## SURFICIAL GEOCHEMICAL SURVEYS OVER CONCEALED URANIUM ORE OF THE PHOENIX AND MILLENNIUM DEPOSITS IN THE ATHABASCA BASIN, SASKATCHEWAN

KEIKO HATTORI<sup>1</sup>, MICHAEL J. POWER<sup>1.5</sup>, AUSTIN KRAHENBIL<sup>1</sup>, CHAD SORBA<sup>2</sup>, TOM G. KOTZER<sup>3</sup>, AND ERIC G. POTTER<sup>4</sup>

1. Department of Earth Sciences, University of Ottawa, 25 Templeton Street, Ottawa, Ontario, K1N 6N5; khattori@uottawa.ca

2. Denison Mines Corporation, 230 22nd Street East, Saskatoon, Saskatchewan, S7K 0E9

3. Cameco Corporation, 2121 11th Street West, Saskatoon, Saskatchewan, S7M 1J3

4. Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, K1A 0E8

5. current address: Dillon Consulting Limited, 137 Chain Lake Drive, Halifax, Nova Scotia, B3S 1B3

### Abstract

Geochemical surveys of surficial media (soil, water, and gas) have been conducted to evaluate and prioritize methods of detecting the presence of deeply-buried unconformity-related U deposits. The study selected two sites: the Phoenix and Millennium deposits in the eastern Athabasca Basin, Saskatchewan. The Phoenix deposits lie at a depth of ca. 400 m along the unconformity between Athabasca sandstones and the basement rocks, and the Millennium deposit at a depth of ca. 750 m along a major shear deformation zone in the basement. Humus and B-horizon soil samples show elevated metal contents including U directly above the ore bodies and WS Shear Zone at the Phoenix deposits, and broad areas over shear zones at the Millennium property. The elevated values of metals in the soil samples were reproduced in subsequent years of sampling in both properties. Laboratory leach experiments on humus using a variety of acids indicate that the elevated contents of metals are tightly held in organics, not adsorbed on the surface of clays or organic matter.

Examination of sandstone geochemistry over the Phoenix deposits shows a chimney-like distribution of elevated metal contents from the deposits to the upper sandstones. The uppermost sandstones contain elevated metal contents, including U. Principal component analysis reveals high scores of elements associated with U, such as rare earth elements and Pb in the basal Read Formation and the uppermost Dunlop Member of the Manitou Falls Formation. The evidence suggests that metals were dispersed in the sandstones during hydrothermal alteration related to ore-formation but were recently dispersed into the surface media. The proposed interpretation is consistent with low <sup>206</sup>Pb and <sup>207</sup>Pb in humus samples and high contents of <sup>222</sup>Rn in ground waters. With a half-life of 3.8 days, <sup>222</sup>Rn cannot be transported from the deeply-seated ore to the surface in several days, and likely originated from U and/or <sup>226</sup>Ra (direct parent of <sup>222</sup>Rn) present in upper sandstones and soil.

The concentrations of He are extremely high in groundwater close to the surface projection of the Millennium ore body and higher at deeper levels. The data appears to suggest upward diffusion of He from the U ore, but the distribution of high He in two study sites suggests its dispersion both vertically and laterally with groundwater flow. In summary, deeply-buried U deposits produce geochemical anomalies in surface media, but the expression of anomalies and media vary at different sites in response to local glacio-fluvial history, soil development and hydrological conditions.

### Introduction

Many large U deposits are located along the eastern margin of the Athabasca Basin, Saskatchewan (Fig. 1), and are associated with the unconformity between the crystalline basement and the overlying Athabasca sandstones (Jefferson et al., 2007). In the eastern margin, the unconformity is relatively shallow compared to the interior of the Basin. However, discoveries of high-grade deposits indicate that U mineralization took place also in deeper sections of the basin and significantly below the unconformity, in some cases up to 400 m along structures (Thomas et al., 1998). They include the Millennium, Centennial, and Eagle Point deposits located ca. 650-750 m, 800-830 m and 50-500 m below the present day surface, respectively (Lemaitre 2006; Cloutier et al., 2009; Jiricka, 2010; Cloutier et al., 2011; Alexandre et al., 2012; Reid et al., 2014). These discoveries expand the possibility of finding more concealed deposits below thick sandstones in the interior of the Athabasca Basin and in basement rocks peripheral to the basin. Since the late 1970s, a variety of surficial geochemical exploration techniques have been employed in the Athabasca region, including lake sediments

(Coker and Dunn, 1981; Maurice et al., 1985; Wasyliuk, 2006), and noble gases (Dyck, 1980; Cameron, 1983). A recent CAMIRO project examined soil and plant samples over Cigar Lake and McClean Lake deposits and reported geochemical anomalies close to the surface projection of the deposits (Bonham-Carter and Hall, 2010; Dunn, 2010). Based on these previous studies, we initiated a TGI 4-supported project in the summer of 2011 to identify the best techniques and reliable surface media in detecting concealed U deposits, and evaluate the pathways and trapping mechanisms of elements in the surface media. In order to track the movement of metals through the overlying sandstone column (building on previous studies such as Sopuck et al., 1983 and Clark, 1987), examination of drill core databases were done in conjunction with the surficial media sampling. Two sites were selected for the study (Fig. 1): the Phoenix deposits with indicated resource of 70.2 million lb  $U_3O_8$ (Roscoe, 2014) and the Millennium deposit with indicated resource of 75.9 million lbs U<sub>3</sub>O<sub>8</sub> (Cameco Corporation, 2013). Both sites have no apparent surface expression of the buried uranium ore. The Phoenix deposits occur at ca. 400 m

