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# **POTENTIAL PATHFINDER ELEMENTS: FOOTPRINT OF 3D LITHOGEOCHEMISTRY OF THE MILLENNIUM UNCONFORMITY-TYPE URANIUM DEPOSIT, ATHABASCA BASIN, SASKATCHEWAN**

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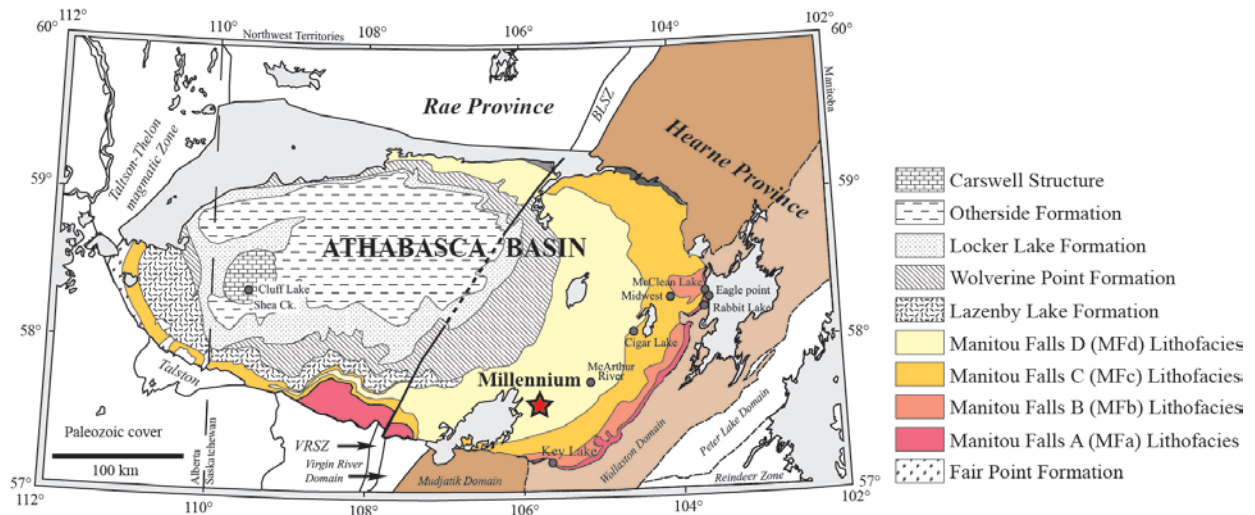
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## **Introduction**

The Athabasca Basin, Saskatchewan, hosts world-class unconformity-type uranium deposits that are important contributors to global uranium production. The Millennium deposit, southeastern Athabasca Basin, is a basement-hosted deposit with ~75.8 million pounds grading 2.4% U<sub>3</sub>O<sub>8</sub> (indicated), ~28.9 million pounds grading 3.2% U<sub>3</sub>O<sub>8</sub> (inferred), and occurs at ~650 m depth (Fig. 1). The aim of this project is to examine the litho geochemical footprint associated with alteration, mineralization, and lithostratigraphic variations around the deposit, and potential litho geochemical vectors toward mineralization.

Whole rock geochemistry results utilizing partial and total extraction methods from the quartz arenite (sandstones) of the Manitou Falls Formation illustrate distinctive patterns of anomalously high concentrations of various elements commonly associated with polymetallic, unconformity-related uranium deposits that span the basement-sandstone contact. Select rare earth elements (Pr, Nd, Sm, Gd, Dy) appear restricted to specific members of the Manitou Falls Formation, whereas other elements (Ag, As, Bi, Co, Cr, Ge, Mo, Ni, Sb, Te) exhibit high concentrations that extend vertically from the unconformity to the surface. These vertical patterns are proximal to the deposit and extend from 500-3000 m along strike and 300-450 m across strike as a halo around uranium mineralization. While the Millennium deposit is considered to be basement-hosted (Cloutier et al. 2009), a significant amount of mineralization occurs in the sandstone above the unconformity; therefore, these potential pathfinder elements may be highlighting the areas of mixing between oxidizing basinal and reducing basement fluids potentially responsible for deposit formation, or post-mineralization secondary dispersion.



