

Evaluation of Rare Earth Element-enriched Sedimentary Phosphate Deposits Using Portable X-ray Fluorescence (XRF) Instruments

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KEYWORDS: Portable XRF, rare earth elements, phosphate, exploration

EXECUTIVE SUMMARY

Sedimentary phosphate deposits (Mineral deposit profile F07; Simandl *et al.*, 2012), consist mainly of the apatite group mineral $[(Ca_5(PO_4)_3(OH,F,Cl))]$ commonly referred to as francolite. Such deposits supply most of the phosphate rock used by the ammonia phosphate fertilizer industry. The 2010 world phosphate rock production is estimated at 176 million tonnes (Cordier, 2011). In recent years sedimentary phosphate deposits have also been considered as a potential fluorine resource (Simandl, 2009) and it is possible that rare earth elements (REE) may also be recovered from some sedimentary deposits as by-products (Simandl *et al.*, 2011a, b). Portable XRF technology is relatively new. To the authors' knowledge there are no publicly available documents describing its use in the exploration and development of sedimentary phosphate deposits containing elevated concentrations of lanthanides and Y as by-products. Thirty-two samples of phosphate rock (pulps) from the Fernie Formation (southeastern British Columbia) were analysed using a hand-held XRF analyser as well as by a lithium metaborate fusion–inductively coupled plasma (LMB-ICPMS) method. The results from both methods were compared; correction factors for the portable XRF analyser were established and their effectiveness was tested. Portable hand-held XRF analysers that are currently on the market have their technical limitations. If correction factors are established, hand-held instruments can be used in exploration for phosphate deposits by analyzing samples directly for phosphorus (P), identifying zones of phosphate rocks rich in rare earth elements (REE), and delineating zones with unacceptable levels of deleterious elements such as uranium (U).

INTRODUCTION

British Columbia is known to host at least 62 known occurrences of sedimentary type phosphate. Several of these occurrences were previously investigated and documented as potential sources of phosphates (Butrenchuk, 1987, 1988, 1996; Norman and Renning, 2009a, b), Y (Pell, 1991) and REE (Simandl *et al.*, 2011a, b); however, none of them are currently in production. In recent years, prices of REE have risen sharply due to an imbalance between supply and demand (Simandl 2010, 2011a, b). The REE and Y content of many phosphate rocks could now justify more detailed investigations of their recovery during fertilizer production from phosphate rocks.

Portable XRF technology was derived from the traditional XRF during the late 1960s and further technological evolution led to the development of hand-held XRF analysers. Laboratory XRF instruments commonly rely on careful sample preparation in the form of pressed powder pellets and fused beads or glass disks to maximize precision and accuracy of the readings. Portable hand-held XRF analysers are subject to the same analytical constraints as their large laboratory equivalents as well as additional limitations due to limited voltage and power at the x-ray source. When used in the field, hand-held XRF analysers do not benefit from sample homogenization and sample preparation of their larger stationary laboratory counterparts. For these reasons initial orientation studies are required prior to any large scale use of hand-held portable XRF equipment. The first stage of any orientation study relies on finely ground and homogenized samples (pulps) in order to minimize errors due to natural textural variations of rocks. In case of sedimentary phosphate deposits the textural variations can be: bedding, laminations, graded bedding, as well as clasts and post-depositional fracture fillings, veinlets, the presence of non-pervasive alteration and weathering (in sedimentary rocks). The effects of uneven broken rock surfaces on hand samples or drill cores are also eliminated using finely ground samples. Additional limitations are described in the “Operator of Portable X-ray Fluorescence Analysers Certification Information and Examination Preparation Booklet” (Murphy *et al.*, 2010). The use of these instruments is well established in a variety of industrial applications including recycling, scrap metal testing, and consumer safety controls.

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The main objectives of this study were; to determine the practical limitations of hand-held XRF technology in phosphate exploration, to determine whether or not calibration is needed for portable XRF technology to be effective at analyzing both major and trace elements within a phosphatic matrix, and to determine the effectiveness of the calibration factors on pulps.

Thirty-two samples from the Fernie Formation were selected with concentrations of P ranging from 0.15 to 27.5% and concentrations of REE ranging from 99.1 to 1498.98 ppm. These samples were originally collected and analysed by Butrenchuk (1987) but have recently been re-analysed using modern analytical methods (Simandl *et al.*, 2011b). The results of portable XRF data were compared with the results of modern analytical methods.

INSTRUMENTATION

The hand-held portable XRF used for this study was a Thermo Scientific Niton XL3t (serial number 67749, manufactured in the U.S.A., 2011), supplied by Elemental Controls Limited (Toronto). The instrument (Figure 1) uses a Ag x-ray tube (no radioactive source), with a maximum current of 0.2 mA, a maximum voltage of 50 kV, and a maximum power of 2 watts. The instrument was used in “Mining Cu/Zn mode” for all analyses. The instrument operates on four different filters in order to obtain accurate measurements of a wide range of elements (Table 1). An optional calibration allowing for La, Ce, Pr, and Nd analysis on the “High” filter was done by Elemental Controls Limited (Toronto). This instrument is one of the first able to be able to analyse Pr and Nd without the use of a radioactive source. Other instruments with radioactive sources have already been used for mapping and grade control, and have even been applied to heavy REE. For example, Avalon uses a Thermo-Scientific Niton XLP-522K hand-held analyser for mapping and



Figure 1. The hand-held portable XRF used for this study was a Thermo Scientific Niton XL3t.

grade control of fine grained REE minerals present in their drill core (Bakker *et al.*, 2011).