Hattori, K., Power, M.J., Krahenbil, A., Sorba, C., Kotzer, T.G., and Potter, E.G., 2015. Surficial Geochemical Surveys Over Concealed Uranium Ore of the Phoenix and Millennium Deposits in the Athabasca Basin, Saskatchewan, *in* Targeted Geoscience Initiative 4: unconformity-related uranium systems, (ed.) E.G. Potter and D.M. Wright; Geological Survey of Canada, Open File 7791, p. 32–42. doi:10.4095/295776

Surficial Geochemical Surveys Over Concealed Uranium Ore of the Phoenix and Millennium Deposits in the Athabasca Basin, Saskatchewan



FIGURE 1. Locations of study areas and simplified geology of the Athabasca Basin (modified after Jefferson et al., 2007)

depth, mostly along the unconformity and at its intersection with the WS Shear (Fig. 2A). The Millennium deposit is a basement-hosted deposit located 650–750 m beneath the surface along the Marker Fault, a major shear deformation zone in the basement (Cloutier et al., 2009; Wood et al., 2012; Fig. 2B). This paper presents a summary of the findings.

### **Study Areas**

The Athabasca Basin is primarily comprised of fluvial sandstones and conglomerates that were deposited over the metamorphosed basement rocks of Archean to Paleoproterozoic granite and gneiss. The sandstones in the study areas in the southeastern margin of the Athabasca Basin (Fig. 1) are about 400 m in thickness and divided into the Read Formation at the base and the overlying Manitou Falls Formation (Jefferson et al., 2007). The Manitou Falls Formation is further divided into Bird Member (MFb), Collins Member (MFc) and Dunlop Member (MFd) in ascending order (Fig. 2B). The Phoenix deposits occur along the unconformity and also a steeply dipping shear deformation zone, WS Shear, in graphitic pelitic gneisses in the basement (Kerr, 2010; Fig. 2A). The basement rocks are metasedimentary rocks and granitic gneisses of the Paleoproterozoic Wollaston Domain of the Trans Hudson orogeny (Yeo and Delaney, 2007). The metasedimentary rocks are graphitic and non-graphitic pelitic gneisses that are intensely altered near the mineralization. The Millennium deposit lies at a depth of ca. 750 m from the surface and 100 m below the unconformity along a major reverse fault, the Marker Fault, in the basement (Fig. 2B). The Marker Fault is rooted in graphite-rich pelitic gneisses. The Paleoproterozoic basement rocks in the area belong to the transition zone between the Wollaston and Mudjatik Domains of the Trans Hudson orogeny (Smith et al., 2010). The rocks of the Mudjatik Domain are similar to those of the Wollaston Domain, but the former is dominated by granitic gneisses.

The study areas are mainly covered by gently rolling hills of well-drained, glacial sediments, that consist of eskers, outwash sand plains, drumlins (Schreiner, 1984; Campbell, 2007). Black spruce is the dominant tree species in the area with minor jack pine. A thin layer of caribou moss covers the forest floor. The Millennium property experienced a forest fire in 2008, which burned much of the vegetation. Therefore, trees are sparse and short (< 2 m). Logging data of exploration drilling shows that glacial sediments are mostly 20–30 m thick, except for the top of eskers. The general ice flow direction in the eastern part of the Athabasca Basin is southwest (Campbell, 2007). This glacial dispersal direction



FIGURE 2. (A) Schematic cross section of the Phoenix deposits (modified from Gamelin et al., 2010). The uranium deposits (dark shaded) lie ca. 400 m beneath the present day surface along the unconformity between the Athabasca sandstone and Paleoproterozoic basement rocks. Minor mineralization extends below the unconformity along the reverse fault of the WS Shear. (B) Cross section of the Millennium deposit (red) at ca. 750 m below the surface along the Marker fault in the basement. Modified after Smith et al. (2010) and Wood et al. (2012).

is consistent with the general morphology of drumlins in the study areas.

The region has a sub-arctic climate with long, cold winters and mild summers with moderately high precipitation, approximately 482 mm of annual precipitation (Dimitrov et al., 2014).

## Sampling and Analytical Techniques

# Soil sample sampling

Although the last glacier retreated from the study area only ca. 9000 years ago (Campbell, 2007), soil horizons are well developed in both properties partly due to well drained sandy glacial sediments on the surface of the properties (Figs. 3A, B). Boggy areas are only developed around a small swamp close to the north end of the surface projection of the Millennium deposit and close to Slush Lake, in the western part of the study area in the Millennium property (Fig. 4B). The thickness of humus varies up to 5 cm and that of B-horizon soil varies from 20 to greater than 60 cm (Figs. 3A, B). The 2008 forest fire at the Millennium property produced charcoal and fragments common in humus.

Sampling (1–2 kg each) was conducted at 15–20 m interval along traverses covering the surface projections of major faults and ore bodies (Figs. 4A, B). Before the sampling, the topography and surface conditions were carefully examined to select sampling traverses to collect similar media. Considering the southwest directing ice dispersion, the orientation of sampling traverses was set perpendicular to this ice flow so that samples possibly affected by glacial dispersal would not be collected along the entire traverse. At the Millennium property, the traverses only covered the northern tip and southern tip of the surface projection of the deposit (Fig. 4B) because the central area was highly disturbed due to extensive drilling and the presence of a swamp directly above the northern body of the deposit. After removing caribou moss and forest litter including dead leaves and twigs, soil samples were collected using a hand-held Dutch auger. Samples were collected of humus, E-horizon soil, B-horizon soil and C-horizon (till). At several locations, B-horizon soil was well developed and extends down to a depth of 100 cm.

To evaluate the reliability of soil data, a test was conducted by repeated sampling at different times at given sites. The site that was selected from the Phoenix deposit property yielded the highest U content in humus in 2011 (indicated with a triple circle in Fig. 4A). It is directly above the Phoenix Deposit B. The site in the Millennium property was directly above the projection of the Marker Fault, the main ore-hosting structure (indicated with an arrow in Fig. 4B).

