

1.0. Summary

Carbonatites, associated fenitization zones, and their weathered equivalents are the most importan sources of Nb and some contain significant concentrations of Ta and rare earth elements (Simandl et al 2012). They contain important deposits of vermiculite, apatite (phosphate), badelleyite (zirconia), fluorite, U and magnetite (Mariano 1989a, 1989b, Birket and Simandl, 1999).

One of the objectives of the Specialty Metals component of the Targeted Geoscience Initiative 4 (TGI-4) is to determine if indicator minerals can guide explorationists toward carbonatite-related mineralization. Heavy mineral processing and analysis of indicator minerals are expensive and time consuming. We measured the concentrations of Nb, Ta, REE, P, Sr, Ba, U, and Th in different grain size fractions of sediments sampled from streams draining three deposits (Fig. 1). Using portable X-ray fluorescence (pXRF) minimizes the cost, improves output, and optimizes the sampling procedure. Concentrations of these pathfinder elements are expected to correlate with the presence of indicator minerals such as pyrochlore, columbite-tantalite, fersmite, apatite, REE-bearing fluorocarbonates, monazite, allanite, zircon, xenotime, and minerals of celestite-barite solid solution.

Three carbonatites, Lonnie (Nb prospect), Aley (large Nb deposit), and Wicheeda (high grade REE deposit), are the subject of an indicator mineral orientation surveys to improve the efficacy of Nb, Ta, and REE exploration techniques (Fig. 1). This study summarizes the methodology used in the above orientation surveys; however, it focusses on the Lonnie Nb prospect.

The results for key pathfinder elements were precise (most having a mean %RSD less than 6%). In order to acheive the best possible accuracy pXRF results were correlated with results from laboratory techniques for recalibration. Results for eight size fractions separated by laboratory sieves indicate a systematic distribution of key elements, with the highest abundances found in the finer size fractions. Of these, the +125µm fraction was chosen for further consideration due to its suitability for continued indicator mineral studies. With the exception of Ba, Sr, and possibly Nb samples upstream from the Lonnie deposit display higher concentrations of carbonatite pathfinder elements than samples downstream of the deposit. This indicates source(s) farther upstream, probably the Vergil carbonatite and Nb and TREE + Y soil geochemical anomalies. Indicator mineral studies are ongoing.



Fig. 1. Geological Setting of the Lonnie, Aley, and Wicheeda carbonatites. Map modified from Colpron and Nelson (2011). Inset from Pell (1994).

2. Geology of the Lonnie carbonatite

The Lonnie carbonatite belongs to a series of metacarbonatites, syenite complexes, and other alkaline rocks forming the British Columbia alkaline province (Fig. 1 inset; Pell, 1994; Simandl et al., 2012). It is in the southern Omineca Mountains, which straddle the boundary between the Intermontane and Omineca belts. The Lonnie metacarbonatite outcrops along the projection of the Wolverine fault (Fig. 2), an extensional structure sub-parallel to the nearby dextral, 1-5 km wide Manson Creek fault system (Simandl et al., 2013a). The Wolverine fault is a probable metallotect connecting the Lonnie deposit to the Virgil carbonatite 4.5 km to the northwest. This fault system, considered part of the Rocky Mountain Trench, separates the Quesnel terrane from the Slide Mountain and Cassiar terranes (Ferri and Melville, 1994).

Northeast of the Wolverine fault zone the Granite Creek drainage area is underlain by amphibolite-grade schist and quartzite of the Wolverine metamorphic complex (Neoproterozoic; Fig. 2). Bordering these rocks along the hanging wall of the Wolverine fault zone is the Lonnie carbonatite. Farther southwest, siliciclastic and carbonate rocks of the Stelkuz Formation, limestone of the Epsee Formation, and metapelites of the Tsaydiz Formation make up the Wolverine antiform (Ferri and Melville, 1994; Simandl et al., 2013a). Farther to the west are the Nina Creek and Big Creek Groups (Paleozoic; Fig. 2).

The Lonnie carbonatite has been traced by trenching over an area of 650 m by 50 m. Several Nb ± REE soil anomalies were identified near the deposit (Fig. 2; Helmel, 2012). The deposit consists of biotite-bearing sövite, aegerine-amphibole sövite, and a variety of quartz-free feldspathic rocks produced by fenitization. Blue-green amphiboles and aegirine decrease away from the carbonatite in fenitized metasediments (Simandl et al., 2013a). A 1955 trenching program (predating NI-43-101) reported a mineralized zone 530 metres long and approximately 17 metres wide grading 0.21% Nb₂O₅ (Rowe, 1958; Chisholm, 1960). In this zone, the Na-amphibole-bearing carbonatite assayed 0.16% Nb₂O₅ over 6 metres. The feldspathic rocks averaged 0.23% Nb₂O over nearly 10 metres. Furthermore, the central portion of this zone averaged 0.3% Nb₂O₅ across 8.3 metres over a length of 283 metres (Rowe, 1958). Recent analyses (Simandlet al., 2013a) failed to confirm these grades. Pyrochlore seems to be the main Nbbearing mineral (Simandl et al., 2013a); however, columbite was also reported (Hankinson, 1958; Halleran, 1980; Pell, 1994) and Nb-bearing rutile was reported in polished thin sections. Pell (1994) reported up to 20% apatite in the carbonatites and 3-15% zircon in associated nepheline syenite.





