Geochemical surface expression of the Phoenix and Millennium uranium deposits, Athabasca Basin, Saskatchewan.

Michael James Power, B.Sc. (Hons)

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Ottawa-Carleton Geoscience Centre
Department of Earth Sciences
Faculty of Science
University of Ottawa

Thesis Abstract

The geochemistry of surface media above two known U deposits were examined to observe any possible dispersion products could be detected from them, and based on these findings, improved geochemical exploration techniques are proposed to reduce cost of finding undiscovered U resources. This study examined the materials overlying the Phoenix deposits, which have indicated resources of approximately 58.2 million lbs U_3O_8 grading 15 wt% that lie at 400 m depth below surface at the unconformity between the overlying Athabasca sandstones and Paleoproterozoic basement rocks. Aqua regia digestion, ammonium acetate at pH 5 and hydroxylamine leaches revealed U, Pb, Co, Ni, Mo, and W anomalies in humus and U, W and As anomalies in B-horizon soils above the ore zones and the basement location of a deposit-hosting, northeast-trending "WS Hanging Wall" shear zone over a three year period. These metal signatures suggest likely upward transport of metals from the deposits to overlying sandstones, and subsequently into the overlying till and soils.

This study also looked at materials above the Millennium U deposit, which has indicated resources of 68.2 million lbs U_3O_8 grading 4 wt% at ~750 m depth that occurs along a major fault in granites & metamorphosed pelites of Paleoproterozoic age below the Athabasca sandstones. Soil samples taken over the surface projections of an ore-hosting fault and the ore zone yielded anomalous values in U, Ni, Cu and Pb in aqua regia digestion of humus and U, Cu and Pb values in ammonium acetate leach of pH 5 of B-horizon soils. Hydroxylamine leach did not yield as many anomalies as ammonium acetate leach. Measured $^{4}He/^{36}Ar$ ratios of gas dissolved in water-filled drill holes were observed to be up to about 700 times the atmosphere value for air-saturated water, revealing the presence of

radiogenic ^{4}He that was likely produced from decaying U and released in the groundwater above the deposit.

Our results suggest upward migration of metals to surface through porous sandstone and fault systems at Phoenix, and upward migration of metals along faults and He gas at Millennium. Both studies indicate the importance of the traverse method of sampling over targets perpendicular to the last major ice-flow event to discern U deposits that are defined by other means.

Résumé de These

La géochimie des sols à la surface de deux gisements connus d'uranium a été examinées afin d'observer de possibles produits de dispersion et de proposer de nouvelles techniques d'exploration, dans le but de réduire les coûts associés à la découverte de nouveaux gisements uranifères. Cette étude examine les sols situés au-dessus du gisement Phoenix, qui a des ressources indiquées d'approximativement 58,2 millions lbs d'U_3O_8 à un grade de 15 % U, et qui se situe à 400 m de profondeur où se trouve la discordance entre le grès d'Athabasca et les roches du sous-sol Paléoprotérozoïque. La digestion par aqua regia, la lixiviation par acétate d'ammonium à un pH 5 et par hydroxylamine révèlent, sur une période de trois ans, des anomalies en U, Pb, Co, Ni, Mo et W dans l'humus et des anomalies en U, W et As dans l'horizon-B, dans les sols sus-jacents aux gisements et au toit d'une zone de cisallement uranifère de direction north-ouest qui se situe dans le sous-sol. Ces anomalies en métaux sont suggestives d'un transport ascendant de métaux provenant des gisements jusqu'aux grès sus-jacents, et par la suite dans les sols recouvrant les gisements.

Cette étude a aussi permis d'examiner les sols au-dessus du gisement Millennium, qui a des ressources indiquées de 68,2 millions lbs d'U_3O_8 à un grade de 4 % U, et qui se situe à une profondeur de 750 m le long d'une faille majeure passant à travers des sédiments métamorphisés et des granites d'âge Paléoprotérozoïque sous le grès d'Athabasca. Des échantillons de sols pris suivant la projection de la faille et du gisement à la surface montrent des anomalies en U, Ni, Cu et Pb avec la digestion aqua regia de l'humus et des anomalies en U, Cu et Pb avec la lixiviation par acétate d'ammonium à un pH 5 des horizons-B. La lixiviation à l'hydroxylamine n'a pas générée autant d'anomalies que la lixiviation à l'acétate d'ammonium. Les ratios $^{4}He/^{36}Ar$ mesurés à partir de gaz dissous provenant de certains trous de forage remplis d'eau sont jusqu'à 700 fois le niveau

atmosphérique mesuré dans l'eau saturée d'air, ce qui révèle la présence d'^{4}He radiogénique provenant probablement de la dégradation d'U relâché dans l'eau sous-terraine au-dessus du gisement.

Nos résultats suggèrent donc une migration ascendante des métaux à travers les grès très poreux et les nombreux systèmes de failles de Phoenix, ainsi qu'une migration ascendante des métaux et d'He par l'entremise de failles à Millennium. Les deux études indiquent l'importance de l'échantillonnage en traverses suivant des objectifs perpendiculaires au dernier écoulement glaciaire, afin de pouvoir discerner des gisements d'uranium.

Acknowledgments

I would like to thank Dr. Kéiko Hattori for providing me with the opportunity to pursue this research, and for her critical review of this thesis. Her patience, eagerness and positivity with this project are greatly appreciated, as is her continued support to see this work presented at both national and international geoscience conferences and submitted to scientific journals. I also gratefully acknowledge those who have helped me along the way, especially Jack Dann for software & sampling assistance, Dr. Daniele Pinti for noble gas analyses & discussions, Dr. Nimal De Silva for ICP-MS analyses, Dr. Tara Kell for providing XRF analyses, and Monika Wilk for tritium analyses. I would also like to thank Austin Krahenbil for his resampling work completed in 2013, some of which is included in this thesis. I would like to acknowledge the Research Affiliate Program bursary I received from Natural Resources Canada. This project was funded by Targeted Geoscience Initiative 4 Uranium Ore Systems program at Natural Resources Canada through a research grant to KH, and I thank Dr. Eric Potter at the Geological Survey of Canada for providing support. The Society of Economic Geologists is gratefully acknowledged for a Graduate Student Fellowship Award that I received in 2012. I would like to recognize the Academic and Travel Grants from GSAED and FGPS at the University of Ottawa I received that helped make the presentation of this research possible at the meeting of the Society of Geology Applied to Mineral Deposits and Goldschmidt Meeting in August 2013 in Sweden and Italy. Denison Mines Corp. and Cameco Corp. are acknowledged for providing logistical support at the project sites. Chad Sorba and Dr. Tom Kotzer are also thanked for their continued suggestions and feedback of the work contained in this thesis. I wouldn't have gotten through grad school without the Ottawa Senators, Rosebery homebrew, and an occasional shawarma. Friends new and old of Office 225 in Marion Hall, especially Lindsay Coffin, Stacey Wetmore, Erin Adlakha, April Coombs, Adam Tate, Mary Devine, and Octavia Bath are thanked for many laughs and Café Nostalgica visits. Matt Herod and Dr. John Jamieson are especially acknowledged for their assistance with conference talks, TAing, the consumption of wine, and company on European adventures. Thanks especially to my wonderful parents and family for all of their collective love and support – it was quite the journey turning this ol' trout into an (aspiring) geochemist!

List of Manuscripts, Reports and Presentations

This is a paper-format thesis. It is based on work presented in the following manuscripts:

I M. J. Power[1*], K. Hattori[1], C. Sorba[2] & E. G. Potter[3]
Surficial geochemical survey over the concealed Phoenix uranium deposits, Athabasca Basin, Canada.
In preparation for submission to: *Geochemistry: Exploration, Environments, Analysis*

II M. J. Power[1*], K. Hattori[1], D. L. Pinti[2] & E. G. Potter[3]
Anomalous abundances of He and mobile metals in surface media over the deeply buried Millennium uranium deposit, Athabasca Basin, Canada.
In preparation for submission to a refereed journal

Selection of Abstracts and Publications

Power, M. J., Hattori, K., Pinti, D. L. & Potter, E. G. 2013. Anomalous abundances of He and mobile metals in surface media over the deeply buried Millennium U deposit, Athabasca Basin, Canada. Goldschmidt 2013 Meeting, Florence, Italy. Oral Presentation.

Power, M. J., Hattori, K., Sorba, C., Kotzer, T. & Potter, E. G. 2013. Surface media expressions of buried uranium: the Phoenix & Millennium deposits, Athabasca Basin, Saskatchewan, Canada. SGA 2013 Meeting, Uppsala, Sweden. Oral Presentation.

Power, M. J., Hattori, K., Sorba, C., Kotzer, T., Pinti, D. L. & Potter, E. G. 2013. Surface media expressions of buried unconformity-related uranium: The Phoenix and Millennium deposits, Athabasca Basin. Annual Meeting of the Geological Association of Canada and Mineralogical Association, Winnipeg, MB. Oral Presentation.

Power, M. J., Hattori, K., Sorba, C. & Potter, E. G. 2012. Geochemical anomalies in the soil and uppermost siliciclastic units overlying the Phoenix uranium deposit, Athabasca Basin, Saskatchewan, Canada. Geological Survey of Canada Open File Report 7257.

Power, M. J., Hattori, K., Sorba, C. & Potter, E. G. 2012. Geochemical anomalies in surface media and uppermost sandstones overlying the concealed Phoenix uranium deposit, Athabasca Basin, SK. Geological Survey of Canada Open File Report Poster 7235.

Power, M. J., Hattori, K., & Sorba, C. 2012. Geochemical anomalies overlying the concealed Phoenix uranium deposit, Athabasca Basin, Canada. Geo-mapping for Energy and Minerals (GEM) and Targeted Geoscience Initiative (TGI) Uranium Workshop, St John's, NL. Oral Presentation.

Power, M. J., Hattori, K. & Sorba, C. 2012. The Surface Expression: What do geochemical anomalies in surface media and shallow sandstones overlying the Phoenix uranium deposit, Athabasca Basin, Saskatchewan, tell us?" Ottawa-Carleton Geoscience

Centre Seminar Series. Department of Earth Sciences, Carleton University. Oral Presentation.

Statement of Originality

The work presented in this thesis was written by myself with crucial input and critical review by Dr. Kéiko Hattori. The lab work was conducted in part by myself at the University of Ottawa, Université du Québec à Montréal, the Geological Survey of Canada (Ottawa), with the commercial analytical work completed by ACME Labs in Vancouver, BC.

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CHAPTER 1

Introduction

Preamble

Mineral deposits are highly sought after because as they are essential in the manufacturing and construction of most materials that modern-day societies require. The Athabasca Basin in northern Saskatchewan is home to the world's largest U deposits, and most of those that have been discovered are situated in the eastern margin of the Basin. Explorers are now looking west deeper into the basin for ore that is buried under extensive glacial overburden and sandstone. Geological, geophysical, and geochemical exploration methods are the three main tools used in the hunt to find these resources. The dispersion of elements from deposits has applications from mineral exploration, to environmental remediation, and long-term nuclear waste storage. These can include studies of dispersion products directly from the mineralization itself. Other processes can also rework dispersion products after displacement away from their place of initial dispersion, such as the distribution of elements in glacial overburden, groundwaters, lake bottom sediments, vegetation, and soils in the surrounding environment (Hawkes & Webb 1962).

A commonly used geochemical method to identify buried mineral deposits is selective leaching of soil samples (Cameron *et al.* 2004), especially in Canada where soil is young (<10,000 years old). Those data will be the main focus of this study, along with till, sandstone, gas and water geochemical datasets in a geographic-information systems (GIS) based approach in order to detect anomalies that may be related to deeply buried U deposits several hundred metres below the surface.

Previous Work

Geochemical Exploration for Mineral Deposits

Biogeochemistry, geomicrobiology, soil gases, heavy indicator mineral geochemistry, isotopes of Pb, and groundwater geochemistry have all been used to vector in to mineralization (Coker 2010). Dunn (2007) reviewed the use of various plant species and their use in exploration for a variety of mineral deposit types. Various types of bacteria, from aerobic, anaerobic, to sulphate reducing, have all been used to identify the development of secondary geochemical features associated with a range of ore deposits as reported by several workers (Parduhn 1987; Goodhue & Southam 2004). These "reduced chimneys" developed above concealed volcanogenic massive sulphide deposits require sulfate, which is presumably sourced from the mineralization (Goodhue & Southam 2004). Indicator minerals have been used for centuries to explore for a wide range of deposit types (McClenaghan 2005); minerals dispersed in glacial till from diamond-hosting kimberlite pipes in Canada's north being a notable example. Isotopic signatures for some elements (e.g., Pb) are now be determined by high resolution and multi-collector ICP-MS techniques for fingerprinting the source(s) of the element accumulated in a given sample medium (surface and groundwaters or surficial materials) within the surficial environment (Caughlin 2010). Groundwater geochemistry, through virtue of water being chemically reactive with mineralized zones and often flowing away from them, has the potential to be a powerful mineral exploration tool as exploration for deeply buried deposits under thick cover increases (Leybourne & Cameron 2010). Improved exploration methods using a combination of these media are therefore required to effectively "see" under this cover to hopefully reduce discovery costs and continue to develop new mineral deposit resources.

Geochemical Exploration for Uranium

Geochemical exploration methods for U using surface media have been conducted in other countries as well as in Canada. According to Bradshaw & Lett (1980), direct indication of U mineralization can be achieved in a cost-effective manner using soil and soil gas sampling methods for U, He and Rn, and can provide an indicator of deep ore. Although at the Bear Creek sandstone-type U deposit in the Powder River Basin of Wyoming, mineralization is covered by 90 m of barren shale and sandstone, a significant U anomaly was observed in the top 0.5-1.0 mm of soil (Bradshaw & Thomson 1979; Bradshaw & Lett 1980). Snelling (1984), based on his soil geochemistry orientation survey with two traverses above a U deposit in Koongarra, Australia, concluded that Cu and Pb, and to a lesser extent Co, Ni and Be, are suitable pathfinder elements for U. Peuraniemi & Aario (1991) documented bedrock, till, sand and peat containing high U concentrations in the area underlain by a U-rich Precambrian granite in northern Finland. In Hoffman's (1983) overview of soil and lake sediment surveys for U deposits in the Hornby sandstone basin in Northwest Territories, he concluded that Cu and Ra as pathfinder elements for U, and that methods for drill testing of geochemical soil anomalies depend on the relationship between the geochemical anomaly and a fault zone. In addition, he found that soil anomaly generation is favored by active hydromorphic processes in geochemically homogeneous overburden containing an average background of 0.5 ppm U, and anomaly contrasts typically 2 to 3 times this value, with anomalous U values exceeding 1.5 ppm that are highly reproducible (Hoffman 1981).

There are also numerous studies of these types of surface media, including those examining groundwater, overburden and soil gas above U deposits. Clarke and Kugler (1973) found He contents of up to 600 times atmosphere in groundwater above U deposits at

Elliot Lake, Ontario and Inda Lake, Labrador. Butt and Gole (1986) observed He in excess of atmosphere in groundwaters around U mineralization at Honeymoon, Mayingee, Bennett Well and Stuart-Shelf/Roxby Downs in Australia. Anomalous He has also been found in overburden gas and soil gas over U mineralization in U deposits in the U.S.A. and Australia (Reimer *et al.* 1979; Butt & Gole 1985). However, above some deposits Butt & Gole (1985) examined, overburden and water data did not display anomalous He, leading them to presume that equilibration between overburden gas and atmosphere may be far more rapid than that between overburden gas and groundwater, so that any He released from the water may be quickly dispersed. Though He may escape into the atmosphere or is carried away by circulating groundwaters in porous soils, it can be observed as increasing gradient over the deposit in stagnant groundwater or impervious soils (Dyck 1976). A study by Reimer *et al.* (1979) conducted in Weld County, Colorado, U.S.A. showed that values for He in soil gas can be contoured to outline an anomalous area, and that the anomaly is displaced from the deposit in the direction of groundwater flow. Additional soil gas studies by Reimer *et al.* include the Schwartzwalder U mine in Colorado where He anomalies may be related to geologic structure; and near Ambrosia Lake, New Mexico, where the location of He anomalies are related to groundwater movement.

Geochemical Exploration in the Athabasca Basin

This thesis follows up on a multi-year, multi-site study supported by the Canadian Mining Innovation and Research Organization, which concluded that the buried U deposits might be detected using mobile metals sourced from deposits (Bonham-Carter & Hall 2010). In their multi-media study of soils, vegetation and soil gas hydrocarbons over the Cigar Lake (~400 m depth) and McClean Lake (~150 m depth) deposits in the Athabasca basin, Saskatchewan, they found U, Co, and Ni anomalies in soil over the surface trace of ore zones

at both locations and were best in the humus horizon, with less convincing results in the B and C horizons. In addition, the anomalies they observed in humus did not spatially coincide with the spruce needles anomalies they observed (Bonham-Carter & Hall 2010). At the Wheeler River property in the basin where the Phoenix U deposits in this study are located, AGIP Canada Ltd. performed a two-season biogeochemical survey of young twigs of jack pine in the area including the current study area (Stewart 1981). Results of their 1980 survey yielded anomalous (more than two standard deviations (σ) above the mean population, Stewart 1981) U values ranging from 0.2 up to 10.3 ppm in ash on Wheeler River claim blocks. However, twigs adjacent to lakes and swamps also had high values, which may have been the result of U scavenging from large amounts of water through tree roots (Stewart 1981). Additionally, they were unable to reproduce the highest value that was found over the "WS Conductive Zone", which corresponds to WS Shear zone, the main structural feature associated with the deposits.

Shallow sandstone, gas, and water sampling have been used in addition to traditional soil sampling to explore for buried U deposits (Dyck & Tan 1978; Earle & Drever 1983; Clark 1987; Holk *et al.* 2003; Uravan Minerals 2011). $^{238}U/^{206}Pb$ and $^{206}Pb/^{204}Pb$ ratios in sandstone and basement rocks are useful in determining the timing and nature of U and Pb migration before, during and after mineralization in Proterozoic basins (Holk *et al.* 2003). This is because they can indicate the presence of radiogenic Pb isotope ratios – ratios that provide geochemical vectors toward sites of potential economic U mineralization. These radiogenic Pb ratios can also be found in surface media above sandstone. Surficial geochemical studies by Uravan Minerals (2011) found radiogenic $^{207}Pb/^{206}Pb$ signatures in C-horizon clay samples and tree cores above the Cigar Lake deposit and Uravan's Outer Ring exploration project (Uravan Minerals 2011). Clark (1987) sampled the uppermost

sandstone of the Athabasca Group and found anomalies of U, Pb and other elements over the Cigar Lake deposit, buried 400 m deep. Dyck and Tan (1978) tested seasonal variations of He, Ra, and U in lake waters near the Key Lake U deposit buried 150 m beneath surface. In the lakes they tested, the highest He concentrations of nearly four times atmospheric concentrations were obtained during a winter survey, taken under the ice in two bottom lake samples where the sandy overburden extends for some 50 m directly to the ore zone (Dyck & Tan 1978). Rn and U values in water at these sites were also anomalous, but the highest values of Rn and U in water were obtained in a shallow lake about 2 km south of the ore zone, where a radioactive boulder train was present at surface. Earle and Drever (1983) followed up this work in the Key Lake area, and were able to prove that groundwater samples in exploration drill holes collected from the vicinity of U mineralization have consistently high levels of U, Ra, and He up to tens of meters away from mineralization. Dyck and Da Silva (1981) also found that Vulture and Candy lakes in northern Saskatchewan in close proximity to U mineralization at McClean Lake at were found to contain anomalous He and Rn in the sediment.

Dispersion of Elements from Ore Deposits

Among various mineral deposit types, there are many theories that attempt to explain the vertical movement of elements from ore to surface, and depending on the sampling environment, these migration mechanisms can dictate the surface media in which to explore. These include electrochemical dispersion (Hamilton 1998), which proposes an upward propagation of reduced species to the water table that forms a reduced ion column over volcanogenic massive sulphide deposits, and the subsequent development of geochemical anomalies in the overlying surficial clay overburden. To create the features seen at surface at Cross Lake study site, where at least 30 m of clay overlie the sulphide lens and within a

period of 8,000 years since the clays were deposited, requires rates of migration well beyond that of chemical diffusion (Cameron *et al.* 2004), so other processes likely play a role. Evaporation, transpiration, and convection are also processes that also likely play a role in element redistribution in the soil profile above mineral deposits. Mann *et al.* (2005) carried out laboratory experiments that suggest capillary rise and evaporation may play a role in where elements accumulate in soil, and found that root-zone transpiration may also affect solute deposition and adsorption in the evapotranspiration zone. Their modeling also suggested that convection heat from deposit oxidation could be a method for rapid rise of ions below the water table (Mann *et al*. 2005). Other mechanisms are also well known in the literature. Vapor transport of gas has also been proposed as an upward migration mechanism (Smee 1998) for buried epithermal Au deposits in arid environments. Smee's model suggests that H+ released during the oxidation of sulphide mineralization travels directly to the surface, or may react with carbonate in wall rocks producing CO_2, which in turn migrates to the surface over time. This builds on a longstanding theory by Govett (1976), who advocated chemical dispersion of H + resulting from oxidation of near-surface sulphides and electrochemical dispersion of H + from deeply buried sulphides, facilitated by ground and soil water advection or diffusion. Cyclical dilatancy pumping (Cameron *et al.* 2002) is a method proposed to explain surficial geochemical anomalies in areas with a thick vadose zone, the region between the surface of the ground to the top of the water table. Results of soil and groundwater analyses from a study at a porphyry copper deposit in northern Chile, buried beneath 50 to 100 m of gravels, are consistent with the vertical movement of saline metal-rich groundwaters along fractures during earthquakes in this seismically active area (Cameron *et al.* 2002; Cameron *et al* 2005). Earthquake-driven seismic pumping up along

faults is a mechanism of element transport that has also been proposed (Cameron 2013), including along faults to surface media of the Athabasca basin – the study area for this thesis.

Thesis Objectives

The main objectives of this study were to identify the dispersion of U and related metals as well as daughter product radionuclides in surface media above deeply buried U deposits to provide improved geochemical exploration tools for U. Thus, the aim of this thesis was to study the geochemical expression of surface media over two deeply buried U deposits, with implications for mineral exploration in sporadic permafrost regions of northern Canada. Multiple methods of sampling and analysis of surface media over the deposits are discussed in this thesis, and possible explanations of the geochemical processes responsible for anomaly formation are discussed. These anomalies were identified and scrutinized within a geological, geochemical and geophysical context with relation to these U deposits at depth. This is to reduce the cost of exploration by reducing drilling, as it is among the most expensive costs for explorers.

The Proterozoic-age Phoenix and Millennium U deposits were chosen as study sites. Surficial geochemistry was long known to be useful in detecting shallow U mineralization (Dyck & Tan 1978; Clark 1987), however the depth of these deposits (Phoenix, ~400 m; Millennium, ~750 m) from surface was recently thought to be possible for dispersion products to travel (Cameron 2013). Surface disturbance above these sites was also minimal, which allowed for intact soil horizons at sampling locations. While buried under hundreds of meters of sandstones and Quaternary glacial till, both deposits appear to be discernible in the geochemistry of the various surface media overlying them.

Thesis Outline

This thesis is presented as two manuscripts, both of which were written to address similar themes of this study, as soil, till and sandstone geochemistry is addressed in one, and soil and gas geochemistry in the other.

Chapter 2 is a paper focusing on the trace metal abundances in soils and sandstones above the Phoenix U deposits. The manuscript will be submitted to the journal *Geochemistry: Exploration, Environments, Analysis.*

Chapter 3 is a paper focusing on trace metals in soils and noble gas abundances in drill-holes above the Millennium U deposit. The manuscript will be submitted to a refereed journal.

Methodology

Soil samples from multiple soil horizons (humus, B-, E- and C-horizon till) were collected by Dutch auger and trowel along sampling transects over ore and fault zones. These traverses were sampled in lines perpendicular to the last major ice flow direction to avoid any possible smearing and contamination of materials up-ice. Water samples were collected from drill holes intersecting mineralization and from nearby lakes. Gas samples were collected using diffusion gas samplers submerged in water-filled drill holes, monitoring wells, and a swamp. Geochemical leach data from uppermost sandstones above the Phoenix deposits was donated by Denison Mines Corp. Humus and till samples underwent aqua regia total digestion, and B-horizon soil samples underwent both ammonium acetate at pH 5 and hydroxylamine leaches (2011 only) prior to analysis by inductively coupled plasma mass spectrometer (ICP-MS). Leaching experiments on humus involved leaching humus in water, weak HBr, HNO_3 and HF:HBr digestions. X-ray fluorescence (XRF) analysis was performed on till samples to determine whole-rock composition. Tritium analysis was by filtered water

samples mixed with a low level tritium cocktail and counted using an ultra-low level liquid scintillation counter. Noble gas abundance analyses were by quadrupole mass spectrometer (QMS). Sandstone samples were leached by partial HNO_3:HCl digestion and analyzed with ICP-MS and inductively-coupled plasma optical emission spectrometry (ICP-OES).

Contributions of the Author

I assisted in planning fieldwork and conducted the sampling of soil, water and gas samples and descriptions at both project locations, as well as performed metal leaching experiments on soil at the University of Ottawa. I also prepared samples for noble gas analysis at Université du Québec à Montréal. I mapped geochemical data in the ArcMap function of the ArcGIS software platform, and created raster maps from the sandstone data to identify areas of correlation between high sandstone and high soil metal values.

Contribution to Knowledge

I have published two Open File Reports with the Geological Survey of Canada (OF 7257 and OF 7235), with a third currently in review. I am also preparing to submit a manuscript to the refereed journal *Geochemistry: Exploration, Environments, Analysis* based on my research at the Phoenix deposits, and a manuscript to a refereed journal based on my research at the Millennium deposit.

Regional Geology of the Study Area

Significant unconformity-associated U deposits occur at the base of flat lying, fluvial redbed strata on peneplaned tectono-metamorphic complexes in the interiors of large cratons, with the Athabasca Basin regionally located on the western Churchill Province between the eroded remnants of two major orogenic belts: the 1.9 Ga Taltson magmatic zone, and the 1.8 Ga Trans-Hudson Orogen (Jefferson *et al.* 2007a). This Proterozoic basin in northern Saskatchewan is a virtually undeformed, 1750 m thick, mainly fluvial siliclastic sedimentary

succession deposited between 1740 and 1500 Ma (Creaser & Stasiuk 2007). The Paleoproterozoic Athabasca Group sandstones, which in the eastern part of the basin consist of 500 to 700 m of four members of the Manitou Falls Formation, are named MFa, MFb, MFc and MFd in shallowing order (Ramaekers 1990; Roy *et al*. 2005). The Manitou Falls sandstones consist of coarse to fine-grained, hematite-rich conglomerates along thin stratigraphic horizons, with oxidation of heavy mineral layers and silty sandstones (Ramaekers 1990). The sandstones are differentiated by their proportions of conglomerate and clay intraclasts (Ramaekers *et al.* 2007; Bosman & Korness 2007).

Local Geology of the Wheeler River Property

This formation unconformably overlies metamorphosed basement rocks consisting of Archean to Paleoproterozoic granitoid and gneiss (Jefferson *et al.* 2007a). Basement rocks at the Wheeler River Property hosting the Phoenix deposits are part of the Paleoproterozoic Wollaston Domain of the Trans Hudson-Orogeny and consist of southeastwardly dipping metasedimentary rocks intercalated with granitic gneiss (Yeo & Delaney 2007). These include pelite, semipelitic gneiss, felsic and quartz feldspathic gneiss, quartzite and rare calcsilicate gneiss. The Wollaston quartzite unit forms a prominent basement ridge that is entirely covered by Athabasca Group sandstones and whose crest to the west of the study area is up to 200 metres above the adjacent basement surface. Garnetiferous pelite, graphitic pelite and pelite of the Wollaston Supergroup are interpreted structurally and stratigraphically overlie the quartzite unit (Kerr 2011).

Local Geology of the Cree Extension Property

Basement rocks at the Cree Extension Property hosting the Millennium deposit lie within a transition zone between the Wollaston Lithostructural Domain to the east, and the Mudjatik Lithostructural Domain to the west (Millennium Project Report 2009). The

Mudjatik Domain consists predominantly of granitoid gneisses, which contain discontinuous arcuate zones of Paleoproterozoic supracrustal rocks (Lewry & Sibbald 1980). The Wollaston Domain is a Paleoproterozoic metasedimentary sequence divided into two distinct rock assemblages: the lower assemblage comprising pelitic, semipelitic, and arkosic gneisses with interlayered calc-silicates and quartzites (Ray 1975), and the upper assemblage comprising semipelitic and arkosic gneisses.

Statement of Original Contribution

These manuscripts present new digestion data of humus, C-horizon glacial till and sandstone, leach data of B-horizon soils, whole-rock chemistry of till, noble gas abundances in water-filled drill holes and tritium concentrations in water. Our samples from above the Phoenix and Millennium U deposits, which are 400 m and 800 m deep, respectively, provide important data for future mineral exploration efforts in the basin.

This study involved several weeks of fieldwork in September 2011 and August 2012. Michael Power, Jack Dann, and Keiko Hattori collected soil, gas and water samples. Soil data from samples collected in 2013 by Austin Krahenbil is contained in the Phoenix paper and used with his permission. The soil and till (silt fraction) data was analyzed by ACME Analytical Labs in Vancouver, B.C. Leaching experiments were performed by Michael Power at the University of Ottawa. ICP-MS analyses of humus, whole-rock XRF analysis of till, and tritium analysis of water were completed by Nimal de Silva, Tara Kell and Monika Wilk, respectively, at the University of Ottawa. Daniele Pinti at Université du Québec à Montréal analyzed noble gas abundances. Sandstone leach data was provided by Denison Mines Corp. and used with their permission.

The work contained in the manuscript "*Surficial geochemical survey over the concealed Phoenix uranium deposits*" was presented as posters at the 2011 and 2012

Saskatchewan Geological Open House, as well as orally at the Advances in Earth Sciences Research Conference in Kingston, ON in March 2012. It was also presented at 2012 and 2013 Geological Association of Canada-Mineralogical Association of Canada (GAC-MAC) Annual Meetings, as well as the 11th Biennial Society of Geology Applied to Mineral Deposits Meeting 2013 in Uppsala, Sweden. The work contained in the manuscript "*Anomalous abundances of He and mobile metals in surface media overlying the deeply buried Millennium U deposit, Athabasca Basin, Canada*" was presented as a poster at the 2012 Saskatchewan Geological Open House and orally presented at the 2013 GAC-MAC Annual Meeting and the Goldschmidt 2013 Meeting in Florence, Italy (selected abstracts in Appendix E).

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CHAPTER 2

Article I. Surficial geochemical survey over the concealed Phoenix uranium deposits, Athabasca Basin, Canada.

Michael J. Power[1*], Keiko Hattori[1], Chad Sorba[2] & Eric G. Potter[3]

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Surficial geochemical survey over the concealed Phoenix uranium deposits, Athabasca Basin, Canada.

M. J. Power[1*], K. Hattori[1], C. Sorba[2] & E. G. Potter[3]

1. *Department of Earth Sciences, 140 Louis-Pasteur, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada*
2. *Denison Mines Corporation, 200-230 22nd St East, Saskatoon, Saskatchewan, S7K 0E9, Canada*
3. *Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada*

Abstract

The Phoenix uranium deposits in the Athabasca Basin, Saskatchewan lie 400 m beneath surface at the unconformity between basement rocks and sandstones, above which sits 25-30 m of glacial till. Soil samples were collected in traverses & spot sampling over the deposits in 2011-2013, with multiple background sites. Humus samples underwent aqua regia digestion, and B-horizon soils leaching with ammonium acetate (pH=5) & 0.25 M hydroxylamine. Results show U, Pb, Co, Ni, Cu, Mo, As and W anomalies in soils above the deposits and basement location of the deposit-hosting WS Shear zone. High-density sampling in 2012-2013 around the highest U site from 2011 confirmed anomaly reproducibility. Peak to background ratios of sample sites are up to 28 for U, 44 for Mo, 17 for Co, 18 for W, 5 for Cu and 1.9 for Ni in humus, and 36 for U, 16 for W and 125 for As in B-horizon soil. Uppermost sandstones display elevated metal values in partial HNO_3:HCl and total digestions. The data indicates the traverse method of geochemical prospecting is enhanced by correlating metal values in soil and till to those of the sandstones, suggesting upward transport of metals from sandstones to soils is originating from buried uranium deposits.

Introduction

The Athabasca Basin in northern Saskatchewan, Canada is home to the worlds largest and highest-grade unconformity related U deposits. Discovered in 2008, the Phoenix deposits at Denison Mine Corporation's Wheeler River Property represent one of the Basin's most significant recent discoveries of unconformity-related U mineralization (Fig. 1). Exploration for new buried U deposits remains very difficult due to their lack of outcrop at surface and the depth at which new deposits are being discovered; factors which are forcing explorers westward and deeper into the Basin. For example, the Millennium deposit at Cameco Corporation's Cree Extension property, discovered in 2000, has indicated resources of 68.2 million lbs. U_3O_8, and lies at approximately 750 m depth in basement rocks below the unconformity.

Geochemical exploration methods for U deposits using surface media are well established globally as well as in Canada. According to Bradshaw & Lett (1980), direct indication of U mineralization can be achieved in a cost-effective manner using soil and soil gas sampling methods for U, He and Rn, and can provide an indicator of deep ore. Although at the Bear Creek sandstone type U deposit in the Powder River Basin of Wyoming mineralization is covered by 90 m of barren shale and sandstone, a significant U anomaly was observed in the top 0.5 to 1.0 mm of soil (Bradshaw & Thomson 1979; Bradshaw & Lett 1980). Snelling (1984), based on his soil geochemistry orientation survey with two traverses above a U deposit in Koongarra, Australia, concluded that Cu and Pb, and to a lesser extent Co, Ni and Be, are suitable pathfinder elements for U. Peuraniemi & Aario (1991) documented bedrock, till, sand and peat containing high U concentrations in the area underlain by a U-rich Precambrian granite in northern Finland. In Hoffman's (1983) overview of soil and lake sediment surveys for U deposits in the Hornby sandstone basin in

Northwest Territories, he concluded that Cu and Ra as pathfinder elements for U, and that methods for drill testing of geochemical soil anomalies depend on the relationship between the geochemical anomaly and a fault zone. In addition, he found that soil anomaly generation is favored by active hydromorphic processes in geochemically homogeneous overburden containing an average background of 0.5 ppm U, and anomaly contrasts typically 2 to 3 times this value, with anomalous U values exceeding 1.5 ppm that are highly reproducible (Hoffman 1981).

Previous studies of geochemical exploration for these deposits in the surface media of the Athabasca Basin are numerous. Surficial geochemical studies by Uravan Minerals found radiogenic $^{207}Pb/^{206}Pb$ signatures in C-horizon clay samples and tree cores above the Cigar Lake deposit and Uravan's Outer Ring exploration project (Uravan Minerals 2011). Dyck and Tan (1978) tested seasonal variations of He, Ra, and U in lake waters near the Key Lake U deposit buried 150 m beneath surface. Dyck and Da Silva (1981) also found that Vulture and Candy lakes in northern Saskatchewan in close proximity to U mineralization at the McClean Lake deposit at were found to contain anomalous He and Rn in the sediment. Clark (1987) sampled the uppermost sandstone of the Athabasca Group and found anomalies of U, Pb and other uranium indicator elements over the Cigar Lake U deposit, buried 400 m beneath surface. The previous operator of the Wheeler River property, AGIP Canada Ltd., performed a two-season long biogeochemical survey of young twigs of jack pine in the area, including the current study area (Stewart 1981). Results of 1980 survey yielded anomalous (more than two standard deviations (σ) above the mean population, Stewart 1981) U values ranging from 0.2 to 10.3 ppm in ash on Wheeler River claim blocks. However, high values were also found in twigs adjacent to lakes and swamps, and were interpreted to have been the result of U scavenging from large amounts of water through tree roots (Stewart 1981).

Though their highest value in 1980 was found over the "WS Conductive Zone", which corresponds to the WS Shear zone, the main structural feature associated with the Phoenix deposits; the anomaly was not reproduced in 1981.

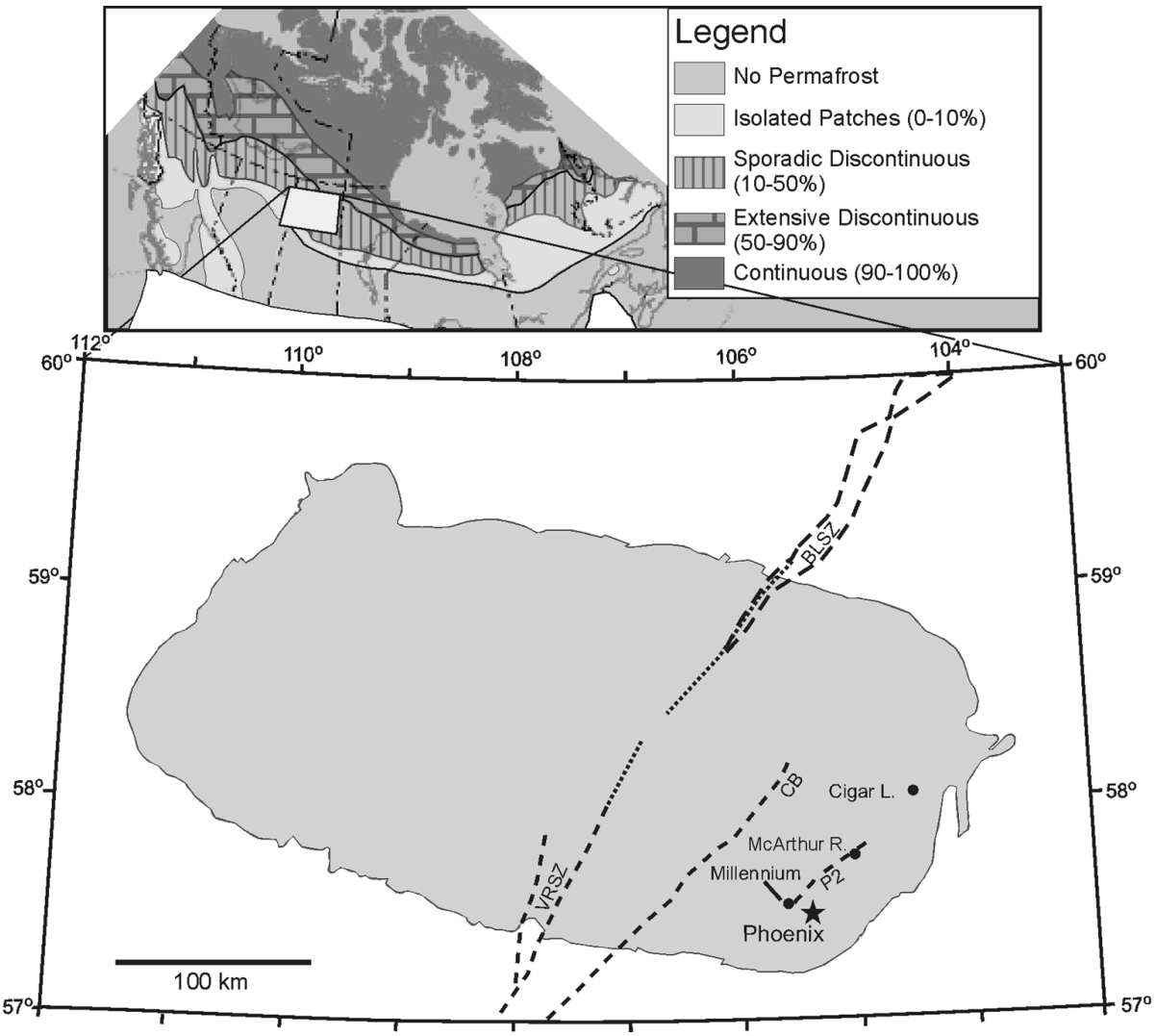


Figure 1: Simplified map in grey of the Athabasca Basin (inset) in the province of Saskatchewan, Canada, in a region of sporadic discontinuous permafrost, with the study area (black star) hosting Denison Mines' Phoenix uranium deposits in the southeastern Basin at Wheeler River. Millennium, McArthur River & Cigar Lake deposits (black circles) are shown for reference to the northeast, as well as the P2 regional fault in the area. The Cable Bay (CB), Virgin River (VRSZ) & Black Lake (BLSZ) basin-scale shear zones/faults in the Eastern basin are also displayed, which also generally trend northeast. Basin information from Jefferson *et al.* (2007a), and permafrost information modified from Burgess *et al.* (1999).

To develop new exploration methods for deposits under sandstones and thick glacial overburden, a surficial geochemical study over a known deposit was undertaken. This involved a three-year geochemical survey of soil, till and sandstone horizons to evaluate geochemical signatures that may be related to the Phoenix U deposits situated 400 m below the surface.

This study builds on a surficial geochemical study by Hall and Bonham-Carter (2010) supported by Canadian Mining Innovation and Research Organization (CAMIRO), which concluded that the buried U deposits may be detected using mobile metals sourced from deposits. At their study site above the Cigar Lake U deposit, they detected anomalies of U, Co, Ni, and As using aqua regia digestion of humus samples taken over the surface projection of the ore zones. Based on these results, they recommended aqua regia digestion of humus in geochemical exploration for U deposits in conjunction with partial leaches of sodium pyrophosphate and ammonium acetate on B-horizon soil. We are building on their work by using similar soil leaches, digestions and analytical techniques, but more importantly by conducting dense resampling of metal anomalies in soils and spatially correlating these to the same U indicator elements that have high values in the uppermost sandstone below the glacial till cover. This is in hopes of detecting metal signatures from deeply buried U deposits; metals that were possibly transported to shallow sandstones, and eventually till and soils directly above via fluid pathways in reactivated faults and porous sandstone.

