

Uranium, molybdenum and thallium isotopes in clay-sized material (<2 µm size fraction) from the McArthur River uranium deposit (Saskatchewan, Canada): a moving story

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ABSTRACT

Clay-sized material (<2 µm size fraction) separated from rock samples from the McArthur River U deposit in the Athabasca Basin (northern Saskatchewan, Canada) was analyzed for U, Mo and Tl isotopes to assess their potential to track ore-forming fluids and secondary remobilization processes. These isotope systems were selected for their ability to 1) track changes in redox reactions, which are the main driver behind U mobilization and precipitation mechanisms, and 2) provide key information on the origin of fluids and secondary water/rock interaction processes. Thallium isotope signatures of the ore-forming fluids are well preserved throughout the mineralized system all the way up to the top of the silicified sandstone layer, although U and Mo isotopic signatures are readily impacted by secondary remobilization, except for samples with high illite content, which seemingly preserve the original ore-forming fluid signature. The potential for these isotope systems to be used as pathfinders for U ore deposits is also discussed.

INTRODUCTION

The International Atomic Energy Agency (IAEA) estimates that the world nuclear capacity will increase by a factor of 2.5 in the context of transition towards cleaner energy (NEA/IAEA 2025). Canada, as the second largest producer and exporter of U in the world (15%) behind Kazakhstan (43%) (NEA/IAEA 2025), has an important part to play in the future of U resources at the global level.

The mobility of U in natural systems is greatly influenced by its redox state. The oxidized species, U(VI), forms oxy-anions that are highly mobile in surficial environments, whereas the reduced species, U(IV), tends to combine with oxygen and form U-rich minerals such as uraninite (UO₂) (Giblin et al. 1981; Bots and Behrends 2008; Cumberland et al. 2016). Developing robust proxies of redox conditions is thus of prime importance, as these will give valuable insight into not only the formation and alteration of U-ore deposits, but also the long-term evolution of nuclear waste repositories and mine tailings or possibly the development of new pathfinders for U exploration.

In this context, several non-traditional stable isotope systems, such as Cr, Fe, Cu, Se, Te, Sb or U, have been used in a variety of contexts to study changes in redox conditions in the current and past environments (Markl et al. 2006; Johnson et al. 2008; Nielsen et al. 2011; Scholz et al. 2017; Johnson et al. 2022; Voinot et al. 2024). Amongst these, we have selected U, Mo and Tl to use in this study, due to their ubiquity at high concentrations in U-ore deposit samples and demonstrated ability, especially for U and Tl isotopes, to successfully track and record change in redox conditions (Bopp et al. 2009; Brennecke et al. 2010; Uvarova et al. 2014; Keatley et al. 2021; Voinot et al. 2024).

In this study, we focus on clay-sized material (<2 µm size fraction) separated from bedrock samples collected around the McArthur River deposit in the Athabasca Basin of northern Saskatchewan, Canada. This unconformity-related U deposit exhibits some of the highest grades in the world (>15 wt% U₃O₈) and offers a unique geological context, with the deposit being overlain by a thick silicified sandstone layer that possibly focused fluids responsible for ore deposition (McGill et al. 1993; Derome et al. 2005). For this purpose, clay fractions were sampled throughout a bedrock stratigraphic profile to assess the evolution of the isotopic signature of several redox sensitive elements — U (δ²³⁸U, δ²³⁴U), Mo (δ⁹⁷Mo) and Tl (ε²⁰⁵Tl) — from the ore deposit at depth to the overlying sandstone units in the Athabasca group.

GEOLOGICAL SETTING

The McArthur River U deposit belongs to the unconformity-related class of U deposits (IAEA 2018), along with all the other high-grade U deposits in the Proterozoic Athabasca Basin (e.g. Key Lake, Millennium, and Cigar Lake U deposits; Fig. 1) (Cuney and Kyser 2009). The McArthur River deposit, discovered in 1988, is one of the world's largest and highest

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grade U deposits, with 327 million pounds (Mlbs) of U_3O_8 produced between the start of production in 1999 and 2018, and total reserves of 392 Mlbs U_3O_8 at a grade of 6.9% (Bray et al. 2019). Individual assays from delineation drilling in 1990 gave grades of more than 77% U_3O_8 (Marlatt et al. 1992). Uranium mineralization has been delineated by surface and under-ground drilling along a strike length of at least 1700 metres and occurs in nine areas at depths between 500 and 640 m below the surface (Bray et al. 2019) (Fig. 2a). Uranium mineralization, predominantly uraninite, is distributed in both the overlying Manitou Falls Group sandstone and the underlying graphite + cordierite pelitic gneiss of the Wollaston Group along the southeast-dipping P2 reverse fault that has accommodated 60–80 m of offset (Marlatt et al. 1992) (Fig. 2b). Minor pyrite, chalcopyrite, galena and Ni+Co sulphides and arsenides accompany the uraninite. Host-rock alteration associated with the deposit includes alkali-free dravite ('dravite'), kaolinite, chlorite, and illite in the sandstone, and chlorite and illite in the basement rocks (Fig. 3) (Kotzer and Kyser 1995; Alexandre et al. 2005; Ng 2012; Ng et al. 2013). A characteristic diagenetic feature at McArthur River is a ~200 m thick