Fig. 3. Most of the sample sites are in the lee of large boulders or logs where the material was deposited in the final stages of bedload transport. The fraction of sediments that passed through an 8mm sieve was kept. Samples were contained in permeable canvas bags and stored in plastic pales. a) Common rounded granite gneiss and angular schist boulders predominate. b) Sampling media typically comprise quartz, feldspar, biotite, white mica, sericite schist, and trace garnet cobbles in a coarse sand matrix. c) A gravity slide observed directly downstream of sample LO-13-04.

3.1. Sample Preparation

Samples were processed at the British Columbia Geologic Survey Laboratory in Victoria. Procedure included drying and seiving in to the following size fractions: +4mm, 2mm to 4mm, 1mm to 2mm, 500µm to 1mm, 250µm to 500µm, 125µm to 250µm, 63µm to 125µm, and -63µm.

Each size fraction was split to permit pXRF analyses and for magnetic separation using an isodynamic separator (Frantz). Milling was carried out with Rocklabs Limited tungsten carbide mills consisting of a ring and roller bowl for three minutes. The pXRF samples were prepared according to the procedure described by Luck and Simandl

3.2. Portable X-Ray Fluorescence

Analyses were carried out using a Thermo Fisher Scientific Niton FXL-950 (Fig. 4) with factory calibrations. The instrument is equipped with an Ag anode x-ray tube capable of a maximum voltage of 50kV, current of 0.2 mA, and power of 4W. Four beams were used to detect elements.

Detection limits for Nb, Ta, La, Ce, Pr, Nd, Y, Ba, Sr, and P as well as pXRF methodology in this study are described in Simandl et al. (2013c) and Luck and Simandl (2014).

Stream sediment geochemical/indicator mineral orientation survey, Lonnie Nb Prospect, British Columbia, Canada **P. Luck¹ and G.J. Simandl^{1,2}**

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Fig. 2. Geological setting of the Lonnie deposit and location of stream sediment samples. Modified from Ferri and Melvill, (1994)



Fig. 4. The pXRF Thermo Fisher Scientific Niton FXL-950 instrument used in this study.

3.3. Data Enhancement

Representative samples spanning a wide compositional range of pathfinder elements (Table 1) from the Lonnie (4 samples), Wicheeda (6 samples), and Aley (6 samples) carbonatite areas were analysed by inductively coupled plasma mass spectrometry following lithium metaborate fusion (LB-ICPMS) and laboratory XRF following lithium metaborate fusion (LB-XRF). Data from all 16 samples (Universal; Tables 1 and 2), as well as separately for Lonnie, Wicheeda, and Aley (Project Specific; Table 2), was linearly regressed against corresponding pXRF results (Fig. 5). Calibration of pXRF data was performed using the method described in Simandl et al. (2013b).

Calibrations were performed by:

Precision was determined by: %RSD = [standard deviation/mean]x100%

Table 1. Summary of correlations between portable x-ray fluorescence and laboratory techniques. Precision of samples used in the cross correlation analysed by pXRF was good (mean %RSD < 10%) while mean % Difference ranged from 3.9 to 645.5% relative to laboratory methods. For Ta, Nd, and Pr high % Difference is due to the low concentrations of these elements, which border on nXRF detection limits. Coefficients of determination (R^2) varied from

