

Secondary geochemical signatures in glaciated terrain

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The geochemistry of soils is a widely used tool in mineral exploration but it is the geochemical signature obtained by partial or selective leaches which is of particular advantage in exploration for deeply buried deposits (e.g. 20-200 m), often under exotic cover. The objective of a partial extraction is to target, by designing the appropriate chemistry of the leach solution, only that portion of the element that can be considered 'labile' or previously mobile, perhaps migrating from mineralisation below; the more crystalline structures (e.g. silicates, oxides) and organic matter, reflecting natural soil genesis, ideally remain undissolved. Some commercial leaches are proprietary or patented, such as the series of Mobile Metal Ion ('MMI') extractions or variations on the Enzymeh leach. Others include weak digestions such as ammonium acetate at pH 5 or 7 ('AA5', targeting carbonates and weakly held; 'AA7' for exchangeable), hydroxylamine hydrochloride in HNO₃ (targeting Mn oxides) or HCl (amorphous Fe and Al oxides), and even water to dissolve the 'soluble' component of a soil. While there have certainly been successes in applying this approach over the past decade, there have also been 'false' anomalies produced by other sources of elements (e.g. hydromorphic dispersion), inappropriate sampling strategies, changes in the nature of the overburden and incorrect leach procedures. Clearly, understanding the processes involved in element migration and fixation would enable the development of effective exploration methodologies. Such was the major objective of a multi-partnered project at the Cross Lake VMS deposit, located in the Abitibi Greenstone Belt (AGB) 50 km SE of Timmins, Ontario, Canada and covered by glacial sediments *ca.* 8000 years ago. This paper describes the surficial geochemical signatures identified at Cross Lake, assumed to be representative of other mineral deposits in the AGB and elsewhere, provides recommendations on sampling and analytical strategies, and suggests mechanisms of element migration.

Site Description

A full description of the Cross Lake deposit and the two survey lines, '6' and '40' studied in detail, can be found in Cameron *et al.* (2004) and Hamilton *et al.* (2004). Briefly, the VMS mineralisation is similar in composition and age (Archean) to the well-known Kidd Creek Zn-Cu-Ag deposit and is hosted in felsic pyroclastic rocks, intruded by feldspar porphyry and diabase dykes. The mineralisation-hosting sericite-altered tuff and silica exhalite has been fractured and the interstitial pore space filled with sulphides, in decreasing abundance of pyrite, Fe-deficient sphalerite, chalcopyrite and galena. Assays indicate that Zn can reach 26 % whereas Cu is much lower, with a maximum of only 1.3%.

Lines 6 and 40 provide the different surficial terrains typical of the region: clay, sand and peat (Figure 1). On Line 6, gleysolic soils formed on silty-clayey glaciolacustrine sediments, whereas on Line 40, podzolic soils formed on sandy glaciofluvial sediments. The width of the VMS subcrop underlying Line 6, centred at 200S, is ~25 m and is covered by 30 m of varved clay with silty laminae. Samples from a borehole at 200S contain up to 1% ZnS and over 10% total sulphides but no visible CuFeS₂. Groundwater on Line 6 is within a few meters of the surface and depressions are saturated. Line 40 is sandy along most of its surface but this changes to sand mixed with clay along its northern lower-lying extension which can be seasonally wet and peaty. The projected subcrop of mineralisation on Line 40 is between 1400 and 1420S; diamond drill-hole results show that the deeper mineralisation (up to ~150 m) is of higher grade.