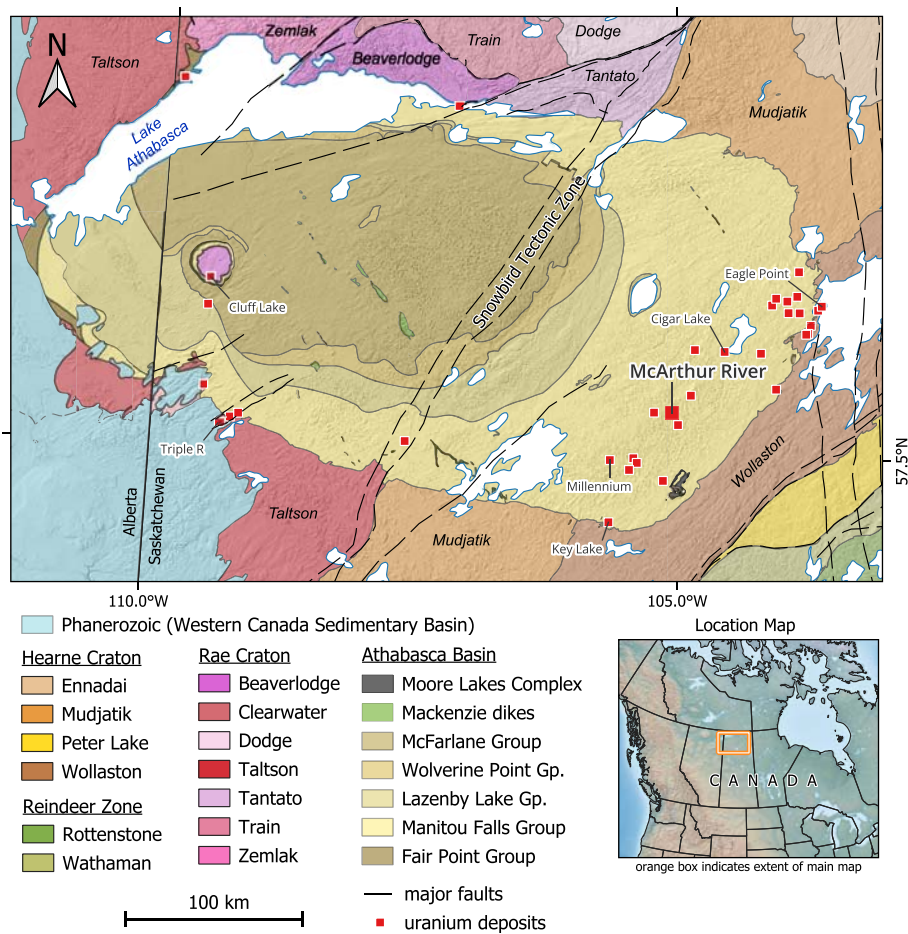


Fig. 1. Location of the Athabasca Basin in central Canada and the locations of U deposits, including the McArthur River deposit.

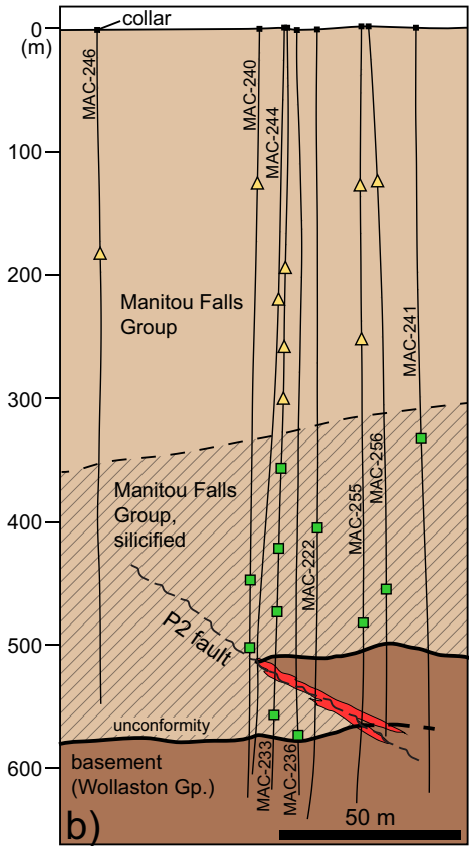
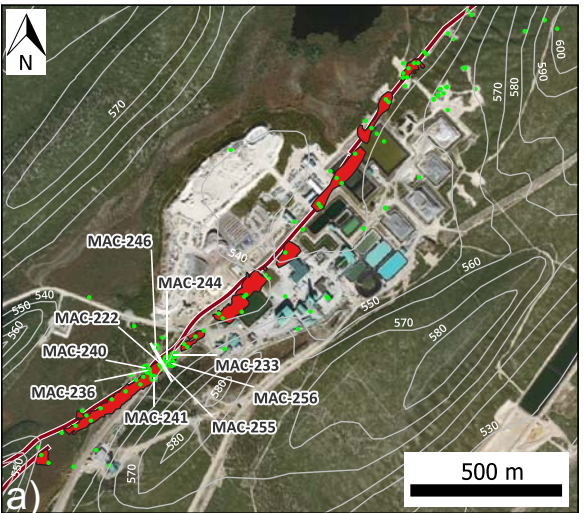


Fig. 2. a) Map of the McArthur River U deposit, showing the surface trace of the ore bodies and P2 fault, and the drill holes sampled for this study; the line of section for Fig. 2b is shown in white; b) cross-section of the McArthur River U deposit, looking northeast; yellow triangles denote non-silicified sandstone samples; green squares denote silicified sandstone samples.

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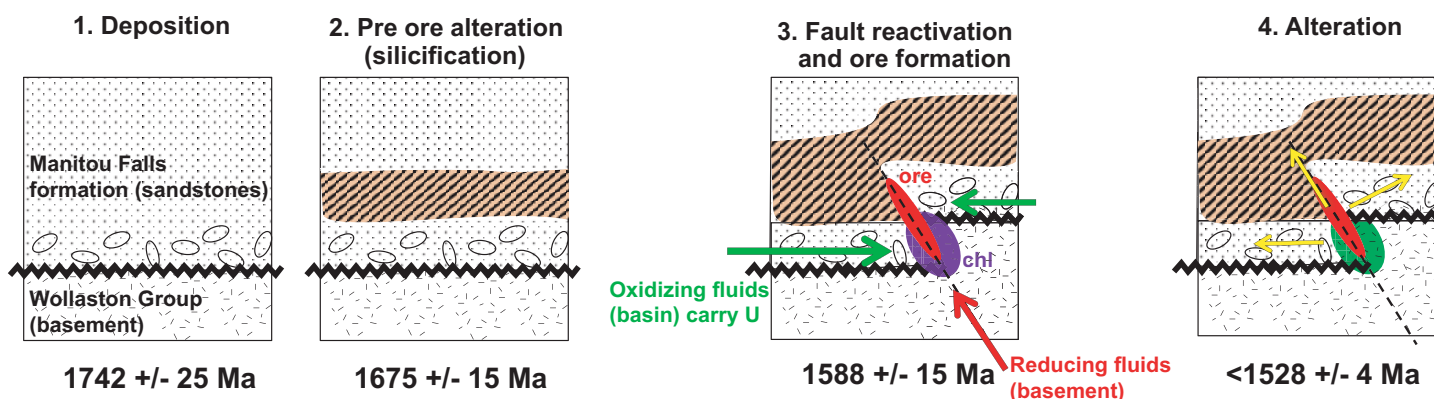


Fig. 3. Chronology of significant geological events in the Athabasca Basin (dates adapted from Alexandre et al. 2009). The green arrows represent the oxidizing fluids coming from the basin and carrying U and other metals (Kotzer and Kyser 1995; Cuney and Kyser 2009); the red arrow represents reducing fluids coming from the basement (Kotzer and Kyser 1995; Cuney and Kyser 2009); the purple represents areas of chlorite alteration (Ng 2012; Ng et al. 2013); the yellow arrows represent secondary remobilization by later fluid events (Ng 2012; Ng et al. 2013).

zone of strongly silicified sandstone that occurs between around 350 m below the natural land surface downward towards the unconformity at 500–550 m below the surface (Marlatt et al. 1992; Ng et al. 2013) (Fig. 2b). Silicified sandstone retains diagenetic purple Fe oxides and dickite, and has been interpreted as either an early diagenetic (Hiatt and Kyser 2007) or as a post-diagenetic hydrothermal feature (McGill et al. 1993; Derome et al. 2005) that likely focused U-mineralizing fluids and thus contributed to the anomalously high grade. The age of U mineralization in the Athabasca Basin is between 1500 and 1600 Ma, and significant Pb loss from the deposits is indicated by discordance that is frequently observed in geochronology of Athabasca uraninite (Fayek et al. 1997; Alexandre et al. 2009; Fayek et al. 2010; Cloutier et al. 2011; Sheahan et al. 2016).