0.85	08 to 0.	9996. Dif	ference	es in mea	an % D	ofference	between t	ne pXRF initial		Nb			Sr			Th			U		
resul	ts and	those of	obtaine	d by th	e "Un	iversal" ı	recalibratio	n indicate an		Initial		Project	Initial		Project	Initial		Project	Initial		Project
impro	ovemen	t in accur	acy for a	all eleme	nts exc	ept Y.				Result	Universal	Specific	Result	Universal	Specific	Result	Universal	Specific	Result	Universal	Specific
Mean % Difference									Lonnie	4.2	0.7	2.6	7.2	0.6	1.3	21.9	16.3	6.7	15.1	20.1	8.7
		pXRF					Initial	Universal		9.1	5.8	2.4	8.7	2.9	3.5	11.0	18.4	0.7	36.2	3.2	1.4
· ·	MIN	MAX	%RSD	m	b	R^2	n Result	Recalibration		1.3	2.3	2.7	6.3	0.4	0.6	13.9	26.7	2.0			
Nb	22	9968	1.27	0.9648	0 ^a	0.9966	16 5.2	2.8		1.5	2.1	4.6	4.6	1.9	4.2	12.7	147.9	14.0	26.7	16.8	14.9
Та	24	236	12.15	1.0293	36	0.9300	12 645.5	220.1	Mean	4.0	2.7	3.1	6.7	1.5	2.4	14.9	52.3	5.8	26.0	13.4	8.3
Y	12	170	1.72	0.9992	0 ^a	0.9979	16 3.9	3.9	\\/; ala a a da	10 1	C O	A A	11 1	2.2	0.7	24.0	0.4	2.0	1 4 1 2		110.0
La	40	4778	5.37	0.9589	8	0.9923	16 19.4	17.3	wicheeda	10.1 E E	0.8	4.4		2.3	9.7	34.U	9.4 1 E	2.9	141.3 217 E	00.4 110 E	62.2
Ce	76	6927	4.48	0.9030	7	0.9878	16 20.5	20.5		5.5	Z.1 1 1	1.9	7.0	1.0	1.0	20 7	1.5 12.2	1.0	217.5	110.5 6 /	22.5
Nd	92	2248	9.23	1.0049	209	0.8508	16 137.1	135.5		4.0	1.1	1.2	2 2 2	1.3	0.7	30.7	13.5 7 3	0.3	20.0 81.3	24 0	6.8
Pr	62	834	11.33	1.1451	125	0.7509	16 308.0	217.6		4.5 1 9	1.0	0.1	83	1.3	2.5	20.5 40 5	95	1.2	01.5	24.0	0.8
Ва	232	2002	2.88	0.7019	146	0.9862	16 37.6	28.9		4.5	0.6	1.5	6.1	3.2	7 1	42.5	4.5	3.2	58.5	69	184.8
Sr	162	2013	0.62	0.8706	12	0.9999	16 9.5	1.1		п <u>-</u>	2.2	1.0	0.2	1.0	1.0	27.0	7.0	1.0	107.1		70.0
Р	166	7051	11.83	0.7083	-349	0.9960	5 53.5	10.5	Iviean	5.0	2.2	1.0	8.0	1.0	4.0	37.8	7.0	1.6	107.1	44.4	/8.8
U	3	81	13.65	1.3861	0	0.9924	14 59.6	20.8	Alev	3.2	0.4	5.2	11.7	0.3	4.0	76.7	9.0	4.1	37.3	1.8	5.1
Th	5	730	6.42	1.7170	-15	0.9904	16 45.1	18.3	,,	6.0	2.6	2.2	12.1	0.1	1.4	64.7	0.9	3.5	28.5	7.7	6.9
Zr	183	1087	1.86	0.9551	21	0.9996	16 4.9	2.1		2.8	6.5	5.6	12.5	0.1	5.8	57.8	5.6	5.9	24.9	10.5	6.4
Si	29195	337981	1.45	0.8973	5123	0.9931	15 13.1	6.8		7.7	4.3	2.5	12.2	0.2	0.4	80.1	8.5	5.2	43.4	3.0	3.5
Fe	5164	90027	0.79	1.0495	267	0.9977	16 5.5	2.7		7.5	4.1	4.4	11.9	0.6	9.4	69.8	1.0	3.2	44.8	4.2	1.2
Ca	8079	209648	0.59	1.0523	-3531	0.9975	16 7.7	4.4		6.6	3.2	0.2	12.8	1.0	8.5	86.3	13.4	5.6	41.6	1.5	4.8
Ti	922	6626	8.65	0.8535	-40	0.9913	16 16.4	5.9	Mean	5.6	3.5	3.4	12.2	0.4	4.9	72.6	6.4	4.6	36.8	4.8	4.7
^a Cali	bration	line was f	orced th	hrough th	e oriair	າ.															





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[corrected pXRF result] = [initial pXRF result – b]/m Where m is the slope and b is the y-intercept of the calibration line.

Accuracy was determined by: % Difference = [|pXRF value - laboratory value]/laboratory value]x100%

Comparison of accuracy for "Project Specific" and "Universal" recalibrations for Nb, Sr, Th, and U. Both ecalibrations consistently improve the accuracy initial results. In the case of U and Th the Project Specific recalibration is better at reducing bias. The exception is U at Wicheeda, where concentrations border on the limit of detection (Fig. 3). With Sr the best results are achieved with the Universal calibration factors.





Fig. 6. Concentrations of elements expected to coincide with the greatest concentrations of indicator mineral grains for eight size fractions. The three finest fractions contain the highest abundances of pathfinder elements. Based on corroborating data from the Aley and Wicheeda study areas (Mackay and Simandl 2014a; 2014b) the +125µm fraction was chosen for detailed study.

