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Analysis of powdered reference materials and known samples with a benchtop, field portable x-ray fluorescence (pXRF) spectrometer: evaluation of performance and potential applications for exploration lithogeochemistry

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ABSTRACT: Powdered international reference materials and samples with previously obtained conventional geochemical data were analysed using a benchtop portable X-ray fluorescence (pXRF) spectrometer to test the abilities of pXRF in silicate rock lithogeochemistry. Results from international reference materials illustrate that pXRF can provide very precise data for many major, minor, and trace elements, generally with RSD values of <7.5% and many <5%, except at very low concentrations (i.e. approaching the limit of detection). Despite good precision, accuracy is highly variable and ranges from excellent to reasonable for many major and minor elements (±15–20% relative difference, RD, for Al_2O_3, SiO_2, K_2O, CaO, Fe_2O_3, TiO_2, and MnO±S), base metals (±20% for Cu, Zn), the low field strength (LFSE) and high field strength elements (HFSE) (±15% RD for Rb, Ba, Zr; ±20% RD for Nb). Poor accuracy was obtained for MgO, P_2O_5, and the transition elements (V, Cr, Ni); Sr shows variable accuracy.

Comparison of pXRF results to independent samples with data from conventional analyses illustrates very poor correlation for MgO, P_2O_5, V, Cr, and Ni, suggesting they have poor accuracy by pXRF. Aluminum (Al_2O_3), SiO_2, and Zn have r^2 values of *c.* 0.6–0.7 illustrating reasonable correlation, whereas most other elements (S, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Co, Cu, Pb, Rb, Sr, Ba, Zr, Nb, U, As, and Mo) have very good to excellent correlation between pXRF data and conventional analysis (i.e. r^2 >0.80). In addition, many of the elements with r^2 >0.8 have slopes that are close to 1 or within 20% of ideal, indicating that pXRF is replicating the results of conventional analyses and likely within ±20% of what can be obtained by conventional methods. Down-hole profiles of pXRF data and element ratios replicate the geometry of the profiles from conventional analyses and illustrate the ability of the pXRF to discriminate rock type, alteration, and mineralization in unknown samples.

Portable XRF can provide fit-for-purpose data that is useful in discriminating lithogeochemical variations related to lithology, alteration, and mineralization. However, pXRF should be considered a preliminary screening tool for sample selection and not a substitute for conventional lithogeochemical methods (e.g. XRF, fusion ICP-ES and ICP-MS), particularly when important economic decisions are to be made using such data (e.g. NI-43-101 resource calculations).

SUPPLEMENTARY MATERIAL: Collated data for repeat analyses of reference materials in Mining Plus (Table 1) and Soil 3 Beam (Table 2) modes. Tables 3-9 contain plots comparing results from pXRF to accepted values for various reference materials. All tables are available at at www.geolsoc.org.uk/SUP18735

KEYWORDS: *portable XRF, lithogeochemistry, alteration, assessment*

Lithogeochemistry is a very powerful tool in petrology, chemostratigraphy, and mineral exploration (e.g. Barrett & MacLean 1999; Eilu *et al.* 2001; Richards 2011). With conventional lithogeochemical methods there is often a time lag between field sample collection and results from the analytical laboratory. This lag often results in a delay, in some cases years,

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between data acquisition and the utilization of results in active exploration and development. Field-portable X-ray fluorescence (pXRF) technology, however, has the potential to provide explorationists with the ability to obtain real time lithogeochemical data, thereby allowing immediate decisions to be made about rock types, alteration, mineralization, and the exploration potential of an area or project.

Despite the development of pXRF units, there is remarkably little published information on the utilization of these instruments in exploration lithogeochemistry and exploration geochemistry. Abundant research has been undertaken on the development of pXRF as an analytical tool (e.g. Potts *et al.* 1995; Potts *et al.* 1997*a*; Potts *et al.* 1997*b*; Hou *et al.* 2004; Potts & West 2008), in environmental research and contaminated soil analysis (e.g. Argyraki *et al.* 1997; Kalnicky & Singhvi 2001; Ramsey 2008; Haffert & Craw 2009; Kenna *et al.* 2011; Higueras *et al.* 2012), and geoarcheaology (e.g. Williams-Thorpe 2008; Liritzis & Zacharias 2011). Only recently has there been a concerted effort towards their utilization in exploration lithogeochemistry and geochemistry (e.g. Morris 2009; Gazley *et al.* 2011; Hall *et al.* 2012). Furthermore, the presence of pXRF in lithogeochemistry and mineral exploration is growing due to the increasing availability and commercialization of pXRF instruments by various providers.

Despite their availability and expanded usage, until recently there has been insufficient documentation of the operation, calibration, data quality, and independent testing of pXRF instruments (Hall *et al.* 2012). This manuscript presents the results of a study of whole rock lithogeochemical powders for international reference materials and previously analysed samples with rock types, matrixes, and compositional ranges commonly seen in exploration lithogeochemistry. We have utilized a single point calibration approach akin to the method of Longerich (1995) for conventional XRF. We provide estimates of precision and accuracy of the various international reference materials, for previously analysed standards, and discuss the potential application of pXRF data in exploration lithogeochemistry.

METHODOLOGY

Data were obtained using a field portable benchtop Olympus/Innov-X X5000 energy dispersive pXRF equipped with a Ta X-ray tube with a maximum tube voltage of 50 kV, maximum tube power of 10 W, detector area of 25 mm^2, and <165 eV spectral resolution. The samples were analysed using both the 2-beam mining plus mode and the 3-beam soil mode. Elements determined in the mining mode were measured at 50 kV (V, Cr, Co, Ni, Cu, Zn, W, As, Pb, Bi, Zr, Mo, Ag, Cd, Sn, Sb, and *Ti, Mn, and Fe*) and 10 kV (Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe). Elements determined in the soil mode were measured at 50 kV (U, Sr, Zr, Th, Nb, Mo, Rh, Pd, Ag, Cd, Sn, Sb, Ba, and *Ti, V, Mn, Fe, Co, Cu, Zn, Hg, As, Se, Tl, Pb, Bi, Rb, Nd*), 35 kV (Fe, Co, Ni, Cu, Zn, Hg, As, Se, Tl, Pb, Bi, Rb, and *Ti, V, Cr, Mn, U, Sr, Zr, Th, Nb, Mo, Rh, Pd, Ag, Cd, Sn, Sb*), and 15 kV (P, S, Cl, K, Ca, Ti, V, Cr, Mn, and *Fe*). Elements in italics above are those collected at that voltage but this is not their primary beam for data collection. Beam times were 60 seconds for all voltages in both soil and mining modes (White & Goodwin 2011; Hall *et al.* 2012). The limits of detection for the various elements by the instrument are generally in the ppm range, except for MgO, SiO$_2$, and Al$_2$O$_3$, which are generally >0.5 % (e.g. Hall *et al.* 2012).

