APPLICATION OF REGIONAL GEOCHEMICAL DATASETS TO URANIUM EXPLORATION IN THE ATHABASCA BASIN, SASKATCHEWAN

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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, which is host to some of the world's most significant high-grade unconformity-associated uranium deposits.

Composite geochemical features based on components of four lithogeochemical signatures highlight specific chemical-spatial relationships important to ongoing exploration for unconformity-associated uranium in the Athabasca Basin. Geospatial integration of these geochemical signatures with regional lineaments and the exploration model highlights that they: 1) correspond with known uranium occurrences and deposits; 2) occur in the exposed and near-surface rocks, including locations overlying ore at significant depths; and 3) correspond with lineament traces and highlight lineament intersections that are fertile for uranium enrichment.

Geochemical Signature 1 illustrates uranium enrichment relative to thorium, emphasizing two distinct types of uranium anomalism. Geochemical Signature 2 illustrates yttrium enrichment relative to phosphorous, which reflects chemo-stratigraphic signatures in the upper Athabasca Group and also displays a spatial (and perhaps temporal) association with known zones of uranium mineralization. Geochemical Signatures 3 and 4, represented by magnesium behaviour relative to lithium, and copper behaviour relative to cobalt, respectively, provide further refinement of the proximal to distal alteration signatures around known deposits.

Introduction

The analysis of large, public datasets can provide important context for deposit-focussed studies that define and refine techniques used to identify mineral exploration targets. The regional lithogeochemistry of the Athabasca Group of northern Saskatchewan was examined to define inter-element relationships that are significant to unconformity-associated uranium mineralization. Taking advantage of the continual advances in analytical techniques that permit accurate determination of lower concentrations and broader suites of elements, this study builds on earlier work such as Sopuck et al. (1983) and Clark (1987). Using only near-total digestion, multi-element data, inter-element behaviour patterns were primarily identified using statistical and spatial Exploratory Data Analysis techniques. The spatial distribution of multi-element signatures in the upper 50 m of bedrock were plotted relative to Athabasca Group stratigraphy, structural features, and known uranium occurrences in order to highlight key relationships. Several geochemical signatures are defined herein and are cumulatively significant in that: 1) they are present in the exposed and near-surface rocks of the Athabasca Basin; 2) correspond with inferred and/or known structures, and highlight structural intersections that are the loci for uranium mineralization; and 3) record potential linkages between diagenetic-hydrothermal alteration in certain sedimentary formations and uranium deposition.

Data and Methodology

The lithogeochemical data for the Athabasca Group used in this study were taken from the Athabasca Uranium Geochemistry (AUG) database (Wright et al., 2014; in press), a regional compilation of lithogeochemical data for the Athabasca Basin based on public and assessment file sources. The element relationships within the Athabasca Group data discussed in this report were identified primarily through: 1) the identification of elements currently important to the uranium exploration model (e.g. Jefferson et al., 2007), and/or 2) the application of Exploratory Data Analysis techniques (Tukey, 1977), including scatterplots, boxplot analysis, and multivariate correlation analyses to identify distinct element patterns. Numerous inter-element relationship groups were identified but only a select group were chosen for further discussion in this report. The definition of thresholds for each of the parameters discussed in this report is based primarily on statistical differences in sample populations related to Athabasca Group stratigraphy, where defined within the AUG Database. Additional and/or alternate criteria for threshold definition are described below for each element system. To emphasize the regional significance and application of the signatures identified, only those samples within 50 metres of surface were modeled spatially relative to the stratigraphy, structure, and known areas of uranium mineralization within the Athabasca Basin (Annesley et al., 2005; Jefferson et al., 2007; Ramaekers et al., 2007; Bosman et al., 2012; Sask. Geol. Atlas, 2013).