Three samples (LO-13-04, LO-13-23 and LO-13-26) were selected for detailed study to identify grain size fractions that have the best potential to carry carbonatite indicator minerals (Fig. 6). Sample LO-13-04, not sieved through an 8mm screen in the field, consists mainly of grains coarser than +250µm. Sample LO-13-23 displays a positively skewed grain-size distribution. LO-13-26 contains nearly equal mass in the +2mm, +1mm, +500µm, and +250µm size fractions.

Niobium, Y, La, Ce, U, and Th are relatively enriched in the +125µm, +63µm, -63µm size fractions (Fig. 6). Barium, Sr, Pr, Nd, and Ta show less consistent patterns, nevertheless they are always detectable. Phosphorus is consistently detectable only in the +125µm fraction. Based on this information, similar findings from Aley carbonatite and Wicheeda drainages (Mackay and Simandl 2014a; 2014b), and because of other work (McClenaghan, 2011) indicating that the +250 µm, +125µm, +63µm fractions can be effectively used for indicator mineral studies, the +125µm fraction was chosen for systematic study.

The +125µm fraction of each of the seven samples collected in the Lonnie area was analysed for major ar selected trace elements using pXRF. The ranges in abundance for major oxides are: 64.1-69.2 wt% SiO₂, 6.6-7 wt% Al₂O₃, 2.6-5.9 wt% Fe₂O₃, 1.5-2.3 wt% CaO, 0.3-1.1 wt% TiO₂, 0.3-0.5 wt% MgO, and 1.1 to 1.5 wt% $\tilde{K_2O}$.

Sediment size fractions commonly examined and hand picked for indicator minerals include 0.25-0.5mm, 0. 0.5mm, and 0.25-0.86mm (McClenaghan, 2011). The three finest size fractions from this study, +125µm, +63µm and -63µm, have the highest abundances of all potential pathfinder elements (Fig. 6). The +125µm is the only size fraction that consistently returned results above the 90 ppm detection limit for P, a constituent of apatite, monazite, and xenotime, which are indicator minerals in REE exploration. The +125µm size fraction is also the coarses fraction of those enriched in carbonatite pathfinder elements, making it potentially the most versatile from the explorationist's point of view. However, both the +125µm and +63µm size fractions will be the subject of quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN®)-based indicator mineral studies that we are initiating in collaboration with ACME Labs $^{\text{TM}}$.

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References



7. Pathfinder element files of stream sediments from Granite Creek. The solid dotted blue lines follow lected samples from the reek's northwestern and northeastern tributaries (Fig. 2). he samples upstream of the rospect (LO-13-23, LO-13-25 -13-26, LO-13-27; Fig. 6) were taken to establish ackground concentrations of carbonatite pathfinder elements. wo of these (LO-13-23 and LO-3-26) have higher ncentrations of Ta, La, Ce, Pr, Nd, Y, P, U, and Th than sediments sampled downstream onnie (LO-13-01, LO-13-02 O-13-04). Only Ba and Si incentrations are consistently gher downstream of the deposit. Upstream sources of a, La, Ce, Y, P, U, and Th are most likely the Vergil carbonatite I.5 km to the northwest) and/or number of Nb and TREE + Y oil geochemical anomalies (Fig identified by Rara Terra linerals Corp. Irregular sample ribution downstream of the onnie carbonatite prevents us from concluding if the prospect is letectable with bulk stream diment chemistry. The lack of pathfinder element anomaly ownstream of the Lonnie arbonatite may be the result of dilution resulting from the gravity slide observed downstream of LO-13-04 (Fig. 3c).

7. Conclusions

Methodology

- 1) Portable XRF is a rapid and effective tool to determine the most appropriate size fraction for indicator mineral orientation surveys over specialty metal deposits. Data enhancement does not change these findings and is not required where relative values are sufficient.
-) Based on the distribution of pathfinder elements (Fig. 6) as well as similar findings from the Aley and Wicheeda carbonatite drainages (Mackay and Simandl 2014a; 2014b) the +125 µm size fraction is most appropriate for consideration in carbonatite indicator mineral studies.
- 3) Uncorrected pXRF data for Nb and Y have good accuracy relative to laboratory techniques (mean % Difference < 6%; Table 1). Recalibration of these elements is not necessary.
- 4) Further research involving Electron microprobe (EMP) and Quantitative Evaluation of Materials by Scanning electron microscopy (QEMSCAN) should start with the +125 µm size fraction.

Lonnie Carbonatite Study Area

- 5) Irregular sample distribution downstream of the Lonnie carbonatite prevents us from concluding if the prospect is detectable with bulk stream sediment chemistry.
- 6) Higher concentrations of pathfinder elements upstream from the Lonnie carbonatite complex are probably derived from the Vergil carbonatite 4.5km to the Northwest or soil Nb and TREE + Y anomalies detected by Rara Terra Minerals Corp.