The materials analysed were in powdered form and were *c.* 200 mesh (74 µm) or finer. Having materials in powder form ensured homogeneity of the material and therefore removes the potential particle size effects associated with the pXRF results (e.g. Potts *et al.* 1997*b*; Markowicz 2008). Powdered samples were placed in 30.9 mm sample cups with 6 µm-Prolene thin films. Samples were shaken prior to analysis by pXRF to ensure continued homogenization (e.g. Hall *et al.* 2012).

The X5000 was calibrated using a single point calibration approach (rather than calibration lines) and utilized certain standards for certain elements, akin to approaches used by some labs for conventional XRF (e.g. Longerich 1995). Standards chosen for the single point calibration were of similar matrix and ranges of compositions as the materials being analysed as unknowns. The single point calibration approach was chosen as it increases the rapidity whereby the instrument can be calibrated, which in turn allows the instrument to be calibrated multiple times during an analytical session so as to minimize drift, and also allows much quicker data processing. The single point calibration approach requires that the samples being analysed are of similar matrix to the calibration standards and have concentration values similar to the calibration standards. The speed of calibration and data processing using this method, however, are reasonable trade-offs to provide rapid, fit-for-purpose data for real time decision-making. Nevertheless, samples with different matrixes and for which the anticipated values are much higher (or lower) in concentration than the calibration standards (i.e. order(s) of magnitude different) should utilize different reference materials to undertake single point calibrations (e.g. samples with ore-grade metal values should use an ore metal standard to get reasonable metal grades).

The calibration standards used for the calibrations in this study include: Japan Geological Survey reference material JR-1 (rhyolite), United States Geological Survey (USGS) reference materials DTS-2b (dunite) and BHVO-2 (basalt), and Canadian Certified Reference Materials Program (CCRMP) reference materials SY-3 (syenite) and PACS-1 (marine sediment). These standards were chosen as they have similar concentrations and matrixes to the reference materials and samples being analysed in the study. The list of calibration values and calibration standards are shown in Table 1. A silica blank provided by the manufacturer in a similar XRF cup with a Prolene thin film was utilized to monitor contamination.

A typical run involved the analysis of the five reference materials used as calibration standards, a blank, 20 unknown samples, and a blank. The procedure was then repeated for the next suite of samples.

Data processing of blank and unknown data was done in single batches with the calibration standards utilized for 20 unknowns and 2 blanks. Raw values obtained for all data were converted from elemental to oxide form for major and minor elements (e.g. Mg, Al, Si, P, K, Ca, Mn, Ti, and Fe); all other elements were left in elemental form. The raw data were then calibration-corrected using the single point calibration. To obtain a calibration-correction, the raw data for a given element from the calibration standards ($[\mathrm{w}]_{\text{reference material, raw}}$) were divided by literature values ($[\mathrm{w}]_{\text{literature}}$) to provide a correction factor (Corr_i) for a given element i:

$$\mathrm{Corr}_i = [\mathrm{w}]_{\text{literature}} / [\mathrm{w}]_{\text{reference material, raw}} \tag{1}$$

This correction factor was then applied to the raw concentration of element i in the unknown sample or blank j (i.e. $[\mathrm{i}]_{\mathrm{raw},j}$) to provide a calibration corrected concentration for element i in sample j:

$$[\mathrm{i}]_{\text{corrected},j} = \mathrm{Corr}_i * [\mathrm{i}]_{\mathrm{raw},j} \tag{2}$$

Table 1. *Calibration standards and values used for calibration of the X5000 pXRF*

Element/oxide	Calibration standard	Value[1]	Preferred mode
MgO	BHVO-2	7.23%	Mining
Al_2O_3	SY-3	11.8%	Mining
SiO_2	BHVO-2	49.9%	Mining
P_2O_5	SY-3	0.54%	Mining
S	PACS-1	13200	Soil
Cl	PACS-1	23900	Soil
K_2O	SY-3	4.23%	Mining
CaO	SY-3	8.25%	Mining
TiO_2	BHVO-2	2.73%	Soil
V	BHVO-2	317	Soil
Cr	DTS-2B	15599	Soil
MnO	SY-3	0.32%	Soil
Fe_2O_3	DTS-2B	7.76%	Mining
Co	BHVO-2	45	Soil
Ni	DTS-2B	3780	Soil
Cu	BHVO-2	127	Soil
Zn	BHVO-2	103	Soil
As	PACS-1	211	Soil
Se*	PACS-1	1.09	Soil
Rb	SY-3	206	Soil
Sr	BHVO-2	389	Soil
Zr	JR-1	101	Soil
Nb	JR-1	15.5	Soil
Mo*	JR-1	3.1	Soil
Sn*	PACS-1	41.1	Soil
Sb*	PACS-1	171	Soil
Ba	BHVO-2	130	Soil
Pb*	JR-1	191	Soil
Th*	SY-3	1003	Soil
U*	SY-3	650	Soil

[1] all values are in ppm except where shown as %

*These elements had very few values above detection limits.