METHODOLOGY - DATA ACQUISITION

All samples were collected by Butrenchuk prior to 1988. Samples were crushed, milled, homogenized, and then analysed using a bench top Philips 1440 wavelength dispersive x-ray fluorescence spectrometer and volumetric techniques by British Columbia Geological Survey Analytical Sciences Laboratory. The results of that analytical work were reported by Butrenchuk (1996). The samples pulps were re-analysed in 2009 (Simandl *et al.*, 2011b) using lithium-borate fusion followed by ICP-MS (LMB-ICPMS) at ALS Laboratories in Vancouver. The re-analysis was required since the results reported by Butrenchuk (1996) do not include most of the REEs.

Before hand-held XRF analysis began, the analyser was allowed to warm up for 150 seconds and a system check was conducted. Three standards were tested first before a phosphate rock pulp was analysed. These standards consisted of a certified 99.995% SiO₂ blank, Standard Reference Material 2780 (May and Rumble 2004), and Certified Reference Material “TRLK” Rare Earth Ore “CGL 124” (Registration Number: USZ 42-2006; Mongolia Central Geological Laboratory). All standards were contained in sample cups covered by a 4.0μ thick polypropylene film. Standards were placed into a portable field test stand and then analysed using the instrument in “Mining Cu/Zn” mode with all 4 beam times set to 45 seconds for a total of 3 minutes.

The same sample cups and 4.0μ thick polypropylene film (Figure 2) were used to hold phosphate pulps because our preliminary investigations concluded that analyzing through the Kraft® paper bags in which the pulps were stored resulted in unacceptable levels of x-ray attenuation, especially when determining concentrations of light elements such as P (Figures 3 and 4). The improvement in quality of the data achieved through the use of polypropylene is also readily apparent by comparing the coefficient of determination, R², from measurements made through the Kraft® paper bags and through polypropylene (Figures 3 and 4). Sample cups were filled to the three quarter mark (~19 mm) with pulp, then filled with gauze and capped (Figure 2). After use, the samples were immediately placed into individual plastic bags to avoid contamination on the film and to preserve them for follow-up research. Both standards and pulp samples were analysed using the instrument in “Mining Cu/Zn” mode. The instrument’s 4 beam times were set to 45 seconds for a total of 3 minutes per reading. Five measurements were taken on each pulp sample. After every five phosphate pulp samples (or 25 measurements), the same three standards (as described above) were re-analysed. Systematic re-analysis of the standards showed negligible instrument drift throughout the experiment. A survey meter was used at all times to alert the operator an unexpected release of radiation.

Table 1. Filters used, time of analysis and elements analysed by the portable XRF. Cr, V and Ti were analysed using the “Main” filters and then these were re-analysed using the “Low” filter for higher accuracy at low concentrations. Similarly, Sb, Sn, Cd and Ag were re-analysed using the “High” filter for higher accuracy at low concentrations. Bal* stands for balance. It represents x-ray energy levels that the analyser does not attribute to a particular element.

Filter	Analytical time interval (seconds)	Elements Analysed
Main	45	Sb, Sn, Cd, Ag, Mo, Nb, Th, Zr, Bal*, Y, Sr, U, Rb, Bi, Au, Se, As, Pb, W, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti
Low	45	Cr, V, Ti, Ca, K
High	45	Nd, Pr, Ce, La, Ba, Sb, Sn, Cd, Ag
Light	45	Al, P, Si, Cl, S, Mg



Figure 2. Typical sample cups covered by 4.0 μ thick polypropylene film.

Both authors are certified by Natural Resources Canada to operate portable XRF instruments in compliance with the Health Canada Safety Code 34/ISO 20807 and followed all required safety procedures specified by Murphy *et al.* (2010).

METHODOLOGY - DATA PROCESSING AND INTERPRETATION

The practical usefulness of portable XRF and its limitations in mineral exploration can be visually assessed using X-Y scatter diagrams, with the Y-axis representing the portable XRF data (XRF) and the X-axis representing the results of the ICP-MS analysis after a lithium borate fusion (Figures 5 and 6). Each point on these graphs represent one of the 5 XRF measurements versus a corresponding LMB-ICPMS analysis.

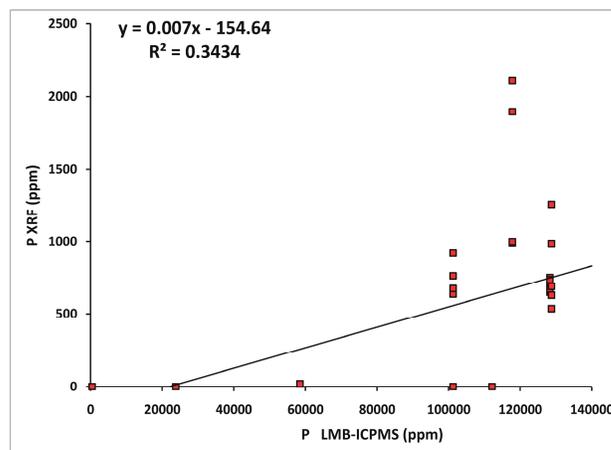


Figure 3. Qualitative comparison of hand-held portable XRF readings obtained by analysing pulps for phosphorus through standard Kraft® paper bags relative to LMB-ICPMS results.

