $R^2 = 0.9899$), Y (pXRF $R^2 = 0.9907$; WDXRF $R^2 = 0.9889$), and Zn (pXRF $R^2 = 0.9928$; WDXRF $R^2 = 0.9244$). These elements are therefore suitable candidates for either method, provided that concentrations fall within the reporting range of the instrument and the sample matrix is comparable to the CRM suite. For these elements, pXRF offers the practical advantages of shorter measurement times and rapid preliminary screening, while WDXRF provides laboratory-based quantification under more controlled analytical conditions. Although pXRF is portable and field-deployable, the present study used pressed powder pellets prepared under laboratory conditions to provide a standardized basis for comparison between the two techniques. Direct field analysis of unprepared geological materials would introduce additional sources of variability associated with sample heterogeneity, surface condition, moisture, and measurement geometry. Consequently, analytical precision and accuracy may be lower than those demonstrated for the homogenized pressed pellets evaluated in this study. Thus, pXRF may be used for preliminary assessment, sample triage, or high-throughput screening, whereas WDXRF is preferred when greater control of calibration, geometry, and matrix correction is required.

Some elements showed clear method-specific advantages. Ba showed Good calibration performance by pXRF ($R^2 = 0.9825$) but only Moderate performance by WDXRF ($R^2 = 0.8325$), indicating that pXRF may provide more reliable CRM-based estimates for Ba under the present calibration conditions. Pb also showed Good performance by pXRF ($R^2 = 0.9880$) but Poor performance by

WDXRF ($R^2 = 0.5361$), suggesting that pXRF is the more useful of the two XRF methods for Pb in this CRM suite, provided that measured concentrations are above LOD. In contrast, Zr showed Good calibration performance by WDXRF ($R^2 = 0.9738$) but only Moderate performance by pXRF ($R^2 = 0.8270$), indicating that WDXRF is preferred for Zr quantification. V also requires caution: although the pXRF regression showed high R^2 ($R^2 = 0.9535$), only 36.8% of the certified CRMs yielded pXRF values above LOD. Therefore, WDXRF is preferred for V because it showed Good calibration performance ($R^2 = 0.9193$) and broader positive reporting coverage.

Nb, Th, U, and Mo were not reliably quantified by the XRF approaches evaluated here. For pXRF, Nb, Th, and U showed high apparent linearity, with R^2 values of 0.9259, 0.9971, and 0.9718, respectively, but were limited by insufficient >LOD coverage. Mo was not reported in the pXRF dataset. For WDXRF, Nb ($R^2 = 0.7744$), Th ($R^2 = 0.4403$), U ($R^2 = 0.0232$), and Mo ($R^2 = 0.1684$) showed Poor calibration performance despite positive measured values for several CRMs. The weak WDXRF linearity likely reflects that many measured values for these elements were close to the practical detection or reporting limits of the constructed calibration. These results indicate that the present pXRF and WDXRF methods should not be used as stand-alone quantitative methods for Nb, Th, U, and Mo at the concentration levels represented by this CRM suite.

These findings are consistent with previous pXRF studies showing concentration-dependent performance for U and Th. Proctor et al. (2020) reported a U quantification limit of 13.1 mg kg⁻¹ and good agreement with ICP-MS for highly U-enriched soils, whereas performance was poorer at concentrations near the detection limit. Similarly, Melquiades et al. (2024) reported quantification limits of 9.9 mg kg⁻¹ for U and 11.0 mg kg⁻¹ for Th, with satisfactory performance for Th but overestimation of U at natural soil concentrations. These reported quantification limits are consistent with the reduced pXRF reporting coverage observed in the present CRM suite, where many U and Th concentrations are near or below the practical reporting range. Together, our findings highlight the limitations of XRF techniques for reliable quantification of U and Th at lower concentrations typical of similar geochemical materials. For these elements, more sensitive complementary techniques, such as ICP-MS/MS, are recommended, particularly when low-level concentrations or high-confidence geochemical interpretation are required.