Table 2. *Range of precision, expressed as RSD (relative standard deviation), and accuracy, expressed as relative difference, for various elements in international reference materials by pXRF*

	Range, %			
Element/oxide	RSD[1]	RD[1]	RSD[2]	RD[2]
MgO	18.5 to 28.1	-5.35 to 57.2	19.1 to 22.4	-5.35 to 4.33
Al_2O_3	1.84 to 2.91	-4.49 to 25.7	1.84 to 2.91	-4.49 to 25.0
SiO_2	1.22 to 1.91	1.21 to 17.5	1.22 to 1.91	1.21 to 17.5
P_2O_5	3.79 to 11.9	-1.33 to -50.9	3.79 to 9.29	-1.33 to -50.9
S	5.44 to 6.11	-6.50 to -10.0	5.44 to 6.11	-6.50 to -9.97
K_2O	0.99 to 3.27	-54.2 to 12.4	0.99 to 1.54	-21.3 to 12.4
CaO	0.96 to 3.30	-56.9 to 29.5	0.96 to 3.30	-56.9 to 29.5
TiO_2	2.53 to 4.18	-10.3 to 11.2	2.53 to 3.87	-8.70 to 6.69
V	4.20 to 7.20	-23.4 to 640	4.20 to 7.20	-23.4 to 138
Cr	3.50 to 7.90	-15.2 to 34.7	3.50 to 5.00	-13.4 to 0.70
MnO	2.50 to 4.00	-5.61 to 7.07	2.50 to 3.93	-5.61 to 3.25
Fe_2O_3	0.91 to 1.39	-3.58 to 153	0.91 to 1.39	-3.58 to 153
Co	2.70 to 5.90	-38.4 to 68.8	2.70 to 5.90	-38.4 to 39.9
Ni	4.6 to 25.6	-84.5 to -46.9	4.60 to 25.6	-84.5 to -46.9
Cu	2.80 to 6.70	-9.10 to 46.1	2.80 to 6.70	-9.10 to 46.1
Zn	2.05 to 6.20	-18.4 to 39.1	2.50 to 6.20	-18.4 to 39.1
As	4.40 to 4.90	49.4 to 51.0	-	-
Rb	3.20 to 7.30	-30.5 to 23.6	3.20 to 4.60	-6.72 to 23.5
Sr	1.30 to 2.60	0.80 to 25.8	1.30 to 2.60	0.8 to 25.8
Zr	1.20 to 21.9	1.50 to 4.50	1.20 to 21.9	1.50 to 4.50
Nb	1.70 to 6.40	-11.1 to 47.9	1.74	6.43
Mo*	21.5 to 21.8	-18.4 to -41.3	-	-
Ba	10.9 to 16.5	-13.5 to 4.10	10.9 to 16.5	-13.5 to 4.10
Pb*	11.7	-32.2	-	-
U*	16.2 to 45.6	74.9	-	-

[1] ranges shown are for average values for the reference materials that are above the limit
limit of quantification (LOQ = 3.3 × limit of detection).

[2] ranges shown are for average values for the reference materials that are 10 times the limit of detection.

Limit of detection used for LOQ and 10× values are from Hall *et al.* (2012).

Accepted values of concentrations for the reference materials were utilized to determine
relationship of results to detection limit.

*Only a few values are above LOQ and data not reliable.

APPLICATION TO POWDERED LITHOGEOCHEMICAL MATERIALS

To test the capabilities of the X5000 we have undertaken three experiments. The first experiment involves the utilization of international and internal reference materials run as unknowns and results were compared to accepted values from the literature. The second test compared powders for lithogeochemical samples from the archives of the senior author that had conventional lithogeochemical data. While these materials had elements measured by a variety of methods (e.g. ICP-ES, ICP-MS, conventional XRF), they do provide a second independent test of the potential utility of pXRF. A third experiment involved a series of contiguous samples from a single drill-core that have had independent conventional analyses. This experiment was designed to illustrate the potential utility and ability to replicate spatial relationships in an exploration/development environment. All pXRF analytical work was undertaken between October and December 2012.

International and internal reference materials

Reference materials analysed as part of this experiment include: 1) USGS reference materials (AGV-2, BCR-2, BIR-1A, DNC-1A, GSP-2, QLO-1, SDC-1, SCo-1, SDO-1, SGR-1b, W-2a); 2) Japan Geological Survey (JG-1A, JR-3); 3) CCRMP reference materials (MRG-1); and 4) Multi-National Andean Project internal reference materials from the Geological Survey of Canada (BAMAP-01, CHA-1, PER-1).

Precision and accuracy results for the various reference materials are shown in Supplementary Data Tables 1 and 2, a summary of which is provided in Table 2, and representative examples of precision are shown in Figure 1. Precision was measured using the percent relative standard deviation (% RSD$_i$). Using the criteria of Jenner (1996), we suggest that excellent precision is 0–3 % RSD, very good precision is 3–7 % RSD, good precision is 7–10 % RSD, and greater than 10 % RSD is poor precision. Accuracy was determined using the percent relative difference (% RD) between elemental values found in the reference materials versus that in the literature. The literature values for the reference materials were obtained from the original USGS certificates, from the Govindaraju (1994) archive of values, and more recent updates from the online GeoREM archive (http://http://georem.mpch-mainz.gwdg.de). The source of the accepted values for each standard is noted in Appendices 1 and 2.

Precision. Precision by pXRF is good to excellent for most elements, especially those with elevated concentrations (Fig. 1; Table 2; Supplementary Data Tables 1, 2). To remove potential precision outliers due to low concentrations, in Table 2 we have summarized the precision for a given element where the element concentration is above the limit of quantification (LOQ = 3.3x the limit of detection) and 10 times the limit of detection. This allows a more robust evaluation of precision than if the entire dataset is utilized. With minor exceptions