Geochemical Signature 1: Uranium – Thorium Behaviour

Cuney (2010) emphasized the importance of modeling uranium content relative to thorium, which reflects the primary association of these elements under igneous conditions, and the preferred mobility of hexavalent uranium (U^{6+}) under hydrothermal, oxidizing conditions (Grandstaff, 1976; Romberger, 1984). Uranium-thorium relationships within the Athabasca Group are defined in Figure 1, illustrating dif-

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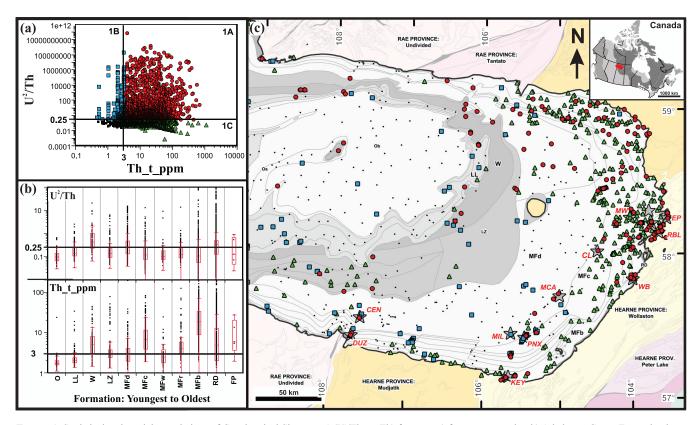


FIGURE 1: Statistical and spatial associations of Geochemical Signature 1 (U^2 /Th vs. Th) features : a) feature scatterplot, b) Athabasca Group Formation boxplots, and c) spatial distribution in surfaces samples (depth < 50 m). Grey stars represent deposits and occurrences (CEN = Centennial, CLF = Cluff Lake, EP = Eagle Point, DUZ = Dufferin Lake Zone, KEY = Key Lake, PNX = Phoenix, MIL = Millennium, MCA = McArthur River, CL = Cigar Lake, WB = West Bear, MW = Midwest, RBL = Rabbit Lake). Athabasca Group (youngest to oldest): Ob – Otherside Fm, Birkbeck Member; Oa – Otherside Fm, Archibald Member; LL – Locker Lake; W - Wolverine Point Fm; LZ – Lazenby Lake Fm; Manitou Falls Formations: MFd –Dunlop Member; MFc – Collins Member; MFb –Bird Member; and RD – Read Formation.

ferences in composite ratio U²/Th [gross uranium multiplied by the ratio of uranium to thorium (U/Th)] versus gross thorium content. A basic threshold for both U^2/Th and Th are based on distinct differences in statistical populations (Fig. 1b) between the Wolverine Point Formation ($X = 25^{th}$ percentile) and other formations of the Athabasca Group (X =75th percentile), emphasizing a lithogeochemical boundary within the Athabasca Group. The threshold for **Th** is based solely on the 25th percentile for the Wolverine Point Formation. Uranium enrichment from most known deposits represented in the AUG display both elevated U2/Th ratios and elevated gross thorium contents (Fig. 1: Sub-suite 1A). Subsuite 1A signatures at surface display a clear spatial association with several known uranium deposits located at depth. A second type of uranium enrichment is characterized by elevated U2/Th ratio values, yet lack significant thorium concentrations (Fig. 1: Sub-suite 1B), interpreted to represent uranium mobilized under lower temperature, oxidizing conditions. The distribution of suite 1B samples at surface displays a distal association with known uranium occurrences. Thorium enrichment in the absence of distinct U²/Th enrichment (Fig. 1: Sub-suite 1C) is characteristic of lower Manitou Falls and Read Formations, consistent with the presence of thorium-bearing aluminum phosphate-sulphate (APS) minerals in altered, heavy mineral-rich layers (Mwenifumbo and Bernius, 2007; Yeo et al., 2007; Carson et al., 2002; and references therein).