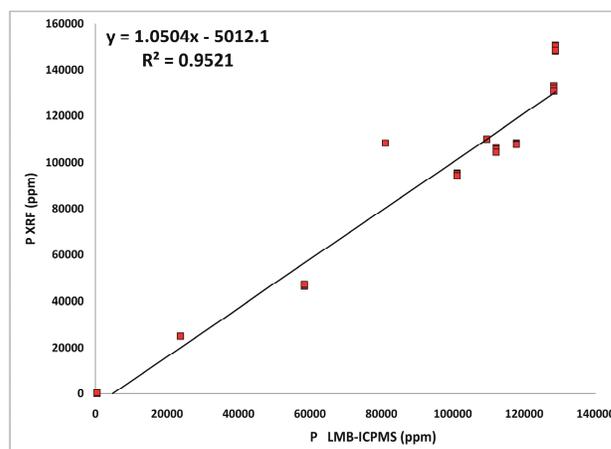


Figure 4. Qualitative comparison of hand-held portable XRF readings obtained by analysing pulps for phosphorus through 4 micron thick polypropylene relative to LMB-ICPMS results.

Based on the total of 160 measurements taken on 32 pulps of phosphate rock samples, the hand-held portable XRF analyser was able to provide an effective quantitative measurement with excellent correlation ($R^2 > 0.85$) to the LMB-ICPMS data (Table 2) for 13 elements (Ba, Mo, Y, Sr, U, Rb, Zn, Fe, Ca, P, Si, S and Mg). A reasonable quantitative or semi-quantitative estimates with good correlation ($0.5 < R^2 < 0.85$) between the hand-held XRF and LMB-ICPMS data sets were achieved for 6 elements (Nd, Ce, La, Zr, W, and Al).

Table 2. Comparison of the correlation between the portable XRF readings and LMB-ICPMS data using the coefficient of determination R². The range of analyses (minimum and maximum value) for each element is provided in ppm.

Filter	Element	R ²	ICP-MS	
			Min*	Max*
High	Nd	0.5417	13.4	347.0
	Pr	0.3677	4.3	79.1
	Ce	0.6258	45.0	247.0
	La	0.8303	29.3	388.0
	Ba	0.98520	295.0	7660.0
High/Main	Sn	-	<1	2.0
	Ag	-	<1	<1
Main	Mo	0.97450	<2	67.0
	Nb	0.29250	1.8	20.4
	Th	0.0406	2.1	15.5
	Zr	0.69810	104.0	350.0
	Y	0.9955	5.9	871.0
	Sr	0.9941	118.0	1365.0
	U	0.9611	2.4	53.6
	Rb	0.98780	10.2	68.8
	Pb	0.00006	<5	11.0
	W	0.75940	9.0	229.0
	Zn	0.96070	24.0	572.0
	Cu	0.43150	8.0	58.0
	Ni	0.0757	12.0	174.0
	Co	-	2.7	24.3
	Fe	0.99360	4686.3	31754.9
	Mn	-	77.4	309.8
Low/Main	Cr	-	50.0	250.0
	V	-	30.0	146.0
	Ti	-	659.4	3237.4
Low	Ca	0.97380	4431.0	316604.0
	K	0.90080	2905.5	18429.0
Light	Al	0.83480	9261.7	80179.0
	P	0.9411	436.4	128741.0
	Si	0.9598	58664.0	362268.0
	S	0.98280	900.0	37500.0
	Mg	-	1327.0	21471.0

Legend	
Excellent Correlation	(Green)
Good Correlation	(Light Blue)
Correlation Observed	(Orange)
No Correlation	(Pink)

R² is the coefficient of determination. It ranges from 0 to +1.0. Zero indicates complete absence of a systematic relationship, while 1 indicates a perfect relationship.

Using the same approach, only limited interpretation (0.25<R²<0.5) can be achieved for 3 elements (Pr, Nb, Cu). There was no practically significant correlation (0.25<R²) between portable XRF analyser and the LMB-ICPMS data sets for three elements (Th, Pb and Ni). Eleven elements (Bi, Au, Co, Mn, Cr, V, Ti, Sb, Sn, Cd and Ag) were not detected by the analyser in any of the samples. The REE with atomic numbers greater than 60 (heavier than neodymium) were not able to be analysed using this instrument.

The hand-held portable XRF analyser was also programmed to detect Se, As, Au, Bi, Cd, Sb and Cl. However, these elements were not analysed by the LMB-ICPMS method used, so a comparison between these data sets was not possible. These elements are excluded from the following discussion. For the purpose of this study, the data on the X axis (LMB-ICPMS) can be considered as nearly error-free relative to the data on the Y axis (hand-held portable XRF).

If there was a near perfect match between the LMB-ICPMS and hand-held portable XRF data, there would be minimal scatter of points over an element concentration range. Ideally, the resulting regression line would have a slope of unity (m=1), and would pass through the origin (b=0). The coefficient of determination (R²) would be equal to one. If the hand-held portable XRF systematically under-estimated or overestimated the “true” (ICP-MS) value, then the slope of the regression line will not be one. Mathematical processing and testing of relationships between corresponding hand-held XRF and LMB-ICPMS data for selected elements allows us to create correction factors based on this premise. The use of such factors does to some extent, correct the bias, revealed in plots so that the corrected XRF values are closer a hypothetical (perfect) relationship.

