Fine-tuning stream sediment chemistry and indicator mineral methodology in exploration for carbonatite-related REE targets, Wicheeda Lake, BC, Canada

Geofile 2014-06

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Suggested Reference:
Mackay, D.A.R., and Simandl, G.J., 2014. Fine-tuning stream sediment chemistry and indicator mineral methodology in exploration for carbonatite-related REE targets, Wicheeda Lake, BC, Canada British Columbia Ministry of Energy and Mines, British Columbia Geological Survey Geofile 2014-06.

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Abstract:

The Wicheeda carbonatite-hosted deposit is one of the most promising rare earth element (REE) prospects in British Columbia. It is one of the three mineralized carbonatites selected for orientation studies. The main objectives of this orientation study are to determine the best size fraction in stream sediments for indicator mineral and exploration programs, and to characterize the geochemical gradients of Nb, Ta, REEs, Ba, Sr, and Th in sediments downstream of the Wicheeda carbonatite complex using Portable x-ray fluorescence (pXRF). This allows for determination of several pathfinder elements (Nb, Ta, REEs, Th, Ba, and Sr) in stream sediment samples collected downstream of this deposit. These samples are expected to contain indicator minerals derived from the carbonatite complex such as monazite, REE-bearing carbonates and fluorocarbonates, pyrochlore, columbite-(Fe), barite-celestine, and apatite. The +250µm, +125µm, and +63µm size fractions contain high concentrations of Nb, La, Ce, and Th relative to other size fractions. The +125µm fraction was chosen for systematic chemical analyses and future pathfinder element studies. There is co-variation of Nb, Ta, La, Ce, Pr, Nd, Y, and Th in the stream sediments. This reflects the presence of multiple mineral phases including pyrochlore, monazite-(Ce), REE-fluorocarbonates, and REE-carbonates. Instead of using traditional processing techniques, followed by hand-picking (as with diamond indicator minerals), we will test an automated approach following gravity ±magnetic separation. Mineralogical studies using optical microscopy, scanning electron microscopy (SEM), electron microprobe (EMP), and Quantitative Evaluation of Materials by Scanning electron microscopy (QEMSCAN) are required to identify and quantify minerals and their distributions downstream of the deposit. These will help assess geochemical and indicator minerals methods for Wicheeda-type carbonatite-hosted REE-deposit exploration.

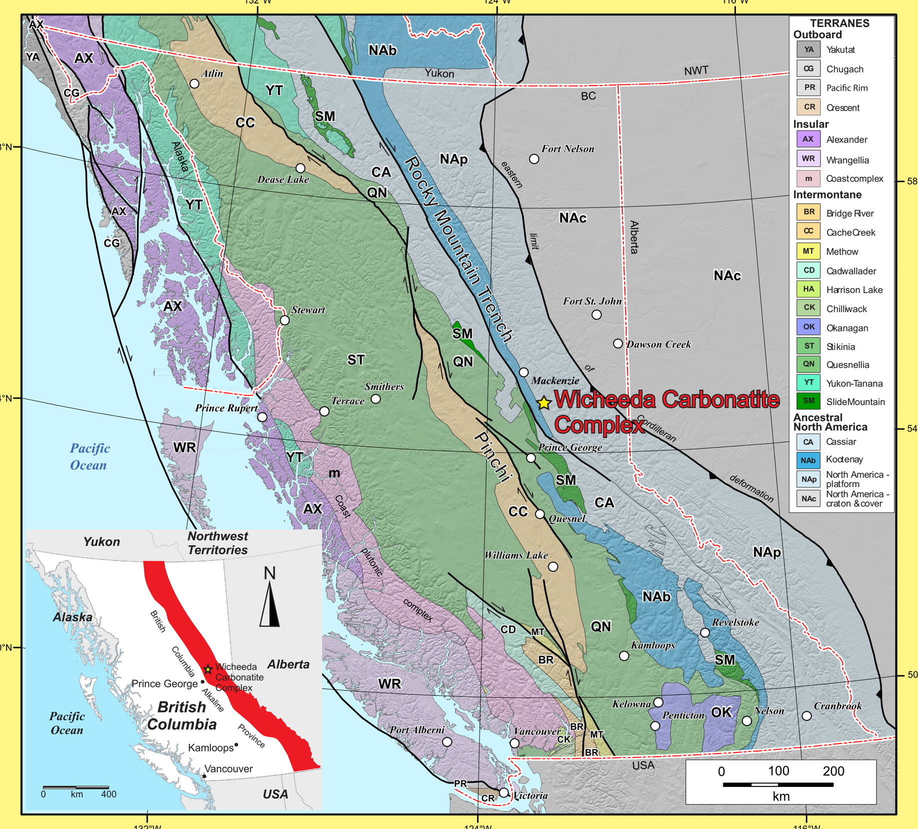

Fig.1. Tectonic setting of the Wicheeda carbonatite complex (yellow star). British Columbia alkaline province shown in red (inset map). Municipalities are denoted by white circles. Modified after Colpron and Nelson (2011). Inset modified after Pell (1994).

Introduction:

Increased use of REE in consumer and green technologies has spurred demand and made these elements a focus of economic and strategic mineral development in the past few years. With 95% of world production of REE in China from deposits such as the carbonatite-related Bayan Obo, and recent export restrictions, western industrialised nations are faced with supply uncertainties. Hence, increased exploration for and development of REE mineral deposits is taking place outside of China.

