



**GEOLOGICAL SURVEY OF CANADA
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**Regional Surface Rock Geochemistry,
Athabasca Basin, Saskatchewan**

D.M. Wright and E.G. Potter

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Saskatchewan**

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2014

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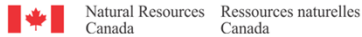
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Regional Surface Rock Geochemistry, Athabasca Basin, Saskatchewan

Wright, D.M. and Potter, E.G.

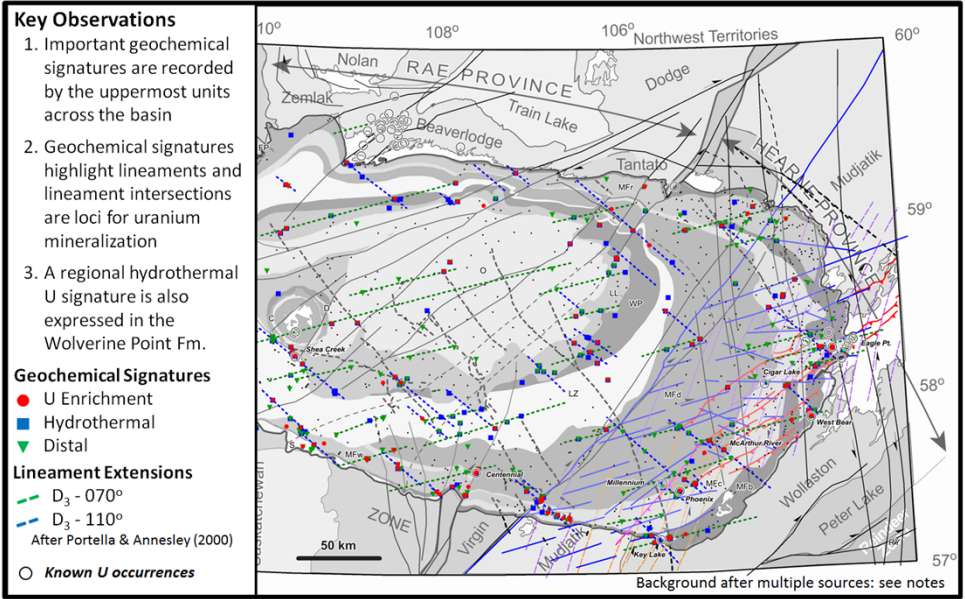


Abstract:

Regional examination and integration of geochemical data with other components of the uranium exploration model can influence mineral exploration. This approach was applied to regional geochemical data for the Athabasca Basin, northern Saskatchewan, Canada, which is host to some of the world's most significant high grade unconformity-associated uranium deposits. Four distinct geochemical signatures are described, each reflecting portions of processes responsible for uranium mineralization, associated alteration, and background geology. These signatures are significant in that they 1) are present in the exposed and near-surface rocks of the Athabasca Basin; 2) correspond with lineament traces, and highlight lineament intersections that are loci for uranium mineralization, and 3) partially define a distinct but locally stratabound hydrothermal signature that is possibly temporally and genetically related to focused uranium deposition elsewhere in the Athabasca Basin, but is also expressed in the Wolverine Point Formation.

Regional Surface Sedimentary Rock Geochemistry

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Regional examination and integration of geochemical data with other components of the uranium exploration model can influence mineral exploration.

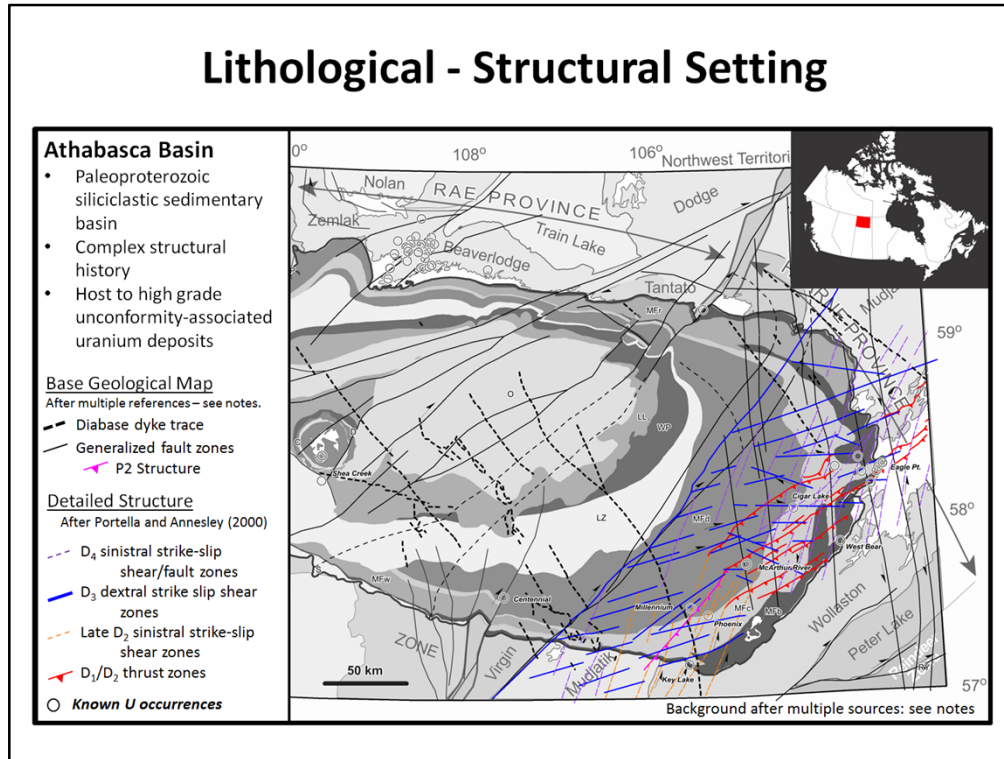
Key Observations:

1. Geochemical signatures of alteration and focused uranium mineralization are present in the upper exposed and near-surface units of the Athabasca Basin;
2. Geochemical signatures correspond with lineaments and highlight lineament intersections are loci for uranium mineralization; and
3. A distinct but locally stratabound hydrothermal signature that is possibly temporally and genetically related to focused uranium deposition elsewhere in the Athabasca Basin is also expressed in the Wolverine Point Formation.

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

Lithological - Structural Setting

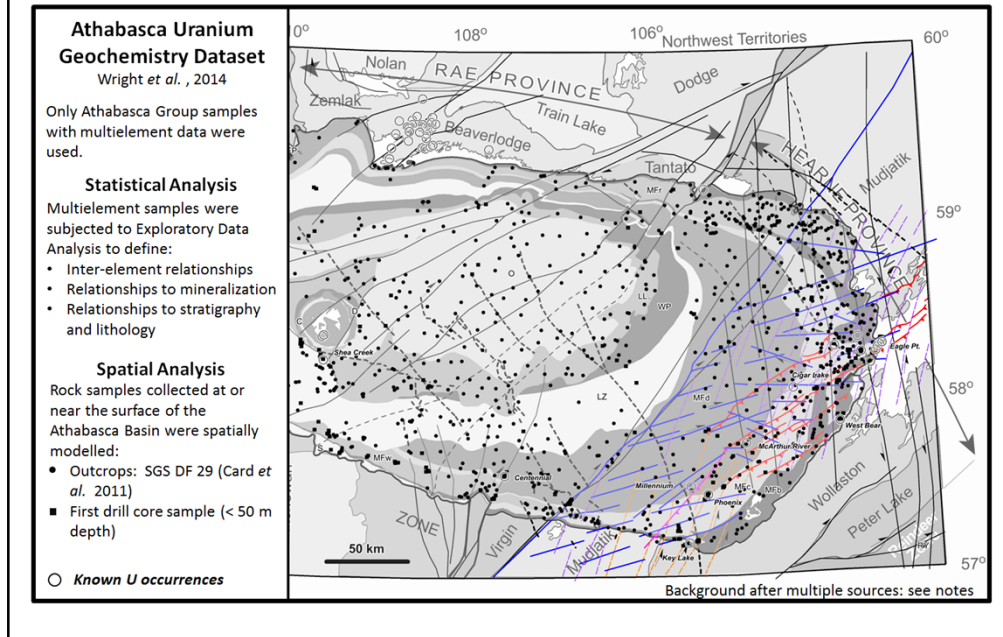


- The Athabasca Basin is a dominantly quartzose, Paleoproterozoic siliciclastic repository located in northern Saskatchewan and Alberta, Canada.
- The basin was filled from ca. 1740 to 1500 Ma as a series of four sub basins with respective westerly, westerly, northerly and westerly paleocurrent trends. The overall basins included sub-basins and were controlled by major Hudsonian age and older faults in the basement rocks that were reactivated in various ways over time in response to far field tectonics (Ramaekers *et al.*, 2007).
- The Athabasca Group is subdivided into ten formations which constitute four fluvial, unconformity-bounded sequences corresponding to the four major basins (Ramaekers *et al.*, 2007; Yeo *et al.*, 2007).