Geochemical Anomalies In The Soil

Sampling was carried out from 1999 to 2003, under CAMIRO- (Canadian Association of Mining Research Organisation) and OMET (Ontario Mineral Exploration Technology)-funded projects. Initial sampling at 25-m intervals of humus and B-horizon soil (a 20-cm interval well separated from the Ah or Ae horizons) failed to provide any significant base metal anomalies, using sodium pyrophosphate and aqua regia digestions on the organic material (humus, peat) or Enzymeh, hydroxylamine hydrochloride, and ammonium acetate leaches on the inorganic sample. However, MMI extraction did result in a multi-

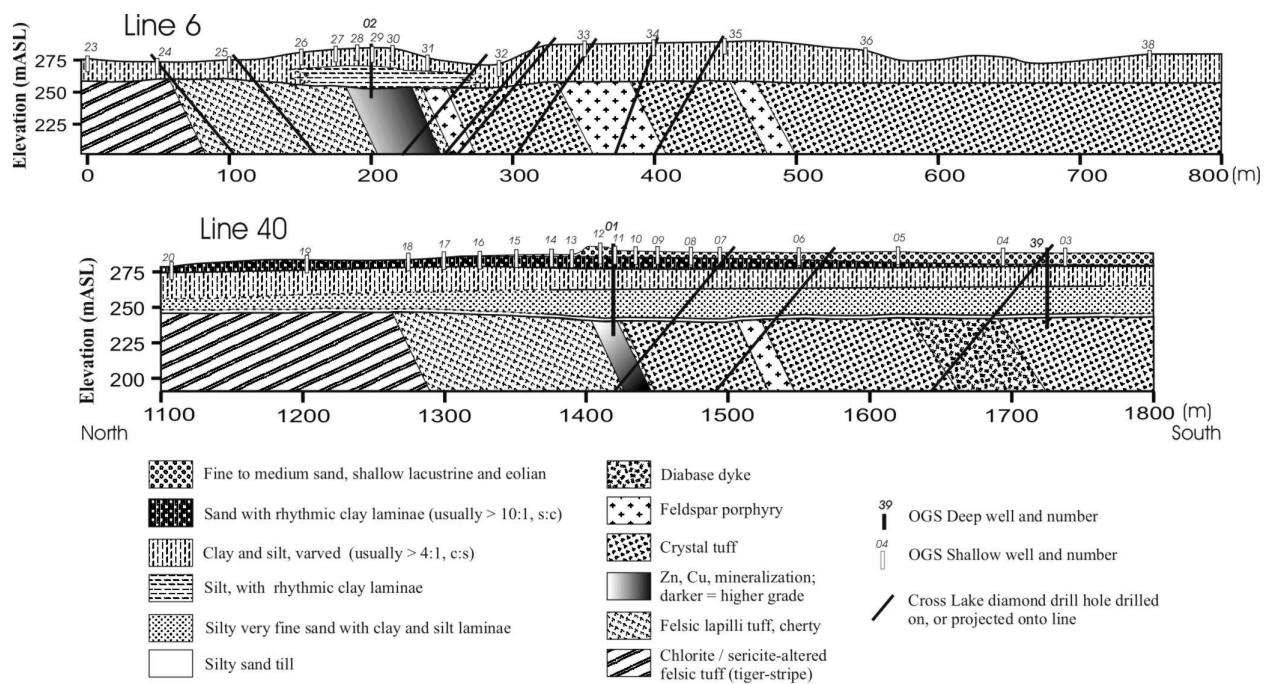


Figure 1. Geological cross-sections of Lines 6 SE and 40W based on diamond drill-hole data by Cross Lake Minerals Ltd and overburden drilling by the OGS; from Hamilton et al. (2004)