The Wicheeda carbonatite complex is the most promising REE prospects in British Columbia. It is located 80 km northeast of Prince George, British Columbia (Fig. 1). Between 1979 and 1987 the complex was the subject of 1:5000-scale geological mapping and trenching (Betmanis, 1987), soil sampling and stream silt sampling (Lovang and Meyer, 1987), and geophysical surveying (Bruland, 2011). Chris Graf acquired the claims for the Wicheeda carbonatite complex, incorporated Spectrum Mining Corporation (Spectrum), vended the claims into it, and did prospecting from 2001 to 2006. Spectrum conducted diamond drilling in 2008 and 2009 (Graf et al., 2009; Lane, 2009).

Geologic Setting:

The Wicheeda carbonatite complex is part of a series of carbonatite, syenite, and alkaline rock complexes forming the British Columbia alkaline province, which coincides with the approximate margin of the Laurentian craton (Pell, 1994; Fig. 1). Carbonatites in British Columbia were emplaced during three main periods of extensional tectonics ca. 800-700 Ma, 500 Ma, and 360-340 Ma (Pell, 1994; Millonig et al., 2012). Subsequent phases of deformation and sub-greenschist to amphibolite grade metamorphism between ~155 and 50 Ma overprint the carbonatites along this trend (Pell, 1994; Millonig et al., 2012).

The Wicheeda Lake carbonatite is west of the Rocky Mountain Trench and intrudes Lower to Middle Paleozoic platformal successions deposited on the western margin of Laurentia. These rocks consist of limestone, argillite, and calcareous siltstone of the Kechika Formation (Cambrian to Early Ordovician; Fig. 2; Armstrong et al., 1969). The Kechika Formation is in fault contact with limestone, slate, siltstone, and argillite of the Gog Group (Neoproterozoic) and unassigned Devonian to Permian felsic volcanic rocks to the west, and unassigned Cambrian to Devonian carbonates, slates, and siltstones to the east (Armstrong et al., 1969; Lane, 2009). Lower greenschist grade regional metamorphism overprints the country rocks (Lane, 2009). Faulting in the area follows the major northwest-southeast trend of the Rocky Mountain Trench.

Dalsin (2013) reported a Sm-Nd whole rock isochron age of 316 ± 36 Ma for samples from the carbonatite dikes ~3km southeast of the main Wicheeda carbonatite complex. The carbonatite and syenite dikes and the Wicheeda complex follow the same northwest-southeast structural trend and are assumed to be related.

Geology of the Wicheeda carbonatite complex:

The Wicheeda carbonatite complex is described as sub-circular to ellipsoidal in plan (<500m in diameter), based on previous mapping and a Th radiometric anomaly (Lovang and Meyer, 1988; Mäder and Greenwood, 1988; Lane, 2009; Bruland, 2011). Fieldwork in 2013 suggests that emplacement of this complex was controlled by the intersection of two faults (Fig. 2). Carbonatite dikes have been identified northwest of the main carbonatite complex near Wicheeda Lake; a larger syenite-carbonatite dike complex is ~3km to the southeast (Fig. 2).

The carbonatite complex consists of three units: dolomite carbonatite; calcite carbonatite; and fenitised zones formerly referred to as syenite breccias. The carbonatite consists mainly of dolomite (75-97%) ± ankerite. Calcite, plagioclase, potassium feldspar, biotite/phlogopite, chlorite, and pyrite are minor constituents, and quartz, barite, strontianite, Fe-Ti oxides, molybdenite, galena, fluorite, apatite (Le Couteur, 2008, 2009; Lane, 2009), and possibly powellite are present in trace amounts. The main REE-bearing phases disseminated in dolomite carbonatite are monazite [(Ce, La, Nd, Th) PO_4] and REE-bearing fluorocarbonates [such as bastnasite-(Ce)] and carbonates (Fig. 3). Apatite, columbite, and pyrochlore may also contain REEs. The main Nb-bearing mineral is pyrochlore [$(Na, Ca)_2Nb_2O_6(OH,F)$; Fig. 3b]. Columbite [$(Fe, Mn)Nb_2O_6$] and Nb-rutile [$(Ti, Nb, Fe)O_2$] may also be present (Fig. 3c). Calcite increases in abundance with depth. Le Couteur (2008, 2009) identified zones of predominantly calcite (85%), which contains biotite, strontianite, and magnetite. The carbonatite is overlain by a brick-red soil or regolith horizon, 5cm to 50cm thick.

Grey potassic fenite envelopes and forms xenoliths in the carbonatite. The fenitised zones (altered wall rock) contain abundant feldspar-rich (90%) xenoliths cemented by a dolomite matrix (Fig. 3c). Blue-green, Na-amphibole (±pyroxene)-bearing fenite is observed in contact with dolomite carbonatite. Sodic fenitization (Fig. 3d) surrounds the potassic fenite zone (Trofanenko et al. 2014).