Humus samples were digested with aqua regia and Bhorizon soil with ammonia acetate leach after drying at temperatures below  $60^{\circ}$ C and sieving – 80 mesh (0.177 mm) at Acme Labs Ltd., Vancouver. To evaluate different techniques, a suite of B-horizon soil samples was subjected to ammonia acetate and hydroxylamine leaches plus aqua regia digestion. For quality control, one every ten samples was split into two and the two were given different labels for the analysis. The results show reproducibility of greater than 90%.



FIGURE 3. Well-developed soil horizons at the Wheeler River (A) and Millennium properties (B).

### Leach test of humus samples

Laboratory tests were conducted at the University of Ottawa to evaluate the leaching of metals in humus with a variety of acids. First, the samples were dried at 60°C, and sieved -80 mesh (0.177 mm) using stainless steel sieves. They were placed in Milli-Q water at 25 °C, 0.02 N hydrobromic acid (HBr) at 25 °C, 1 N nitric acid (HNO<sub>3</sub>) at 25 °C, and concentrated mixture of hydrofluoric (HF)-hydrobromic (HBr) (3:2) at 100°C. The samples in solutions were agitated frequently for the first hour and every hour for over 4 hours. The concentrations of metals (Cu, Ni, Co, As, U, Pb) in the solutions and blank solutions were measured using a Thermo-Agilent HP-7700 inductively coupled plasma mass spectrometer (ICP-MS) at the University of Ottawa. Reagents used for the laboratory analysis were double-distilled at sub-boiling temperatures and purchased from Seastar Chemicals, British Columbia.

## Lead isotope analysis of humus samples

Solutions used for the leaching tests of humus were used for Pb isotope analysis. After the solutions were evaporated at low temperatures, they were re-dissolved in HBr solution for the separation and purification of Pb, following a standard procedure using Dowex AG1-8X anion resin (200-400 mesh) and elution using HBr solution at the University of Ottawa (Hinchey and Hattori, 2007). The total procedure blanks for Pb were less than 200 picograms. The isotope compositions of Pb were determined using Thermo-Agilent HP-7700 ICP-MS and also a Thermo-Finnigan Triton thermal ionization mass spectrometer. The mass fractionation was 0.13 % a.m.u. based on the measured values of NBS 981 and the values given by Todt et al. (1995). For the ICP-MS analysis, <sup>204</sup>Pb was counted for a long time, 3.0 sec, in each cycle to give the uncertainty of 0.1 % (2 $\sigma$ ) of the quoted values. The two instruments yielded similar results.

## Till samples

The major and minor element abundance of till samples were determined using a Philips PW 2400 X-ray fluorescent spectrometer at the University of Ottawa after fusing the sample powder with a flux composed of 78.5%  $Li_2B_4O_7$  and 21.5 %  $LiBO_2$ .



**FIGURE 4.** (A) Uranium concentrations in ammonia acetate leach of B-horizon soil (circles) and in aqua regia of the uppermost sandstones above the Phoenix deposits. Reproducibility of soil data was tested at PHX 28 shown with brown triple circle. Modified after Power et al. (2012). (B) Sampling traverses (white and blue circles, Tr 1, Tr2, Tr3) and sites (yellow circles) for helium survey by Power et al. (2012) and Krahenbil et al. (2014). A=DDH CX-86, B=DDH CX52, C=DDH CX98, D=DDH CX40, E=DDH CX43, F=DDH CX45, G=DDH CX63, H=DDH CX58, I=DDH CX49, J=Monitoring well ML 07-02, K=Monitoring well BH127, L = swamp). The surface projection of the Millennium deposit is shown in red. Major shear deformation zones in the basement rocks are extended to the surface (shown in yellow dashed lines). Modified after Krahenbil et al. (2014). The reproducibility of soil sample was collected in 2013 at MLN 145 (shown with a yellow arrow along transect 2 (Tr2))

Water

Groundwater was collected from monitoring wells and exploration drill holes using a bailer made of Cu tube with one end closed. Both groundwater and surface water samples were subjected to analysis of the abundance of cations and anions, tritium, dissolved carbon, and isotope compositions of hydrogen and oxygen. Water samples were also used to determine dissolved Rn contents.

#### Noble Gases

Radon gas dissolved in groundwater and surface water was measured after extracting Rn gas using mineral oil following the method described by Leaney and Herczeg (2006). Radon gas contents were also measured in soil pore fluids close to drill holes. Helium gas dissolved in water was collected using a diffusion gas sampler, which is made of a Cu tube ( $\frac{1}{4}$ " OD, ~ 8 cm in length) connected to a ca. 5 cm long silicon tube (e.g. Sanford et al., 1996; Hamilton et al., 2005). The samplers were submerged in a small swamp, shallow environmental monitoring wells and exploration drill holes in the Millennium property, and in exploration drill holes in the Phoenix property.

## Results

The 17 till samples collected from the two properties show remarkably similar major and minor element abundances. They are characterized by high SiO<sub>2</sub> (avg. 89 %), moderate Al<sub>2</sub>O<sub>3</sub> (avg. 4.5 %), and low CaO (avg. 0.50 %), Na<sub>2</sub>O (avg. 0.83 %), K<sub>2</sub>O (avg. 0.93 %), MgO (avg. 0.21 %), and Fe<sub>2</sub>O<sub>3</sub> as total Fe (avg. 0.56%) (Power et al., 2014).

#### Soil

C-horizon (Till)

Humus samples show very low concentrations of Al, less than 0.1 %, confirming that humus samples contain very little minerals, such as clays. Both humus and B-horizon soil show elevated concentrations of U, Pb, Mo, Ag, Co, Ni and W directly above the Phoenix deposits and WS Shear (Fig. 2A). Arsenic values are also high in selected samples (Power et al., 2012).