This paper presents multi-element data for soil, till and sandstones samples collected above the Phoenix deposits in 2011 through 2013, as well as the results of leaching experiments of humus. The data displays reproducible metal anomalies over the deposits over a three-year period.

Study Area

Geological Setting

The Proterozoic Athabasca Basin (Fig. 1) is a virtually undeformed, 1750 m thick, mainly fluvial siliclastic sedimentary succession deposited between 1740 and 1500 Ma (Creaser & Stasiuk 2007). These unconformably overlie metamorphosed basement rocks consisting of Archean to Paleoproterozoic granitoid and gneiss (Jefferson *et al.* 2007a). Basement rocks at the study site are part of the Paleoproterozoic Wollaston Domain of the Trans Hudson-Orogeny and consist of southeastwardly dipping metasedimentary rocks intercalated with granitic gneiss (Yeo & Delaney 2007). These include graphitic and non-graphitic pelite, semipelitic gneiss, felsic and quartz feldspathic gneiss, quartzite and rare calcsilicate gneiss. Near the Phoenix deposits, the Wollaston quartzite unit forms a prominent basement ridge that is entirely covered by Athabasca Group sandstones and whose crest to the west of the study area is up to 200 metres above the adjacent basement surface. Garnetiferous pelite, graphitic pelite and pelite of the Wollaston Supergroup are interpreted structurally and stratigraphically overlie the quartzite unit (Kerr 2011).

In the general area, only the Read and Manitou Falls Formations of the Athabasca Group are preserved. As noted by Kerr (2011), the Read Formation can generally be subdivided into a lower unit of pebble-cobble conglomerate to pebbly sandstone and an upper unit of well-sorted sandstone to pebbly sandstone. From bottom to top, the Manitou Falls Formation comprises three members; the Bird (MFb), Collins (MFc) and Dunlop (MFd). They are differentiated by their proportions of conglomerate, and clay intraclasts (Ramaekers *et al.* 2007; Bosman & Korness 2007). The gradationally overlying Dunlop member contains no conglomerate interbeds, and has greater than 0.6 % clay intraclasts (Yeo *et al.* 2001; Ramaekers *et al.* 2007; Bosman & Korness 2007).

Study Area and Uranium Mineralization

Denison Mine Corporation's Wheeler River Property is located 35 km northeast of the Key Lake, SK. The Property has experienced approximately 30 years of exploration, which culminated in the discovery of the Phoenix A & B1 deposits in 2008. Following the initial discovery, drilling yielded one of the highest-grade intersections of U in the Basin the next summer (6.0 m of 62.6% U_3O_8 in deposit A, drill hole WR-273; Press Release by Denison Mines Corp. August 2nd, 2009; Fig. 2). The mineral resources drilled to date are estimated to contain 52.3 (indicated) to 59.9 (inferred) million lbs of U_3O_8 in deposits A and B1 at grades of 15.6 wt.% and 29.8 wt.% U_3O_8, respectively (Arseneau & Revering 2010; Roscoe 2012). In these deposits, the mineralization is mostly fine-grained uraninite (pitchblende) with large amounts of Cu (up to 3,100 ppm), Pb (up to 9.83 wt %), Ni (up to 461 ppm), Co (up to 119 ppm), As (up to 170 ppm), and Zn (up to 1,070 ppm) (Kerr 2011). The ore is proximal to the unconformity between the early Paleoproterozoic crystalline basement rocks and the overlying quartz arenite, breccia, conglomerate and pebbly quartz arenite, approximately 400 m beneath the present day surface (Fig. 2). The ore bodies are located within or near the graphitic pelite of the Wollaston Supergroup and are elongate and narrow, approximately 25-50 m in width, generally striking NE-SW (Fig. 3). The WS Shear, the main structural feature associated with this deposit, is a NE-SW trending (055° azimuth) reverse fault that dips 55° to the SE at the base of the graphitic pelite along the footwall of the quartzite ridge (Arseneau & Revering 2010). The closely associated WS Hanging Wall Shear, running parallel east of the ore zones, is thought to have been the conduit for the mineralizing fluids along with the WS Shear (Arseneau & Revering 2010). Both shear zones are well defined in the basement rocks, but splay into secondary faults in the overlying sandstones (Fig. 2).

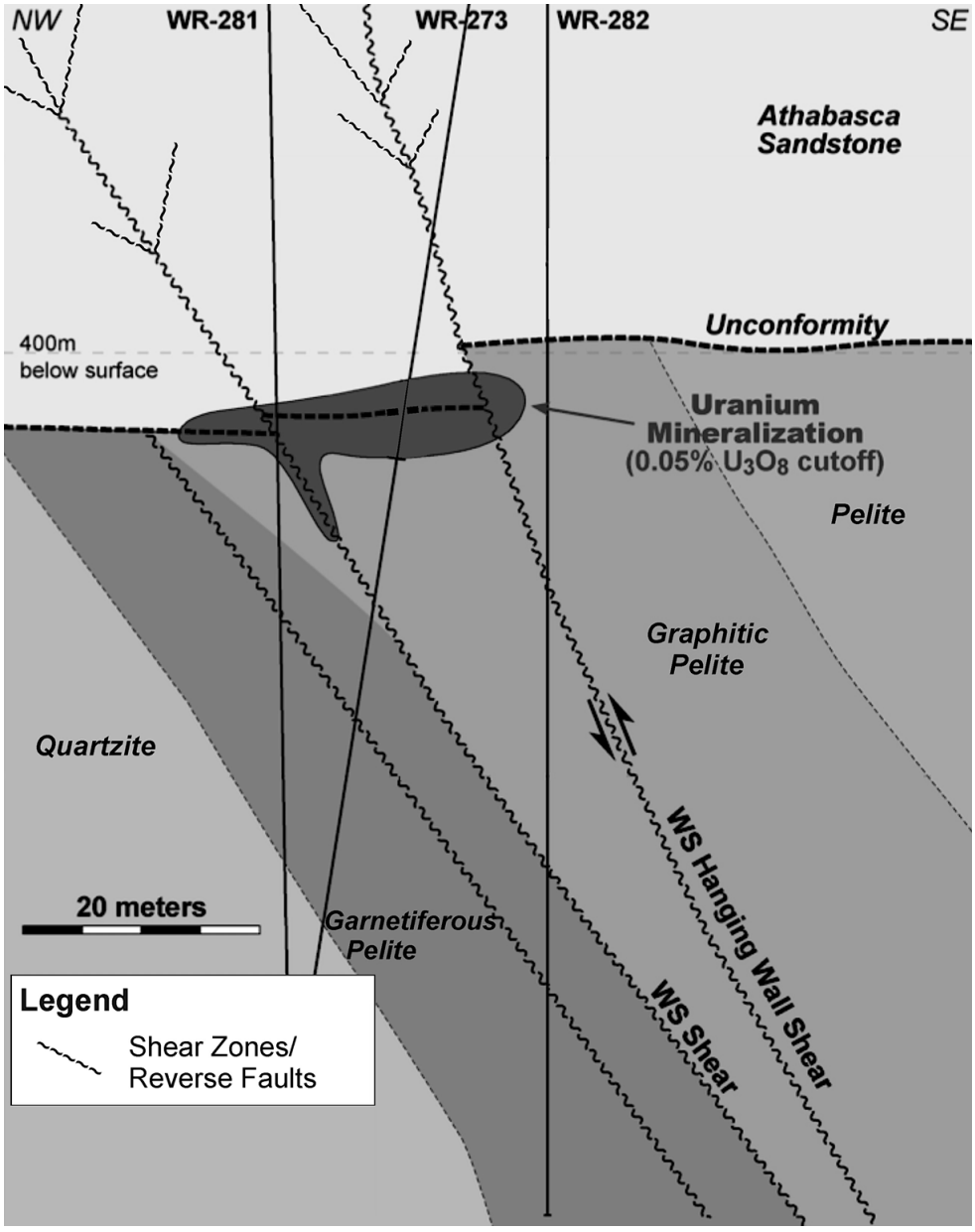


Figure 2: Schematic cross section of the Phoenix deposits (modified from Gamelin *et al.* 2010). The deposits are proximal to the unconformity between the early Paleoproterozoic crystalline basement rocks and the overlying quartz arenite, breccia, conglomerate and pebbly quartz arenite, approximately 400 m beneath the present day surface. The WS Shear & associated Hanging Wall Shear (curved dotted lines) are the main structural features associated with these deposits. The WS Shear is a NE-SW trending (055° azimuth) reverse fault that dips 55° to the SE at the base of the graphitic pelite along the footwall of the quartzite ridge. Both shear zones are well defined in the basement rocks, but splay and become diffused in the overlying sandstones.

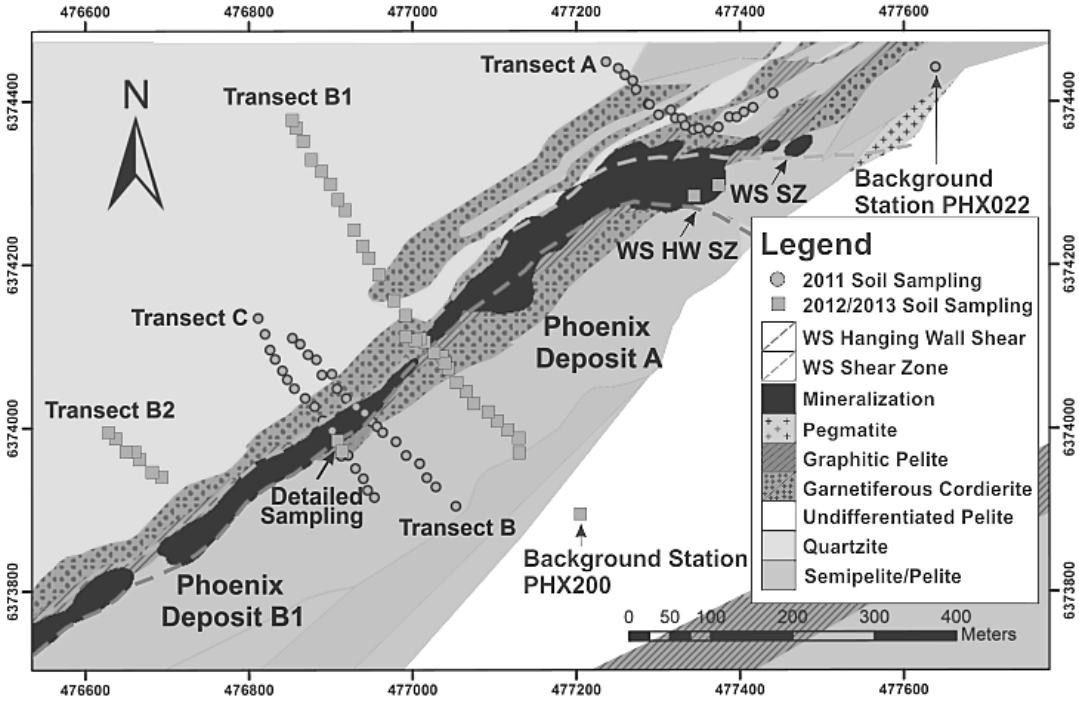


Figure 3: 2011 (circles) & 2012/2013 (squares) soil sampling sites plotted on Denison Mines Corp's basement geology map hosting the Phoenix A & B1 deposits, with the WS (WS SZ) & WS Hanging Wall (WS HW SZ) shear zones bounding them to the west and east, respectively. 2011 sampling sites comprise Transects A through C, while Transects B1, B2 (off-strike transect), and detailed sampling sites encompass 2012 and 2013 follow-up sampling. The sampling sites are approximately 10-15 metres apart. Background sampling sites PHX022 (2011) & PHX200 (2012) are shown to the northeast and south approximately 150 and 130 m away from the ore zones, respectively. Coordinates are projected in UTM, NAD 83, Zone 13.

Climate, Topography & Quaternary Glacial Sediments of the Study Area

The Athabasca Basin lies in a region of sporadic discontinuous permafrost within Northern Saskatchewan (Fig. 1) with sub-arctic climate characterized by long, cold winters followed by warm, wet summers, and approximately 482 mm of annual precipitation (Dimitrov *et al*. 2014). The surface topography consists mainly of gently rolling hills of glacial deposits. These are composed of eskers, outwash sand plains, drumlins, till plains and glaciofluvial moraine plain deposits (Campbell 2007). This geomorphological setting is

typical of the "taiga" forestland emblematic to the Basin area, and typically contains more than 90% young jack pine in the order of 2 to 3 m tall (Fig. 4) with rare older stands up to 5 to 10 m high. Black spruce is usually limited to the fringes of water bodies and low boggy areas. The trees are set in a thin carpet of white caribou moss (lichen) with local clumps of shrubs.

The regional ice flow record in the Basin is related to the late stages of the Wisconsinan deglaciation that began 9000 to 8700 years ago (Campbell 2007), with the area becoming ice-free by 8100 BP (Schreiner 1984; Dyke *et al*. 2003). During the Wisconsinan, the Keewatin Lobe of the Laurentide Ice Sheet advanced to the southwest from Nunavut in a fan shape across the Athabasca Basin with a flow direction of almost due west (Schreiner 1984; Dyke & Dredge 1989). However, evidence for older ice flow directions have been reported at various locations in the eastern Athabasca Basin (Campbell 2007). Along the northern margin of the Athabasca Basin, straie and provenance of multiple till units indicate a southwestward ice flow onto the Basin that predated the main westward flow (Ramaekers 1976; Schreiner 1984; Campbell 1998). This is consistent with the most dominant ice flow direction observed in the eastern Basin (Fig. 5, top), which is interpreted to be this southwesterly direction as deduced from the morphology of large drumlins (Campbell 2007). This ice flow direction is believed to represent the flow of Keewatin ice during the initial Late Wisconsinan glacial ice advance (Campbell 2007). The Eastern Athabasca has extensive glacial till cover which varies in thickness both regionally and at the study area. Glacial till cover can reach thicknesses of more than 100 m in parts of the eastern Athabasca Basin (Campbell 2007) but is approximately 25 to 30 m thick on the Wheeler River property. The surficial geology (Fig. 5, inset) of the property, like the southeast Basin, is characterized by relatively flat-lying glacial moraine plain in a larger region of moraines, drumlins and

subordinate eskers (Schreiner 1984; Campbell 2007). No drumlins or eskers occur directly on top of the sandstone bedrock at the study area; rather, these features appear several km to the northeast, which themselves trend southwest (210–225°; Campbell 2007).

Figure 4: Typical view of the forested study area, covered in 2-3 m high jack pine and in lower-lying areas, black spruce trees (not shown). The sampling area is relatively flat and homogenous, with similar soil horizons at each site, and extensive caribou moss on the forest floor. Photograph taken in September 2011.

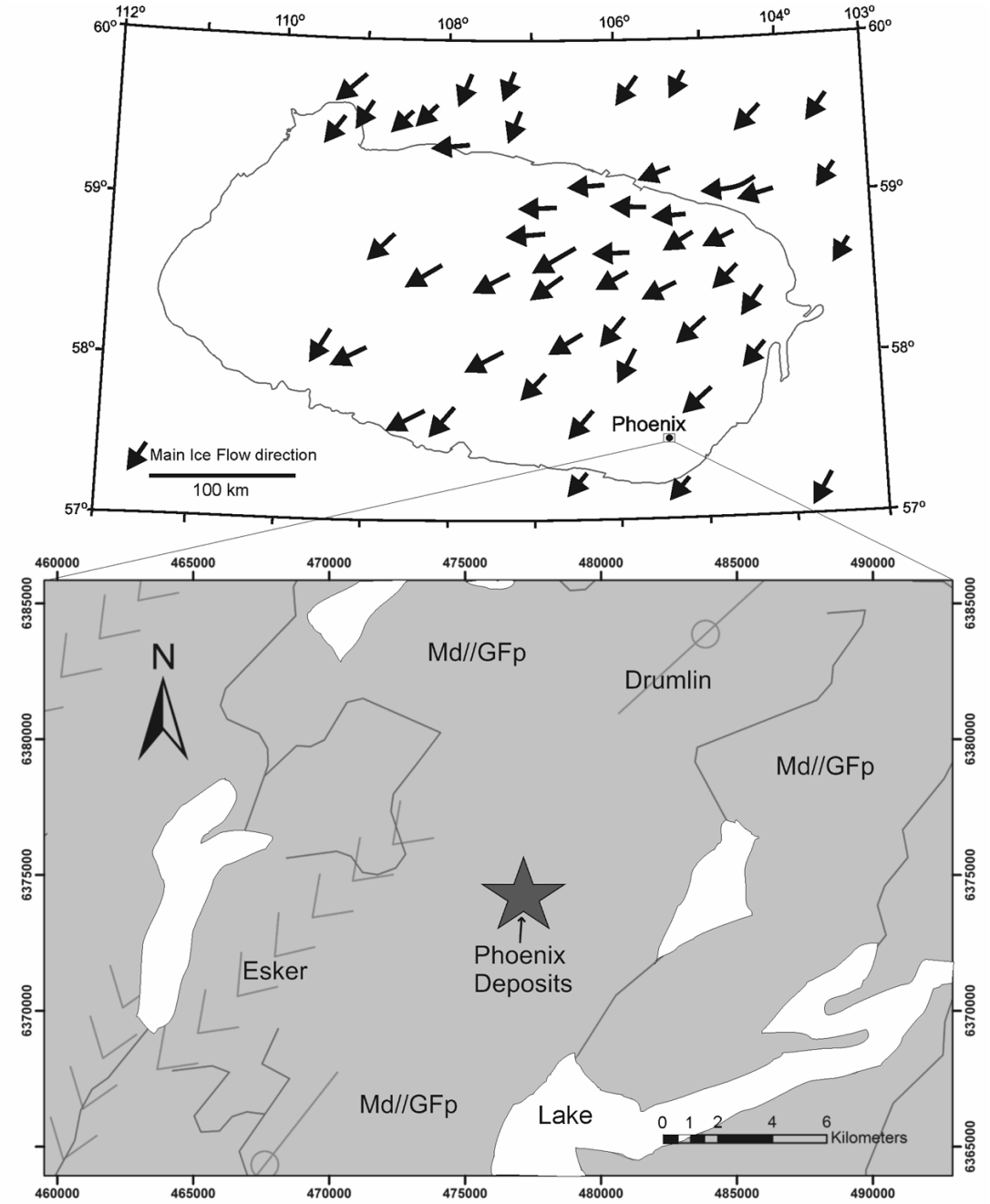


Figure 5: Deglaciation of the Athabasca Basin beginning approximately 9000 to 8700 years ago in Northern Saskatchewan. The dominant ice flow direction in the Eastern Athabasca is to the southwest as shown by the black arrows (modified from Campbell 2007, basin outline from Jefferson *et al.* 2007a). Inset shows property scale (approximately 1:60,000 scale) surficial geology map at Wheeler River (modified from Schreiner 1984) with location of the Phoenix deposits (shown in middle). The deposits are situated in an area of glaciofluvial moraine plain often molded into drumlinoid form (Md//GFp), within an area of streamlined moraine and subordinate eskers, though none of these features directly overlie them. The southwest-trending eskers and drumlins are symbolized by sinuous herringbone patterns and drumlins by lines through open circles. Coordinates are projected in UTM, NAD 83, Zone 13.

Soil Conditions

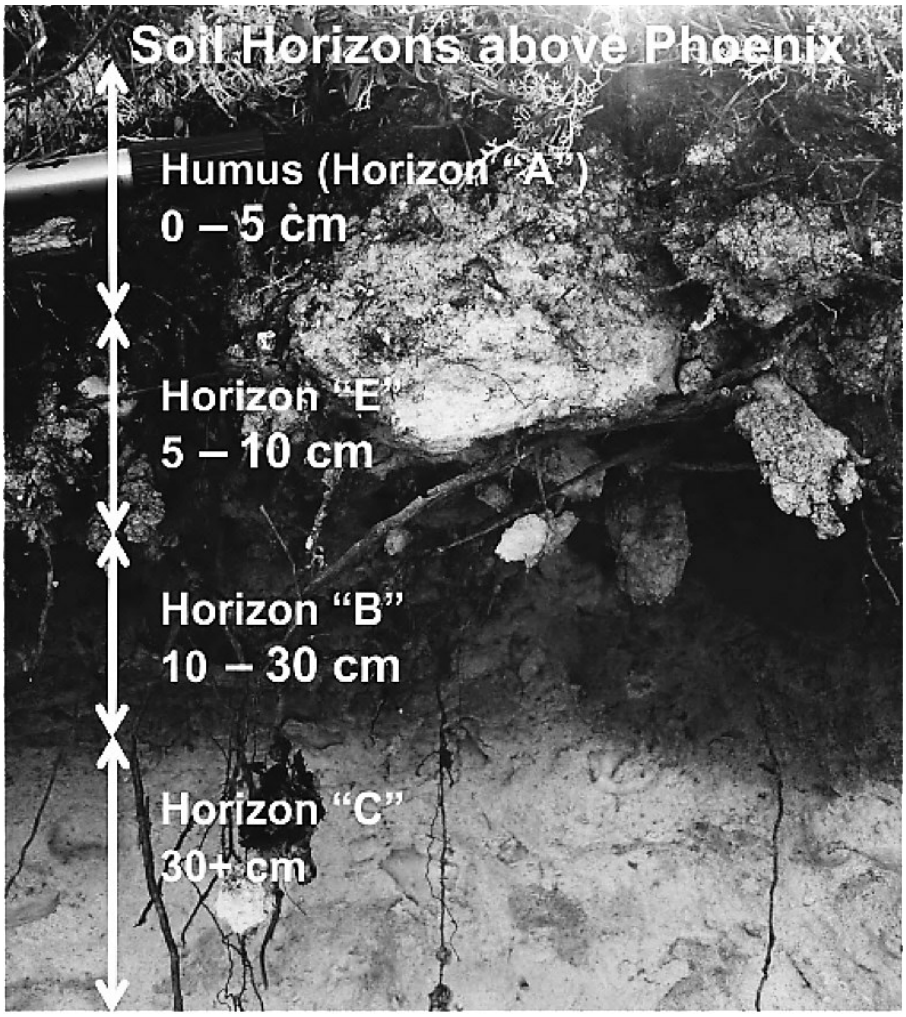


Figure 6: Typical soil horizon profile at the study area. The humus layer includes charcoal from a previous forest fire event. The photo was taken at 57° 30' 32.285" N, 105° 23' 10.768" W.

At most sampling sites, well-developed soil horizons are present (Fig. 6). The organic matter (0 to 5 cm from surface) is usually expressed morphologically by a darkening of the surface soil (very dark black) and is relatively dry. Horizon E (5-10 cm) is sandy, greyish-white and the boundary with the overlying humus is gradational in a cm thickness in many places. The B-horizon ranges in thickness from 10 to 30 cm, is yellowish-brown in color, and has a well-defined contact with the overlying E-horizon, which in some places is very rich, dark brown. The top-most C-horizon is a glaciofluvial, sand-rich till, occurs deeper than 30

cm, and comprised of medium to coarse-grained sand with minor cream coloured silt with quartz and potassium feldspar clasts and little to no clay.

Samples

Selection of Soil Sampling Sites

Great care was taken to collect samples from similar surficial conditions including topography, vegetation, and water drainage, as a homogenous soil sampling environment is one of the most important aspects of a surficial geochemical survey (Kelley & Kelley 2003). The study area is dry, with well-drained glacial sediments, and there are no swamp or bogs in the immediately vicinity of the deposit. Surficial geochemical anomalies over concealed mineral deposits are commonly offset from the centers of deposits, and some are located over the edges of deposits (Hattori *et al.* 2009). Therefore, over a three-year period, soil samples for this study were collected along transects, at locations over the deposits and sample sites off-strike of the mineralized zones (Fig. 3). The transect, or traverse, method facilitated sampling "background values" at sites relatively far away from the ore zones in the specific soil environments being studied (Kelley & Kelley 2003). More importantly, this method also allowed for sampling perpendicular to the last main ice flow direction from northeast to southwest. To provide further confidence of background values, background sites, >100 meters away from the deposits, were sampled in 2011 to 2012, as well as a background sampling traverse sampled off-strike from the known mineralization in 2012.

2011 Sampling

Three transects (A, B and C) were sampled at 10 to 15 m spacing (dark grey dots in Fig. 3). Such spacing between sample points was required to detect any anomalies possibly sourced from the narrow ore bodies below. Transect A (northernmost line of circles, Fig. 3) was sampled from the northwest to southeast across the northern extension of the area over

deposit A and included 22 sampling locations over a length of 464 m. Transects B (length of 298 m) and C (length of 271 m), comprising 19 and 18 sampling sites, respectively, were sampled from the northeast to southwest across the area over the B1 deposit (middle and southernmost lines of circles, Fig. 3). A total of 226 soil samples (humus, B-, E-, and C-horizon) were collected at a total of 59 sites in undisturbed forest.

2012 Sampling

Transects B1 (634 m in length) and B2 (88 m in length), which consisted of 30 and 7 sampling sites, respectively, were sampled from northwest to southeast across the surface projection of the B1 deposit at 10 to 15 m sample spacing (gray squares, Fig. 3). Transect B1 was sampled farther to the northwest and longer in length than Transect B, as to detect possible metal dispersion from the southeast dipping (55°) WS Shear zone. Assuming a consistent strike and dip, the surface projection of the fault should lie 280 m west of the deposits. However, since the fault splays steepen and become diffuse in the sandstones, the secondary faults may project considerably closer to the ore (Fig. 2). Sampling along Transect B2 was carried out off-strike to the west of the B1 deposit to obtain background values. Apart from sampling along transects, dense sampling was completed at 7 sites around the site of the most elevated U value (PHX028, 5.7 ppm U) from 2011 to evaluate reproducibility of results. Two sites southeast of the surface projection of the A deposit were also sampled close to Transect A, mainly for additional C-horizon till samples. A total of 112 soil samples were taken at 55 sampling sites in 2012.

2013 Sampling

Detailed sampling of humus and B-horizon was also completed at 5 sites around the site containing the highest U concentrations in humus from 2011-2012 to evaluate the reproducibility of the results for a third year in a row. A total of 9 soil samples (4 humus, 5

B-horizon) were taken at 5 sampling sites in 2013.

Till Samples

The upper C-horizon glacial till sampled in this program (30-50 cm depth) was well-sorted medium to coarse-grained sand with minor cobbles and K-feldspar grains. This was underlain by mostly cobbles (1-2 cm diameter) and boulders (>5 cm diameter) intermixed with the above sandy material, which indicates that it may be lodgement till. The Till 2 unit in the eastern Athabasca, according to Campbell (2007) comprises of a soft, matrix-rich sandy upper till with a lodgement and basal melt-out facies, and an ablation facies forming a veneer locally.

Sample Collection

Sampling along each transect was completed over a one to two day period using a Dutch auger and trowel after careful visual examination of the soil profile at each site to ensure homogenous samples. We sampled humus (~0.5 kg), E- (~1 kg), B- (~1 kg) and C-horizon (~2kg), and placed the samples in freezer bags. Every 20 sites, where material was available, large amounts were collected from all horizons to make duplicate samples. Till samples were not collected at all sites because large, tightly-packed boulders (>20 cm) prevented till material from being collected.

Analytical Methods

In Field

On the same day of sampling, the pH and conductivity of E-horizon and B-horizon samples were measured in a slurry of soil and distilled water (1:1) using an Oakton pHTestr 2 for pH and Combo PH/EC/TDS/Temperature meter for electric conductivity. We mixed 2-3 grams of soil with equal parts water in small plastic cups, and mixed vigorously with a popsicle stick for 5-10 seconds before taking the readings.

Till Samples

Bulk-composition of till was measured with Philips PW 2400 X-ray fluorescent spectrometer at the University of Ottawa, after a glass disk was made from rock powder mixed with 78.52% $Li_2B_4O_7$, and 21.47% $LiBO_2$.

Leaches and Digestion

Trace element composition data of soils and till were measured at ACME Analytical Labs in Vancouver, British Columbia, Canada. All samples were dried at 60°C and sieved to -80 mesh (0.177 mm) before leaching and digestion. Humus and silt (<64 μm) fractions of C-horizon till samples were digested by aqua regia (AR). B-horizon samples were leached by ammonia acetate, pH 5 (AA5) and 0.1 M hydroxylamine (Ox, 2011 samples only). 3 sets of duplicate samples from 2011 and 2012 were given different sample numbers, and this data were used to evaluate the precision of the overall data. The data suggests a reproducibility of ±2% for humus samples. Lab standards used were OREAS45CA for humus, DS3 for B-horizon, DS8 and OREAS45C for C-horizon silt fraction samples. The whole rock geochemical compositions of sandstone samples collected from drill cores were provided by Denison Mines Corp., who submitted them to the Saskatchewan Research Council laboratories for partial HNO_3-HCl & aqua regia digestions. Analyses were completed via inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission (ICP-OES) (analytical detection limits, Table 1). Geochemical values reported as less than detection limit were reassigned values of zero for calculation of basic statistics.

Table 1. *Detection limit of analytical methods*

Method 1F-MS: Geochemical Ultratrace Aqua Regia Digestion (Acme Labs)									
Analyte	Mo	Cu	Pb	Ag	Ni	Co	As	U	W
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
DL	10	10	10	2	100	100	100	100	100

Method 1SLE: Ammonium acetate (pH=5) leach (Acme Labs)									
Analyte	Mo	Cu	Pb	Ag	Ni	Co	As	U	W
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
DL	10	20	20	3	50	20	100	5	10

Method 1SLM: Hydroxylamine leach (Acme Labs)									
Analyte	Mo	Cu	Pb	Ag	Ni	Co	As	U	W
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
DL	10	20	20	3	50	20	100	5	10

Method ICPMS1: Sandstone Exploration Package (SRC Labs)									
Analyte	Mo	Cu	Pb	Ag	Ni	Co	As	U	W
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
DL	10	10	20	10	10	10	10	10	100

Leaching Experiments

To evaluate the sites of metals in humus, several samples were subjected to various acid leaches at the University of Ottawa. The samples were dried at 60°C, and sieved to -80 mesh. After adding Milli-Q water, the samples were manually shaken every hour for a 2-hour period at room temperature. The solution was centrifuged to separate the solution from the residue for the measurements of the concentrations of U, Pb, Mo, Cu, Ni and Co using Agilent 7700 ICP-MS. Similar procedures were repeated with 0.02 M HBr, 1 N HNO_3 (25°C) and a hot (100°C) concentrated mixture of 3:2 HF-HBr. For the weak HBr leach, the sample was placed in an ultrasonic bath for at least 1 hr. For the HNO_3 leach, the sample was left at room temperatures (or 100°C) overnight after 1 hr of ultrasonic bath. For the concentrated HF-HBr, samples in a screw-top Teflon vial were placed on a hot plate for 100-

120°C overnight. All acids used are double distilled at sub-boiling temperatures, and purchased from Seastar Chemicals, BC.

Separation of Silt Fractions in Till Samples

Till samples were dried at room temperature for 24 hours and sieved with stainless steel sieves. The silt fraction (<64 μm) was then sent to ACME Labs for aqua regia digestion followed by analyses with ICP-MS.

Mapping Software

The spatial distributions of soil and sandstone data were analyzed and plotted using the ArcMap™ function of the ESRI ArcGIS™ 10.0 software platform. The sandstone data were further interpolated element-by-element, inside a predefined shape, by the inverse weighted distance (IDW) method to determine unknown values based on proximity to known values in a defined neighborhood (De Smith *et al*. 2008).

Results

Background Values and Defining Anomalies

Anomalies were defined three ways. The first method involved calculating the ratios of metal values in the sampling area to background site values. In 2011 sampling, metal values from sampling site PHX022 were considered to be background to the sampling area above the known mineralization. This site, more than 150 m, or 10 times sample collection spacing, away from the defined edges of the deposit surface projections at the time was considered far enough from deposits to provide background values. In addition, the metal values at this site are similar to those obtained from sites near the ends of three transects, which supports this assumption (Table 2, Figs. 7 to 10). Peak to background ratios of greater than 3 for U and related metals were considered to be anomalous. This number was chosen for these datasets because it seems like a reasonable multiplication factor to effectively

isolate outlier values from the population of metals of interest. This numerical factor has been used in geochemical exploration for U previously, as Dyck (1975) defined radioactive anomalies in groundwater to be a threefold or greater increase in content compared to the background measurement. However, to ensure our values passed an anomalous threshold considered to be geostatistically valid, two additional definitions of geochemical anomalies were used.

The second method of defining anomalies is calculating mean and standard deviations of an entire population of metals of interest. Statistically, metal values are considered anomalous when they are more than 2 standard deviations above the mean value of the normally distributed population (Hawkes & Webb 1962).

The third method in defining anomalies used quantile–quantile (Q-Q) plots (Fig. 7). In this study, values were considered anomalous when they appeared in a distinct population apart from normally distributed values on a normal Q-Q plot. The normal Q-Q plot for the 2011 humus data shows a polymodal distribution for U, confirming the presence of a highly anomalous value distinct from the approximately normal distribution of data (Fig. 7A). The normal Q-Q plot for B-horizon data in 2011 also displays a polymodal distribution of the data similar to the humus data, a single point that appears distinctly apart from the normally distributed population (Fig. 7B).

Values yielding the highest peak to background ratio are considered anomalous by the other two definitions, so the highest values for U and relevant pathfinder elements in each transect pass all three criteria for being true anomalies. For example, the 5.7 ppm U value obtained for humus in 2011 has the highest peak to background (28 times) of U values in the survey, is the highest above the population mean+2σ (1.9 ppm), and easily observable as a distinct population in the Q-Q plot for humus in 2011 (Fig. 7a).

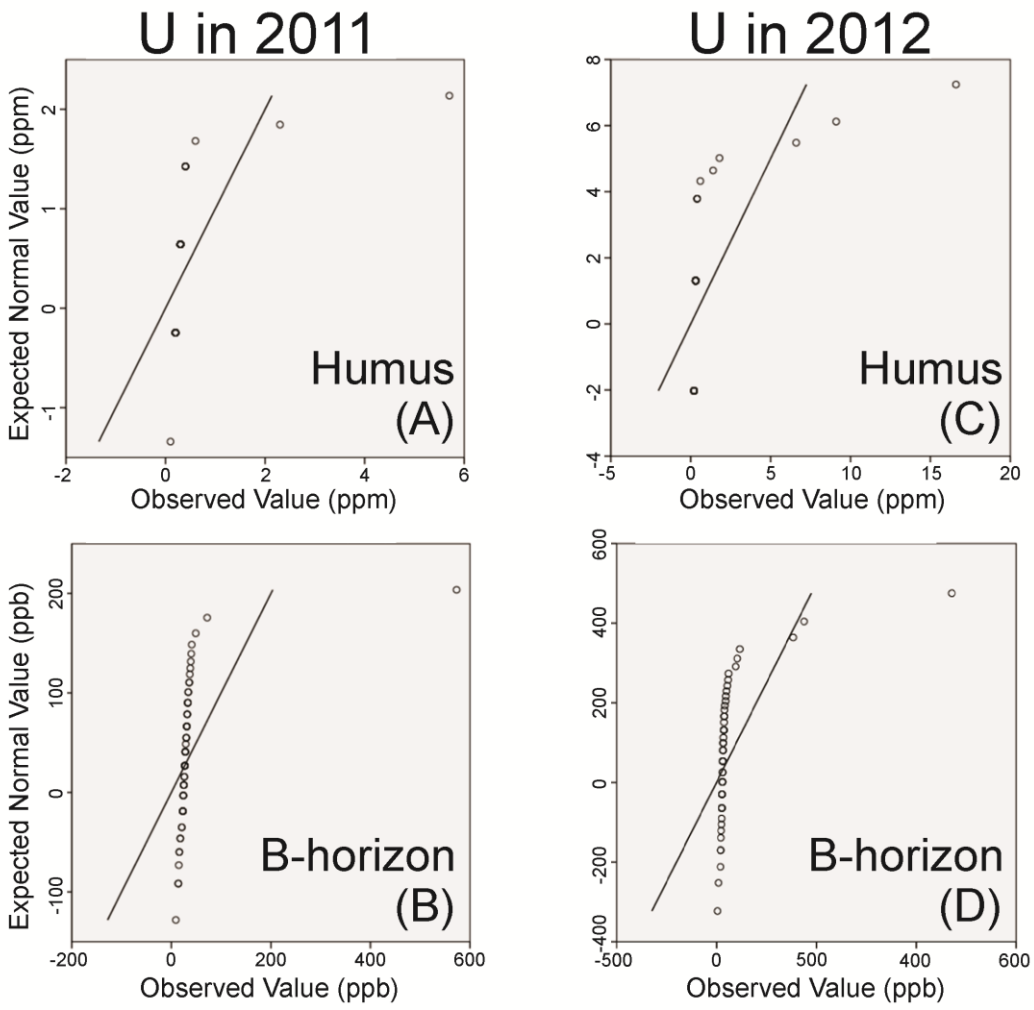


Figure 7: Q-Q plots (A = humus results in 2011, B = humus results in 2012, C = B-horizon results in 2011, D = B-horizon results in 2012) of U in humus & B-horizon soils using aqua regia digestion & ammonium acetate leach, respectively. Values are considered anomalous when they appear in a distinct population apart from the linear, normally distributed values usually observed in normal Q-Q plots. Anomalous values are overlying or immediately adjacent to the surface projections of the ore zones & basement location of the deposit-hosting WS Shear zone.

Table 2. *Values in humus & B-horizon soil from the background sampling sites and B2 "barren" traverse in 2011-2012.*

	Soils from background site PHX022 No. of sites = 1 Value	Soils from background site PHX200 No. of sites = 1 Value	Minimum	Soils from "barren" B2 Traverse No. of sites = 7 Mean	Maximum
pH	5.6	8.0	8.4	8.7	9.0
Conductivity	6.0	323.0	12.0	30.0	49.0
ORP	na	281.0	117.0	178.0	203.0
Aqua regia digestion - Humus					
As (ppm)	0.50	1.10	0.20	0.53	1.00
Al (%)	0.27	0.26	0.26	0.31	0.39
Ba (ppm)	166.0	247.0	167.0	264.0	366.0
Ca (%)	0.31	0.36	0.24	0.35	0.51
Co (ppm)	0.3	0.6	0.4	0.5	0.6
Cu (ppm)	9.00	14.20	10.00	12.40	14.60
Fe (%)	66.40	0.21	0.19	0.23	0.26
K (%)	0.03	0.05	0.03	0.04	0.05
Mn (ppm)	269	387	76	152	259
Mo (ppm)	0.11	0.19	0.08	0.12	0.16
Na (%)	0.003	0.004	0.001	0.001	0.002
Ni (ppm)	3.5	50.0	3.7	5.4	6.5
Pb (ppm)	24.10	36.00	19.00	23.00	26.00
Zn (ppm)	66.0	49.0	30.0	34.0	42.0
U (ppm)	0.2	0.3	0.2	0.3	0.3
W (ppm)	bd	bd	0.1	0.1	0.1
Ammonium acetate leach (pH=5) - B-horizon					
As (ppb)	bd	bd	bd	bd	bd
Al (ppm)	5234	420	395	478	575
Ba (ppb)	4364	7736	2964	5010	8057
Ca (ppm)	bd	28	3	11	23
Co (ppb)	bd	41	10	11	20
Cu (ppb)	47	109	35	74	148
Fe (ppm)	24.00	33	17	32	51
K (ppm)	bd	bd	bd	bd	bd
Mn (ppb)	516	3777	153	695	2807
Mo (ppb)	bd	bd	bd	bd	bd
Ni (ppb)	bd	bd	bd	bd	bd
Pb (ppb)	200	1118	433	773	1207
Zn (ppb)	295	227	bd	bd	235
U (ppb)	16	39	25	32	46
W (ppb)	bd	bd	bd	bd	bd

Notes: na = not analyzed, bd = below detection limit

2011 Results

Humus Data

The humus samples collected in 2011 display significant variations in the concentrations of U, Pb, Co, Ni, Mo, and W. These metals, especially Co and Ni, are considered to be pathfinder elements for U deposits in sandstones, till, peat and soil in the Athabasca region (Jefferson *et al.* 2007b). All the aforementioned element abundances are highest at soil sampling sites overlying the surface projection of the deposits, and are also found directly above the WS Hanging Wall Shear zone where it occurs at the unconformity.

In the 2011 survey, peak to background ratios of element concentrations are up to 28 for U (up to 5.7 ppm, 0.2 ppm background value), 44 for Mo (up to 4.8 ppm, 0.11 ppm background), 17 for Co (up to 5.2 ppm, 0.3 ppm background), 18 for W (up to 100 ppm, 0.5 ppm background), 5 for Cu (up to 50 ppm Transect C, 9 ppm background) and 1.9 for Ni (up to 6.5 ppm, 3.5 ppm background) (Fig. 8).

These values are confirmed to be anomalous when compared to the metal population means from the 3 sampling transects. For U, outliers are present above 1.9 ppm (0.4ppm+1.5 ppm), and for Mo values are present above 2.77 ppm (0.25 ppm+2.52 ppm). They are also anomalous in Co, with values present above 1.84 ppm (0.52 ppm+1.32 ppm). W, Cu and Ni also display anomalies, with values present above 21.3 ppm (9.1 ppm+12.2 ppm) for Cu, above 6.7 ppm (0.69 ppm+5.96 ppm) for W, and above 7.14 ppm for Ni (3.4 ppm+3.76ppm). In both the A and C transects, U anomalies (2.3 ppm Transect A, 5.7 ppm Transect C) occur above the surface projection of the shear zone at the unconformity. Mo (0.9 ppm Transect A, 4.8 ppm Transect C) is anomalous above deposit B1 along Transect B and above the WS Hanging Wall shear zone adjacent to the surface projection of the mineralized zone in Transects A and C. Co concentrations (1.8 ppm Transect A, 5.2 ppm Transect B) are

anomalous in the area above the shear zone in Transect A and C, as well as above the B1 mineralization surface trace in Transect B. Ag anomalies (0.98 ppm Transect A, 0.19 ppm Transect C) are located both above the Hanging Wall shear on Transect A, and above the surface trace of the B1 mineralization in Transect B. Sharp W anomalies (17 ppm Transect A, 100 ppm Transect C) are also located above the WS shear in Transect A, and above the B1 mineralized zone in Transect C. Elevated values of Cu are also present in these same locations (18 ppm Transect A, 50 ppm Transect C) as are those of Ni (6.5 ppm Transect A, 15 ppm Transect C).