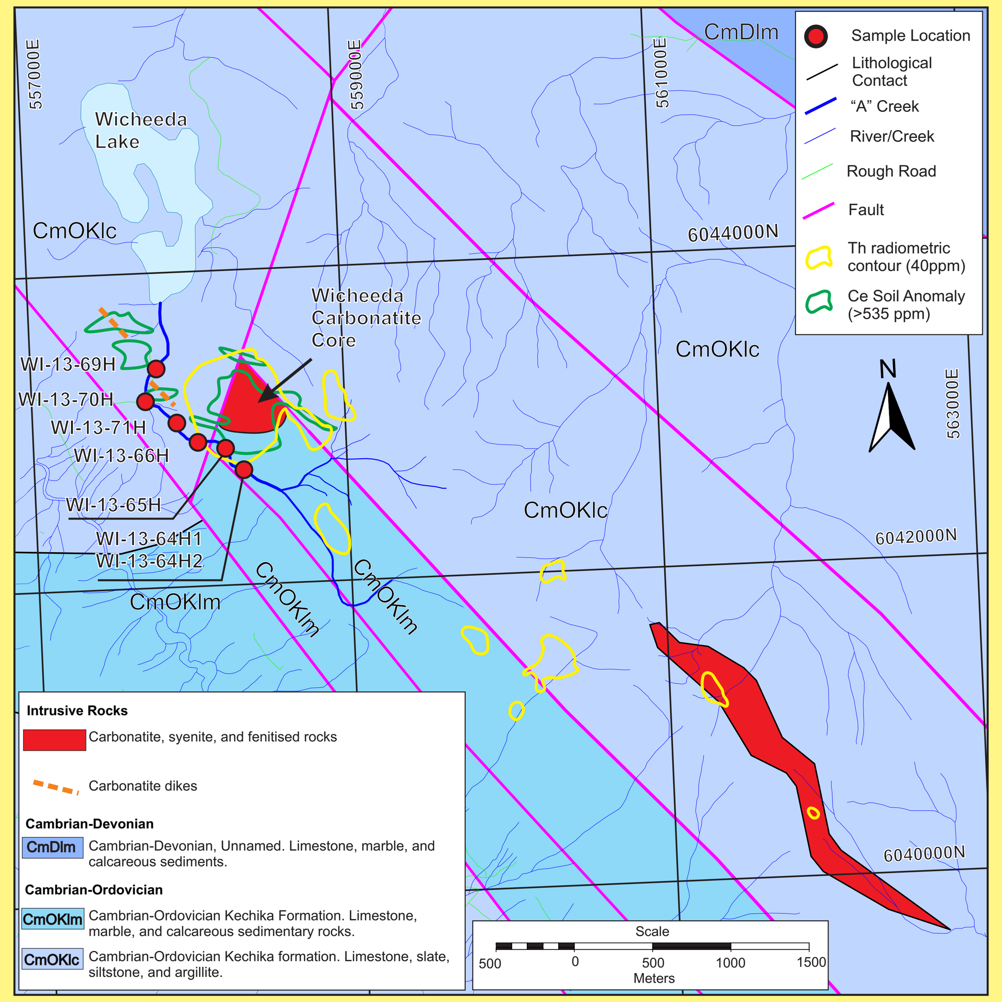

Fig. 2. Geological setting of the Wicheeda carbonatite complex, associated dykes, and locations of stream sediment samples. Base map modified after Massey et al. (2005). Thorium radiometric anomalies from Bruland (2011) shown by yellow traces. Cerium soil anomaly from Lane (2009) shown by green traces.

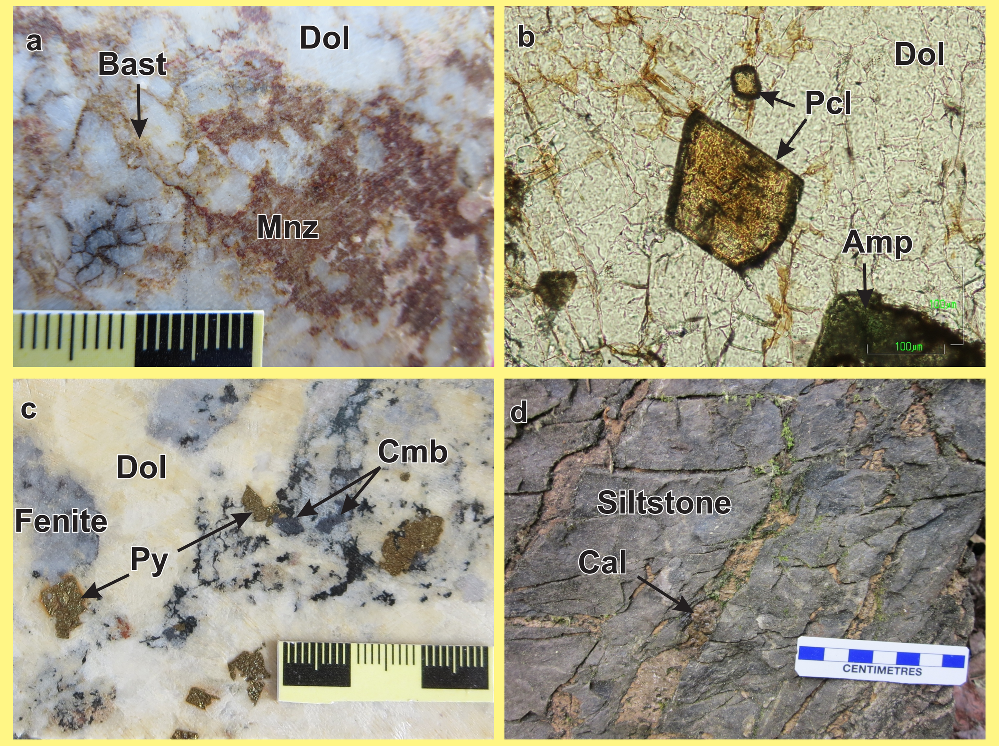

Fig. 3. Core photos from the Wicheeda carbonatite complex. a) Monazite (Mnz) with REE-fluorocarbonates (bastnasite; Bast) in dolomite (Dol) carbonatite (smallest unit = 1mm). b) Pyrochlore (Pcl) with Na-amphibole (Amp) in dolomite carbonatite. Plane polarized light image. c) Pale grey feldspathic (K-spar) fenite xenoliths are surrounded by dolomite carbonatite. Grey Nb-rich minerals (predominantly columbite; Cmb) with pyrite (Py) are found in the fenite. d) Grey sodic altered (fenitized) siltstone with calcite (Cal) veins at oblique angle to bedding.

