Exploration geochemistry: Principles and practices for the strategic commodities Nb, Ta, Zr, and rare earth elements

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1. Introduction: Challenges and opportunities

Geochemical exploration for Nb, Ta, Zr and rare earth element (REE) mineralization associated with carbonatite, pegmatite, and peralkaline intrusions presents unique challenges and opportunities. The challenges are mainly due to the tendency of these elements, as High Field Strength Elements (HFSE), to be relatively immobile in surface environments in addition to commonly forming minerals that are resistant to weathering. In addition, many of the host minerals are resistant to routine exploration geochemistry digestions, which are typically aimed at dissolving soluble oxides or extracting more labile ionic forms (Reimann et al., 2014).

Opportunities arise because host rocks typically represent relatively rare end products of the magmatic processes that generate peralkaline magmas including, at the far end of the spectrum, carbonatites. Hence host rocks are relatively easy to identify geochemically and commonly define classic lithological zoning (e.g., Modreski et al., 1995). In addition, many of the minerals that contain these elements are resistant to weathering, mechanically durable, have relatively high densities, and have the have the potential to form heavy mineral concentrates when released by weathering. This is particularly so for Zr, Nb, and Ta, which form primary minerals such as tantalite (Ta Nb), pyrochlore (Nb), coltan (Ta Nb), columbianite (Ta Nb), dysanalite-perovskite (Nb) and zircon (Zr). In contrast, the REE are mobile in the weathering environment and commonly re-locate from primary carbonate and phosphate minerals (e.g., synchysite, monazite, xenotime, bastnäsite, allanite) to secondary phosphate minerals such as churchite (Lottermoser, 1990) and gorceixite (Mariano, 1989).

2. Sample media

Depending on the phase and scale of exploration, diverse materials can be sampled to search for Ta, Nb, Zr, and REE. These include soils, tills, stream sediments, lake sediments, vegetation, and rock samples (Ryghaug, 1983; McConnell and Batterson, 1987; Moller et al., 1989; Galeschuk and Vanstone, 2007). Indirect detection of potential host rocks for further evaluation using host rock rather than mineralization chemistry (for example P, Ba, Zn, Be, U) should always be considered as an exploration tool, such as at Allan Lake (Ford et al., 1988).

Soils concentrate elements in amounts reflecting the resistance to weathering of individual minerals. Unless soil materials get transported physically or chemically, these elements will concentrate directly above a mineral deposit, and a broad halo is unlikely. Hence sampling design needs to consider the likely size of a target and recognize that regional-scale soil sampling densities may not directly locate mineralization.

In glaciated terrains, deposits may be buried by till. Nonetheless, evidence of mineralization may be preserved for many kilometres down the former ice-flow direction as dispersal trains comprising sediments eroded from a deposit. Geochemical sampling of soil, till, and till-derived lake and stream sediments may identify the transport paths of the commodities of interest and of ancillary pathfinder elements. Such responses have been documented at the Strange Lake deposit, Labrador (McConnell and Batterson, 1987; Batterson, 1989, McClenaghan et al., 2007), where a dispersal train in a variety of media exceeds 40 km as a narrow 4-5 km wide ribbon, and at the Allan Lake carbonatite, Ontario (Ford et al 1988)

Because of the low mobility of Ta, Nb, Zr, ions in the surface environment, dispersion of ions from a deposit buried by till via mechanisms such as proposed by Hamilton (2000) is unlikely, and partial leach techniques are unlikely to respond well.

In stream sediments, minerals with Nb, Ta, Zr and REE tend to concentrate at heavy mineral trap sites where flow deceleration causes sedimentation (e.g., sand bars; in the lee of obstacles such as logs) that can be preferentially sampled (Stendal and Theobald, 1994). In glaciated terrains, stream sediments may be sampling the till dispersal train from a deposit rather than the deposit itself (e.g., McConnell and Batterson, 1987).

Because the HFSE are generally considered insoluble in aqueous solutions, hydrogeochemistry is unlikely to generate a significant response, and concentrations are typically in the sub-ppb to sub-ppt range (Protano and Riccobono, 2002; Gassama et al., 2012; Mason, 2013; Tepe and Bau, 2013), effectively at the detection limit of typical commercial hydrogeochemical methods. However, Y in ground water was indicated as a potential element of interest to target REE mineralization at the Strange Lake deposit, Labrador (McConnell and Batterson, 1987).

Certain plants can accumulate some of these elements as essential trace elements (Kovalevsky, 1987, Dunn, 2007; Miao et al., 2008), but owing to low element mobility, concentrations are generally low and responses subtle (Dunn, 2007). Bluemel et al., (2013) demonstrated the potential to use primitive ferns (Dryopteris Filix-mas) as a biogeochemical indicator for REE deposits, with this particular species showing LREE enrichment above mineralization.