Geochemical Signature 2: Yttrium – Phosphorous Oxide Behaviour

Fluorapatite or apatite-(CaF) [Ca₅(PO₄)₃(OH,F,Cl)] and xenotime [YPO₄] have been identified in several locations in the Athabasca Basin, including the uranium deposits and occurrences (Fayek and Kyser, 1997), the uranium-poor, REE-rich Maw Zone (MacDougall, 1990; Quirt et al., 1991), and the Wolverine Point Formation (Rainbird et al., 2003, 2007; Davis et al., 2008). Aluminum phosphate-sulphate minerals have also been noted throughout the basin and associated with several ore deposits (Wilson, 1985; Gaboreau et al., 2007). The inter-element behaviour of yttrium and phosphorous were examined relative to select immobile elements to model mineralogy associated with hydrothermal alteration (xenotime, fluorapatite and other immobile element-bearing minerals) from mineralogy associated with predominantly diagenetic alteration (e.g. APS minerals). Yttrium-phosphorous relationships within the Athabasca Group are defined in Figure 2, illustrating differences in the composite ratio Y^{2}/Th [gross yttrium (Y) multiplied by the ratio of yttrium to thorium (Y/Th] versus the composite ratio $P_2O_5^2/TiO_2$ [gross phosphorous oxide (P_2O_5) multiplied by the ratio of phos-

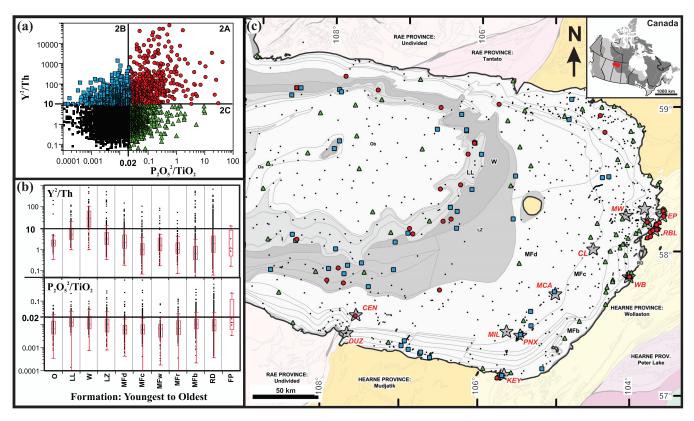


FIGURE 2: Statistical and spatial associations of Geochemical Signature 2: $(Y^2/Th vs. P_2O_5^2/TiO_2)$ features: a) feature scatterplot, b) Athabasca Group Formation boxplots, and c) spatial distribution in surface samples (depth < 50 m). Deposit, occurrence, and stratigraphic labels as per Fig. 1.

phorous oxide to titanium oxide (P₂O₅/TiO₂)]. Basic thresholds for Y²/Th is based on a distinct difference in statistical populations (Fig. 2b) between the Wolverine Point Formation (X = 25^{th} percentile) and other formations of the Athabasca Group ($X = 75^{th}$ percentile), emphasizing a lithogeochemical boundary within the Athabasca Group. The basic threshold for $P_2O_5^2/TiO_2$ (Fig. 2b) approximates the 75th percentile of most formations of the Athabasca Group, and is intended to represent a more general enrichment of phosphorous independent of lithogeochemical stratigraphy. Relative enrichment of both yttrium and phosphorous (Fig. 2: Sub-suite 2A) perhaps indicate evidence for a strong hydrothermal signature including the presence of xenotime and fluorapatite. This signature is observed in portions of the Wolverine Point Formation and areas of known uranium occurrences. Elevated concentrations of trace elements (including yttrium) have also been observed in sandstones above the Phoenix deposit (Power et al., 2012; Dann et al., 2014). Enrichment of yttrium relative to thorium and phosphorous (Fig. 2: Sub-suite 2B), is perhaps indicative of relict xenotime signatures subjected to later alteration, or overall lower xenotime contents. This signature is more widely spatially associated with the Wolverine Point and Locker Lake Formations, and with areas of known uranium mineralization. Phosphorous enrichment in the absence of yttrium enrichment (Fig. 2: Sub-suite 2C) is interpreted to reflect the genesis and or modification of APS minerals during lower temperature alteration. A wide spatial association with areas of known uranium occurrences is observed in the eastern Athabasca Basin. This feature is observed in all formations, with some linear trends crosscutting stratigraphy (presumably along late structure).