Stream Sediment Orientation Survey

Sample Collection:

Seven stream sediment samples along "A" creek adjacent to the Wicheeda carbonatite complex were collected during the 2013 field season (Figs. 2, 4, Table 1). Sample sites are spaced 200-300 metres apart. There is more than 160m elevation difference between sample WI-13-64H1 and WI-13-69H (Table 1). The streambed consists mainly of boulders, cobbles, and pebbles. Samples were collected in the lee of boulders and logs, and from inside stream bends, typically over areas < $1 m^2$.

	Location		Elevation	Channel Characteristics			Clast Size (cm)		Dry wt. (<8 mm diameter)	Sample Site Characteristics
Sample ID	Northing	Easting	(m)	Width (m)	Depth (m)	Flow	Average	Max	(kg)	
WI-13-64H1	6042772	558279	1077	1.5	0.10	rapid	0.5-1.5	5-7	1.7	Lee of fallen trees; steep-sided gully, upstream of trail; predominantly shale, siltstone, and carbonate clasts.
WI-13-64H2	6042772	558279	1077	1.5	0.10	rapid	0.5-1.5	5-7	1.1	2-3 m upstream of WI-13-64H1.
WI-13-65H	6042901	558198	1015	2.0	0.20	rapid	0.5-1.5	5-10	2.6	Inside of stream bend; steep-sided gully; grey slate clasts predominant.
WI-13-66H	6042929	558020	973	2.0	0.30	rapid	0.5-1.5	5-7	1.5	Pools below rapids (protected by fallen tree); steep sided gully; grey slate clasts predominant.
WI-13-71H	6043031	557916	935	1.5	0.15	slow	2-5	35	5.4	Lee of fallen tree; low relief topography; grey slate and limestone predominant.
WI-13-70H	6043178	557731	920	1.5	0.10	slow	1-2	10	2.6	Sample from matrix between cobbles; low relief topography; grey slate and limestone predominant; upstream of trail.
WI-13-69H	6043384	557792	911	1.0	0.15	moderate	0.2-0.5	5-7	2.8	Sample from matrix between cobbles; low relief topography; grey slate and limestone predominant; upstream of trail.

Table 1. Characteristics of stream channel and sample sites. Samples are in order of increasing distance downstream of the Wicheeda carbonatite complex. UTM zone 10, NAD 83.

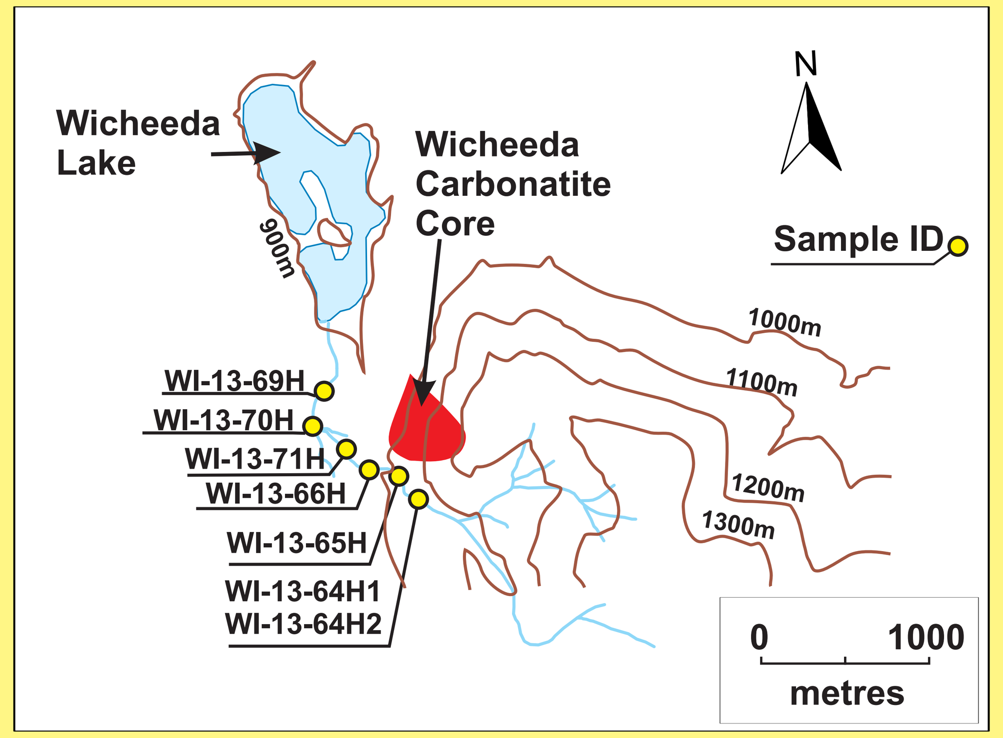

Fig 4. Location of stream sediment samples. Samples are downhill of the Wicheeda carbonatite complex (100m contour interval). Modified after Massey et al. (2005).

Portable X-ray fluorescence results:

Two samples (WI-13-66H and WI-13-71H) were chosen for detailed study. Sample WI-13-66H was collected ~175 metres down slope from the deposit (Fig. 4); WI-13-71H was collected 220 metres downstream of sample WI-13-66H. In both samples, the +125µm size fraction contains higher concentrations of pathfinder elements relative to other size fractions (Fig. 5). Based on these characteristics, the +125µm fractions of the remaining samples were analysed. Samples WI-13-66H and WI-13-71H show a grain-size distribution that is skewed toward coarse-grained material (Fig. 5). Concentrations of major oxides and trace elements (Table 2) obtained by pXRF analyses using a Thermo Fisher Scientific Niton FXL-950 instrument, as described by Luck and Simandl (2014). This pXRF data has acceptable precision; however, it has not been recalibrated using results of standard laboratory analyses (as described in Simandl et al., 2013) to correct for matrix effects and analytical biases to improve accuracy. Portable XRF is not a substitute for conventional laboratory analyses.