Overall, WDXRF is recommended for quantitative major-oxide analysis and for elements such as S, V, and Zr, where it showed stronger CRM-based performance than pXRF. pXRF is recommended as a rapid screening method for selected trace elements with Good calibration performance and sufficient >LOD coverage, including Cr, Ba, Cu, Ni, Pb, Rb, Sr, Y, and Zn. For elements that performed well in both methods, pXRF can be used for rapid preliminary assessment, while WDXRF can serve as a more controlled laboratory method. However, both techniques remain element-specific, and their outputs should be interpreted using CRM-based correction equations, reporting coverage, and calibration class rather than relying on instrument-reported concentrations alone.

CONCLUSION

This study examined whether pXRF and WDXRF can provide reliable, element-specific measurements of major oxides and selected trace elements in geological reference materials relevant to nuclear source material assessment. Using 21 certified reference materials prepared as pressed powder pellets, the results showed

that XRF performance is strongly element-specific. Portable XRF showed good CRM-based calibration performance for Cr, Ba, Cu, Ni, Pb, Rb, Sr, Y, Zn, Ca, Fe, K₂O, Ti, and Mn, supporting its use as a rapid screening method when concentrations are above reporting limits and sample matrices are comparable to the CRM suite. However, pXRF showed insufficient reporting coverage for Nb, Th, U, and V, and poor calibration performance for S, MgO, and P. In contrast, WDXRF showed strong performance for most major oxides, including Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, MnO, and Fe₂O₃, as well as selected trace elements such as Cr, Cu, Ni, Rb, S, Sr, V, Y, Zn, and Zr, indicating its suitability for laboratory-based quantitative analysis. Overall, WDXRF is recommended for major-oxide determination and elements such as S, V, and Zr. Portable XRF is recommended for rapid screening of selected elements, including Cr, Ba, Cu, Ni, Pb, Rb, Sr, Y, and Zn, when CRM-based correction equations and reporting coverage criteria are applied. For nuclear source material assessment, U and Th should not be quantified solely by the present XRF methods. The limitation for U and Th primarily reflects their low concentrations in geochemical materials of the type represented by the CRM suite, which approach or fall below the practical reporting capability of both XRF methods. Although pXRF showed good apparent linearity when U or Th was within the instrument's working range, <50% >LOD coverage indicates that reliable quantification is generally limited to more U- or Th-enriched samples. More sensitive complementary techniques such as ICP-MS/MS are recommended for U and Th, particularly for low-level concentrations, regulatory-grade confidence, or high-resolution geochemical interpretation. Future work should include matrix-matched LOD determination, independent validation of the correction equations, and application of the calibrated methods to Philippine nuclear source materials and related geological samples.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

CONTRIBUTIONS OF INDIVIDUAL AUTHORS

ATBVII: Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Data curation, Formal analysis, Funding acquisition, Supervision; **JKGB:** Writing – review & editing, Data curation, Formal analysis; **GBMB:** Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Data curation, Formal analysis; **RAHM:** Writing – review & editing, Data curation, Formal analysis; **AdCP:** Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Data curation, Formal analysis, Funding acquisition, Supervision; **RCGR:** Writing – review & editing, Data curation, Formal analysis; **JIBR:** Writing – review & editing, Data curation, Formal analysis; **LGFS:** Writing – review & editing, Data curation, Formal analysis.