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

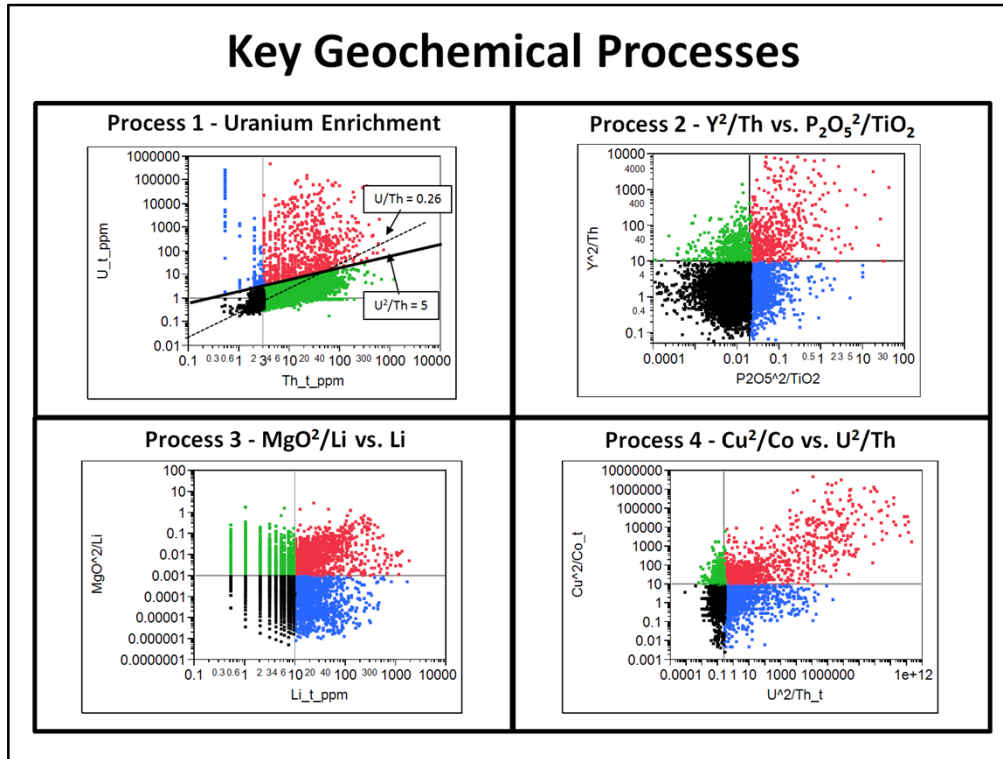
Athabasca Uranium Geochemistry Database



Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

Key Geochemical Processes

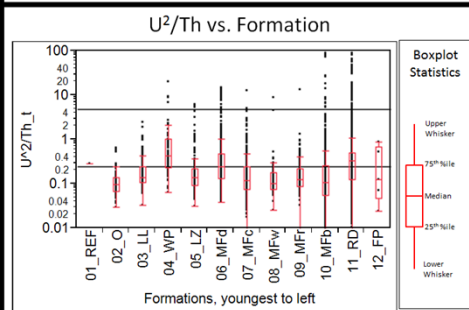
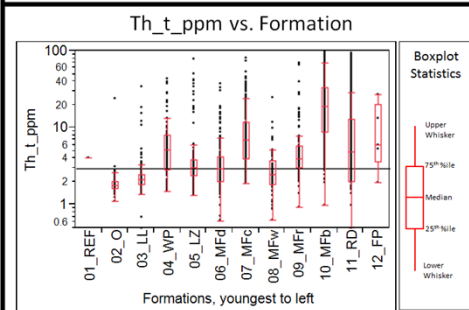
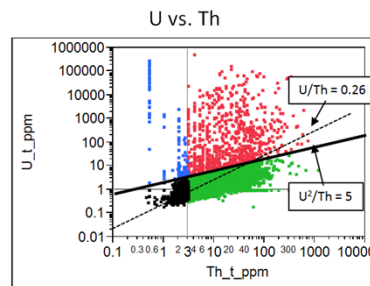


Discussion

- Four key chemical systems highlight different alteration and mineralization processes in the Athabasca Basin:
 - Process 1: Uranium Enrichment
 - Process 2: Hydrothermal/Diagenetic alteration
 - Process 3: Hydrothermal/Diagenetic alteration
 - Process 4: Alteration/remobilization
- The spatial distribution of distinct groups of samples within each of the suites highlighted correspond with mineralization, alteration, basin stratigraphy, and lineament trends.
- Details for each process are presented in the following slides.
- Colours used to represent different classes of sample within each Process are not shared between Process descriptions.

Process 1 - Uranium Enrichment

- Uranium mineralization = enrichment of uranium relative to thorium
- The above process is best modeled using the ratio $U^2/Th = U \times U/Th$ to isolate mobilized U from background U-Th patterns
- Note: $U/Th = 0.26$ (Upper Continental Crust Average, Cuney 2010) does not model actual U-Th relationship.
- Several formations display high average Th contents, requiring the use of the U^2/Th ratio to clearly distinguish uranium enrichment
- The highest average U^2/Th values occur in the Wolverine Point Formation (25th %ile = 0.25) (related to regional stratabound U-rich F-apatite cement)



Discussion

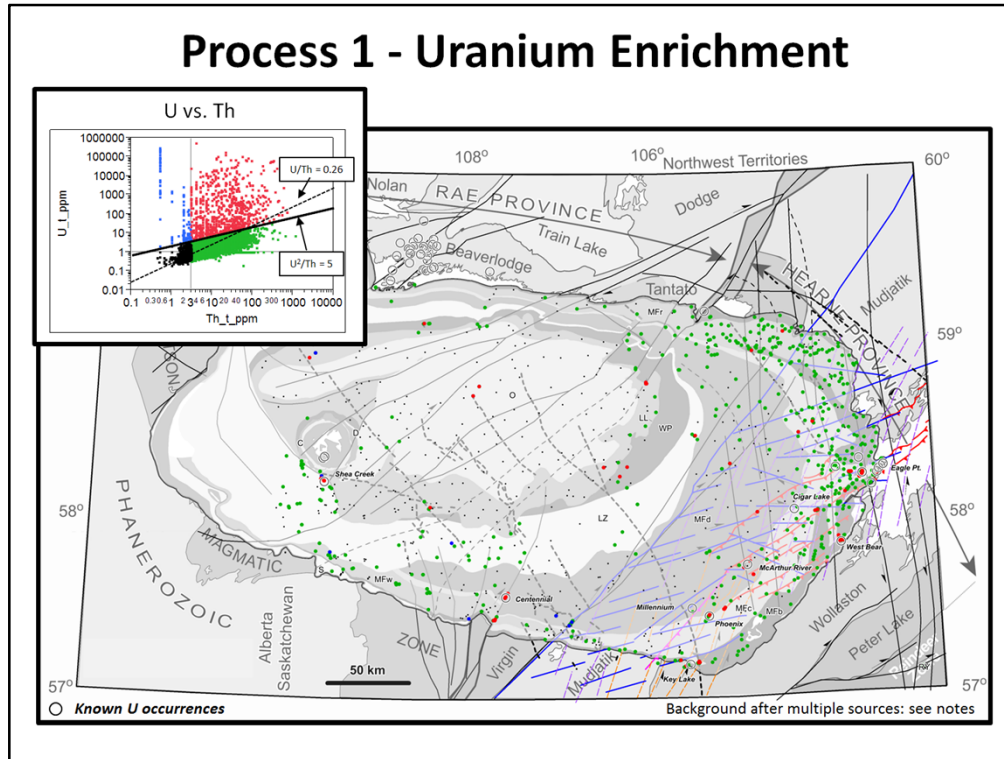
The ratio $U \times U/Th = U^2/Th$ is a ratio commonly employed by geophysicists to model uranium versus thorium behavior in radiometric data (Brian Powell, pers. comm.). This is consistent with their different mobilities in that Th^{4+} complexes are relatively insoluble in hydrothermal systems at pH values from 5 to 8 whereas U^{6+} forms numerous complexes that are highly soluble in a wide range of temperatures and pH values under oxidizing conditions (Boyle, 1982; Cuney, 2010).

- $U^2/Th = 5$ threshold defined from visual examination of the uranium versus thorium plot. Lower thresholds may be applied, but may also increase risk of including uranium associated with the “background” U-Th trend.
- $Th_t_ppm = 3$: A wide range of “average” thorium contents were observed for individual formations of the Athabasca Group. An arbitrary threshold of $Th_t_ppm = 3$ was selected based on the 25th percentile value of Wolverine Point Formation.

Legend for uranium vs. thorium Plots.

- Red = $[U^2/Th \geq 5] + [Th_t_ppm \geq 3]$
 - Hydrothermal uranium enrichment, accompanied by elevated thorium.
- Green = $[U^2/Th < 5] + [Th_t_ppm \geq 3]$
 - Strata of the Athabasca Group displaying distinctly elevated thorium contents.
 - Thorium enrichment is most distinct in the lower Manitou Falls Formation sandstone and conglomerate units with altered heavy mineral bands and relatively abundant aluminum phosphate-sulphate (APS) minerals (consistent with Mwenifumbo *et al.*, 2007; Yeo *et al.*, 2007, Carson *et al.*, 2002, among others), but a correlation of elevated thorium with the Wolverine Point Formation is also apparent.
 - Although a positive linear association of uranium with thorium is observed, distinct enrichment of uranium relative to thorium is not observed ($U^2/Th < 5$).
- Blue = $[U^2/Th \geq 5] + [Th_t_ppm < 3]$
 - Enrichment in uranium relative to thorium, independent of elevated thorium.
 - At least two explanation for this pattern are possible:
 - Distinct uranium enrichment in the absence of significant thorium could represent low temperature remobilization of uranium.
 - Patterns of thorium values may also reflect issues related to the lower limits of detection for thorium.
- Black = $[U^2/Th < 5] + [Th_t_ppm < 3]$
 - Background strata – no enrichment of either thorium or uranium.

