



Use of Portable XRF in evaluation of Rare Earth Element-bearing Phosphate Deposits G.J. Simandl^{1,2}, R. Fajber², E.A. Prussin¹, S. Paradis^{2,4} and K. Grattan³



Executive Summary:

The 2010 world phosphate rock production was estimated at 176 million tonnes (Cordier 2011 Sedimentary phosphate deposits (Mineral deposit profile F07; Simandl et al. 2012), account for most of it. Apatite-bearing carbonatites (Mineral deposit profile N01;Birket and Simandl, 1999) and peralkaline intrusions account for the balance. Current production of guano as a phosphate fertilizer source relative to the above sources is negligible. Sedimentary phosphate deposits consist mainly of the apatite group mineral [(Ca₅(PO4)₃(OH,F,CI)] commonly referred to as francolite. In recent years these 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 potentially recoverable lanthanides and Y as by-products. Thirty two samples of phosphate rock (pulps) from the Fernie Formation, collected from the Fernie Basin (Figure 1), south-eastern British Columbia were analyzed using a hand-held XRF analyzer as well as by the lithium metaborate fusion – inductively coupled plasma method (LMB-ICPMS). The results from both methods were compared; correction factors for the portable XRF were established and their effectiveness was tested. Hand-held XRF analyzers that are currently on the market have their technical limitations. 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).



Figure 1. Sedimentary carbonatite-related and single hydrothermal phosphate occurrences in British Columbia. All of the sedimentary phosphate deposits that were sampled for this study are located within the un-metamorphosed to low-grade metamorphic rock of the Foreland Belt within the Fernie Basin.

Introduction:

British Columbia MINFILE contains at least 65 known sedimentary phosphate and 11 carbonatite-related occurrences plus one miscellaneous (volcanic rock-related) showing. 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, price 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. When used in the field, hand-held XRF analyzers do not benefit from sample homogenization and sample preparation of their larger stationary laboratory XRF counterparts and other laboratory techniques. In the case of sedimentary phosphate deposits, the textural variations (bedding, laminations, graded bedding, clasts and post-depositional fracture fillings, veinlets, presence of non-pervasive alteration and weathering) are the main cause of such inhomegeneities. 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 Analyzers Certification Information and Examination Preparation Booklet" (Murphy et al. 2010).

For these reasons, initial orientation studies are required prior to any large scale use of handheld portable XRF equipment. The first stage of orientation studies rely on finely ground and homogenized samples (pulps) in order to minimize errors due to natural textural variations of rocks. Present study represents only this first stage. Its main objectives 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 ppm to 1498.98 ppm. These samples were originally collected and analyzed by Butrenchuk (1986) but have recently been re-analyzed using modern analytical methods (Simandl et al. 2011b). The results of the portable XRF data were compared to results obtained from modern analytical methods.

Instrumentation:

The hand-held portable XRF used for this study was a Thermo Scientific Niton XI3t equipped with GOLDD+ technology (serial number 67749, manufactured in the U.S.A., 2011), supplied by Elemental Controls Limited (Toronto). The instrument (Figure 2) uses a Ag X-ray tube (no radioactive source), with a maximum current of 0.2 mA, a maximum voltage of 50kV, 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 ac rate measurements of a wide range of elements (Table 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 analyse Pr and Nd without the use of a radioactive source. Instruments with radioactive sources have previously been used for



Thermo Scientific Niton XL3t.

mapping and grade control of heavy REE-bearing ore deposits. For example, Avalon Minerals Inc. uses a Thermo Scientific Niton XLP-522K handheld analyser for mapping and grade control at their Nechalacho deposit in Northwest Territories (Bakker *et al.*, 2011).

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 the lightelements within the sample not excited by the analyser.

Filter	Analytical time interval (seconds)	Elements Analysed
Main	45	Sb, Sn, Cd, Ag, Mo, Nb, Th, Zr, Ba Pb, W, Zn, Cu, Ni, Co, Fe, Mn, Cr,
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

Data Aquisition:

Samples were crushed, milled, homogenized and then analysed using lithium-borate fusion followed by ICPMS (LMB-ICPMS) at ALS Laboratories in Vancouver. 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 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

The same sample cups and 4.0µ thick polypropylene film (Figure 3) were used to hold phosphate pulps. Sample cups were filled to the three quarter mark (~19 mm) with pulp, then filled with gauze and capped. 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. Same as the standards, rock pulps were also analysed using the instrument in "Mining Cu/Zn" mode with the 4 beam times 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.

Interpretation:

The usefulness of portable XRF and its limitations in exploration can be 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 ICPMS analysis after a lithium borate fusion (Figures 4 - 5). Each point on these graphs represents one of the 5 XRF measurements versus a corresponding LMB-**ICPMS** analysis

Based on the total of 160 measurements taken on 32 pulps of phosphate rock samples, the hand-held XRF analyser was able to provide an effective quantitative measurement with excellent correlation R²>0.85) to the LMB-ICPMS data (Table 2) for 12 elements (Ba, Mo, Y, Sr, U, Rb, Fe, Ca, P, Si, S and Mg). A reasonable guantitative or semi-guantitative estimate with good correlation (0.5<R²<0.85) exists between the hand-held XRF and LMB-ICPMS data sets for 6 elements (Nd, Ce, La, Zr, W, and AI). Using the same approach, only limited interpretation (0.25<R²<0.5) was achieved for Pr. Nb and Cu. These elements were present in concentrations near the lower detection limit of the analyser. There was no practically significant correlation (0.25<R²) between the portable XRF analyser and the LMB-ICPMS data sets for three elements (Th, Pb and Ni). Twelve elements (Bi, Au, Co, Mn, Cr, V, Ti, Sb, Sn, Cd and Aq) 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 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.