Sample	Size Fraction (mm)	Nb	Ta	Y	La	Ce	Nd	Pr	Ba	Sr	P	U	Th	% SiO_2	% CaO
WI-13-64H1	+0.125	144	<22	46	455	761	319	172	1707	305	<90	<5	100	47.68	6.27
WI-13-64H2	+0.125	140	<22	41	467	771	344	148	1805	328	<90	5	101	49.42	4.80
WI-13-65H	+0.125	253	<22	45	733	1176	442	192	1802	311	<90	<5	141	52.15	4.70
WI-13-66H	+2.00	87	<22	25	171	310	196	97	1363	243	<90	7	46	50.10	4.87
WI-13-66H	+1.00	85	24	27	151	315	216	119	1379	214	<90	<5	48	50.24	3.95
WI-13-66H	+0.500	85	<22	31	239	455	305	142	1501	216	<90	7	80	52.70	3.06
WI-13-66H	+0.250	119	<22	36	358	671	294	154	1690	253	<90	<5	86	52.60	3.41
WI-13-66H	+0.125	163	<22	40	482	819	361	172	1698	298	<90	<5	107	53.69	4.77
WI-13-66H	+0.063	119	<22	38	396	655	269	139	1463	277	<90	5	82	50.09	5.01
WI-13-71H	+4.00	62	23	19	135	244	300	178	806	257	<90	<5	24	47.78	8.20
WI-13-71H	+2.00	64	22	23	117	215	234	144	1216	190	<90	<5	30	51.49	4.10
WI-13-71H	+1.00	73	25	26	164	305	268	140	1291	192	<90	<5	42	51.88	3.74
WI-13-71H	+0.500	83	<22	30	214	444	282	160	1506	203	<90	<5	55	52.20	3.32
WI-13-71H	+0.250	108	<22	34	344	648	348	194	1661	244	<90	<5	80	52.87	3.66
WI-13-71H	+0.125	159	<22	40	480	806	378	184	1644	284	<90	<5	101	53.13	4.69
WI-13-71H	+0.063	100	<22	37	358	581	286	146	1391	255	<90	<5	69	51.56	4.65
WI-13-71H	-0.063	57	<22	38	193	341	167	97	1250	233	<90	<5	51	42.76	5.09
WI-13-70H	+0.125	251	26	46	886	1301	482	225	1329	231	<90	<5	129	55.86	3.06
WI-13-69H	+0.125	283	35	43	725	1119	424	191	1295	230	<90	<5	130	57.92	2.07

Table 2. Relative major oxide and trace element concentrations. Samples are in order of increasing distance downstream of the Wicheeda carbonatite complex.