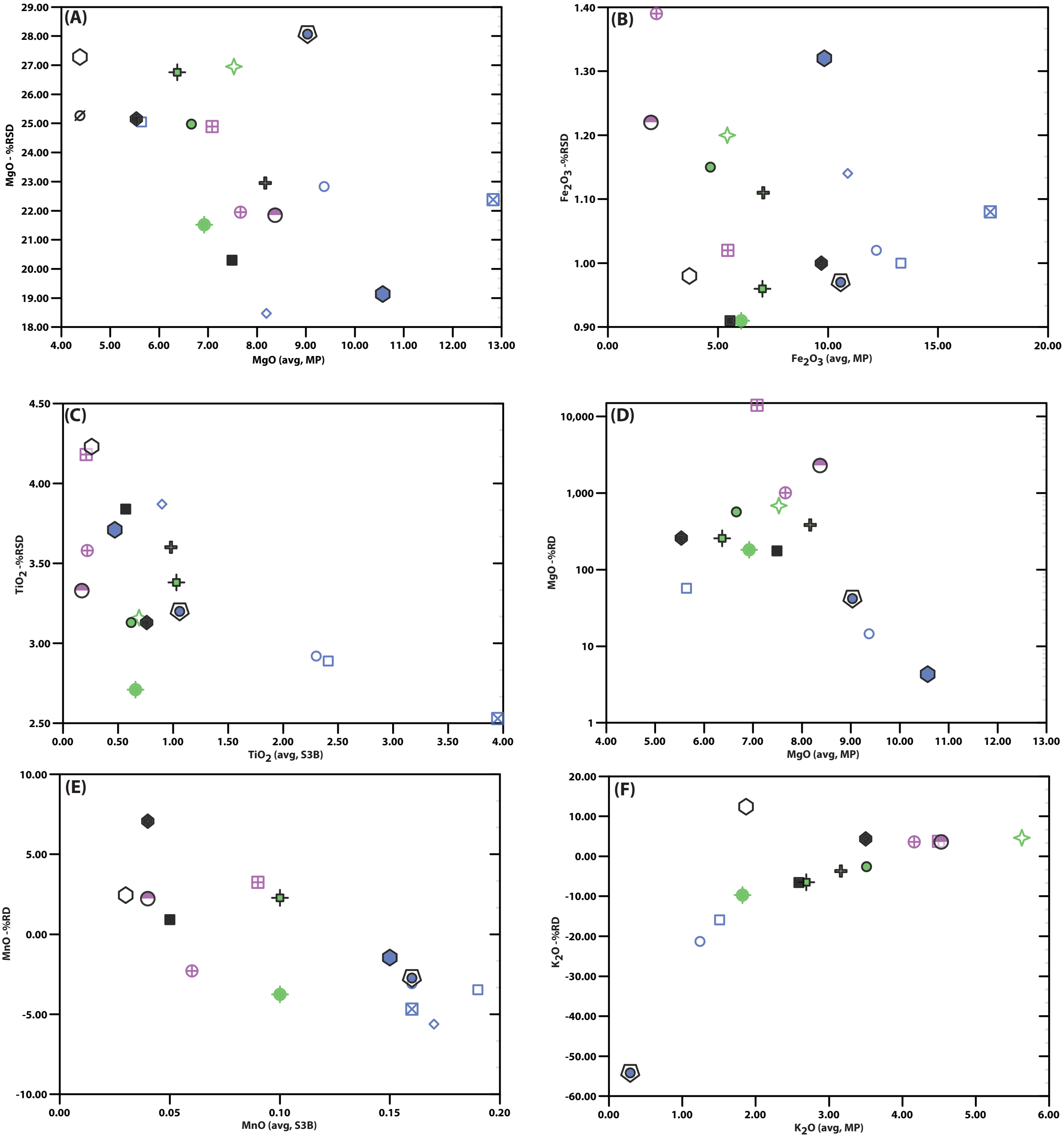

Fig. 1. Representative plots illustrating precision and accuracy of reference materials results for pXRF data. Precision is shown as relative standard deviation (RSD) against average analyte values (in %) recorded by pXRF for (**A**) MgO, (**B**) Fe_2O_3 and (**C**) TiO_2. MgO illustrates typically poor precision, Fe_2O_3 shows very good precision, and TiO_2 shows good precision but decreasing precision with decreasing concentration. Accuracy is shown as relative difference (RD) versus average concentration of the analyte (in %) recorded by pXRF for (**D**) MgO; (**E**) MnO; and (**F**) K_2O. MgO shows extremely poor accuracy, MnO shows good accuracy, and K_2O illustrates a decrease in accuracy with decreasing concentration. MP, mining mode; S3B, soil mode.

precision is good to excellent for most elements with many samples having an RSD of <7.5% (Fig. 1b). Poorer precision exists for MgO, Ni, Ba, and for elements with only a few analyses above the LOQ (e.g. Pb, U, Mo). In some cases precision decreases with concentration (e.g. TiO_2, P_2O_5; Fig. 1c).

Accuracy. While precision is good across most elements, the accuracy of pXRF data for the international reference materials exhibits significant variability (Fig. 1; Table 2; Supplementary Data Tables 1, 2). The light elements (MgO, Al_2O_3, SiO_2, P_2O_5, and S) exhibit very high variability in accuracy unless they are 10x the LOD, and even then the accuracy is poor for many reference materials (Fig. 1d). Other major elements have better accuracy, including K_2O, TiO_2, MnO, Fe_2O_3 (Figs. 1e, f) and to a lesser extent CaO, but are still of lower quality compared to conventional analyses (e.g. Longerich 1995). The transition metals (V, Cr, Co, and Ni) show highly variable accuracy, but are generally poor, as are base metals (Cu, Zn), albeit to a lesser extent. The elements Rb, Sr, Zr, Ba, and Nb provide surprisingly reasonable results and are roughly ±20% RD. Arsenic, Mo, Pb, and U have insufficient results to elaborate on quality; however, given their low concentrations in most surface materials it is assumed that their accuracy would be poor by pXRF when at low concentrations.

Comparisons to independently analysed whole rock samples

The goal of this experiment is to compare results from conventional methods and pXRF and to evaluate whether pXRF can replicate lithogeochemical patterns, if not absolute data, for powders/rocks in real time. Conventional data from the unknown samples were obtained by total methods, either via utilization of solid source methods, including pressed pellet and fused disc conventional XRF, or total digestion methods (e.g. fusion or bomb dissolution) and subsequent analysis by inductively coupled plasma emission spectroscopy (ICP-ES) and/or inductively coupled plasma mass spectrometry (ICP-MS). The samples used for this test include: peralkaline felsic volcanic and plutonic rocks from central Newfoundland (Topsails Igneous Complex and Springdale Group (Courage 2013); variably altered subalkalic rhyolitic to basaltic rocks from the Ming volcanogenic massive sulphide deposit, Newfoundland (Piercey, unpublished data); subalkalic dacitic to basaltic rocks from the Pilley's Island Terrane, central Newfoundland (McKinley 2013 (submitted)); three Mineral Deposit Research Unit (UBC) internal reference materials previously reported by Piercey *et al.* (2001) and Piercey (2001); a sample of subalkalic (tholeiitic) greenstone from the Yukon-Tanana terrane, Yukon (Piercey *et al.* 2004); within-plate, weakly alkalic VMS-related rhyolite flows to porphyritic intrusive rocks from the Yukon-Tanana terrane (Piercey *et al.* 2001, 2008); and two sulphide- and metal-rich hydrothermal mudstones from the Lemarchant VMS deposit, central Newfoundland (Piercey, unpublished data).