At the Millennium property, elevated contents of U, Pb and Cu were observed in broad areas covering several major deformation zones. B-horizon soil samples indicate that ammonia acetate leaches yield the most relevant results in this study area. Hydroxylamine is designed to target the dissolution of Fe and Mn oxides (Cameron et al., 2004), but it dissolves other phases, such as carbonates, and leaches adsorbed metals. Aqua regia dissolves not only sulphides but also carbonates, clays and metal-oxyhydroxides. Higher concentrations of elements in the analytical solutions decreases the detection limits of most elements, but can increase detection limits of trace elements targeted. This obscures the detection of anomalies.

At the Phoenix property, the site that yielded the highest U content in humus in 2011 was resampled in 2012 and 2013 approximately 1m from the original site (Fig. 4A). Both visits reproduced elevated values (Figs. 6A, B). At the Millennium property, two sampling sites above the Marker Fault were revisited in 2013 (Fig. 4B). The subsequent sampling around (< 2 m) the original site reproduced elevated values (Figs. 4B, 6C; Krahenbil et al., 2014). Although the absolute values are different, the data indicates the reliability of soil geochemical anomalies.

Leach testing of humus using a variety of acids shows that metals are released only when the organic material is decomposed (Fig. 5; Power et al., 2013a). The results suggest that metals are not adsorbed on the surface of material in the humus, but they are tightly bound within organic matter.

Lead isotope compositions of various humus leach fractions (water, 0.02N HBr leach, 1 N HNO<sub>3</sub> leach, and concentrated HF-HBr digestion) show  $^{206}Pb/^{204}Pb$  values ranging from 17.3 to 1.6 and  $^{207}Pb/^{204}Pb$  from 15.4 to 15.6.

#### Water

Analyses of inorganic carbon dissolved in water yielded low values of  $\delta^{13}$ C, from -6 to -20 ‰ <sub>PDB</sub> (Power et al., 2012; Dudek et al., in press). The values are lower than that in equilibrium with the atmospheric CO<sub>2</sub>, indicating oxidation of significant amounts of organic carbon in groundwater.

## Radon Gas

Radon contents are high and variable in groundwaters above the Phoenix deposits. There is no systematic variation



**FIGURE 5.** Concentrations of U and Pb in leach tests of a humus sample, after Power et al (2013a). The amounts of metals leached are expressed as percent of the total metals extracted in aqua regia; 5.7 ppm U and 15.2 ppm Pb.  $H_2O = Milli Q$  water, HBr = hydrobromic acid, HNO3 = nitric acid, HF=hydrofluoric acid.

of Rn contents with increasing depths; Rn contents increase or decrease with increasing depths. The data suggest a local source of Rn or <sup>220</sup>Ra, a direct parent nuclide of <sup>222</sup>Rn Radium is highly soluble in water and <sup>222</sup>Ra has a relatively long halflife, 1600 yrs. Radon contents in pore fluids of soil were all below the detection limit of 3 Bq/L. Sporadically high values were noted in soil just around recent drill holes, but high values were not reproduced in the second measurement, 15 min after the first data collection.

#### Helium Gas

Swamp and monitoring wells in the Millennium property show low He concentrations (Power et al., 2013b; Fig. 7A). Deeper water samples show greater concentrations of He (Power et al., 2013b; Krahenbil et al., 2014; Fig. 7B). The sample sites east of the deposit show rather low He values, which suggests He transport by groundwaters that flow



FIGURE 6. Uranium contents in humus after aqua regia digestion (A) and ammonia acetate leach of B-horizon soil (B) at PHX028 site (shown as a triple circle in Fig. 4A) in 2011 (C) at MLN 145 (shown with an arrow in Fig. 4B). Soil data after Power et al. (2012) and Krahenbil et al (2014). Background values (bkgr) are shown as gray lines. The location of PHX028 and MLN 145 are shown in Figs.4A and 4B.



**FIGURE 7.** (A) Helium and the ratio of He/Ar in gas dissolved in water and in the Millennium property. The ratio of 1 indicates that He/Ar ratio of sample gas is identical to that in water in equilibrium with the atmosphere. The gray circles are the values from shallow environmental monitoring wells, BH127 and ML0702, and a swamp, and red circles are from exploration drill holes in the Millennium property. The blue star denotes the values of water in equilibrium with the atmosphere after Power et al (2013b), and Krahenbil et al. (2014). (B) Depth profile of He/Ar in gases dissolved in water. Location of sampling sites indicated in Fig. 4B.

Soil data

westwards toward the lake.

Groundwater in the exploration drill holes above the Phoenix deposits show low He contents, similar to water in equilibrium with the atmosphere (Dudek et al., in press)

### C-horizon (Till)

The SiO<sub>2</sub> contents of the C-horizon samples are high, supporting the Athabasca sandstones as the dominant source of glacial sediments. However, the Na<sub>2</sub>O contents vary from 0.4 to 1.32 wt. % and are much higher than average contents of Athabasca Group sandstones. For example, the uppermost sandstone unit, MFd, in the Athabasca sandstones contain Na<sub>2</sub>O less than 0.05 wt. % (Card et al., 2011; Bosman and Card, 2012). The data suggests the glacial sediments are derived not only from Athabasca Group sandstones but also from granitic basement rocks in the up-ice direction. The finding is consistent with the occurrence of glacial erratics of granitic and gneissic rocks on the surface of the study areas. Furthermore, granitic basement rocks are exposed ca. 150 km to the northeast (Fig. 1).

#### Sandstones

Sandstones above the Phoenix deposits show chimneylike vertical distribution of elevated metal contents (Dann et al., 2014). The patterns are especially apparent for elements, such as rare earth elements, Y and W (Figs. 8A, B). Furthermore, high metal contents including U are present in the uppermost sandstones on the Phoenix property (Fig. 4A, Power et al., 2012). Principal component analysis of total digestion data of sandstones confirms that the Dunlop Member of the Manitou Falls Formation has high scores of PC1, which includes U, B and rare earth elements (Chen et al., 2014, 2015; Fig. 9).