**Figure 1. Geology of the Athabasca Basin, northern Saskatchewan. Coloured areas indicate the lithofacies of the Manitou Falls Formation and location of the Millennium deposit (red star), hosted in the basement rocks of the Hearne Province, within the transition zone between the Mudjatik and Wollaston domains. Figure modified from Cloutier et al. (2009) and Sibbald & Quirt (1987).**

## Methodology

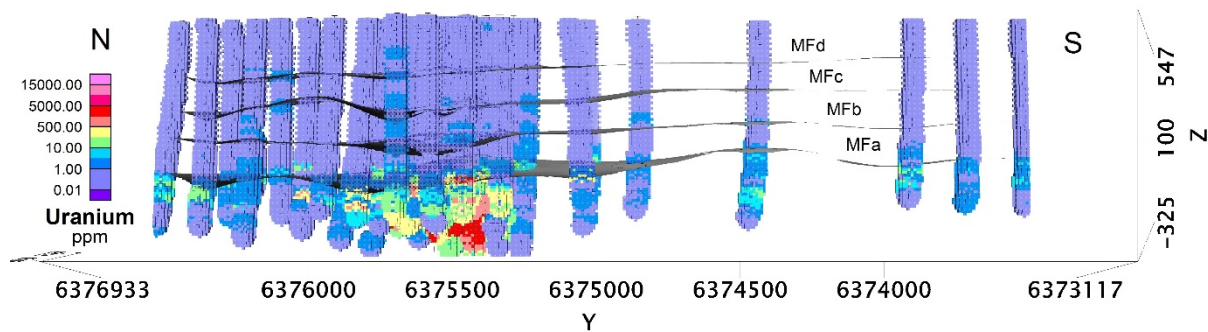
### Whole rock geochemistry

All samples were collected from diamond drill cores and analysed at the Geoanalytical Laboratories of the Saskatchewan Research Council. Sandstone samples consist of core collected at 10 or 20 metre intervals and are considered representative of lithology over that interval. Samples were crushed and underwent both total (3 acid) and partial digestion (aqua regia). Partial digestion is preferred for the investigation of mobile elements, as it is less aggressive than the total digestion preferred for mineral composition and immobile elements. Solutions were analysed for trace elements by inductively coupled plasma mass spectrometry (ICP-MS) and major elements were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Geosoft Target was used for data analysis and 3D mapping to visually identify patterns of elements, combinations of elements, and their spatial relationships to uranium mineralization. In addition, quantification of patterns in the data was undertaken using conventional statistical methods.

Samples for the study cover an area that extends for 3.2 km N-S along strike of the deposit with over 50 collar locations. The angled holes were drilled east to west from the hanging wall side, through the unconformity and therefore contain elemental analyses for both basin and basement rock, although only basin samples are examined in this summary.

## Geology and Mineralization

The Manitou Falls Formation sandstone consists of quartz arenite with minor clay minerals. It is unmetamorphosed, extensively altered, and lies subhorizontally above the basement (Ramaekers, 2007; Cloutier et al. 2009). Alteration processes include prograde diagenesis associated with basin burial as well as hydrothermal events leading to uranium mineralization, and later meteoric events (Kyser & Cuney, 2008). Four lithofacies define the Manitou Falls Formation and are identified as MFd (uppermost, at surface), MFc, MFb, and MFa. The bottom surface of the lowest unit (MFa) is considered to be the unconformity within this dataset (Fig. 2). Uranium distribution throughout the study area (Fig. 2) indicates that the majority of mineralization occurs in the basement, well beneath the unconformity. Uranium is also present at the unconformity and in lower abundance in the sandstones above the unconformity; within the scope of this dataset, samples containing greater than 1000 ppm U in the sandstones were not included in order to avoid results directly related to mineralization itself.



**Figure 2. Uranium distribution in the Manitou Falls Formation. While Millennium is a basement-hosted deposit (yellow to pink areas), uranium is present in the sandstones above the unconformity as well.**