Representative examples of element behavior are shown in graphical form in Figure 2 (MgO, SiO_2, Fe_2O_3) and in Supplementary Data Tables 3–9, and linear relationships between the conventional analyses and pXRF results and their relevant coefficients of determination (r^2) are given in Table 3. These results corroborate many of the results from the international reference materials and illustrate extremely poor correlations for MgO, P_2O_5, V, Cr, and Ni, suggesting they have poor accuracy. Oxides Al_2O_3 and SiO_2 have r^2 values between 0.60 and 0.70 and all other elements have r^2 values, when filtered for outliers, that are >0.8, implying very significant correlations. Furthermore, most of the samples with r^2 values of >0.8 have slopes that are ±20% of 1, with the exception of U and Mo, implying that pXRF is replicating the results of conventional analyses by *c.* ±20%.

Applications to chemostratigraphy

To test the potential utilization of pXRF data in a spatial context, a down-hole profile of pXRF data relative to conventional data, comprising both element concentrations and element ratios, is shown in Figures 3–6. The drill-hole utilized is from the Ming VMS deposit, Newfoundland, Canada, and was chosen because the hole had a wide range of concentrations of major and trace elements due to lithologic variation, alteration, and mineralization. Therefore, this drill-hole tests whether pXRF can replicate spatial lithogeochemical relationships in an exploration context. Samples were collected during mapping of the drill-core in 2010 and were prepared by conventional crushing and pulverizing at a commercial laboratory. These powders were then analysed by fusion ICP-ES for major elements, and by bomb dissolution and ICP-MS for trace elements (i.e. HFSE, LFSE, metals) and rare earth elements. These same powders were then used for pXRF determinations.

For major elements, the pXRF data for Al_2O_3 and MgO show broadly similar shapes to the conventional data; however, there is significant offset in the results (Fig. 3). In contrast, SiO_2, K_2O, and Fe_2O_3 are much better with most results nearly identical to the conventional data (Fig. 3). Elements that are indicative of mineralization (e.g. base metals Cu, Zn, and Pb), or are pathfinder elements (As, Sb), have variable behavior (Fig. 4). The base metals (Cu, Zn, and Pb) and As replicate the results from conventional data but with some offset, whereas Sb only approximates the conventional data (Fig. 4). Elements typically used for chemostratigraphy (e.g. Barrett & MacLean 1999; Piercey 2009) show fairly good coincidence with conventional data, except for values that are approaching the LOD/LOQ of pXRF (e.g. Nb; Fig. 5). Similarly, alteration-sensitive mobile elements and element ratios (e.g. Barrett & MacLean 1999; Piercey 2009) yield similar patterns and considerable overlap between pXRF and conventional data, except for those that are close or below the LOD/LOQ (e.g. some Rb and Ba values) (Fig. 6).

DISCUSSION AND SUMMARY

The single point calibration method provided in this paper illustrates that calibration using a minimal number of calibration standards results in reasonably good precision and accuracy. While it is acknowledged that multiple calibration points per element (i.e. calibration lines) would likely extend the dynamic range of precision and accuracy, the results we have obtained on international reference materials are very similar to the more extensive study of Hall *et al.* (2012). Replicate analyses of international reference materials using the X5000 are excellent to good for most major to minor elements (K_2O, CaO, TiO_2, MnO) including many light elements (Al_2O_3, SiO_2, P_2O_5). In contrast, the major element MgO has poor precision, and there are insufficient data to evaluate the precision of S and Cl. Similarly, the X5000 can produce precise data for trace elements, including transition metals (V, Cr, Co), base metals (Cu, Zn), LFSE (Rb, Sr), and HFSE (Zr, Nb), except at lower concentrations (i.e. approaching LOD and LOQ), with most having RSD values below 7.5% and many with RSD values below 5%. The exceptions include Ni, which has limited data and low precision, and Ba, which is also less precise.

While the precision of the X5000 is good for most elements, the accuracy is variable. Most reference materials have accuracy of ±15–20% RD for the major and minor elements Al_2O_3, SiO_2, K_2O, CaO, Fe_2O_3, TiO_2, and MnO, except where the elements are at low concentrations. Sulphur shows promise as the two reference materials with S >1.5 wt% (>15000 ppm) have an accuracy that is <10% RD. In contrast, MgO and P_2O_5 have poor accuracy. The transition metals have very poor accuracy, whereas base metals Cu and Zn have 20% RD or better. The poor accuracy for the transition elements is likely due to X-ray peak overlaps that are not resolved by the X5000 software (e.g. Fe Kα and Kβ peaks overlapping with Co Kα peak) (Thompson *et al.* 2009; Hall *et al.* 2012). The lower accuracy for the base metals is possibly due to matrix effects, as most base metals in the reference materials are likely associated with sulphides, whereas the calibration standard for the base metals is a silicate matrix (i.e. basaltic). Using a calibration standard with a sulphide matrix