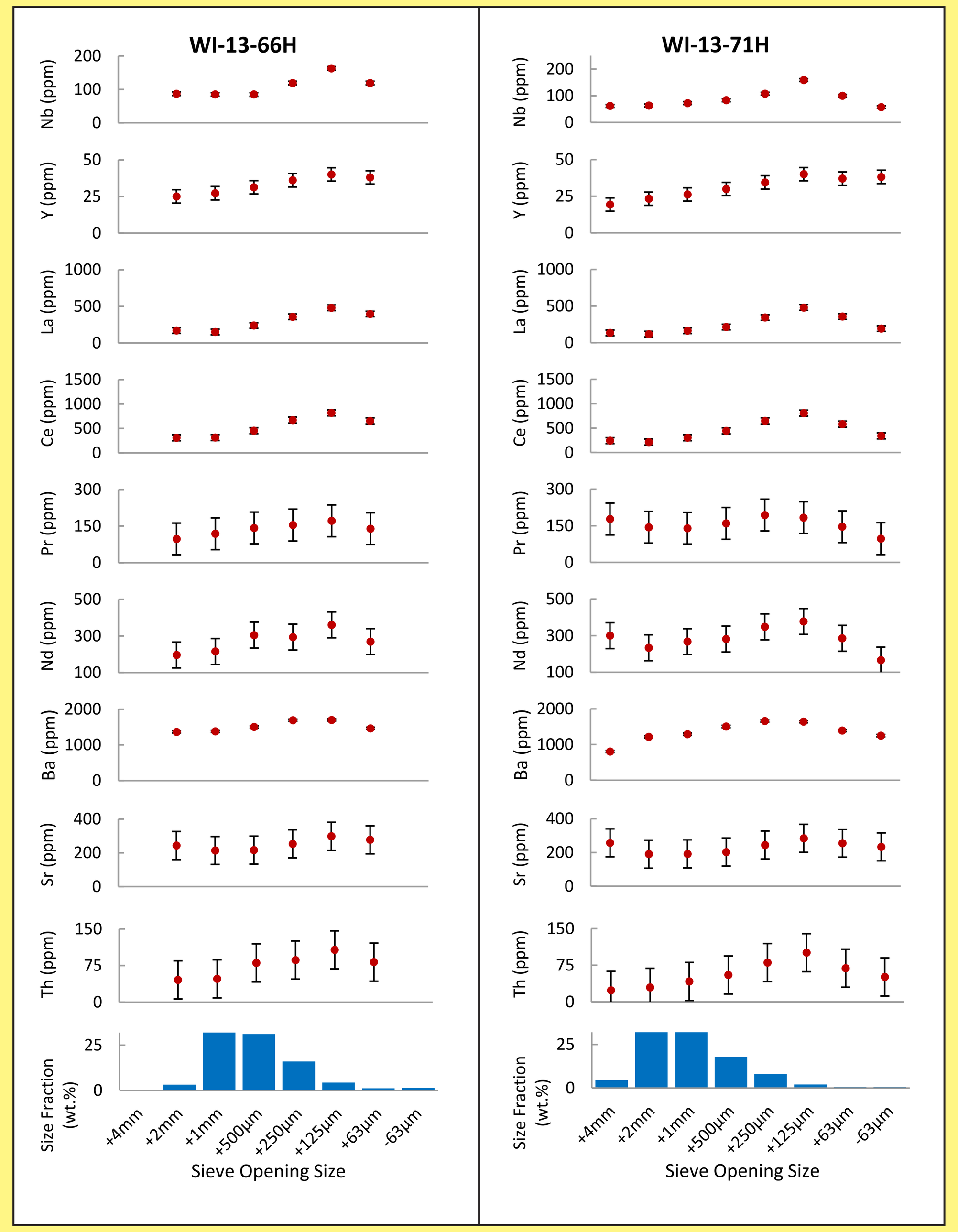

Fig. 5. Relative concentrations of pathfinder elements determined by pXRF (Niton FXL-950 instrument) and grain size fraction distributions of samples WI-13-66H and WI-13-71H. The +250µm, +125µm, and +63µm size fractions are enriched in Nb, La, Ce, and Th relative to other size fractions.

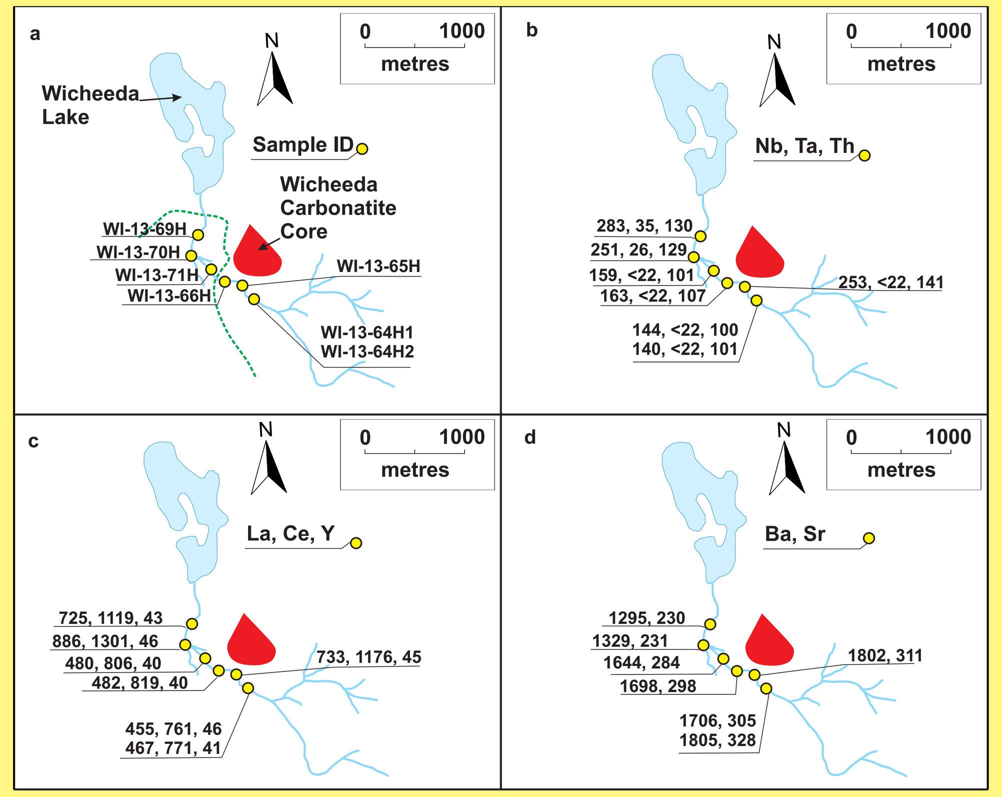

Fig. 6. Relative trace element concentrations in stream sediment samples. a) Sample numbers. b) Nb, Ta, and Th. c) La, Ce, and Y. d) Ba and Sr. Concentrations in ppm. The edge of the cut block and the area of low topographic relief are denoted by the green dotted line.

Discussion:

High concentrations of Nb, Ta, REEs, Th, Ba, and Sr suggest the detectable presence of prospective indicator minerals in the +125µm size fraction. Barium and Sr show a noticeable decrease in concentrations from southeast to northwest (Figs. 6, 7). This may reflect input of material from other carbonatite-related showings in the area, or be related to sediment influx from limestones and marbles of the Kechika Formation. A slight decreasing trend is observed in CaO with increasing distance downstream. The opposite trend for SiO_2 may reflect a change in lithology across a fault from predominantly limestone and marble on the southeast to a predominantly pelitic assemblage on the northwest (Fig. 7).

Samples WI-13-71H and WI-13-66H have consistently lower concentrations of pathfinder elements than the samples immediately upstream and downstream (WI-13-65H and WI-13-70H; Fig. 7). Calcite carbonatite dikes are reported by Lane (2009) northeast of the main carbonatite complex. One of the dikes was observed near sample WI-13-70H (Fig. 2, 7). These dikes coincide with Ce soil and Th radiometric anomalies in the area (Fig. 2). Input of material from these dikes probably contributes to increased pathfinder element concentrations in samples WI-13-69H and WI-13-70H (Fig. 7).