## Discussion

This study produced two encouraging results in the use of soil in surficial geochemical exploration for concealed U deposits. First, a variety of acid leach and digestion on humus samples show that metals are tightly held within the organic material, not on the surface of organics or minor clays (Fig. 5). The data rejects a possible incorporation of metals into humus as the result of drilling and other exploration activity. The analytical results of this study suggest that digestions to decompose organic, such as aqua regia, are necessary for the analysis of humus samples in U exploration. This is in accord with the procedure, aqua regia digestion of humus, recommended by the CAMIRO-sponsored project (Bonham-Carter and Hall, 2010). As proposed by (Dunn, 1983), plants may have extracted U from groundwater and soils prior to decomposition into a humus layer.

Repeated sampling tests show reliable nature of elevated metal contents in soil. Samples of humus as well as B-horizon soil collected in the vicinity, ca. 1–2 m, from the original sites of collection both at the Phoenix and Millennium properties yielded elevated values of metals in subsequent years (Fig. 6). The absolute values vary, but they are elevated relative to the surrounding soils. Considering different months of sampling, the data is encouraging for soil geochemical surveys.

Traverse sampling of soil samples shows that elevated metal contents are close to the surface projections of U ore of the Phoenix deposits (Fig. 4A). To evaluate the contribution of glacial dispersion to the metal contents, sampling was conducted along Transect B1, which runs above the barren area between the Phoenix Deposit A and Deposit B (Fig. 4A). Transect B1 did not yield elevated metal contents. The

Surficial Geochemical Surveys Over Concealed Uranium Ore of the Phoenix and Millennium Deposits in the Athabasca Basin, Saskatchewan



FIGURE 8. (A) Yttrium and Tb (B) concentrations in sandstones above the Phoenix Deposit A and B, after Dann et al. (2014). MSL = metres above sea level.

data suggest that glacial dispersion is unlikely source for elevated metal contents in soil samples.

### Metal Sources

The data from the Phoenix deposit suggest that metals in soils were most likely derived from sandstones. This is supported by chimney-like elevated concentrations of metals in sandstones above U ore (Figs. 8A, B), and relatively high metal contents in the upper sandstones (Figs. 4A; 8). Elevated concentrations of U and W in soil samples are consistent with oxidized conditions of groundwaters where organic carbon is oxidized. These elements are mobile as  $U^{6+}$  and  $W^{vl}O_4^{-2}$  under oxidized conditions.

At the Millennium site, the composition data is not available for sandstones above the Millennium deposit because their exploration drill holes are all from the east of the deposit. Therefore, it is difficult to evaluate the source of metals whether sandstones or deep-seated U ore. In the Millennium property, reactivation of basement shear deformation zones produced abundant faults in sandstones, which are clearly imaged in seismic surveys (Wood et al., 2012). Elevated metal contents in soil samples directly above such major faults suggest that faults are conducive in transferring elements from deep levels.

## Sandstones

Anomalous compositions of sandstones above the Phoenix deposits are consistent with the sandstone compositions above U deposits at the Key Lake, Midwest Lake and Eagle Point (Sopuck et al., 1983) and at the Cigar Lake, Dawn Lake and Wolf Lake deposits (Clark, 1987). The data suggests that sandstones above U deposits commonly show elevated concentrations of elements associated with the deposits. The dispersion of elements in sandstones may have taken place during the U mineralization (primary dispersion) or long after the mineralization (secondary dispersion; c.f. Cameron et al., 2004). The primary dispersion is supported by extensive occurrences of alteration minerals in the overlying sandstones (Jefferson et al., 2007; Gamelin et al., 2010; Kerr, 2010). Furthermore, heavy REE and W are considered to be immobile at low temperatures. The dispersion of such

elements in sandstones suggests that elevated metal contents are likely produced during the hydrothermal activity related to the U mineralization.

## Noble Gases

Noble gases are chemically inert, which makes them disperse quickly along fractures in rocks and soil. Among noble gases, He and Rn are decay products of U and therefore they are expected to be in higher concentrations around U deposits. Helium is light, stable, and able to diffuse more quickly in water than Rn (Yaws, 2009; Dudek and Hattori, in press). The high diffusivity of He, however, poses a problem. Gas sampled near the surface of water in environmental monitoring holes, exploration drill holes, and swamps yielded low contents of He, identical to the amount expected in water in equilibrium with the atmosphere (Power et al., 2013b). The results suggest that He gas should be collected in water at a depth greater ca. 5 m below the top of the water table.

Although He contents were high in deeper waters in proximity to the surface projection of the Millennium deposit, low contents of He are noted in the eastern part of the property where water is flowing towards the deposit and the lake (Fig. 4B). If He is transported through diffusion process either vertically or radially, it should be detected above U ore. The data suggests that He is not ascending vertically but rather transported laterally by groundwater flow. This is also consistent with low He contents in waters above the Phoenix deposits.

High and variable contents of Rn in groundwater above the Phoenix deposits are similar to the results reported from the Millennium property by Devine et al. (2013). If Rn is ascending from deep sources, the values of Rn should be greater at deeper levels. High values of Rn at shallower depths in several drill holes suggest proximal sources of Rn at shallow levels. Furthermore, the short half-life, 3.8 days, of <sup>222</sup>Rn makes it impossible to migrate from deeply-seated U deposits to the surface. Although <sup>226</sup>Ra, Rn's immediate parent, has a reasonably long half-life of 1600 years, it would be more difficult for Ra to be vertically diffused in groundwaters from the deposits to the surface.