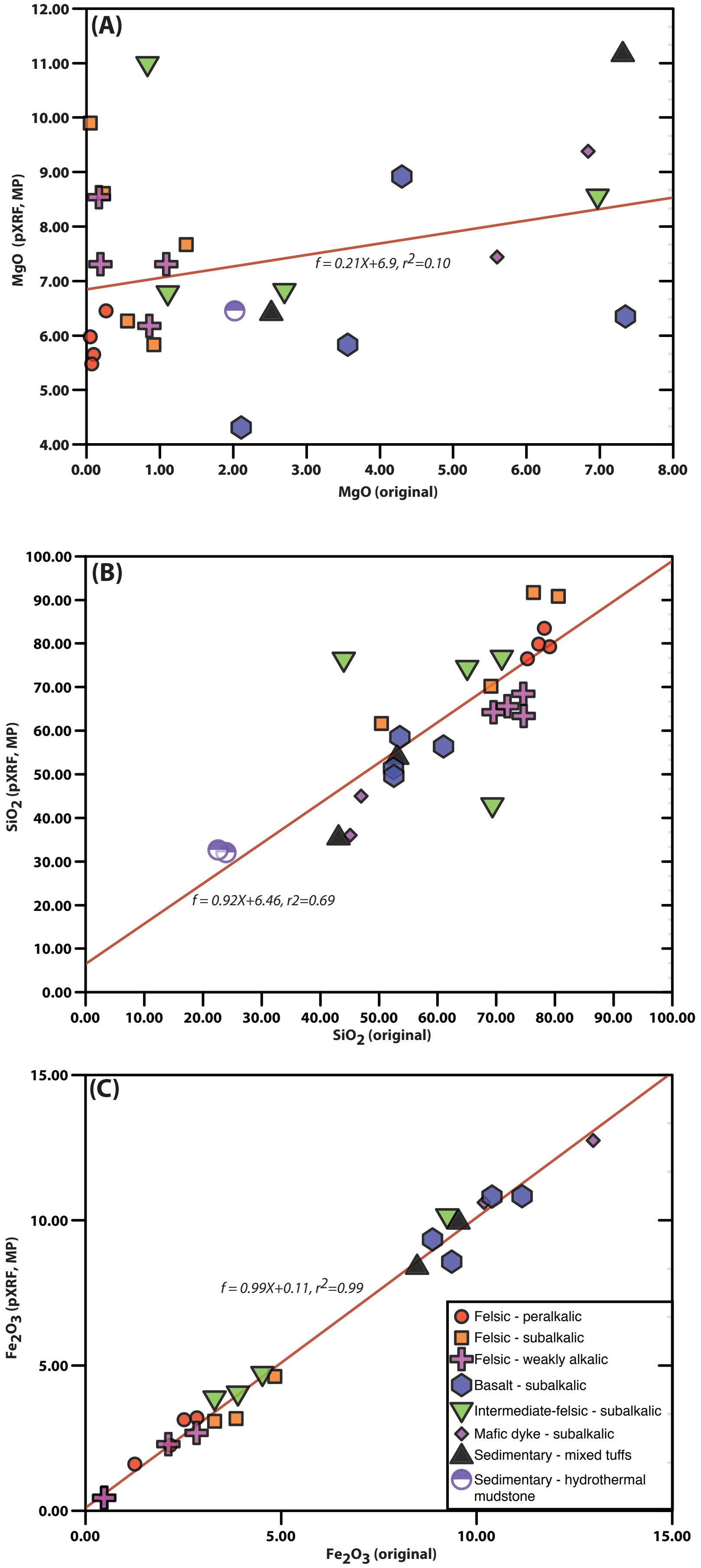

Fig. 2. Representative plots comparing pXRF results (in %) to conventionally determined data for (**A**) MgO; (**B**) SiO_2; and (**C**) Fe_2O_3, which are examples of poor, moderate, and excellent pXRF replication of conventional results, respectively.

Table 3. *Results of comparison between data obtained by pXRF to that obtained by conventional total digestion/solid source methods (e.g. XRF, ICP-ES, and/or ICP-MS). Shown are the equations of the lines for the comparisons (y, pXRF results; x, original results) and their respective coefficients of determination (r^2)*

Element/oxide	Mode	Equation	r^2	Notes
MgO	Mining	$y = 0.21x + 6.90$	0.10	-
Al_2O_3	Mining	$y = 0.74x + 4.45$	0.64	-
SiO_2	Mining	$y = 0.92x + 6.46$	0.69	-
P_2O_5	Mining	$y = 0.34x + 0.07$	0.33	-
S	Soil	$y = 1.15x - 0.38$	0.99	-
K_2O	Mining	$y = 1.06x - 0.12$	0.96	-
CaO	Mining	$y = 0.98x + 0.09$	0.86	-
TiO_2	Soil	$y = 0.82x + 0.11$	0.88	-
V	Soil	$y = 0.71x + 188$	0.06	-
Cr	Soil	$y = 0.68x + 34$	0.68	-
MnO	Soil	$y = 0.92x + 0.11$	0.99	-
Fe_2O_3	Mining	$y = 0.99x + 0.11$	0.99	Two Fe_2O_3- and sulfide-rich samples removed from dataset (Fe_2O_3 <20%).
		$y = 0.79x + 1.24$	0.99	All data included.
Co	Soil	$y = 0.93x +5.7$	0.86	Two Fe_2O_3- and sulfide-rich samples removed from dataset (Fe_2O_3<20%).
		$y = 0.71x +19$	0.09	All data included. Poor correlation due to two Fe-rich samples causing Fe-Co overlaps (e.g., Thompson *et al.* 2009)
Ni	Soil	$y = 0.11x + 1.4$	0.40	
Cu	Soil	$y = 1.08x + 4.0$	0.99	
		$y = 0.95x + 13.8$	0.94	High Cu sample removed from the data array.
Zn	Soil	$y = 1.52x + 63.8$	0.99	All data included.
		$y = 1.02x - 0.04$	0.74	Samples greater than 250 ppm removed from array.
Pb	Soil	$y = 1.18x - 4.1$	0.99	All data included.
		$y = 1.05x + 3.2$	0.93	High Pb sample removed from the data array.
Rb	Soil	$y = 0.53x + 23.1$	0.46	All data included.
		$y = 1.03x - 0.2$	0.99	Two carbonate samples rich in Y removed from data array due to potential Y-Rb overlaps (e.g., Thompson *et al.* 2009).
Sr	Soil	$y = 1.08x + 1.2$	0.96	-
Ba	Soil	$y = 0.92x + 7.4$	0.99	All data included.
		$y = 1.05x - 18.7$	0.99	Barite-rich samples removed from the array.
Zr	Soil	$y = 0.80x + 16.3$	0.99	All data included.
		$y = 0.94x - 1.0$	0.97	Zr < 300 ppm
Nb	Soil	$y = 1.02x +3.3$	0.88	All data included.
		$y = 1.21x + 0.8$	0.78	Nb < 10 ppm.
U	Soil	$y = 1.87 - 3.3$	0.86	Line constrained by only a few samples with > 5 ppm U.
As	Soil	$y = 1.46x -18.5$	0.99	All data included.
		$y = 1.01x + 20.3$	0.99	Samples with As < 700 ppm
Mo	Soil	$y = 0.35x + 1.5$	0.95	Line constrained by only a few samples with >10 ppm Mo.