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Figure 2. The hand-held portable XRF used for this study was a





Figure 3. Typical sample cups covered by 4.0µ thick polypropylene

 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, unless otherwise specified.

Filtor	Element	R ²	ICP-MS	
Filter			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
/Main	Sn	-	<1	2.0
High	Ag	-	<1	<1
	Мо	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
. <u>E</u>	Rb	0.98780	10.2	68.8
Σ	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
in	Cr	-	50.0	250.0
w/Me	V	-	30.0	146.0
2	Ti	-	659.4	3237.4
ş	Са	0.97380	4431.0	316604.0
2	к	0.90080	2905.5	18429.0
	AI	0.83480	9261.7	80179.0
	Р	0.9411	436.4	128741.0
Light	Si	0.9598	58664.0	362268.0
	S	0.98280	900.0	37500.0
	Mg	-	1327.0	21471.0
Legend				
	Excellent Good Co	Correlation prrellation		
	No Cor	relation		



Figure 4. Scatter diagrams, with the Y-axis representing the portable XRF data (XRF) and the X-axis representing the results of the LMB-ICPMS analysis for P, Y, La, Ce, Pr and Nd. In each case, the purple dotted line represents a perfect theoretical regression line with a slope of unity (m=1). The black line represents the actual regression line. Bias revealed in a comparison between the two lines is explained in the text.

If there was a near perfect match between the LMB-ICPMS and hand-held 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 (R^2) would be equal to one. If the hand-held XRF systematically under-estimated or overestimate the "true" (ICPMS) value, then the slope of the regression line will not

Pr LMB-ICPMS (ppm)

Data Processing:

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 to 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:

$$m = \frac{y_2 - y}{x_2 - x}$$

Where x_1 , y_1 is one pair of LMB-ICPMS (x) and handheld XRF (y)

analytical values corresponding to the first sample and x_2 , y_2 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 4 and 5 the expression can be written as:

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

definitions of m, b, n and c.



Total of 32 samples



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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 analysis for U, Th, Si, S, K and Fe. In each case, the purple dotted line represents a perfect theoretical regression line with a slope of unity (m=1). The black line represents the actual regression line. Bias revealed in a comparison between the two lines is explained in the text.

Table 3. Comparison of accuracy of the portable XRF results before and after correction using the Mean Absolute Percentage approach. See the text for formulae used and

| Mean % E (w/o cor) | m | b | n | c Mean % E (w/ cor) 63.48% 53.63% 41.48% 15.31% 5102 21.537 1 17.65% 6.72% 33.52% 19.52% 47.45% 11.84% 45.95% 22.26%
 18.63%
 1.0512
 -324.7
 0.951294
 500.000

 0.7017
 42264
 1.42511
 -617
16.25% 48280 32.14% 18.68%

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

- [Corrected hand-held XRF reading] = ([Hand-held XRF reading] b)
- [Corrected hand-held XRF reading] = n [hand-held 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 a correction factor will be able to be analysed using this instrument. 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. The comparison between raw hand-held XRF readings and corrected data is shown in Figures 6, 7, 8, 9 and 10.

Comparison Between Processed and Raw Data:

A simple test was used to compare the relative error between the portable XRF analytical results without calibration and the corrected results (after calibration). The same process was repeated for the corrected values afterwards. This quantity is called the mean absolute percentage error (Nau, 2005). It can be expressed as:

[Mean Absolute Percentage Error] = $\frac{1}{n} \sum \frac{|([XRF]_i - [LMB-ICPMS]_i)|}{[LMB-ICPMS]_i]}$

where "n" is the number of measurements. Similarly, the mean absolute percentage error can be



100000 20000 40000 60000 80000 100000 120000 140000 P LMB-ICPMS (ppm)

Figure 6. 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 purple 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 praseodymium (Pr). Red squares and green circles represent uncorrected and corrected data respectively. The dotted purple line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ÌCPMS data.

calculated for the corrected 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.

Conclusion:

Hand-held XRF analysers can be used to determine quantitative. semiquantitative or qualitative concentrations of major, minor and trace elements present in phosphate rocks, as demonstrated by this orientation survey of REEbearing phosphate occurrences of the Fernie Formation. From the field geologist's point of view, P concentrations were detected and measured accurately enough within the tested range of concentrations in all the samples. The few random discrepancies between LMB-ICPMS analyses and hand-held portable XRF data are probably due to 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, N Sr, U, Rb, Zn, Fe, 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 concentrations established through use of an appropriate laboratory method. The portable XRF determinations of REE are of special interest to exploration geologists. Light REE (La, Ce, Pr, Nd, Y) concentrations determined using the hand-held XRF on



Figure 7. 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 purple 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 uranium (U). Red squares and green circles represent uncorrected and corrected data, respectively. The dotted purple line coincides with a perfect (theoretical) correlation between the portable XRF and LMB-ICPMS data.

samples from the Fernie Formation are subject to systematic over-estimation 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 are present in low concentrations and the use of portable hand-held XRF instruments without a radioactive source is not recommended.

Summary:

Hand-held portable XRF instruments, such as Thermo Scientific Niton XL3t, can be effectively used in exploration and development of phosphate (± REE) deposits; 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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