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SUPPLEMENTAL INFORMATION

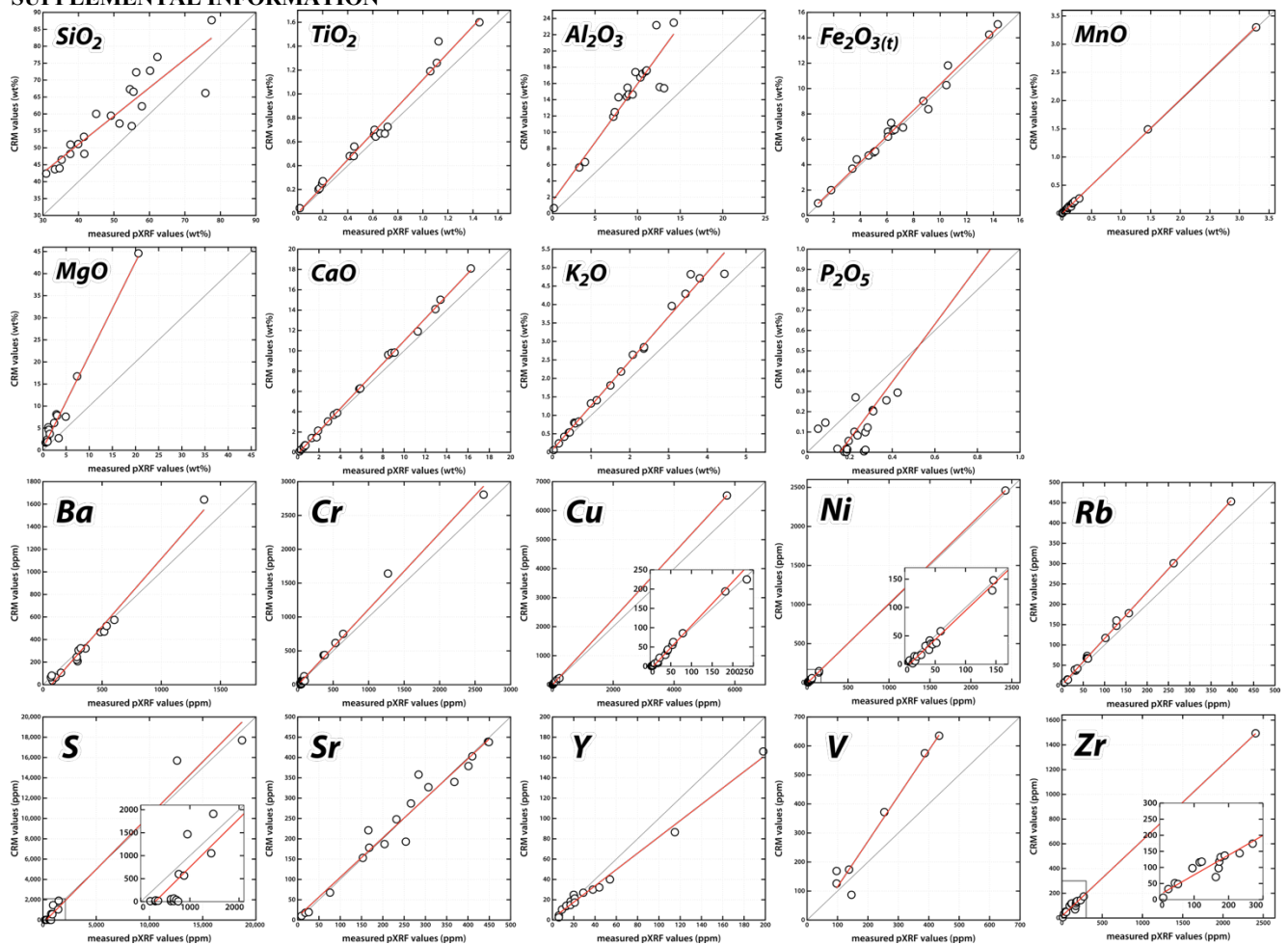


Figure S1: CRM-based calibration plots for pXRF measurements. Certified concentrations of the 21 geochemical reference materials are plotted against pXRF-reported concentrations for each element or oxide. Red lines indicate the linear regression used to derive the CRM-based correction equations. Insets show expanded views of low-concentration regions where high-concentration samples dominate the full-scale plot. Elements with insufficient reporting coverage were interpreted cautiously because fewer than 50% of CRMs with certified values yielded pXRF concentrations above the manufacturer-provided LOD.