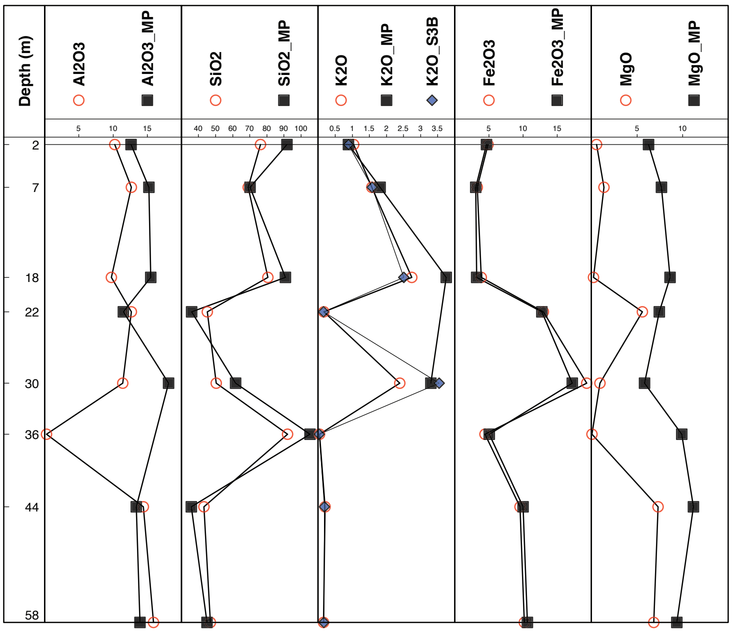

Fig. 3. Down-hole profile for key major elements (in %) used in the discrimination of lithology, alteration, and mineralization. MP suffix at the end of the element implies analysis by mining mode. Elements without suffixes were data obtained by conventional methods (fusion ICP-ES and ICP-MS).

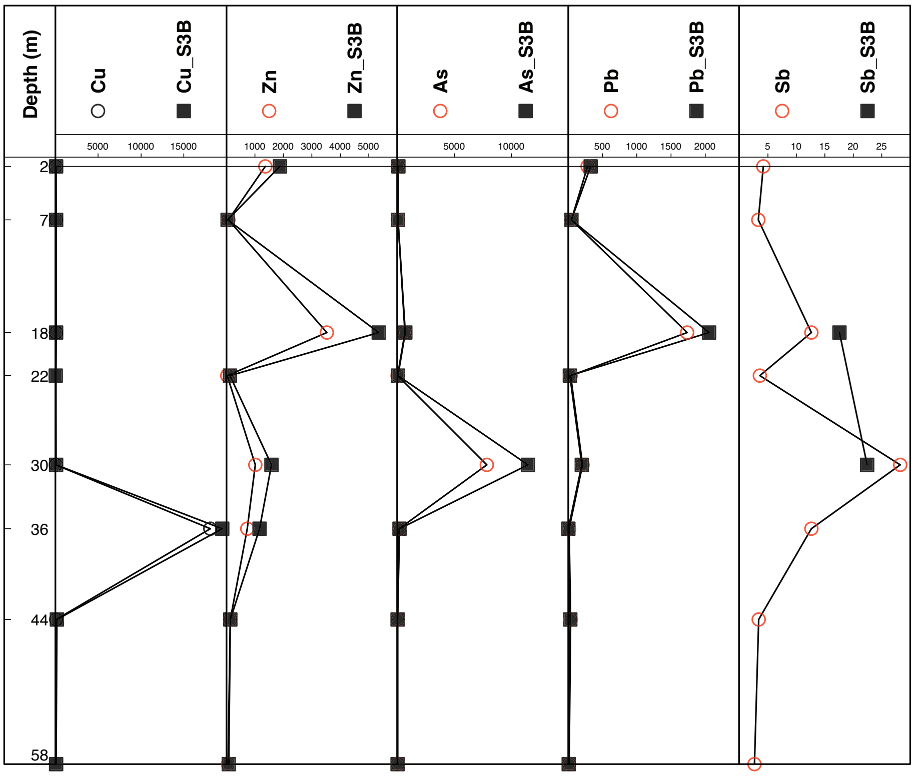

Fig. 4. Down-hole profile for key trace elements (in ppm) used in delineating mineralization, including metals (Cu, Zn, Pb) and metalloids (As, Sb). S3B suffix at the end of the element implies analysis by soil mode. Elements without suffixes were data obtained by conventional methods (fusion ICP-ES and ICP-MS).