Geochemical Signature 3: Magnesium Oxide – Lithium Behaviour

The inter-element behaviour of magnesium and lithium was primarily examined to model chemical anomalism possibly related to dravite, magnesiofoitite, and chlorite alteration often associated with uranium occurrences in the Athabasca Basin (Jefferson et al., 2007 and references therein). The relationship of boron to magnesium and lithium was also reviewed, but was not presented due to fewer boron analyses in the AUG dataset. Magnesium-lithium relationships within the Athabasca Group are defined in Figure 3, illustrating differences in the composite ratio MgO²/Li [gross magnesium oxide (MgO) multiplied by the ratio of magnesium oxide to lithium (MgO/Li)] versus gross lithium (Li) content. Basic thresholds for both MgO²/Li and Li are based on distinct differences in statistical populations (Fig. 1b) between the Wolverine Point Formation ($X = 25^{th}$ percentile) and other formations of the Athabasca Group (X =75th percentile), emphasizing primarily a lithogeochemical boundary within the Athabasca Group. Relatively elevated magnesium with high lithium concentrations (Fig. 3: Subsuite 3A) display a proximal spatial association with known uranium occurrences (e.g. Phoenix Deposit, Centennial, West Bear). These signatures also reflect enrichment of MgO relative to boron (not shown), likely indicative of a

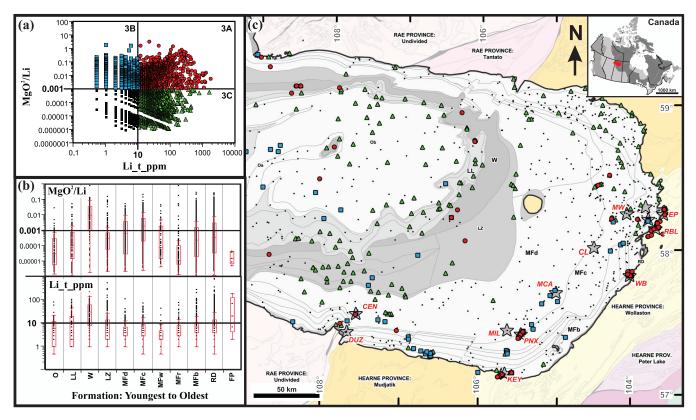


FIGURE 3: Statistical and spatial associations of Geochemical Signature 3 (MgO^2/Li vs. Li) features: a) feature scatterplot, b) Athabasca Group Formation boxplots, and c) spatial distribution in surface samples (depth < 50 m). Deposit, occurrence, and stratigraphic labels as per Fig. 1.

magnesium-enriched chlorite (c.f. Adlakha et al., 2013). Elevated relative magnesium with low lithium contents (Fig. 3: Sub-suite 3B) appear to represent a distal alteration signature, with broad spatial associations with known uranium occurrences that mimics the distribution of dravite in the southeast Athabasca Basin (Earle and Sopuck, 1989; Adlakha et al., 2013). A more direct positive association between magnesium and boron is also observed for the 3B suite (not shown). Gross lithium enrichment in the absence of relative magnesium enrichment (Fig. 3: Sub-suite 3C) is interpreted to represent a possible proxy for late hydrothermal alteration, inferred primarily from the wide spatial distribution of this signature within the upper stratigraphy of the Athabasca Group (excluding the Douglas and Carswell Formations. A distinct and consistent association between lithium, magnesium, and boron is also observed within the Subsuite 3C samples, and may reflect an important background mineralogical relationship, such as detrital tourmaline within the Athabasca Group (c.f. Sopuck et al., 1983).