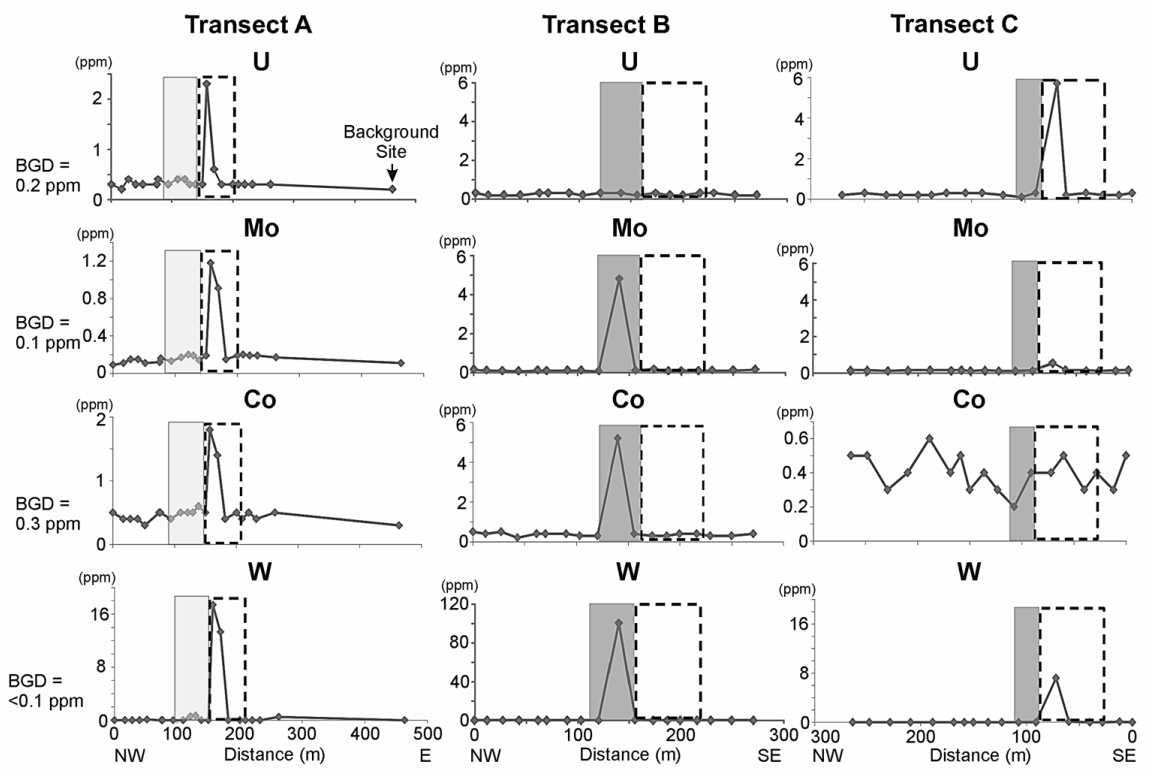


Figure 8: Abundances of trace metals in humus along Transects A, B and C, after aqua regia digestion (2011 sampling programme). The light grey box (Transect A) indicates the area directly above deposit A, dark grey (Transects B & C) the area above deposit B1, and the dotted rectangle encompasses the likely surface projection of the splayed WS Hanging Wall Shear Zone in the underlying basement rocks. Background (BGD) metal concentrations are denoted on the y-axis of each chart.

B-horizon Data

The concentration of U in both AA5 and Ox leaches of the B-horizon soil samples in 2011 also displays high concentrations with respect to the background values (Fig. 9). Peak to background ratios of element concentrations are up to 36 for U (up to 573 ppb U, background of 16 ppb for AA5; 533 ppb U, background of 44 ppb for Ox). Concentrations of W and As are also high in the B-horizon; up to 15 ppb W in AA5, up to 16 ppb in Ox, and up to 174 ppb As. Values are also anomalous in the B-horizon. Anomalous values are observed in the area directly above the surface projection of the mineralization and the WS Hanging Wall shear zone at the unconformity. For U, anomalies exist above 182 ppb in AA5 leach (37.8 ppb+144.2 ppb), and in Ox leach, above 172 ppb (44.9 ppb+144.2 ppb). Anomalies also exist in W values above 4.5 ppb (0.27 ppb+4.2 ppb) in Ox leach, and in AA5 leach with W values above 7.11 ppb (0.71 ppb+6.2 ppb). High values are also present for As above 79.5 ppb (9.3 ppb+70.2 ppb).

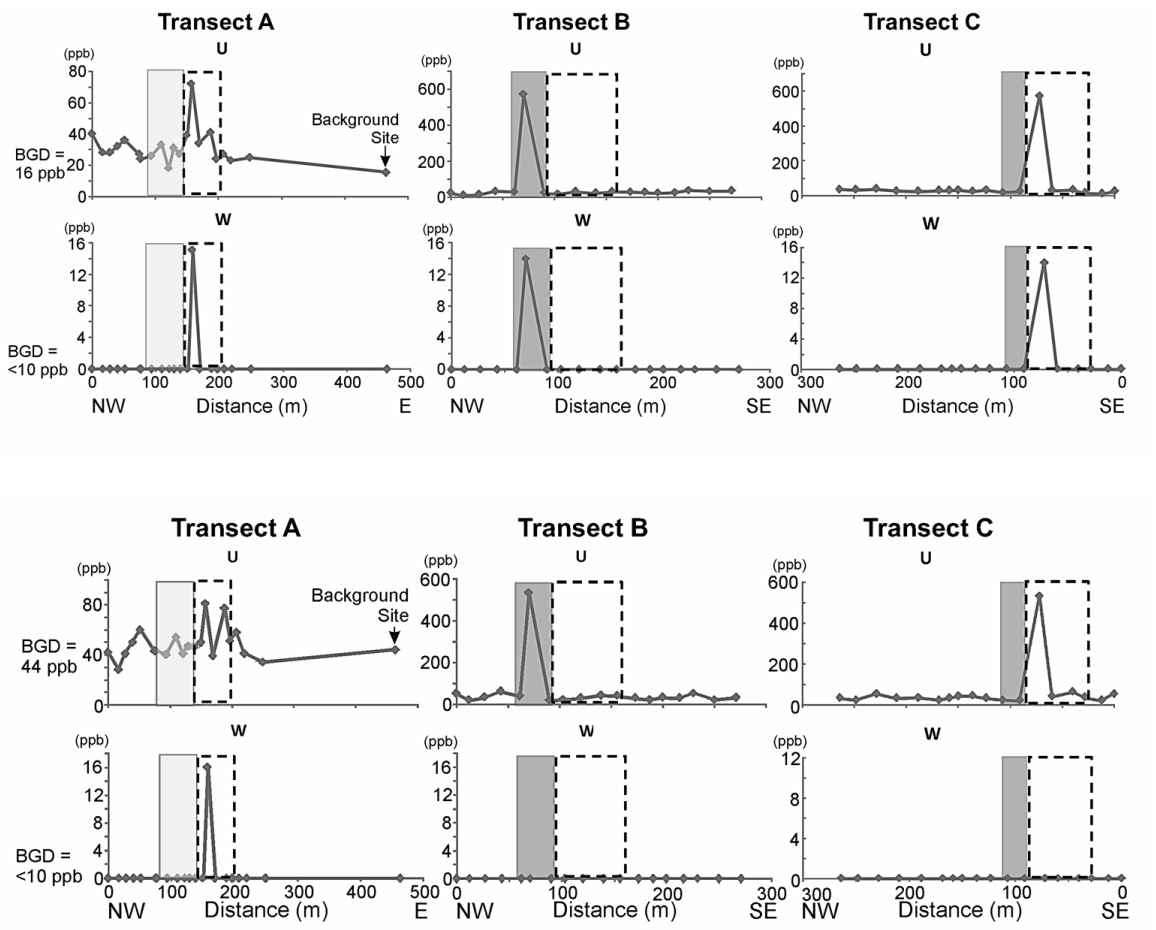


Figure 9: Trace metal abundances along the 2011 transects (top): U & W in ammonium acetate pH 5 leach of B-horizon soil. Traces of ore and fault zones denoted as in Figure 8. 9b: Trace metal abundances along the 2011 transects (bottom): U & W in B-horizon soil after hydroxylamine leach. Ore and fault zones denoted as in Figure 8. This leach does not detect as many anomalies in U or its respective pathfinder elements as the ammonium acetate leach, especially for U and W in Transects B & C. Background (BGD) metal concentrations are denoted on the y-axis of each chart.

Till Geochemical Data

The silt fraction of selected C-horizon till samples in 2011 contain high values of Mo, Cu and Ni, but the values are not qualified as anomalous based on the criteria outlined above (Fig. 10). Peak to background ratios of element concentrations are greater than 1 for Mo (up to 0.21 ppm and 0.15 ppm background), 2 for Cu (up to 2.2 ppm and 0.98 ppm background)

and 2.5 for Ni (5.5 ppm and 2.2 ppm background), with all being more pronounced over the surface trace of deposit A. Anomalous U values were not observed in the till.

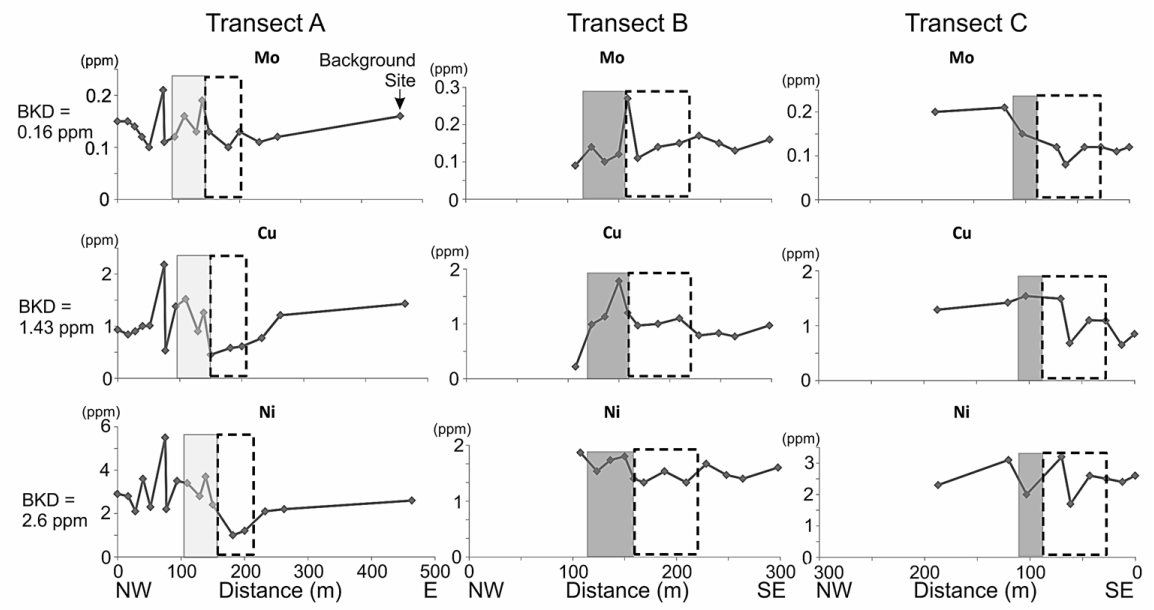


Figure 10: Trace metal abundances along the 2011 transects: Mo, Cu and Ni in the silt fraction of C-horizon glacial till after aqua regia digestion. Ore and fault zones denoted as in Figure 8. The metal values do not have as strong peak to background ratios as humus digestion and B-horizon soil leaches, and are not anomalous. Background (BGD) metal concentrations are denoted on the y-axis of each chart.

2012 Results

Background Values

Background values were measured two ways. The first method was similar to 2011 sampling since metal values from sample site PHX200, more than 130 m southeast of the mineralization, were considered background. The highest values from all sampling sites were compared to this site. Peak to background ratios were then measured using sampling sites with the highest metal values above the mineralization and shear zones and comparing them to the values of the PHX200 site (values, Table 2). Metal concentrations at PHX200 are low, and very similar to the PHX022 background site from 2011 sampling.

The second method was sampling a traverse considered "barren", the B2 Transect, to provide an additional measure of background metal concentrations off strike from the known mineralized zones on the northwest side of the B1 deposit. This also provided a chance to test background measurements on the opposite side of the sample area, and see how much these values differed from using a single background site, potentially avoiding a biasing of results. This method was used to evaluate any anomalies present from highest peak to background measurements using values of the PHX200 site. Metal values from Transect B1 and dense sampling were considered anomalous when observed to be greater than two standard deviations above the mean values of Transect B2 (Table 2). Values from the Transect B2 were low when compared to metal values in the B1 Transect sampled in between deposits A and B1.

B1 Transect

Peak to background concentrations for samples from the B1 transect in 2012 were highest in U and several of its pathfinder elements, especially when compared to peak to background ratios from 2011 (humus and B-horizon, Fig. 11). Although the data did not display very pronounced peak to background ratios for Ni with a ratio of only 1.5 (up to 6.6 ppm, 4.5 ppm background), they were quite pronounced for other elements; up to 1.9 for Cu (up to 27 ppm, 14 ppm background) in humus. As well, they were up to 3 times for U (up to 117 ppb, 39 ppb background) and higher for As (up to 448 ppb, <100 ppb background) in the B-horizon soil. Various metal values are also anomalous when compared to the mean+2σ of metal values from B2 Transect samples. Anomalous values for Cu are present above 15.5 ppm (12.4 ppm+3.06 ppm). In the B-horizon, anomalous values for U and As are observed above 45.6 ppb for U (31.7 ppb+13.9 ppb), and above 100 ppb for As (773 ppb+536 ppb).

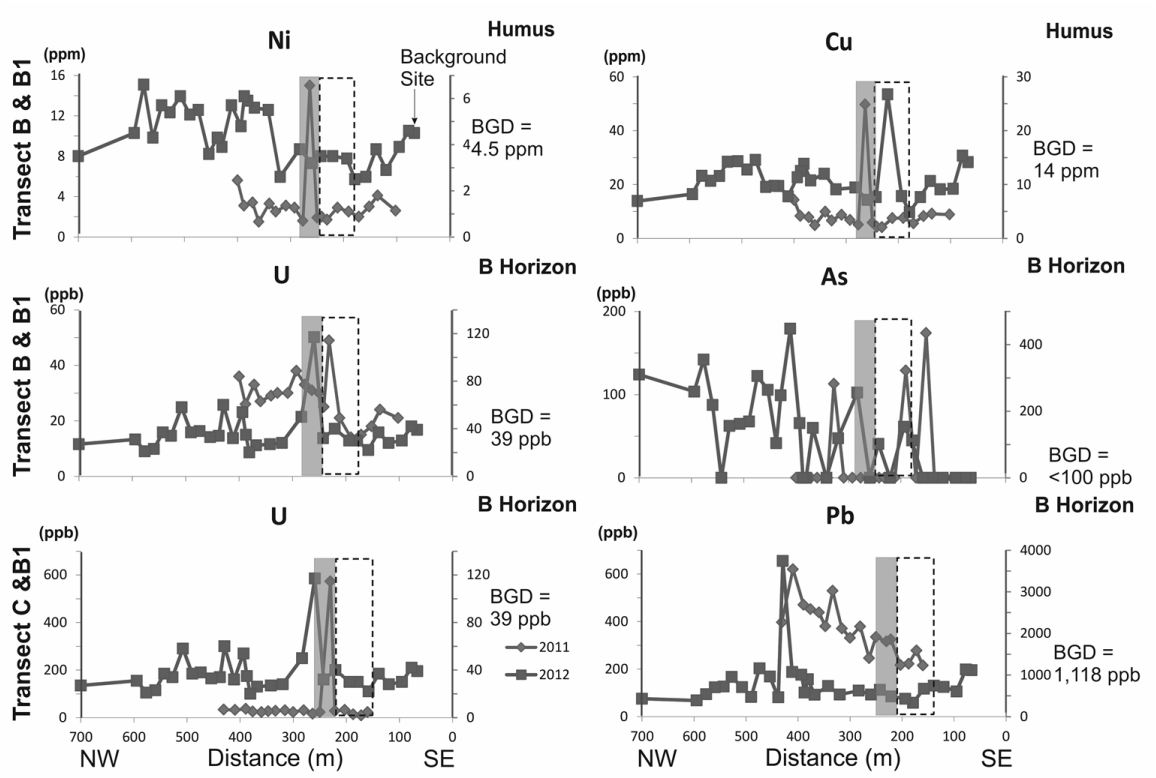


Figure 11: Trace metal abundances along Transects B & C in 2011 (denoted in diamonds) and B1 in 2012 (denoted in squares): U, Pb, Ni, Cu and As in humus and B-horizon soil after aqua regia digestion and ammonium acetate weak leach. Ore (deposit B1) and fault zones denoted as in Figure 7. U, along with pathfinder metals Cu and Pb, displayed excellent reproducibility of values from year to year. Background (BGD) metal concentrations are denoted on the y-axis of each chart.

Detailed Sampling in the Area with the Highest Metal Values

Additional soil samples were collected via dense sampling near the PHX028 sampling site, which yielded the highest U value in humus in 2011. This site is located immediately above the southern edge of the B1 deposit surface trace, where values of 5.7 ppm and 16.6 ppm U were obtained from humus in 2011 and 2012 (Fig. 12, top). The 2012 results confirmed the reproducibility of the 2011 anomalies, especially for U, W, Mo and Cu in humus, and U, Pb and As in the B-horizon. At sites PHX231 to PHX237 (samples 1 to 7 in Fig. 12, bottom) where dense sampling was conducted, peak to background ratios in

humus are as great as 161 for W (up to 16.9 ppm, 0.1 ppm background), 80 for U (up to 16.6 ppm, 0.3 ppm background) and 5 for Mo (up to 1.0 ppm, 0.19 ppm background). In the B-horizon, peak to background ratios are more than 30 times for U (up to 1178 ppb, 39 ppb background) and 4 times for As (up to 428 ppb, 100 ppb background) and 2 times for Pb (up to 2058 ppb, 1118 ppb background). Similar to 2011, these values occur over the surface trace of the B1 deposit, as well as over the WS Shear and the splay of the associated Hanging Wall shear zone. Moreover, there are broader, elevated values to the northwest of the mineralization in the B1 Transect, and to a lesser degree in the B2 Transect off strike to the south.

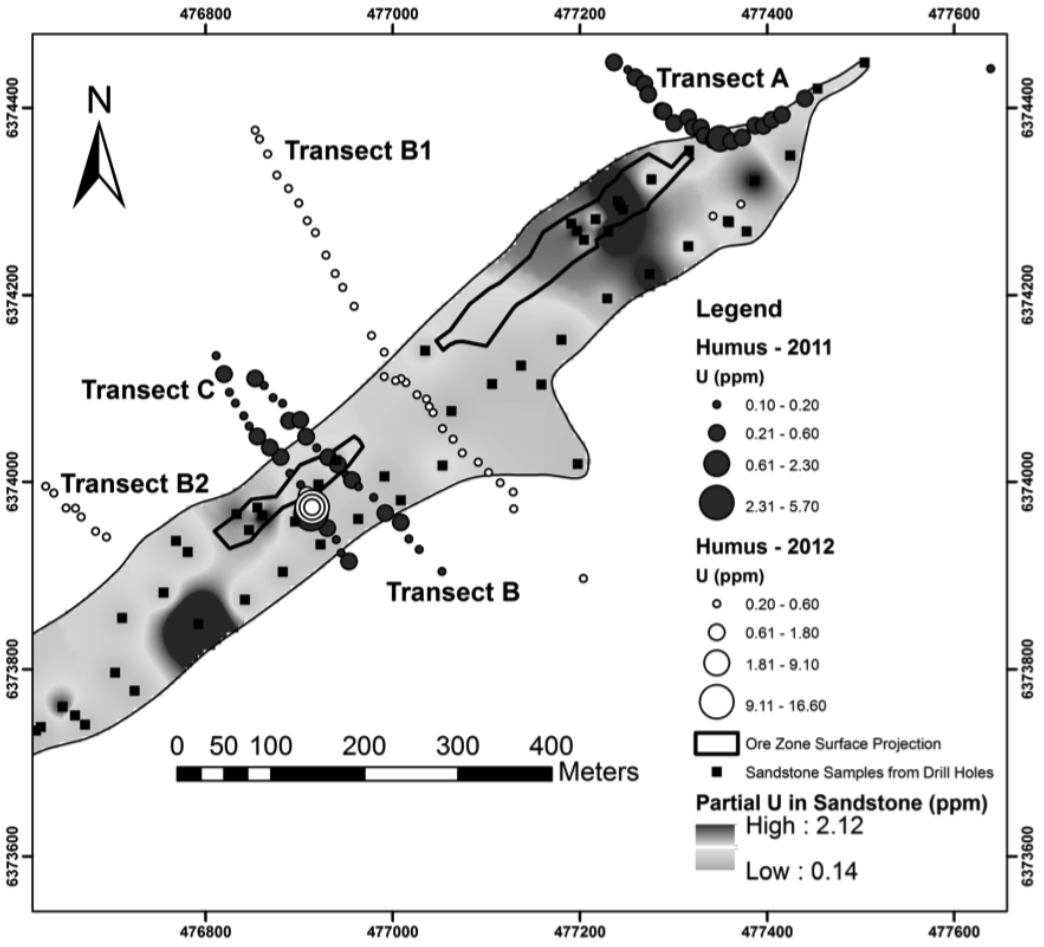
Table 3. *Metal concentrations in sandstone samples (partial HNO_3:HCl & aqua regia digestion)*

Sample #	Easting (m)	Northing (m)	Depth (m)	Ag (ppm)	As (ppm)	Co (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	U (ppm)	W* (ppm)
WR-268	477106	6374104	30.0	0.05	2.20	0.10	2.90	0.05	1.40	1.00	0.25	0.50
WR-289	477053	6374017	30.0	0.22	1.60	0.10	2.02	0.49	1.19	0.82	0.48	0.50
WR-354	477035	6374140	30.0	bd	0.50	0.10	1.99	0.05	1.15	0.46	0.49	bd
WR-262	477009	6373980	30.0	0.05	0.40	0.60	1.60	0.10	1.70	0.47	0.25	1.00
WR-265	476991	6374005	28.0	0.05	0.30	0.05	1.00	0.05	1.00	0.32	0.25	0.50
WR-261	476963	6373960	27.6	0.20	0.30	0.10	1.80	0.10	1.00	0.58	0.25	0.50
WR-266	476781	6373925	27.6	0.05	0.25	0.05	0.70	0.05	0.30	0.36	0.25	0.50
WR-347	476940	6374023	27.2	bd	0.22	0.06	1.31	0.04	0.77	0.50	0.52	bd
WR-325	477378	6374268	27.0	bd	0.21	0.12	0.66	0.08	0.90	1.34	0.47	bd
WR-260	476842	6373874	27.0	0.05	0.21	0.20	1.60	0.05	1.40	1.35	0.25	1.00
WR-293	476833	6373965	26.8	0.15	0.20	0.18	7.10	0.19	2.72	0.80	0.68	0.20
WR-259	476883	6373904	26.7	0.05	0.18	0.20	1.10	0.05	0.60	0.28	0.25	0.50
WR-294	476855	6373972	26.2	bd	0.18	0.08	1.20	0.21	0.88	0.49	0.29	bd
WR-264A	476921	6373997	26.0	0.05	0.18	0.10	1.20	0.05	0.80	0.39	0.25	1.00
WR-271	476768	6373937	25.8	bd	0.17	0.06	1.01	0.07	0.51	0.42	0.27	bd
WR-258	476923	6373933	25.6	0.05	0.17	0.10	1.20	0.05	0.80	1.18	0.25	0.50
WR-291	476861	6373964	25.5	bd	0.16	0.08	1.32	0.03	0.83	0.33	1.02	bd
WR-256	476896	6373957	25.5	0.05	0.16	0.05	1.00	0.05	0.90	0.61	0.25	1.00
WR-287	477191	6374276	25.3	bd	0.16	0.12	0.98	0.06	1.16	0.52	0.50	bd
WR-280	477063	6374075	25.2	bd	0.16	0.04	0.83	0.03	0.75	0.35	0.22	bd
WR-190A	477198	6374019	25.0	0.05	0.15	0.80	3.40	1.80	4.40	0.57	0.25	1.00
WR-267	477137	6374124	25.0	0.05	0.15	0.05	0.90	0.05	0.60	0.36	0.25	0.50
WR-281	477217	6374281	24.7	0.08	0.15	0.13	1.20	0.10	0.82	2.76	0.34	0.20
WR-249	477159	6374104	24.4	0.05	0.15	0.05	0.90	0.05	0.60	0.42	0.25	1.00
WR-286	477197	6374268	24.2	bd	0.15	0.14	2.34	0.04	1.14	0.55	0.94	bd

Sample #	Easting (m)	Northing (m)	Depth (m)	Ag (ppm)	As (ppm)	Co (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	U (ppm)	W* (ppm)
WR-295	476846	6373948	24.0	bd	0.15	0.15	2.23	0.10	1.24	0.57	0.53	bd
WR-323	477504	6374448	24.0	bd	0.14	0.20	0.78	0.12	0.62	0.50	0.45	bd
WR-339	476792	6373848	23.6	bd	0.14	0.09	1.59	0.08	1.21	2.62	2.14	bd
WR-282	477230	6374267	23.6	bd	0.14	0.10	1.32	0.05	1.02	0.70	1.07	bd
WR-285	477425	6374349	23.5	0.02	0.14	0.05	0.33	0.03	0.42	0.34	0.16	bd
WR-360	477454	6374420	23.4	bd	0.13	0.12	0.95	0.05	1.01	0.43	0.38	bd
WR-269	477180	6374152	23.3	0.05	0.13	0.05	0.80	0.05	1.10	0.31	0.25	0.50
WR-277	477387	6374322	22.9	bd	0.13	0.09	8.37	0.06	1.31	1.28	0.81	bd
WR-276	477358	6374279	22.1	bd	0.13	0.25	0.54	0.04	0.78	0.50	0.35	bd
WR-272	477229	6374196	21.5	bd	0.13	0.05	1.89	0.04	0.56	0.62	0.50	bd
WR-283	477204	6374259	21.5	bd	0.13	0.08	1.17	0.05	0.82	0.46	0.41	bd
WR-290	477240	6374300	21.5	bd	0.12	0.12	0.86	0.11	1.11	0.53	1.36	bd
WR-353	476711	6373854	21.5	bd	0.12	0.08	0.94	0.05	0.68	0.37	0.27	bd
WR-251	476647	6373759	21.4	0.05	0.12	0.10	1.40	0.05	2.10	0.63	0.80	0.50
WR-274	477316	6374252	21.2	0.02	0.12	0.06	0.55	0.03	0.70	0.50	0.40	bd
WR-273	477274	6374222	21.0	bd	0.11	0.06	2.87	0.03	0.82	0.44	0.81	bd
WR-288	477246	6374291	21.0	bd	0.11	0.10	0.69	0.06	0.98	0.45	0.66	bd
WR-292	477243	6374295	21.0	0.03	0.11	0.14	0.74	0.18	0.96	1.83	0.80	bd
WR-330	477276	6374323	21.0	bd	0.11	0.09	0.51	0.11	0.89	0.58	0.35	bd
WR-351	476755	6373881	21.0	bd	0.11	0.06	1.02	0.12	0.70	0.46	0.26	bd
WR-275	477359	6374278	20.7	0.09	0.11	0.10	0.90	0.06	0.80	0.54	0.48	bd
WR-252	476703	6373796	20.6	0.05	0.11	0.10	1.50	0.05	1.50	0.62	0.25	0.50
WR-253	476660	6373750	20.4	0.05	0.10	0.10	1.80	0.20	1.30	0.75	0.25	0.50
WR-263	476724	6373776	20.1	0.05	0.10	0.05	0.90	0.05	1.10	0.30	0.25	0.50
WR-254	476671	6373740	17.9	0.05	0.10	0.10	2.10	0.05	1.20	0.58	0.25	1.00
WR-328	476536	6373678	15.7	bd	0.10	0.15	1.06	0.36	1.12	1.91	0.28	bd
WR-326	476528	6373762	15.0	bd	0.10	0.13	2.48	0.04	1.72	0.42	0.15	0.20
WR-257	476597	6373808	14.8	0.05	0.10	0.10	1.20	0.05	0.90	0.45	0.25	0.50
WR-255	476624	6373738	14.7	0.05	0.10	0.20	1.70	3.10	1.50	0.76	0.25	0.50

Sample #	Easting (m)	Northing (m)	Depth (m)	Ag (ppm)	As (ppm)	Co (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	U (ppm)	W* (ppm)
WR-384	477317	6374354	14.5	bd	0.10	0.06	0.47	0.03	0.80	0.73	0.25	bd
WR-370	476619	6373734	12.0	bd	0.10	0.12	2.09	0.04	1.24	0.54	0.21	bd
WR-364	476128	6373454	11.0	bd	0.10	0.10	1.06	0.05	0.61	0.72	0.65	bd
WR-355	476494	6373644	10.5	bd	0.10	0.17	0.87	0.02	1.31	0.45	0.18	0.20
WR-270	476580	6373705	10.4	0.10	0.10	0.08	1.28	0.04	0.72	1.95	0.27	0.20
WR-378	475867	6373290	10.3	bd	0.10	0.05	0.89	0.05	0.60	0.81	0.26	0.20
WR-375	476075	6373521	10.2	bd	0.10	0.12	2.42	0.05	0.95	0.99	0.36	bd
WR-314	475775	6372902	10.0	bd	0.10	0.14	0.60	0.10	1.11	0.97	0.35	bd
WR-317	476193	6373382	10.0	bd	0.10	0.04	0.98	0.04	0.44	0.49	0.17	bd
WR-357	476433	6373635	9.8	0.02	0.10	0.15	1.18	0.04	1.49	0.51	0.25	bd
WR-372	476433	6373696	9.0	bd	0.10	0.27	1.66	0.06	1.51	0.65	1.63	bd
WR-361	476344	6373657	8.8	bd	0.10	0.10	2.68	0.04	1.53	0.56	0.21	bd
WR-365A	476537	6373755	8.8	bd	0.10	0.12	2.07	0.08	1.31	0.65	0.52	bd
WR-380	475932	6373231	8.6	bd	0.09	0.04	0.38	0.02	0.26	0.45	0.14	bd
WR-374	476403	6373668	7.7	bd	0.09	0.20	1.16	0.05	1.68	0.49	0.18	bd
WR-368	476483	6373728	6.0	bd	0.08	0.12	1.64	0.03	0.92	0.49	0.24	bd
WR-362	476225	6373499	5.4	bd	0.08	0.12	1.19	0.04	1.04	0.48	0.21	bd
WR-359	476328	6373538	4.6	bd	0.08	0.05	0.62	0.03	0.52	0.41	0.20	bd
WR-358	476411	6373598	3.8	bd	0.07	0.16	1.85	0.04	1.03	0.57	0.37	bd

Notes: Analysis by ICP-MS & ICP-OES
bd = below detection limit
* = denotes total digestion
Co-ordinates are in UTM NAD 83, Zone 13


476800
477000
477200
477400
477600
6374400
6374200
6374000
6373800
6373600
N
Transect A
Transect B1
Transect C
Transect B2
Transect B
0 50 100 200 300 400
Meters
Legend
Humus - 2011
U (ppm)
0.10 - 0.20
0.21 - 0.60
0.61 - 2.30
2.31 - 5.70
Humus - 2012
U (ppm)
0.20 - 0.60
0.61 - 1.80
1.81 - 9.10
9.11 - 16.60
Ore Zone Surface Projection
Sandstone Samples from Drill Holes
Partial U in Sandstone (ppm)
High : 2.12
Low : 0.14

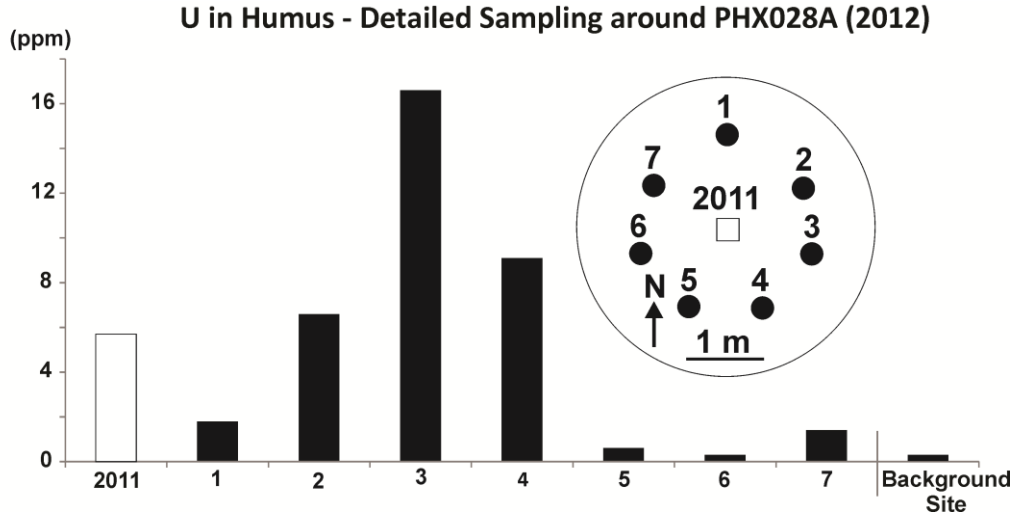

U in Humus - Detailed Sampling around PHX028A (2012)
(ppm)
16
12
8
4
0
2011
1
2
3
4
5
6
7
Background Site
1
2
3
4
5
6
7
2011
N
1 m

Figure 12: Contoured geochemical results for U in aqua regia digestion of humus soil samples from 2011-2012 and in partial leach of the uppermost Dunlop Member sandstone of the Manitou Falls Formation (top). Values were interpolated inside of a pre-defined shape in order to avoid extrapolation of data too far outside the known data points. The sandstone map showing interpolated U abundance from partial leachwere used as an independent base on which the soil transect results from aqua regia digestion were plotted. The surface traces of the A and B1 deposits are also outlined for reference. Coordinates are projected in UTM, NAD 83, Zone 13. Detailed 2012 humus soil sampling near the 2011 site (PHX028, furthest left on graph) that showed the highest U value (bottom). The results, (samples PHX231-237 & background site value) confirm the reproducibility of anomalous U observed in 2011.

Metal values are anomalous in the humus and B-horizon soils at the dense sampling sites. For U in humus, a very high value of 16.6 ppm is observed, which is greater than the anomalous threshold value of 0.38 ppm (0.27 ppm+0.1 ppm). Mo values are also present above the anomalous threshold value of 0.18 ppm (0.12 ppm+0.06 ppm). Anomalous values exist in Cu above the threshold of 15.5 ppm (12.4 ppm+3.06 ppm). In the B-horizon, anomalous values for U and Pb are observed above the threshold 45.6 ppb for U (31.7 ppb+13.9 ppb), and above 1,309 ppb for Pb (773 ppb+536 ppb). The results indicate that sampling in 2012 reproduced anomalies that were identified during the 2011 sampling programme.

These anomalies are also identified in normal Q-Q plots of the humus data for 2012, including that of the dense sampling. The U data display several populations, two of which appear to be anomalous (Fig. 7C). The Q-Q plot for U in the B-horizon also exhibits a polymodal population in 2012, two of which appear to approximate the linear observed versus the expected trend, but one that is clearly anomalous (Fig. 7D). Anomalous values in Q-Q plots from 2011–2012 correspond to those overlying or immediately adjacent to the surface projections of the ore zones or basement location of the deposit hosting WS Shear zone. Though only U was plotted in Q-Q plots, the other metals of interest in this study

behave similarly to U with respect to concentrations and backgrounds (Figs. 8-9, 11; Table 2).

2013 Results

Additional dense sampling of soil was completed in 2013 near the PHX028 site and reproduced high values for metals in humus. Sampling also yielded anomalous values in the B-horizon soils. Aqua regia digestion of humus samples yielded the highest value of 3.9 ppm for U, but measured 406 ppb for U using AA5 leach of the B-horizon, comparable in magnitude to the results for both 2011 and 2012 (Fig. 13).

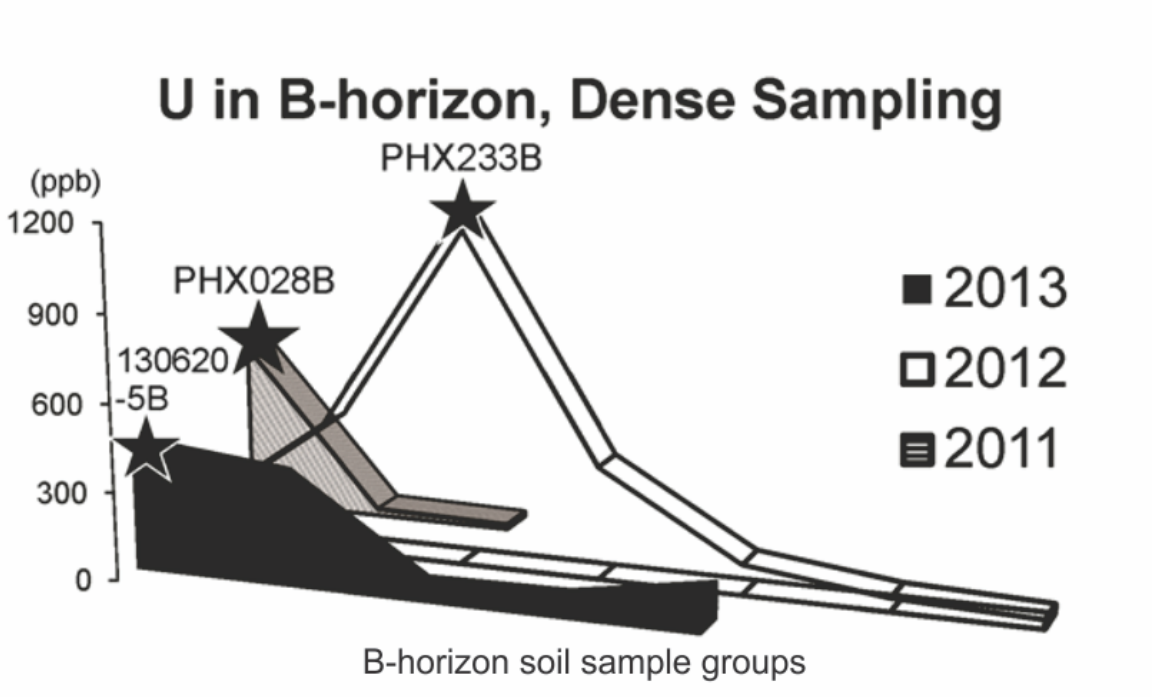


Figure 13: Results of detailed sampling of B-horizon soil from 2011 to 2013 using ammonium acetate leach, with stars illustrating the highest concentrations. In 2011, sample PHX028B showed the highest U value. Based on the results, seven samples were taken near this area in 2012, and confirm the reproducibility of anomalous U (PHX233B). The anomaly was reproduced once again in 2013 (130620-5B). This shows reproducibility of metals over a three-year sampling period at the same location.

pH and Conductivity Results, 2011-2012

pH and conductivity measured in soil-water slurries from the B-horizon soils in 2011 to 2012 varied significantly. In 2011, the highest pH value of 6.5 was measured in B-horizon soils near the southern end of Transect C at site PHX055, whereas the mean value of B-horizon samples was 4.5. Conductivity values were at maximum at the northern tip of Transect A (444 µS/cm), with a mean of 33.9 µS/cm. In 2012, the most alkaline value (9.6) in the B-horizon soil was measured directly over the deposit between the A and B1 deposits at site PHX216 of Transect B1, whereas the mean value was 8.7. The conductivity was also highest at this part of the traverse (480 µS/cm), and had a mean of 114 µS/cm.

Leaching Experiments

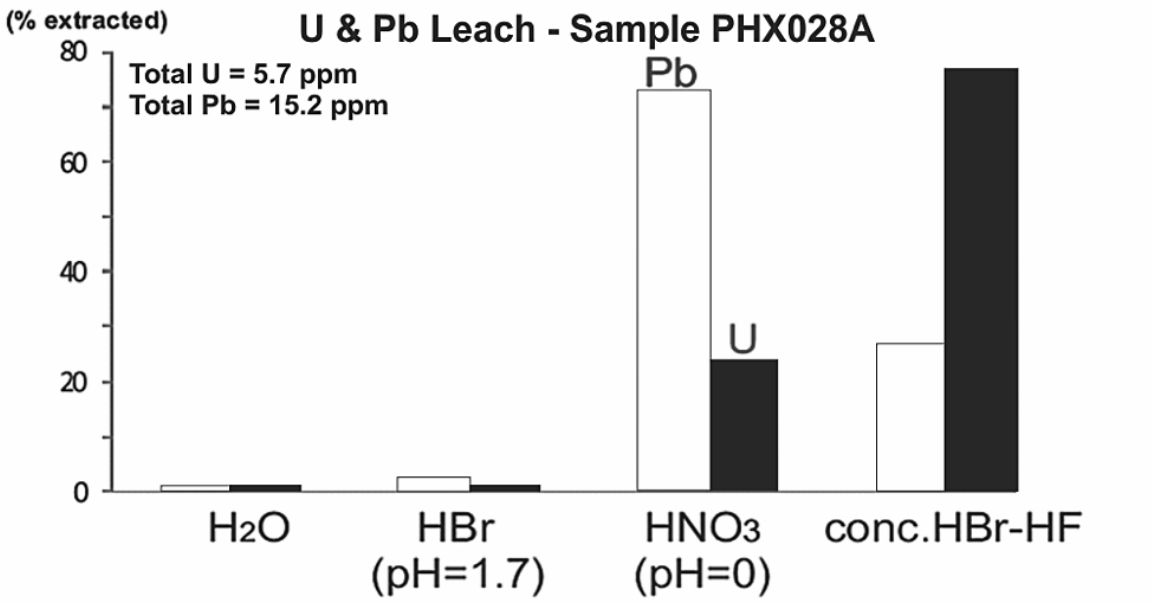


Figure 14: U and Pb extracted from humus sample PHX028A (2011) by water and a variety of acidic solutions. Humus did not release significant amounts of metals in water and weak HBr (pH =1.7) in ultrasonic bath for several hours. Metals are instead released from humus in HNO_3 (pH = 0 at 25°C) and hot, concentrated HBr-HF mixture. The experiment suggests that metals are not on the surface of organic material in humus. Instead, metals are tightly fixed in organics in humus.