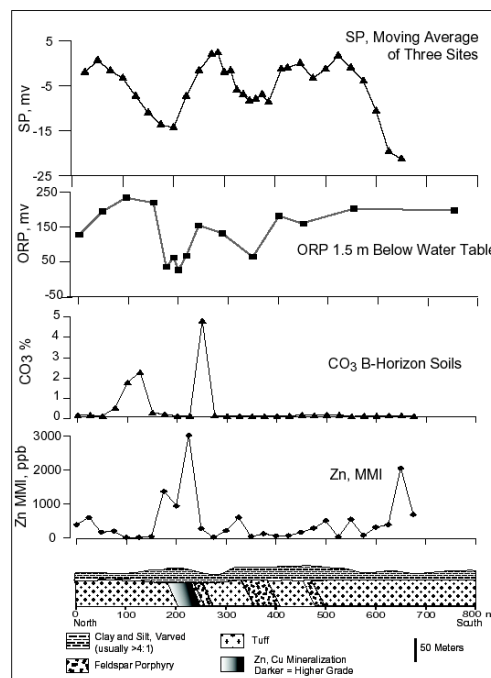


Figure 2. Line 6: spontaneous potential (SP), ORP measurements of redox conditions at 1.5 m below water table, carbonate content of B-horizon soils, and Zn by MMI sampled at 10-25 cm below decomposing vegetation; from Cameron et al. (2004)

point Zn anomaly directly over mineralisation, shown in Figure 2 for Line 6; this sample had been collected according to the company's protocol, 10 to 25 cm below the decomposing vegetation (i.e. 20 to

35 cm below surface) and consisted mostly of B-horizon sometimes mixed with Ae and occasionally Ah. Coincident with this MMI Zn anomaly are lows in SP (spontaneous potential), ORP (oxidation-reduction potential) (Fig. 2), and in the pH of soil slurries. Strong carbonate peaks, up to 5% CO₃ over a background of <0.1% CO₃, flank the subcropping mineralisation (Fig. 2).

Resampling in 2000 focussed on the issue of depth: two samples, the ‘upper’ 10 cm of the B-horizon (i.e. average sample depth of 15 to 25 cm) and the ‘lower’ 10-20 cm interval of the B. Density of sampling was increased but the lines were decreased from ~700 m to ~200 m, centred over mineralisation. This time all partial extractions, Enzymeh, the two ammonium acetates, as well as MMI, showed strong Zn anomalies directly over the deposit in the Upper B horizon sample, and not in the Lower B (Fig. 3). Aqua regia digestion did not result in such an anomaly, in either B-horizon sample (note the different magnitudes of Zn extracted by these leaches). Thus, depth has an important control on the ‘metal accretion zone’. Perhaps even more interesting is the observation that the Ae-horizon shows an equally significant anomaly to the Upper B-horizon, shown in Figure 4 for Line 40. This is the zone of eluviation, from which major elements such as Fe, Al and Mn are leached by organic acids to accumulate in the B-horizon below. Consequently, this horizon has been avoided traditionally in geochemical exploration in favour of the B-horizon where there are abundant Fe and Al oxides to sorb labile trace elements. By collecting the uppermost mineral soil, whether Ae or B or a mixture of the two, a distinctive multi-point Zn anomaly is obtained (Fig. 4).