Geochemical Signature 4: Copper – Cobalt Behaviour

Base metal enrichment is commonly associated with uranium occurrences in the Athabasca Basin (Jefferson et al., 2007). The inter-element behaviour of copper and cobalt was examined to model the relationships between copper mobility and subtle uranium enrichment. The diagram Cu^2/Co vs. U^2/Th (Fig. 4) defines three distinct suites in terms of copper-cobalt versus uranium-thorium behaviour within the Athabasca Group. Copper-cobalt relationships within the Athabasca Group are defined in Figure 4, illustrating differences in the composite ratio Cu²/Co [gross copper (Cu) multiplied by the ratio of copper to cobalt (Cu/Co)] versus the composite ratio U^2/Th [gross uranium (U) multiplied by the ratio of uranium to thorium (U/Th)]. A basic threshold for Cu²/Co (Fig. 4b) approximates the 75th percentile of most formations of the Athabasca Group, and is intended to represent a more general enrichment of copper, independent of lithogeochemical stratigraphy. The basic threshold for U²/Th is identical to that defined above. Elevated relative copper with sympathetic uranium enrichment (Fig. 4: Sub-suite 4A) suggests that some copper enrichment may be directly related to uranium enrichment processes (e.g. Geochemical Signature 1). Elevated copper contents have been reported in soils above the Cigar Lake and Phoenix deposits (Bonham-Carter and Hall, 2010; Power et al., 2012). Elevated relative copper without sympathetic weak uranium enrichment (Fig. 4: Sub-suite 4B) may represent more distal copper alteration related to uranium ore-forming processes, or localized copper enrichment related to the alteration of other copper-bearing features. Weak uranium enrichment in the absence of relative copper enrichment (Fig. 4: Sub-suite 4C) is interpreted to represent a lower temperature, perhaps diagenetic or remobilization phase, inferred primarily from the wide spatial distribution of this signature.

Spatial and Temporal Geochemical Associations

Composite geochemical features based on the inter-element signatures described above display broad temporal and

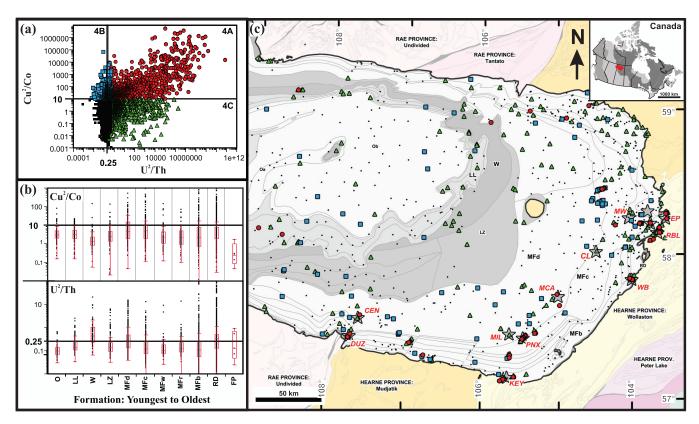


FIGURE 4: Statistical and spatial associations of Geochemical Signature 4 ($Cu^2/Co vs. U^2/Th$) features: a) feature Scatterplot, b) Athabasca Group Formation boxplots, c) spatial distribution in surface samples (depth < 50 m). Deposit, occurrence, and stratigraphic labels as per Fig. 1.

spatial associations with known uranium occurrences, stratigraphy, and structure within the Athabasca Basin (Fig. 5). These associations are important to applying these geochemical signatures to active exploration projects, evaluating the intensity and concentrations of these signatures relative to potential uranium deposits. In addition, elevated Y²/Th signatures suggest a genetic and temporal relationship between high-grade uranium mineralization and the Wolverine Point and Locker Lake Formations of the Athabasca Group.

Most high-grade occurrences captured in the AUG dataset display a combined signature of both elevated U²/Th and elevated Y²/Th values (Fig.5; Geochemical Feature 1). Samples of the Read and Manitou Falls Formations at surface with this combined signature display a spatial association with known deposits at depth (Fig. 5). Elevated U²/Th and Y²Th also occur within the Wolverine Point and Locker Lake Formations (Signature 1a), but are considered more likely a coincidental feature than indicative of higher-grade uranium mineralization (discussed in more detail below).