MATERIAL AND METHOD

Clay mineralogy was determined by short-wave infrared spectroscopy (SWIR) on drill core samples (see Ng (2012) for more details on the method). Twenty samples from various depths around the McArthur River deposit (Acevedo and Kyser 2015) were prepared using the clay separation procedures (<2 µm fraction) that included ultrasonic disintegration and centrifugation as described in Ng (2012). X-ray diffraction analyses of the clay-sized material after separation indicate that it is dominated by phyllosilicates (Ng 2012; Ng et al. 2013).

About 100 mg of powdered clay separate was weighed into a perfluoroalkoxy (PFA) Savillex container in a class 1000 clean laboratory at the Queen's Facility for Isotope Research (Queen's University, Kingston, Canada), and digested with a 3:2:1 mixture of HCl:HNO₃:HF at 180°C until no solid residue was visible, typically within 24 to 48 hours. Samples were then evaporated to dryness at 80°C, before being refluxed in a 1:1 mixture of 1.4% H₃BO₃ and concentrated HCl to remove excess F from the samples. Samples were then evaporated to dryness again and then brought up in 2% HNO₃. An aliquot was set aside for U, Mo and Tl chromatography and subsequent isotope analyses by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS, Thermo Finnigan Neptune). Another aliquot was saved for trace and major element concentration analyses by high-resolution (HR)-ICP-MS using a Thermo Finnigan Element XR. The procedure is described in more detail in Voinot et al. (2024).

High-purity reagents were used throughout the entire procedure to minimize sample contamination. Concentrated

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HCl and HNO₃ were prepared from technical grade acids (Fisher) using an in-house distillation apparatus. High-purity HF was sourced from Seastar (Baseline), whereas high-purity H₃BO₃ was prepared by passing the solution prepared from technical grade powdered H₃BO₃ through a chromatography column loaded with 10 ml of Biorad AG50W-X8 cation exchange resin. Ultrapure water (Milipore MiliQ 18.2 MΩ.cm) was used for all dilutions.

Isotope compositions are expressed as deviation from reference standards in either ‰ or ε-units, as per the following equations:

$$\delta^{238}\text{U}_{\text{CRM112A}} = \left(\frac{{}^{238}\text{U}/{}^{235}\text{U}_{\text{sample}}}{{}^{238}\text{U}/{}^{235}\text{U}_{\text{CRM112A}}} - 1 \right) \times 1000 \quad (\text{eq. 1})$$

$$\delta^{234}\text{U}_{\text{CRM112A}} = \left(\frac{{}^{234}\text{U}/{}^{238}\text{U}_{\text{sample}}}{{}^{234}\text{U}/{}^{238}\text{U}_{\text{CRM112A}}} - 1 \right) \times 1000 \quad (\text{eq. 2})$$

$$\delta^{97}\text{Mo}_{\text{NIST3134}} = \left(\frac{{}^{97}\text{Mo}/{}^{95}\text{Mo}_{\text{sample}}}{{}^{97}\text{Mo}/{}^{95}\text{Mo}_{\text{NIST3134}}} - 1 \right) \times 1000 \quad (\text{eq. 3})$$

$$\varepsilon^{205}\text{Tl}_{\text{NIST997}} = \left(\frac{{}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{sample}}}{{}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{NIST997}}} - 1 \right) \times 10,000 \quad (\text{eq. 4})$$

As the ²³⁴U/²³⁸U ratio of the U standard CRM112A is lower than secular equilibrium, a correction factor was applied to ²³⁴U values, so that samples in secular equilibrium exhibit a ²³⁴U value of 0‰ (Cheng et al. 2013; Voinot et al. 2024).

Procedure blanks were measured and accounted for less than 0.1% of the total U, Mo and Tl extracted from the samples by ion-exchange chromatography and analyzed by MC-ICP-MS for isotope ratios, making them negligible. Reference materials (McArthur River 653 in-house uraninite standard as well as SDO-1 and SGR-1 shale reference material) were analyzed, and values were within the uncertainty of reported isotope values for U, Mo and Tl isotopic compositions (Crawford et al. 2021; Knaack et al. 2023; Voinot et al. 2024). Uncertainties (2 SD) are hereafter reported in the figures.

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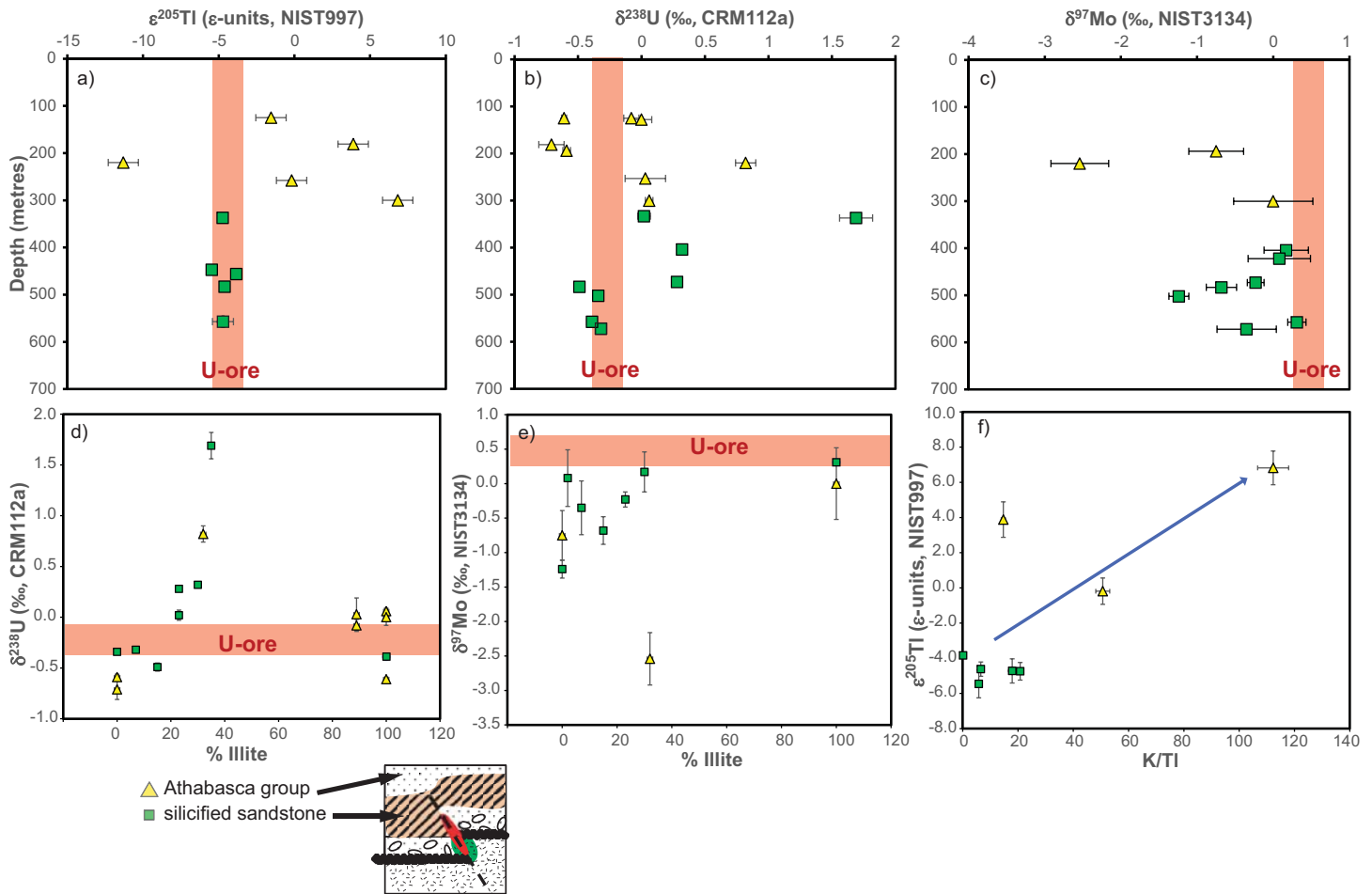