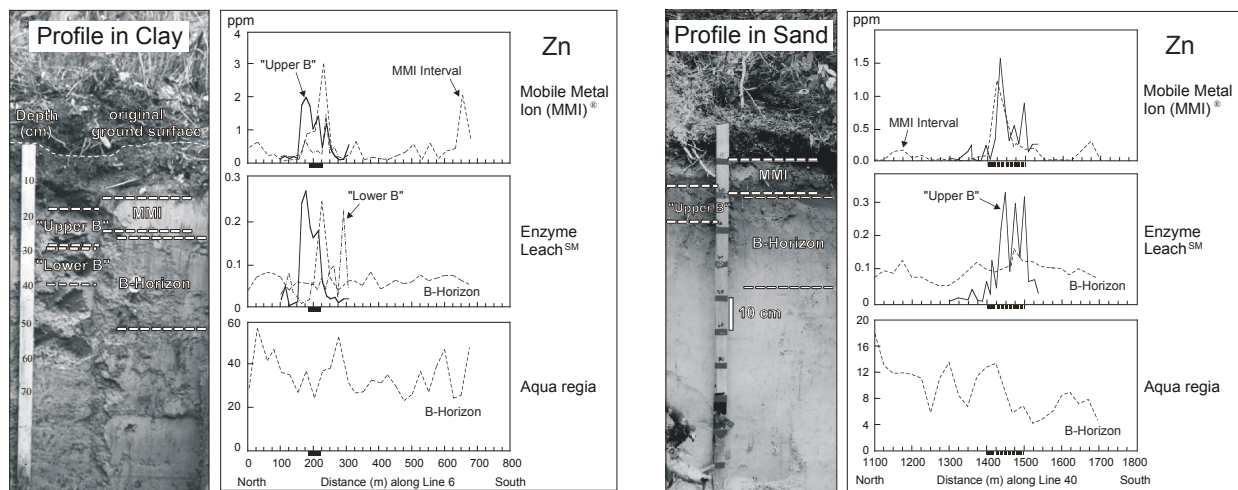


Figure 3. Zn geochemical profiles for MMI, Enzyme, aqua regia leaches of samples from (a) Line 6, covered by ~30 m of clay and (b) Line 40, covered by ~50 m of sand and clay

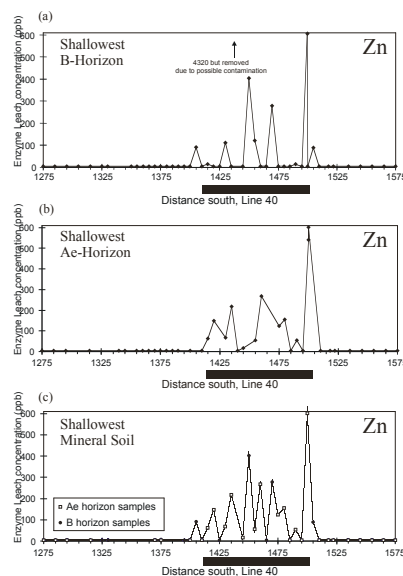


Figure 4. Zn responses on Line 40 by Enzyme leach for (a) shallowest B-horizon, (b) shallowest Ae-horizon and (c) shallowest mineral soil, either Ae or B

In order to map out element distribution in the top ~ 1 m above the deposit, a trench, 200-300 m long, was dug on each line and samples taken every 5 m along its length. Samples (O, Ah, Ae, B) were collected with depth at 10-cm intervals. The soils were analysed for 50-60 elements following aqua regia, Enzymeh leach, ammonium acetate (AA5 and 7) and weak HCl digestions, and for various other parameters in addition to pH and ORP. Figure 5 shows the distribution of Zn on Line 6 by (a) aqua regia and (b) Enzymeh, normalized to aqua regia Zn; the latter shows a consistent anomaly near surface extending for ~60 m and centred over the deposit at depth. The pattern of Zn by Enzymeh is similar to this but of less contrast. The aqua regia pattern, however, shows a depletion in this region as it is dominated by Zn in the humus (sparse humus over mineralisation) and by the colluvial material from ~235 m southwards. The first two principal components for the Enzymeh leach are shown in Figure 6: PC1 comprises the REEs and the high field strength elements (e.g. Hf, Th, Zr) and PC2 Zn, Cd, pH (-), Cu (-) with Ba, Rb and Tl. The PC2 anomaly coincides with the dramatic pH low (to ~5 from 7-8) that exists in the top metre overlying the deposit and is shown in the solid line.