Process 1 - Uranium Enrichment



Spatial Discussion

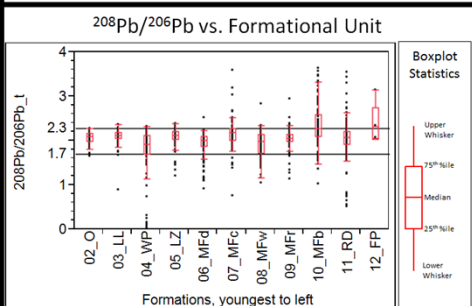
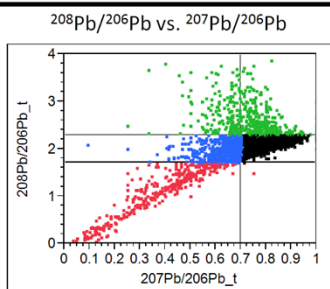
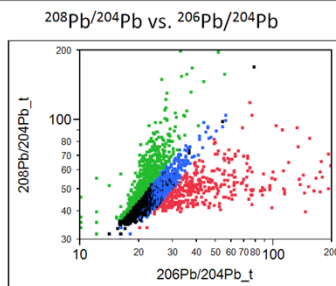
- Red = $[U^2/Th \geq 5] + [Th_t_ppm \geq 3]$
 - Hydrothermal uranium enrichment, accompanied by elevated thorium.
 - Spatial association with McArthur River, Phoenix, Centennial, and Shea Creek deposits, among others.
- Green = $[U^2/Th < 5] + [Th_t_ppm \geq 3]$
 - Athabasca Group strata displaying distinctly elevated thorium contents.
 - Thorium enrichment is most distinct in the coarser grained lower Manitou Falls Formation with altered heavy mineral bands and relatively abundant APS minerals (consistent with Mwenifumbo *et al.*, 2007; Yeo *et al.*, 2007; Carson *et al.*, 2002, among others), but a subtle correlation of elevated thorium with the Wolverine Point + Locker Lake Formations is also observed.
 - Although a positive linear association of uranium with thorium is observed, distinct enrichment of uranium relative to thorium is not observed ($U^2/Th < 5$).
- Blue = $[U^2/Th \geq 5] + [Th_t_ppm < 3]$
 - Enrichment in uranium relative to thorium, independent of elevated thorium.
 - At least two explanations for this pattern are possible:
 - Distinct uranium enrichment in the absence of significant thorium could represent low temperature remobilization of uranium.
 - Patterns of thorium values may also reflect issues related to the lower limits of detection for thorium.
- Black = $[U^2/Th < 5] + [Th_t_ppm < 3]$
 - Background strata – no enrichment of either thorium or uranium.

Map compiled from several sources, including:

- Base lithological map: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.*, (2012); Saskatchewan Geological Atlas.

Process 1a - Lead Isotopes

- Uranium oxidation (U^{4+} to U^{6+} ; leaching and transportation) depletes U relative to Th whereas reduction (U^{6+} to U^{4+} ; mineralization) enriches U relative to Th *at low to moderate temperatures*
- The above process can also be modeled using the lead isotope ratio $^{208}\text{Pb}/^{206}\text{Pb}$ (reflecting $^{232}\text{Th}/^{238}\text{U}$)
- Most $^{208}\text{Pb}/^{206}\text{Pb}$ ratios range between 1.7 to 2.3
- Uranium mineralization = $^{208}\text{Pb}/^{206}\text{Pb} < 1.7$
- Thorium residual "enrichment" = $^{208}\text{Pb}/^{206}\text{Pb} > 2.3$
- $^{207}\text{Pb}/^{206}\text{Pb}$ ratio models $^{235}\text{U}/^{238}\text{U}$ (Holk *et al.*, 2003)
- Lead isotope analysis was only completed for a subset of the AUG dataset



Primary Observations:

- Lead isotope geochemistry is intimately associated with uranium and thorium, making it an ideal chemical system to model uranium enrichment / mineralization (e.g. Gulson, 1986; Holk *et al.*, 2003).
- Lead isotope analyses were only completed for a subset of the AUG dataset, but were completed for all of the DF29 SGS dataset (Card *et al.*, 2011), allowing for review of lead isotope patterns across the top (outcrop) of the Athabasca Group units.
- Four suites of lead isotope ratio values may be used to model uranium enrichment relative to thorium:
 - Red = $[^{208}\text{Pb}/^{206}\text{Pb} < 1.7]$
 - Interpreted to represent enrichment of uranium (^{206}Pb) relative to thorium (^{208}Pb), paralleling uranium enrichment due to hydrothermal and oxidation-reduction processes.
 - Green = $[^{208}\text{Pb}/^{206}\text{Pb} > 2.3]$
 - Interpreted to represent apparent enrichment of thorium (^{208}Pb) relative to uranium (^{206}Pb). Due to relatively immobility of thorium in hydrothermal systems, this pattern is interpreted to represent removal of uranium.
 - Blue = $[^{208}\text{Pb}/^{206}\text{Pb} < 0.7] + [1.7 < ^{208}\text{Pb}/^{206}\text{Pb} < 2.3]$
 - Interpreted to represent anomalous levels of parent uranium (e.g. Holk *et al.* (2003), applied to Weak Acid Leach data), yet does not distinguish uranium enrichment relative to thorium. It is likely that samples that display the above characteristics are closely associated with samples that display both elevated uranium and thorium contents.
 - Black = $[^{208}\text{Pb}/^{206}\text{Pb} > 0.7] + [1.7 < ^{208}\text{Pb}/^{206}\text{Pb} < 2.3]$
 - Background strata

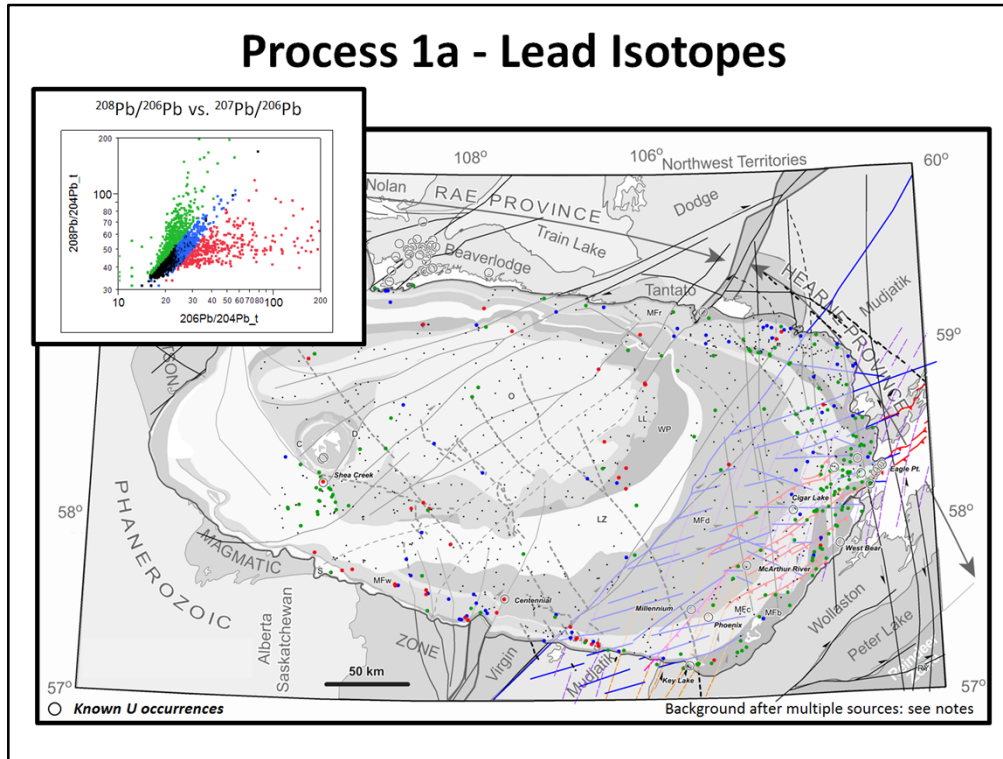
Athabasca Group geochemical associations according to formational unit:

- Most $^{208}\text{Pb}/^{206}\text{Pb}$ ratios range between 1.7 to 2.3.
- $^{208}\text{Pb}/^{206}\text{Pb} > 2.3$ locally associated with the lower Manitou Falls Formation, Bird Member (MFb) documents significant uranium removal at an early stage. Mwenifumbo and Bernius (2007) documented the thorium-bearing mineral as crandallite (APS mineral) which is associated with hematitic heavy mineral bands. Mwenifumbo *et al.* (2007) noted that the APS forms small clusters about the diameter of detrital grains within with coarser-grained beds and interpreted them as possible altered monazite. Jefferson *et al.* (2007, p. 51) noted that workers such as Madore *et al.* (2000), Hecht and Cuney (2000) Gaboreau *et al.* 2003, and Cuney *et al.* (2003) had documented the replacement of monazite by APS in basement rocks wherein partially replaced monazite retains uranium but the APS replacement minerals lack uranium while retaining thorium and REE. Jefferson *et al.* (2007) hypothesized that this same reaction had gone to completion on a regional scale within the Manitou Falls Formation, thereby releasing sufficient uranium to account for all known deposits in the Athabasca Basin.

Lead Isotopes:

- ^{204}Pb : Non-radiogenic "common" Lead
- ^{206}Pb : Radiogenic Lead; derived from decay of ^{238}U
- ^{207}Pb : Radiogenic Lead; derived from decay of ^{235}U
- ^{208}Pb : Radiogenic Lead; derived from decay of ^{232}Th

