Location of Uranium-Rich Brines Determines the Distribution and Grade of Unconformity-Related Uranium Deposits

Xu Xu¹, Hua Lin², and Jianwen Yang¹

¹College of Material Science and Engineering, Guilin University of Technology, Guangxi, China; ²College of Environmental Science and Engineering, Guilin University of Technology, Guangxi, China; ³School of the Environment, University of Windsor, Windsor, ON, Canada

Abstract Recent fluid inclusion analysis indicates that uranium-bearing brines were present in both the sandstone and the basement at the time of ore genesis in the Athabasca Basin, Canada. However, the question of how the location of uranium-rich brines controls the formation of unconformity-related uranium deposits remains unresolved. In this study, four reactive flow modeling scenarios are designed to address this outstanding issue. Our numerical results confirm that the basement-hosting uranium-rich brines are capable of forming high-grade concentrated uranium deposits in the footwall region of the fault zone below the unconformity interface. In contrast, the sandstone-hosting uranium-rich brines lead to the formation of low-grade sheet-like uranium mineral precipitates above the sandstone layer rather than in the basement. Therefore, this study reveals that unconformity-related uranium deposits tend to be formed when the basement unit serves as the main uranium source. Taking the sandstone layer as the main uranium source, no unconformity-related uranium deposits can be formed since the resultant uranium precipitation has no spatial relation with the unconformity interface.

1. Introduction

Unconformity-related uranium deposits represent the most profitable uranium resource due to their exceptionally high grade and large tonnage (Cuney, 2009). They are located in or around the unconformities between Proterozoic basin fill and underlying Archean to lower Proterozoic metamorphic basement rocks, where faults exist (Jefferson et al., 2007). The largest and highest grade deposits of this type occur in Paleoproterozoic sedimentary basins, particularly in the Athabasca Basin, Canada, and the Northern Territory, Australia (Bruce et al., 2020).

Geological, structural, geochemical, and mineral paragenetic studies have resulted in a widely accepted model in which unconformity-related uranium deposits formed when oxidizing brines mixed with basement-derived reducing fluids or reacted with reducing minerals in the basement, at or near the regional unconformity between Proterozoic conglomeratic sandstones and Archean to Paleoproterozoic metamorphosed basement rocks that were intersected by reactivated fault systems (e.g., Fayek & Kyser, 1997). Despite this general understanding, the exact origin of the large amount of uranium remains uncertain and continues to be a debated topic. Two possible uranium sources have recently been proposed (Bruce et al., 2020), though the surface and near-surface evaporitic conditions might also enhance the uranium concentration in the brines (Richard et al., 2011). One version considers the overlying basal sediments as the source of both uranium and oxidized brines (e.g., Fayek & Kyser, 1997; Kotzer & Kyser, 1995), and the other uses the basement as the uranium source while oxidized fluids still originate from sedimentary basins (e.g., Hecht & Cuney, 2000; Mercadier et al., 2010). Recent fluid inclusion analysis exhibits the presence of uranium-rich brines in both the sandstone and the basement at the time of ore genesis in the Athabasca Basin, Canada, and the uranium concentration is over two orders (in the sandstone) and three orders (in the basement) of magnitude higher than that of typical natural geofluids (Chi et al., 2019; Richard et al., 2012, 2016). This paper does not intend to explore the origin and formation mechanism of such uranium-rich brines. Instead, it is to evaluate whether the basement-hosting uranium-rich brines or the sandstone-hosting brines are more favorable for the formation of uranium deposits from the perspective of reactive transport modeling.