3. Sample preparation

With the exception of preparing heavy mineral concentrates, no special treatment is required for conventional soil and stream-sediment samples beyond sieving using a mesh that ensures the minerals of interest pass through the sieve. As noted above, many elements may still reside in primary magmatic minerals that have undergone minimal grain-size reduction during weathering and transport. This physical partitioning contrasts greatly with the behaviour of more labile elements such as Cu and Zn, that are commonly bound to clays or Fe-Mn oxide particles during dispersion.

In a lithogeochemical survey, consideration must be made to the expected concentration of the elements of interest and the coarseness of the mineral grains such that a large enough sample is collected to represent the source rock. Mineral grains, particularly in pegmatite and carbonatite intrusions can achieve sizes of several centimetres, hence collecting a representative sample can be difficult. Following collection, rock samples require crushing and grinding before digestion and analysis.

4. Sample digestion and analysis

For Nb, Ta, REE and Zr, a strong multi-acid (four acid) digestion (e.g., HF, $HClO_4$, HCl and HNO_3) is required to ensure an effective dissolution of the refractory minerals and retention of elements from the mineral phase in the solution (Reimann et al., 2014). Weaker digests such as aqua-regia, although still likely to release metal into solution, are likely to produce both poor geochemical responses and contrasts. Even a four-acid digest will produce poor responses for minerals such as zircon, which is particularly resistant to HF attack (Lett and Patterson, 2011). A superior option would be to use a fusion digest with a flux such as sodium or lithium tetra/metaborate, which will effectively liberate the elements of interest. Inductively coupled plasma mass spectrometry (ICP-MS) is commonly used by commercial laboratories to measure Nb, Ta, REE, Zr, concentrations in solution following multi-acid digestion or a lithium borate fusion. The major oxide content of lithium borate fusion solutions are determined with inductively coupled plasma emission spectroscopy (ICP-OES). Total concentration of some of the elements (e.g., REE, Ta) can be accurately determined by non-destructive, instrumental neutron activation (INAA).

All of these elements, can be analyzed by X-ray fluorescence (XRF), using either a field portable (Luck and Simandl, 2014) or desk-top field or laboratory based instrument. For the latter, either a press powder or fusion disk may be appropriate. Consultation with the laboratory would be appropriate, particularly if high element concentrations outside of the calibration and dynamic range of the analytical equipment are expected.

5. Quality assurance and quality control

An established laboratory quality control scheme is an industry standard requirement. Randomly imbedding field duplicates, preparation blanks, and certified reference materials with samples for analysis, in addition to ensuring that the laboratory also has appropriate control materials to routinely monitor quality control, is key to maintaining acceptable and consistent accuracy and precision. Certified reference materials with elevated concentrations of some of these elements are available, particularly for the REE, however matrix matching the reference with that of the project samples could prove problematic. For example, at an advanced level of exploration (e.g., detailed drilling resource estimation), it may be prudent to generate project-specific certified reference materials through a commercial supplier.

6. Exploration geochemistry

Although the commodity being sought will likely be key to driving or directing the exploration program, the extreme end-member composition of many of the rock types hosting Nb, Ta, REE and Zr mineralization provides a unique suite of lithological pathfinder elements for delineating exploration targets.

In a typical soil geochemical survey, carbonatites can be clearly identified by negative Si, K, Na, and Al anomalies relative to surrounding lithologies. In particular, the Si contents over a carbonatite core can be well below 30%. Conversely, Ca, REE, Th, U, P, Cl, and F +/-Nb tend to be elevated, with distinct high La/Yb ratios, reflecting light-REE enrichment. There are also low K/Th ratios, which reflect Th enrichment and depletion in K relative to surrounding lithologies, a pattern reflected by radiometric imaging. Particular relationships such as a Ca-P-Cl association will clearly indicate the presence of Ca-phosphates (e.g., apatite), which may correlate well with REE-indicating mineral phases associated with the elements of interest, particularly in the secondary environment.

Other lithological phases in an alkaline complex, ranging from K to Na-K dominated units through to mafic units, can likewise be identified by careful major and trace element selection (Fig. 1) and simple ratios specifically selected to contrast adjacent rock types.

