Hand-held, Portable XRF in Exploration for Carbonate-hosted Sulphide and Nonsulphide Pb-Zn Deposits

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Extended Abstract:

Carbonate-hosted, nonsulphide base metal mineralization is derived from sulphide deposits by supergene processes. Pb and Zn can be trapped locally (replacing the protore), forming direct-replacement nonsulphide deposits ("red ores"), or transported by percolating waters down and away from the protore, forming wallrock-replacement nonsulphide deposits ("white ores") as shown on Figures 1a and 1b.

In the Kootenay and Cariboo terranes (Figure 2), red ores (Figure 3) consist mainly of Fe-oxyhydroxides, goethite, hematite, hemimorphite, and minor smithsonite, hydrozincite and cerussite (Figure 1). Vestiges of galena may be present. Red ores are difficult to distinguish macroscopically from barren gossan. White ores consist mainly of hemimorphite, smithsonite, hydrozincite, and minor Fe-oxyhydroxides (Figure 4, Table 1). In some cases, they are difficult to distinguish macroscopically from enclosing carbonate host rock.

Samples from carbonate-hosted nonsulphide deposits of the Kootenay and Cariboo terranes were analysed first using portable hand-held X-Ray Fluorescence (XRF) spectrometry and secondly using laboratory ICP-MS/ICP-ES methods (following lithium metaborate fusion). The portable hand-held Alpha series Innov-X Delta analyzer (Figure 5) was set-up in "mining" mode for analyses of heavy elements, such as Pb, Zn, Cu, Mo, Ni, Cr, W, Fe and Cd . The instrument was calibrated by the manufacturer for silica-rich volcanogenic massive sulphides, sedimentary-hosted exhalative deposits (SEDEX) and porphyry Cu±Au environments. The analytical procedure described in "Innox-X Systems ALPHA Series™ X-Ray Fluorescence Spectrometers" (Innov-X Systems, 2007) was strictly adhered to and is not repeated here.

The portable hand-held XRF analyses were performed directly on hand specimens (Figure 5), thin section slabs (Figure 6), crushed rocks granules measuring 3 to 5 mm (Figure 7) and pulps (Figure 8).

Hand specimens and thin section slabs show textural heterogeneity (Figure 6) and could lead to a disagreement between the lab analyses and the data gathered by the portable hand-held XRF instrument (Figure 9).

When used with granules the instrument was shutting down prematurely and testing was discontinued. No data is shown from these tests.

The best results were achieved using finely ground (pulp) material. Six analyses were performed on each pulp sample (60 to 90 seconds count time each; there was little difference in the quality of the data if the count time exceeded 60 seconds). The six pulp analyses were averaged out and compared statistically with the ICP-MS/ICP-ES results (Figure 10). The portable hand-held XRF instrument is useful for rapid decision making; however, it is not a substitute for ICP-MS or other established analytical techniques.