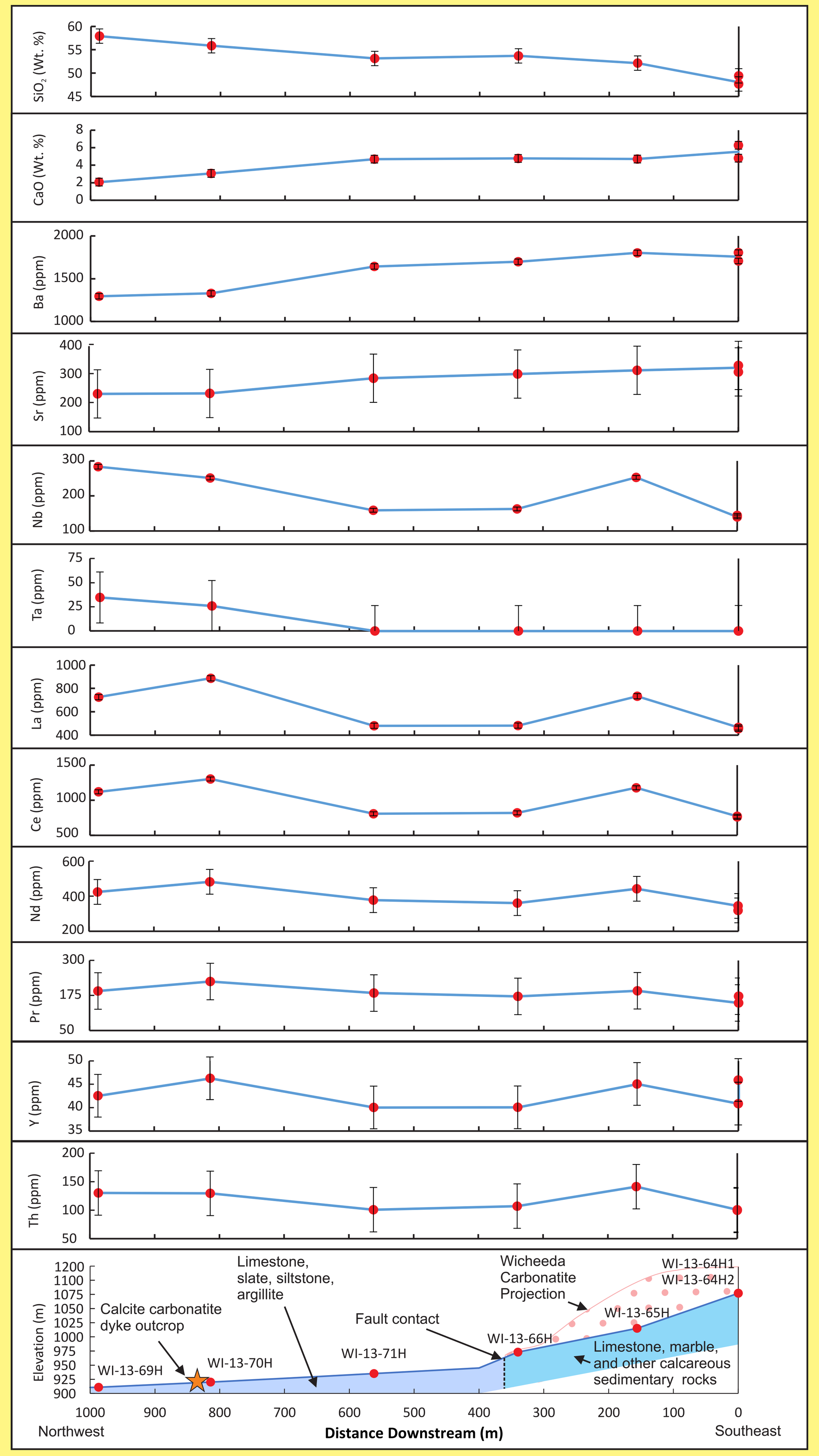

Fig. 7. Relative concentrations of key pathfinder elements in the +125µm size fractions of stream sediments and corresponding geological section.

Correlations of pathfinder elements observed in the +125 µm size fraction (Fig. 8) can be used to predict indicator minerals found in stream sediments. Strong correlations between Ce and La (R^2 =0.99), Nd (R^2 = 0.94), and Pr (R^2 =0.74) is expected due to ready substitution of these elements in the same minerals. Cerium-Th (R^2=0.87; Fig. 8a) linear dependency suggests the presence of monazite-(Ce), which is consistent with observed REE-mineralogy for the Wicheeda carbonatite complex where monazite-(Ce) and REE-fluorocarbonates and carbonates predominate.

Strong dependence between Nb-Ce (R^2= 0.85; Fig. 8b) and Nb-La (R^2 = 0.82) probably indicates co-occurrence of Nb- and REE-bearing minerals. This is expected as REE-fluorocarbonates [such as bastnasite-(Ce), parisite-(Ce), or synchysite-(Ce)], monazite-(Ce), and pyrochlore have similar densities (4.0-5.0 g/cm^3, 4.5-5.5 g/cm^3, and 4.2-6.4 g/cm^3 respectively) and probably, settling velocities.

There is an excellent linear dependence between Nb and TiO_2 (R^2 = 0.98; Fig. 8c). This relationship may indicate that pyrochlore contains significant amounts of Ti, or the presence of Nb-rutile within stream sediments. The moderate correlation between Nb and Fe_2O_3 (R^2 = 0.73; Fig. 8d) may reflect co-existence of Nb-bearing minerals (pyrochlore, columbite, and Nb-rutile) with pyrite or magnetite. Correlation between Nb and Ta is poor (R^2=0.61; including below detection limit data).