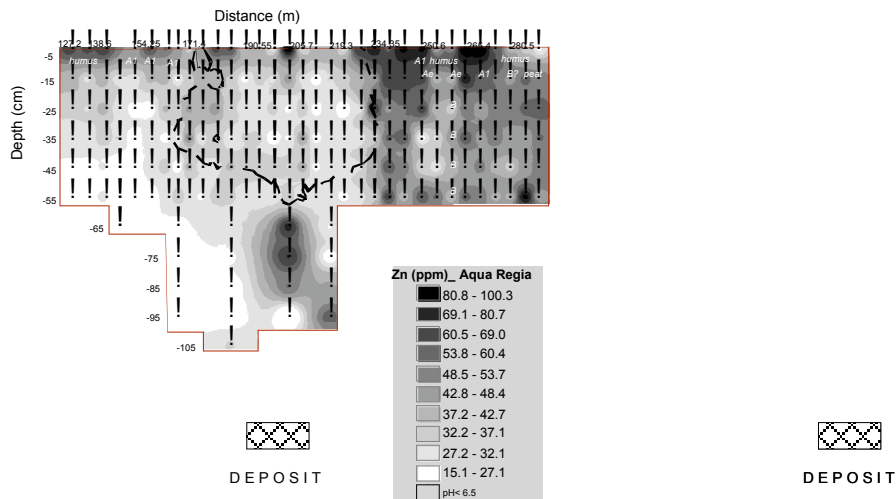


Figure 5. Distribution of (a) Zn by aqua regia and (b) $(Zn \text{ by Enzymeh leach}) / (Zn \text{ by aqua regia}) \times 10^{-3}$ in trench samples on Line 6, showing completely different patterns

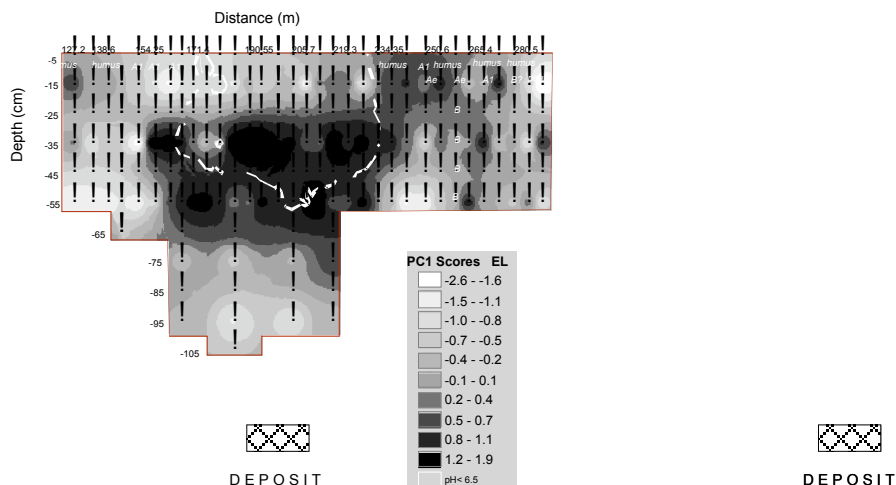


Figure 6. Distribution of (a) PC1 (REEs, HFSEs) and (b) PC2 (Zn, pH (-), Cu (-), Ba, Tl, Rb) for Enzymeh leach applied to the trench samples on Line 6. PC2 coincident with the pH low near surface above mineralisation