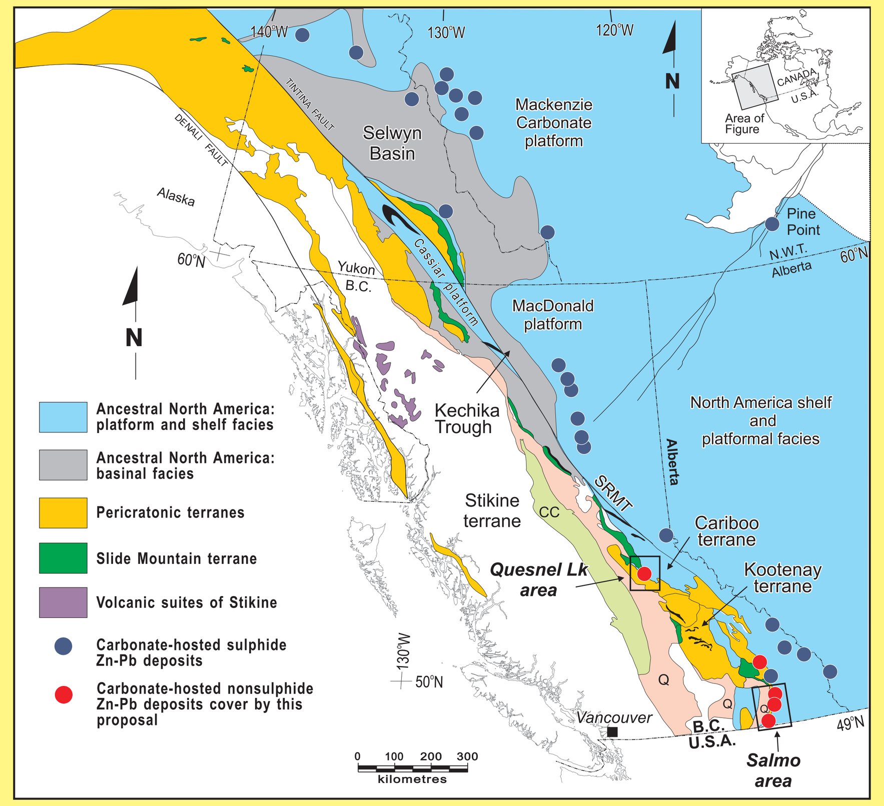

Figure 2: Location of significant carbonate-hosted sulphide and nonsulphide occurrences in the northern cordillera (modified from Nelson et al., 2002, 2006, Paradis et al., 2011). Abbreviations: St - Stikine terrane, CC - Cache Creek, Q-Quensnel terrane, SRMT - Southern Rocky Mountain Trench.

Table 1: Selected zinc-, lead-, and iron- bearing minerals (modified from Simandl and Paradis, 2009).

Main zinc-bearing minerals	Formula	Colour	Lustre	Density	Hardness	Comments
Smithsonite	$ZnCO_3$	white	earthy to dull	4.5	4.4	HCl-soluble, botroidal habit
Hemimorphite	$Zn_4Si_2O_7(OH)_2 \cdot H_2O$	white, brown, greenish gray	vitreous	3.6	5	weakly soluble in HCL, massive, botroidal, stalactitic
Hydrozincite	$Zn\,(CO_3)_2(OH)_6$	white, pale yellow, pale gray	pearly	3.6-3.8	2-2.5	massive, fibrous, bladed aggregates
Sauconite	$Na_{0.2}Zn_3Si_3AlO_{10}(OH)_2 \cdot 4(H_2O)$	white, pale brown, reddish brown	earthy to dull	2.45 (variable)	1.0-2.0	earthy or clay-like texture
Willemite	$ZnSiO_4$	white, green, red, brown, black, pinkish, bluish	vitreous/resinous	3.9-4.2	5.5	massive, granular, prismatic
Zn-bearing aragonite	$(Zn,Ca)\,CO_3$	white, gray, yellowish	vitreous	3	3.5-4.0	HCl-effervescence, fibrous, prismatic, columnar
Minrecordite	$Ca\,Zn\,(CO_3)_2$	white to colourless, brown, blue green	vitreous to pearly	3.5	3.5-4	rhombohedral, sometimes saddle-shaped
Hopeite	$Zn_3(PO_4)_2 \cdot 4H_2O$	colourless to grayish white and pale yellow	vitreous	3.05	3.25	easily soluble in dilute HCl
Tarbuttite	$Zn_2(PO_4)(OH)$	colourless to white, yellowish to pale pink	vitreous	2.7	4.5-5	soluble in hot concentrated HCl

Main lead-bearing minerals	Formula	Colour	Luster	Density	Hardness	Comments
Cerussite	$PbCO_3$	colourless, white, tan, gray	adamantin	6	3	massive granular, reticulate, well formed prisms
Anglesite	$PbSO_4$	white, colorless, gray, bluish, yellow	vitreous to adamantin	6.3	3	granular, anhedral to subhedral crystals
Pyromorphite	$Pb_5(PO_4,AsO_4)_3\,Cl$	green, brown, yellow	resinous/adamantin	6.7-7	4	prismatic or reniform and globular textures
Plumbojarosite	$PbFe_6(SO_4)_4(OH)_{12}$	brown, yellowish brown	dull to vitreous	3.6	1.5-2.0	HCl soluble, earthy, concreationary, encrustations
Litharge	PbO	red	greasy	9.14-9.3	2	encrustations
Mimetite	$Pb_5(AsO_4,PO_4)_3Cl$	brown, yellow, tan, brown, white	resinous	7.1-7.3	3.5-4	reniform, globular, sometimes prismatic