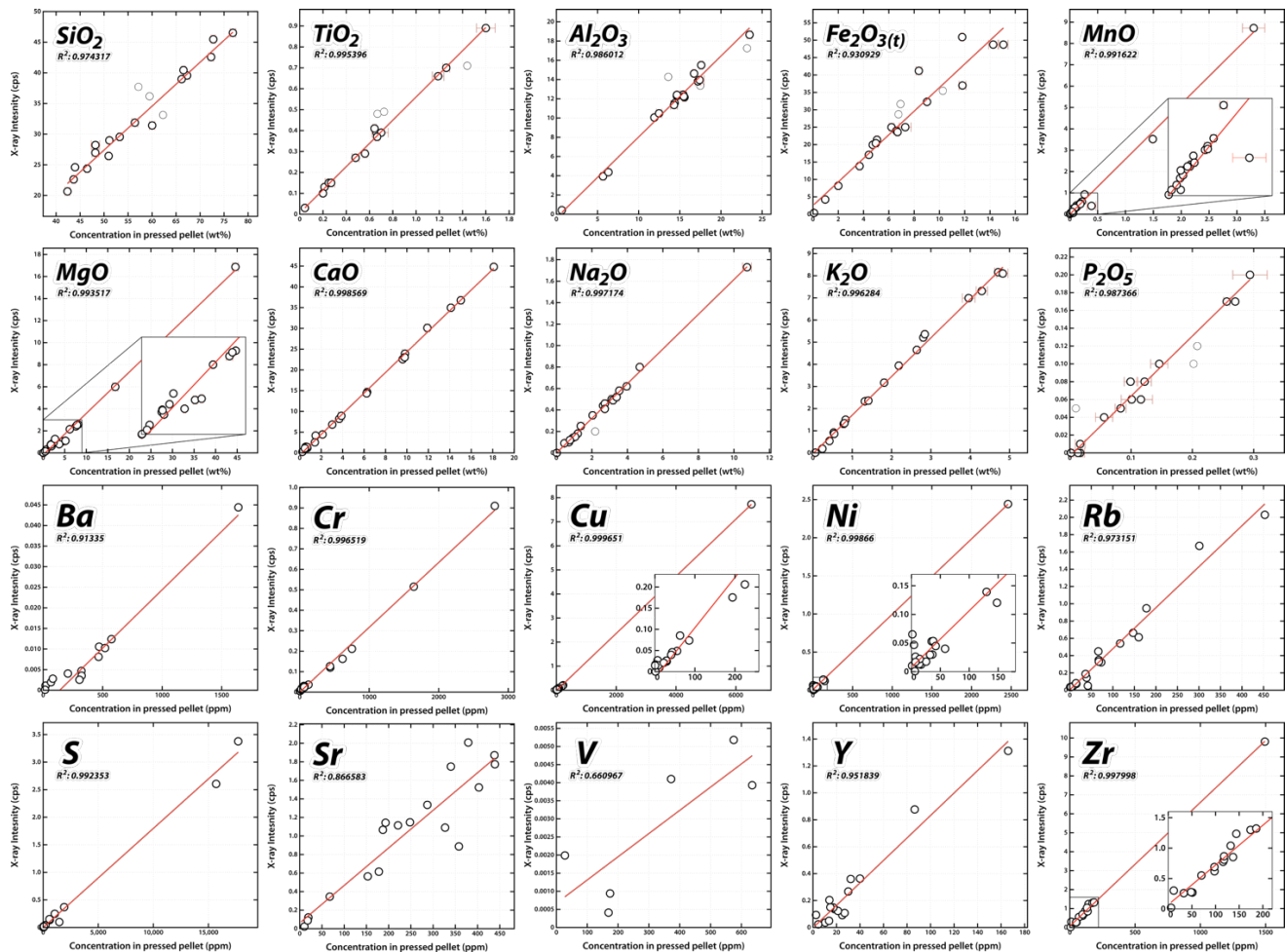


Figure S2: CRM-based calibration plots for WDXRF measurements. Certified concentrations of the 21 geochemical reference materials are plotted against WDXRF-measured intensities or concentrations for each element or oxide. Red lines indicate the empirical CRM-based calibration relationships used to evaluate WDXRF performance. Insets show expanded views of low-concentration regions where high-concentration samples dominate the full-scale plot. Error bars indicate replicate variability where shown.

Table S1: Empirical Calibration Constants per Element for WDXRF

Comp.	Type	C(Linear)	D(Constant)
SiO2	Empirical	1.30E+00	1.19E+01
TiO2	Empirical	2.03E+00	2.92E-02
Al2O3	Empirical	1.36E+00	5.73E-01
MnO	Empirical	5.39E-01	2.10E-02
MgO	Empirical	2.30E+00	2.40E-01
CaO	Empirical	3.20E-01	2.27E-02
Na2O	Empirical	6.16E+00	4.95E-02
K2O	Empirical	4.94E-01	7.91E-02
P2O5	Empirical	9.78E-01	3.59E-03
Fe2O3	Empirical	2.07E-01	-1.18E-01
Ba	Empirical	1.55E+04	1.24E+02
Cr	Empirical	2.59E+03	-1.52E+01