The general equation of the regression line is

$$y = mx + b$$

where “m” is the slope of the line and “b” is the y-intercept. The slope can be determined using the formula

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

Where x₁, y₁ is one pair of LMB-ICPMS (x) and hand-held XRF (y) analytical values corresponding to the first sample and x₂, y₂ is a pair of analytical results corresponding to the second sample (plotting directly on the line). In the case of our regression lines shown in Figures 5 and 6 the expression can be written as:

$$[Hand-held XRF reading] = m[LMB-ICPMS result] + b$$

Since we are assuming that the results of LMB-CPMS analyses are almost error-free (compared to the XRF values), then the correction equation will be in the form

$$[Corrected XRF reading] = \frac{1}{m} ([Hand held XRF reading] - b)$$

OR

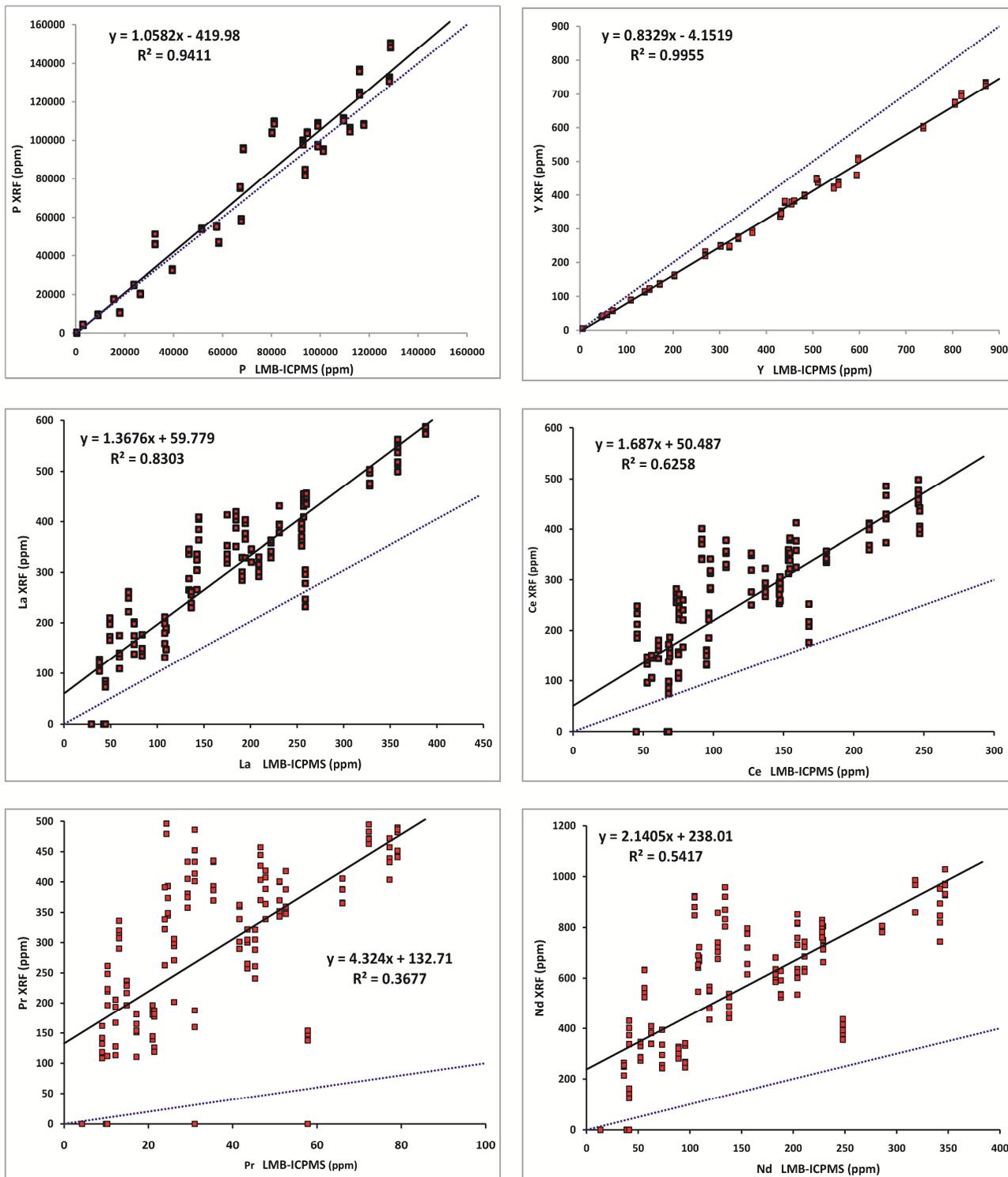


Figure 5. Scatter diagrams, with the Y-axis representing the portable XRF data (XRF) and the X-axis representing the results of the LMB-ICPMS for P, Y, La, Ce, Pr and Nd. In each case, blue dotted line represents perfect theoretical regression line with a slope of unity ($m=1$). Black line represents actual regression line. Bias revealed in a comparison between the two lines is explained in the text.