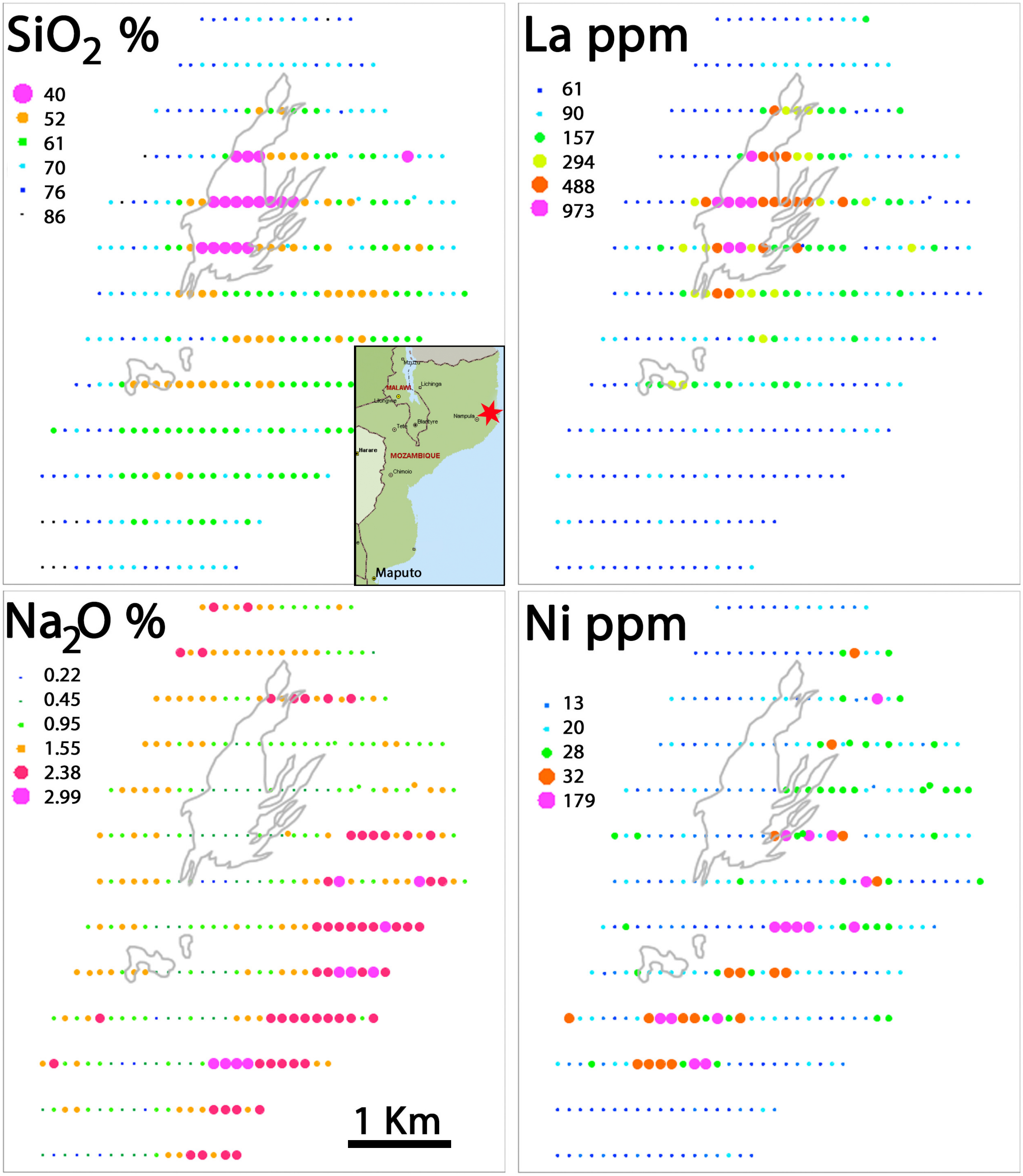

Fig. 1. La, SiO_2, Ni and Na_2O distribution in <180micron B-horizon, residual surface soils around the Evate carbonatite, Monapo complex, Mozambique. Samples analyzed by Li-Metaborate fusion ICPOES/MS. Sampling is on a 400 m by 100 m grid centred on the carbonatite phase (outlined in grey), which formed the exploration target. High La and low SiO_2 highlight the carbonatite phase. Ni highlights mafic units in the complex with Na_2O highlighting an alkali rich unit to the southeast. Inset map shows the location of the Evate carbonatite. The carbonatite itself is hosted in undifferentiated granite gneisses (Macy et al., 2013). Geochemical data published with kind permission from Vale Exploration.

7. Conclusions

Geochemical exploration for Nb, Ta, REE, and Zr mineralization in peralkaline-carbonatite and pegmatites is aided by the extreme end-member composition of the host rocks, which potentially provide a range of elements for lithological discrimination as well as resource identification. However, the resistant nature of many of the minerals that contain these elements can result in poor dispersion of the commodity signal. Because target sizes are likely to be small, relatively tight sample spacing is required for soil surveys. Heavy mineral sampling techniques are suitable for stream-sediment and till geochemical surveys because many minerals bearing Nb, Ta, REE, and Zr have high densities and are chemically stable and mechanically durable. Extensive dispersal trains can form in glaciated terrains, and tills may feed anomalous material into stream sediments and lakes. Unfortunately, due to the resistive nature of some of the minerals and low mobility of the elements of interest, partial extraction techniques are ineffective for discovering mineralization concealed beneath till or other post-mineralization units.

Geochemical analytical methods for Nb, Ta, REE, and Zr must recognize the resistant nature of the host minerals, and hence require HF, $HClO_4$, HCl and HNO_3 digestion or, preferably, lithium borate fusions followed by ICP-MS analysis or, alternatively, XRF and INAA analysis. However careful quality control is required to ensure that the required and acceptable accuracy and precision of the analyses is maintained, given the extremes of chemical composition encountered during typical geochemical surveys.

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