Fig. 4. Evolution of $\epsilon^{205}\text{Tl}$, $\delta^{238}\text{U}$ and $\delta^{97}\text{Mo}$ values as a function of depth in various clay samples from the present study (4a, 4b and 4c, respectively); $\delta^{238}\text{U}$ and $\delta^{97}\text{Mo}$ values as a function of illite content (4d and 4e, respectively); $\epsilon^{205}\text{Tl}$ values as a function of K/Tl ratios (4f).

RESULTS

The $\delta^{97}\text{Mo}$ and $\epsilon^{205}\text{Tl}$ values cover a wide range of isotopic compositions in the clay separate samples ($\delta^{97}\text{Mo}$ from -2.54 to +0.31‰, $\epsilon^{205}\text{Tl}$ from -11.3 to +6.8 ε-units, Fig. 4). Uranium isotope compositions also span a range of $\delta^{238}\text{U}$ values of about 2.40‰, from -0.71 to +1.69‰ (Fig. 4).

Samples collected from the silicified sandstone show increasing $\delta^{238}\text{U}$ values with decreasing depth ($\delta^{238}\text{U}$ values from -0.49 to +1.69‰), with the deepest samples showing values similar to that of the uraninite from the ore deposit ($\delta^{238}\text{U} = -0.25\text{‰}$, Voinot et al. 2024), though $\epsilon^{205}\text{Tl}$ values span a very narrow range from -5.5 to -3.8 ε-units, within analytical uncertainty of the values of the U ore ($\epsilon^{205}\text{Tl} = -4.6 \pm 0.7$ ε-units) (Fig. 4) (Voinot et al. 2024). The $\delta^{97}\text{Mo}$ values of these samples ($\delta^{97}\text{Mo} = -1.24$ to +0.31‰) are significantly lower than those of uraninite from the ore deposit itself ($\delta^{97}\text{Mo} = +0.5\text{‰}$, Voinot et al. 2024).

Samples of non-silicified Manitou Falls Group sandstone show higher dispersion for Mo and Tl isotope compositions ($\delta^{97}\text{Mo}$ from -2.54 to +0.01‰, $\epsilon^{205}\text{Tl}$ from -11.3 to +6.8 ε-units, respectively), as well as overall lower Mo and Tl concentrations (see Fig. 4 and [Appendix 1](#)). Uranium isotope

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compositions cover $\delta^{238}\text{U}$ values ranging from -0.71 to 0.82‰ (Fig. 4).

Lastly, $\delta^{234}\text{U}$ values are variable, ranging from -170 to +276‰, with only one sample being at or close to secular equilibrium (sample MAC_255_483 from the silicified sandstone layer, with a value of about -3‰).

DISCUSSION

Timing of U remobilization

Uranium mobility is heavily dependent on its redox state, with U(VI) forming very mobile oxyanions in oxidizing conditions, whereas U(IV) precipitates as uraninite in reducing conditions (Grenthe et al. 1992). In addition, ^{234}U is highly mobile in geological environments because it is ejected from the structure of minerals by alpha recoil when it is produced during the fission of ^{238}U (Kigoshi 1971). If the system is opened and ^{234}U loss occurs, the $\delta^{234}\text{U}$ value of the system will decrease, though the opposite is true when U gain occurs (Uvarova et al. 2014; Voinot et al. 2024). Once the system is closed again, the U activity ratio ($^{234}\text{U}/^{238}\text{U}$) returns to secular equilibrium within about 2.5 Ma (Ivanovich 1994).

The high mobility of U in the samples from the current study is highlighted by the wide range of $\delta^{234}\text{U}$ values, as all samples significantly depart from secular equilibrium ($\delta^{234}\text{U} = 0$ ‰) (see Appendix 1). This wide range of $\delta^{234}\text{U}$ values indicates that most samples have seen significant U gain (positive $\delta^{234}\text{U}$ values) or U loss (negative $\delta^{234}\text{U}$ values) within the last 2.5 Ma (Uvarova et al. 2014). Variable $\delta^{234}\text{U}$ values have been documented in other U ore deposits around the globe and showcase the dynamic nature of these systems (Uvarova et al. 2014; Keatley et al. 2021; Voinot et al. 2024).

Isotopes systematics and bonding environment of U, Mo and Tl in clays

Molybdenum and U have a high affinity for clay mineral surfaces, as they form inner sphere complexes during adsorption (Goldberg et al. 1996; Sylwester et al. 2000) (Fig. 5). Adsorption efficiency of Mo and U varies with pH, with maximums observed at lower pH values for Mo (pH <4) than U (pH between 5 and 9) (Goldberg et al. 1996; Echevarria et al. 2001; Bachmaf and Merkel 2011). Preferential adsorption of light Mo isotopes onto clay minerals has been observed in several studies (Wang et al. 2018; Greaney et al. 2020; Greaney et al. 2021), similar to what can be seen with other mineral phases like oxides and hydroxide minerals, with $\delta^{97}\text{Mo}_{\text{solution-solid}}$ values ranging from 0.5 to around 2‰ (Kendall et al. 2017 and references within). Our data agree, exhibiting a preferential adsorption of the light isotope onto clay minerals at the McArthur deposit, with $\delta^{97}\text{Mo}$ values rapidly declining away from the ore body into the sandstone above it.