Main iron-bearing minerals	Formula	Colour	Luster	Density	Hardness	Comments
Goethite	$FeO(OH)$	dark or rusty brown, black	dull/resinous	4-4.4	3.5-4	earthy, botroidal, stalactitic
Hematite	Fe_2O_3	red to nearly black	dull	5.2	5	coatings, stains, fracture fillings

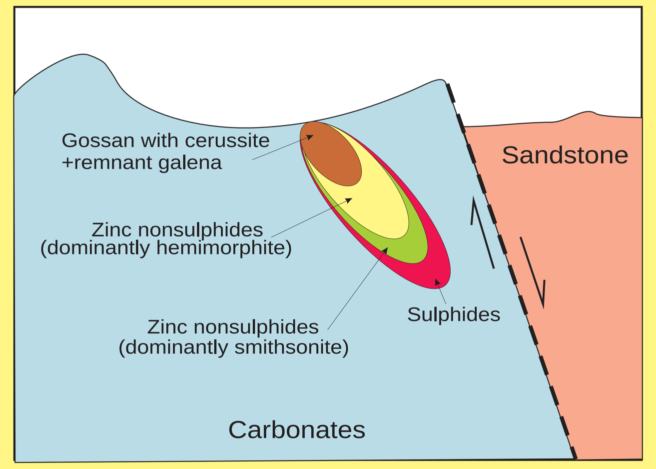

Figure 1a: Idealized representation of the "direct-replacement" carbonate-hosted nonsulphide Pb-Zn deposit. Modified from Hitzman et al. (2003).

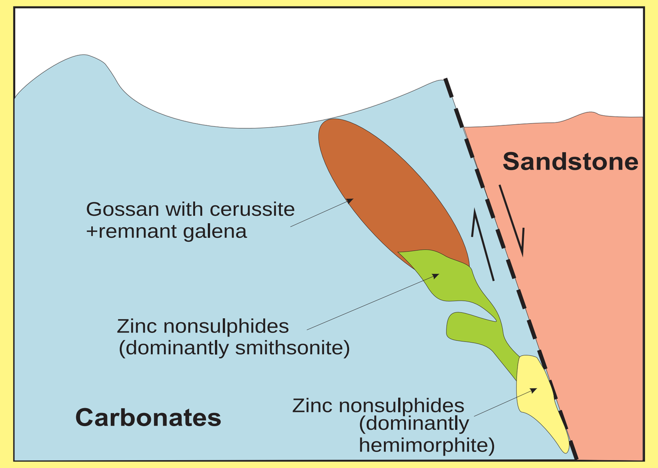

Figure 1b: Idealized representation of the "wallrock-replacement" carbonate-hosted nonsulphide Pb-Zn deposit. Modified from Hitzman et al. (2003).

Figure 3: Dolomite-hosted nonsulphide mineralization, occurring as iron-rich gossan, Red Bird, Salmo area, BC.

Figure 4: Internal texture of a hemimorphite nodule, Oxide deposit, Salmo area, BC.

Figure 5: ALPHA Series™ Portable X-Ray Fluorescence Spectrometer produced by Innov-X Systems, Inc.

Figure 6: Textural heterogeneity (on sample scale) is typical of nonsulphide and "mixed" (sulphides and nonsulphides) bearing mineralization.

Figure 7: Crushed rock granules (right) and corresponding pulp (<200 mesh, left)

Figure 8: Typical pulps of nonsulphide rocks and host rocks, crushed and milled to -200 mesh, homogenized and analysed by ICP-MS after lithium metaborate fusion. The same samples were analysed using the portable XRF instrument.

Interpretation:

Scatter plot diagrams between laboratory ICP-MS/ICP-ES data and the results of the portable XRF analysis on hand samples and pulps are given on figures 9 and 10, respectively. Laboratory data is plotted on the vertical scale and portable XRF data on the horizontal scale. For each sample, the range of the readings are represented by horizontal bars (in red), and the means are plotted (in black). Least squared linear regression lines, related equations and corresponding coefficient of determination (R^2) are shown in blue. Quadratic regression curves, related equations and corresponding coefficient of determination are shown in green. The linear and quadratic regression curves were produced by only considering the average XRF reading for each set of readings and corresponding laboratory reading.