Computational numerical modeling that couples thermal-hydraulic-mechanical-chemical processes has been employed to investigate ore-forming processes and controlling factors for various ore genesis scenarios (e.g., Feltrin et al., 2009; Ju & Yang, 2011; Liu et al., 2018; Liu et al., 2021; Liu & Xiao, 2020; Wang et al., 2021;
Yang et al., 2010). In association with the formation of unconformity-related uranium deposits, previous numerical studies have largely concentrated on coupling fluid flow with heat transport and/or mechanical deformation (e.g., Cui et al., 2012a, 2012b; Eldursi et al., 2020; Li et al., 2016, 2017; Pek & Malkovsky, 2016). Only very limited studies have coupled hydrothermal fluid flow with chemical reactions. For instance, Raffensperger and Garven (1995) simulated the formation of uranium deposits under equilibrium conditions with methane as a reducing agent. Aghbelagh and Yang (2014) set up more robust kinetic behavior for mineral dissolution and precipitation, and addressed the role of a faulted graphite zone. More recently, they examined the effect of fault dip angles and permeabilities on uranium mineralization (Aghbelagh & Yang, 2017). However, all the previous studies have assumed that uranium-rich brines are contained only in the sandstone layer, ignoring the fact that uranium-bearing brines are also present in the basement. Furthermore, they only emphasized the importance of fluid circulation within the sandstone layer, without addressing the role of fluid flow in the confining cover and basement unit. Therefore, this study aims to fill these knowledge gaps through evaluating the role of the location of uranium-rich brines in controlling uranium ore genesis.

2. Conceptual Model Development

As shown in Figure 1, our conceptual model is 5 km deep and 6 km wide, with the top boundary 3 km below the surface, which is based on some common features of typical deposits of this type in the Athabasca Basin. The solution domain is discretized uniformly by 160 cells vertically and horizontally, containing a confining cover, an intermediate sandstone layer, a basement unit, and an unconformity interface separating the sandstone and basement. Previous numerical studies have also employed similar layered models (e.g., Cui et al., 2012a; Li et al., 2016).

In this paper, it is assumed that aqueous methane is produced by dissolving graphite in fault zones at typical ore-forming brine temperatures, according to reaction 1:

$$C + \frac{3}{2}H_2O \rightarrow \frac{1}{2}H^+ + \frac{1}{2}HCO_3^- + \frac{1}{2}CH_4(aq).$$

(1)

which is then used as a reducing agent to reduce uranium ore (Aghbelagh & Yang, 2014, 2017; Raffensperger & Garven, 1995), following reaction 2:

$$\text{UO}_2^{2+} + \frac{3}{4}H_2O + \frac{1}{4}CH_4(aq) \rightarrow \text{UO}_2 + \frac{1}{4}HCO_3^- + \frac{9}{4}H^+.$$

(2)