There are several possible local sources of U or Ra in drill holes: upper sandstones, soil and U brought to the surface by drilling (contamination by human activity). If mineralized cores brought U and Ra to the surface. Rn contents should be high in water samples collected from drill holes that intersected the mineralization. There is no significant difference in Rn contents between water from holes intersected and not-intersected the mineralization. To evaluate a possible contribution of soil to Rn in water, Rn contents in soil pore fluids were measured in the area close to drill holes. but high values were not confirmed. Although sporadic high values were recorded in highly disturbed soil adjacent to drill holes, the values were not reproduced. Another possible source of Rn is preferential enrichment of Rn or Ra by organic matter in water or soil because Rn has a strong affinity with organic material (Leanev and Herczeg, 2006). It is also known that plant roots incorporate Ra (Gunn and Mistry, 1970). Radium incorporated in plants would release Rn in shallow depths.

The fourth possibility is elevated U and Ra concentrations in sandstones at shallow depths. Power et al. (2012) documented high contents of metals including U, in the uppermost sandstones in the area directly above the Phoenix uranium deposits (Fig. 4A). Principal component analysis of sandstones by Chen et al., (2014, 2015) also shows high metal contents including U in the MFd (Fig. 9). The distribution of high metal contents form "chimney" like shape from the deposits to the uppermost sandstones (Dann et al., 2014). Uranium contents in the MFd are mostly below 1 ppm, but values greater than 1 ppm are not uncommon (Dann et al., 2014). Furthermore, many humus and B-horizon soil contain U greater than 1 ppm. The amount is sufficient to explain Rn contents in most samples. Therefore, we conclude that it is highly likely that U and probably Ra in sandstones at shallow levels and soil are the sources of Rn observed in groundwater.

The fifth possibility is U in granitic boulders and erratics in glacial sediments. This cannot be discounted, but we do not consider this as the most likely source of Rn and He. It is too fortuitous for high U-granitic boulders to be present in the areas directly above U deposits.

#### **Implications for Exploration**

- 1. Sampling over the Phoenix and Millennium deposits has demonstrated that geochemical anomalies are detectable in surface media, even from deeply-seated deposits situated 400 m and 750 m below the surface, respectively. The surficial geochemical anomalies are influenced by many factors, such as groundwater flow, abundance of faults, and glacial sediments. Anomalies may not be apparent in a single medium in individual site. Different media, such as soil and gases need to be examined in concert.
- The distributions of geochemical anomalies in soil suggest that faults are implicated in metal transfers to the surface media, perhaps through water movement. Multiyear surveys of soil show repeatable soil geochemical anomalies.
- 3. The chemical composition and alteration of sandstones at



**FIGURE 9.** Vertical scores of Principal Component 1 of sandstones above the Phoenix deposits. Elements in component 1 are rare earth elements, Y, U, B, Na, Mg, K, Li and Pb (after Chen et al., 2014). The score of PC1 for U is shown with a red line. Note that sandstones of RD and MFd plot close to the vertical line of U.

shallow levels may provide a clue for the presence of deeply-seated U deposits. The information is very useful in exploration, especially in the interior of the basins where drilling of thick sandstone covers would be expensive.

4. Helium dissolved in water far below the water table level yielded promising results in the detection of buried U deposits in the Millennium property. Since He moves with water, a careful selection of sites is essential, particularly with respect to porous till and sand. While elevated Rn concentrations were detected at both properties, the short half-life and relatively slow transport mechanisms from the deeply-buried ore likely prevents it from reaching surface media. Therefore, Rn observed in groundwater in drill holes likely originated from a proximal source such as U or Ra in the upper sandstones and/or soil.

## Acknowledgments

We thank Denison Mines Corporation and the Exploration and Mining departments at Cameco Corporation for their logistic support. The project was funded by a grant from Natural Resources of Canada through the Targeted Geoscience Initiative Four program. The manuscript benefited from helpful reviews by Donald Wright, Janet Campbell and Paul Gammon.

#### References

- Alexandre, P., Kyser, T.K., Jiricka, D., and Witt, G., 2012. Formation and Evolution of the Centennial Unconformity-Related Uranium Deposit in the South-Central Athabasca Basin, Canada; Economic Geology, v. 107, p. 385–400.
- Bonham-Carter, G., and Hall, G., 2010. Multi-media techniques for direct detection of covered unconformity uranium deposits in the Athabasca Basin, Phase III, Final report of results of soil geochemistry using selective leaches; Canadian Mining Industry Research Organization (CAMIRO) Exploration Division, 280 p.

<a href="https://www.appliedgeochemists.org/index.php/publications/other-publications/2-uncategorised/116-camiro-project-08e01">https://www.appliedgeochemists.org/index.php/publications/other-publications/2-uncategorised/116-camiro-project-08e01</a>