Cu	Empirical	6.95E+02	3.23E+00
Mo	Empirical	1.71E+03	1.73E+01
Nb	Empirical	-1.65E+03	1.02E+03
Ni	Empirical	2.04E+03	-1.88E+00
Pb	Empirical	4.15E+03	-8.59E+01
Rb	Empirical	5.87E+02	-1.05E+01
S	Empirical	2.91E+03	2.76E+01
Sr	Empirical	6.20E+02	-1.54E+00
Th	Empirical	2.06E+01	7.98E+00
U	Empirical	5.80E+02	5.17E+01
V	Empirical	2.18E+04	-4.22E+00
Y	Empirical	1.43E+02	1.39E+00
Zn	Empirical	1.97E+03	-5.47E+01
Zr	Empirical	1.75E+02	7.45E-01

Table S2: Matrix Correction Coefficients Derived for Analyte Signal Compensation Based on Coexisting Element for WDXRF

Analyte	El.line	Type	1st comp.	Coefficient	Analyte	El.line	Type	1st comp.	Coefficient
SiO ₂	Si-KA	A	Al ₂ O ₃	3.78030E-03	Mo	Mo-KA	A	SiO ₂	-1.36439E-02
SiO ₂	Si-KA	A	P ₂ O ₅	-3.26969E-02	Mo	Mo-KA	A	MnO	-1.09094E-01
SiO ₂	Si-KA	A	MgO	1.15830E-03	Mo	Mo-KA	A	MgO	-5.61008E-03
TiO ₂	Ti-KA	A	SiO ₂	-4.82189E-03	Ni	Ni-KA	A	SiO ₂	-1.14002E-02
TiO ₂	Ti-KA	A	Na ₂ O	3.36840E-02	Ni	Ni-KA	A	Al ₂ O ₃	7.03531E-03
TiO ₂	Ti-KA	A	V	1.01922E-04	Ni	Ni-KA	A	TiO ₂	8.25741E-02
Al ₂ O ₃	Al-KA	A	SiO ₂	-1.97152E-03	Ni	Ni-KA	A	Na ₂ O	-2.58911E-02
Al ₂ O ₃	Al-KA	A	S	-4.33793E-05	Ni	Ni-KA	A	P ₂ O ₅	2.37965E-01
MnO	Mn-KA	A	SiO ₂	-7.26750E-03	Ni	Ni-KA	A	Cu	1.05235E-05
MnO	Mn-KA	A	Fe ₂ O ₃	1.21000E-02	Ni	Ni-KA	A	Zn	-6.75761E-04
MnO	Mn-KA	A	TiO ₂	-5.59362E-02	Pb	Pb-LA	A	SiO ₂	-9.57128E-03
MnO	Mn-KA	A	MgO	-4.97667E-03	Pb	Pb-LA	A	Al ₂ O ₃	-2.25356E-02
MnO	Mn-KA	A	Al ₂ O ₃	-2.66659E-04	Rb	Rb-KA	A	SiO ₂	-5.87827E-03
MnO	Mn-KA	A	K ₂ O	-2.10511E-02	Rb	Rb-KA	A	Al ₂ O ₃	-1.81155E-02
MnO	Mn-KA	A	V	-8.27952E-05	Rb	Rb-KA	A	TiO ₂	7.72861E-02
MgO	Mg-KA	A	Al ₂ O ₃	9.32648E-03	S	S -KA	A	SiO ₂	1.21193E-02
MgO	Mg-KA	A	Na ₂ O	3.43348E-02	Sr	Sr-KA	A	SiO ₂	-8.77823E-03
MgO	Mg-KA	A	K ₂ O	-7.14825E-02	Sr	Sr-KA	A	Al ₂ O ₃	-8.84928E-03
MgO	Mg-KA	A	Fe ₂ O ₃	1.63305E-02	Sr	Sr-KA	A	MnO	6.54946E-02
CaO	Ca-KA	A	SiO ₂	5.48371E-03	Sr	Sr-KA	A	MgO	-7.06829E-03
CaO	Ca-KA	A	K ₂ O	2.08075E-02	Sr	Sr-KA	A	Na ₂ O	6.21307E-03
Na ₂ O	Na-KA	A	Cr	-6.44212E-05	Sr	Sr-KA	A	Fe ₂ O ₃	2.88091E-03
K ₂ O	K -KA	A	SiO ₂	1.60775E-03	U	U -LA	A	Al ₂ O ₃	-9.25541E-02
K ₂ O	K -KA	A	Fe ₂ O ₃	-7.69375E-03	U	U -LA	A	TiO ₂	3.04157E-01