These findings, along with those from other studies (Wang et al. 2018; Greaney et al. 2020; Greaney et al. 2021), contrast with the negligible Mo isotopic fractionation during the formation of clay minerals observed by Sibert et al. (Sibert et al. 2015). This discrepancy could be attributed to 1) differences in physicochemical conditions of the fluids

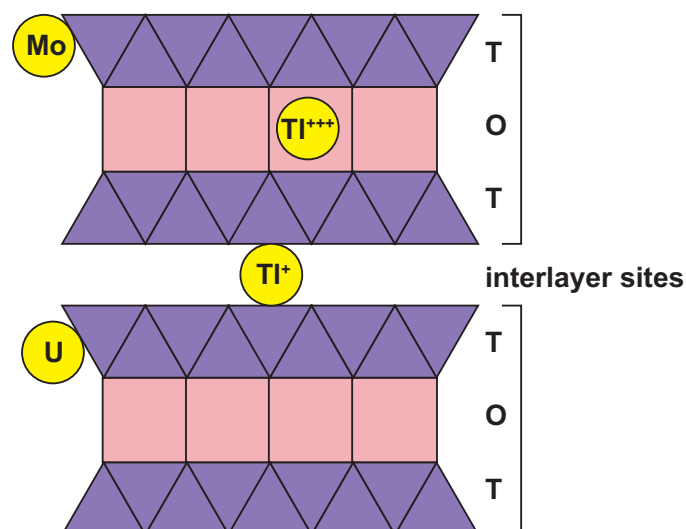


Fig. 5. Expected site occupancy for U, Mo and Tl in clay minerals (Goldberg et al. 1996; Wick et al. 2018; Sylwester et al. 2000). T: tetrahedral sheets; O: octahedral sheets.

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(pH, Eh), which could have a high influence on Mo adsorption systematics and associated isotope fractionation (Goldberg et al. 1996; Kendall et al. 2017); or 2) differences in context between the various studies, including the mineralogy of clays and other associated mineral phases, that will greatly influence the isotopic fractionation associated with adsorption reactions (Siebert et al. 2015; Kendall et al. 2017; Wang et al. 2018; Greaney et al. 2020; Greaney et al. 2021).

Similarly, preferential adsorption of the light isotope ^{235}U is observed during U adsorption onto various mineral phases (birnessite, goethite, quartz), with clay minerals like illite exhibiting a $\delta^{238}\text{U}_{\text{solution-solid}}$ of about 0.2‰ (Brennecke et al. 2011; Dang et al. 2016; Jemison et al. 2016). In our data, the U isotope signature of ore-forming fluids seems to be somewhat better preserved initially below a depth of about 500 m, above which $\delta^{238}\text{U}$ values start increasing (Fig. 4b). This distribution suggests that the U isotopic composition of the fluids evolves with increasing distance from the deposit, with ^{238}U being progressively enriched in the residual fluid, and likely indicates that the light U isotopes are preferentially adsorbing onto other mineral phases first before adsorption onto clay minerals. This divergence between Mo and U isotopes could potentially shed some insight into the physicochemical conditions during the formation of the clay minerals. For example, low pH conditions (pH <4) would lead to high adsorption efficiency for Mo (Goldberg et al. 1996), but would be sub-optimal for adsorption of U onto clay minerals (Echevarria et al. 2001; Bachmaf and Merkel 2011) leading to competition and preferential adsorption of U onto other mineral phases (such as oxides and hydroxides), resulting in a fluid relatively enriched in ^{238}U .

Thallium, on the other hand, is capable of adsorbing onto the surface of clay minerals, but can also substitute for K in its reduced form Tl(I) in interlayer sites of phyllosilicates like illite and, as such, can undergo significant adsorption when these mineral phases are present (Martin et al. 2018; Wick et al. 2018; Voegelin et al. 2022) (Fig. 5). Thallium can also be incorporated in its oxidized form Tl(III) in these mineral phases, where it can substitute for Fe in octahedral sites, similar to the Fe/Tl substitution observed in other mineral phases like jarosite (Dutrillac et al. 2005). As Tl isotopes do not exhibit fractionation during mineral weathering and alteration (Nielsen et al. 2017), changes in the redox state of Tl are necessary to explain isotopic fractionation during such processes. At McArthur River, the Tl isotopic composition in the clay minerals from the silicified sandstone are within error of the $\epsilon^{205}\text{Tl}$ value of the ore deposit (Fig. 4c), which suggests that no change in redox conditions was involved during the transport of Tl and the formation of these clay minerals in the samples from the silicified sandstone (Nielsen et al. 2017). Samples collected from non-silicified sandstone show much higher variability in $\epsilon^{205}\text{Tl}$ values (Fig. 4a), which could be attributed to either 1) differences in source of the Tl for these samples, with contribution from a different source within the basin with a much higher $\epsilon^{205}\text{Tl}$ signature; or 2) later remobilization of Tl

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associated by a change in its redox state, similar to what has been observed in the B-horizon of soils from the Erzmatt in Switzerland, where high $\epsilon^{205}\text{Tl}$ values are attributed to a 2-step process of weathering of Tl(III)-bearing phases followed by a Tl(I) remobilization, leading to an enrichment in the heavy isotope, ^{205}Tl , in secondary phases like illite (Vaněk et al. 2020).

These findings corroborate observations made on other U ore deposit samples (intrusive, granite-related, metamorphic and other unconformity-related deposits, Voinot et al. 2024), showing that the initial $\epsilon^{205}\text{Tl}$ value is being preserved despite secondary remobilization processes, although Mo isotopes are heavily impacted, likely due to their lighter mass, bonding environment, and higher overall mobility in these environments (Voinot et al. 2024). Samples of non-silicified sandstone do not appear to reflect the U, Mo or Tl isotopic compositions of the ore deposit. This is potentially related to the fact that this unit is hydrologically isolated from the ones below it by the silicified sandstone layer that acted as an impermeable layer (McGill et al. 1993; Derome et al. 2005; Ng et al. 2013).

Relations with clay mineralogy

Samples showing high proportions of illite (85% or higher) determined using SWIR exhibit a tight population of $\delta^{97}\text{Mo}$ and $\delta^{238}\text{U}$ values that are systematically close to the isotopic compositions of the U ore material at McArthur River (Fig. 4d, e). This similarity in isotopic compositions likely indicates that either 1) the Mo and U trapping mechanism is very efficient and all Mo and U present in solution is being adsorbed onto the illite (Goldberg et al. 1996; Sylwester et al. 2000); or 2) negligible isotopic fractionation occurs during adsorption for both elements (Siebert et al. 2015). The data available does not allow us to clearly distinguish between the two potential mechanisms, however it is worth noting that secondary clay formation does not fractionate Mo isotopes (Siebert et al. 2015), and that adsorption on other surfaces (oxides, organic matter) is usually accompanied by isotopic fractionation for both U and Mo (Siebert et al. 2015; Jemison et al. 2016). It is thus more likely that the Mo and U adsorption on illite is happening very efficiently, quantitatively removing all U and Mo from the solution. We can go as far as to postulate that the process is likely happening in a range of more favourable acidic pH conditions, as discussed previously.