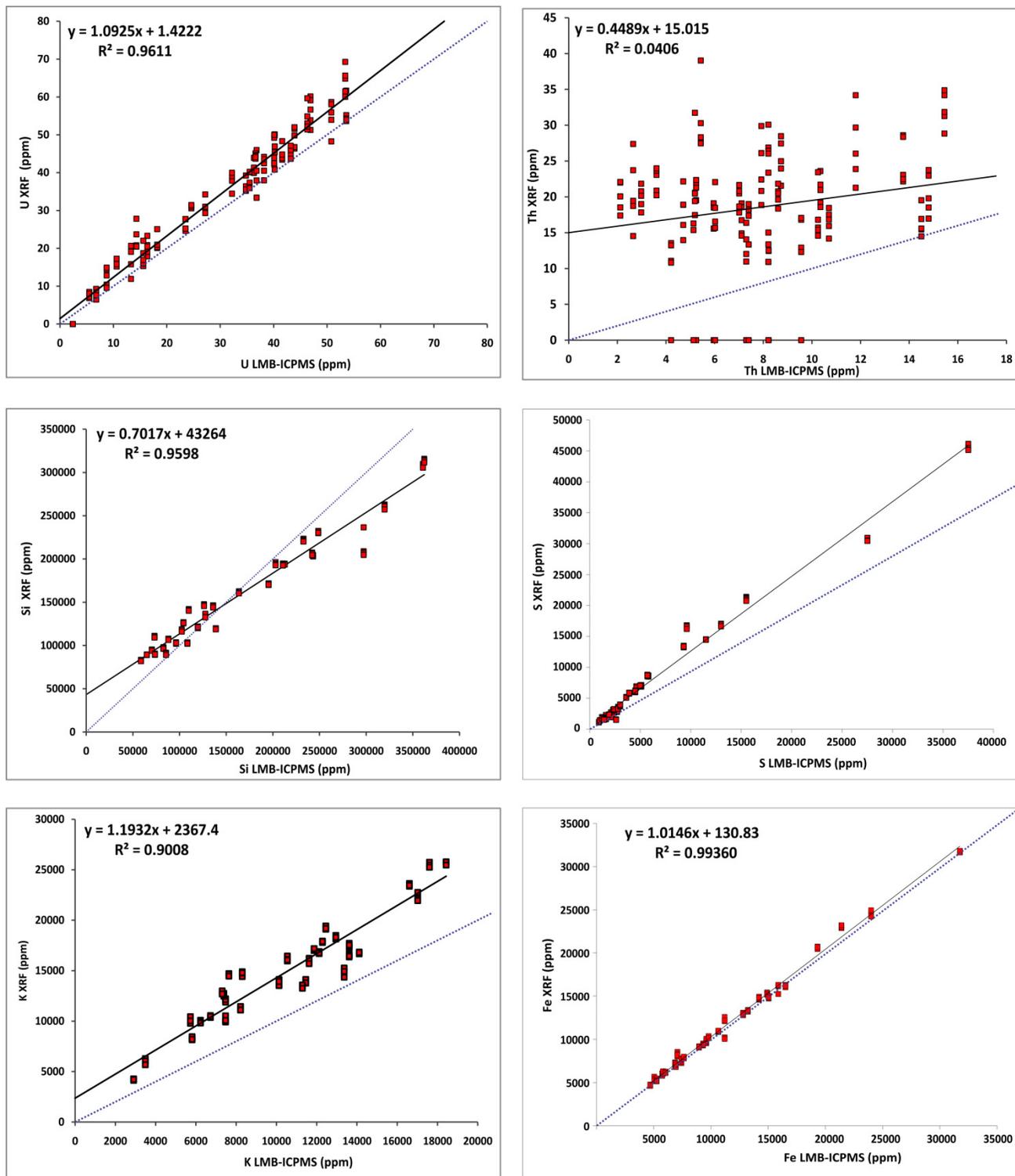


Figure 6. Scatter diagrams, with the Y-axis representing the portable XRF data (XRF) and the X-axis representing the results of the LMB-ICPMS for U, Th, Si, S, K and Fe. In each case, blue dotted line represents perfect theoretical regression line with a slope of unity ($m=1$). Black line represents actual regression line. Bias revealed in a comparison between the two lines is explained in the text.

$[Corrected\ XRF\ reading] = n[XRF\ reading] + c$

where $n = \frac{1}{m}$ and $c = \frac{-b}{m}$

A value of “m” greater than 1 represents overestimation by hand-held XRF relative to the LMB-ICPMS value; a value of “m” less than 1 represents an underestimation. If “n” is greater than 1, then the use of correction factor will reduce the bias (improve the accuracy); however, it will increase the spread of the portable XRF data. If the value of “n” is less than 1 then the correction factor will reduce the bias (improve the accuracy) and decrease the spread of the values (improve precision). If the value of b is greater than 0, then b represents the lowest theoretical value of that element that will be given even if that element is not present in a sample. If the value of b is less than 0, then it can be used to calculate the x intercept of the regression line. This intercept represents the smallest concentration of a given element that the XRF can be expected to read.

A simple test was used to compare the relative error between the hand-held XRF analytical results without calibration and the corrected results (after calibration). The absolute value of the difference of data for each portable XRF measurement and the corresponding lab (LMB-ICPMS) measurement was then divided by the lab (LMB-ICPMS) measurement. The average of this value was taken over all measurements. This quantity is called the mean absolute percentage error (Nau, 2005). It can be expressed as:

$$[Mean\ Absolute\ Percentage\ Error] = \frac{1}{n} \sum \frac{|[XRF]_i - [Lab]_i|}{[Lab]_i}$$

where n is the number of measurements. Similarly, the mean absolute percentage error was calculated using corrected hand-held XRF values. The mean absolute percentage error estimates (Table 3) were used to provide numerical indication of the improvements achieved through the use of correction factors. The mean absolute percentage error estimate may not be statistically the best approach (Swanson *et al.*, 2011); however, it is the simplest way to convey the information to geologists and prospectors.