Process 1a - Lead Isotopes



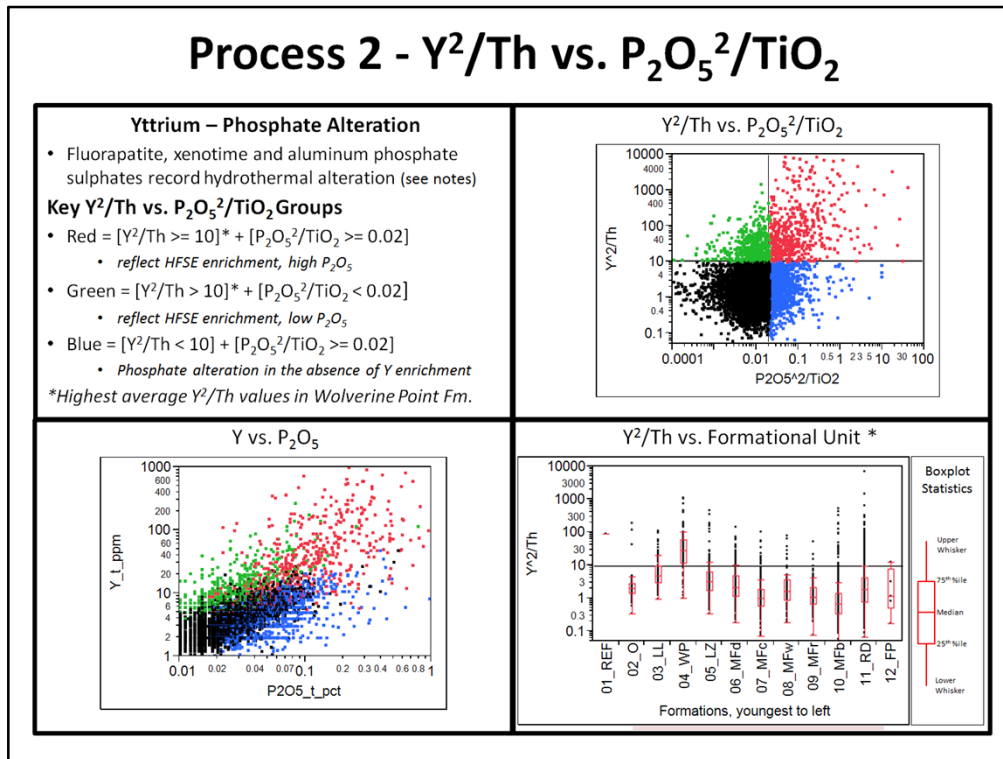
Lead Isotope Spatial Discussion

- NOTE: Lead isotope analyses were only completed for a subset of the AUG dataset, but were completed for the DF29 SGS dataset (Card *et al.*, 2011), allowing for review of lead isotope patterns across the top (outcrop) of the Athabasca Group strata.
- Red = [$^{208}\text{Pb}/^{206}\text{Pb} < 1.7$]
 - Interpreted to represent enrichment of uranium (^{206}Pb) relative to thorium (^{208}Pb), paralleling uranium enrichment due to hydrothermal and oxidation-reduction processes.
 - Local spatial association with areas of known uranium occurrences, e.g. Centennial and Shea Creek deposits.
- Green = [$^{208}\text{Pb}/^{206}\text{Pb} > 2.3$]
 - Interpreted to represent apparent enrichment of thorium (^{208}Pb) relative to uranium (^{206}Pb). Due to relatively immobility of thorium in hydrothermal systems, this pattern is interpreted to represent removal of uranium.
 - Local association with the Manitou Falls Formation, particularly in the basal (MFb = Bird) member.
- Blue = [$^{208}\text{Pb}/^{206}\text{Pb} < 0.7$] + [$1.7 < ^{208}\text{Pb}/^{206}\text{Pb} < 2.3$]
 - Interpreted to represent anomalous levels of parent uranium (e.g. Holk *et al.* (2003), applied to Weak Acid Leach data), yet does not distinguish uranium enrichment relative to thorium. It is likely that samples that display the above characteristics are closely associated with samples that display both elevated uranium and thorium contents.
 - Local association with the Manitou Falls Formation and the Wolverine Point Formation.
- Black = [$^{208}\text{Pb}/^{206}\text{Pb} > 0.7$] + [$1.7 < ^{208}\text{Pb}/^{206}\text{Pb} < 2.3$]
 - Background strata

Map compiled from several sources, including:

- Base lithological map: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.*, (2012); Saskatchewan Geological Atlas.

Process 2 - Y^2/Th vs. $P_2O_5^2/TiO_2$



Primary Observation

The discrimination diagram Y^2/Th vs. $P_2O_5^2/TiO_2$ can be used to discriminate hydrothermal alteration (Y^2/Th ; xenotime, fluorapatite and other HFSE-bearing minerals) from diagenetic alteration (e.g. APS):

- Hydrothermal alteration: $Y^2/Th > 10$ (with or without P_2O_5 , although presence of higher than average P_2O_5 could indicate more intense sections of the system)
- Diagenetic alteration: $[P_2O_5^2/TiO_2 > 0.02] + [Y^2/Th < 10]$.

Discussion

Fluorapatite $[Ca_5(PO_4)_3(OH,F,Cl)]$ and xenotime $[YPO_4]$ have been identified in several locations in the Athabasca Basin, including associations with the Maw Zone (e.g. MacDougall, 1990; Quirt *et al.*, 1991), the Wolverine Point Formation (Rainbird *et al.*, 2003, 2007; Davis *et al.*, 2008). Aluminum phosphate-sulphate minerals have been noted throughout the basin and associated with several ore deposits (Hoeve and Quirt, 1984; Wilson, 1985; Quirt *et al.*, 1991; Mwenifumbo and Bernius, 2007; Mwenifumbo *et al.*, 2007; Lorilleux *et al.*, 2003; Gaboreau *et al.*, 2007; Reid *et al.*, 2014).

The inter-element behaviour of yttrium, calcium, and phosphorous were examined:

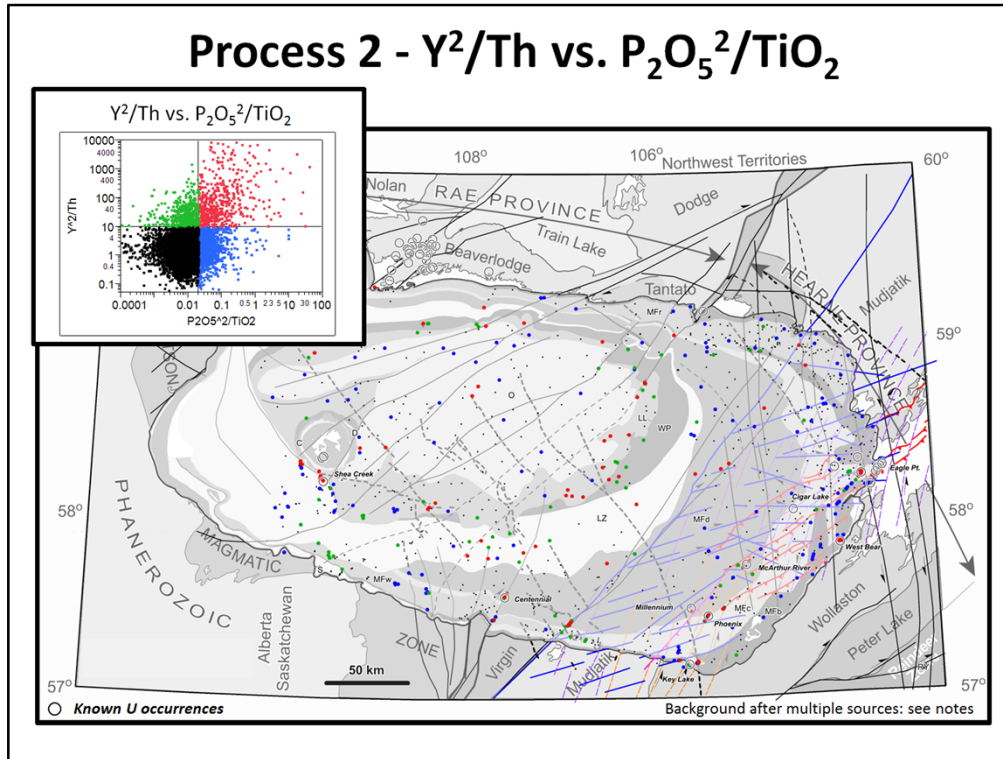
- Yttrium modeled relative to thorium (Y^2/Th)
 - $Y^2/Th = 10$ threshold defined from the 25th percentile value for the Wolverine Point Formation – distinct from other units, as discussed below.
- Phosphorous modeled relative to titanium ($P_2O_5^2/TiO_2$)
 - $P_2O_5^2/TiO_2 = 0.02$ threshold defined from the 75th percentile value for the Wolverine Point Formation - relatively consistent with 75th percentile of other formations.
 - No distinct differences in average range (25th to 75th percentile) for $P_2O_5^2/TiO_2$ were observed between formations.

Observations

All plots are coloured using the same legend, based on the Y^2/Th vs. $P_2O_5^2/TiO_2$ plot.

- Y^2/Th vs. $P_2O_5^2/TiO_2$ discrimination Plot:
 - Red = $[Y^2/Th \geq 10] + [P_2O_5^2/TiO_2 \geq 0.02]$
 - Relative enrichment of both yttrium and phosphorous, perhaps indicative of strong xenotime, fluorapatite, and similar HFSE-bearing minerals
 - Green = $[Y^2/Th \geq 10] + [P_2O_5^2/TiO_2 < 0.02]$

- Enrichment of yttrium relative to thorium and phosphorous:
 - perhaps indicative of relict xenotime (HFSE) signatures, subjected to later alteration, or,
 - Weaker xenotime contents.
 - Blue = $[Y^2/Th < 10] + [P_2O_5^2/TiO_2 \geq 0.02]$
 - Phosphorous enrichment in the absence of yttrium enrichment
 - Diagenetic signature, perhaps related to APS minerals
 - Black = $[Y^2/Th < 10] + [P_2O_5^2/TiO_2 < 0.02]$
 - Background
- Y vs. P_2O_5 Plot
 - A prominent weakly positive linear relationship is observed between Y and P_2O_5 (black samples). This pattern is interpreted to represent primarily a background signature for the Athabasca Group strata, yet higher P_2O_5 values along this trend (blue samples) could represent a form of enhanced diagenetic alteration.
 - Samples with elevated yttrium relative to thorium ($Y^2/Th > 10$; red and green samples) appear to display a higher than normal yttrium content relative to phosphorous, possibly representing a separate process (phosphate alteration).
 - Y^2/Th vs. Formation
 - Average (25th to 75th percentile) Y^2/Th values for the majority of the Athabasca Group strata are low relative to average crustal compositions (Taylor and McLennan, 2009).
 - The highest average (25th to 75th percentile) values for Y^2/Th are observed for the Wolverine Point Formation.



Spatial Discussion: Y^2/Th vs. $P_2O_5^2/TiO_2$ Discrimination Plot.