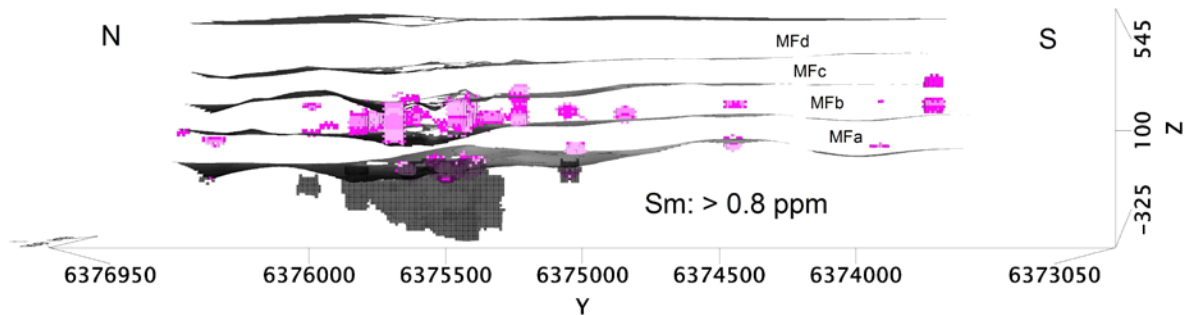
All data from the Manitou Falls Formation were examined with a map generated for each element in 3D. All maps were created in Geosoft Target utilizing an inverse distance weighting function with a cell size of 10 metres. The maps were analysed visually for patterns that have a spatial relationship of high concentrations with uranium. The patterns for all digestions available were examined, and in most cases the signal resolution for the partial result of a particular element was preferable for that spatial relationship. Where a distinctive pattern was found, the raw data were examined in an attempt to quantify that pattern in dimensions across and along strike. “Anomalous” concentrations for each element were defined as those values above the 90<sup>th</sup> percentile.

## Results

Several trace elements are well known to be mobile pathfinders coincident with uranium mineralization, namely Bi, Cr, Cu, Zn, Ni, Co, Mo, Mn, As, Ag, Te, and others (Hoeve & Sibbald, 1978; Sopuck et al., 1983, Ng et al. 2013). Rare earth

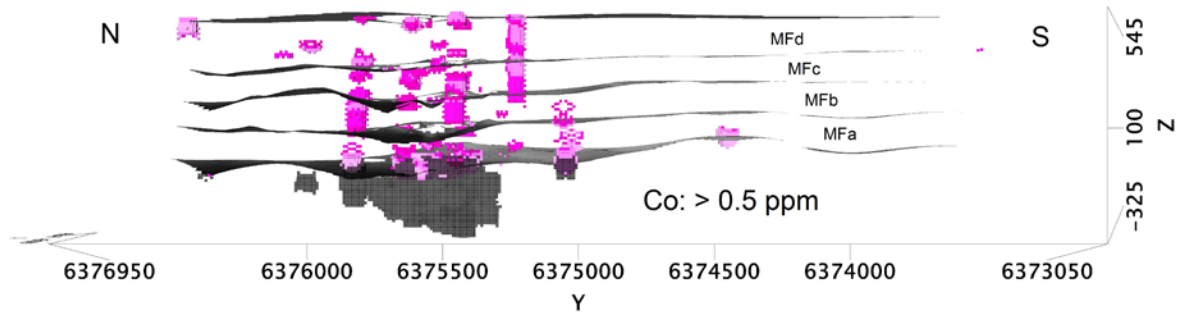
elements are also used as pathfinders (Fayek & Kyser, 1997; Fisher et al., 2013). At the Millennium deposit, all of these are found to be spatially related to elevated levels of uranium in the sandstone, as well as mineralization in the basement, along with Rb, Ga, and Sb.

Within the sandstone rocks that contain elevated levels of uranium, elements with anomalously high concentrations that are proximal to mineralization tend to fall into two categories: 1) those patterns that are horizontally constrained within the mid- to lower lithofacies and centred over the deposit in the basement (50 ppm U and greater); or 2) centred over the deposit and exhibiting high values in a vertical pattern from the unconformity through all lithofacies to the surface. The lanthanides, plus Y, fall into the first category (Fig. 3). Their patterns do not mirror the uranium distribution in the sandstone but instead highlight the location of the basement deposit.



**Figure 3. Rare Earth Element distribution in the Millennium deposit. Rare earth elements Gd, Nd, Pr, Sm, Dy, and HFSE Y (partial extraction) are concentrated in the MFb lithofacies. 90<sup>th</sup> percentile values of Sm are shown and illustrate localization in the MFb. Uranium in the basement (50 ppm and greater) shown in grey.**

The second category of elements is vertically distributed and more likely to be constrained by conduits for fluid flow than elemental variation in the sandstones. These elements include partial digestion results for As, Ga, Rb, Cu, Ag, Bi, Co, Mo, Ni, Sb, and Te, and total digestion values for Cr (partial digestion unavailable). These elements appear directly above mineralization and extend towards the surface. The halo of anomalous values for each element is not continuous throughout each drill core and can be scattered, but the larger-scale spatial relationship is apparent.