- Bosman, S.A. and Card, C.D., 2012. Data File Report 31, Geochemical analyses of Athabasca Group drillholes in Saskatchewan (NTS 64L, 74F to 74K, and 74N to 74P)-Supplementary to Data File Reports 24, 29, and 30; Saskatchewan Ministry of Energy and Resources.
- Cameco Corporation, 2013. The strength to dig deeper, 2013 Annual Report; Cameco Corporation, http://www.cameco.com/invest/ financial-information/annual-reports/2013
- Cameron, E.M., 1983. Uranium Exploration in Athabasca Basin, Saskatchewan, Canada; Geological Survey of Canada Paper 82-11, 310 p.
- Cameron, E.M., Hamilton, S.M., Leybourne, M.I., Hall, G.E.M., and McClenaghan, M.B., 2004. Finding deeply buried deposits using geochemistry; Geochemistry: Exploration, Environment, Analysis, v. 4, p.7–32.
- Campbell, J. E. 2007. Quaternary geology of the eastern Athabasca Basin, Saskatchewan; in EXTECH IV: Geology and Uranium Exploration TECHnology of the Proterozoic Athabasca Basin, Saskatchewan and Alberta, (ed.) C.W. Jefferson and G. Delaney; Geological Survey of Canada Bulletin v. 588, p. 211–228
- Card, C. D, Bosman, S. A., Simmon, W. L., Zmetana, D. J. and Delaney, G. D., 2011. Data File Report 29, Geochemical Analyses of Athabasca Group Outcrops in Saskatchewan (NTS 64L, 74F to 74K, & 74N to 74P); Saskatchewan Ministry of Energy and Resources.
- Chen, S., Hattori, K. and Grunsky, E.C., 2014. Principal component analysis of sandstones overlying the Phoenix uranium deposits, Athabasca Basin; Geological Survey of Canada, Open File 7578. doi:10.4095/29492
- Chen, S., Hattori, K., Grunsky, E.C., and Liu, Y., 2015. Geomathematical study of sandstones overlying the Phoenix uranium deposits and the REE-rich Maw Zone, Athabasca Basin, Saskatchewan; *in* Targeted Geoscience Initiative 4: unconformity-related uranium systems, (ed.) E.G. Potter and D.M. Wright; Geological Survey of Canada, Open File 7791, p. 21-31. doi:10.4095/295776
- Clark, L.A.C., 1987. Near surface lithogeochemical halos as an aid to discovery of deeply buried unconformity-type deposits, Athabasca Basin, Canada; Journal of Geochemical Exploration, v. 28, p. 71–84.
- Cloutier, J., Kyer, T.K., Olivo, G.R., and Brisbin, D., 2011. Geochemical, isotopic, and geochronologic constraints on the formation of the Eagle Point basement-hosted uranium deposit, Athabasca Basin, Saskatchewan, Canada and recent remobilization of primary uraninite in secondary structures; Mineralium Deposita, V. 46, p. 35–56.
- Cloutier, J., Kyer, T.K., Olivo, G.R., Alexandre, R., and Halaburda, J., 2009. The Millennium uranium deposit, Athabasca Basin, Saskatchewan, Canada: An atypical basement-hosted unconformity-related uranium deposit; Economic Geology, v.104, p. 815–840
- Coker, W.B., and Dunn, C.E., 1981. Lake water and sediment geochemistry; NEA-IAEA Athabasca Basin-Wollaston lake test area, Saskatchewan; Geological Survey of Canada, Open File 779, 100 p. doi:10.4095/129693
- Dann, J., Hattori, K., Potter, E.G., and Sorba, C., 2014. Discrimination of elemental assemblages in the alteration halo of the Phoenix deposit, Saskatchewan, Through Applied GIS; Geological Survey of Canada,

Open File 7463, doi: 10.4095/293122.

- Devine, M., Hattori, K., and Kotzer, T., 2013. Radon concentrations of groundwater in the Millennium property, Athabasca Basin; Saskatchewan Geological Survey Open House.
- Dimitrov, D.D., Bhatti, J.S., and Grant. R.F. 2014. The transition zones (ecotone) between boreal forests and peatlands: Modelling water table along a transition zone between upland blackspruce forest and poor forested fen in central Saskatchewan; Ecological Modelling, v. 274, p. 57–70.
- Dudek, N., and Hattori, K., in press. Radon distribution and concentrations above buried uranium ore: Denison Mine's Phoenix deposits, Saskatchewan; Geological Survey of Canada, Scienific Presentation, 1 poster.
- Dunn, C., 2010. Biogeochemical Surveys at Cigar West, and McClean South: Athabasca Basin, Saskatchewan; Unpublished CAMIRO Final Report, 39p.
- Dyck, W., 1969. Development of uranium exploration methods using radon; Geological Survey of Canada, Paper 69-46, 26 p.
- Gamelin, C., Sorba, C., and Kerr, W., 2010. The discovery of the Phoenix deposit: A new high-grade, Athabasca Basin unconformity-type uranium deposit, Saskatchewan, Canada; in Saskatchewan Geological Survey Open House 2010, Abstracts, 17, p. 10.
- Gunn, K.B. and Mistry, K.B., 1970. The effect of chelating agents on the adsorption of radium by plants; Plant and Soil, v. 33, p. 7-16.
- Hamilton, S.M., Hattori, K.H., Clark, I.D., 2005. Investigation into the source of forest-ring-related natural gas in northern Ontario; Ontario Geological Survey Open File Report 6172, p.19-1–19-4.
- Hinchey, J.G., and Hattori, K., 2007. Lead isotope study of the late Archean Lac des lles palladium deposit, Canada: Enrichment of platinum group elements by ponded sulfide melt; Mineralium Deposita, v. 42, p.601–611.
- Jefferson, C.W., Thomas, D.J., Gandhi, S.S., Ramaekers, P., Delaney, G., Brisbin, D., Cutts, C., Portella, P., and Olso, R.A., 2007. Unconformity-associated uranium deposits of the Athabasca Basin, Saskatchewan and Alberta; in EXTECH IV: Geology and Uranium Exploration TECHnology of the Proterozoic Athabasca Basin, Saskatchewan and Alberta, (ed.) C.W. Jefferson and G. Delaney; Geological Survey of Canada, Bulletin 588, p.23–67.
- Jiricka, D., 2010. The Centennial deposit—an atypical unconformity-related uranium deposit—an update; International Association on the Genesis of Ore Deposits (IAGOD), 13th Quadrennial IAGOD Symposium, Adelaide, Australia, 6–9 April 2010, Proceedings.
- Kerr, W.C., 2010. The discovery of the Phoenix deposit: a new high-grade Athabasca Basin unconformity-type uranium deposit, Saskatchewan, Canada; in The Challenge of Finding New Mineral Resources: Global Metallogeny, Innovative Exploration, and New Discoveries, Volume II: Zinc-Lead, Nickel-Copper-PGE, and Uranium, (ed.) R.J. Goldfarb, E.E. Marsh and T. Monecke; Society of Economic Geologists, p. 703–725.
- Krahenbil, A., Hattori, K., Power, M., and Kotzer, T., 2014. Surficial geochemistry associated with the deeply buried Millennium and Phoenix uranium deposits, Athabasca Basin, Northern Saskatchewan; Geological Survey of Canada, Open File 7611, doi:10.4095/293928
- Leaney, F.W. and Herczeg, A.L., 2006. A rapid field extraction method for determination of radon-222 in natural waters by liquid scintillation counting; Limnology and Oceanography; Methods v. 4, p. 254–259.
- Maurice, Y.T., Dyck, W., and Strand, J.G., 1985. Secondary dispersion around the uranium-nickel deposit at Key Lake, northern Saskatchewan; in Geology of Uranium Deposits, (ed.) T.I.I. Sibbald and W. Petruk; Canadian Institute of Mining and Metallurgy, v. 32, p. 38–47.
- Power, M.J., Hattori, K., Sorba, C. and Potter, E.G., 2012. Geochemical anomalies in the soil and uppermost sandstones overlying the Phoenix uranium deposit, Athabasca Basin, Saskatchewan, Canada; Geological Survey of Canada, Open File 7257, 36 p., doi:10.4095/291981
- Power, M.J., Hattori, K., Sorba, C., Kotzer, T., Potter, E.G. 2013a. Surface media expressions of buried uranium: the Phoenix and Millennium deposits, Athabasca Basin, Saskatchewan, Canada; 12<sup>th</sup> Biennial meeting of Society for Geology Applied to Mineral Deposits, Uppsala, Sweden. v. 1, p. 426–429.