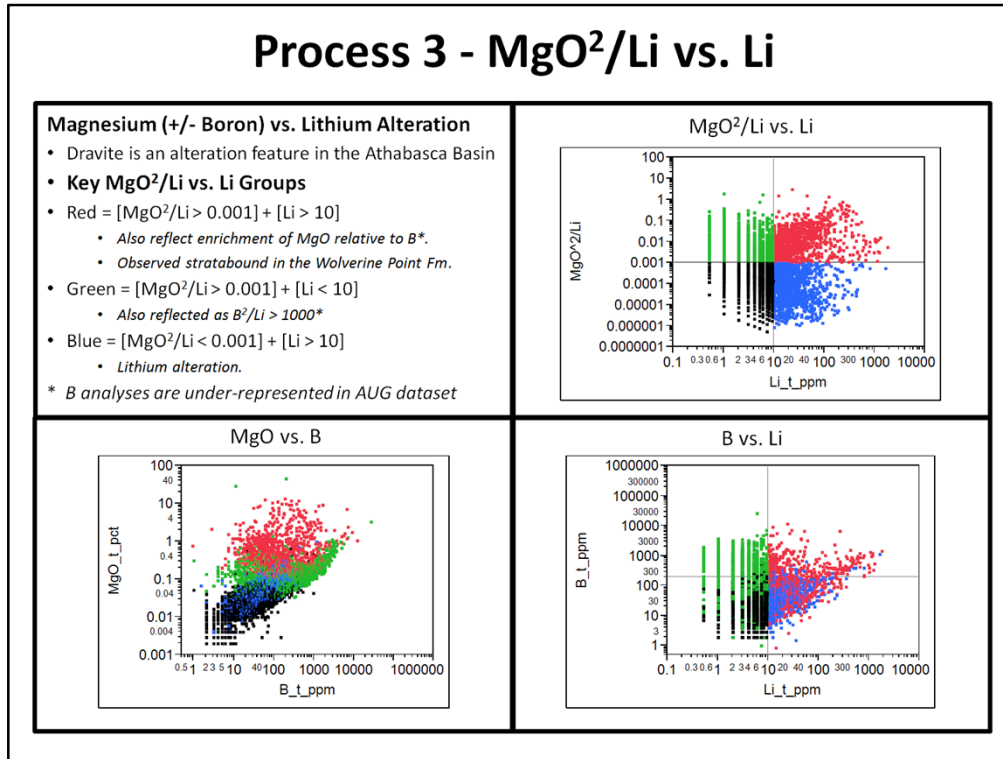
The discrimination diagram Y^2/Th vs. $P_2O_5^2/TiO_2$ can be used to differentiate hydrothermal alteration (Y^2/Th ; xenotime, fluorapatite, other HFSE-bearing minerals) from diagenetic alteration:

- Hydrothermal alteration: $Y^2/Th > 10$
- Diagenetic or late alteration: $[P_2O_5^2/TiO_2 > 0.02] + [Y^2/Th < 10]$.
- Red (hydrothermal alteration with P_2O_5) = $[Y^2/Th \geq 10] + [P_2O_5^2/TiO_2 \geq 0.02]$
 - Local spatial association with areas of known uranium occurrences outside of the Wolverine Point Formation.
 - Above the Phoenix Deposit, Dann *et al.* (2014) identified “yttrium chimneys”, extending to the preserved top of the Manitou Falls Formation.
 - Similarly, Power *et al.*, 2012 identified tungsten anomalies in surface media over the Phoenix Deposit. In the AUG dataset, W^2/Th anomalies display a similar spatial distribution to $Y^2/Th + P_2O_5$ anomalies (not shown).
 - Local spatial (and stratigraphic) association with the Wolverine Point Formation.
- Green (hydrothermal alteration without P_2O_5) = $[Y^2/Th \geq 10] + [P_2O_5^2/TiO_2 < 0.02]$
 - More distal spatial association with areas of known uranium occurrences than Red samples outside of the Wolverine Point Formation.
 - More widely distributed spatial (and stratigraphic) association with the Wolverine Point Formation than Red samples.
- Blue = $[Y^2/Th < 10] + [P_2O_5^2/TiO_2 \geq 0.02]$
 - Occurs in all formations, although some subtle linear trends crosscutting stratigraphy are observed.
 - Interpreted to represent mobilization of P_2O_5 – a wide spatial association with areas of known uranium occurrences is observed in the eastern Athabasca Basin, possibly manifested in the localized enrichment of APS minerals.
- Black = $[Y^2/Th < 10] + [P_2O_5^2/TiO_2 < 0.02]$
 - Background.

Map compiled from several sources, including:

- Base lithological map: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.

Process 3 - MgO²/Li vs. Li



Discussion

Dravite and magnesiofoitite are B-bearing tourmaline alteration minerals related to uranium occurrences in the Athabasca Basin, most commonly identified using spectral (e.g.: Wasyluk, 2002) or chemical techniques (e.g. Earle and Sopuck, 1989, McGill *et al.*, 1993) and/or petrography (e.g. Hoeve and Sibbald, 1978; Rosenberg and Foit, 1986; Rosenberg and Foit, 2006)

The discrimination diagram MgO²/Li vs. Li can be used to discriminate three separate subgroups of samples likely related to separate processes:

- 1) Hydrothermal alteration: MgO + lithium
- 2) B-dominated alteration (also hydrothermal due to associated MgO²/Li signature?), and
- 3) Diagenetic (?) alteration: lithium-dominated alteration.

- Red: [MgO²/Li > 0.001] + [Li_t_ppm > 10]
 - High MgO and lithium contents interpreted to represent a hydrothermal signature.
 - Also reflect enrichment of MgO relative to boron.
 - Strong statistical association with the Wolverine Point Formation.
- Green: [MgO²/Li > 0.001] + [Li_t_ppm < 10]
 - Also reflected as B²/Li > 1000
 - Distinct boron and MgO-bearing alteration phase, lacking significant lithium content.
 - Considered a separate alteration event from Li-rich suite (Red).
- Blue: [MgO²/Li < 0.001] + [Li_t_ppm > 10]
 - Distinct, consistent association between lithium, MgO, and boron.
 - Values above 10 ppm Li are considered to represent a separate alteration phase (associated with weak sympathetic MgO and boron enrichment, perhaps diagenetic).

Observations

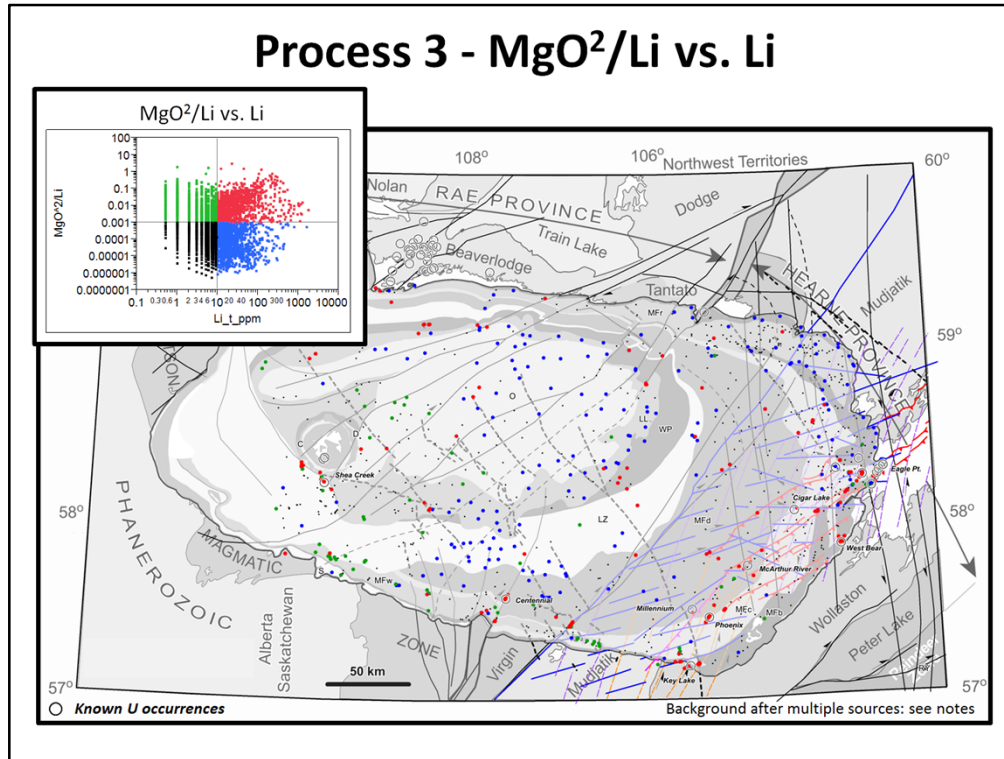
All plots are coloured using the same legend, based on the MgO²/Li vs. Li discrimination plot.

The thresholds used (MgO²/Li = 0.001 and Li_t_ppm = 10) are both based on the 25th percentile value for the Wolverine Point Formation. The average ranges (25th to 75th percentile) for the Wolverine Point Formation are elevated relative to the average ranges for other formations in the Athabasca Basin (not shown).

Note: Boron analyses were under-represented in the AUG dataset, including the outcrop samples analyzed by the SGS (Card *et al.*, 2011); this limited our ability to conduct extensive statistical and spatial interpretation.

- Plot: MgO vs. B
 - Samples displaying elevated MgO₂/Li (> 0.001) and gross Li (> 10) also display a strong relative enrichment of MgO to boron.
- Plot: B vs. Li
 - Elevated boron relative to lithium ($B^2/Li > 1000$) are distinct from a linear boron-lithium trend. These values typically occur at low lithium contents ($Li_t_ppm < 10$), and are accompanied by elevated MgO₂/Li (>0.001).
 - A minimum threshold of $B_t_ppm > 200$ (e.g. McGill *et al.*, 1993) will identify samples from all three subgroups, but will not properly classify the samples.