Phosphorus, REE and Y

Correlation between P values measured by the portable XRF and LMB-ICPMS data is excellent. The values obtained using the hand-held portable XRF analyser are very similar to the laboratory data (Figure 5). Correlation between the corresponding LMB-ICPMS and portable XRF for Y is also excellent across a wide range of concentrations; however, the portable XRF does significantly underestimate the Y content relative to the LMB-ICPMS (Figure 5). Good correlation exists between the portable XRF data and the LMB-ICPMS data for La (Figure 5), although the portable XRF overestimates the La content. Ce and Nd also display good correlation (Figure 5), but the overestimation of portable XRF values compared with LMB-ICPMS values is even more

significant. In the case of Nd, overall, the portable XRF overestimates lab values by more than 100%.

The data from the portable XRF for Pr displays a wide range of scatter, and only a weak correlation with the LMB-ICPMS (Figure 5). This weak correlation is at least in part due to low concentrations of Pr (<100 ppm) in phosphate rocks. Only a qualitative trend can be inferred from the data. The analyser also overestimates Pr concentrations by more than 300% relative to LMB-ICPMS laboratory results.

Other Elements of interest

Uranium and thorium (Th) concentrations are carefully monitored by fertilizer manufacturers. High concentrations of these elements in ammonia phosphate fertilizers are not desirable as they can potentially accumulate in agricultural soil due to repetitive application of fertilizer, and eventually be incorporated into food crops in unacceptable concentrations. If these elements are not incorporated into phosphate fertilizer products or recovered during fertilizer production, they move into effluents associated with phosphogypsum stockpiles and could pose a danger to public health. Reasonable agreement exists between the U data acquired using the hand-held portable XRF unit and corresponding LMB-ICPMS data (Figure 6). The use of hand-held XRF to monitor U concentrations in the phosphate rock is therefore justified as a viable field-based method. Similar relation exists between hand-held XRF unit and corresponding LMB-ICPMS analyses for Mo and Rb.

Thorium content of phosphate rocks used in this study is very low (<20 ppm) and in some cases below the detection limit of the LMB-ICPMS. As expected at low concentrations, there is a much higher degree of scatter between the hand-held portable XRF data and results (Figure 5), and no meaningful correlation can be obtained. Other elements that are present in low concentrations and display similar patterns to Th are Nb, Pb and Ni. Silicon (Si) concentrations determined using hand-held XRF display good precision and excellent correlation when compared to the LMB-ICPMS (Figure 6) but the concentrations obtained using hand-held XRF tend to be significantly underestimated. Similar tendencies are apparent for Ca, Al, Sr and Ba. Sulphur displays slight increase in scatter for samples containing concentrations above 10 000 ppm (Figure 6).

Potassium and Fe illustrate two distinct trends (Figure 5). In the case of K, the hand-held XRF analyser overestimates K concentrations relative to the LMB-ICPMS with an intercept larger than 2000 ppm (0.2%). This indicates that the hand-held XRF analysed could display over 0.2% on a sample where the LMB-ICPMS would not detect any K. It is possible that the high intercept of K is due to spectral overlap with other elements. In the case of Fe, there is a very good match between hand-held XRF and LMB-ICPMS methods; however, unlike in the case of K, the Fe regression line has only a small intercept (130.83 ppm, compared with

Table 3. Comparison of accuracy of the portable XRF results before and after correction using the Mean Absolute Percentage Error approach. See the text for formulae used and definitions of m, b, n and c. Mean % E (w/o cor) stands for the "Mean Absolute Percentage Error" prior to correction. Mean % E (w cor) stands for the "Mean Absolute Percentage Error" after correction.

Element	R ²	Mean % E (w/o cor)	m	b	n	c	Mean % E (w cor)
Nd	0.5417	356.00%	2.1405	238.01	0.4671806	-111.19365	63.48%
Pr	0.3677	993.17%	4.324	132.71	0.2312673	-30.691489	64.64%
Ce	0.6258	53.63%	1.687	50.487	0.5927682	-29.92709	41.48%
La	0.8303	96.49%	1.3676	59.779	0.731208	-43.71088	23.94%
Ba	0.98520	15.31%	0.8268	50.595	1.2094823	-61.193759	15.06%
Mo	0.97450	22.51%	0.7467	0.5137	1.3392259	-0.6879604	9.95%
Zr	0.69810	28.05%	0.6102	21.537	1.6388069	-35.294985	11.65%
Y	0.9955	17.65%	0.8329	-4.1519	1.2006243	4.9848721	6.72%
Sr	0.9941	33.52%	0.6622	0.2542	1.5101178	-0.3838719	2.53%
U	0.9611	19.52%	1.0925	1.422	0.9153318	-1.3016018	9.84%
Rb	0.98780	47.45%	0.492	0.8044	2.0325203	-1.6349593	4.83%
Zn	0.96070	17.46%	0.9388	-3.6733	1.0651896	3.912761	17.01%
Fe	0.99360	3.93%	1.0146	130.83	0.9856101	-128.94737	3.01%
Ca	0.97380	11.84%	0.8758	1694.5	1.1418132	-1934.8025	7.08%
K	0.90080	45.95%	1.1932	2367.4	0.8380825	-1984.0764	12.02%
Al	0.83480	22.26%	0.454	11005	2.2026432	-24240.088	24.73%
P	0.9239	18.63%	1.0512	-324.7	0.9512938	308.88508	16.64%
Si	0.9598	16.25%	0.7017	43264	1.4251104	-61655.978	9.40%
S	0.98280	32.14%	1.2089	529.03	0.8271983	-437.61271	18.68%