Water and a variety of acids were used to extract metals (Cu, Ni, Co, As, U, Pb) from humus in sample PHX028A collected in 2011 (U and Pb, Fig. 14). Humus did not release significant amounts of metals in water, nor in a weak HBr solution that was placed in an ultrasonic bath for over 12 hours. Metals were instead released in 1.0 N HNO_3 solution at room temperature after reaction for the same amount of time, and also in a concentrated hot (100°C) HBr-HF mixture after 12 hours.

Geochemical Data of Uppermost Sandstones

Elevated values of U and its associated pathfinder elements are present in the uppermost sandstones above the deposits (Table 3). Values of up to 2.14 ppm in U are observed, with highest values observed above the northern part of the A deposit surface projection, just southeast of deposit A, above the southern part of the B1 deposit surface projection, and to the southwest of the deposit (Fig. 12a). High Pb values (up to 2.76 ppm Pb) appear in similar areas to U, as well as showing elevated values to the east of the deposit projections. Elevated Co values (up to 0.8 ppm) occur between the two deposits to the east, and south of the B1 deposit surface projection. Elevated values of Ni (up to 4.4 ppm) only occur southeast of the deposit A surface projection, and over the surface projection of the B1 deposit. Large Cu values (up to 8.37 ppm Cu) were measured, with values highest above and southeast of the A deposit surface projection, as well as in the southern section over the B1 deposit surface projection. Mo appears to have quite a similar distribution, with highest values (up to 3.1 ppm) to the southeast of the deposit A surface projection. As values are highest (2.2 ppm) in the area adjacent to B1 deposit, and much farther to the south of the B1 deposit. W values (up to 1 ppm) appear highest immediately adjacent to the east of the B1 deposit projection, and southeast of the A deposit surface projection. Ag values (up to 0.22 ppm) appear highest adjacent to the east of the northern portion of the B1 deposit projection.

Raster maps of the interpolated metal values show that the areas with high concentrations of U, Pb, Co, Ni, Cu, Mo, As and W are similar to those of anomalies in humus and B-horizon soils.

Discussion

Glacial Till

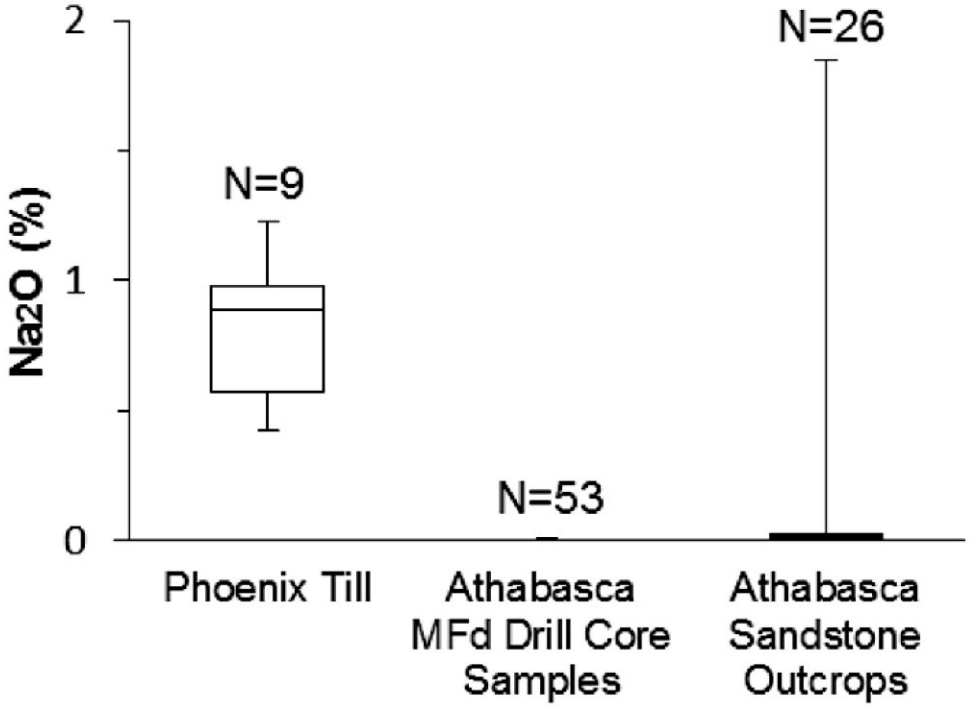


Figure 15: Box-whisker plot of Na_2O content in tills from above Phoenix and from both Athabasca sandstone outcrop and drill core in the area (Card *et al*. 2011, Bosman & Card 2012). Till contains much higher Na_2O than the sandstones, likely indicating input from rocks sourced outside the basin from the up-ice direction (Simpson & Sopuck 1983; Campbell *et al.* 2002; 2007).

Bulk rock compositions of till contain moderately high Na_2O, 0.42 to 1.23 wt. % (Fig. 15, Table 4), which is 20 times greater than that of the Athabasca sandstones below (0.001 to 0.05 wt. % Na_2O, Fig. 14; Card *et. al.* 2011). Sandstones of the Dunlop member in drill holes yield similar values (0.03 to 0.001 wt. % Na_2O) to the outcrop data (Bosman & Card 2012). The till values with high Na contents (PHX223C, 1.23 wt. % Na_2O, PHX247C, 0.98 wt. % Na_2O) are north and slightly west of the surface projection for deposit A. The

distribution suggests a possible down ice dispersion of high Na from some source to the northeast by the last major glacial event, though this is not entirely clear for this specific property based on the small sample population. The high Na contents in tills also indicate that the glacial sediments are derived not only from Athabasca sandstones, but also from granitic basement rocks.

The results are not a surprise considering basement rocks outcrop up-ice along the strike of the last major glacial flow direction approximately 150 km to the northeast (Fig. 15), and this geochemical influence on Athabasca till material is well documented in the literature. Simpson and Sopuck (1983), who compared the geochemistry of the uppermost sandstone to the overlying till near the Midwest U deposit, also in the eastern Athabasca Basin. They found high Na_2O (~2%), Al_2O_3, MgO and K_2O as well as low SiO_2 contents in the till chemistry, which they interpreted was indicative of contamination of material derived from a basement complex to the northeast (Simpson & Sopuck 1983). In Earle's 2001 study of eastern Athabasca till, he found that on average, 85% of the larger clasts in the till are Manitou Falls Formation sandstone and most of the remaining 15% are basement derived granite and gneiss from outside (north and east) of the Athabasca Basin. According to Campbell (2007) extrabasinal material in Athabasca till comprises pebble to boulder-sized erratics of igneous and metamorphic rock and pink feldspar, phyllosilicate minerals, and heavy minerals in the fine fraction. She argues that this extrabasinal material was predominantly derived from immediately up-ice from the northeast margin of the basin as suggested by Simpson & Sopuck and Earle, however, several erratics of dominant lithology indicate transport distances, for a smaller component of the till, of greater than several 100 km from sources in Nunavut (Campbell 2002, 2007). This, along with the other workers results, suggests that the extrabasinal component is the dominant influence on the

geochemical signature of the till (Campbell 2007). Further adding to this hypothesis is how the relative proportions of intra- and extrabasinal material are related to the type of till deposit, the till unit, and the till thickness. As till that forms a thin veneer over sandstone is primarily composed of localized sandstone, the proportion of extrabasinal detritus increases with till thickness (Campbell 2002, 2007). This could explain the high extrabasinal component in relation to the tills of moderate thickness observed above the Phoenix deposits.

Table 4. *Whole rock data for Phoenix till samples*

Sample #	PHX203C	PHX206C	PHX211C	PHX223C	PHX229C	PHX237C	PHX243C	PHX246C	PHX247C
SiO2(%)	94.02	93.78	88.57	85.18	86.50	93.00	89.56	87.68	89.85
TiO2	0.046	0.062	0.104	0.204	0.118	0.063	0.089	0.124	0.091
Al2O3	2.53	2.93	4.61	6.45	5.02	3.08	3.98	5.65	4.74
Fe2O3	0.215	0.228	0.420	1.210	0.640	0.265	0.476	0.637	0.649
MgO	0.08	0.12	0.20	0.34	0.19	0.11	0.17	0.37	0.29
MnO	0.003	0.003	0.006	0.013	0.007	0.004	0.004	0.007	0.010
CaO	0.26	0.34	0.46	0.75	0.55	0.33	0.39	0.86	0.67
Na2O	0.42	0.57	0.93	1.23	0.89	0.55	0.76	1.18	0.98
K2O	0.394	0.541	0.877	1.361	0.929	0.522	0.747	0.821	1.078
P2O5	0.021	0.020	0.026	0.027	0.013	0.020	0.020	0.026	0.034
L.O.I.	1.70	1.43	1.83	2.40	2.13	1.55	2.17	1.32	2.76
Conc.	98.01	98.63	96.25	96.85	94.94	97.99	96.25	97.41	98.46
Total	99.71	100.06	98.08	99.25	97.07	99.54	98.42	98.73	101.22
Ba (ppm)	80	112	158	300	160	133	129	136	44
Rb	14	19	32	53	37	22	28	37	95
Sr	53	66	91	123	106	67	80	93	13
Th	5	6	7	34	20	13	7	8	7
V	12	5	9	16	17	6	14	17	7
Y	5	6	7	10	8	5	6	7	94
Zr	69	115	242	364	349	121	198	114	52
Ce	5	35	14	29	15	21	16	47	52
Nd	5	21	5	9	8	10	5	12	21

Notes: Major and trace element data by X-ray fluorescence. PHX = Phoenix.
bd = below detection limit

Metal Sites in Humus Samples

The results of the leaching experiments (Fig. 14) suggest that metals are not adsorbed on the surface of material in humus nor on Al-O-OH or Fe-O-OH compounds in the samples, because metals adsorbed on these compounds would be released in weak acids (Drever 1997). Instead, the metals are likely tightly fixed in the organics of the humus. The result supports earlier studies suggesting that many metals are incorporated in organics in humus. Hattori and Cameron (2004) also demonstrated that metals, such as Pd, are tightly bound in organics.

Our leaching experiments also reject a possible cause of metal anomalies from activity related to exploration and drilling. Metals in the drilling fluids would have been easily dissolved in weak acids. Furthermore, the surface of the property is slightly sloped towards a lake in the northeast corner of the property (Fig. 5, bottom) and most of the sampling transects are on all topographically higher ground than drilling sites so are thereby safe from fluids that may have been carried down-slope by rainwater or groundwater.

Comparison of Ammonium Acetate and Hydroxylamine Leaches for B-horizon Samples

When comparing the two different partial extraction methods, AA5 was much better at displaying anomalies in B-horizon than the hydroxylamine leach. The 0.25 M Ox leach is a stronger acid than AA5 and dissolves not only carbonates, but also amorphous Fe and Mn oxyhydroxides. More metals in solution raise the detection limits of elements, which create less prominent peaks of anomalies. For example, AA5 leaches yield more anomalies of U and other pathfinder elements than Ox leaches. For W, the Ox leach produces one anomaly over the A deposit, whereas the AA5 leach produces anomalies over the A deposit and two adjacent to the area above the B1 deposit. We therefore agree with Bonham-Carter and Hall's (2010) recommendation to use ammonium acetate leach on B-horizon soils as it seems

better to detect anomalies for several elements, but we also recommend the use of hydroxylamine in discerning anomalies of U and W.

Spatial Correlations of Anomalies in Soil (Humus and B-horizon soil)

Our results show that anomalies in U and pathfinder elements occur in humus and B-horizon over the surface trace of the U ore bodies, as well as the area over the WS Hanging Wall shear zone as it is present in the basement rocks. Dense sampling of both humus and B-horizon over the B1 deposit near the PHX028 sample site confirmed multi-year reproducibility of metal anomalies. There may also be anomalous concentrations of these elements above shear zone splays that emanate to the northwest of the ore zones, which could be sourcing the more diffuse and broad anomalies that we observe in sandstone, and subsequently in Ni for aqua regia digestion of humus, and for As and Pb in ammonium acetate leach of the B-horizon soil (Fig. 11). Though these minor shears are not well defined, the WS Shear likely contributes to the development of these splays in the basement rocks and also into the Athabasca sandstones near the southern portion of the A deposit (Fig. 2). A change in the principal stress to an east-west direction led to later strike-slip movement along the WS Shear, and later extension is indicated by northwest-striking normal faults, which dip steeply to the southwest (Roscoe 2012). This prolonged stress likely built the fracture network emanating from the WS Shear, creating space for increased upward fluid flow in sandstone. This may have also contributed to the heterogeneous metal signals observed in the sandstones, till and soils.

Spatial Correlations of Anomalies Between Soil and Till

The spatial distribution of anomalies in the humus and B-horizon soils correlate with the results from the silt-fraction (<64 μm) of the till, but these values were not as pronounced as those from the humus or the B-horizon. Ni, Cu and Mo in till samples show moderately

higher than background values over the surface traces of the ore zones, and were highest over the B1 deposit and to the northwest of deposit A. This is in contrast to the pronounced anomalies in the humus and B-horizon, as they were observed both above the B1 deposit and adjacent to both deposits.

It is often argued that metal anomalies in till reflect down-ice dispersion from a sub-cropping mineralization (Ainsworth 2012). We reject this possibility for two reasons. Firstly, these deposits located at 400 m of depth, are too deep to outcrop on surface. Secondly, samples along the B1 transect did not yield as many anomalies as the other sampling areas. If the anomalies were produced by glacial till materials, they should be detected along the B1 transect, as this traverse is in between the two deposits. Instead, the anomalies in surface media are restricted in areas directly above ore zones and the WS Shear, and do not appear to be smeared in the down-ice direction of the most dominant south-westerly ice flow direction in the area.

Spatial Correlations of Anomalies Between Soil and Sandstones

U shows an excellent spatial correlation between the geochemical anomalies in soil and elevated values in the uppermost sandstones (Fig. 12a). It is especially evident in the region northeast of deposit B1 and southwest of deposit A. The evidence suggests that the anomalies in these soil horizons reflect high metal values from areas directly below in the underlying sandstones. High values of U and its pathfinder elements have been observed to be present in sandstone above known U deposits, and are well documented in the literature (Golightly *et al.* 1983; Sopuck *et al.* 1983; Clark 1987). Golightly *et al*. found that where U zones have been found in the basement rocks, regolith and lower Athabasca sandstone, U values greater than 2 to 3 ppm consistently occur in the overlying sandstones at or near surface, similar to this study. But though Sopuck *et al.* (1983) caution that U, Ni, As and Co

in sandstone have limited use as targeting vectors except tens of metres away from mineralization, they conclude that U can form anomalies when steeply dipping mineralization is related to fault structures. In Clark's 1987 study, orientation surveys were undertaken by sampling the uppermost 10 m of sandstone in a selection of holes from the Cigar Lake, Dawn Lake, and Wolf Lake areas where the deposits are, respectively, 430, 160, and 210 m deep. Leachable anomalies of U up to 14 and 16 times background measurements were observed for samples above the Cigar Lake and Dawn Lake deposits. More unusual patterns occurred at Wolf Lake, which the authors concluded might have been related to post-alteration tectonism.

Anomalous values of pathfinder metals, as documented here, occur at the northern end of the B1 Transect. The WS Shear zone was reactivated and splays into several faults with near vertical dips within the sandstone, and any surface projections of these should be closer to the ore zone. This is confirmed by the lack of faults in drill hole WR-281 (Fig. 2). Movement on these faults must have continued after deposition of rocks of the Read Formation and probably the MFd member (Roscoe 2012). Therefore, basement-hosted shear zones and their splays in the Athabasca sandstone likely provided conduits for the upward-transport of elements from the ore zones.

Upward Movement of Elements from Sandstones to the Surface

Transport mechanisms of elements from concealed mineral deposits to surface media have been debated in the literature (e.g., Bajc 1998; Cameron *et al.* 2004) and are not fully understood**.** The widely accepted genetic model for the formation of unconformity-related uranium deposits involves mixing of oxidized uraniferous brines in the sandstones with reduced fluids emanating from the basement (Jefferson *et al.* 2007b). Where U deposits occur, they are often accompanied by large alteration haloes created by fluid-flow and

extensive fluid-rock interactions in the sandstone. Hydrothermal alteration, including desilicification, had the net effect of increasing permeability along the faults and the adjacent wall rocks; thus sub-vertical, high permeability channels rise through sandstone that otherwise would have been impermeable due to silica cement or fine-grained intergranular material (Cameron 2013). Cameron (2013) also argues that these faults or fracture zones are commonly reactivated during late tectonic events and important for bringing metals perhaps as far upwards as the uppermost sandstone. Fluid flow through this porous sandstone, carrying metals post-Holocene after deposition of the glacial cover, could offer a possible explanation for anomalies in soil above the Phoenix deposits.

Broad geochemical anomalies in soils at the property show distribution of elements could exist over the deposit, thought the exact location of these pathways through the sandstone remain unclear. Our results suggest upward migration of metals to surface, detectable by geochemical exploration methods for U using different types of surface media.

Implications for Uranium Exploration

Surficial geochemical surveys have been proven to be an efficient and inexpensive exploration tool in detecting shallowly buried deposits (*cf* Cameron *et al.* 2004). This study overlying the Phoenix deposits at a depth of 400 m shows that such analysis is also capable of detecting metals related to deeply buried unconformity-related U deposits, even in sporadic discontinuous permafrost regions of Canada, where the dispersion of metals is slow. In addition, this study suggests that geochemical analysis of shallow siliciclastic rocks provides additional valuable information perhaps related to the presence of a buried deposit at great depths. The use of geochemical data of the uppermost sandstone may reduce the number of deep, expensive drill holes in U exploration programmes.

This study also documents that narrow geochemical anomalies in soil and high metal values in sandstone exist directly above the underlying U deposit but also exist at less pronounced levels to the northwest of the deposit. For similar surveys in deposit-scale exploration campaigns, soil samples should be collected along transects over a target defined by other methods starting at least 100 m away from the target perpendicular to the last major ice flow direction. Transects should be designed to collect similar media under homogenous surface conditions and relatively uniform topography. The sampling spacing should be determined based on the size and shape of a target. Shorter spacing is recommended for narrow targets. Background sampling sites at least several hundred meters away from the target, as well as background sampling transects off-strike of the target are also recommended to have a reasonable idea of background metal values when evaluating possible anomalies.

After collecting humus, B-horizon and C-horizon materials, U and its associated pathfinder elements should be concentrated in humus and B-horizon, as the organics in humus and Fe/Mn hydroxides in B-horizon scavenge mobile metals (Cameron *et. al* 2004). This study finds that Ox leaches were not as useful at detecting trace metals in the B-horizon as AA5 leaches. Ox leaches would be effective in dissolving metals in Fe-O-OH and Mn-O-OH, but the very young soil in the study area, at ca. 4000 years old, would not have crystalline Fe-O-OH and Mn-O-OH compounds. Therefore, even weaker leaches may have been able to remove metals on these compounds and Al-O-OH.

Shallow sandstones should be subject to partial leach to add geochemical information about adsorbed metal distribution in the shallow sandstone environment. The IDW method of interpolation is one possible method to "grid" the samples, and is considered by De Smith *et al.* (2008) to be the best for a small drill hole population that usually exist in relatively

unexplored properties, or for soil samples if there is enough (approximately 50) in a rectangular orientation.

All methods suggested in this paper are inexpensive when compared to cost of drilling. At a reasonable cost, these methods used in a soil, till and sandstone geochemical survey serve as complementary methods to other geochemical and geophysical methods in discerning targets prior to exploration drilling for uranium deposits in glaciated terrains.

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CHAPTER 3

Article II. Anomalous abundances of He and mobile metals in surface media over the deeply buried Millennium uranium deposit, Athabasca Basin, Canada.

Michael J. Power, Keiko Hattori, Daniele L. Pinti & Eric G. Potter

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Anomalous abundances of He and mobile metals in surface media over the deeply buried Millennium uranium deposit, Athabasca Basin, Canada.

M. J. Power[1*], K. Hattori[1], D. L. Pinti[2] & E. G. Potter[3]

1. *Department of Earth Sciences, 140 Louis-Pasteur, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada*
2. *GEOTOP, Université du Québec à Montréal, Montréal, Québec, H2X 3Y7, Canada*
3. *Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada*

Abstract

The composition of soil and noble gases dissolved in water were examined over the Millennium deposit that has indicated resources of 68.2 million lbs U_3O_8 ~750 m below surface. Aqua regia digestion of humus yielded anomalous values in U (≤0.6 ppm), Pb (≤35 ppm) and Cu (≤15 ppm). Anomalous values were also detected for U (≤102 ppb), Pb (≤2100 ppb) and Cu (≤220 ppb) in ammonium acetate leach of B-horizon soil. Anomalies were present directly above surface projections of the deposit and faults, including the mineralization-hosting Marker fault. Broad geochemical anomalies suggest fault-controlled redistribution of metals. Gas samples collected in drill holes and monitoring wells yielded anomalous $^4He/^{36}Ar$ ratios of 715, 239 and 108 times the A.S.W. (Air Saturated Water) value. Results suggest present-day upward migration of ^4He, and likely metals, to surface through rocks and tills. The observations suggest deeply buried U deposits are detectable by geochemical exploration of surface media.

Introduction

The Athabasca basin in northern Saskatchewan, Canada hosts high-grade U deposits. The eastern Athabasca is considered a maturing mining district, and exploration farther west into the interior of the basin is bringing present-day exploration deeper into and below the basin itself. Most of the Athabasca deposits are classified as unconformity-type deposits, since U deposition is spatially related to the unconformity between the fluvial sandstones and underlying basement rocks (Roy *et al.* 2005). However, mineralization can extend deep into the basement rocks, and many of these basement-hosted deposits have only been discovered in recent times. The Millennium deposit is one of such deposits. At Cameco's Cree Extension property, the deposit was discovered in 2000 with indicated resources of 68.2 million lbs U_3O_8 grading at 4.1% U_3O_8, lies at approximately 750 m depth in the basement rocks, mostly below overlying Athabasca sandstone.

This study follows a multi-year, multi-site study supported by the Canadian Mining Innovation and Research Organization (CAMIRO), which concluded that the buried U deposits might be detected using mobile metals sourced from deposits (Bonham-Carter & Hall 2010). This paper presents soil geochemical data, as well as noble gas data from the property hosting the Millennium deposit. Helium is a decay product of U and it does not react with rocks. Abundance of He in ground waters in exploration drill holes and environmental monitoring wells was examined. The data show anomalous values of metals and He above the deposit.

Study Area

Geological Setting

The Athabasca basin (Fig. 16), deposited between 1740 and 1500 Ma is a virtually undeformed, mainly fluvial, over 1750 m thick sedimentary succession of Proterozoic age (Creaser & Stasiuk 2007). It unconformably overlies metamorphosed basement rocks consisting of Archean to Paleoproterozoic granitoid and pelitic gneiss (Jefferson *et al.* 2007a). The Millennium deposit (Fig. 17, modified from Wood *et al.* 2012) occurs on the hanging wall of a major reverse basement fault in the eastern Athabasca basin, in close proximity to a graphitic horizon at a depth of ~750 m from the surface below the unconformity (Roy *et al.* 2005). Basement rocks at the Cree Extension Property lie within a transition zone between the Wollaston Lithostructural Domain to the east, and the Mudjatik Lithostructural Domain to the west (Millennium Project Report 2009). The Mudjatik Domain consists predominantly of granitoid gneisses, which contain discontinuous arcuate zones of Aphebian supracrustal rocks (Lewry & Sibbald 1980). The Wollaston Domain is a Paleoproterozoic metasedimentary sequence divided into two distinct rock assemblages: the lower assemblage comprising pelitic, semipelitic, and arkosic gneisses with interlayered calc-silicates and quartzites (Ray 1975), and the upper assemblage comprising semipelitic and arkosic gneisses.

These are overlain by the Paleoproterozoic Athabasca Group sandstones, which consist of 500 to 700 m of four members of the Manitou Falls Formation, named MFa, MFb, MFc and MFd in shallowing order (Ramaekers 1990; Roy *et al*. 2005). The Manitou Falls Formation sandstones consist of coarse to fine-grained, hematite-rich conglomerates along thin stratigraphic horizons, with oxidation of heavy mineral layers and silty sandstones (Ramaekers 1990).

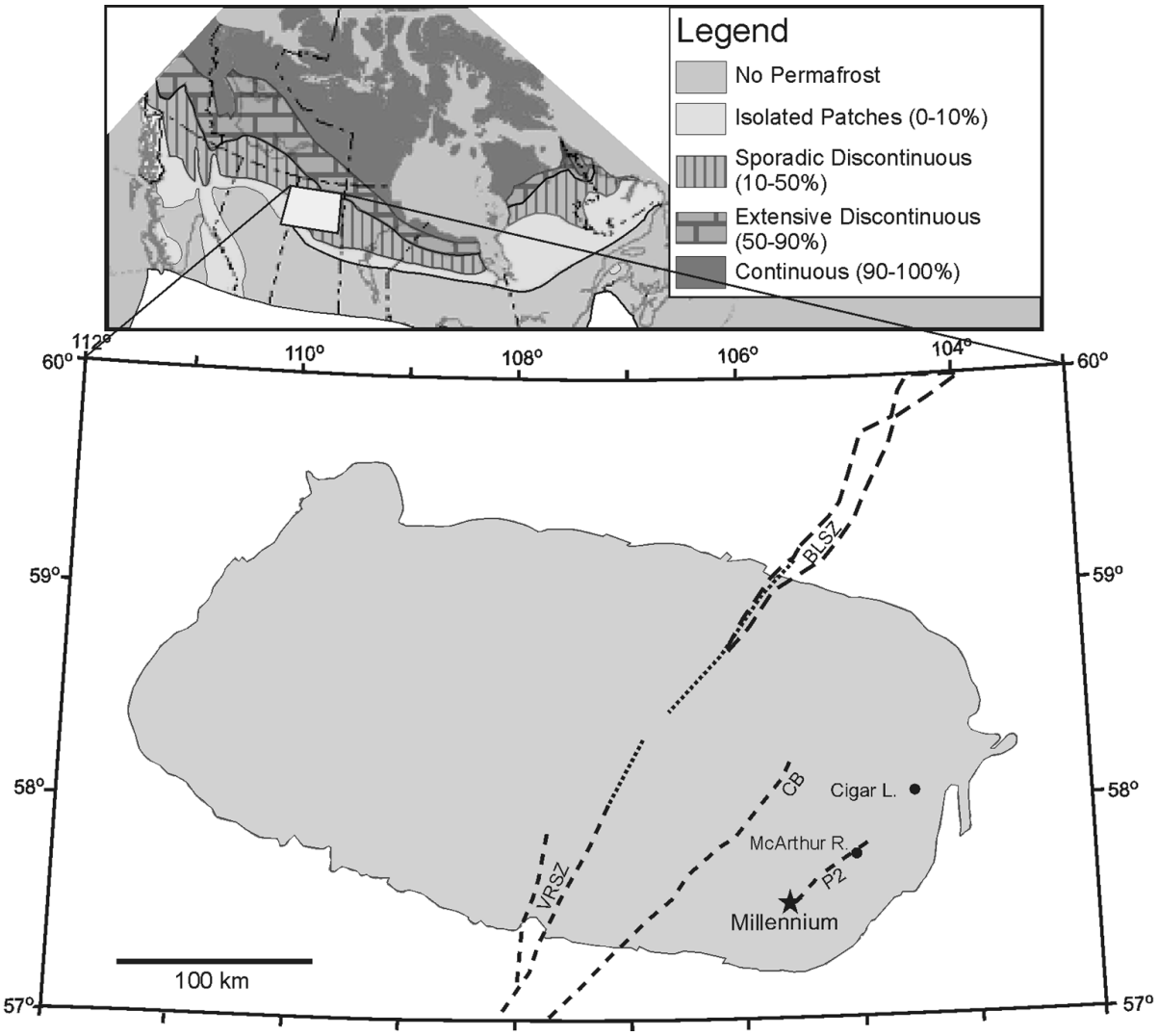

Figure 16: Simplified map in grey (inset) of the Athabasca Basin in northern Saskatchewan, Canada, in a region of sporadic discontinuous permafrost, with the study area hosting Cameco's Millennium deposit in the southeast Basin. Nearby U deposits Phoenix, McArthur River and Cigar Lake are also shown. The regional P2 fault is also displayed as a dashed line between Millennium and the other deposits, while the Virgin River (VRSZ), Black Lake (BLSZ) and Cable Bay (CB) basin-scale shear zone/faults are displayed, and also trend generally northeast. Basin outline from Jefferson *et al.* (2007a), and permafrost information modified from Burgess *et al.* (1999).

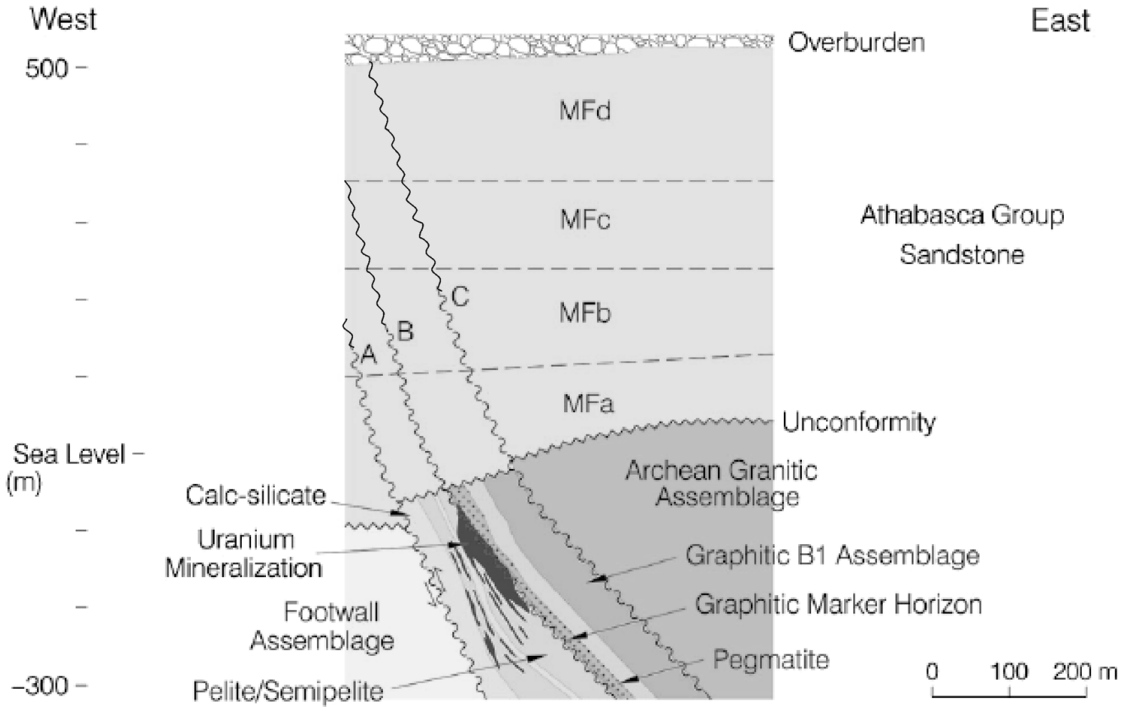

Figure 17: Schematic cross section of the geology through the Millennium deposit (modified from Wood *et al.* 2012). The mineralization is mostly within Paleoproterozoic metasedimentary rocks at 600 to 750 m depth below the Manitou Falls (MFa-d) sandstones of the Basin, with the deposit is situated along the major ore-hosting Marker reverse fault. The Main Zone has been defined for a minimum strike length of 230 m, and overall grades approximately 4% U_3O_8 (Roy *et al.* 2005).

Quaternary Sediments

The research area has experienced several major glacial events involving multiple ice flow events and secondary reworking of glacial material, with the last major event occurring approximately 9000-8700 years ago (Campbell 2007). Southwesterly was the most dominant ice flow direction (Fig. 18) as deduced from the morphology of the largest drumlins, although these features were weakly overprinted by later west-southwesterly ice flow (Campbell 2007). The study area is characterized by a relatively flat-lying region of glacial

moraine plain and ground moraine in a larger region of moraines, eskers, outwash, aeolian, and lacustrine deposits (Schreiner 1984; Roy *et al*. 2005; Campbell 2007). Several drumlins and eskers appear immediately on and near the project area, and also regionally, trending northeast southwest, 210-225° (Roy *et al.* 2005; Campbell 2007) with abundant granite boulders present locally. Glacial till can reach more than 100 m thickness in the eastern Athabasca basin (Campbell 2007), but it is only several meters thick in most sample sites of this study. West of the study area across Slush Lake, cross-bedded fluvial sandstones of the Mfd formation are well exposed.

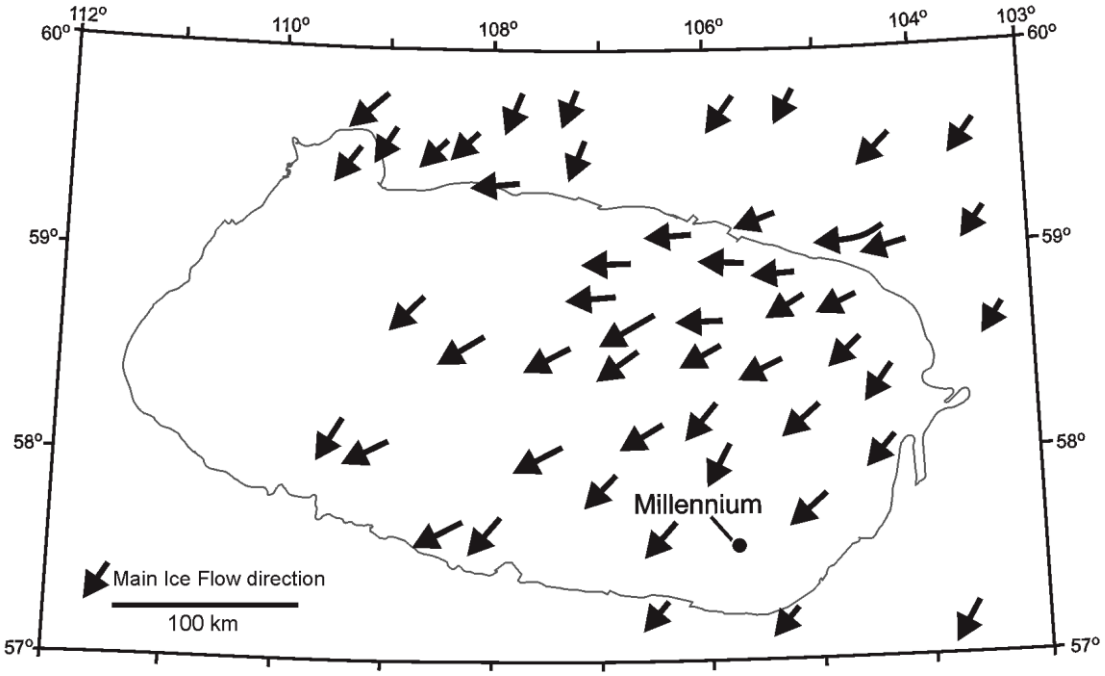

Figure 18: Regional ice flow pattern of the last glacial event in Northern Saskatchewan; the last dominant ice flow direction is shown by the black arrows (modified from Campbell 2007). Deglaciation of the eastern Athabasca Basin began in the southwest at 9000-8700 BP, with the entire area becoming completely ice-free by 8200 BP (Campbell 2007).

The upper part of glacial till (Fig. 19) was examined during sampling. It is well-sorted, whitish, medium to coarse-grained quartz sand with minor cobbles of granitic rocks and K-feldspar grains. This is underlain by mostly a mixture of cobbles (1-2 cm diameter) and boulders (>5 cm diameter) at approximately 30 cm depth from surface. This coarse material is mixed with sand-rich-material, which indicates that it could be lodgement till. This is similar to the Till 2 unit in the eastern Athabasca defined by Campbell (2007), which comprises of a soft, matrix-rich sandy upper till with a lodgement and basal melt-out facies, and an ablation facies forming a veneer locally.

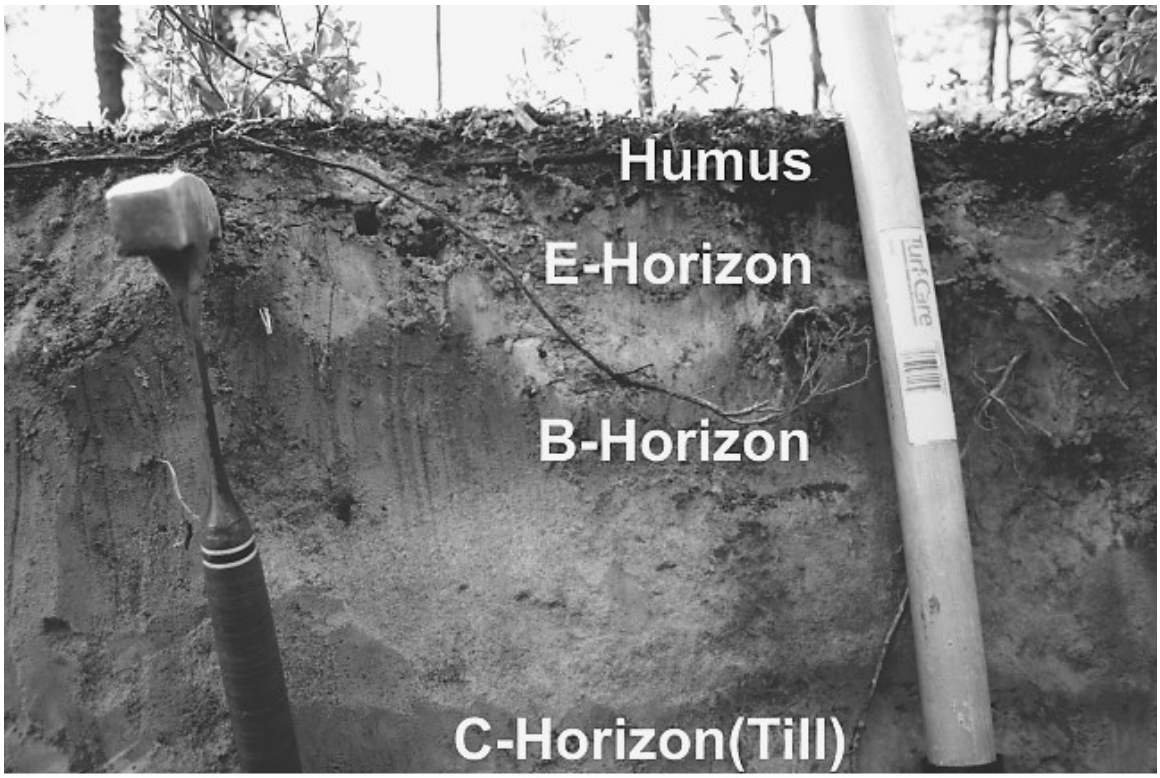

Figure 19: Typical soil horizon profile at the study area, with a hammer on the left for scale. The humus layer includes charcoal from a previous forest fire event. Though the soil horizons are not thick, they are fairly homogenous in texture and easy to collect without cross-contamination, while cobbles and boulders prevented collection of C-horizon till material at some sampling sites. The photo was taken near the main camp location (GPS coordinates 460853 E, 6375247 N). Coordinates are in UTM NAD 83, Zone 13.

Study Area, Exploration History and U Mineralization

The study area may be accessed via all terrain vehicle through a gravel road, 35 km north of the Key Lake mill facility in northern Saskatchewan. Early exploration at the Property included airborne electromagnetic and ground geophysical methods accompanied by geochemical and radiometric surveys (Roy *et al.* 2005). In the 1980's, four distinct electromagnetic conductors were identified in the basement rocks, and initial drilling identified weak unconformity-hosted U mineralization along A1 and B1 conductors, subsequently focusing towards the B1. This is where indications of reactivated faulting and anomalous geochemistry in the sandstone coincided with the southern portion of the B1 conductor (Roy *et al.* 2005). This included the review of a historic drill core that averaged 0.9 ppm U over nearly 200 m in the lower sandstones and extensive hydrothermal overprinting in the upper 80 m of basement rocks, which included anomalous Pb and B values throughout both intervals. More importantly, a strong foliation in basement rocks was also observed, and along with the local graphitic conductor was projected as a drill target up-dip of this drill hole. The Millennium discovery hole CX-40, drilled in the spring of 2000, intersected weak to moderate U mineralization 40 m below the unconformity, continuous over 29 m strike length, grading 1% U_3O_8 (Roy *et al.* 2005).

The mineralization at Millennium occurs along the Marker fault, which is steeply dipping in sandstone, hosting uraninite, and is broadly stratabound in the basement rocks (Roy *et al.* 2005). The mineralization hosted along the basement fault is low in Ni, As, Cu and Co contents, which are each generally less than 200 ppm, with Mo, Pb and V contents increasing with U content (Roy *et al*. 2005). The oldest U-Pb age date obtained at the deposit is approximately 1600 Ma, which is estimated from the age of unaltered uraninite.