Process 3 - MgO²/Li vs. Li



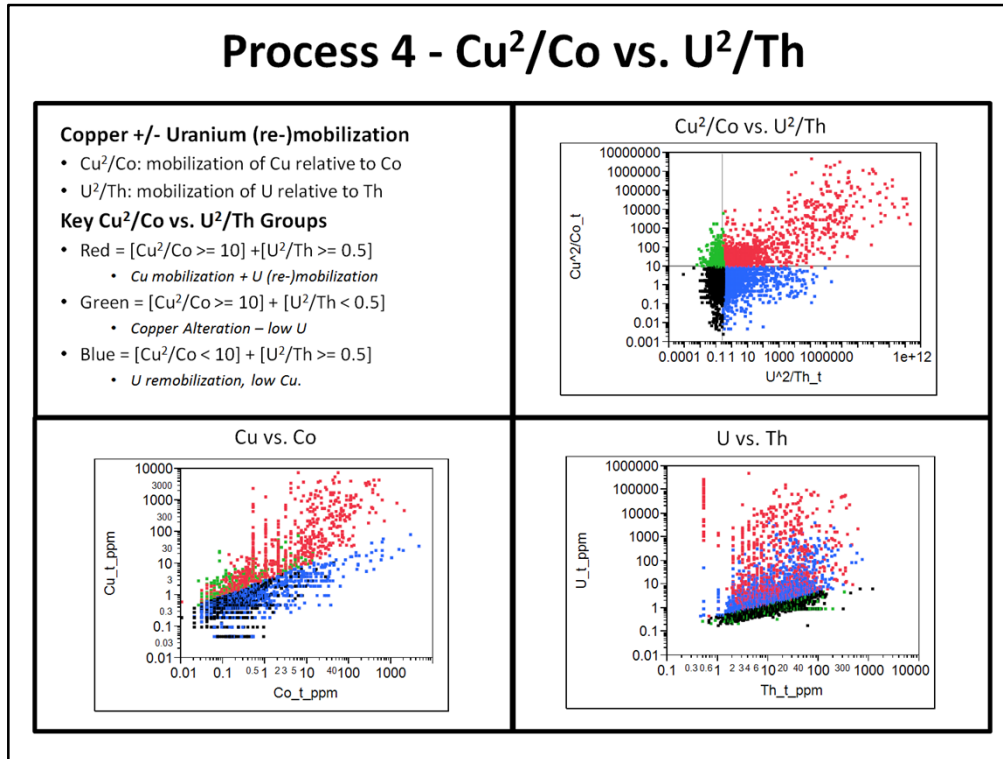
Spatial Discussion: Process 3 - MgO²/Li vs. Li

- Red: $[MgO^2/Li > 0.001] + [Li_t_ppm > 10]$
 - High MgO and lithium contents are interpreted to represent a hydrothermal signature.
 - Also reflect enrichment of MgO relative to boron.
 - Strong statistical association with the Wolverine Point Formation.
 - Local spatial association with areas of known uranium occurrences outside of the Wolverine Point Formation.
- Green: $[MgO^2/Li > 0.001] + [Li_t_ppm < 10]$
 - Also reflected as $B^2/Li > 1000$
 - Distinct boron- and MgO-bearing alteration phase, lacking significant lithium content.
 - Considered a separate alteration event.
 - Appear to represent a distal alteration signature, especially in the southern and southwestern Athabasca Basin.
- Blue: $[MgO^2/Li < 0.001] + [Li_t_ppm > 10]$
 - Distinct, consistent association between lithium, MgO, and boron.
 - Values above 10 ppm Li are considered to represent a separate alteration phase (associated with weak sympathetic MgO and boron enrichment, perhaps diagenetic).
 - Widespread distribution in upper stratigraphic units of the Athabasca Group (excluding the Douglas and Carswell Formations).

Map compiled from several sources, including:

- Base lithological map: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.

Process 4 - Cu²/Co vs. U²/Th



Primary Observation

The discrimination diagram Cu²/Co vs. U²/Th emphasizes three groups of samples, interpreted to highlight zones of copper and uranium enrichment relative to cobalt and thorium, respectively:

- 1) Red: uranium and copper enrichment
- 2) Blue: uranium only
- 3) Green: copper only

Elevated copper contents have been reported in surficial media above the Phoenix Deposit (Power *et al.*, 2012)

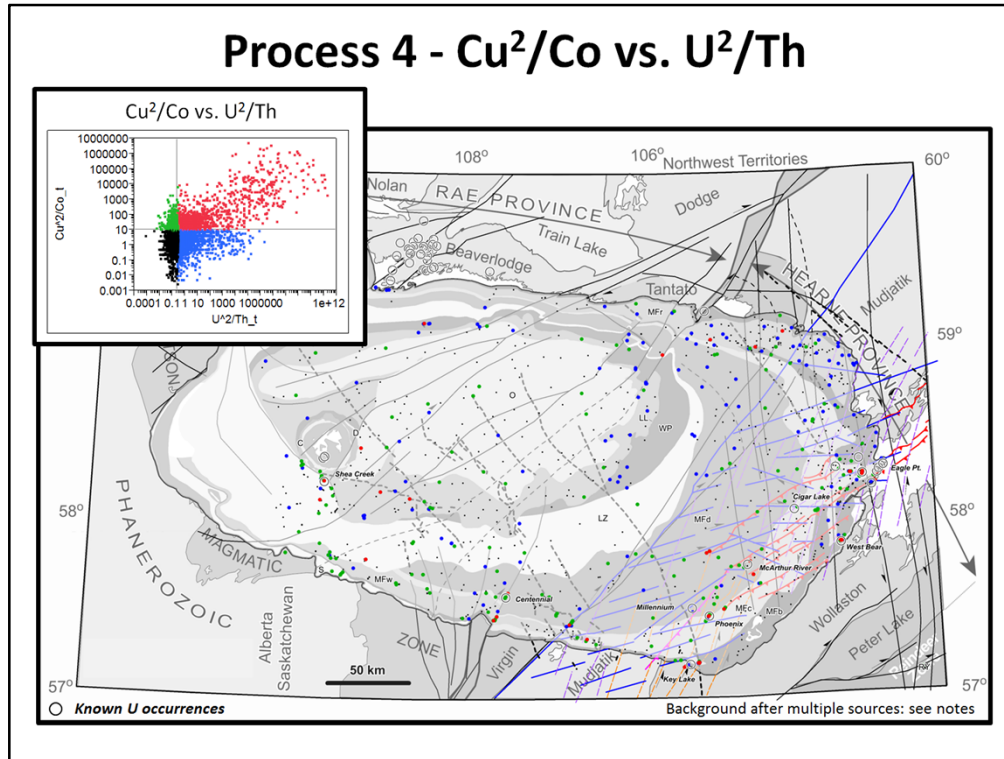
Geochemical Discussion:

Plot: Cu²/Co vs. U²/Th

- Red = [Cu²/Co >= 10] + [U²/Th >= 0.5]:
 - Copper and uranium enrichment
- Green = [Cu²/Co >= 10] + [U²/Th < 0.5]
 - Copper enrichment
- Blue = [Cu²/Co < 10] + [U²/Th >= 0.5]
 - Uranium enrichment
- Black = [Cu²/Co < 10] + [U²/Th < 0.5]
 - Background strata.
- Plot: Cu vs. Co
 - A linear correlation of copper and cobalt is visible at relatively low Cu²/Co values (< 10).
 - Above the Cu²/Co = 10 threshold, and with increasing cobalt content, a distinct increase in copper relative to cobalt is observed. This trend is interpreted to represent either the addition of, or remobilization of, copper within the strata relative to cobalt.
 - The association of very high Cu²/Co values with high U²/Th values suggests that some copper enrichment may be due to hydrothermal processes (sympathetic to Y and HFSE enrichment observed in Process 2).
- Plot: U vs. Th
 - Although a threshold of U²/Th = 5 was applied in Process 1 to highlight distinct evidence of mineralization, lower

- thresholds may be applied, but also increase the risk of including uranium associated with the “background” U-Th trend.
- The threshold of $U^2/Th = 0.26$ was applied in Process 4 based on the 25th percentile (lower end of the average range) of the Wolverine Point Formation. Most of the average ranges for other stratigraphic units are below this threshold.

Process 4 - Cu^2/Co vs. U^2/Th



Spatial Discussion: Cu^2/Co vs. U^2/Th

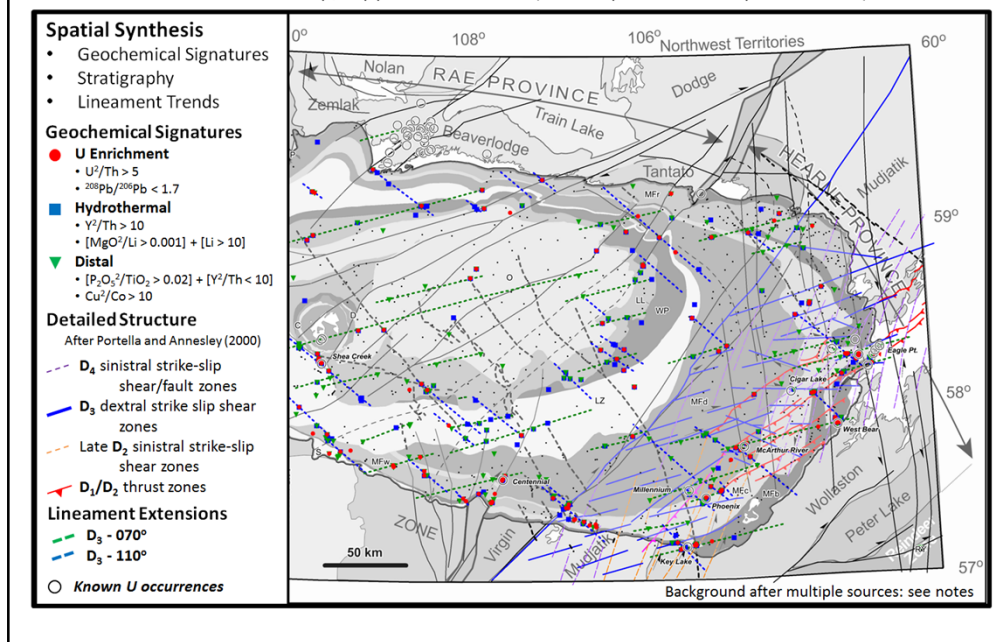
- Red = $[\text{Cu}^2/\text{Co} \geq 10] + [\text{U}^2/\text{Th} \geq 0.5]$:
 - Copper and uranium enrichment
 - Localized within zones of known uranium occurrences – but not ubiquitous (association with 075° lineaments)
 - Elevated copper values have been reported in surficial media above the Phoenix Deposit (Power *et al.*, 2012)
- Green = $[\text{Cu}^2/\text{Co} \geq 10] + [\text{U}^2/\text{Th} < 0.5]$
 - Copper enrichment
- Blue = $[\text{Cu}^2/\text{Co} < 10] + [\text{U}^2/\text{Th} \geq 0.5]$
 - Uranium enrichment
 - Strong concentration in the NE Athabasca Basin – related to another phase of alteration, such as late, low temperature meteoric waters (?)
- Black = $[\text{Cu}^2/\text{Co} < 10] + [\text{U}^2/\text{Th} < 0.5]$
 - Background strata.