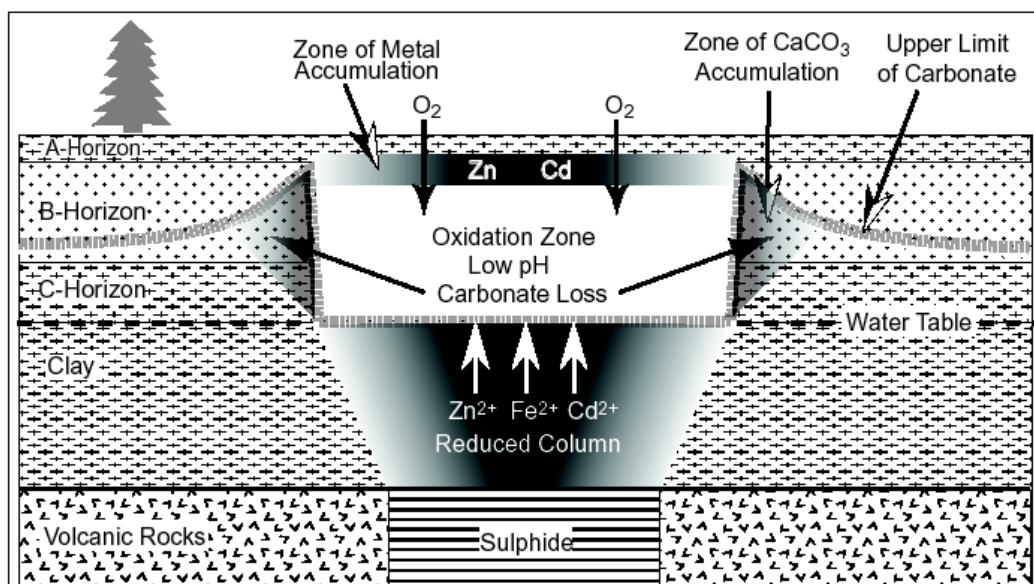


Figure 7. Model by Hamilton for development of anomalies through exotic overburden at Cross Lake. A reduced chimney/column is generated above the sulphide body. Reduced metal ions are oxidized at and above the water table by infiltrating oxygen and thereby generate H^+ ions which in turn dissolve carbonate (from C-horizon clay soils) that reprecipitates on the flanks of the zone of low pH. From Cameron *et al.* (2004)

Much of the data obtained at Cross Lake, on both lines, support Hamilton's model (2000) of reduced columns in saturated overburden above mineralisation that are overlain by acidic areas which are developed in the vadose zone. As H^+ is the most mobile of species, its continued presence in the near surface directly over the deposit in carbonate-rich terrain must imply a constant source and that probable source is the upward ongoing movement of reduced ions to continue the oxidation process (Figure 7). Clearly the continued presence of H^+ ions will have a large effect on trace elements in this area and some elements will be desorbed from exchange sites on the soil to be resorbed in a higher pH environment, perhaps in a different binding mechanism that will have different solubility characteristics in a partial leach (and hence produce an anomaly). For example, the PC1 anomaly in Figure 6, showing higher concentrations (by Enzymeh leach) of the REEs and HFSEs at 25 to 75 cm depth, could simply be due to redistribution of these elements by the effect of pH. Furthermore, pH has an effect on unbuffered leaches such as the Enzymeh leach so that some elements may dissolve to different extents that could confound interpretation. Whether a leach should be buffered and not influenced by the soil pH is under review as, in this case, pH changes reflect mineralisation below.

Various mechanisms (e.g. those based on diffusion or advection) have been proposed to explain element migration from deeply buried mineralisation and are discussed in Cameron *et al.* (2004) and by Kelley (2004). As diffusion (chemical, electrochemical) is much too slow a process to explain element migration through ~30 m of overburden in 8000 yrs, Smee (2003) concludes that the anomalies observed in partial extraction applications are the result of indirect responses to the pH low and can all be negated by appropriate normalizing to other parameters such as the number of binding sites (e.g. C) and the distribution of pH-sensitive elements such as Fe, Mn and Ca. While exact mechanisms remain unclear, Pb isotopic studies at Cross Lake strongly suggest that Pb has indeed moved to the surface from the deposit at depth. The only leach to show a clear Pb anomaly on Line 6 is the ammonium acetate pH 7 leach applied to the shallowest mineral soil (Ae or B); the stronger AA pH 5 leach obscures the anomaly by its higher background. A sequential extraction was applied to six samples collected from the trench survey: the Ae sample over mineralisation showing the highest Pb AA7 anomaly (at 200 m South, #200); surface organic-rich samples (at 154, 181 m S); and deeper unoxidised clays (at 214, 270, 280 m S). The Pb isotopic results (Fig. 8) for the extraction – AA7, followed by AA5, followed by aqua regia (AR) – clearly show that the AA7 signature of sample 200, the sample and leach showing the Pb anomaly over mineralisation, is close to that of the Cross Lake (CL) aqua regia ore signal and is distinct from its own AR signal and from both weak and strong leach signatures of the deeper unoxidised samples. These data show that the Pb AA7 anomaly in the metal accretion zone near surface is caused by Pb migrating from the underlying mineralisation, and not from redistributed Pb from adjacent clay sites or from atmospheric deposition.