The Manitou Falls Formation sandstones show the typical alteration mineralogy

observed above other U deposits in the basin with illite, minor chlorite, kaolinite and dravite, with B enrichment and Na_2O and Zn depletion (Roy *et al.* 2005). The footwall reverse fault, known as the Mother fault, is filled with preore quartz, and the hanging wall reverse fault, known as the B1, is associated with a cordierite-graphite metapelitic gneiss unit (Roy *et al.* 2005; Wood *et al.* 2012). Basement-hosted mineralization is often in close proximity such graphitic units related with pre-Athabasca basin steeply to moderately dipping fractures and breccias, units which may extend hundreds of meters into the basement rocks (Thomas *et al.* 1998). The alteration surrounding the Millennium deposit extends downward along the B1 bedding parallel fault, and is bounded by a fault footwall to the Mother Fault.

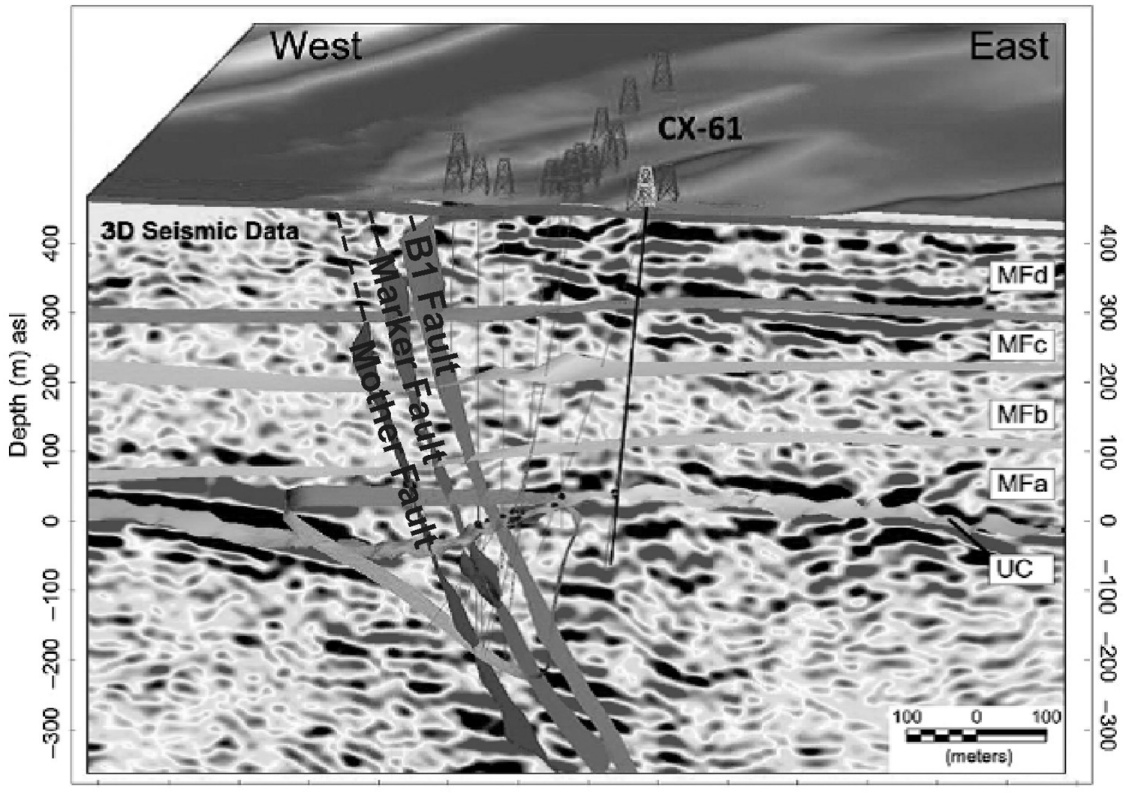

Figure 20: West-east profile (line 65) from the 3D surface seismic cube displayed with a slice though the interpreted 3D geologic model (modified from Wood *et al.* 2012). Vertical structures are from left (dark grey) to right (light grey: the Mother, Marker and B1 faults, respectively) and are interpreted to extend to surface from the basement rocks up through the Athabasca basin sandstones. Depth scale is in meters (asl).

Climate and Topography of the Study Area

The region has a sub-arctic climate with long, cold winters and warm summers with extensive precipitation, approximately 482 mm of annual precipitation (Dimitrov *et al.* 2014). The area lies in a region of sporadic discontinuous permafrost (Burgess *et al.* 1999, Fig. 15). This environment is typical of the "taiga" forestland emblematic to the basin, and is more than 90% young jack pine in the order of 2 to 3 m tall (Fig. 6) with rare older stands up to 5-10 m high. Forest fires at the study site in 2008 burned much of the vegetation along the southern surface projection of the mineralized zone. Black spruce is usually limited to the fringes of Slush Lake and boggy sections of topographic lows. Minor local stands of white birch are found in some well-drained areas. The trees are set in a thin carpet of white caribou moss (lichen) with local clumps of shrubs.

Figure 21: Typical view of a property access road looking south with the forested study area covered in 2-3 m high jack pine and in lower-lying areas, black spruce trees & shrubs. The sampling area is relatively flat and homogenous, with very similar soil horizons at each sampling site, and extensive caribou moss on the forest floor. Evidence of a forest fire in 2008 is apparent from the burned trees on the ground. Photograph taken in August, 2012.

Soil Conditions

At most sampling stations, even-textured, homogenous soil horizons are present (Fig. 19) at Millennium, but in places the till is thin with abundant cobbles and pebbles, with some sampling sites even preventing sampling of the C-horizon till. The accumulated organic matter (humus, 0-4 cm from surface) is very dark black, with minor charcoal from recent forest fire in 2008, though thicker closer to Slush Lake. Horizon E (4-10 cm) is sandy, greyish-white and the boundary with the overlying humus is gradational in a cm thickness in

many places. The B-horizon ranges in thickness from 10 to 30 cm, is yellowish-brown in color, and has a well-defined rich, dark brown contact with the overlying whitish-grey E-horizon. The top-most C-horizon (Fig. 19), essentially free of weathering, is a glaciofluvial light grey sand-rich till deeper than 30 cm, and comprised of medium to coarse-grained sand with minor cream coloured silt with quartz and potassium feldspar clasts, and little to no clay.

Samples

Selection of Sampling Sites

The mineralized bodies are narrow. In addition, surficial geochemical anomalies over concealed mineral deposits are commonly offset from the centres of deposits (Hattori *et al.* 2009). Therefore, soil samples were collected along linear transects over the mineralized zones. The transect method of soil sampling facilitates values at stations relatively far away from a defined target, whether mineralized or fault zones, in the specific soil environments being studied (Kelley & Kelley 2003). Great care was taken to choose sampling transects that have similar surficial conditions including the topography, vegetation, and water drainage, as a uniform sampling environment is among the most important aspects of planning a surficial geochemical survey. The transect direction was chosen to be perpendicular to the last main ice flow direction from northeast to southwest, in order to avoid any potential "smearing" effects the till might have from rocks up-ice. The study area is dry, underlain by well-drained glacial sediments, with no swamp or bog, which are known to concentrate redox-sensitive metals (Bogle & Nichol 1981). In the immediate sampling area, however, the western edge of the sampling area near Slush Lake had very thick (~10 cm) humus, but the thickness appears no effects on metal contents. A swamp (100 m in diameter) is present to the southeast of Transect 1, and though no soils were sampled in the

swamp, a gas sampler was placed close to the surface of the swamp water. Gas samples were collected in westward-inclined drill holes intersecting the mineralization and in nearby environmental monitoring wells (Figs. 22, 23). Drill holes were cemented after completion of drilling to prevent water flow into the basement and radioactive material from entering the shallow groundwater. A soil sampling station was taken ~1 km south of the sampling area to provide a background site. Similarly, gas samples were also collected several hundred meters away from the mineralization to provide a background values to samples in drill holes intersecting mineralization.

Gas Sampling

Diffusion gas samplers were constructed at the University of Ottawa, using ¼ inch copper tubing, silicon tubes and Pyrex beads, with the 2 lengths of copper tubing fastened to the silicon with stainless steel wire. The design is identical to that described by Sader *et al.* (2013). Two 10 cm portions of tubing were cut, and each crimped on one end. The other ends were placed into a silicon tube after it was filled with the beads. Care was taken to place coiled wire in each end of the silicon tube as to prevent beads from going into copper samplers. Samplers were then tightly coiled shut with the wire. Once in the field, washers were taped to the samplers and attached via duct tape to a roll of fishing wire, and lowered down into both drill holes and shallow environmental monitoring wells until submerged in the water table. Of the 6 gas samples taken, 2 were taken from environmental monitoring wells (MLNG01, MLNG03), 1 was taken from a nearby swamp (MLNG04), and three were taken from drill holes intersecting mineralization (MLNG05, MLNG06, MLNG07). After being submerged for approximately 72 hours, samplers were retrieved and immediately crimped to seal the gas inside the copper tubes.

Soil Sampling

Two transects (1 and 2) were traversed at 10-15 m sampling intervals (Fig. 22). Spacing of 10-15 m between sample points was selected based on the detection of possible dispersion products from narrow mineralized bodies. Transect 1, 503 m in length consisting of 33 sampling locations, was sampled from the southeast to northwest across the northern extension of the mineralized zone surface projection, whereas Transect 2 (total length of 333 m) consisting of 19 sampling stations was sampled from the northeast to southwest across the southern surface trace of the mineralized zone. The values at station MLN159 (Fig. 22) were used as a background site to the values of samples taken above the deposit, as it is approximately 1000 meters south of the sampling area. A total of 139 soil samples (humus, B- and C-horizon) from 43 sites along 2 traverses and a background station were collected in undisturbed forest. Site duplicates of all three horizons were taken once every ten to fifteen stations at the site where sufficient material is available. The Dutch auger and trowel were used for of sampling, and the sampling along each transect was completed over a one to two day period after careful visual examination of the soil profile at each site to ensure homogeneity of the soil samples. We sampled humus (~0.5 kg), E- (~1 kg), B- (~1 kg) and C-horizon (~2 kg), and placed the samples in freezer bags. Samples were split, sent to ACME Labs in Vancouver and also to the University of Ottawa.

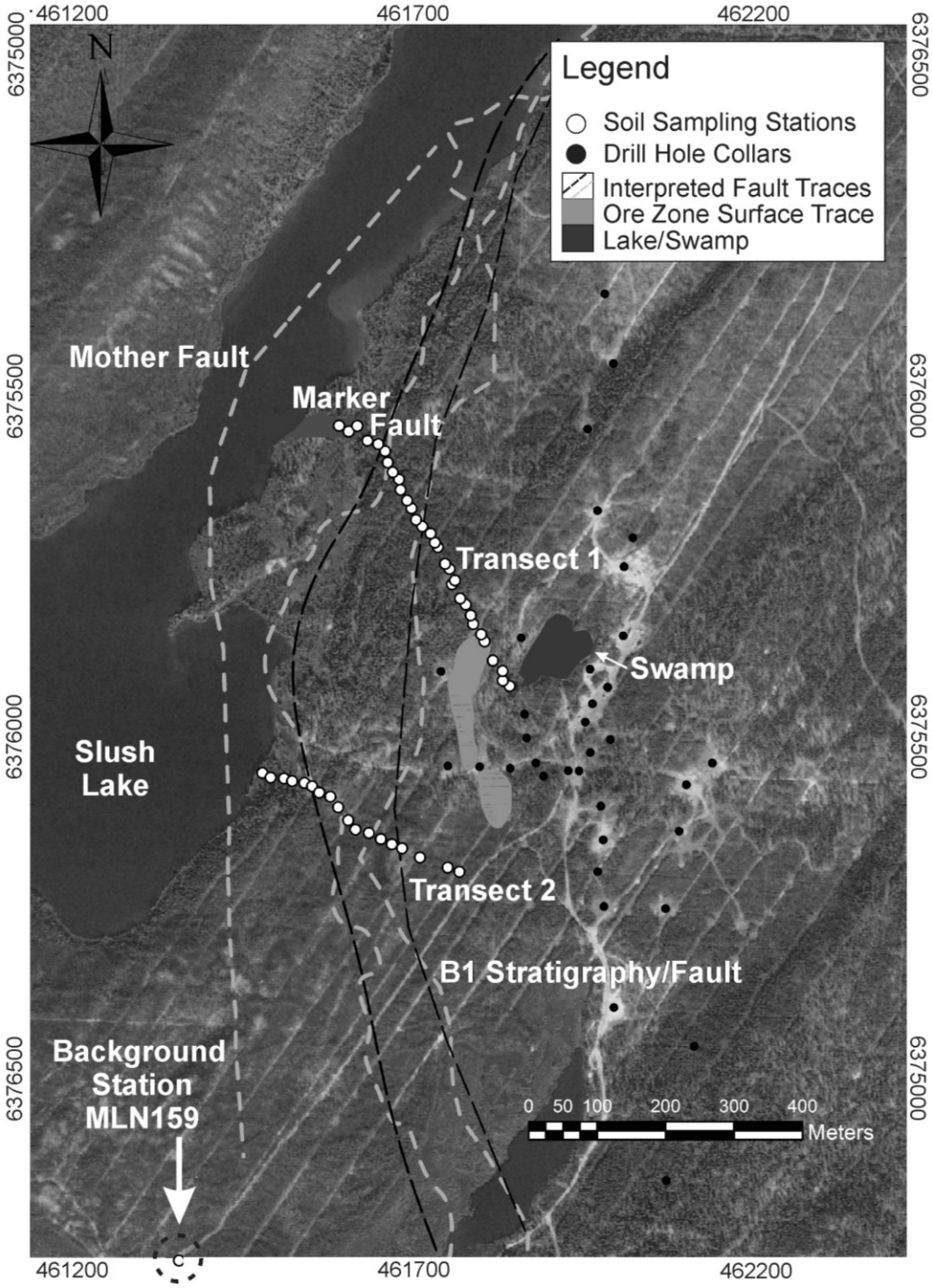

Figure 22: Soil sampling stations (white circles) plotted on an aerial photograph of the study area, with the surface trace of the ore zone in the middle and interpreted surface projection of basement faults plotted as dashed lines on the left, generally striking north-south. Soil sampling stations make up Transects 1 and 2. The sampling sites are approximately 10-15 metres apart. Background soil sampling site MLN159 was sampled more than 1 km south of the main sampling area. Interpretations based on a 3D seismic survey trace the Mother, Marker & B1 faults from the basement through the sandstones to the surface, where the surficial geochemical surveys in this study were conducted. The spatial distributions of soil and gas data were analyzed and plotted using the ArcMapTM utility of the ESRI ArcGISTM 10.0 software platform. Coordinates are in UTM NAD 83, Zone 13.

Water Sampling

A bailer for water sampling was constructed at the University of Ottawa from 1-inch diameter copper tubing 10 cm long, welded shut at one end. Once the sample was collected the temperature and pH of the water were measured. It was then filtered with a Millipore Sterivex-HV filter with 0.45 μm pore size and placed in high density polyethylene sample bottle (~25 ml) for tritium analysis at the University of Ottawa.

Analytical Methods

In Field

On the same day of sampling, the pH and conductivity of B-horizon samples were measured in a slurry of soil and distilled water (1:1) using a ExStik pH/ORP Meter for pH and Combo PH/EC/TDS/Temperature meter for electric conductivity. 2-3 grams of soil was mixed with equal parts water in small plastic cups, and mixed vigorously with a popsicle stick for 5-10 seconds before taking the readings.

Gas Analysis

Samples were again pinched off using a clamp. The extremity of the copper tube was cut, and was connected to an extraction line by using an NPT-conflat connector. The gas amount was read on a vacuum gauge. The gas volume was diluted 10,000 times, and the residual was purified on a Ti-sponge and two ST707 SEAS getters. Getters were heated for 15 minutes (600˚C for the Ti-sponge and 200˚C for the ST707) and then cooled down for 10 mn. The residual gas was sent to a Balzers C-200 quadrupole mass spectrometer (QMS). The noble gas species were measured isotopically: ^{4}He, ^{22}Ne, ^{36}Ar, ^{40}Ar, ^{84}Kr and ^{132}Xe. These masses were measured 20 times cyclically, and analytical precision on the measurements is less than 2% for each isotope. Errors reported are propagated uncertainties (1σ) that take into account analytical precision on the sample and standard measurements and volume

uncertainties of the copper tube extraction system. The QMS was calibrated against pipettes of standard air. Analyses were run starting from a blank, two samples and finally a standard reference gas. The final concentrations in ccSTP/cc were transformed in ccSTP/g of water by using the Bunsen solubility coefficient (ccgas/ccliquid) of each gas species at the sampling temperature.

Till Samples

Bulk-composition of till was measured with a Philips PW 2400 X-ray fluorescent spectrometer at the University of Ottawa. Samples were ground to less than 2 mm, and a glass disk was made from rock powder mixed with 78.52% $Li_2B_4O_7$, and 21.47% $LiBO_2$.

Soil Leaches and Digestion

Trace element composition data of soils were measured at ACME Analytical Labs, Vancouver, British Columbia, Canada. Every 15-20 sampling stations, where material was available, large amounts were collected from all horizons to make duplicate samples. All samples were dried and sieved to -80 mesh (0.177 mm) before leach and digestion. Humus samples were digested by aqua regia after drying at 60° C. B-horizon soil samples were leached by ammonia acetate (pH 5) (AA5). Duplicate samples were given different sample numbers and the data were used to ensure quality control during the analytical procedures. The duplicate analysis of samples suggests a reproducibility of +- 3%. Analysis of soils was via inductively coupled plasma mass spectrometer (ICP-MS) (Table 5).

Table 5. *Detection limit of analytical methods*

Method 1F-MS: Geochemical Ultratrace Aqua Regia Digestion (Acme Labs)									
Analyte	Mo	Cu	Pb	Ag	Ni	Co	As	U	W
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
DL	10	10	10	2	100	100	100	100	100

Method 1SLE: Ammonium acetate (pH=5) leach (Acme Labs)									
Analyte	Mo	Cu	Pb	Ag	Ni	Co	As	U	W
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
DL	10	20	20	3	50	20	100	5	10

Water Samples

For tritium analysis, 10 ml filtered water samples were mixed with 10 ml Ultima Gold LLT cocktail in high density polyethylene plastic vials, counted using a 1220 Quantulus ultra-low level liquid scintillation counter at the University of Ottawa. Tritium concentrations are reported in tritium units (TU) where 1 TU is defined as the presence of one tritium in 10^{18} atoms of hydrogen (H) (Clark & Fritz 1997).

Results

Background Value and Defining Anomalies

Anomalies are defined one way for gas samples, and three ways for soil samples. If gas samples displayed a $^{4}He/^{36}Ar$ ratio higher than the Air Saturated Water (A.S.W.) ratio of 1 (normal atmosphere), they were considered anomalous. Soil sample values in transects were compared to those of the background site. If peak to background ratios were greater than 3, they were considered to be anomalous. Though this number is arbitrary, high values are consistent with the other classification methods used. In the second method, metal values from the traverses are considered anomalous when they are greater than 2 standard deviations above the mean value of the population of both traverses ($\mu \pm 2\sigma$, Hawkes & Webb

1962). To confirm this graphically, and as a third method of defining anomalies, values were plotted in normal Q-Q plots to observe if anomalies indeed appear in a distinct grouping apart from the remainder of the population.

Gas Data

Measured ^{4}He concentrations range from 6.89×10^{-8} to 4.23×10^{-5} ccSTP/g. The lower amount is identical to that equilibrated with the atmosphere (A.S.W.), and three samples (MLNG01, MLNG03, MLNG04) displayed this low amount (Table 6). MLNG04 was collected 30 cm below the surface in a swamp and also exhibited values very similar to those of the atmosphere. However, three samples (MLNG05, MLNG06 and MLNG07) yielded anomalous $^{4}He/^{36}Ar$ ratios 715, 239 and 108 times the A.S.W. value, clearly indicating the addition of radiogenic ^{4}He (Figs. 23 and 24). Ratios of $^{4}He/^{22}Ne$ (790, 340 and 130 times A.S.W. value), $^{4}He/^{84}Kr$ (690, 240 and 110 times A.S.W.), and $^{4}He/^{132}Xe$ (580, 210 and 95 A.S.W.) were also observed, confirming the anomalous ^{4}He results. These three samples were all submerged in westward dipping drill holes that intersected mineralization along the unconformity or along the Marker fault, or the vicinity of the deposit (Fig. 23).

Table 6. *Gas & water data from drill holes & monitoring wells*

Gas Sample	MLNG01	MLNG03	MLNG04	MLNG05	MLNG06	MLNG07
Drill Hole Number	ML-07-02	BH-127	SWAMP	CX-052	CX-086	CX-40
Easting (m)*	461994	461177	461946	461958	461855	461796
Northing (m)*	6375251	6374578	6375617	6375599	6375645	6375461
Depth (m)	6.5	8.4	0.3	49.0	11.0	10.0
Altitude (m ASL)**	520	528	525	529	536	533
^{4}He (ccSTP/ccwater)	6.93E-08	6.89E-08	7.34E-08	4.23E-05	1.04E-05	4.40E-06
$^{4}He/^{36}Ar$_sample	0.94	0.97	1.05	714.73	238.99	108.34
$^{4}He/^{36}Ar$_ASW						
$^{4}He/^{22}Ne$_sample	1.02	1.08	1.09	786.17	335.77	128.86
$^{4}He/^{22}Ne$_ASW						
$^{4}He/^{84}Kr$_sample	0.93	0.99	1.07	690.33	240.37	107.1
$^{4}He/^{84}Kr$_ASW						
$^{4}He/^{132}Xe$_sample	0.88	0.84	0.97	575.34	205.52	95.04
$^{4}He/^{132}Xe$_ASW						
Water Sample	MLNW01	MLNW02	MLNW03	MLNW05	MLNW06	MLNW07
Tritium Contents (TU)	8.18	13.06	N/A	N/A	12.85	4.62
pH	8.4	9.2	9.1	7.8	10.6	9.4
Temperature (°C)	10.5	10.0	9.0	7.8	10.6	9.4
Conductivity (µ/m)	148	234	85	381	520	190

Notes: ASW=Air Saturated Water
TU=Tritium Units
ASL=Above Sea Level
*UTM NAD 83 Zone 13.
** The top of the drill hole

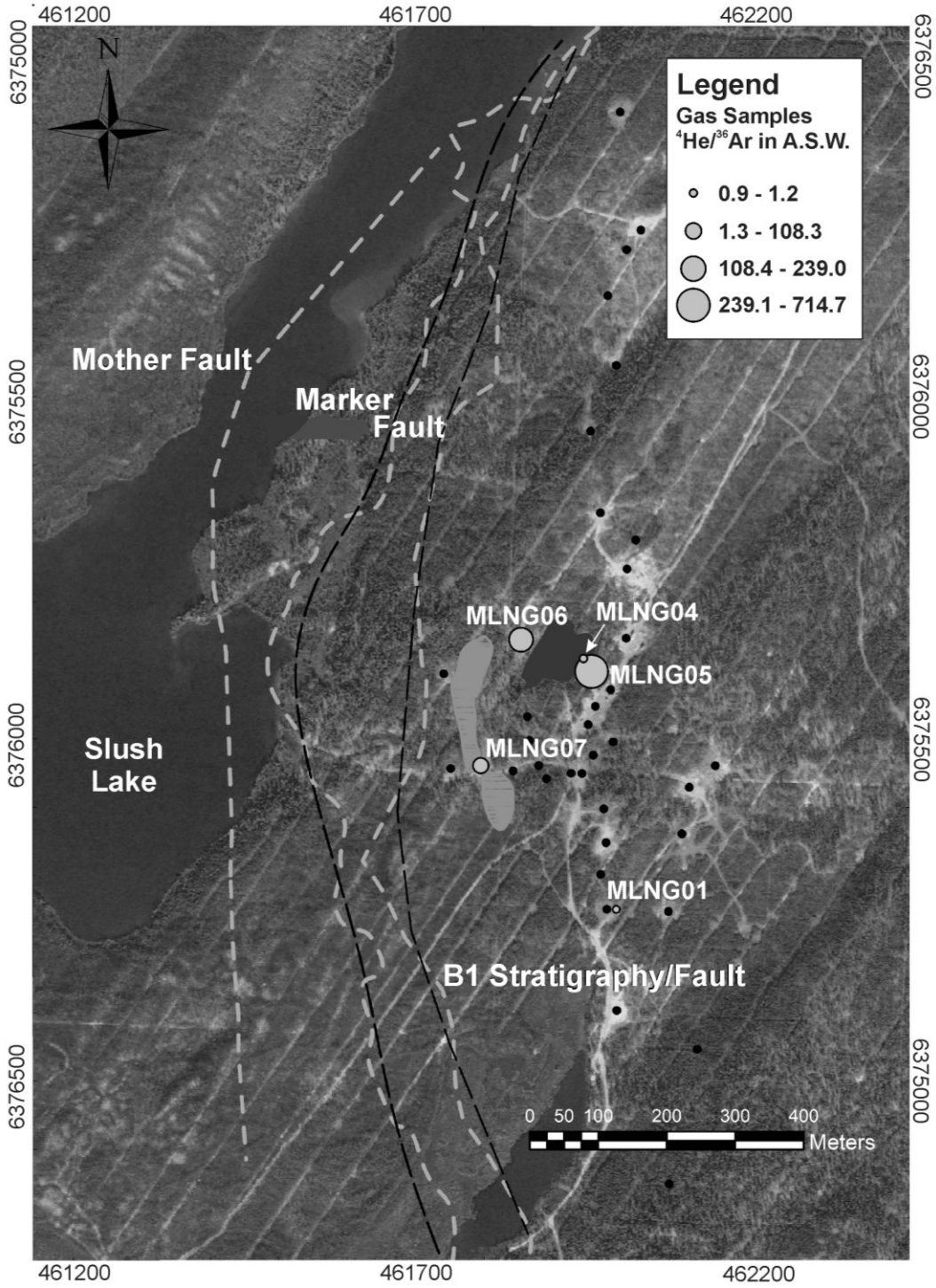

Figure 23: Gas samples (grey circles) MLNG01 & MLNG04-07 are shown as bubble plots on the aerial photo of the property as ratios of $^{4}He/3^{6}Ar$ gas in each sample to the calculaed $^{4}He/^{36}Ar$ gas in air-saturated water (A.S.W.). Samples MLNG05-07 display $^{4}He/^{36}Ar$ ratios from 100 to more than 700 times the value for atmosphere in drill holes intersecting mineralization. Sample MLN G04, which was sampled in the swamp adjacent to the deposit to the east, displayed atmospheric values, as did samples MLNG01-03 (not shown), ~200 m southeast of the study area. Coordinates are in UTM NAD 83, Zone 13.

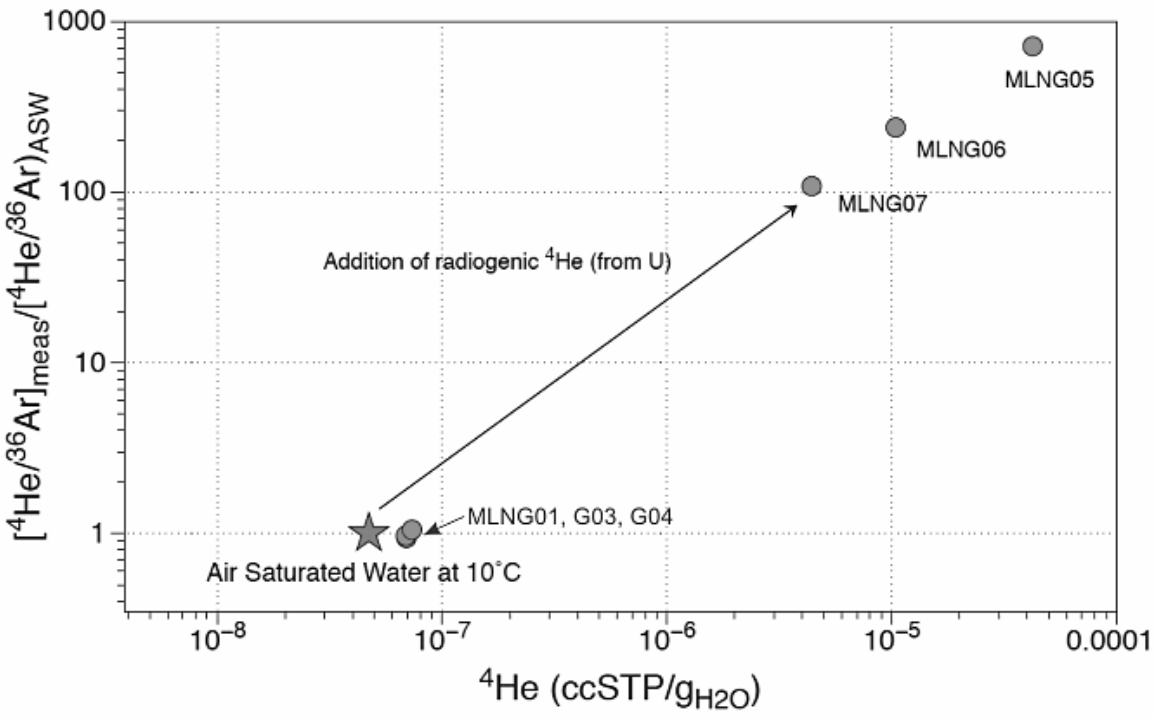

Figure 24: Ratios of $^{4}He/^{36}Ar$ in sample over the $^{4}He/^{36}Ar$ in the calculated value for air-saturated water (A.S.W.) vs. the abundance of ^{4}He in each gas sample. Three samples (MLNG05, MLNG06 and MLNG07) display extremely radiogenic values of ^{4}He, while samples placed in shallow environmental monitoring wells (MLNG01 and MLNG03) and nearby swamp (MLNG04) plot nearly identically to the atmosphere value (atmosphere = $^{4}He/^{36}Ar$ ratio of 1). The radiogenic ^{4}He observed in these water-filled drill holes could possibly be sourced from the U deposit at depth.

Soil Data

Humus Data

Humus samples show substantial variability in the concentrations of U, Ni, Cu and Pb (Cu and Pb, Fig. 25). These metals, especially Ni and Cu, are considered to be pathfinder elements for U deposits in sandstones, till, peat and soil in the Athabasca region (Jefferson *et al.* 2007b). Peak to background values were measured using values from both soil sampling traverses and comparing them to the values at site MLN059 (Table 7). The highest U value yielded a peak-to-background ratio of 2 (0.6 ppm, 0.3 ppm background). Similarly, the

highest Ni value also yielded a peak-to-background ratio of 2 (1.1 ppm, 0.5 ppm background), also double the background. To a lesser extent, Cu and Pb values yielded 14.5 ppm and 35.4 ppm (9.6 ppm and 21.2 ppm background values), peak-to-background ratios that are 1.5 and 1.7, respectively.

Metal values in Transect 1 and 2 are considered statistically anomalous. All of the aforementioned metals U (0.2 ppm+0.3ppm), Ni (3.7 ppm+2.2 ppm), Cu (8.8 ppm+3.6 ppm) and Pb (14.2 ppm+11.4ppm) have values that are above the anomalous threshold of $\mu \pm 2\sigma$. All the aforementioned metals are highest at sites near or overlying the surface traces of the mineralized zones, and are also found directly above the surface traces of the mineralization-hosting Marker Fault and also the B1 Stratigraphy Fault. These faults are interpreted to come to surface from basement rocks through the overlying sandstones based on the seismic survey of the project area.

B-horizon Data

Concentrations of U, Cu and Pb in AA5 leach of the B-horizon soil samples display high values with respect to the B-horizon soil at background site MLN059 (Fig. 25). Peak to background ratios of element concentrations are up to 2.9 for U (maximum 102 ppb U, background 35 ppb) 10 for Cu (220 ppb maximum, background 22 ppb) and 2.4 for Pb (2,122 ppb maximum, 896 ppb background). Values are also anomalous, with U (32 ppb+30 ppb), Cu (73 ppb+108 ppb), and Pb (751 ppb+718 ppb) all more than two standard deviations above the mean for their respective metal populations. Similar to the humus, anomalous values are situated in the surface area directly above the mineralization zones and directly above the surface projection of the Marker and B1 Stratigraphy faults.

Table 7. *Background site MLN159 values*

Sample Soil	MLN159A Humus	Sample Soil	MLN159B B-Horizon
Mo_ppm	0.10	Al_ppm	426
Cu_ppm	9.58	Ba_ppb	4621
Pb_ppm	21.20	Ca_ppm	7
Zn_ppm	29.9	Ce_ppb	173
Ag_ppb	31	Cs_ppb	14
Ni_ppm	4.6	Cu_ppb	22
Co_ppm	0.6	Dy_ppb	14
Mn_ppm	101	Fe_ppm	29
Fe_pct	0.33	Ga_ppb	21
As_ppm	0.4	Gd_ppb	15
U_ppm	0.3	La_ppb	98
Th_ppm	0.5	Mg_ppm	2
Sr_ppm	25.4	Mn_ppb	255
Cd_ppm	0.60	Nd_ppb	102
Sb_ppm	0.05	Pb_ppb	896
Bi_ppm	0.14	Pr_ppb	23
V_ppm	5	Rb_ppb	91
Ca_pct	0.20	Sm_ppb	20
P_pct	0.041	Sr_ppb	133
La_ppm	6.8	Th_ppm	94
Cr_ppm	3.9	U_ppb	35
Mg_pct	0.03	V_ppb	71
Ba_ppm	330.1	Y_ppb	63
Ti_pct	0.008	Yb_ppb	9
Al_pct	0.40	Zn_ppb	134
Na_pct	0.003	Zr_ppb	77
K_pct	0.04		
Sc_ppm	0.6		
Tl_ppm	0.05		
S_pct	0.03		
Hg_ppb	96		
Se_ppm	0.4		
Ga_ppm	1.3		

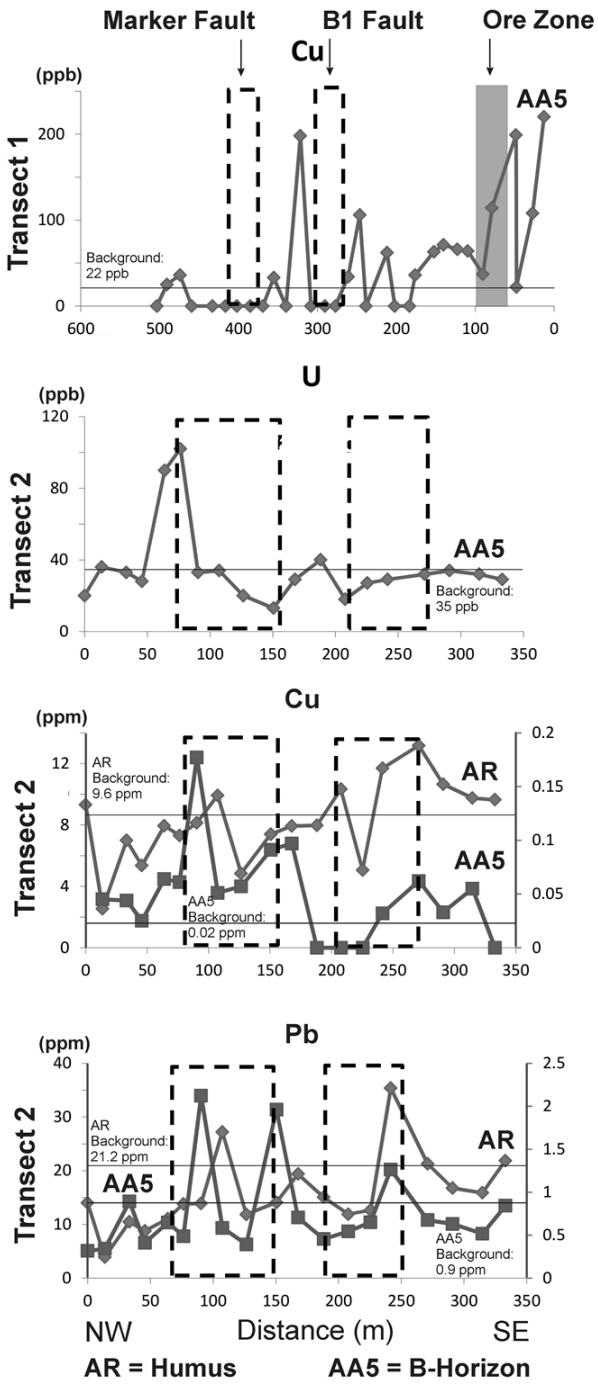

Figure 25: Trace metal abundances in soil sampling transects 1 & 2 at Millennium: Cu, U and Pb after aqua regia (AR) digestion and ammonium acetate (AA5) weak leach of humus and B-horizon soils, respectively. Background station values for each metal value are also plotted as horizontal lines on each graph. The shaded area indicates the area directly above the ore zone, and the dashed lines indicate the interpreted surface expression of the ore-hosting Marker & B1 Stratigraphy faults. Anomalous values indicate the possibility of fault-controlled redistribution of U & its associated pathfinder metals.

Q-Q Plots

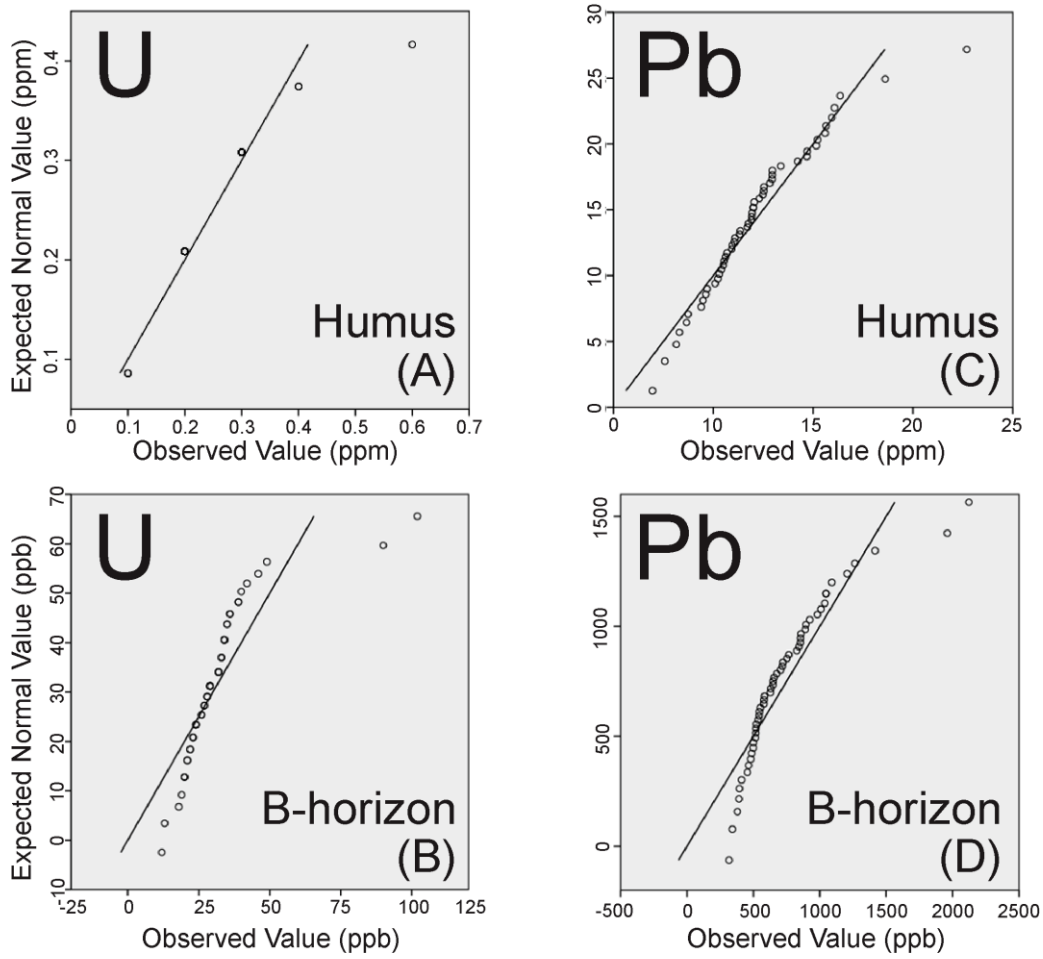

Figure 26: Q-Q plots (A =U in humus, B = U in B-horizon, C = Pb in humus, d = Pb in B-horizon) of U & Pb in humus & B-horizon soils using aqua regia digestion & ammonium acetate leach, respectively. Values are considered anomalous when they appear in a distinct population apart from the linear, normally distributed values usually observed in normal Q-Q plots. Anomalous values are overlying or immediately adjacent to both the surface projections of the ore zones & the deposit-hosting Marker & Mother faults.

The Q-Q plot for U in humus displays a sample isolated from the rest of the values (Fig. 26a). Values for U in the B-horizon appear distinctly polymodal as well, with two values in a distinct grouping apart from the remainder of the Pb population (Fig. 26b). The pattern is similar for Pb in humus, with at least two populations (Fig. 26c). Pb in the B-horizon also displays a polymodal population of two samples that appear to be distributed a

considerable distance from the majority of the data (Figs. 26d). Therefore, humus and B-horizon values for these metals are anomalous statistically and graphically in Q-Q plots. Metal values in Q-Q plots correspond to those soil samples overlying or immediately adjacent to the surface projections of the mineralized zones and deposit-hosting Marker fault and the B1 Stratigraphy fault.

pH and Conductivity Results of B-horizon Soils

pH and conductivity values measured from B-horizon soil-water slurries were observed to be highest towards the eastern part of the sampling area. The highest pH value observed (8.7) was near the eastern end of Transect 2 at station MLN155 at the interpreted surface expression of the B1 Stratigraphy fault, while the mean value of the B-horizon samples was 8.1. Conductivity values are at maximum at the northwestern tip of Transect 1 (227 μS/cm), with a mean of 32.3 μS/cm.