A more distal pattern of uranium enrichment in the absence of relative yttrium enrichment (Fig. 5: Geochemical Feature 2) is interpreted to represent the higher mobility of hexavalent uranium relative to thorium and associated high field strength elements (such as yttrium) under low temperature, oxidizing conditions (i.e. remobilizing fluids). At surface, the spatial distribution of this type of uranium enrichment signature is observed distal to known deposits along known and inferred structural conduits at surface (Fig. 5; Geochemical Feature 2). The occurrence of elevated U^2/Th ratios within the Wolverine Point and Locker Lake formations is considered to be probably more associated with this group (Fig.5; Signature 2a), where remobilized uranium has overprinted the chemostratigraphic Y²/Th signature.

A distal composite alteration feature is represented by relative phosphorous, magnesium oxide, and copper enrichment (Fig. 5; Geochemical Feature 3). A spatial association of this composite alteration feature correspond to late structures, consistent with 070°- and 110–120°-trending lineament features (e.g. Portella and Annesley, 2000; Annesley et al., 2005). This distal alteration crosscuts all units of the Athabasca Group, suggesting that they represent a later alteration event that has been mobilized along pre-existing structures.

A temporal and genetic relationship is implied by an elevated yttrium signature common to the Wolverine Point Formation, Locker Lake Formation, and zones of higher-grade uranium mineralization (Fig. 5: Geochemical Features 1 and 4). Elevated Y²/Th signatures observed in the Wolverine Point and Locker Lake Formations, are suggested to be associated with xenotime and fluorapatite cements in these units (Jefferson et al., 2007) providing a chemo-stratigraphic marker. This chemo-stratigraphic signature may share a genetic association with the enrichment of Y, Th, and other high field strength/incompatible elements observed with high-grade uranium mineralization (Jefferson et al., 2007). Within the Wolverine Point Formation, intraclast zircon grains (1644 \pm 13 Ma; Rainbird et al., 2007) are broadly con-

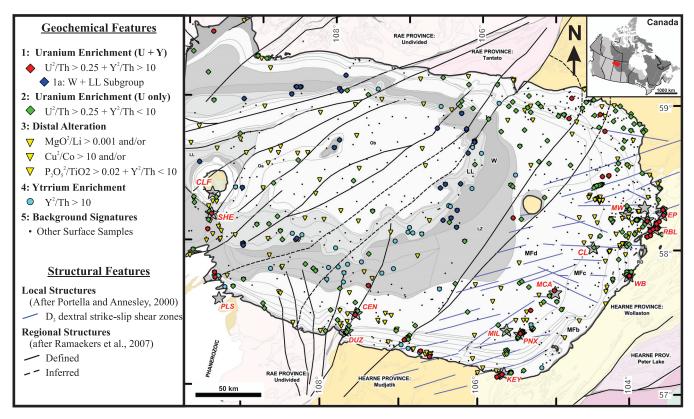


FIGURE 5: Spatial synthesis of composite geochemical features relative to lithology, structure, and known mineral deposit locations in the Athabasca Basin. Deposit, occurrence, and stratigraphic labels as per Fig.1.

current with diagenetic fluorapatite cements (1640–1620 Ma; Rainbird et al., 2003; Davis et al., 2008), both of which are broadly contemporaneous with the timing of pre-ore alteration (1730–1590 Ma; Alexandre et al. 2009) around major uranium deposits in the Athabasca Basin. The unconformable contact at the top of the Locker Lake Formation, demarcated by the 1544 \pm 13 Ma Douglas Formation (Creaser and Stasiuk, 2007), indicates a significant hiatus prior to deposition of the Otherside Formation, which may explain the absence of elevated Y²/Th ratio values in this later unit.

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