**Figure 4. Transition metals and other trace elements. As, Ga, Rb, Cu, Ag, Bi, Co, Mo, Ni, Sb, and Te (partial extraction), along with Cr (total extraction) are concentrated directly above the basement uranium, shown in grey. The 90<sup>th</sup> percentile for Co is shown here as an example, but all extend from the unconformity through all lithofacies to the surface.**

Table 1 summarizes the elements in Figure 3 and Figure 4 above, and the haloes of anomalous concentrations as measured along and across strike of the study area. Although the patterns are not continuous in all directions, the maximum distances along and across strike were chosen for measurements. While these haloes are within those sandstones that exhibit elevated levels of uranium, the patterns do not mirror the U distribution.

**Table 1: Elements exhibiting high concentrations in the sandstones (90<sup>th</sup> percentile) that demonstrate a strong spatial relationship to uranium mineralization in the basement.**

Element	90 <sup>th</sup> percentile (ppm)	Lithofacies present	Across Strike (m)	Along Strike (m)
Pr	>1.3	MFb	450	2800
Nd	>4.6	MFb	450	2800
Sm	>0.8	MFb	450	2800
Gd	>0.8	MFb	450	2800
Dy	>0.3	MFb	450	1200
Y	>1.2	MFc-MFa	450	2800
Cr	>238	MFd-MFa	350	1000
Co	>0.5	MFd-MFa	350	1200
Ni	>4.1	MFd-MFa	350	3000
Cu	>2.3	MFd-MFa	300	2200
Ga	>0.3	MFd-MFa	450	1300
Rb	>0.3	MFd-MFa	450	1600
As	>1.1	MFd-MFa	450	3000
Sb	>0.1	MFd-MFa	300	600
Bi	>0.4	MFd-MFa	300	600
Ag	>0.04	MFd-MFa	300	600
Mo	>0.9	MFd-MFa	300	1200
Te	>0.1	MFd-MFa	300	500

## Discussion

While the high grade mineralization at the Millennium deposit is located within basement rocks (Roy et al., 2006; Cloutier et al. 2009), uranium mineralization is present in the sandstones of the Manitou Falls Formation at and above the unconformity, directly above the basement deposit. For the purposes of geochemical footprint delineation, the elemental relationships within this study have been developed using a maximum cut off value of 1000 ppm uranium. These relationships illustrate that various rare earth elements, transition metals, and other metals and metalloids show anomalously high concentrations in the sandstones that highlight the location of the highest concentrations of uranium in the basement. These anomalous (90<sup>th</sup> percentile) values exhibit patterns in the Manitou Falls Formation, along with elevated values of uranium, that are centred directly above the basement-centric uranium deposit, with haloes that range from 350-450 m across and 500-3000 m along strike (Table 1). Given that many of these potential pathfinder elements are associated with polymetallic, complex-type sandstone-hosted uranium deposits (Kyser & Cuney, 2008), these patterns may be representative of a mixing zone of hydrothermal fluids that produced the lower grade mineralization or, alternatively, may be associated with the movement of post-mineralization fluids as the Athabasca Basin has been affected by multiple fluid events after the main mineralization episodes (Fayek & Kyser, 1997; Alexandre et al., 2009, Cloutier et al. 2009). Previous analysis on this dataset through the examination of lead-lead isotope ratios support both scenarios, as those ratios indicative of mineralization appear both directly above the deposit and at a distance (Guffey et al, 2014).

## Conclusions

Basement-hosted unconformity-related uranium deposits are considered to be difficult exploration targets as associated accessory minerals and alteration haloes tend to be located at or below the unconformity (Kyser and Cuney, 2008). The basement-hosted Millennium deposit, in the southeastern part of the Athabasca Basin, is found at a depth of approximately 650 m, with the majority of mineralization below the unconformity. Whole rock geochemistry of sandstones samples indicates that several elements exhibit anomalously high values directly above the deposit, some of which are present in all four lithofacies that comprise the Manitou Falls Formation.

The 18 elements noted here (Pr, Nd, Sm, Gd, Dy, Y, Cr, Co, Ni, Cu, Ga, Rb, As, Sb, Bi, Ag, Mo, and Te) have the potential to act as pathfinders, especially the latter 12 that show anomalously high concentrations present from the surface to the unconformity. These elements are commonly considered to be indicator elements for classic, unconformity contact type unconformity-related uranium deposits, as opposed to the monometallic character associated with basement-hosted deposits. As a result predominantly basement-hosted deposits that extend to the unconformity

and above may be identified where similar patterns are noted in the Athabasca Basin sandstones, specifically those in the Manitou Falls Formation.

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