When a decrease of the proportion of illite in the samples is observed, the spread in both U and Mo isotope compositions increases, and although the $\delta^{238}\text{U}$ values do not seem to show any correlation with the proportion of illite (Fig. 4d), $\delta^{97}\text{Mo}$ values decrease with decreasing illite content (Fig. 4e). This relationship between Mo isotopes and illite content might provide some insight into the mechanism at play behind Mo adsorption, with preferential uptake of the light isotope (^{95}Mo) from the solution, as observed with other mineral phases (Kendall et al. 2017, and references within). It also reinforces that extreme caution should be used when using Mo isotopes in isolation as tracers of paleoredox conditions, as secondary processes can readily overprint the isotope signature of the initial ore-forming fluid event (Voinot et al. 2024).

Thallium as a robust tracer of ore deposition mechanisms

Though U and Mo appear to exhibit very high mobility and change in isotope composition in the samples from this study, Tl isotope systematics indicate that the isotopic composition of the clays in all samples from the silicified sandstone and basement units is a direct reflection of the isotopic composition of the U ore deposit (Fig. 4a). This is in agreement with what is observed in a variety of U ore deposits around the globe, showing that Tl isotopes are not affected by secondary processes, and as such, can be used as tracers of mechanisms of formation of U ore deposits (Voinot et al. 2024). These results also suggests that no change of Tl redox state occurred in the system, as these would be accompanied by significant isotopic fractionation (Vaněk et al. 2020).

In addition, plotting the $\epsilon^{205}\text{Tl}$ values of the clay separates against K/Tl ratios (Fig. 4f) seems to indicate that two different end-members are controlling Tl isotope compositions in the samples: 1) a low [Tl] but high [K] and $\epsilon^{205}\text{Tl}$ value (around 8 ϵ -units) source, likely representing later contribution from the basin, as high $\epsilon^{205}\text{Tl}$ values are typically found in

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Fe-Mn crusts or pelagic clays or samples with high sulphide contents (Nielsen et al. 2017; Voinot et al. 2024); and 2) a low [K] but higher [Tl] and lower $\epsilon^{205}\text{Tl}$ value (around -5 ϵ -units), likely associated with U-rich fluids, as this corresponds to the Tl isotopic composition of the U ore deposit.

CONCLUSIONS AND POTENTIAL IMPLICATIONS FOR MINERAL EXPLORATION

The data presented here suggests that Tl isotopic compositions of clay-sized material (<2 μm) from the silicified layer share a common Tl source with a fluid that likely led to the formation of the U deposit, and that the initial Tl isotopic composition of the ore-forming fluid appears to be preserved in these geological units (Fig. 4a). The patterns observed here also likely indicate that the clay minerals from these units formed at the same time as the ore deposit and therefore Tl isotopes could potentially be used as pathfinders for U mineralization as they appear to be unaffected by alteration and secondary processes at depth, similar to what was observed in U-ore deposit samples (Voinot et al. 2024). Analyzing sandstone samples for $\epsilon^{205}\text{Tl}$ values to find areas of sandstone with compositions that are similar to that of the ore deposit in the area could potentially prove to be a powerful vectoring tool towards new discoveries.

To a lesser extent, similar results are observed for U isotopes, however, the original signature from the ore-forming fluids seems to be quickly overprinted over a short distance away from the deposit (Fig. 4b), even in the silicified sandstone. Though a more targeted approach using illite-rich samples exclusively might lead to similar results, it also means that this approach remains very limited, as slight changes in clay mineralogy may adversely affect the results and lead to false negatives or positives.

The discrepancy observed in the data between Mo isotopes (showing preferential adsorption of Mo onto clay minerals) and U isotopes (indicating that other mineral phases likely quantitatively remove U from solution before it is being adsorbed onto clays) potentially brings insight into the physicochemical conditions of the fluid during the formation of the clay minerals in the silicified sandstone, likely indicating acidic conditions (pH <4).

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APPENDIX 1

This article is accompanied by a digital data file ([Appendix 1.xlsx](#)) that can be downloaded here.

REFERENCES

- Acevedo, A. and Kyser, T.K. 2015. Fe isotopic composition of alteration minerals from McArthur River Zone 4 Deposit, Athabasca Basin. Geological Survey of Canada, Open File 7791, 61–73. <https://doi.org/https://doi.org/10.4095/295784>
- Alexandre, P., Kyser, K., Polito, P. and Thomas, D. 2005. Alteration mineralogy and stable isotope geochemistry of

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Paleoproterozoic basement-hosted unconformity-type uranium deposits in the Athabasca Basin, Canada. *Economic Geology*, 100, 1547–1563.

<https://doi.org/10.2113/gsecongeo.100.8.1547>

Alexandre, P., Kyser, K., Thomas, D., Polito, P. and Marlat, J. 2009. Geochronology of unconformity-related uranium deposits in the Athabasca Basin, Saskatchewan, Canada and their integration in the evolution of the basin. *Mineralium Deposita*, 44, 41–59. <https://doi.org/10.1007/s00126-007-0153-3>

Bachmaf, S. and Merkel, B.J. 2011. Sorption of uranium(VI) at the clay mineral–water interface. *Environmental Earth Sciences*, 63, 925–934. <https://doi.org/10.1007/s12665-010-0761-6>

Bopp, C.J., IV, Lundstrom, C.C., Johnson, T.M. and Glessner, J.J.G. 2009. Variations in $^{238}\text{U}/^{235}\text{U}$ in uranium ore deposits: Isotopic signatures of the U reduction process? *Geology*, 37, 611–614. <https://doi.org/10.1130/g25550a.1>

Bots, P. and Behrends, T. 2008. Uranium mobility in subsurface aqueous systems: the influence of redox conditions. *Mineralogical Magazine*, 72, 381–384.

Bray, L., Murdock, G.M. and Renaud, A.D. 2019. McArthur River operation, northern Saskatchewan, Canada. National Instrument 43-101 Technical Report for Cameco Corporation. <https://s3-us-west-2.amazonaws.com/assets-us-west-2/technical-report/cameco-2018-mcarthur-technical-report.pdf>

Brennecke, G.A., Borg, L.E., Hutcheon, I.D., Sharp, M.A. and Anbar, A.D. 2010. Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the $^{238}\text{U}/^{235}\text{U}$ fractionation mechanism. *Earth and Planetary Science Letters*, 291, 228–233. <https://doi.org/https://doi.org/10.1016/j.epsl.2010.01.023>

Brennecke, G.A., Wasylenki, L.E., Bargar, J.R., Weyer, S. and Anbar, A.D. 2011. Uranium Isotope Fractionation during Adsorption to Mn-Oxyhydroxides. *Environmental Science & Technology*, 45, 1370–1375. <https://doi.org/10.1021/es103061v>

Cheng, H., Lawrence Edwards, R. et al. 2013. Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth and Planetary Science Letters*, 371–372, 82–91. <https://doi.org/https://doi.org/10.1016/j.epsl.2013.04.006>

Cloutier, J., Kyser, 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*, 46, 35–56. <https://doi.org/10.1007/s00126-010-0308-5>

Crawford, I., Layton-Matthews, D., Peter, J.M., Gadd, M.G., Voinot, A., Leybourne, M.I. and Pufahl, P. 2021. Application of molybdenum and thallium isotopes as indicators of paleoredox conditions and genesis of hyper-enriched black shale deposits, Peel River, Yukon, Canada. *The Canadian Mineralogist*, 59, 1085–1110. <https://doi.org/10.3749/canmin.2000099>

Cumberland, S.A., Douglas, G., Grice, K. and Moreau, J.W. 2016. Uranium mobility in organic matter-rich sediments: A review of geological and geochemical processes. *Earth-Science Reviews*, 159, 160–185.