Map compiled from several sources, including:

- Base lithological map: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.

Spatial Synthesis

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Primary Observation:

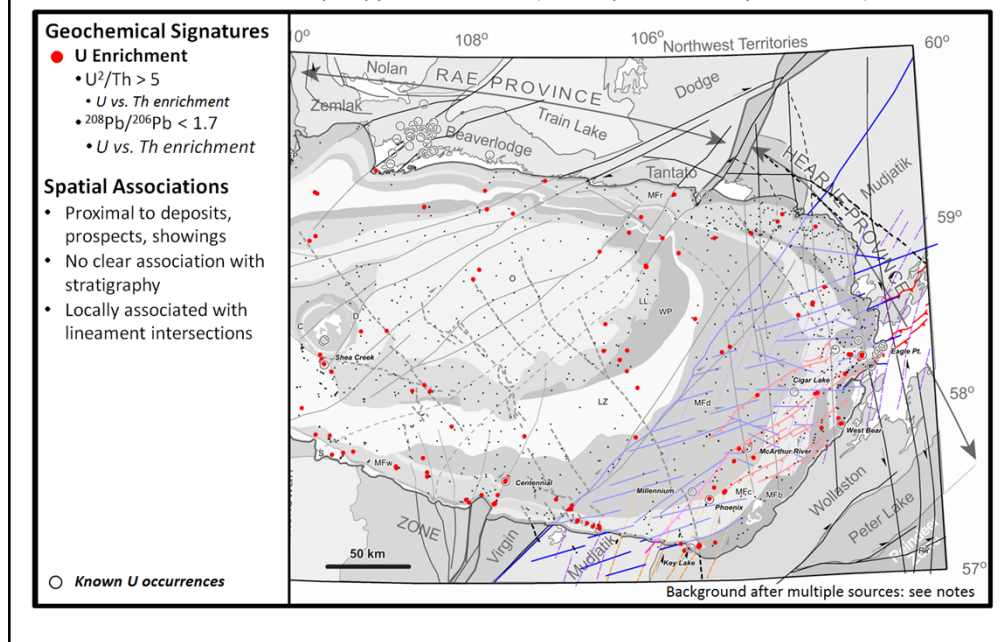
- Several composite geochemical signatures have been identified in the strata of the Athabasca Basin, each reflecting unique geological/geochemical processes.
- In the near-surface and surface strata of the Athabasca Basin, the separate geochemical signatures display spatial associations with known uranium occurrences and specific structural orientations.
- Extensions of some lineament trends appear to correspond well with those defined by Portella and Annesley (2000)

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

Uranium Mineralization Signature

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



U Enrichment Signature:

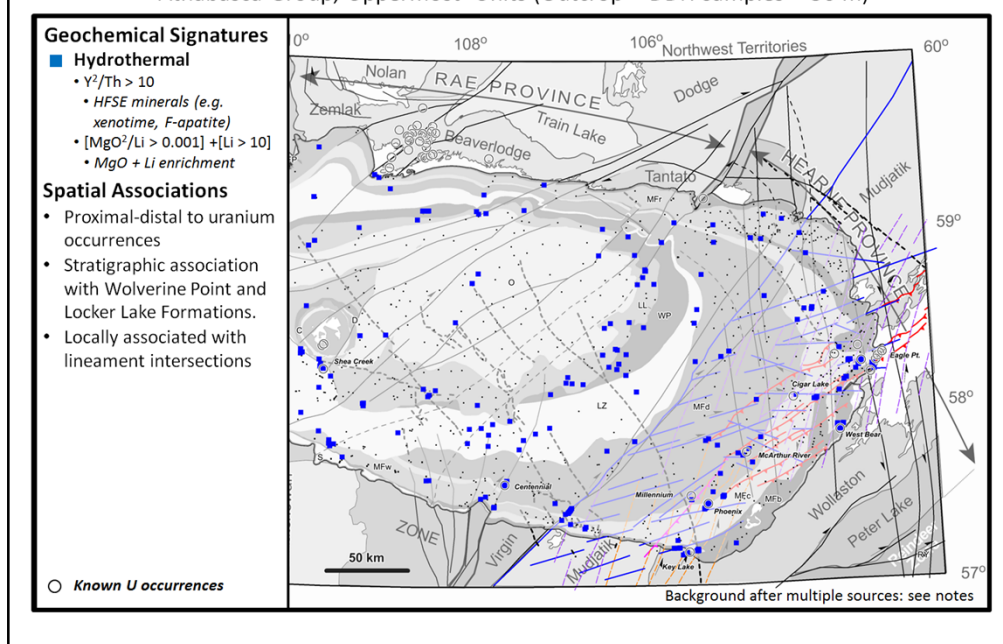
- Distinct chemical signatures of uranium enrichment relative to thorium.
 - Process 1: $U^2/Th > 5$
 - Process 1a: $^{208}Pb/^{206}Pb < 1.7$
- Spatial Associations
 - Proximal to uranium deposits, prospects and/or showings
 - No clear association with stratigraphy
 - Locally associated with lineament intersections

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

Hydrothermal Signature

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Hydrothermal Signature

- Distinct chemical signatures interpreted to represent hydrothermal alteration:
 - Process 2: $Y^2/Th > 10$
 - High Field Strength Element (HFSE) mineral enrichment (e.g. xenotime, fluorapatite)
 - Process 3: $[MgO^2/Li > 0.001] + [Li > 10]$
 - MgO + Li enrichment
 - Additional Features (not shown):
 - $Yb_n > 4 + La/Yb < 20$
 - Reflect both HFSE enrichment in the Wolverine Point Formation (represented by Yb_n) and shallower La/Yb ratios ($La/Yb < 20$) relative to most other formations ($La/Yb > 20$). $Yb_n = Yb$ contents normalized to S1 chondrite (Sun and McDonough, 1989).

Spatial Associations

- Proximal-distal to uranium occurrences
- Stratigraphic association with Wolverine Point and Locker Lake Formations.
- Locally associated with lineament intersections

Significance

- Interpreted to represent a distinct signature for the Wolverine Point Formation (and to some extent the Locker Lake Formation as well), primarily associated with High Field Strength Element chemical signatures.
- Fluorapatite $[Ca_5(PO_4)_3(OH,F,Cl)]$ and xenotime $[YPO_4]$ have been identified in several locations in the Athabasca Basin, including associations with the Maw Zone (e.g. MacDougall, 1990; Quirt *et al.*, 1991), extensively within the Wolverine Point Formation and in various patches within all known units below the Wolverine Point Formation including the regolith (Rainbird *et al.*, 2003, 2007; Davis *et al.*, 2008).
- A close geochemical and temporal similarity between the Wolverine Point Formation and known uranium occurrences away from the Wolverine Point Formation may imply a linkage.
 - Based on the concentration of High Field Strength Elements such as yttrium and ytterbium, it is suggested that the observed signature is hydrothermal in origin (perhaps driven by the event that resulted in deposition of the reworked volcanic tuffs present in the Wolverine Point Formation and/or derived from the uranium-rich fluorapatite cemented stratabound zones present in the Wolverine Point Formation).
 - Similarities in age between early mineralization, apatite-xenotime alteration, and the Wolverine Point Formation include:
 - Wolverine Point Formation: 1644 ± 13 Ma (Rainbird *et al.*, 2007)
 - Fluorapatite ages in the Athabasca Basin between 1640-1620 Ma (Rainbird *et al.*, 2003; Davis *et al.*, 2008)