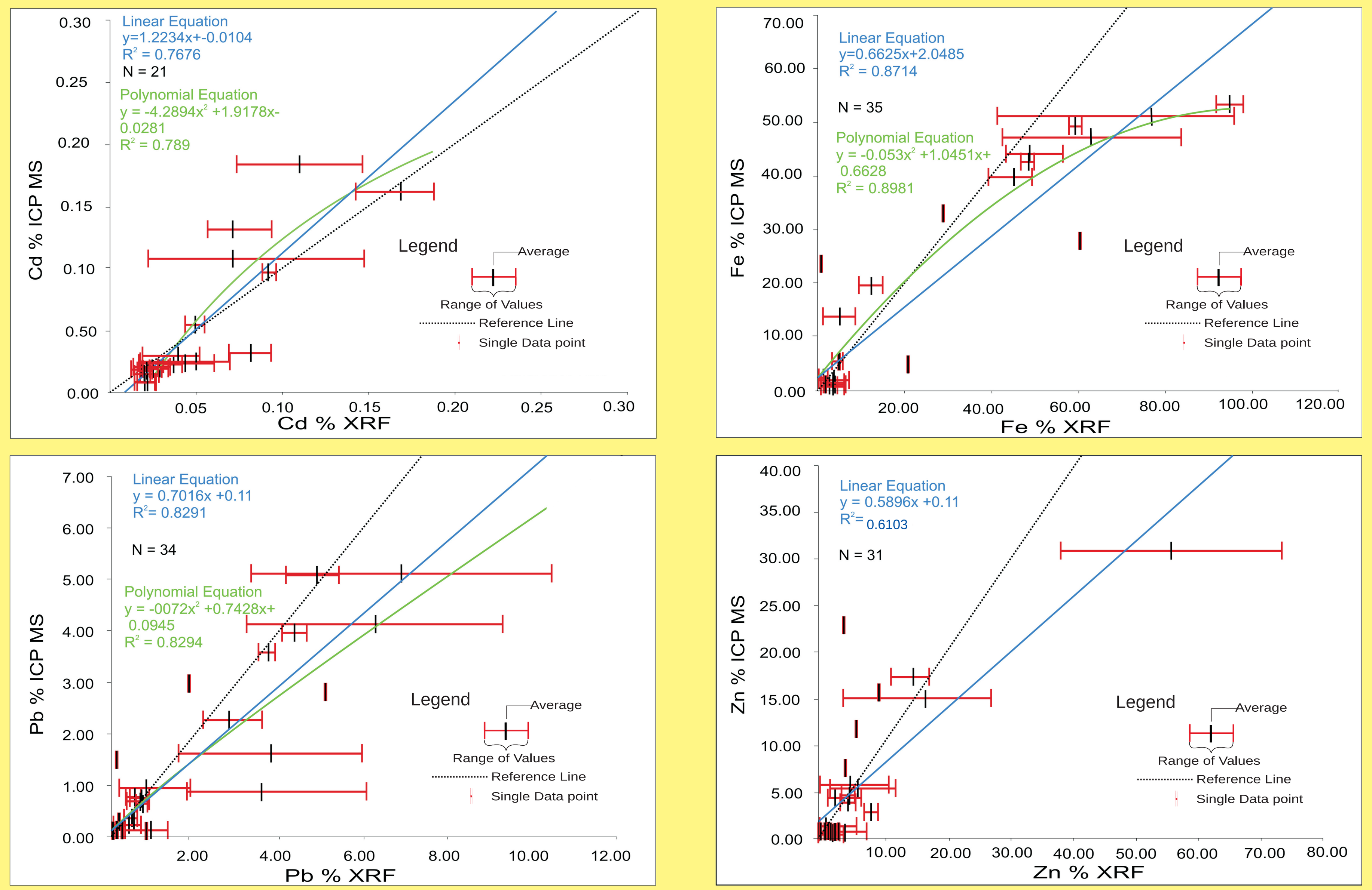

Figure 9: Correlation diagrams comparing results of XRF analysis with corresponding ICP-MS data on hand specimens. Four samples in which the ICP-MS method reports values greater than 40% Zn (without providing more precision) have been omitted. The quadratic curve for Zn became misleading and is not shown.