Cuney, M. and Kyser, K. 2009. Recent and not-so-recent developments in uranium deposits and implications for exploration. *Mineralogical Association of Canada, Short Course Series, Volume 39*.

Dang, D.H., Novotnik, B., Wang, W., Georg, R.B. and Evans, R.D. 2016. Uranium Isotope Fractionation during Adsorption, (Co)precipitation, and Biotic Reduction. *Environmental Science & Technology*, 50, 12695–12704. <https://doi.org/10.1021/acs.est.6b01459>

Derome, D., Cathelineau, M., Cuney, M., Fabre, C.C., Lhomme, T.R.S. and Banks, D.A. 2005. Mixing of sodic and calcic brines and uranium deposition at McArthur River, Saskatchewan, Canada: a raman and laser-induced breakdown spectroscopic study of fluid inclusions. *Economic Geology*, 100, 1529–1545. <https://doi.org/10.2113/gsecongeo.100.8.1529>

Dutrizac, J.E., Chen, T.T. and Beauchemin, S. 2005. The behaviour of thallium(III) during jarosite precipitation. *Hydrometallurgy*, 79, 138–153. <https://doi.org/https://doi.org/10.1016/j.hydromet.2005.06.003>

Echevarria, G., Sheppard, M.I. and Morel, J. 2001. Effect of pH on the sorption of uranium in soils. *Journal of Environmental Radioactivity*, 53, 257–264.

Fayek, M., Janeczek, J. and Ewing, R.C. 1997. Mineral chemistry and oxygen isotopic analyses of uraninite, pitchblende and uranium alteration minerals from the Cigar Lake deposit, Saskatchewan, Canada. *Applied Geochemistry*, 12, 549–565. [https://doi.org/https://doi.org/10.1016/S0883-2927\(97\)00032-2](https://doi.org/https://doi.org/10.1016/S0883-2927(97)00032-2)

U, Mo, Tl isotopes in clay-sized material from the McArthur River U deposit *continued from page 15*

- Fayek, M., Harrison, T.M., Grove, M. and Coath, C.D. 2010. A rapid in situ method for determining the ages of uranium oxide minerals: Evolution of the Cigar Lake Deposit, Athabasca Basin. *International Geology Review*, 42, 163–171. <https://doi.org/10.1080/00206810009465075>
- Giblin, A., Batts, B. and Swaine, D. 1981. Laboratory simulation studies of uranium mobility in natural waters. *Geochimica et Cosmochimica Acta*, 45, 699–709.
- Goldberg, S., Forster, H. and Godfrey, C. 1996. Molybdenum adsorption on oxides, clay minerals, and soils. *Soil Science Society of America Journal*, 60, 425–432.
- Greaney, A.T., Rudnick, R.L., Romaniello, S.J., Johnson, A.C., Gaschnig, R.M. and Anbar, A.D. 2020. Molybdenum isotope fractionation in glacial diamictites tracks the onset of oxidative weathering of the continental crust. *Earth and Planetary Science Letters*, 534, 116083. <https://doi.org/https://doi.org/10.1016/j.epsl.2020.116083>
- Greaney, A.T., Rudnick, R.L., Romaniello, S.J., Johnson, A.C., Anbar, A.D. and Cummings, M.L. 2021. Assessing molybdenum isotope fractionation during continental weathering as recorded by weathering profiles in saprolites and bauxites. *Chemical Geology*, 566, 120103. <https://doi.org/https://doi.org/10.1016/j.chemgeo.2021.120103>
- Grenthe, I., Fuger, J., Konings, R.J., Lemire, R.J., Muller, A.B., Nguyen-Trung, C. and Wanner, H. 1992. *Chemical thermodynamics of uranium*. Elsevier Amsterdam.
- Hiatt, E.E. and Kyser, T.K. 2007. Sequence stratigraphy, hydrostratigraphy, and mineralizing fluid flow in the Proterozoic Manitou Falls Formation, eastern Athabasca Basin, Saskatchewan. In: Jefferson, C.W. and Delaney, G. (eds) *EXTECH IV: Geology and Uranium EXploration TECHnology of the Proterozoic Athabasca Basin, Saskatchewan and Alberta*. Geological Survey of Canada, Bulletin 558, 489–506.
- IAEA. 2018. Geological classification of uranium deposits and description of selected examples. International Atomic Energy Agency, TECDOC-1842.
- Ivanovich, M. 1994. Uranium series disequilibrium: concepts and applications. *Radiochimica Acta*, 64, 81–94.
- Jemison, N.E., Johnson, T.M., Shiel, A.E. and Lundstrom, C. 2016. Uranium isotopic fractionation induced by U (VI) adsorption onto common aquifer minerals. *Environmental Science & Technology*, 50, 12232–12240.
- Johnson, C.M., Beard, B.L. and Roden, E.E. 2008. The iron isotope fingerprints of redox and biogeochemical cycling in modern and ancient Earth. *Annual Review of Earth and Planetary Sciences*, 36, 457–493. <https://doi.org/10.1146/annurev.earth.36.031207.124139>
- Johnson, T.M., Druhan, J.L., Basu, A., Jemison, N.E., Wang, X., Schilling, K. and Wasserman, N.L. 2022. A review of the development of Cr, Se, U, Sb, and Te isotopes as indicators of redox reactions, contaminant fate, and contaminant transport in aqueous systems. In: *Isotopic Constraints on Earth System Processes*. American Geophysical Union, 237–269. ISBN: 978-1-119-59496-3
- Keatley, A.C., Dunne, J.A., Martin, T.L., Nita, D.C., Andersen, M.B., Scott, T.B., Richards, D.A. and Awbery, R.P. 2021. Uranium isotope variation within vein-type uranium ore deposits. *Applied Geochemistry*, 131, 104977. <https://doi.org/10.1016/j.apgeochem.2021.104977>
- Kendall, B., Dahl, T.W. and Anbar, A.D. 2017. The stable isotope geochemistry of molybdenum. *Reviews in Mineralogy and Geochemistry*, 82, 683–732. <https://doi.org/10.2138/rmg.2017.82.16>
- Kigoshi, K. 1971. Alpha-recoil thorium-234: Dissolution into water and the uranium-234/uranium-238 disequilibrium in nature. *Science*, 173, 47–48. <https://doi.org/doi:10.1126/science.173.3991.47>
- Knaack, D.R., Sullivan, K.V., Leybourne, M.I., Dunn, C.E. and Layton-Matthews, D. 2023. Thallium isotopes as indicators of ore mineralization at the Zn-rich sediment-hosted massive sulfide TL Deposit, British Columbia, Canada. *Geochemistry: Exploration, Environment, Analysis*, 23. <https://doi.org/10.1144/geochem2022-042>
- Kotzer, T.G. and Kyser, T.K. 1995. Petrogenesis of the Proterozoic Athabasca Basin, northern Saskatchewan, Canada, and its relation to diagenesis, hydrothermal uranium mineralization and paleohydrogeology. *Chemical Geology*, 120, 45–89. [https://doi.org/10.1016/0009-2541\(94\)00114-n](https://doi.org/10.1016/0009-2541(94)00114-n)
- Markl, G., Lahaye, Y. and Schwinn, G. 2006. Copper isotopes as monitors of redox processes in hydrothermal mineralization. *Geochimica et Cosmochimica Acta*, 70, 4215–4228.
- Marlatt, J., McGill, B., Matthews, R., Sopuck, V. and Pollock, G. 1992. The discovery of the McArthur River uranium deposit, Saskatchewan, Canada. New developments in uranium exploration, resources, production and demand. IAEA, Vienna, 118–127.
- Martin, L.A., Wissocq, A., Benedetti, M.F. and Latrille, C. 2018. Thallium (Tl) sorption onto illite and smectite: Implications for Tl mobility in the environment. *Geochimica et Cosmochimica Acta*, 230, 1–16. <https://doi.org/https://doi.org/10.1016/j.gca.2018.03.016>
- McGill, B.D., Marlatt, J.L., Matthews, R.B., Sopuck, V.J., Homeniuk, L.A. and Hubregtse, J.J. 1993. The P2 North uranium deposit, Saskatchewan, Canada. *Exploration and Mining Geology*, 2, 321–331.
- NEA/IAEA. 2025. Uranium 2024: Resources, Production and Demand. https://www.oecd-neo.org/jcms/pl_103179/uranium-2024-resources-production-and-demand?details=true
- Ng, R. 2012. Geochemical and mineralogical evolution of the McArthur River Zone 4 unconformity-related Uranium ore body and application of iron oxidation state in clay alteration as indicator of Uranium mineralization. M.Sc. thesis, Queen's University, Kingston, Ontario, 220 p.
- Ng, R., Alexandre, P. and Kyser, K. 2013. Mineralogical and geochemical evolution of the unconformity-related McArthur River Zone 4 orebody in the Athabasca Basin, Canada: implications of a silicified zone. *Economic Geology*, 108, 1657–1689.