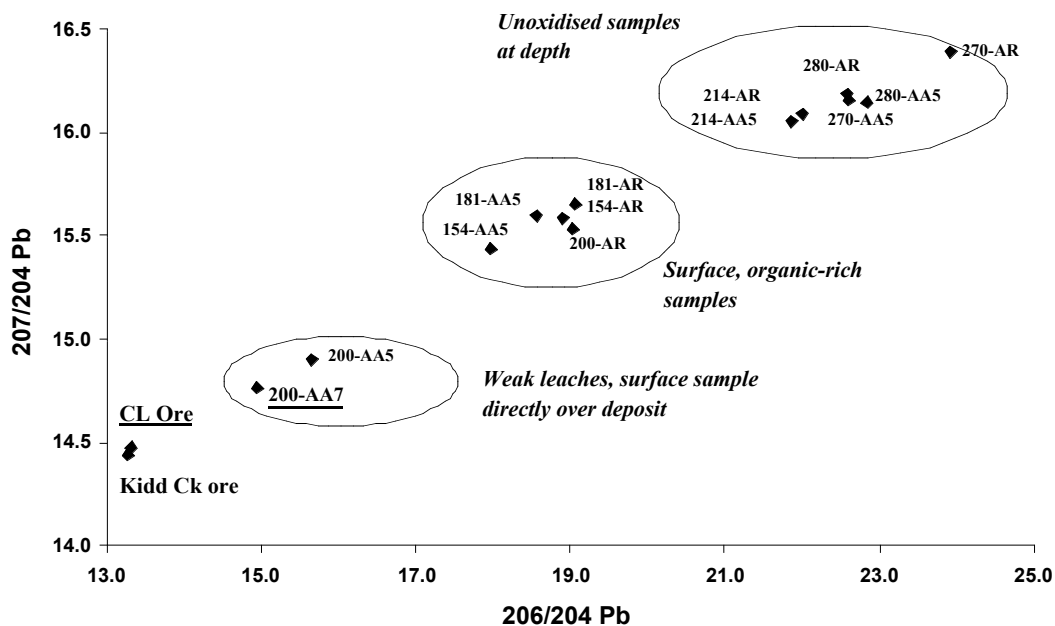


Figure 8. Pb isotopic signatures (by TIMS) of samples at 154, 181, 200, 214, 270 and 280 m south collected from the Line 6 trench, leached in sequence by ammonium acetate pH 7(AA7), ammonium acetate pH 5 (AA5), and aqua regia (AR). The AA7 signature of sample 200 (directly over the VMS mineralisation at depth, in the Ae-horizon) is close to that of the Cross Lake ore.

Analysis of soils (B-horizon) along Line 6 by Soil Desorption Pyrolysis (SDP) also highlights the location of the VMS orebody. The premise underlying this approach is that gases migrate from depth continuously and are adsorbed at surface on, for example, clay-sized particles; the signature of a deposit would differ from that of its host rocks. Numerous aliphatic and aromatic hydrocarbons, as well as gases such as SO₂, H₂S and CO₂, are desorbed from the 0.2-2.0 µm fraction and analysed by mass spectrometry. A template is created using data from samples over and off mineralisation, in order to define the most appropriate parameters. Perhaps the most exciting aspect of this particular study is that the template derived for another VMS orebody in the Abitibi could be used interchangeably with that for Cross Lake, suggesting that one template could have widespread application. Yet another dataset that shows distinct footprints directly over buried mineralisation is that of different populations of bacteria in the soil, hardly surprising as bacteria (e.g. sulphate-reducing) are well known to colonise areas of redox boundaries. The consistency with which all these (bio)geochemical signatures outline the location of the deeply buried mineralisation indicates that the processes involved are highly interactive and that this exploration technique can be extremely effective given the correct sampling and analytical strategies.

Acknowledgements

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