Legend
Excellent Correlation
Good Correlation
Correlation Observed
Total of 32 samples

R² is the coefficient of determination. It ranges from 0 to +1.0. Zero indicates complete absence of a systematic relationship, while 1 indicates a perfect relationship.

a lowest reported LMB-ICPMS value of more than 5000 ppm). The slope of the Fe regression line is nearly matching unity and there is little scatter (similar to phosphorus).

DISCUSSION

Linear regression equations for 20 elements that have good correlation between analytical methods or are economically significant (Table 2) were used to create correction equations for the hand-held XRF relative to the LMB-ICPMS. Significant deviation from the theoretical 1:1 regression line for hand-held XRF versus corresponding LMB-IPMS data exists for most of these elements. In these cases, if there is also a significant correlation indicated by a large positive coefficient of determination (R²) the instrument calibration or equivalent mathematical treatment of the raw hand-held XRF generated data can greatly improve the quality of hand-held portable XRF analyses.

In the case of P (Figure 7, Table 3) the mean percentage error decreases only slightly; while in the case of Y (Figure 8, Table 3), the mean percentage error decreases from 17.65 to 6.75%. This is due to the fact that most of the error in the P calibration curve is random and not systematic, in this case the correction curve can only have a small effect on the overall accuracy of the method. For elements with a high degree of systematic error such as Pr, the correction factors may significantly increase the accuracy (Figure 9, Table 3); however, the resulting values may still be considered as qualitative estimates at best. In the case of La, the correction values improve the accuracy significantly, although several outliers still exist (Figure 10), and these outliers are not improved significantly. For elements at low concentrations such as U (Figure 11), the accuracy improves significantly with the correction factors. Higher concentrations of U need to be tested in order to determine if the correction factors can be used outside of this fairly limited concentration interval. From a practical point of view, the correction

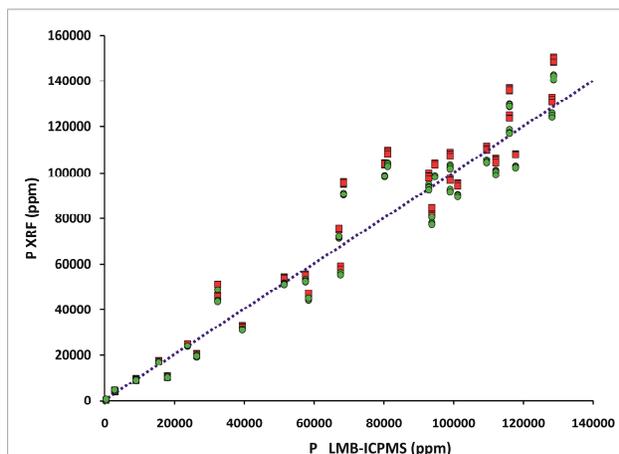


Figure 7. Comparison of uncorrected and corrected hand-held portable XRF data for phosphorus (P). Red squares and green circles represent uncorrected and corrected data, respectively. The dotted blue line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ICPMS data.

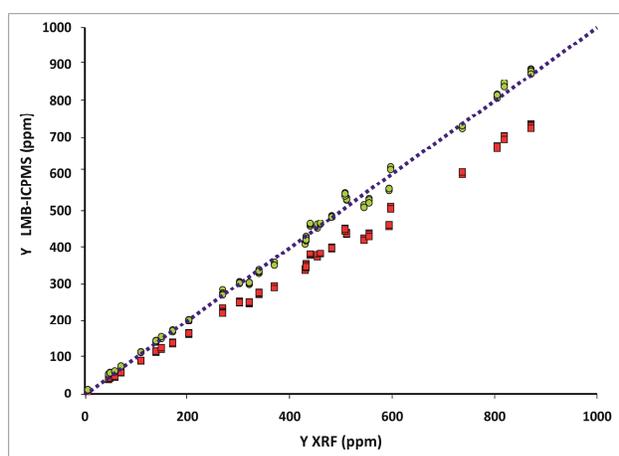


Figure 8. Comparison of uncorrected and corrected hand-held portable XRF data for yttrium (Y). Red squares and green circles represent uncorrected and corrected data, respectively. The dotted blue line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ICPMS data.

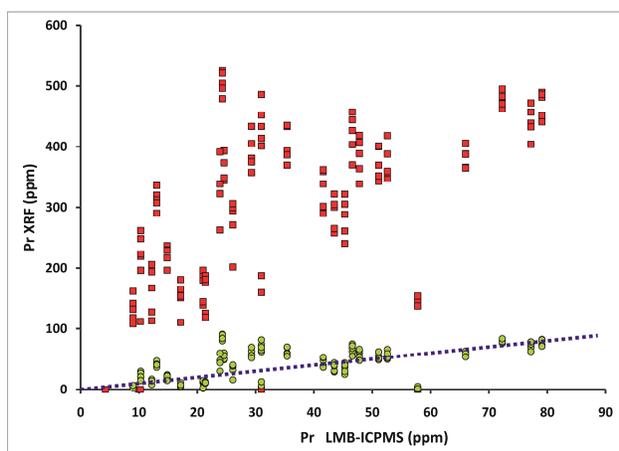


Figure 9. Comparison of uncorrected and corrected hand-held portable XRF data for praseodymium (Pr). Red squares and green circles represent uncorrected and corrected data respectively. The dotted blue line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ICPMS data.