Interpretation cont.:

The dotted reference line has a slope (m) equal to 1. If the linear regression line (shown in blue) lies below the reference line (black dotted line) the XRF instrument overestimates the metal content relative to the laboratory method. If the linear regression line lies above the reference line, the XRF instrument underestimates the metal content relative to the laboratory method.

Quadratic regression curves model the XRF readings with a high degree of fit. A convex quadratic regression curve indicates that the XRF machine tends to underestimate lower values and overestimate higher values. A concave quadratic regression curve indicates that the XRF instrument tends to overestimate lower values and underestimate higher values. Cd and Pb powders are the only data sets that are modeled by a concave curve. In the case of portable hand-held readings on Fe powders, the reference line is crossed twice by the quadratic regression (Figure 10). In this case, the XRF tends to overestimate below 5% Fe and above 35% Fe and has a tendency to slightly underestimate between these two values.

In almost all cases, the coefficient of determination corresponding to the quadratic equation is higher than the corresponding coefficient of the linear equation for the same data set. The only exception is the set of XRF values taken on Cd powders.

The precision of the XRF readings on pulp samples is higher than the precision of the XRF readings on hand samples. This is explained by the lack of homogeneity in the hand samples. The range of the portable XRF readings for any given sample indicates lower levels of reproducibility than conventional laboratory methods. Basing decisions on a single reading per sample could be highly misleading.