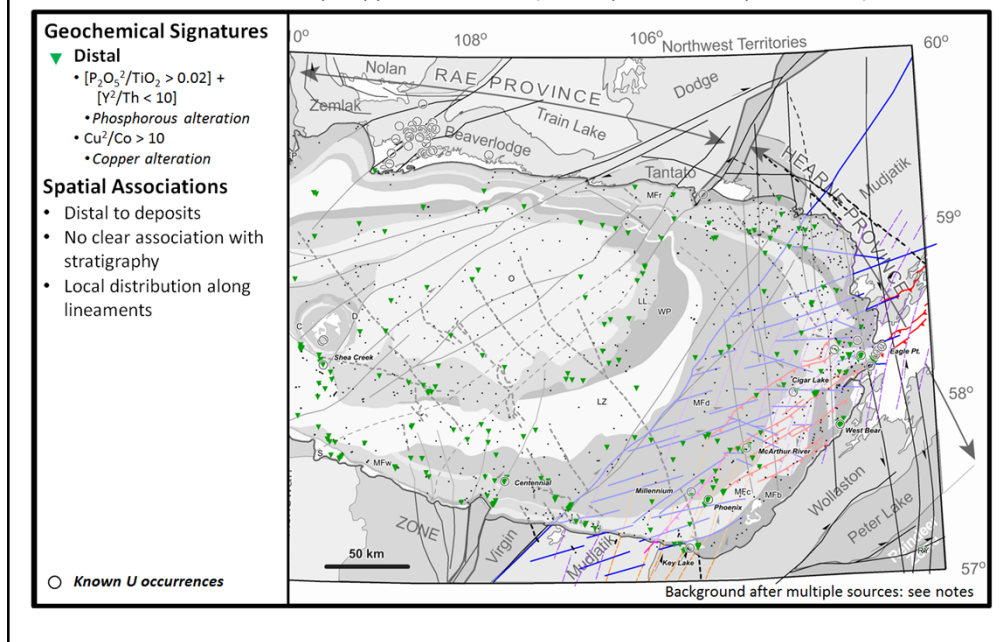
- Regional hydrothermal event at about the same time as localized pre-ore alteration minerals developed (Jefferson *et al.*, 2007)
- Annesley *et al.* (2010): Uraninite from basement granitic pegmatites with greater than 50 wt.% UO₂ yielded ages of **1.84 to 1.485 Ga**. The older group of ages, **1.84 to 1.76 (±0.09) Ga** from the least altered uraninite, is interpreted as an approximate age of crystallization, and probably the age of granitic pegmatite emplacement. The U-Th-Pb chemical age dates from the freshest (i.e. old) uraninite grains indicate a primary magmatic crystallization age of ca. 1770 ±90 Ma. The younger chemical ages along grain boundaries and fractures imply that uraninite started experiencing disturbances of their U-Th-Pb chemical/isotopic system. These younger ages correlate with isotopic disturbance to the Stage 1 and Stage 2 U-mineralization events of Fayek and Kyser (1997).
- Fayek *et al.* (2010): At the **Millennium Deposit**: “disseminated uraninite (style 4) have ²⁰⁷Pb/²⁰⁶Pb ages from 1770-**1650 Ma**. These ages are older than the depositional age for the Athabasca sediments (ca. 1710 Ma) (ed. note: Jefferson *et al.* (2007) suggest that the deposits began to form after the deposition of the WP formation, e.g. after 1644 ± 13 Ma, above. This date is younger than the date quoted by Fayek *et al.* (2010) as the depositional age of the Athabasca sediments) and are similar to the ages from the Beaverlodge vein-type uranium deposits.”
- Alexandre *et al.* (2007): Pre-ore alteration occurred simultaneously around both basement- and sandstone-hosted deposits at ca. **1675 Ma**, as indicated by the ⁴⁰Ar/³⁹Ar dating of pre-ore alteration illite and chlorite. “The uranium mineralization age is ca. **1590 Ma**, given by LA-ICP-MS U/Pb dating of uraninite and ⁴⁰Ar/³⁹Ar dating of syn-ore illite, and is the same throughout the basin and in both basement- and sandstone-hosted deposits. The mineralization event, older than previously proposed...”

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

Distal Signature

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Distal Signature (Late lineaments)

Chemistry:

- $[P_2O_5/TiO_2 > 0.02] + [Y^2/Th < 10]$: Phosphorous enrichment independent of yttrium enrichment.
- $Cu^2/Co > 10$: Copper enrichment relative to cobalt.

Significance:

- Interpreted to represent distal, perhaps later, alteration to mineralization that has exploited brittle lineaments (120° and 075°).

Structural Setting:

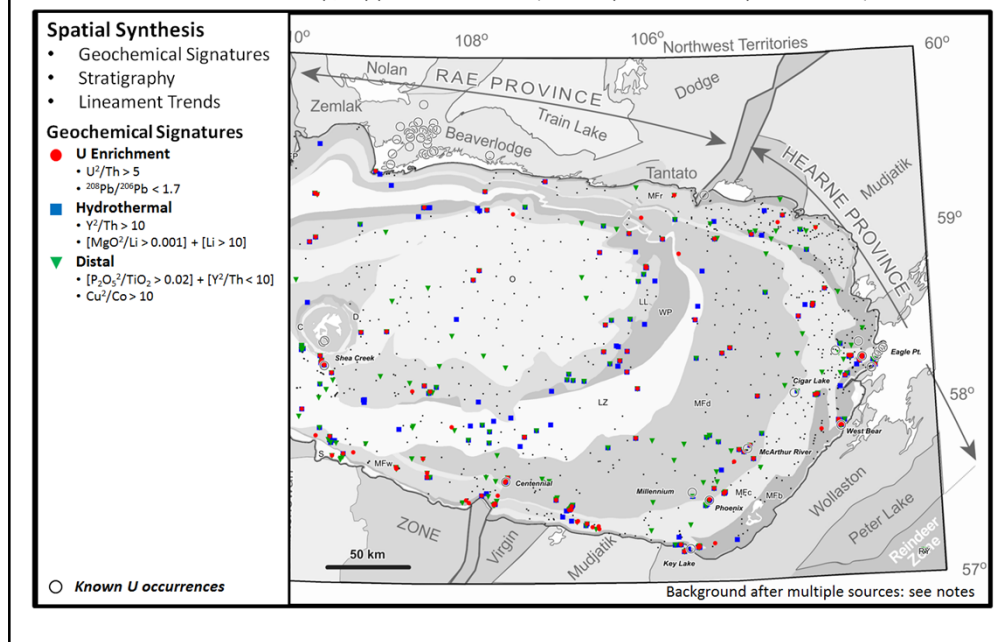
- Appear to parallel / follow SE-trending (~110°) and ENE-trending (070°) lineaments.

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)

Spatial Synthesis

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Primary Observation:

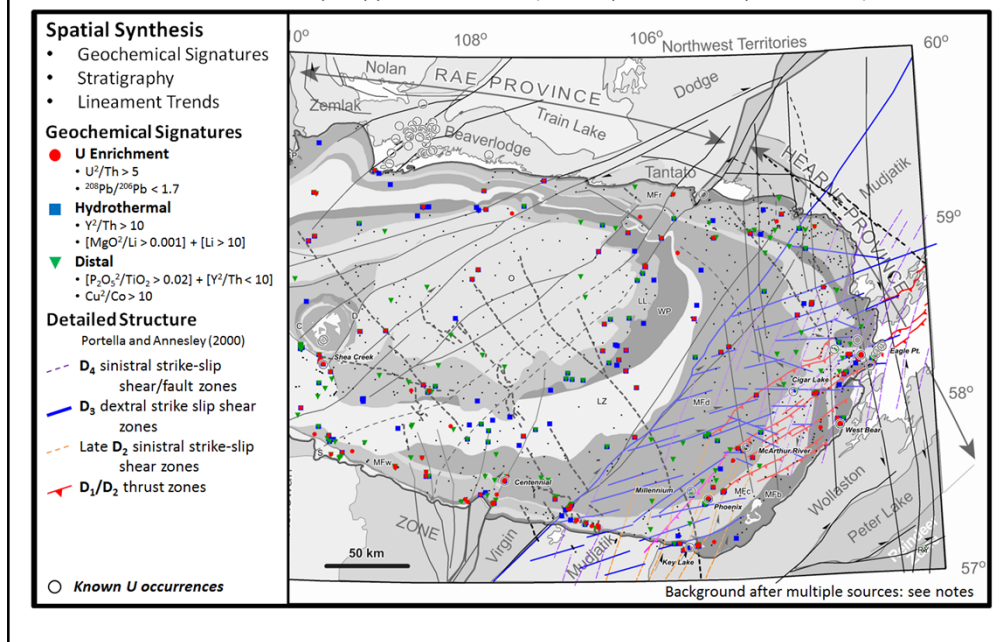
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Spatial Synthesis

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Primary Observation:

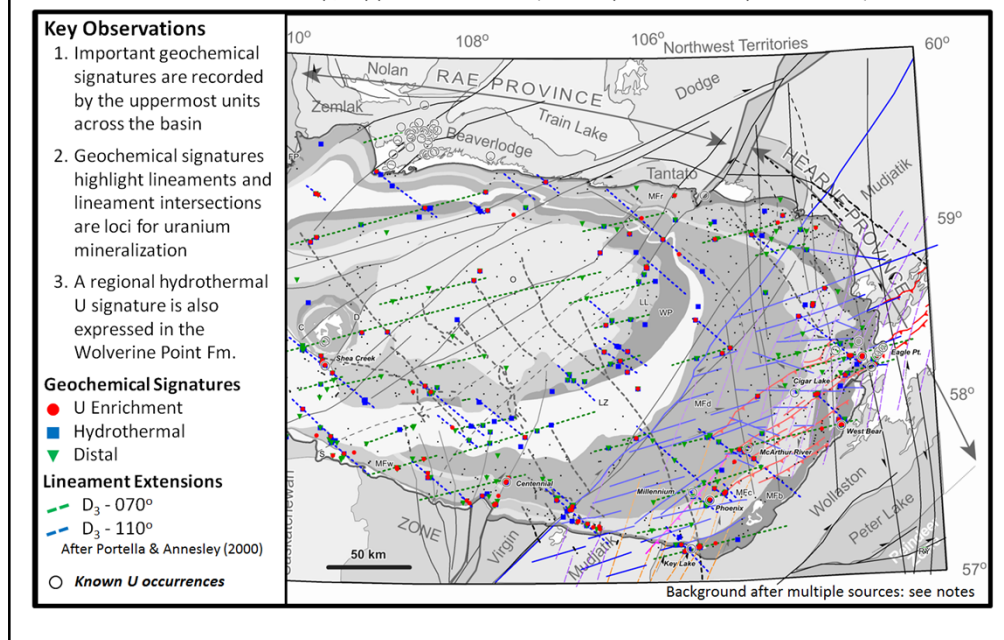
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Regional Surface Sedimentary Rock Geochemistry

Athabasca Group, Uppermost Units (Outcrop + DDH samples < 50 m)



Regional examination and integration of geochemical data with other components of the uranium exploration model can influence mineral exploration.

Key Observations:

1. Geochemical signatures of alteration and focused uranium mineralization are present in the upper exposed and near-surface units of the Athabasca Basin;
2. Geochemical signatures correspond with lineaments and highlight lineament intersections are loci for uranium mineralization; and
3. A distinct but locally stratabound hydrothermal signature that is possibly temporally and genetically related to focused uranium deposition elsewhere in the Athabasca Basin is also expressed in the Wolverine Point Formation.

Map compiled from several sources, including:

- Base lithological map and major structures: Jefferson *et al.* (2007); Ramaekers *et al.* (2007); Bosman and Schwab (2009); Bosman *et al.* (2012); Saskatchewan Geological Atlas.
- Structures in the East Athabasca: Portella and Annesley (2000)



Regional Surface Rock Geochemistry, Athabasca Basin, Saskatchewan

Wright, D.M. and Potter, E.G.

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