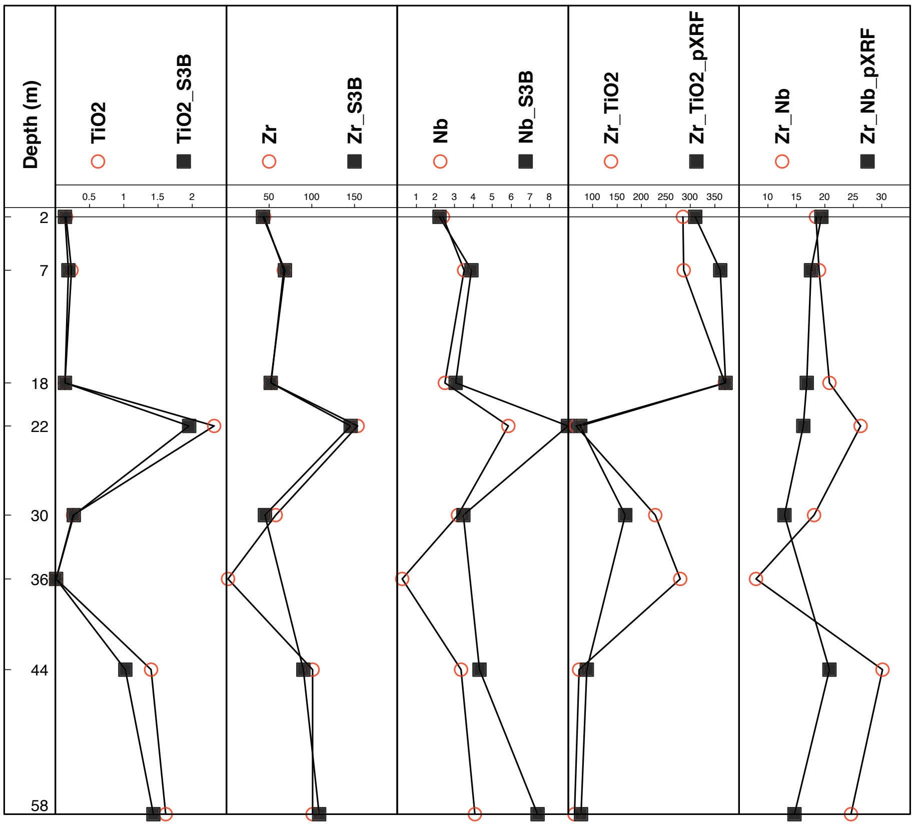

Fig. 5. Down-hole profile for key major (in %) and trace elements (in ppm) and element ratios used in lithologic discrimination and chemostratigraphy (e.g. Winchester & Floyd 1977; Barrett & MacLean 1999). Suffixes S3B and pXRF reflect data obtained by the soil mode and ratios of pXRF data, respectively. Elements and element ratios without suffixes were data obtained by conventional methods (fusion ICP-ES and ICP-MS).

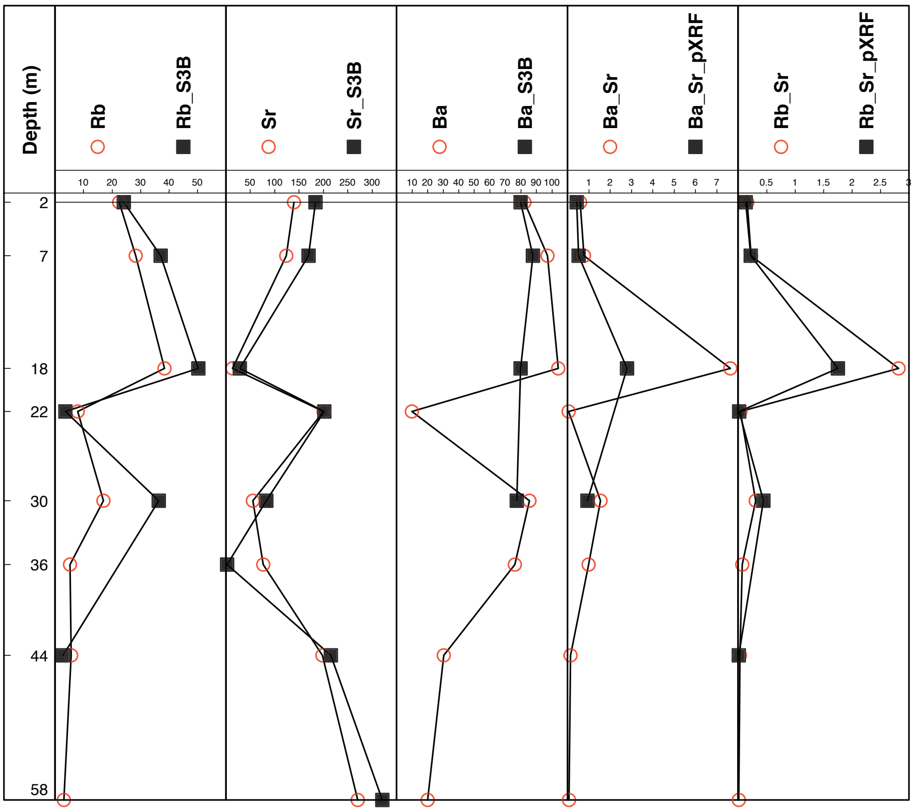

Fig. 6. Down-hole profile for key major (in %) and trace elements (in ppm) and element ratios used in documenting alteration (e.g. Barrett & MacLean 1999; Piercey 2009). Suffixes S3B and pXRF reflect data obtained by the soil mode and ratios of pXRF data, respectively. Elements and element ratios without suffixes were data obtained by conventional methods (fusion ICP-ES and ICP-MS).

may improve accuracy and is the focus of ongoing research by the Memorial University group.

The LFSE and HFSE Rb, Ba, and Zr have accuracy in the range of ±15% RD, whereas Nb is 20% RD or better (with minor exceptions) and Sr is variable. The variability of Sr accuracy contrasts with other research as it is one of the most accurate elements during pXRF testing by Morris (2009) and Hall *et al.* (2012). Further, Sr shows very strong correlations with slopes close to 1, when compared to samples with independent conventional geochemical analyses for Sr.

The results for international reference materials are also replicated in comparisons of pXRF results on samples with existing analyses by conventional geochemical methods. There are extremely poor correlations for MgO, P_2O_5, V, Cr, and Ni, suggesting they have poor accuracy. In contrast, there are strong correlations between pXRF data and conventional analysis (i.e. $r^2 > 0.80$) for S, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Co, Cu, Pb, Rb, Sr, Ba, Zr, Nb, U, As, and Mo. Despite some scatter, there are also weaker correlations for Al_2O_3, SiO_2, and Zn (Table 3; Supplementary Data Tables 3–9). In addition, many of these elements have slopes that are close to 1 or within 20% of ideal, indicating that pXRF is replicating the results of conventional analyses for the aforementioned elements. Furthermore, the down-hole profiles of various elements that are critical for lithogeochemical identification of rock type, mineralization, and alteration are clearly replicated and there is overlap between conventional and pXRF data.

The results of this study illustrate that pXRF can provide reasonable quality (i.e. fit-for-purpose) data for many elements. Furthermore, it can replicate the results of conventional methods and can be utilized in exploration lithogeochemistry. It is clear, however, that pXRF cannot provide data that are a substitute for more robust conventional methods like traditional fused disc or pressed pellet XRF and fusion ICP-ES and ICP-MS (e.g. Hall *et al.* 2012), particularly when economic decisions are to be made (e.g. NI-43-101 resource calculations). Nevertheless, it has a potentially very useful future in the screening samples for which to obtain conventional data and in preliminary chemostratigraphic and alteration studies.

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