Water Data

Measured tritium levels in water display concentrations ranging from 4.6 to more than 13 TUs (Table 6). pH values averaged 9.1, with a maximum value of 10.6. High values are likely due to cement used to fill the unconformity and mineralization of drill holes to prevent the dispersion of high U into the shallow groundwater reservoir and possible in-fill of water during mine development. Conductivity values averaged 260 μ/m, with a maximum value of 560 μ/m. The average temperature of water in the drill holes/monitoring wells was 9.6 °C.

Discussion

Sources of Glacial Till

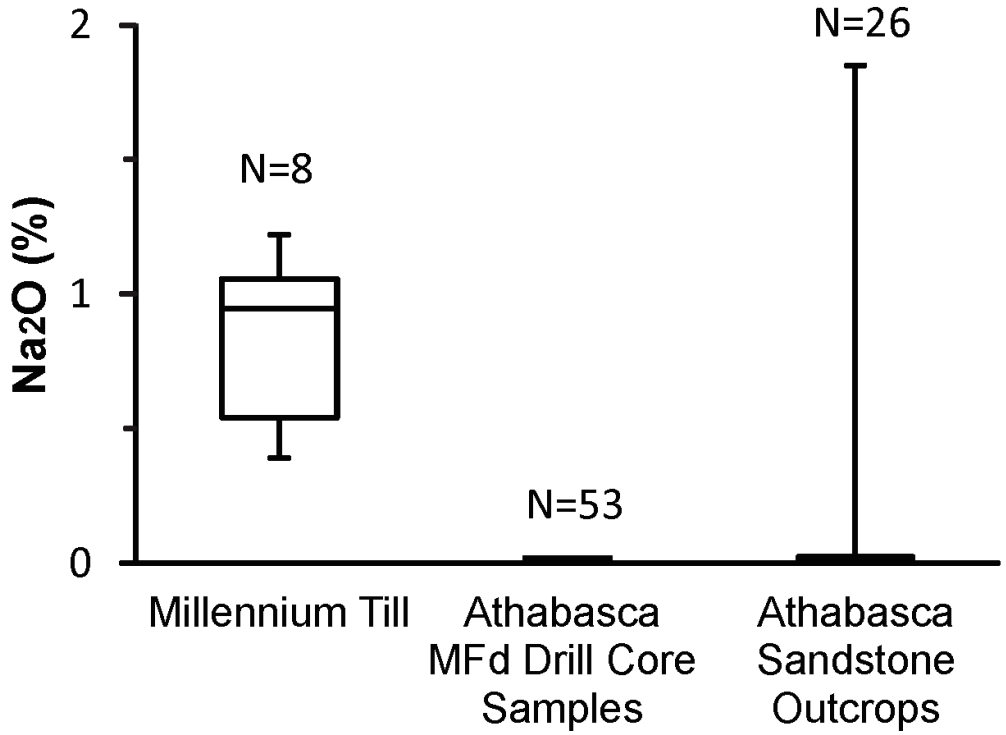

Figure 27: Box-whisker plot of Na_2O content in tills above Millennium (this study) compared to the data for both Athabasca sandstone & drill core in the area (Card *et al.* 2011). Till contains much higher Na_2O than the sandstones, indicating input from rocks in the up-ice direction outside the Athabasca basin.

Glacial till (Table 8) contains high Na_2O, 0.39-1.08 wt %, which is more than 20 times that of the Athabasca sandstones (0.001 to 0.05 % Na_2O; Card *et al.* 2011) in the area (Fig. 27). Drill hole geochemistry was also completed on the Mfd member sandstones by Card (2012), with total Na_2O values on samples from the Dunlop Formation yielding similar values (0.03 to 0.001 % Na_2O) to the outcrop data. The till values with the highest Na content (MLN120C, 1.22 wt %) is northeast of the mineralization on Transect 1, giving a possible indication of down-ice dispersion from some source outside the deposit-area to the northeast by the last glacial event, though this is not entirely clear based on the small sample population. This high Na content in till samples indicates that the glacial sediments have

contributions from granitic basement rocks, perhaps those from the Archean Wollaston Domain northeast of the Athabasca basin. The results are not surprising, considering the distance of approximately 150 km to the exposure of Archean rocks northeast up-ice along the dominant ice flow direction.

Table 8. *Whole rock data for Millennium till samples*

Sample #	MLN100C	MLN105C	MLN114C	MLN120C	MLN125C	MLN146E	MLN150C	MLN159C
SiO2(%)	87.78	86.61	81.71	87.99	94.28	89.20	94.14	86.08
TiO2	0.133	0.126	0.196	0.098	0.073	0.121	0.055	0.147
Al2O3	5.42	5.22	6.98	5.66	2.68	3.57	2.58	5.21
Fe2O3(t)*	0.739	0.589	1.482	0.542	0.163	0.392	0.205	0.628
MgO	0.27	0.21	0.37	0.23	0.10	0.18	0.10	0.26
MnO	0.009	0.006	0.011	0.007	0.003	0.003	0.003	0.007
CaO	0.68	0.49	0.61	0.65	0.31	0.22	0.30	0.56
Na2O	1.08	0.89	1.05	1.22	0.56	0.39	0.48	1.00
K2O	1.123	1.088	1.743	1.328	0.550	1.167	0.462	1.029
P2O5	0.021	0.031	0.056	0.032	0.013	0.023	0.023	0.024
L.O.I.	1.70	1.43	1.83	2.40	2.13	1.55	2.17	1.32
Conc.	97.33	95.34	94.30	97.83	98.77	95.31	98.37	95.02
Total	99.03	96.77	96.13	100.23	100.90	96.86	100.54	96.34
Ba (ppm)	259	257	300	278	115	161	95	209
Rb	42	36	57	48	24	38	20	39
Sr	120	92	116	124	67	46	62	100
Th	14	bd	17	bd	13	bd	bd	19
V	14	15	29	14	bd	15	bd	24
Y	8	6	16	bd	bd	bd	bd	bd
Zr	224	215	349	107	114	203	94	320
Ce	15	42	23	43	bd	17	bd	23

Notes: Major and trace element data by X-ray fluorescence. MLN= Millennium
*: Total Fe expressed as Fe2O3.
bd = below detection limit

Spatial Distributions of Anomalies in Soil (Humus and B-horizon Soil)

Our results show that anomalies in U and pathfinder metals Ni, Co, Cu and Pb occur in aqua regia digestion of humus and ammonium acetate leach of the B-horizon above the deposit, as well as the area over the surface projection of the Marker and B1 Stratigraphy faults. U and its associated pathfinder elements should be concentrated in humus and B-horizon, as the organics in humus and Fe/Mn hydroxides in B-horizon scavenge mobile metal ions extremely well (Cameron *et. al*. 2004). In aqua regia digestion of humus, anomalies of Cu and Pb are all situated above the surface projection of these faults. However, in the ammonium acetate leach of the B-horizon soils, anomalies are more widespread, both directly above and between the fault projections, and also above the mineralized zone in Transect 1 (Fig. 10). The broad distribution of these anomalies suggests that faults are likely contributing to dispersion of metals.

Abundance and Spatial Distribution of ^{4}He Gas Anomalies

Gas samples placed in environmental monitoring wells recorded the value for air saturated water, or atmosphere, but those samples placed in drill holes recorded highly anomalous values. Shallow environmental monitoring wells were only drilled a couple meters into the ground within glacial sediments. The glacial sediments are well-drained sands and were overall dry during the sampling period. The pore water was likely saturated with the atmosphere. The anomaly observed in one gas sample (MLNG07) appeared to be situated in a drill hole (CX-086) overlying the surface trace of the southern mineralized zone at Millennium. The surface traces of multiple faults (Marker and B1) are just to the west of the mineralized zone, and these well-defined basement fault splays become vertical in the sandstone (Fig. 17) where upward migration of He is likely occurring, perhaps even in

fractures that drill holes intersect, and it is possible we observe this phenomenon in our study. However, it is possible He could be travelling both up drill holes, which we observed, and also along faults. For the latter, this could be answered by future sampling, including gas sampling in the areas displaying high metal values or in drill holes that intersect faults.

Tritium Concentrations in Groundwater

Tritium (T) is a naturally occurring cosmogenic nuclide with a half-life of 12.32 years. Tritium was also produced during above ground nuclear weapons testing in the 1960's, causing elevated tritium levels in both surface water and groundwater on a global scale (ODWAC Report 2009). In this context, tritium is considered an event marker, and may only be used for identification of human impacts or relative, and not exact age (Table 9, Clark & Fritz 1997). The tritium concentrations in our water samples indicate that either the modern groundwater system is free of any bomb tritium (4-15 TU, Table 6), or, that these are very old waters that were present before the bomb testing. In shallow, well-circulated groundwater, tritium levels in groundwater are low because the short half-life of tritium allows insufficient time for significant accumulation, even if a deeply buried U deposit lies beneath. This is in agreement with the tritium levels in samples from this study, which all have a residence time between 5 and 15 years.

Table 9. *Approximate groundwater age based on tritium content (Clark & Fritz 1997)*

Tritium Content (TU)	Groundwater Age
<0.8	Submodern (<1950's)
0.8 to 4	Mix of submodern to modern
5 to 15	Modern (<5-10 years)
15 to 30	Contribution of nuclear bomb-related tritium
>30	Recharge occurred in 1960's/1970's

Upward Movement of Elements and Gases from Mineralized Zones to the Surface

Our results indicate that upward movement of metals from the ore to the surface media along faults. Transport mechanisms of metals from concealed mineral deposits to surface media have been in debate (e.g., Cameron *et al.* 2004). Proposed models include upwelling of groundwaters (Sader *et al.* 2011), ground and soil water advections or diffusion (Govett 1976), vapour transport (Smee 1998), upwelling of deep water along faults during seismic activity (Cameron *et al.* 2002), and capillary migration of ions (Mann *et al.* 2005). The spatial correlation between metal anomalies and faults suggest that seismic pumping along faults contributed to upward dispersion of metals from the mineralization to the surface media above (Cameron 2013).

The "grid" method of sampling was tested in the multi-year, multi-media CAMIRO project to evaluate signatures over two U deposits. This included sampling multiple soil horizons over deposits and using multiple leach and digestion methods. In their study, U, Co, and Ni anomalies in soil occur over the surface trace of ore zones at both Cigar Lake (400 m depth) and at McClean Lake (150 m depth) and were best in the humus horizon, with somewhat positive, but less convincing, results in the B and C horizons (Bonham-Carter & Hall 2010). Some of the anomalies at both locations were in close proximity to swamps northwest of the deposits, which may have caused metal accumulation in peat and not the B- and C-horizons. This illustrates that it is crucial to have homogenous sampling conditions, as the swampy conditions at the western edge of their sampling grids was not identical the rest of the sample sites. At the Cigar Lake site, prominent U, Co, Ni, and As anomalies in humus run SW-NE across the westerly tip of the surface trace of the ore zone, and is close to a mapped fault that has the same orientation (Bonham-Carter & Hall 2010). If vertical migration occurs over these extensive distances, the metal signature likely travelled up ore-

hosting faults with upward dispersion of metals through sandstone to till, with metal incorporation into soils occurring within the last 7,000 years. The Cigar Lake and McClean deposits are much shallower than Millennium, and fault-related dispersion is widespread (up to 500 m at Cigar Lake) in soils at surface, whereas it is appears to be narrower at Millennium (~200 m). The CAMIRO study was unable to conclude whether anomalies observed were solely sourced from faults intersecting the underlying mineralization, and attributes "alternate mechanisms" for anomaly formation (Bonham-Carter & Hall 2010). At Millennium, however, metal anomalies were numerous and observable in multiple soil horizons overlying the Marker fault, which likely extend to surface (Wood *et al.* 2012). These faults may have provided conduits for metal migration from ore to surface materials.

The amount of He emanating from a U deposit is substantial. 1 g of ^{238}U, allowing for the 0.7% ^{235}U present with the ^{238}U, produces 12 x 10^{-8} cm^3 He per year (Dyck 1976). Being inert and very light, He has a great tendency to escape into fissures and thence into the groundwater regime (Dyck 1976). Anomalous abundances of He in groundwaters have also been observed around other U deposits. Clarke and Kugler (1973) found He contents of up to 600 times atmosphere in groundwater above U deposits at Elliot Lake, Ontario and Inda Lake, Labrador. Dyck (1973) found as much as a hundred-fold increase in the He content in gases dissolved in in some U mine waste waters in Elliot Lake, Ontario. Dyck and Tan (1978) tested seasonal variations of He, Ra, and U in lake waters near the Key Lake U deposit, and He concentrations of nearly four times atmosphere were obtained in samples near the bottom of lakes where the sandy overburden extends for some 50 m directly to the ore zone. Dyck and Da Silva (1981) found that Vulture and Candy lakes in northern Saskatchewan in close proximity to U mineralization at McClean Lake at were found to contain anomalous He and Rn in the sediment. Butt and Gole (1986) observed helium in

excess of atmosphere in groundwaters around U mineralization at Honeymoon, Mayingee, Bennett Well and Stuart-Shelf/Roxby Downs in Australia. Anomalous He has also been found in overburden gas and soil gas over U mineralization (Goldak 1972; Reimer *et al.* 1979; Butt & Gole 1985). However, the overburden and water above deposits Butt & Gole (1985) examined did not display anomalous He, leading them to presume that equilibration between overburden gas and atmosphere may be far more rapid than that between overburden gas and groundwater, so that any He released from the water may be quickly dispersed. Though He may escape into the atmosphere or is carried away by circulating groundwaters in porous soils, it can be observed as increasing gradient over the deposit in stagnant groundwater or impervious soils (Dyck 1976). A study by Reimer *et al.* (1979) conducted in Weld County, Colorado, U.S.A. showed that values for He in soil gas can be contoured to outline an anomalous area, and that the anomaly is displaced from the deposit in the direction of groundwater flow. Additional soil gas studies by Reimer *et al.* (1979) include the Ambrosia Lake uranium district, New Mexico, where the location of He anomalies are related to groundwater movement; and the Schwartzwalder U mine in Colorado, where He anomalies may be related to geologic structure. Faults or fracture zones are known to be a conduit for bringing dissolved metals to the surface, and spatial correlations exist between anomalies in soil and fault structures (Cameron *et al*. 2004). Therefore, these features are likely too, as for metals, a conduit for upward gas movement, in addition to the groundwaters above the mineralization at Millennium.

Numerous geochemical anomalies in soils and gas at the property show that fault-controlled redistribution of elements possibly exists over the deposit, and based on our ^{4}He results is a process occurring at present-day. Our results suggest upward migration of metals

and He to surface through these geological features, detectable by geochemical exploration methods for U using different types of surface media.

Implications for U Exploration

This study overlying the Millennium deposit 750 m beneath the surface shows that such geochemical analysis is capable of detecting gas and metals related to deeply buried U deposits, even in sporadic discontinuous permafrost regions of Canada, where the dispersion of metals, and likely gas, is slow at low temperatures. In addition, this study confirms that geochemical analysis of gases dissolved in water in drill holes provides valuable information. Gas diffusion samplers are easily constructed, deployed quickly and for a short period, and data can be obtained quickly.

This study shows that broad geochemical anomalies in soil and gas exist both directly above and near the surface projection of the U deposit, but also to the northwest, where the deposit-hosting Marker fault and Mother and B1 faults likely extend to surface. For similar surveys in U exploration campaigns, soil samples should be collected along traverses over a target defined by geophysical techniques, radiometrics and larger, property-scale soil sampling if possible. Detailed, deposit-scale sampling at least 100 m away from the target with 10-15 m sample spacing perpendicular to the last major ice flow direction is recommended to avoid any "smearing" effect glaciers may have had on metal accumulation in the till. Background sample sites, or transects above non-mineralized zones, are recommended to have a good idea of values for which to define as anomalies. Transects should be designed to collect similar media under homogenous surface conditions and relatively uniform topography.

Geochemical exploration methods described in this paper are fairly inexpensive compared to other exploration techniques. It has also been demonstrated that gas sampling at

surface and analysis of ^{4}He is a valid and complementary deposit-scale prospecting method for U deposits. At reasonable cost, the methods shown in this paper used in a combined soil, till and gas geochemical survey serve as complementary techniques to geophysical methods in discerning drilling targets prior to exploration for deeply buried U deposits in glaciated terrains.

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CHAPTER 4

Conclusions

The aim of this thesis was to study the geochemical expression of surface media over deeply buried U deposits, with implications for mineral exploration in sporadic permafrost regions of northern Canada. The Proterozoic Phoenix and Millennium U deposits, buried under hundreds of meters of sandstones and Quaternary glacial till, appear to be discernible in the geochemistry in samples of various surface media above them. Multiple methods of sampling and analysis of surface media over the deposits were discussed in this thesis, and possible explanations of the geochemical processes responsible for anomaly formation were given. These anomalies were identified and scrutinized within a geological, geochemical and geophysical context with relation to these U deposits at depth.

The humus and B-horizon soil profiles above the Phoenix deposits contained the most pronounced anomalies of U, Pb, Co, Ni, Cu, Mo, As and W; metals that are tightly bound to the organic material within the humus, and to Fe- and Mn-hydroxide compounds in the B-horizon. Leaching humus in various acids demonstrated metals were only dissolved in strong acids, eliminating Fe- and Al-hydroxides as possible binding agents, and negating drilling fluid, and likely airborne pollutants, as possible contamination sources. The anomalous data in humus and B-horizon soil were reproducible over a three-year period. This is a very important result because reproducibility is often one of the biggest problems in multi-year geochemical surveys. High values of these metals found in the silt fraction of the C-horizon till, though these were not considered to be anomalous. Uppermost sandstones at Phoenix revealed high values of U and associated pathfinder elements that were broadly distributed in drill holes over the deposits. Anomalies are the most pronounced overlying and adjacent to the surface traces of the ore zones and above the basement location of the ore-

hosting WS shear zone at the Phoenix deposits. The WS shear, though well defined in basement rocks, is observed to have an increasingly vertical dip in sandstones to the immediate northwest of the deposits and splays into multiple fault splays based on drill hole observations. U, and associated metals found in high amounts in the ore, are present in high levels in uppermost sandstone. These elements are also in high amounts in the overlying till and even further concentrated in B-horizon soil and humus likely from groundwater upwelling through physical conduits such as numerous fault splays, and clean, porous quartz-rich Mfd sandstone. This groundwater upwelling may have been aided by post-glacial uplift, though this is somewhat unlikely for upward fluid flow through more than 400 metres of sandstone. More likely is a scenario of seismic pumping of groundwaters through reactivated, post-Athabasca sandstone structures like the WS shear, facilitated by fractured and porous uppermost sandstones, carrying metals formed during Proterozoic time through till cover to plants and soil at surface sometime in post-Quaternary time. This is likely why we do not see anomalies in till but observe them in humus and B-horizon soils. Mechanisms such as groundwater upwelling along faults and through porous rock, and seismic pumping along faults have been studies from the VMS environments of northern Ontario, the porphyry copper settings of Chile, and the Athabasca basin.

The B-horizon soil above Millennium contained the most pronounced anomalies of Pb and Cu in that study, and to a lesser extent these anomalies were also present in the overlying humus. Gas samples taken from water-filled drill holes intersecting mineralization were up to 700 times atmosphere, indicating the presence of radiogenic ^{4}He – a U decay product – that is likely related to the U deposit at depth. Metal values in humus above the Millennium are not as high as those in humus at the Phoenix study site, but are far more pronounced in the B-horizon at Millennium. A possible reason for this is that humus is less

developed then at the Phoenix study site, as a major forest fire in 2008 burned through much of the study area and likely destroyed the established organic material, therefore causing a loss in metal content. A significant difference between the study sites is that the ore-hosting Marker fault at Millennium is clearly defined coming to surface in the seismic survey completed at the property, which may be responsible for more pronounced anomalies in the B-horizon than those observed at Phoenix. Seismic pumping along this fault, bringing metals from the mineralization to surface during earthquakes, is a much more credible upward migration mechanism at this site. It is also possible that the migration of He took place along this and other basement-hosted faults that are observed to come to surface (Mother and B1), but is more likely upward migration of gas is taking place in groundwater above the deposit. The groundwater table is interpreted to be relatively flat with little upwelling, and the tritium data suggest young, well-circulated water, giving further evidence to the He being a process occurring at present-day.

In terms of both study areas, the traverse method of soil sampling across the surface projection of the deposits proved very useful for a number of reasons. It allowed the ends of soil sampling transects to act as a qualitative background to the deposits and their associated fault projections. The whole-rock composition of till showed, through comparison of Na content with the underlying sandstones, that smearing of material from a source up-ice of the deposits is the primary reason transects should be sampled perpendicular to the last major ice flow event as opposed to the grid method of sampling in a square or rectangle. This is because metals in till would be likely be smeared in the same manner, which could lead to errors in interpreting the soil geochemical data if transects were sampled parallel to ice flow or in grids.

Implications of this research are several-fold. One, is that it expands the likelihood of geochemical exploration in areas with extensive till cover that were previously thought to be too deep for geochemical prospecting of surface media to be of any use. This is an exciting development for the exploration industry, because deposits considered previously be "blind" may actually be seen in the surface media overlying them if the geological features allow, and the correct geochemical exploration techniques are utilized. Upward migration mechanisms suggested in this study may be equally applicable elsewhere in this basin environment. Two, as U deposits are well known to be structurally controlled, it stands to reason the dispersal of its ore post-deposition would also be as such. Knowledge of structure at depth and at surface, if possible, would be beneficial when formulating any interpretations of upward element migration. Knowledge of till thickness, local groundwater table information and lithological competency of shallow sandstones overlying prospects would also be useful to know in order to effectively integrate additional interpretations previously suggested that may also be related to upward element migration.

In conclusion, understanding the multi-media surface geochemistry far above these U deposits within the context of their geology and geophysical signature contributes to the understanding of the element migration mechanisms that may present evidence of these previously hidden resources. The characteristics of the deposits, possible pathways of their dispersal to surface, and surface media have all been addressed in this thesis. The observation of reproducible anomalies is attributed to sampling and analytical methods well known in industry, government and academia. Upward movement of metals via seismic pumping in fault splays and porous rock to surface media at Phoenix, and seismic pumping of metals at Millennium along well-defined basement faults and gas upwelling through groundwater through sandstone to surface, have been suggested as ways of interpreting the

geochemical data above these U deposits.

Summary of Conclusions

Phoenix surficial geochemistry study

- Results show U, Pb, Co, Ni, Cu, Mo, As and W anomalies in soils above the deposits and basement location of the deposit-hosting WS Shear zone. High-density sampling in 2012-2013 around the highest U site from 2011 confirmed anomaly reproducibility. Metals in humus are only dissolved by strong acids, indicating they are tightly bound in organic compounds. This negates drilling fluid, and likely airborne pollutants, as possible contaminant sources.
- Uppermost sandstones display elevated metal values in HNO_3:HCl partial & total digestions.
- Evidence suggests upward transport of metals from sandstones to soils through fault splays and porous sandstone, originating from the deposits, likely driven by seismic pumping during earthquakes. The data indicates the traverse method of geochemical prospecting effectively discerns buried U deposits using surface media.

Millennium surficial geochemistry study

- Soil samples along transects over Millennium yielded anomalous values in U (≤0.6 ppm), Pb (≤35 ppm) and Cu (≤15 ppm) in aqua regia digestion of humus. Anomalous values were also detected for U (≤102 ppb), Pb (≤2100 ppb) and Cu (≤220 ppb) in ammonium acetate leach of B-horizon soil. Anomalies occurred directly above surface projections of the deposit and faults, including the ore-hosting Marker fault. Broad geochemical anomalies suggest fault-controlled dispersion of metals.

- Gas samples yielded anomalous $^{4}He/^{36}Ar$ ratios of 715, 239 and 108 times the A.S.W. (Air Saturated Water) value. Tritium concentrations in water are low, indicating recharge of water after the 1960's. Results suggest present-day upward migration of metals and ^{4}He to surface through geological features, likely driven by seismic pumping along the ore-hosting Marker fault in the case of metals, and the movement of gas up structures and through the groundwater column above the deposit for gas. The observations suggest deeply buried U deposits are detectable by geochemical exploration of surface media.

Both studies

- High Na content in whole-rock composition of till samples above the deposits suggests a parent rock, likely alkaline, from some distance in the up-ice direction. If Na is "smeared" down-ice, it is possible trace metals are as well. This emphasizes the importance of sampling in transects above a target perpendicular to the last major ice flow direction.
- Anomalous U and pathfinder metals in soil, and radiogenic ^{4}He in gas were found over and adjacent to the surface traces of these deposits, indicating that geochemical exploration of surface media for U deposits can be used to explore for deeply buried deposits.

Appendices

Appendix A: Pb isotope compositions of humus at the Phoenix study site

Pb Isotope Compositions of Humus

Pb isotope compositions of humus samples were determined using two instruments, the Agilent 7700 ICP-MS and a Thermo-Finnigan Triton thermal ionization mass spectrometer (TIMS). In both cases, Pb was separated and purified by a standard procedure using anion resin and Pb eluted with HBr. Total procedural blanks for Pb were < 200 picograms. The mass fractionation for with a TIMS was corrected using NBS 981, which yielded the measured values of 16.889 + .007 (2σ) for $^{206}Pb/^{204}Pb$, 15.426 + .01 for $^{207}Pb/^{204}Pb$, 36.494 + .031 for $^{208}Pb/^{204}Pb$ in June 2012. The correction was 0.13 % a.m.u. based on the values of NBS981 by Todt *et al.* (1984). For the ICP-MS analysis, the peak of ^{204}Pb was collected for 3.0 seconds in each cycle to improve the counting statistics, and no instrumental mass fractionation correction is applied to the ICP-MS data. Two instruments yielded similar values for identical samples.

Lead isotope compositions show $^{206}Pb/^{204}Pb$ values ranging from 17.3 to 17.6 and $^{207}Pb/^{204}Pb$ from 15.4 to 15.6. The values plot close to 1.0 Ga of the two-stage Pb evolution line of Stacey and Kramers (1975; Figs. A-1 & A2). Values obtained with TIMS are very similar to the results with ICP-MS.

The Role of Pb Isotopes in Interpreting the Movement of Metals

To test the origin of Pb in soil whether it originated from the ore, we calculated the present-day Pb isotope compositions in the Phoenix deposits. The deposits have an average weight ratio of Pb/U of 10. There are several estimates of the mineralization age of U in the Basin, ranging from 1600 to 1350 Ma (Jefferson *et al.* 2007a), from 1600 to 1500 Ma (Alexandre *et al.* 2003) and 1460 to 1350 Ma (Fayek *et al.* 2002). The bulk of the U-Pb isochron ages on uraninite from Phoenix are in the range of 1600 Ma to 1350 Ma (Roscoe 2012). For the calculation, we used 1500 Ma as the mineralization age and assumed that Pb

at the time of the mineralization had average crustal Pb isotope compositions. (taken from the two stage crustal Pb evolution values of Stacey & Kramers, 1975). The calculation yielded a $^{206}Pb/^{204}Pb$ value of 203.3 and a $^{207}Pb/^{204}Pb$ value of 32.9 as the present day Pb values for the deposits (Fig. A-2). Considering the variation in Pb/U weight ratios of the ore, we also calculated the present-day isotope compositions of Pb with Pb/U ratios of 5 (Fig. A-2). Based on these results, we suggest that Pb and other metals in soil were not derived directly from the ore. Instead, these metals were dispersed to the overlying sandstones at ancient time and these metals in sandstones were brought to the surface.

As noted by Alexandre *et al*. (2009) the numerous U-Pb isotopic re-setting events recorded in most of the Athabasca basin uranium deposits (e.g. 1.4 Ga, 1.27 Ga, 1.0 Ga and 0.85 Ga) coincide with continent-wide tectonic events, such as the Masatzal orogeny, Berthoud orogeny, intrusion of MacKenzie mafic dykes, Grenville orogeny and assembly and break-up of Rodina, respectively. Since our results indicate non-radiogenic (common) Pb, then resetting could have coincided with the Pb signature we observe in humus that is perhaps associated with the initial U deposition at 1500 Ma. Therefore, our Pb signature could be associated with ore-related elements that likely migrated upwards with other uranium pathfinder metals in ancient times to sandstone, and eventually transferred to surface materials.

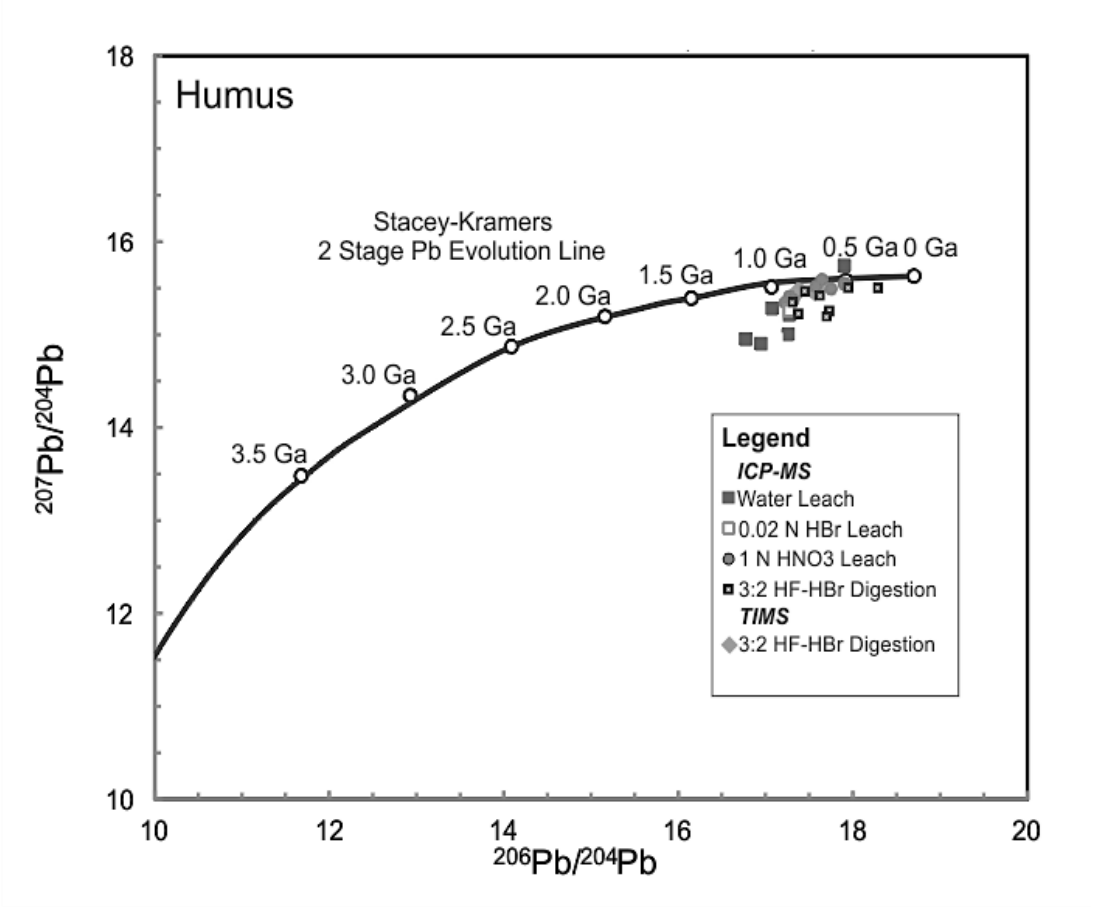

Figure A-1: $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ ratios measured via ICP-MS & TIMS on humus samples leached with water and acids, are shown with the two-stage Stacey & Kramers (1975) two-stage Pb evolution model decay curve. Values are those of common (non-radiogenic) Pb, and the data from those samples measured with TIMS & ICP-MS are nearly identical.

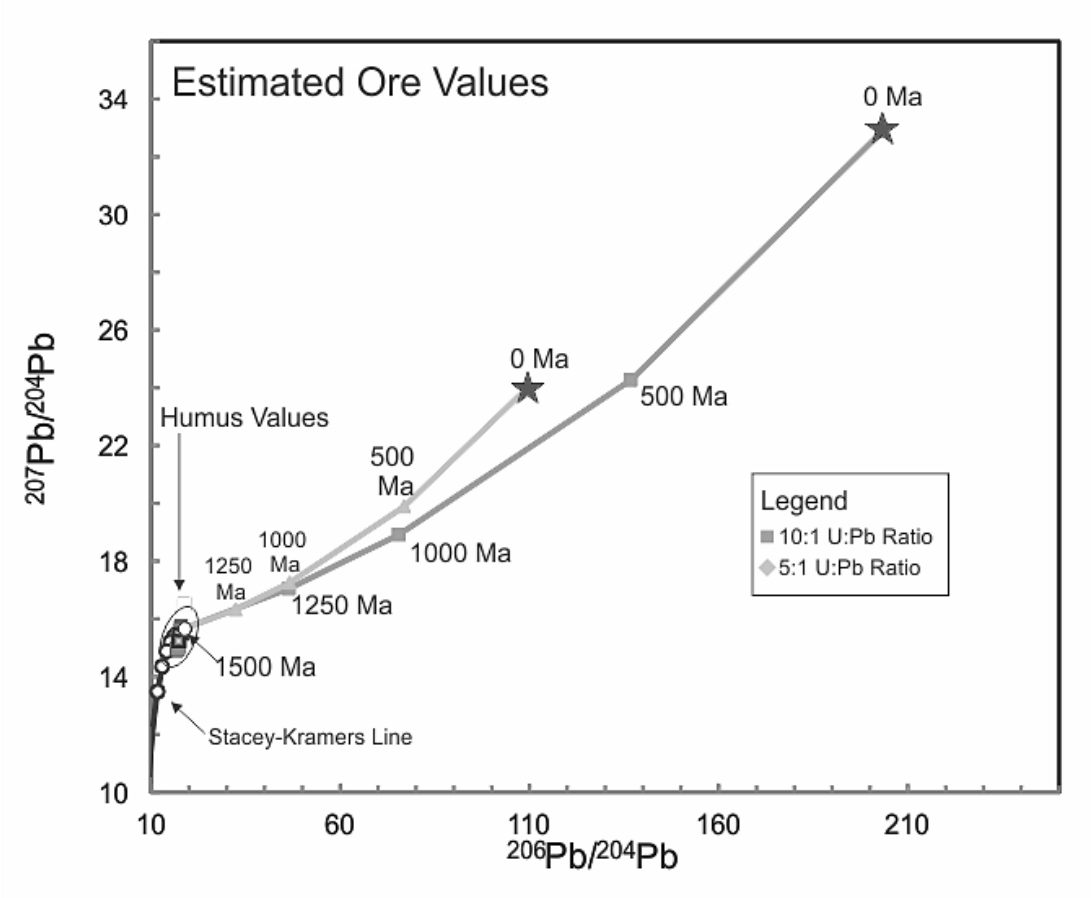

Figure A-2: $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ ratios measured via ICP-MS on humus samples, as well as estimated ore values calculated for the deposit at present-day for both 10:1 and 5:1 U:Pb ratios, are shown with the two-stage Stacey and Kramers decay curve. Both the 10:1 and 5:1 ratios of the estimated ore values are highly radiogenic with large $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ values, and are likely unrelated to the values from the humus; however values in humus could possibly be related to the estimated Pb values of the ore at 1500 Ma.

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Appendix B: Contoured geochemical results for elements in humus & B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone at the Phoenix study site

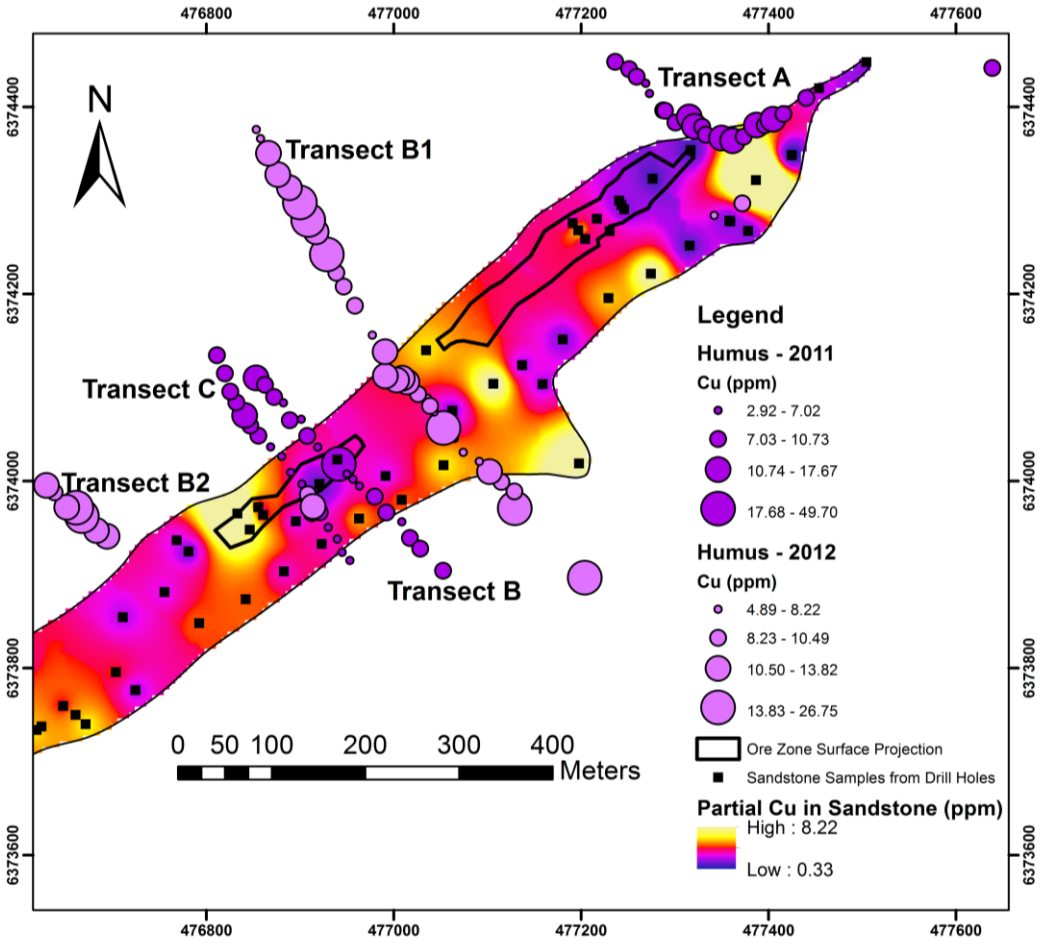

Figure B-1: Contoured geochemical results for Cu in aqua regia (AR) digestion of humus soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

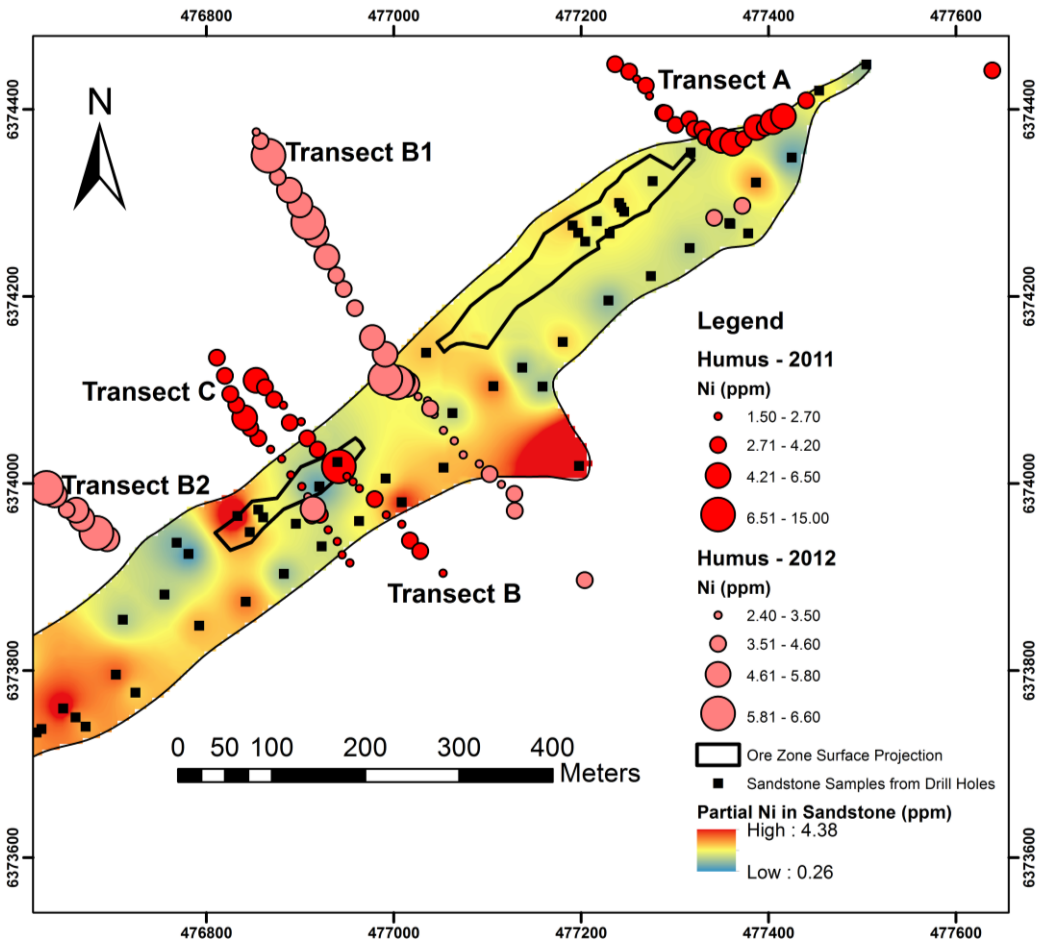

Figure B-2: Contoured geochemical results for Ni in aqua regia digestion of humus soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