K2O	K -KA	A	Ba	2.80960E-05	U	U -LA	A	MnO	-7.54073E-01
K2O	K -KA	A	Na2O	5.42738E-03	U	U -LA	A	CaO	4.22310E-02
K2O	K -KA	A	Rb	7.39675E-05	U	U -LA	A	Na2O	1.96362E-02
K2O	K -KA	A	Cr	2.83148E-05	V	V -KA	B	TiO2	3.00891E+02
K2O	K -KA	A	V	9.20808E-05	Y	Y -KA	A	Al2O3	-2.71244E-02
P2O5	P -KA	A	SiO2	4.11996E-03	Y	Y -KA	A	MnO	1.28127E+00
P2O5	P -KA	A	Al2O3	1.87025E-02	Y	Y -KA	A	MgO	1.55565E-02
Fe2O3	Fe-KA	A	Al2O3	1.75755E-02	Y	Y -KA	A	CaO	2.93675E-02
Fe2O3	Fe-KA	A	TiO2	1.52761E-01	Y	Y -KA	A	Na2O	5.09582E-02
Fe2O3	Fe-KA	A	MnO	3.52207E-02	Y	Y -KA	A	K2O	-5.55381E-02
Fe2O3	Fe-KA	A	MgO	2.39428E-05	Y	Y -KA	A	Fe2O3	1.04207E-02
Fe2O3	Fe-KA	A	Sr	-1.37958E-04	Y	Y -KA	A	Zr	3.60012E-05
Ba	Ba-LA	A	TiO2	1.39634E+00	Y	Y -KA	A	Sr	-3.43255E-04
Ba	Ba-LA	A	CaO	-2.48832E-02	Zn	Zn-KA	A	SiO2	-9.79548E-03
Ba	Ba-LA	A	K2O	8.77287E-02	Zn	Zn-KA	A	TiO2	4.29628E-02
Ba	Ba-LA	A	Na2O	-9.31536E-02	Zr	Zr-KA	A	Al2O3	-1.85258E-02
Cr	Cr-KA	A	SiO2	4.81654E-03	Zr	Zr-KA	A	MnO	7.18983E-01
Cr	Cr-KA	A	TiO2	2.08321E-01	Zr	Zr-KA	A	CaO	-1.04792E-02
Cr	Cr-KA	A	Al2O3	-2.11257E-03	Zr	Zr-KA	A	Fe2O3	1.12647E-02
Cu	Cu-KA	A	TiO2	4.57872E-01	Zr	Zr-KA	A	Sr	-1.62713E-04
Cu	Cu-KA	A	Ni	-1.70434E-04	Zr	Zr-KA	A	V	1.82229E-04
					Zr	Zr-KA	A	Y	-1.22341E-04

Matrix effects arising from coexisting elements, x-ray absorption and secondary fluorescence (type A), as well as spectral overlap (type B), were corrected using the theoretical matrix correction method implemented in the instrument software (SQX). Correction coefficients were calculated using either the Lachance-Trail or de Jong model, automatically chosen by the software depending on the type of composition. Interfering elements included in the correction model were carefully selected based on their concentration and their potential to influence the analyte signal. The set of correction elements was optimized iteratively to maximize calibration accuracy. Table S1 shows the empirical calibration constants and Table S2 shows the generated coefficients of each element used in the matrix correction of analytes following the equation expressed below.

$$W = (CI + D) / (1 + K + \sum(AF_j) + \sum(BF_j))$$

where for each element,

W is the quantified value

I is the X-ray intensity

K is a constant

C, D are calibration curve coefficient and constant

A is the absorption/ enhancement correction coefficient

B is the overlap correction coefficient

Fj, Fk are the analyzed values or X-ray intensities of coexisting elements j and k