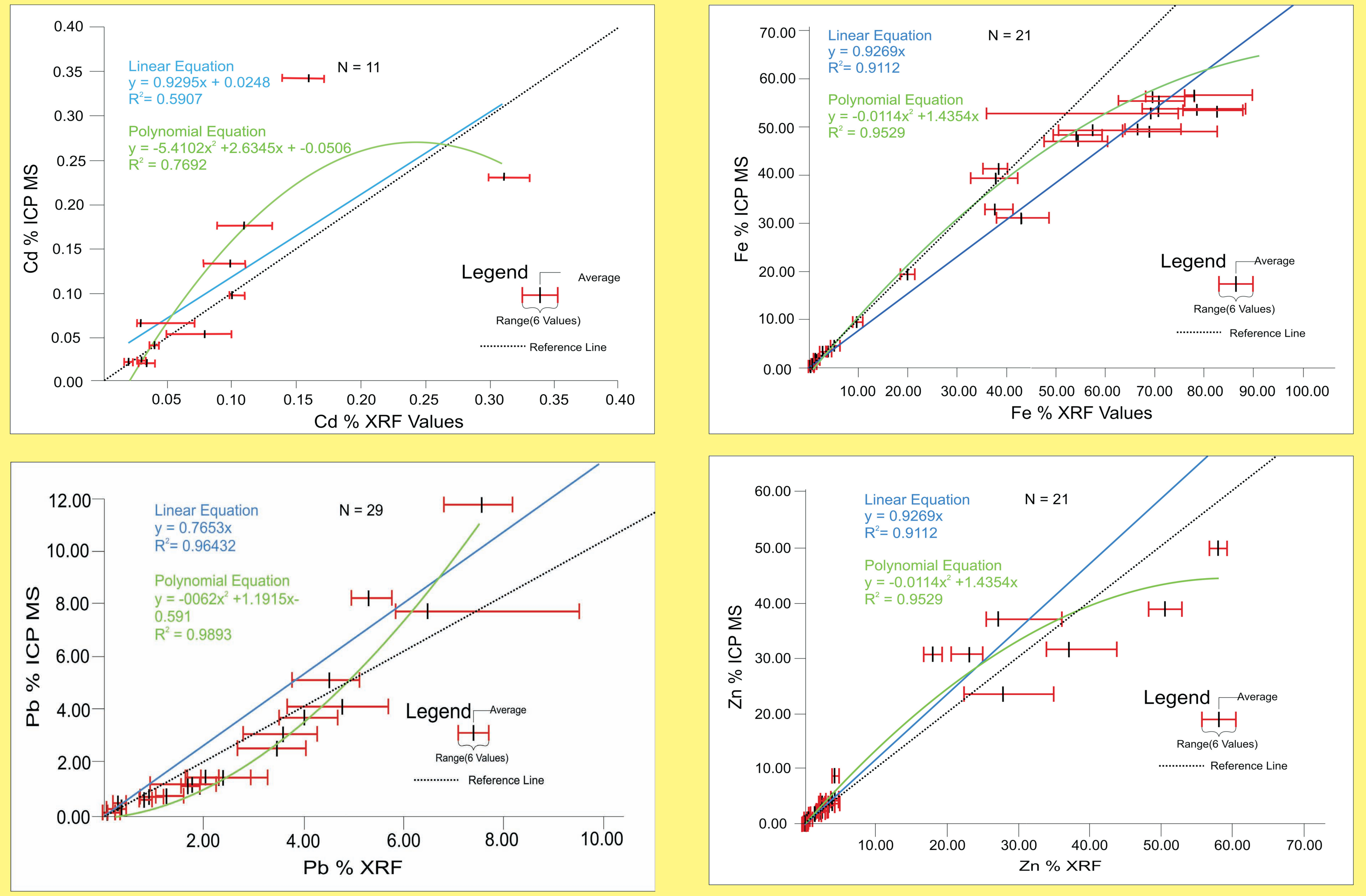

Figure 10: Correlation diagrams comparing results of portable XRF analysis with corresponding ICP-MS data on pulps. Cd had the lowest coeffecient of determination as well as the fewest number of samples. The quadratic curve should not be considered as a good fitting model for higher ICP-MS values.

Conclusion:

As expected, the correlation between the ICP-MS/ICP-ES and the portable hand-held XRF data decreased with increasing coarseness (crushed rock 2-5 mm), decreasing count time (used for less than 60 seconds) and when the portable hand-held XRF was used directly on hand specimens (lack of homogeneity). If the portable hand-held XRF instrument is calibrated specifically for nonsulphide Pb-Zn deposits, better results could be obtained.

These tests indicate that the portable hand-held XRF is a useful field tool in exploration for carbonate-hosted nonsulphide deposits, which are difficult to recognize visually (Table 1). The instrument is able to distinguish between barren, moderately mineralized and high grade samples, making it useful where rapid decisions are needed (on a drill site or during helicopter supported reconnaissance geological work) or for semi-quantitative verification of ore grades on a mine site (if appropriately calibrated). It should not be used as a substitute for analytical laboratory methods (such as ICP-MS/ICP-ES or assays).

For the analyses done on nonsulphide mineralization, only Fe, Zn, Pb, and Cd were present in concentrations detectable by the portable XRF instrument. New generations of portable hand-held XRF instruments will most likely be faster, more precise, more accurate and easier to adjust to the needs of a specific project.

Additional information:

Background Information:
Paradis, S. and Simandl, G.J. (2011): Carbonate-hosted, nonsulphide Zn-Pb (supergene) - Mineral Deposit Profile B09; in: British Columbia Ministry of Forests, Mines and Lands, Geological Fieldwork 2010, Paper 2011-1.

Complete List of References:
Paradis, S., Keevil, H., Simandl, G.J., and Raudsepp, M. (2011): Geology and mineralogy of carbonate-hosted nonsulphide Zn-Pb mineralization in southern (NTS 082F/03) and central British Columbia (NTS 093A/14E, 15W); in: Geoscience BC Summary of Activities, Geoscience BC Report 2011-1.

Portable Hand-Held XRF Instrument:
Innov-X Systems, Inc. (2007): User Instruction Manual; Innov – X Systems ALPHA Series™ X-Ray Fluorescence Spectrometers. March 2007, P/N 100392, Revision B.

Suggested reference:

Simandl, G.J., Paradis, S., Fajber, R., Rogers, N., (2011):
Hand-held, Portable XRF in Exploration for carbonate-hosted culphide and nonsulphide Pb-Zn deposits, British Columbia; British Columbia Ministry of Forests, Mines and Lands; Geofile 2011-6, poster.