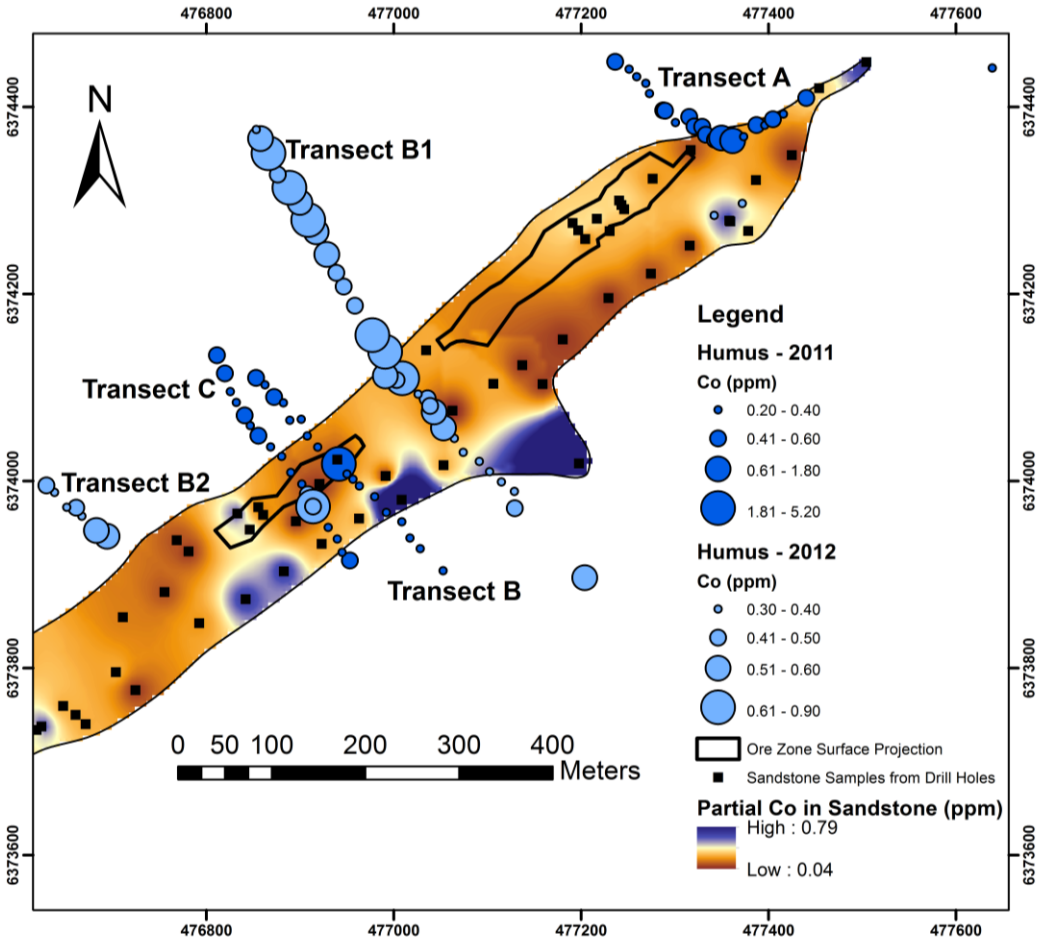

Figure B-3: Contoured geochemical results for Co in aqua regia digestion of humus soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

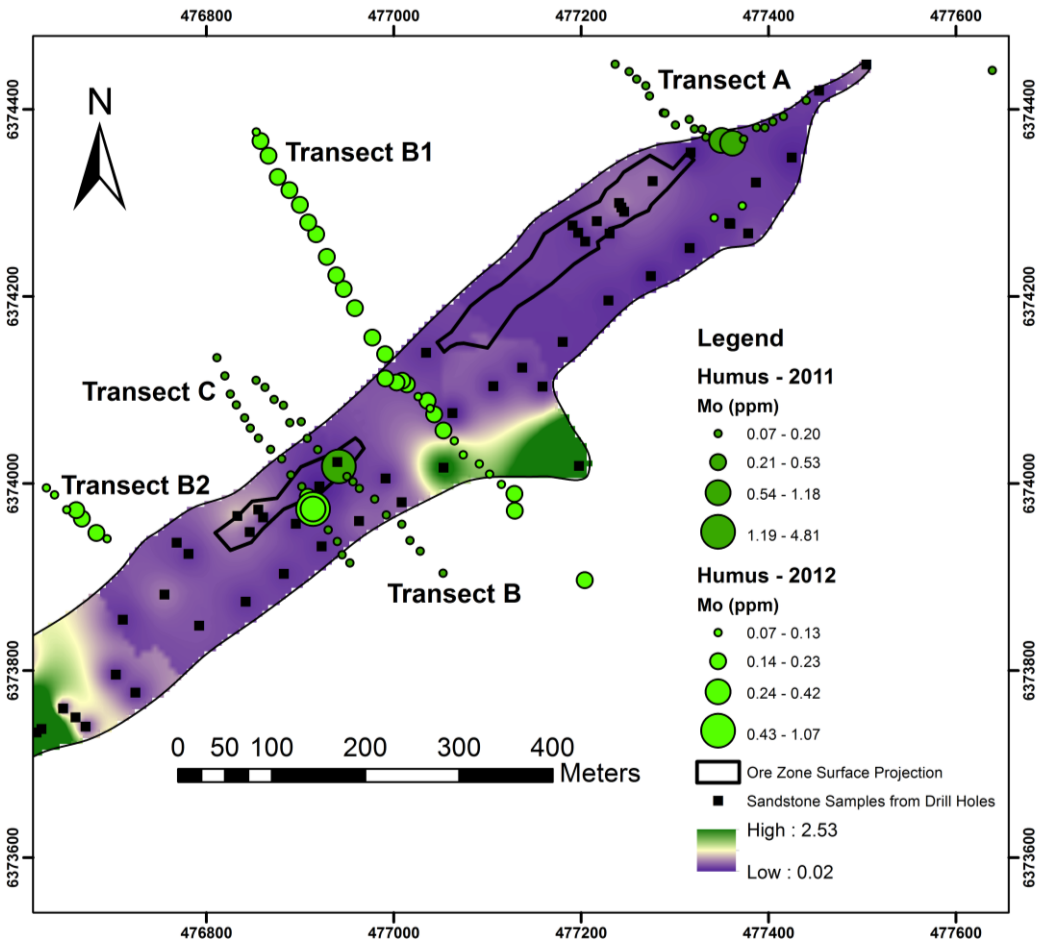

Figure B-4: Contoured geochemical results for Mo in aqua regia digestion of humus soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

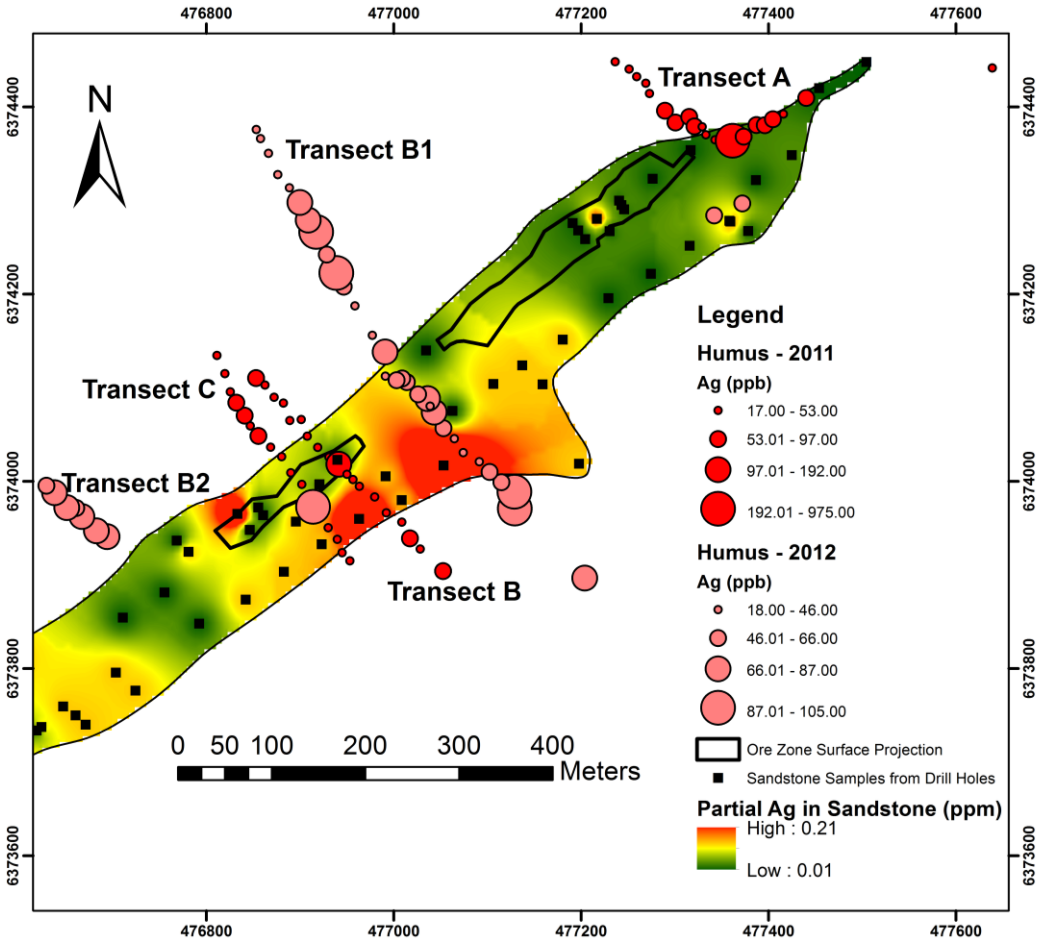

Figure B-5: Contoured geochemical results for Ag in aqua regia digestion of humus soil samples in 2011 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

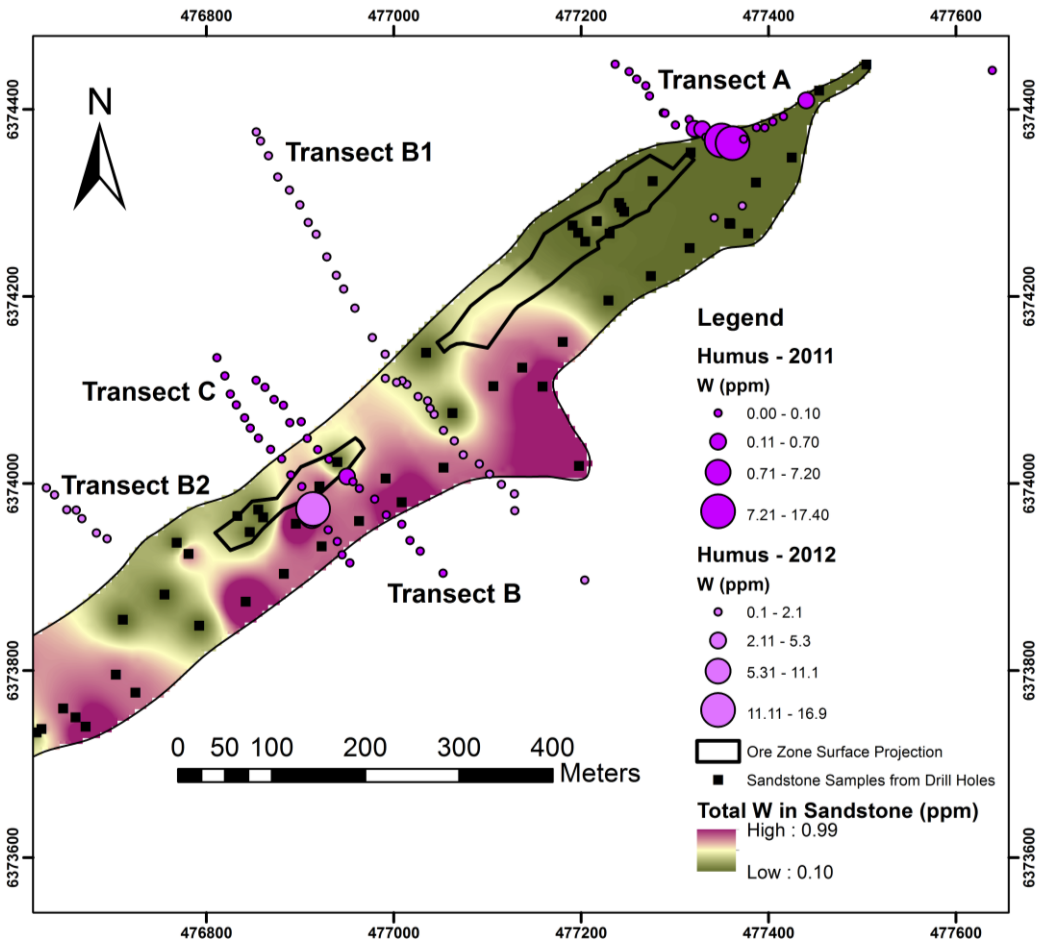

Figure B-6: Contoured geochemical results for W in aqua regia digestion of humus soil samples in 2011 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

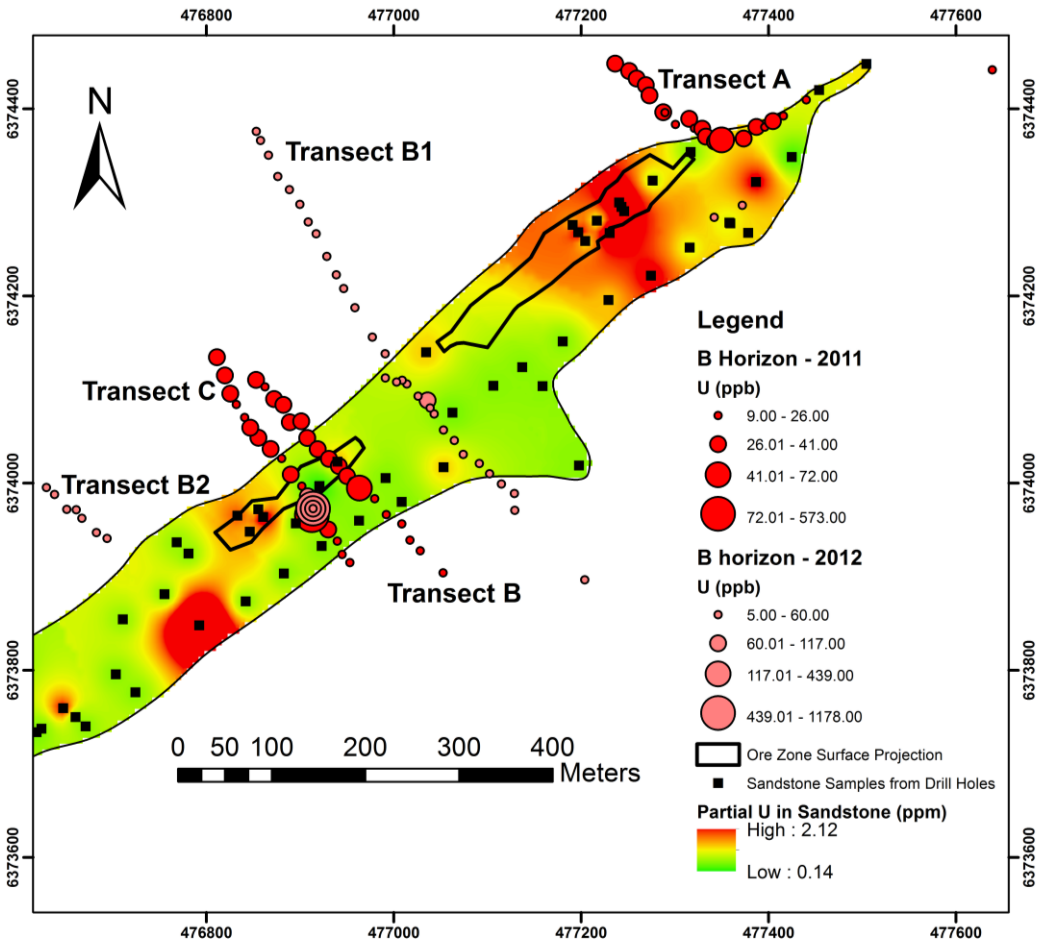

Figure B-7: Contoured geochemical results for U in ammonium acetate pH=5 (AA5) leach of B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

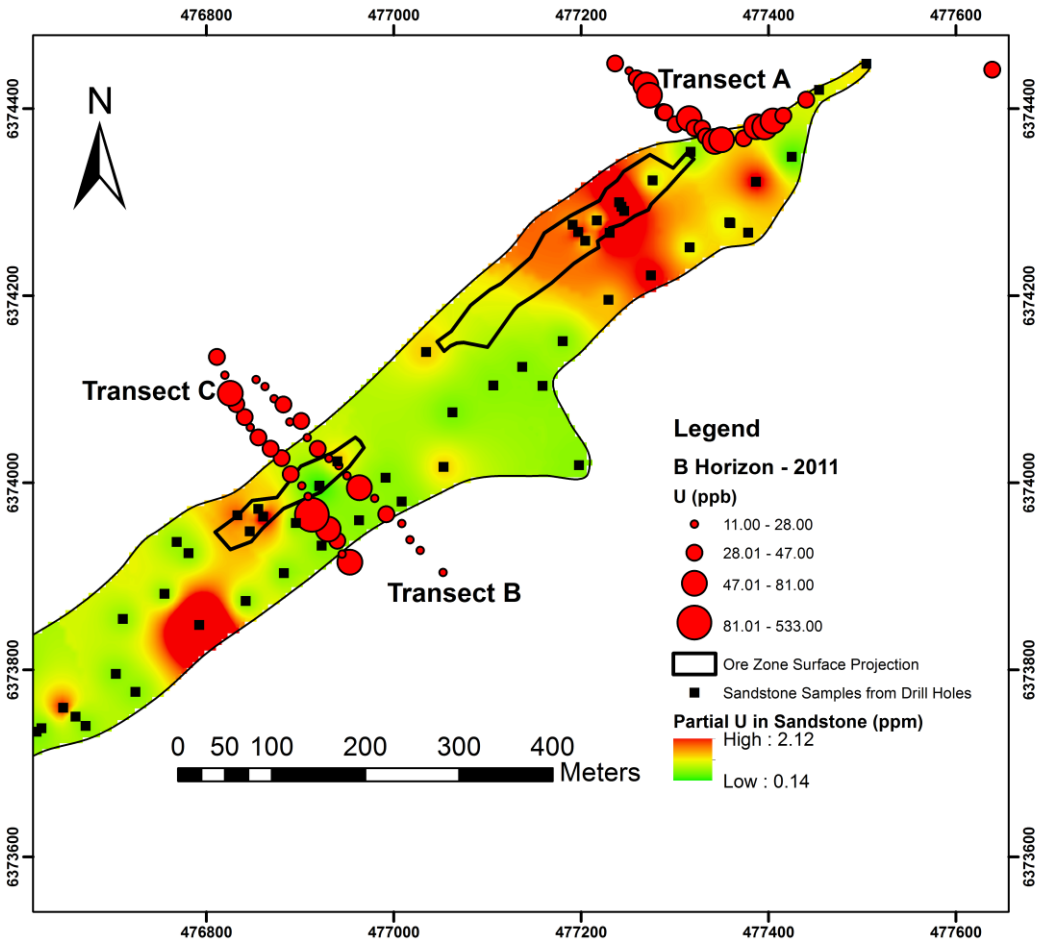

Figure B-8: Contoured geochemical results for U in hydroxylamine (Ox) leach of B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

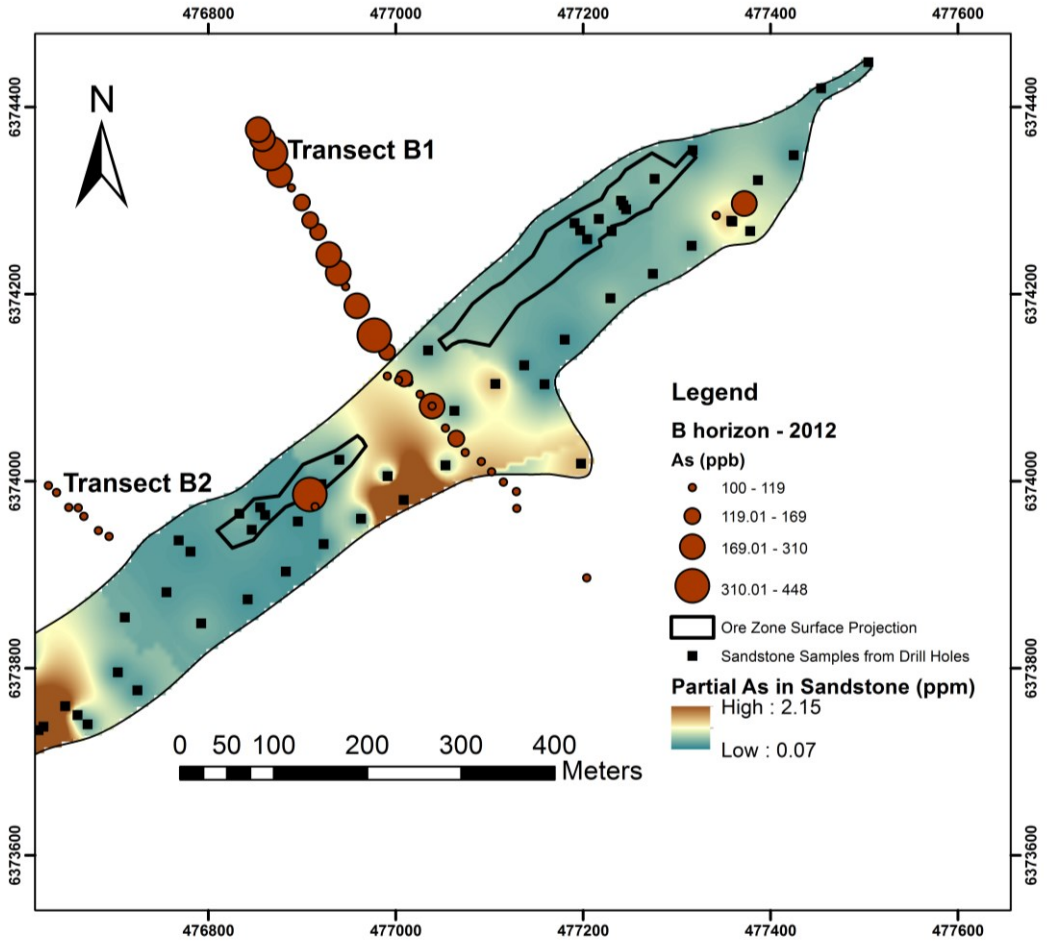

Figure B-9: Contoured geochemical results for As in AA5 leach of B-horizon soil samples in 2011 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

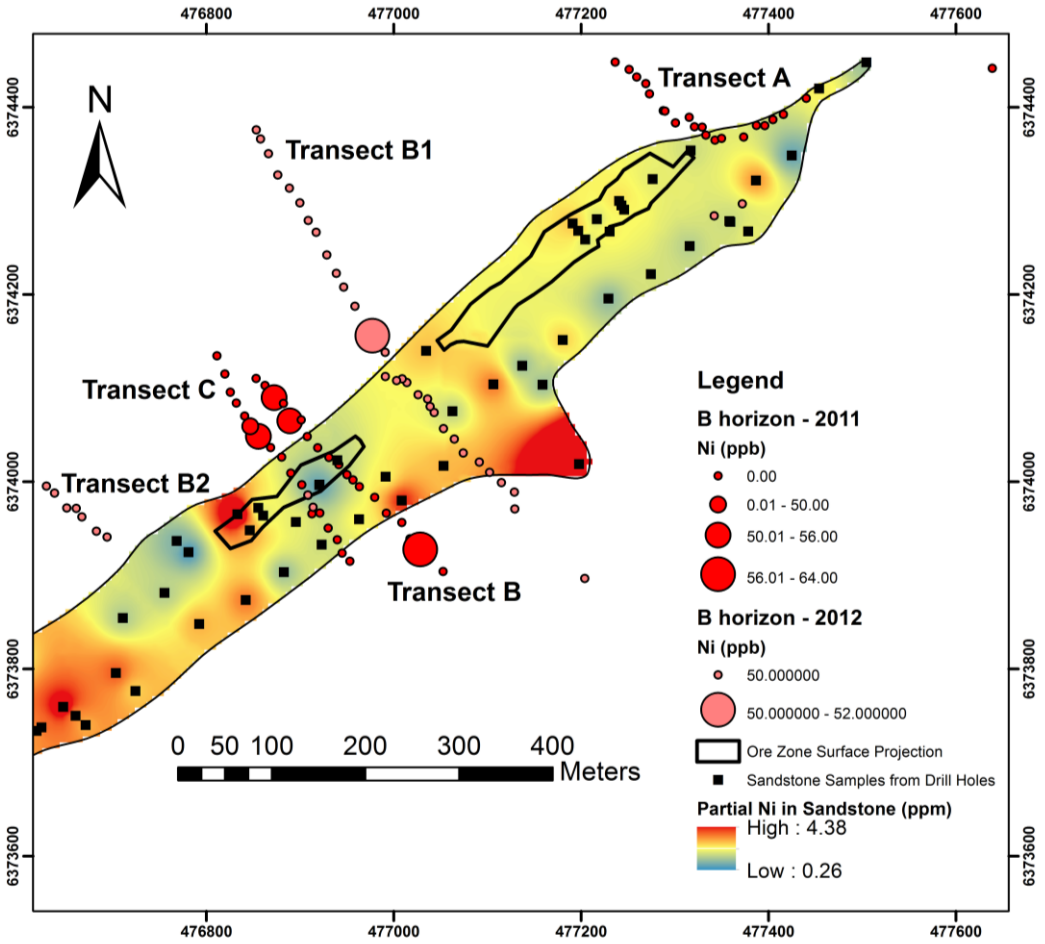

Figure B-10: Contoured geochemical results for Ni in AA5 leach of B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

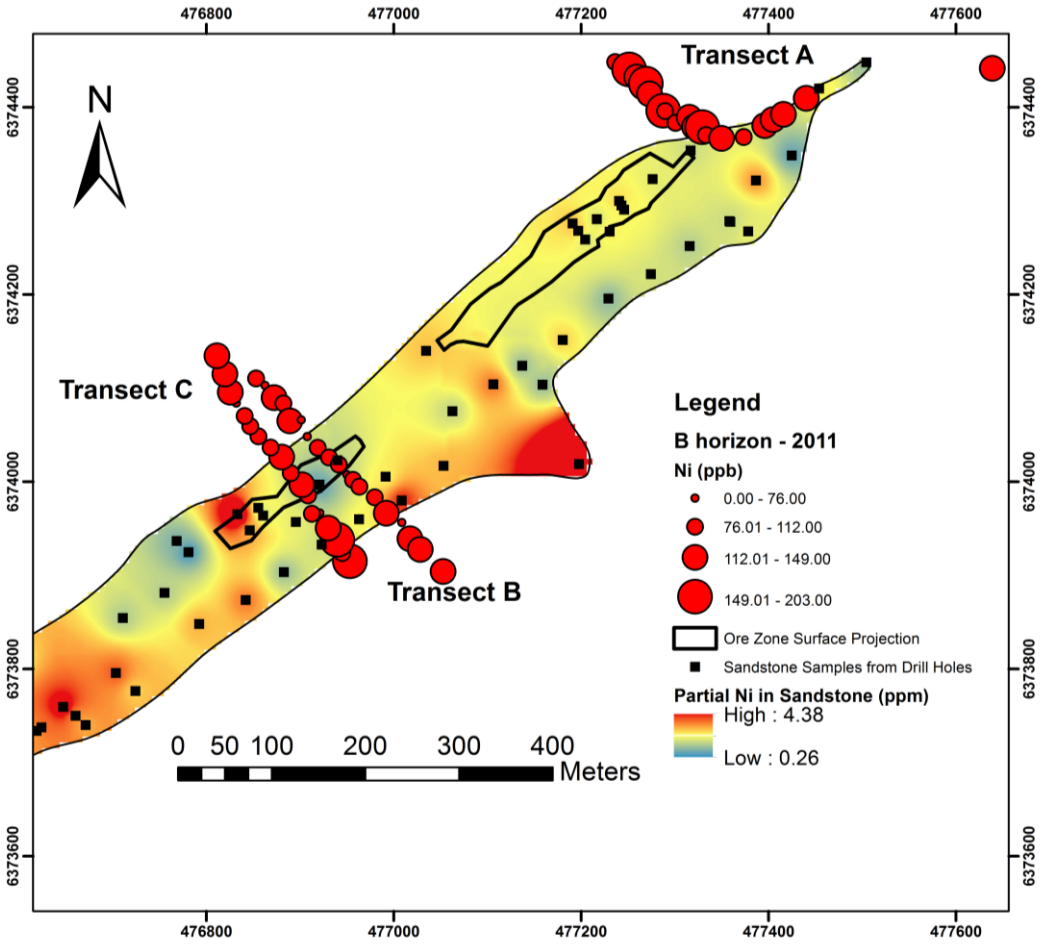

Figure B-11: Contoured geochemical results for Ni in Ox leach of B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

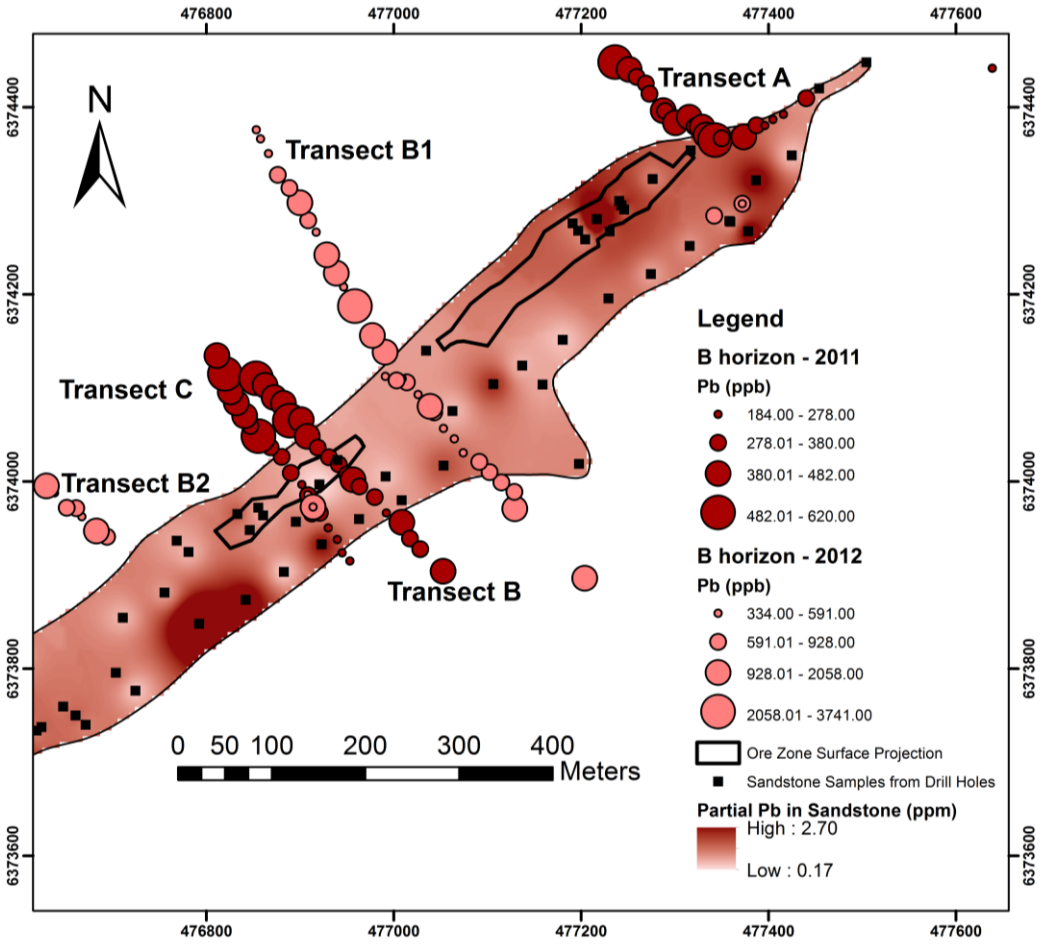

Figure B-12: Contoured geochemical results for Pb in AA5 leach of B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

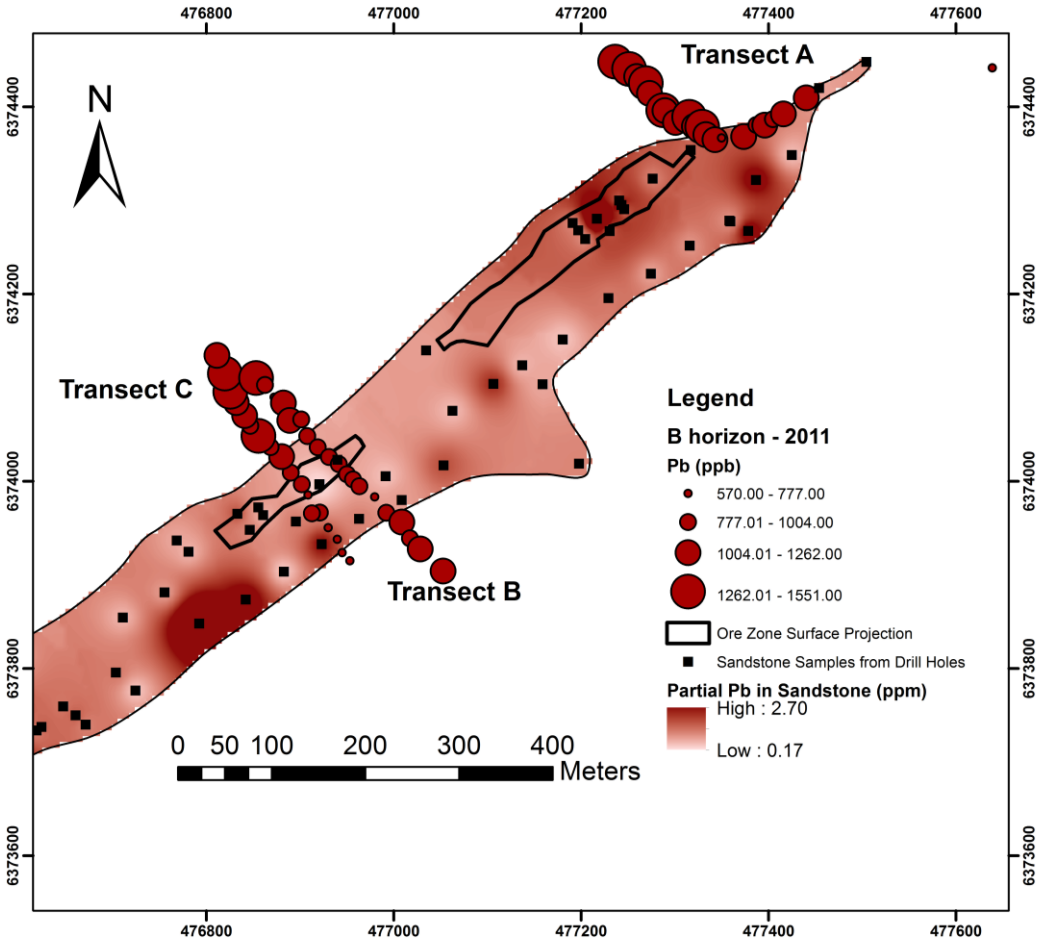

Figure B-13: Contoured geochemical results for Pb in Ox leach of B-horizon soil samples in 2011-2012 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

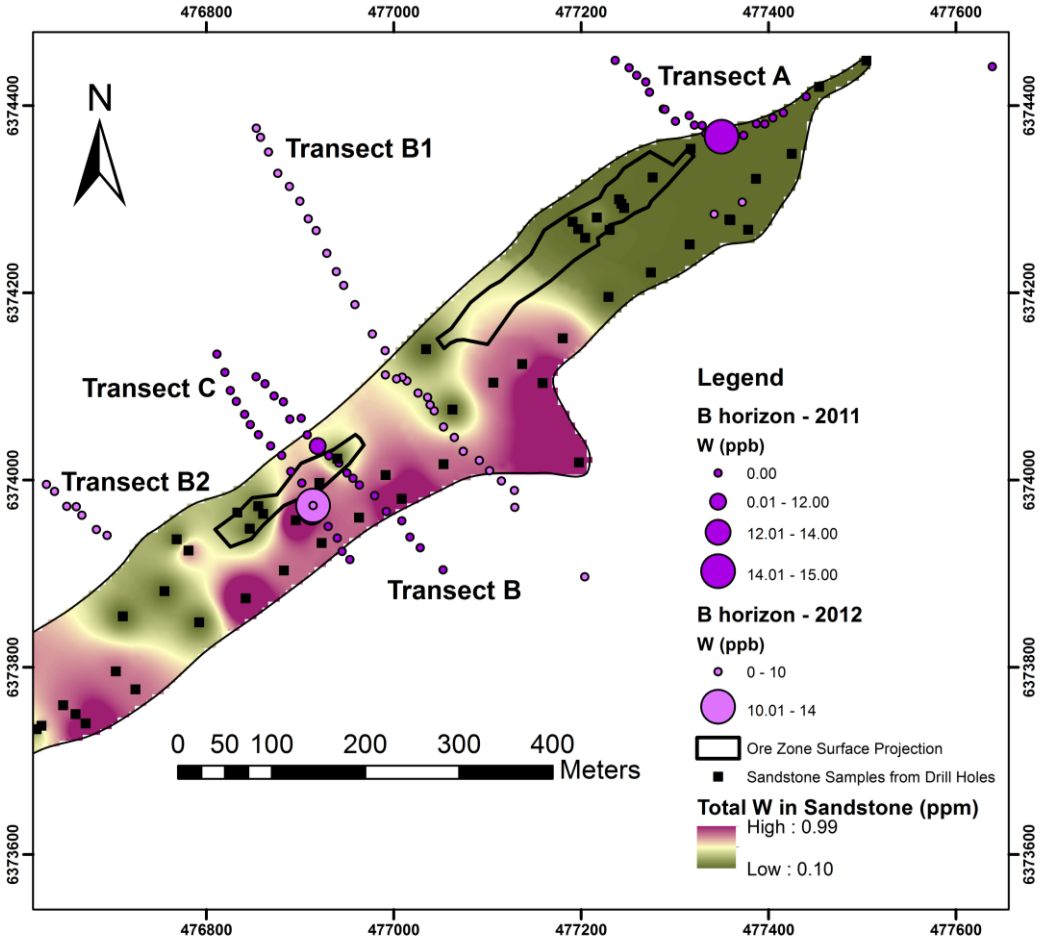

Figure B-14: Contoured geochemical results for W in AA5 leach of B-horizon soil samples in 2011 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

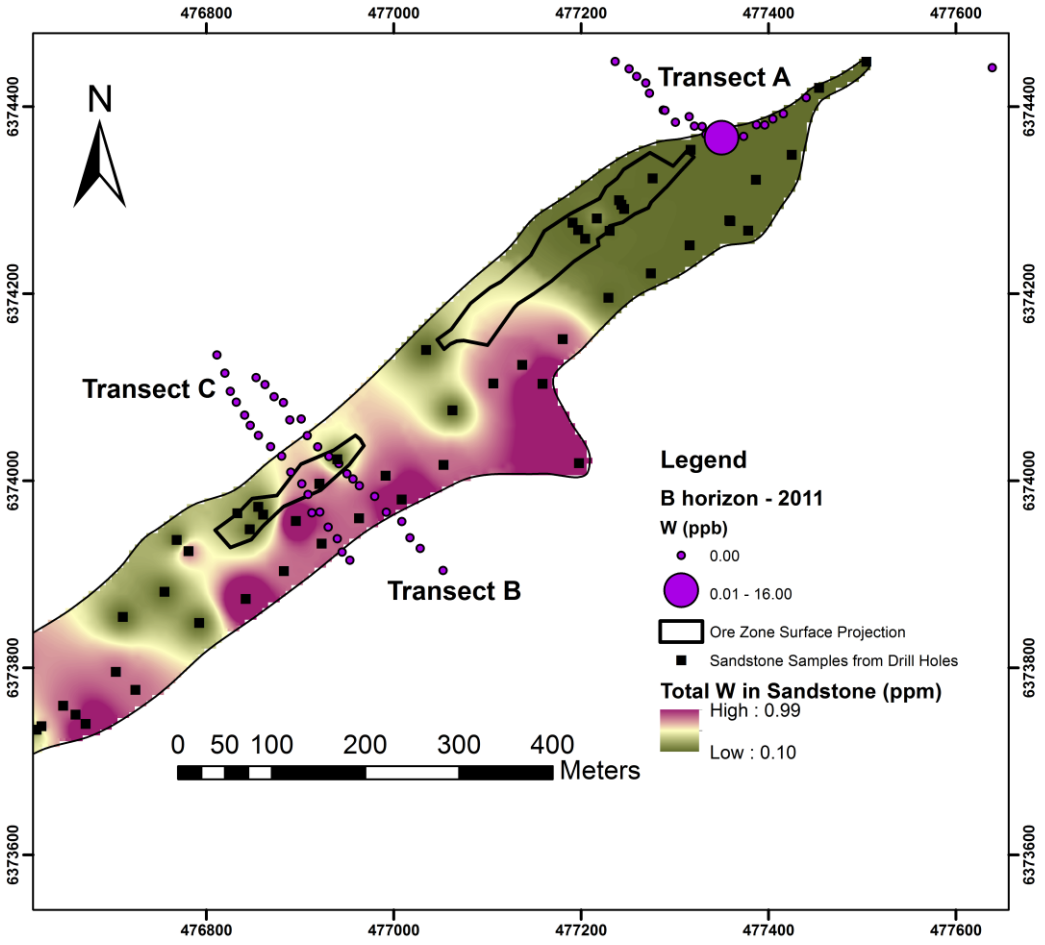

Figure B-15: Contoured geochemical results for W in Ox leach of B-horizon soil samples in 2011 and uppermost Dunlop Member sandstone. Coordinates are projected in UTM, NAD 83, Zone 13.