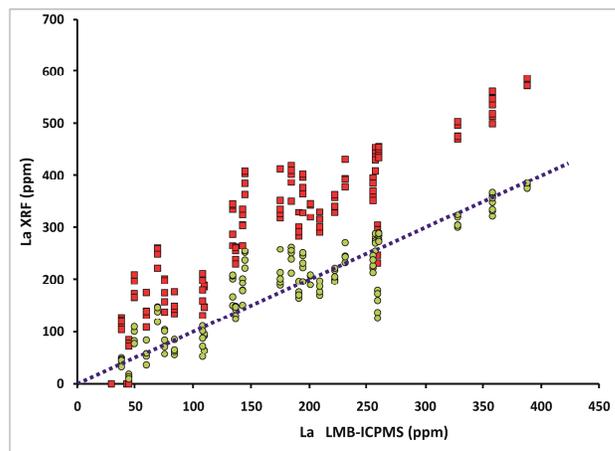


Figure 10. Comparison of uncorrected and corrected hand-held portable XRF data for lanthanum (La). Red squares and green circles represent uncorrected and corrected data, respectively. The dotted blue line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ICPMS data.

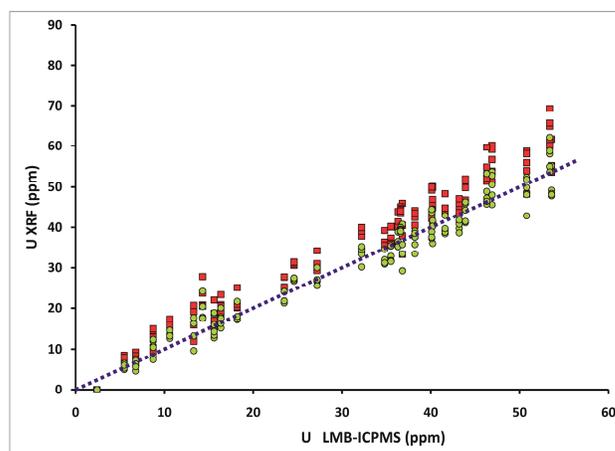


Figure 11. Comparison of uncorrected and corrected hand-held portable XRF data for uranium (U). Red squares and green circles represent uncorrected and corrected data, respectively. The dotted blue line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ICPMS data.

factors suggest that any sample measuring less than 100 ppm U with this method will almost certainly have a concentration of U below the limit (500 ppm U) requiring special precautions for exploration established in the Health, Safety and Reclamation Code for Mines in British Columbia (British Columbia Mines Act).

The increase in accuracy through the use of correction factors is apparent if we compare distribution of corrected and uncorrected hand-held portable XRF readings relative to the results of LMB-ICPMS analyses (Figures 7 to 11, Table 3).

CONCLUSION

Portable, hand-held XRF technology can be used to determine quantitative, semi-quantitative or qualitative concentrations of major, minor and trace elements present in a phosphate matrix, as shown in the phosphate \pm REE occurrences of the Fernie Formation, British Columbia. From the field geologist's point of view, P and Fe

concentrations can be detected in all of the samples and can be measured accurately enough within the tested range of concentrations. The few random discrepancies between LMB-ICPMS analyses and hand-held portable XRF data are probably due to sample inhomogeneity of the pulp. For preliminary assessment of P and Fe content there is no need for use of correction factors.

Acceptable quantitative and semi-quantitative determinations of Nd, Pr, Ce, La, Ba, Mo, Zr, Y, Sr, U, Rb, Zn, Ca, K, Al, P, Si and S could be obtained using the hand-held XRF instrument. However, to achieve these results the readings acquired using the hand-held portable XRF instrument have to be corrected to a known laboratory method using samples of similar concentrations. The portable XRF determinations of Y and REE are of special interest to exploration geologists and geochemists. Light REE (La, Ce, Pr, Nd) and Y results acquired using the hand-held XRF are subject to systematic overestimation relative to laboratory results. Systematic over or under-estimations by XRF instruments are commonly caused by chemical matrix effects (such as absorption and enhancement of the intensity of XRF lines, etc.). Heavy REE (HREE) are present in low concentrations; furthermore, portable hand-held XRF instruments without a radioactive source are not able to analyse for them. Other instruments such as the Thermo Scientific Niton XLP-522K, which allows the detection of HREEs (including Sm, Eu, Gd, Tb and Dy), may be more useful in these applications.

In summary, hand-held portable XRF instruments, such as Thermo Scientific Niton XL3t, can be effectively used in exploration for phosphate (\pm yttrium and REE-bearing) rocks; however, an orientation study is recommended before the use of the hand-held XRF instrument is applied on a large scale. The first stage of the orientation test should be similar to this study. If satisfactory, the second stage should involve analyses of hand specimens corresponding to the pulps to alert the operator of scattered values attributable to effects of textural variations and uneven rock surfaces.

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