U, Mo, Tl isotopes in clay-sized material from the McArthur River U deposit *continued from page 16*

- Nielsen, S.G., Rehkämper, M. and Prytulak, J. 2017. Investigation and application of thallium isotope fractionation. *Reviews in Mineralogy and Geochemistry*, 82, 759–798.
- Nielsen, S.G., Goff, M., Hesselbo, S.P., Jenkyns, H.C., LaRowe, D.E. and Lee, C.-T.A. 2011. Thallium isotopes in early diagenetic pyrite—A paleoredox proxy? *Geochimica et Cosmochimica Acta*, 75, 6690–6704.
- Scholz, F., Siebert, C., Dale, A.W. and Frank, M. 2017. Intense molybdenum accumulation in sediments underneath a nitrogenous water column and implications for the reconstruction of paleo-redox conditions based on molybdenum isotopes. *Geochimica et Cosmochimica Acta*, 213, 400–417.
- Sheahan, C., Fayek, M., Quirt, D. and Jefferson, C.W. 2016. A combined Ingress-Egress model for the Kianna unconformity-related uranium deposit, Shea Creek Project, Athabasca Basin, Canada. *Economic Geology*, 111, 225–257. <https://doi.org/10.2113/econgeo.111.1.225>
- Siebert, C., Pett-Ridge, J.C., Opfergelt, S., Guicharnaud, R.A., Halliday, A.N. and Burton, K.W. 2015. Molybdenum isotope fractionation in soils: Influence of redox conditions, organic matter, and atmospheric inputs. *Geochimica et Cosmochimica Acta*, 162, 1–24. <https://doi.org/https://doi.org/10.1016/j.gca.2015.04.007>
- Sylwester, E.R., Hudson, E.A. and Allen, P.G. 2000. The structure of uranium (VI) sorption complexes on silica, alumina, and montmorillonite. *Geochimica et Cosmochimica Acta*, 64, 2431–2438. [https://doi.org/https://doi.org/10.1016/S0016-7037\(00\)00376-8](https://doi.org/https://doi.org/10.1016/S0016-7037(00)00376-8)
- Uvarova, Y.A., Kyser, T.K., Geagea, M.L. and Chipley, D. 2014. Variations in the uranium isotopic compositions of uranium ores from different types of uranium deposits. *Geochimica et Cosmochimica Acta*, 146, 1–17.
- Vaněk, A., Voegelin, A., Mihaljevič, Ettler, V., Trubač, M., Oborná, V., Vejvodová, K., Penížek, V., Pavlů, L., Drábek, O., Vokurková, P., Zádorová, T. and Holubík, O. 2020. Thallium stable isotope ratios in naturally Tl-rich soils. *Geoderma*, 364, 114183. <https://doi.org/https://doi.org/10.1016/j.geoderma.2020.114183>
- Voegelin, A., Wick, S., Pfenninger, N., Mangold, S., Baeyens, B. and Fernandes, M.M. 2022. Thallium adsorption onto phyllosilicate minerals. *Environmental Science: Processes & Impacts*, 24, 1343–1359. <https://doi.org/10.1039/D2EM00028H>
- Voinot, A., Kyser, T.K., Chipley, D., Valentino, M., Uvarova, Y., Layton-Matthews, D. and Leybourne, M.I. 2024. Tl, Mo and U isotopes in U-ore deposits record Earth's fundamental redox processes. *Chemical Geology*, 661, 122154. <https://doi.org/https://doi.org/10.1016/j.chemgeo.2024.122154>
- Wang, Z., Ma, J. et al. 2018. Fe (hydro) oxide controls Mo isotope fractionation during the weathering of granite. *Geochimica et Cosmochimica Acta*, 226, 1–17. <https://doi.org/https://doi.org/10.1016/j.gca.2018.01.032>
- Wick, S., Baeyens, B., Marques Fernandes, M. and Voegelin, A. 2018. Thallium adsorption onto illite. *Environmental Science & Technology*, 52, 571–580. <https://doi.org/10.1021/acs.est.7b04485>