Appendix C: Sample location, pH and conductivity of B- and E-horizon soil samples from 2011-2012 at the Phoenix study site (UTM NAD 83, Zone 13)

Table C-1. *Sample location, pH and Conductivity of B- and E-horizon soil samples from 2011 (UTM NAD 83, Zone 13)*

Station	pH	Conductivity (µS/cm)	Easting (m)	Northing (m)
PHX001E	4.2	290	477236	6374448
PHX001B	4.3	444	477236	6374448
PHX002E	4.4	277	477251	6374441
PHX002B	4.8	290	477251	6374441
PHX003E	4.4	83	477259	6374432
PHX003B	4.7	408	477259	6374432
PHX004E	4.5	105	477269	6374425
PHX004B	4.9	45	477269	6374425
PHX005E	4.2	98	477273	6374414
PHX005B	5	40	477273	6374414
PHX006E	4.5	125	477288	6374397
PHX006B	5.4	28	477288	6374397
PHX007E	4.1	110	477290	6374396
PHX007B	5.1	55	477290	6374396
PHX008E	4.6	42	477301	6374383
PHX008B	4.6	97	477301	6374383
PHX009E	5.3	4	477316	6374389
PHX009B	5.3	15	477316	6374389
PHX010E	4.3	16	477321	6374379
PHX010B	5.3	4	477321	6374379
PHX011E	4.1	12	477329	6374379
PHX011B	4.8	16	477329	6374379
PHX012E	4.3	3	477333	6374370
PHX012B	4.9	6	477333	6374370
PHX013E	4.8	1	477343	6374365
PHX013B	4.7	2	477343	6374365
PHX014E	4.8	17	477350	6374367
PHX014B	5.2	8	477350	6374367
PHX015E	5.1	11	477362	6374364
PHX015B	5.4	10	477362	6374364
PHX016E	4.5	6	477374	6374368
PHX016B	5.3	6	477374	6374368
PHX017E	4.6	24	477387	6374381
PHX017B	4.6	33	477387	6374381
PHX018E	4.8	26	477396	6374381
PHX018B	5	29	477396	6374381
PHX019E	4.4	11	477405	6374387
PHX019B	5	15	477405	6374387

Station	pH	Conductivity (µS/cm)	Easting (m)	Northing (m)
PHX020E	4.7	12	477416	6374392
PHX020B	5	14	477416	6374392
PHX021E	5.2	5	477440	6374410
PHX021B	5	14	477440	6374410
PHX022E	5.2	4	477639	6374442
PHX022B	5.6	6	477639	6374442
PHX023E	5.3	32	476953	6373915
PHX023B	6.5	57	476953	6373915
PHX024E	5.5	11	476945	6373924
PHX024B	6	6	476945	6373924
PHX025E	5.3	12	476940	6373938
PHX025B	5.8	14	476940	6373938
PHX026E	5.9	18	476930	6373951
PHX026B	5	16	476930	6373951
PHX027E	4.6	10	476921	6373967
PHX027B	5.6	8	476921	6373967
PHX028E	4	8	476913	6373966
PHX028B	4.7	10	476913	6373966
PHX029E	4.1	3	476908	6373985
PHX029B	4.5	8	476908	6373985
PHX030E	3.8	10	476902	6373997
PHX030B	4.8	7	476902	6373997
PHX031E	3.8	7	476890	6374009
PHX031B	4.5	7	476890	6374009
PHX032E	4.1	4	476880	6374026
PHX032B	4.5	5	476880	6374026
PHX033E	4.2	14	476869	6374037
PHX033B	4.5	5	476869	6374037
PHX034E	4	2	476856	6374048
PHX034B	4.1	4	476856	6374048
PHX035E	3.7	5	476847	6374059
PHX035B	4.3	6	476847	6374059
PHX036E	3.6	4	476841	6374070
PHX036B	4.2	4	476841	6374070
PHX037E	4	2	476832	6374084
PHX037B	4.2	4	476832	6374084
PHX038E	3.9	5	476826	6374096
PHX038B	4.1	4	476826	6374096
PHX039E	4	5	476820	6374115
PHX039B	3.8	2	476820	6374115
PHX040E	3.7	7	476811	6374135

Station	pH	Conductivity (µS/cm)	Easting (m)	Northing (m)
PHX040B	4.3	17	476811	6374135
PHX041E	3.8	7	476853	6374110
PHX041B	4.3	1	476853	6374110
PHX042E	3.7	4	476863	6374103
PHX042B	4.1	8	476863	6374103
PHX043E	3.8	2	476872	6374090
PHX043B	3.8	10	476872	6374090
PHX044E	3.7	11	476882	6374084
PHX044B	4.1	7	476882	6374084
PHX045E	4	4	476889	6374065
PHX045B	3.9	10	476889	6374065
PHX046E	3.8	4	476901	6374066
PHX046B	4.3	2	476901	6374066
PHX047B	4.4	5	476908	6374048
PHX048B	3.6	2	476919	6374036
PHX049B	3.7	2	476931	6374026
PHX050B	3.6	4	476941	6374018
PHX051B	3.3	3	476950	6374008
PHX052B	3.3	2	476957	6374002
PHX053B	3.2	3	476963	6373995
PHX054B	3.3	7	476980	6373983
PHX055B	3.4	5	476992	6373966
PHX056B	N/A	12	477009	6373957
PHX057B	N/A	7	477017	6373939
PHX058B	N/A	4	477028	6373928
PHX059B	N/A	1	477053	6373904

Table C-2. *Sample location, pH and conductivity of B-horizon soil samples from 2012 (UTM NAD 83, Zone 13)*

Station	pH	Conductivity (µS/cm)	Easting (m)	Northing (m)
PHX200B	8	323	477204	6373897
PHX201B	8.2	110	477129	6373971
PHX202B	7.8	440	477129	6373989
PHX203B	5.6	138	477115	6373999
PHX204B	8.2	184	477102	6374010
PHX205B	9	37	477091	6374021
PHX206B	9.5	48	477074	6374031
PHX207B	8.1	160	477065	6374046
PHX208B	9.2	151	477053	6374057
PHX209B	9.3	170	477043	6374074
PHX210B	7.8	178	477036	6374088
PHX211B	6.6	180	477039	6374080
PHX212B	7.4	485	477026	6374093
PHX213B	7.4	123	477014	6374106
PHX214B	9.1	119	477009	6374110
PHX215B	9	242	477003	6374108
PHX216B	5.7	223	476991	6374123
PHX217B	9.5	43	476991	6374138
PHX218B	9.3	252	476977	6374156
PHX219B	9	70	476959	6374188
PHX220B	9.5	16	476947	6374208
PHX221B	9.4	200	476939	6374223
PHX222B	8	61	476929	6374242
PHX223B	9.1	28	476917	6374266
PHX224B	8.8	312	476909	6374279
PHX225B	9.3	69	476900	6374298
PHX226B	8.5	30	476889	6374314
PHX227B	8.7	28	476876	6374328
PHX228B	8.7	151	476866	6374350
PHX229B	8.6	316	476858	6374366
PHX230B	9.3	160	476853	6374376
PHX231B	9	35	476908	6373986
PHX232B	9.3	71	476914	6373973
PHX233B	9.1	75	476914	6373973
PHX234B	9.2	14	476914	6373973
PHX235B	9.1	28	476914	6373973
PHX236B	9.3	34	476914	6373973
PHX237B	8.7	72	476914	6373973

Station	pH	Conductivity (µS/cm)	Easting (m)	Northing (m)
PHX238B	8.4	27	476694	6373941
PHX239B	9	49	476683	6373947
PHX240B	8.4	12	476667	6373962
PHX241B	8.8	34	476661	6373972
PHX242B	8.8	23	476651	6373972
PHX243B	8.7	20	476638	6373988
PHX244B	9	44	476629	6373995
PHX245B	9.2	12	477372	6374297
PHX246B	9.2	12	477372	6374297
PHX247B	9.1	14	477342	6374284

Appendix D: Sample locations and metal values of humus, and pH and conductivity of B-horizon soil samples from 2012 at the Millennium study site (UTM NAD 83, Zone 13)

Table D-1. *Metal values in aqua regia digestion of humus soil samples.*

Sample Name	U_ppm	Pb_ppm	Ni_ppm	Cu_ppm
MLN099A	0.40	15.90	3.50	7.50
MLN100A	0.10	9.30	1.40	3.00
MLN101A	0.10	11.20	1.60	3.20
MLN102A	0.20	19.40	2.60	6.50
MLN103A	0.20	20.40	4.20	11.40
MLN104A	0.20	18.50	6.10	14.50
MLN105A	0.20	14.00	4.70	9.30
MLN106A	0.20	20.30	4.60	11.50
MLN107A	0.20	15.90	3.60	9.30
MLN108A	0.20	22.70	4.50	7.60
MLN109A	0.20	13.50	5.30	12.30
MLN110A	0.10	5.20	4.00	6.30
MLN111A	0.20	10.80	3.70	9.00
MLN112A	0.20	9.40	3.20	6.40
MLN113A	0.20	12.20	3.50	10.20
MLN114A	0.20	13.80	3.00	10.70
MLN115A	0.20	12.10	3.80	9.20
MLN116A	0.20	10.20	4.40	12.20
MLN117A	0.20	7.50	3.10	7.00
MLN118A	0.20	12.70	4.30	11.10
MLN119A	0.20	22.10	3.70	12.10
MLN120A	0.20	9.00	2.30	6.70
MLN121A	0.20	15.70	3.50	10.20
MLN122A	0.20	11.00	5.40	15.00
MLN123A	0.20	11.40	4.90	12.70
MLN124A	0.20	14.60	3.30	8.40
MLN125A	0.20	7.30	3.80	8.30
MLN126A	0.30	15.00	3.90	12.90
MLN127A	0.20	10.60	5.40	9.60
MLN128A	0.30	15.10	3.90	8.50
MLN129A	0.20	13.40	3.60	7.40
MLN130A	0.30	6.60	2.90	4.30
MLN131A	0.60	6.30	4.60	7.20
MLN140A	0.20	14.00	4.70	9.30
MLN141A	0.20	3.90	1.20	2.50
MLN142A	0.20	10.50	3.40	7.00
MLN143A	0.20	8.80	2.10	5.40
MLN144A	0.20	11.10	2.60	7.90

Sample Name	U_ppm	Pb_ppm	Ni_ppm	Cu_ppm
MLN145A	0.20	13.80	2.80	7.30
MLN146A	0.20	13.90	2.60	8.10
MLN147A	0.30	27.20	4.70	9.90
MLN148A	0.10	11.90	2.10	4.80
MLN149A	0.20	14.10	2.20	7.40
MLN150A	0.30	19.40	4.00	7.90
MLN151A	0.30	15.10	3.70	8.00
MLN152A	0.30	11.90	4.60	10.30
MLN153A	0.30	12.70	2.70	5.10
MLN154A	0.40	35.40	6.20	11.70
MLN155A	0.30	21.30	5.40	13.20
MLN156A	0.30	16.80	5.00	10.70
MLN157A	0.30	15.90	3.40	9.80
MLN158A	0.20	21.90	4.40	9.60
MLN159A	0.30	21.20	4.60	9.60

Table D-2. *Sample location, pH and conductivity values of soil slurry and metal values in ammonia acetate leach of B-horizon soil samples.*

Station	Easting	Northing	pH	Conductivity (s/m)	U_ppb	Pb_ppb	Cu_ppb
MLN099B	461842.5	6375574	8.1	16	33	519	220
MLN100B	461832.3	6375582	7.9	40	23	395	108
MLN101B	461832	6375596	8.1	36	12	536	22
MLN102B	461817.7	6375611	8.1	19	24	855	199
MLN103B	461818	6375611	8.1	78	33	545	114
MLN104B	461805.7	6375639	8	3	22	520	37
MLN105B	461800.9	6375649	8	61	34	854	64
MLN106B	461789.1	6375664	7	9	39	1091	66
MLN107B	461785.4	6375677	7.7	4	32	858	71
MLN108B	461778.1	6375693	7.1	17	34	767	63
MLN109B	461770	6375702	8.3	14	29	1009	36
MLN110B	461758	6375723	8.2	34	27	982	10
MLN111B	461762.4	6375728	8.1	8	26	500	10
MLN112B	461754.4	6375745	8.2	34	27	753	62
MLN113B	461748	6375753	8.1	29	22	925	10
MLN114B	461737.2	6375777	8.2	6	39	719	106
MLN115B	461733	6375784	8.2	8	42	1416	34
MLN116B	461726.8	6375797	8.1	3	24	723	10
MLN117B	461714.4	6375807	8.1	7	35	1047	10
MLN118B	461705.6	6375817	8	9	19	579	10
MLN119B	461698.9	6375834	8.1	9	32	1038	198
MLN120B	461692.4	6375846	7.8	9	23	501	10
MLN121B	461683	6375861	7.8	10	20	1047	33
MLN122B	461680.7	6375876	8	16	21	480	10
MLN123B	461671.6	6375887	7.7	12	23	827	10
MLN124B	461664.2	6375901	7.8	7	21	522	10
MLN125B	461660.3	6375918	7.9	35	24	1206	10
MLN126B	461650.2	6375928	8.4	208	28	657	10
MLN127B	461634.5	6375933	8.2	118	36	628	10
MLN128B	461619.6	6375955	8.3	227	34	581	36
MLN129B	461607.1	6375947	8.1	38	46	553	25
MLN130B	461592.9	6375955	8.1	7	26	380	10
MLN131B	461592.9	6375955	8	72	49	464	10
MLN140B	461481.1	6375447	8.2	12	20	317	10
MLN141B	461493	6375440	7.9	10	36	342	10
MLN142B	461512.5	6375438	8.2	13	33	892	44
MLN143B	461524.4	6375435	7.9	26	28	411	25
MLN144B	461542.4	6375432	8.4	18	90	648	64
MLN145B	461553.8	6375427	8.2	2	102	487	61
MLN146B	461564.7	6375418	8	36	33	2122	177
MLN147B	461580.5	6375412	8.2	4	34	584	51
MLN148B	461591.7	6375396	8.2	35	20	392	57
MLN149B	461606.4	6375377	8.2	71	13	1960	91
MLN150B	461616.9	6375364	8.2	5	29	705	97
MLN151B	461636.8	6375359	8.7	77	40	455	10

Station	Easting	Northing	pH	Conductivity (s/m)	U_ppb	Pb_ppb	Cu_ppb
MLN152B	461654.1	6375350	8.2	9	18	543	10
MLN153B	461670.1	6375342	8.7	41	27	649	10
MLN154B	461685.1	6375336	8.5	7	29	1264	32
MLN155B	461711.3	6375323	8.1	30	32	676	62
MLN156B	461564	6375418	8.4	7	34	631	33
MLN157B	461751.7	6375308	8.1	10	32	516	55
MLN158B	461769	6375302	8.1	118	29	843	10
MLN159B	461359	6374733	8.2	7	35	896	22

Appendix E: Conference Abstracts and Proceedings

THE "SURFACE" EXPRESSION: WHAT DO GEOCHEMICAL ANOMALIES IN SURFACE MEDIA AND SHALLOW SANDSTONES OVERLYING THE PHOENIX URANIUM DEPOSIT, ATHABASCA BASIN, SASKATCHEWAN, TELL US?

Michael Power[1], Keiko Hattori[1] and Chad Sorba[2]
[1]Department of Earth Sciences, University of Ottawa, Ottawa, ON, K1N 6N5
[2]Denison Mines Corp., 200-230 22nd St East, Saskatoon, SK, S7K 0E9

Many mineral deposits are buried below younger rocks and glacial sediments. We initiated this project to examine whether surficial geochemical anomalies exist for such a deeply buried uranium deposit. For our study, we selected the Phoenix deposit on Denison Mines' Wheeler River Property in the Athabasca Basin. The deposit, situated near the southeastern rim of the Basin in northern Saskatchewan, was originally thought to have no surface expression of any kind. Discovered in 2008, the deposit currently has an indicated resource of approximately 35 million lbs U_3O_8. Mineralization occurs as mainly monominerallic uraninite within four pods termed the A, B, C and D ore zones. This deposit has no surficial expression, and occurs near the unconformity between the crystalline basement rocks and overlying Athabasca sandstones at approximately 400 meters depth. The surficial environment, within the region of discontinuous permafrost, consists of gently rolling hills covered by glacial till and moraines, with overburden varying in thickness from 25 to 100 m. In September 2011, we initiated a study to evaluate whether geochemical anomalies related to such a deeply seated deposit exist in surface media or the overlying sandstones. A total of 226 soil samples (humus, B, E, and C-horizon) from 59 sites along 3 transects over the "A" and "B" ore zones were collected approximately 10 meters apart. In addition, traverse sampling was done to determine "background values" in the study area setting.

Geochemical analyses of the samples revealed the presence of strong U, Mo, Co, Ag and W anomalies in humus, B-horizon soil and uppermost sandstones not only overlying the A and B zones, but also over a nearby northeast-trending "WS Hanging Wall" Shear Zone. Peak to background ratios were up to 6 times (5.7 ppm) for U, 5 for Mo (4.8 ppm), 4 for Co (5.2 ppm) 20 for Ag (0.98 ppm) and 18 for W (100 ppm), respectively, in the various surface media. The geochemical anomalies in the surface media and the uppermost sandstones over the shear zone suggest that the fault is acting as a conduit for upward movement of fluids from the deposit. This fluid movement and resulting geochemical expression in surface media provides excellent exploration tools for deeply seated unconformity-related uranium deposits in Proterozoic sedimentary basins.

The 5.7 ppm U anomaly by aqua regia digestion method of the humus layer yielded among the strongest and most robust geochemical anomalies, and therefore is recommended as the leach of choice in this well-drained area of the Basin.

Abstract, Joint Annual Meeting of the Geological Association of Canada and Mineralogical Association of Canada, St John's, Newfoundland, May 2012

GEOCHEMICAL ANOMALIES IN SURFACE MEDIA AND UPPERMOST SANDSTONES OVERLYING THE CONCEALED PHOENIX URANIUM DEPOSIT, ATHABASCA BASIN, CANADA

M. Power[1], K. Hattori[1] and C. Sorba[2]
[1]Dept. Earth Sciences, University of Ottawa, Ottawa, ON, K1N 6N5
[2]Denison Mines Corp., 200-230 22nd St East, Saskatoon, SK, S7K 0E9

The Wheeler River Property, host of Denison Mine's Phoenix uranium deposit, is situated near the southeastern rim of the Athabasca Basin in northern Saskatchewan. Discovered in 2008, the deposit currently has resource estimates between 52 to 55 million lbs. U_3O_8. Mineralization occurs as mainly monominerallic uraninite with in four pods pods termed the A, B, C and D ore zones. This deposit has no surficial expression, and occurs near the unconformity between the crystalline basement rocks and overlying Athabasca sandstones at approximately 400 meters depth. The surficial environment consists of gently rolling hills covered by glacial tills and moraine, with overburden varying in thickness from 25 to 100 m. In September 2011, we initiated a study to evaluate whether geochemical anomalies related to such a deeply seated deposit exist in surface media or the overlying sandstones. A total of 226 soil samples (humus, B, E, and C-horizon) from 59 sites along 3 transects over the "A" and "B" ore zones were collected approximately 10 meters apart. In addition, traverse sampling was done to determine "background values" in the settings.

Geochemical analyses of the samples revealed the presence of strong U, Mo, Co, Ag and W anomalies in humus, B-horizon soil and uppermost sandstones not only overlying the A and B zones, but also over a nearby northeast-trending "WS Hanging Wall" Shear Zone. Peak to background ratios were up to 6 times (5.7 ppm) for U, 5 for Mo (4.8 ppm), 4 for Co (5.2 ppm) 20 for Ag (0.98 ppm) and 18 for W (100 ppm), respectively, in the various surface media. The geochemical anomalies in the surface media and the uppermost sandstones over the shear zone suggest that the fault is acting as a conduit for upward movement of fluids from the deposit. This fluid movement and resulting geochemical expression in surface media provides excellent exploration tools for deeply seated unconformity-related uranium deposits in Proterozoic sedimentary basins.

The 5.7 ppm U anomaly by aqua regia digestion method of the humus layer yielded among the strongest and most robust geochemical anomalies, and therefore is recommended as the leach of choice in this arid area of the Basin.

Michael Power, Keiko Hattori, Chad Sorba, Tom Kotzer, Daniele Pinti, Eric Potter **(2013)** Surface media expressions of buried unconformity-related uranium: The Phoenix and Millennium deposits, Athabasca Basin. Annual Meeting of the Geological Association of Canada and Mineralogical Association of Canada.

Surface media expressions of buried unconformity-related uranium: The Phoenix & Millennium deposits, Athabasca Basin

Power, M.J.[1], mpowe102@uottawa.ca, Hattori, K.H.[1], Sorba, C.[2], Kotzer, T.[3], Pinti, D.L.[4] and Potter, E.G.[5], [1]Department of Earth Sciences, University of Ottawa, 140 Louis Pasteur Ottawa, ON K1N 6N5; [2]Denison Mines Corp., 200-230 22nd St East, Saskatoon, SK S7K 0E9; [3]Cameco Corp., 2121-11th St West, Saskatoon, SK S7M 1J3; [4]GEOTOP, Université du Québec à Montréal, CP 8888, succ. Centre-Ville, Montréal, QC H3C 3P8; [5]Geological Survey of Canada, 601 Booth St., Ottawa, ON K1A 0E9

In order to evaluate surficial geochemical anomalies over deeply-buried unconformity-related uranium deposits, we selected two deposits with no apparent surface expression of mineralization: The Phoenix and Millennium deposits. The Phoenix deposit, owned by Denison Mines Corporation, has currently defined indicated resources of 52.3 million lbs U_3O_8 situated ~400 m below the surface, whereas Cameco Corporation's basement-hosted Millennium deposit has indicated resources of 46.8 million lbs U_3O_8, at a depth of ~750 m. Both are located in the southeastern margin of the Athabasca Basin in northern Saskatchewan. The area is covered by 25-100 m thick glacial tills comprised of moraine plains, streamlined moraines and subordinate eskers. Whole rock compositions of till samples from both properties suggest that the glacial sediments were sourced from a mixture of granitic basement rocks and Athabasca sandstones.

2011 field sampling above the Phoenix deposit yielded anomalous concentrations of U, Ni, Cu, Mo, Ag and W in humus, B-horizon soil and C-horizon glacial till in the areas directly above the A and B deposits and the WS Shear zone. 2012 sampling reproduced similar geochemical anomalies in soil samples (2-17 ppm U, 10-27 ppm Cu, 4-7 ppm Ni, 1000-1500 ppb As). Furthermore, leaching of humus samples in H_2O, HBr, HNO_3 and HF-HBr solutions show that these metals are not simply adsorbed on the surface; instead, they are tightly held in organics. Finally, analyses of the uppermost Manitou Falls "D" Formation sandstones with partial HF-HNO_3-HCl digestion above the ore zones contain anomalous U (up to 2 ppm).

Following the successes at Phoenix, soil sampling was carried out along the transects over the Millennium deposit in the summer of 2012, and yielded anomalies in U (0.4-0.6 ppm), Pb (15-35 ppm) and Cu (5-15 ppm) in aqua regia digestion of humus as well as anomalies in ammonium acetate leach of B horizon soils again above the ore zones and surface traces of B1 and Marker faults. Broad surficial geochemical anomalies in the property likely reflect abundant faults and fault-bound mineralization. Gas samples placed in water-filled drill holes at depths of several m yielded anomalously high radiogenic ^4He as indicated by $^4He/^{36}Ar$ ratios up to 700 times the atmospheric one, confirming the upward migration of 4He from the Millennium deposit. The combined results suggest upward migration of both mobile metal ions and uranium decay products from the ore zones to the surface.

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Anomalous abundances of He and mobile metals in surface media over the deeply buried Millennium U deposit, Athabasca Basin, Canada

MICHAEL J. POWER[1] *, KEIKO HATTORI[1] , DANIELE L . PINTI[2] AND ERIC G. POTTER[3]
[1]Department of Earth Sciences, University of Ottawa, Ottawa, Canada (correspondence: mpowe102@uottawa.ca)
[2] GEOTOP, Université du Québec à Montréal, Montréal, Canada
[3] Geological Survey of Canada, Ottawa, Canada

We examined soil and noble gas geochemistry over the Millennium uranium deposit, Athabasca Basin, SK, Canada. It has indicated resources of 68.2 million lbs U_3O_8 at ~750 m depth, along a major fault in granites & metamorphosed pelites of Archean to Paleoproterozoic age below the Athabasca sandstones.

110 soil samples along two transects 503 and 333 m long over the deposit yielded anomalous values in U (**!**0.6 ppm), Pb (**!**35 ppm) and Cu (**!**15 ppm) in aqua regia digestion of humus, when compared to the $\mu \pm 2\mathbf{4}_x$ for metal values. Anomalous values were also detected for U (**!**102 ppb) Pb (**!**2100 ppb), and Cu (**!**220 ppb) in B-horizon soils leached by ammonium acetate compared to the $\mu \pm 2\mathbf{4}_x$ of metal values. Most anomalies were directly above the ore zones and surface traces of major faults, including the ore-hosting Marker fault. Gas samples were collected in monitoring wells and drill holes by submerging diffusion samplers at 10 to 42 m below the surface for 3 days. The ^{4}He, ^{22}Ne, ^{36}Ar, ^{40}Ar, ^{84}Kr and ^{132}Xe were measured by quadrupole mass spectrometry at GEOTOP. Analytical uncertainties range from 1.5 to 4.6% of the measured amount. Measured ^{4}He concentrations in water ranges from 6.89×10^{-8} to 4.23×10^{-5} ccSTP/g. The lower amount is identical to that expected by equilibration with the atmosphere (Air Satured Water value or ASW). The higher amount is clearly related to radiogenic ^{4}He produced by the U ore and released in the water. Indeed, three samples yielded anomalous $^{4}He/^{36}Ar$ ratios, 715, 239 and 108 times the ASW value, clearly indicating the addition of radiogenic ^{4}He. Ratios of $^{4}He/^{22}Ne$ (790, 340 and 130 times ASW value), $^{4}He/^{84}Kr$ (690, 240 and 110 times ASW), and $^{4}He/^{132}Xe$ (580, 210 and 95 ASW) were also observed, confirming the results.

Broad geochemical anomalies in soil and gas at the property show that fault-controlled redistribution of elements and gases possibly exists over the deposit. Our results suggest upward migration of metals and He to surface through these geological features – detectable by geochemical exploration methods for U using two different surface media.

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Surface media expressions of buried uranium: the Phoenix & Millennium deposits, Athabasca Basin, Saskatchewan, Canada

Michael J. Power, Keiko Hattori
Department of Earth Sciences, University of Ottawa, Ottawa, ON, Canada K1N 6N5

Chad Sorba
Denison Mines Corp., 200-230 22nd St East, Saskatoon, SK, Canada S7K 0E9

Tom Kotzer
Cameco Corp., 2121 11th St West, Saskatoon, SK, Canada S7M 1J3

Eric G. Potter
Geological Survey of Canada, 601 Booth St, Ottawa, ON, Canada K1A 0E9

Abstract. To detect buried uranium deposits using surficial geochemistry, we selected two known deposits: Phoenix and Millennium. The Phoenix has indicated resources of 52.3 million lbs U_3O_8 at ~400 m depth, whereas Millennium has indicated resources of 68.2 million lbs U_3O_8, at ~750 m depth. Both are located in the southeastern Athabasca Basin, Saskatchewan, Canada. Sampling in 2011 above Phoenix yielded anomalous U, Pb, Ni, Cu, Mo, As and W in humus, B-horizon soil, till and uppermost sandstones above the deposit and WS Shear zone. 2012 sampling reproduced anomalies in soil (2-17 ppm U, 10-27 ppm Cu, 4-7 ppm Ni, 1-1.5 ppm As) in total and partial leaches. Leaching of humus in various acid solutions shows that metals are tightly held in organics. Soil sampling over Millennium in 2012 yielded broad anomalies in U (0.4-0.6 ppm), Pb (15-35 ppm) and Cu (5-15 ppm) in partial leaches of humus and B-horizon soil above the deposit & B1 and Marker faults. Results suggest upward migration of mobile metals from these deposits to surface.

Keywords. surficial geochemistry, uranium exploration, glaciated terrain, Athabasca Basin.

1 Introduction

In order to evaluate surficial geochemical anomalies over deeply buried uranium deposits, we selected two deposits with no apparent surface expression of mineralization: the Phoenix and Millennium deposits (Fig. 1). The Phoenix deposit, owned by Denison Mines Corporation, occurs along the unconformity between the dominantly siliciclastic Athabasca Group sandstones and the crystalline basement rocks. It has currently defined indicated resources of 52.3 million lbs U_3O_8 situated ~400 m below the surface (Roscoe, 2012), whereas Cameco Corporation's basement-hosted Millennium deposit has indicated resources of 46.8 million lbs U_3O_8 at a depth of ~750 m (Cloutier et. al, 2009).

Both deposits are located in the southeastern margin of the Athabasca Basin in northern Saskatchewan, a region of sporadic discontinuous permafrost (Burgess et al., 1999). 25-30 m thick glacial tills comprised of moraine plains, streamlined moraines and subordinate eskers cover the area (Schreiner 1984; Campbell 2007). Whole rock compositions of till samples from both properties suggest that the glacial sediments were sourced from a mixture of granitic basement rocks and Athabasca Group sandstones.

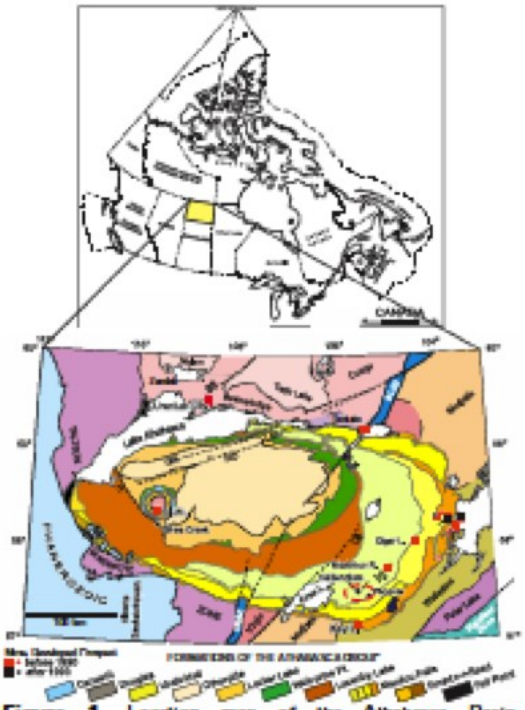

Figure 1. Location map of the Athabasca Basin, Saskatchewan, Canada, and the study area (dashed red oval) hosting the Phoenix & Millennium deposits in the southeastern Athabasca Basin. Geology from Jefferson et al. (2007).

At Phoenix, the mineralization is mostly pitchblende, with anomalous amounts of Cu (up to 3,100 ppm Cu) and Pb (up to 9.83 wt % Pb), and minor Ni (up to 461 ppm Ni), Co (up to 119 ppm Co), As (up to 170 ppm As), Zn (up to 1,070 ppm Zn) and Ag (up to 0.1 ppm Ag) (Kerr, 2011; this study).

For both systems, alteration mineralogy in the overlying Athabasca Group is typical of Athabasca

unconformity-related uranium systems with varying silicification and de-silification, tourmaline, chlorite, illite, kaolinite, hematite and drusy quartz. Of note, both properties also occur within the northeast-trending, regional illite and chlorite trend defined by Earle and Sopuck (1989).

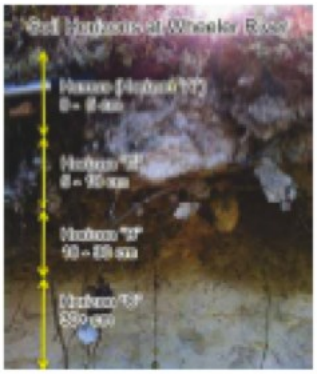

Figure 2. Typical soil horizon profile at Phoenix. The humus layer includes charcoal from a previous forest fire event. The photo was taken at 57° 30' 32.285" N, 105° 23' 10.768" W

2 Results from the Phoenix Study

2011 field sampling (sampling method, Fig. 2) above the Phoenix deposit yielded anomalous concentrations of U, Pb, Ni, Cu, Mo, As and W in humus, B-horizon soil and C-horizon glacial till in the areas directly above the A and B ore zones and the WS Shear zone (humus, Figs. 3 & 4). 2012 sampling reproduced similar geochemical anomalies in soil samples (2-17 ppm U, 10-27 ppm Cu, 4-7 ppm Ni, 1000-1500 ppb As; Figs. 4 & 5). Furthermore, leaching of humus samples in H_2O, HBr, HNO_3 and HF-HBr solutions showed that these metals are not simply adsorbed on the surface; instead, they are tightly held in organics (Fig. 6). Finally, analyses of the uppermost Manitou Falls Dunlop Formation sandstones by partial HF-HNO_3-HCl digestion above the ore zones contain anomalous U (up to 2 ppm, Fig. 4).

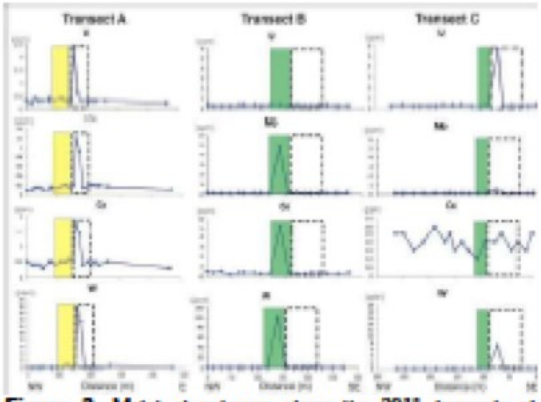

Figure 3. Metal abundances along the 2011 transects at Phoenix: U, Mo, Co, W in humus from the 2011 sampling programme after aqua regia digestion. The boxes indicate the areas directly above ore Zones A & B1, and the dotted rectangle encompasses the expression of the WS Hanging Wall shear at the unconformity.

3 Results from the Millennium Study

Soil sampling was carried out along transects over the Millennium deposit in the summer of 2012. These samples yielded anomalies in U (0.4-0.6 ppm), Pb (15-35 ppm) and Cu (5-15 ppm) from aqua regia digestions of humus as well as anomalies in ammonium acetate leaches of B horizon soils above the ore zones and surface traces of B1 and Marker faults (Fig. 7). Broad surficial geochemical anomalies in the property likely reflect abundant faults and fault-bound mineralization.

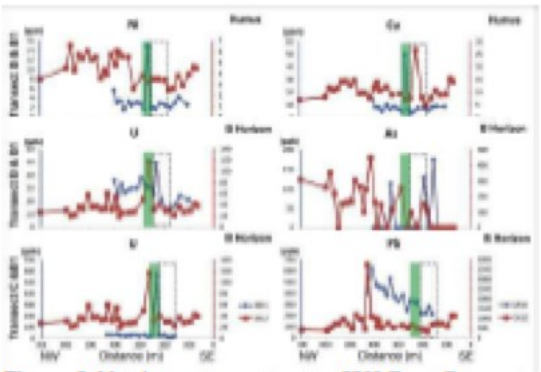

Figure 4. Metal abundances along the 2011 B and C transects & 2012 B1 transect at Phoenix: Ni, Cu, U, As and Pb after aqua regia digestion and ammonium acete leach of humus and B horizon. The box indicates the area directly above Zone B1, and the dotted rectangle encompasses the expression of the WS Hanging Wall shear at the unconformity.

4 Conclusions

The combined results suggest upward migration of mobile metals from the ore zones to the surface. As such, geochemical analysis of surface media is potentially an efficient and inexpensive too identifying deeply-buried uranium deposits among possible targets.

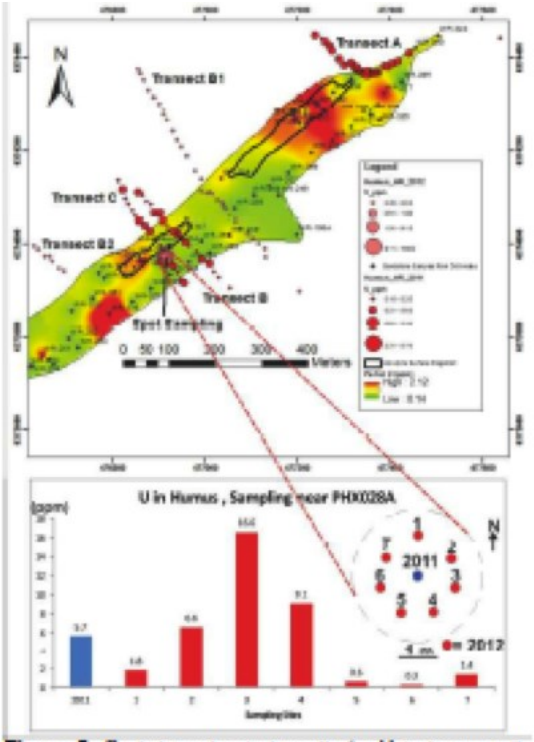

Figure 5. Graded geochemical results for U in humus soil samples from Transects A to C (2011), Transects B1-B2 & spot sampling (2012) and uppermost Dunlop Member sandstone (underlying raster). Inset is of dense 2012 humus soil sampling within 1 m from the 2011 site (PHX028) that showed the highest U value. The value on the left is the highest in the 2011 survey, and data in columns 1-7 are from 2012 spot sampling. The results confirm the reproducibility of the anomalous mobile metals trace elements observed in 2011.

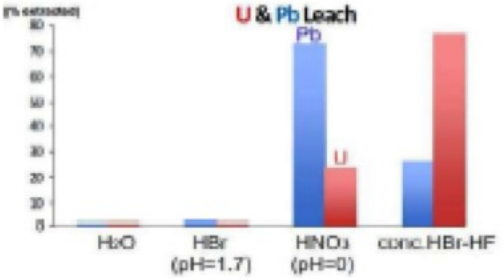

Figure 6. Water and a variety of acids were used to extract metals (Cu, Ni, Co, As, U, Pb) from a humus sample. Humus did not release significant amounts of metals in water and weak HBr (pH=1.7). The samples were dried at 60°C, and sieved to -80 mesh (0.177 mm). After adding Milli-Q water, we manually shook the samples several times and let them stand at room temperature for about an hour, after which they were again shaken manually. After removing the solids, then solution was then centrifuged, and analyzed via ICP-MS. Similar procedures were repeated with 0.02 M HBr, 1 N HNO_3 (25°C) and a hot (100°C) concentrated mixture of 3:2 HF-HBr.

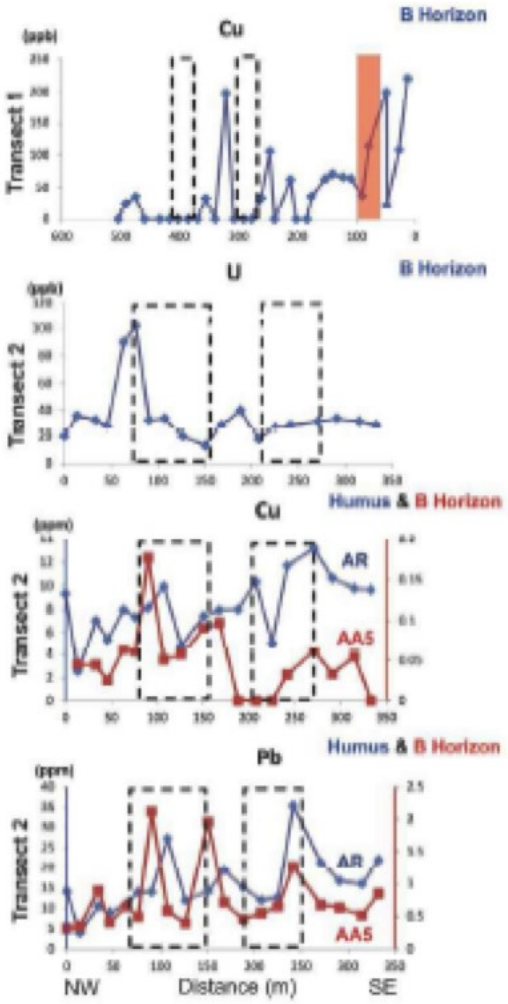

Figure 7. Metal abundances along the transects at Millennium: Cu, U and Pb after aqua regia digestion and ammonium acetate weak leach of humus and B horizon soils, respectively. The shaded area indicates the area directly above the ore zone, and dashed lines indicate the likely surface expression of the Marker and B1 faults.

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Appendix F: Analytical Data - Data are found on CD attached to this thesis

F-1: Phoenix Humus Data (2011)

F-2: Phoenix B-horizon Data (2011)

F-3: Phoenix C-horizon Silt Data (2012)

F-4: Phoenix Humus Data (2012)

F-5: Phoenix B-horizon Data (2012)

F-6: Phoenix Humus Pb Isotope Data (2012)

F-7: Phoenix Uppermost Sandstone Data (2011)

F-8: Millennium Humus Data (2012)

F-9: Millennium B-horizon Data (2012)

F-10: Phoenix & Millennium 2012 C-horizon Whole-Rock Till data (2012)

F-11: Phoenix & Millennium Noble Gas Data (2012-2013)

F-12: Phoenix & Millennium Tritium Data (2013)

F-13: Phoenix Project Sample List (2011)

F-14: Phoenix Project Sample List (2012)

F-15: Millennium Project Sample List (2012)