Linear dependence between Ba and Sr (R^2 = 0.98) may reflect the presence of both elements in a common mineral phase such as REE-bearing fluorocarbonates and/or a consistent composition for barite-celestine solid solution minerals in the area. Input of Sr-Ba sulphates from limestones and marbles of the Kechika Formation cannot be ruled out as a possible source of Ba and Sr. Co-variation in pathfinder element concentrations between Nb, La, Ce, Nd, and Th (Fig. 7) is probably related to the presence of multiple indicator minerals in stream sediments. Further optical microscope, EMP, and SEM analyses, in combination with QEMSCAN, will provide quantitative information on indicator minerals. Sampling of stream sediments downstream of other mineralization in the area and outside the influence of the Wicheeda carbonatite complex could strengthen the findings in this study.

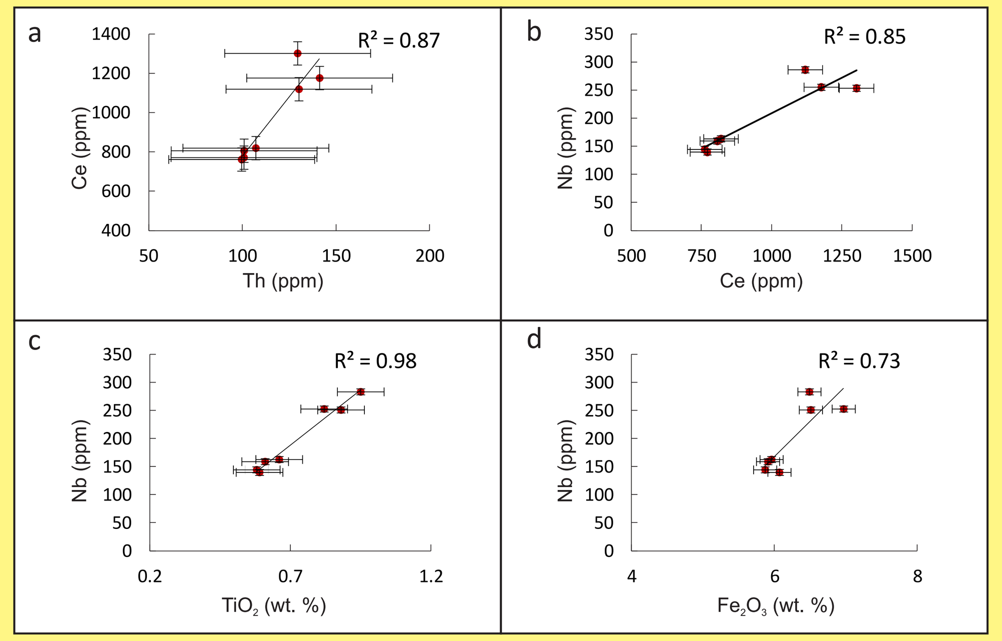

Fig. 8. Correlations between the concentrations of selected elements in the +125 µm size fraction of samples. a) Ce and Th. b) Nb and Ce. c) Nb and TiO_2. d) Nb and Fe_2O_3.

Conclusion:

1. Portable XRF (Niton FXL-950) is an effective tool to measure relative concentrations of pathfinder elements (Nb, Ta, La, Ce, Pr, Nd, Y, and Th) in stream sediments collected near the Wicheeda carbonatite complex.

2. The 125 to 250µm size fraction has the highest concentrations of pathfinder elements and, by extrapolation, indicator minerals.

3. The mineralogy of the Wicheeda carbonatite complex and detectable concentrations of Nb, Ta, La, Ce, Pr, Nd, and Y suggest that monazite, REE-fluorocarbonates and carbonates, and pyrochlore (± columbite) are expected indicator minerals for Wicheeda carbonatite-type REE deposits.

4. Elevated concentrations of pathfinder elements are found in samples where, based on topography, the greatest influence from the Wicheeda carbonatite is expected. A second spike in pathfinder element concentrations is associated with calcite carbonatite dykes located downstream of the main deposit.

5. Further mineralogical analyses using QEMSCAN and electron microprobe are in progress. Development of methodology to process and analyse indicator minerals for REE-bearing carbonatites is in progress.

Acknowledgements:

This project received funding and support from Targeted Geoscience Initiative 4 (2010-2015), a Natural Resources Canada program carried out under the auspices of the Geological Survey of Canada. Discussion with Chris Graf regarding previously identified soil and radiometric anomalies helped focus the perspective of this study. Mr. Graf also permitted us to talk to Bob Lane about Spectrum Mining Corporation's confidential drill results and made it possible to examine the drill core at Falcon Drilling's facilities in Prince George. Critical review by Pearce Luck (British Columbia Ministry of Energy and Mines) and Bob Lane (Plateau Minerals Corp.) greatly improved earlier versions of this manuscript. The authors would also like to thank Pearce Luck for his assistance with sample preparation and analyses and Joel Trofanenko for his assistance in the field.

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For a complete list of references, see: Mackay, D.A.R., and Simandl, G.J., 2014. Portable x-ray fluorescence to optimize stream sediment chemistry and indicator mineral surveys, case 2: Carbonatite-hosted REE deposits, Wicheeda Lake, British Columbia, Canada. In: Geological Fieldwork 2013, British Columbia Ministry of Energy and Mines, British Columbia Geological Survey Paper 2014-1, pp. 195-206.