- Power, M., Hattori, K., Pinti, D., Potter, E.G., 2013b. Anomalous abundances of He and mobile metals in surface media over the deeply buried Millennium U deposit, Athabasca Basin, Canada; in 2013 Goldschmidt Conference, Mineralogical Magazine, v. 77, p.1993. doi:10.1180/minmag.2013.077.5.16
- Power, M., Hattori, K., Krahenbil, A., Sorba, C., Kotzer, T. and Potter, E.G., 2014. Geochemical surface expression of the Phoenix and Millennium uranium deposits, Athabasca Basin: Improving exploration vectors; PDAC-CMIC-SEG Canada Student Minerals Colloquium, http://cmicfootprints.ca/pdac-smc/2014
- Reid, K.D., Ansdell, K., Jiricka, D., Witt, G., and Card, C., 2014. Regional setting, geology, and paragenesis of the Centennial unconformity-related uranium deposit, Athabasca Basin, Saskatchewan, Canada; Economic Geology, v. 109, p. 539–566
- Roscoe, W.E., 2014. Technical report on a mineral resource estimate update for the Phoenix uranium deposit, Wheeler River project, Eastern Athabasca Basin, northern Saskatchewan, Canada; NI 43-101 Technical Report prepared for Denison Mines Corp., 134 p.
- Sanford, W. E., Shropshire, R.G., and Solomon, D. K., 1996. Dissolved gas tracers in groundwater: Simplified injection, sampling, and analysis; Water Resources Research, v. 32, p. 635–1642.
- Schreiner, B.T. 1984. Quaternary geology of the Precambrian Shield, Saskatchewan; Saskatchewan Energy and Mines Report, 221, 1 map, scale 1:1 000 000.
- Smith, R.S., Wood, G.R., Powell, B., 2010. Detection of alteration at the Millennium uranium deposit in the Athabasca Basin: a comparison of data from two airborne electromagnetic systems with ground resistivity data; Geophysical Prospecting, v. 58, p.1147–1158.
- Sopuck, A.J., de Carla, A., Wray, E.M., and Cooper, B., 1983. The applica-

tion of lithogeochemistry in the search for unconformity-type uranium deposits, northern Saskatachewan, Canada; Journal of Geochemical Exploration, v. 19, p. 77-99.

- Thomas, D.J., Matthews, R.B., and Sopuck, V.J., 1998. Athabasca basin unconformity-type uranium deposits: A synopsis of the empirical model and review of exploration and production trends; Canadian Institute of Mining, Metallurgy and Petroleum meeting, Montreal 1998, Proceedings, CD-ROM.
- Todt, W., Cliff, R.A., Houser, A. and Hofmann, A.W., 1995. Evaluation of a <sup>202</sup>Pb -<sup>205</sup>Pb double spike for high precision analyses; in Earth Processes: Reading the Isotopic Code, (ed.) A. Basu and S. Hart; American Geophysical Union Geophysical Monograph v. 95, p. 429–437.
- Wasyliuk, K., 2006. Geochemical methods in the Athabasca Basin: Past, Present and Future; in, Uranium: Athabasca Deposits and Analogues; Canadian Institute of Mining, Metallurgy and Petroleum Field Conference, Saskatoon, CD-ROM.
- Wood, G., O'Dowd, C., Cosma, C., and Enescu, N., 2012. An interpretation of surface and borehole seismic surveys for mine planning at the Millennium uranium deposit, northern Saskatchewan, Canada; Geophysics, v. 77, p.WC20–WC212.
- Yaws, C.L., 2009. Diffusion Coefficients in Water Inorganic Compounds; in Transport of Chemicals and Hydrocarbons, (ed.) C.L. Yaws; Elsevier Inc., p. 594–596.
- Yeo, G.M. and Delaney, G. 2007. The Wollaston Supergroup, stratigraphy and metallogeny of a Paleoproterozoic Wilson cycle in the Trans-Hudson Orogen, Saskatchewan; in EXTECH IV: Geology and Uranium Exploration TECHnology of the Proterozoic Athabasca Basin, Saskatchewan and Alberta, (ed.) C.W. Jefferson and G. Delaney; Geological Survey of Canada, Bulletin 588, p. 89–117.