In the Athabasca Basin, the maximum total thickness of sedimentary rocks was 5–7 km, although due to erosion, the thickness is currently much less (Hoeve et al., 1981). Fluid inclusion analysis of the quartz indicates a homogenization temperature of 150–170°C and a salinity of 25 wt% NaCl equivalent for the basin brine (Jefferson et al., 2007). Reverse faults play a key role in the formation of unconformity-related uranium deposits, as they focused mineralizing fluids to deposition sites and provided reducing agents (i.e., CH_4) for uranium precipitation (e.g., Jefferson et al., 2007; Kotzer & Kyser, 1990; Kyser et al., 1989). The width of the fault zones varies from tens of meters to hundreds of meters (e.g., Bruneton, 1993; Li et al., 2016). They occur predominantly in the basement, with roots up to hundreds of meters deep, generally extending into the basinal sandstone for tens to hundreds of meters (e.g., Bishop et al., 2016; Derome et al., 2005; McGill et al., 1993). In addition, the dip of the fault zones also varies from very low to near vertical (e.g., Bishop et al., 2016; Finch, 1996; Hajnal et al., 2005; Hoeve & Sibbald, 1978). Based on these constraints on the fault zones in the Athabasca Basin, a faulted graphite zone is included in the model as illustrated in Figure 1. It slopes to the right at an angle of 59°, extends 625 m vertically (20 cells vertically deep), and is 128 m thick (4 cells horizontally wide). The fault zone is rooted mainly in the basement, with a vertical extension of 562.5 m below the unconformity and 62.5 m above. Similar fault zone dimensions have been used in previous studies (e.g., Eldursi et al., 2020; Li et al., 2016). Previous studies have reported that fault offsets of the unconformity interface are common in the Athabasca Basin, and
The confining cover consists of low-permeability shallow marine sedimentary rocks (mudstone, siltstone, and sandstone), mainly composed of calcite, kaolinite, quartz, dolomite, anhydrite, muscovite, and hematite. The intermediate sandstone layer is the main aquifer for fluid circulation, and its main minerals include quartz, muscovite, K-feldspar, anhydrite, hematite, and chlorite. The basement unit is almost impermeable and is composed of quartz, muscovite, K-feldspar, chlorite, hematite, and pyrite. The fault zone appears to act as a fluid conduit based on geological evidence that fault zones of this type were reactivated after the filling of the basin (Kotzer & Kyser, 1995) and remained conductive until recently (Hoeve & Quirt, 1984). Graphite is its main mineral together with muscovite, quartz, chlorite, pyrite, and kaolinite. Compiled from the parameters previously employed in related modeling studies and the physical properties obtained from in-lab measurements of the Athabasca group sandstone samples (e.g., Aghbelagh & Yang, 2014, 2017; Cui et al., 2012a; King et al., 1988; Li et al., 2016; Raffensperger & Garven, 1995), Table 1 shows the density, porosity, permeability, and thermal conductivity of the four geological units, whereas Tables 2–5 tabulate the initial mineral volume fractions and aqueous component concentrations for each hydrostratigraphic unit. Table 6 shows the chemical parameters for the minerals involved, including the kinetic rate constant at 25°C $K_{25}$ (mol/m²s), activation energy $E_a$ (kJ/mol), and reactive surface area $A_w$ (cm²/g). Furthermore, the confining cover and the sandstone layer are assumed to be in oxidizing and acidic conditions, with log $f_{O_2} = −14.8$ and pH $= 5.3$, and log $f_{O_2} = −22.8$ and pH $= 5.1$, respectively, where $f_{O_2}$ is oxygen fugacity. The basement unit and the fault zone are assumed to be in reducing and more acidic conditions, with log $f_{O_2} = −46.8$ and pH $= 4.5$, and log $f_{O_2} = −51.3$ and pH $= 4.1$, respectively.

As shown in Table 1, the sandstone layer is assumed to be highly permeable with a permeability of $3 \times 10^{-13}$ m². This is justified by the following: (a) In-lab measurements of the physical properties of the Athabasca group sandstone samples (King et al., 1988). (b) The fluid inclusion study by Richard et al. (2016) indicates that the large-scale fluid circulation was across an entire 3–6-km-thick sedimentary pile and at least several hundreds of meters below the unconformity in the basin in the Athabasca Basin. (c) In previous ore-forming flow modeling studies, the permeabilities assigned for the sandstone unit at similar depth all have the same order of magnitude (e.g., Cui et al., 2012a, 2012b; Oliver et al., 2006; Raffensperger & Garven, 1995). In particular, Li et al. (2018) and Li et al. (2021) assigned the same permeability of $3 \times 10^{-13}$ m² for the sandstone layer in the Athabasca Basin.

The top and bottom boundaries are set at fixed temperatures of 90 and 240°C, respectively, following a typical geothermal gradient of 30°C/km. The side and bottom boundaries are assumed to be impermeable to fluid flow, but the top boundary is set at a fixed fluid pressure of 30 MPa (e.g., Cui et al., 2012a). As for the boundary conditions of the chemical domain, the top and bottom are assumed to have fixed mineral volume fractions and aqueous component concentrations, equal to those of their respective units. For the side boundaries, the normal gradients of the volume fractions and concentrations are set to zero (e.g., Aghbelagh & Yang, 2017). The initial temperature distribution is calculated using the same geothermal gradient, and the initial fluid pressure is determined on a basis of hydrostatic conditions.

| Parameter | Confining cover | Sandstone layer | Basement unit | Faulted graphite zone |
|-----------|------------------|-----------------|---------------|----------------------|
| Density (kg/m³) | 2,400 | 2,500 | 2,650 | 2,400 |
| Porosity | 0.15 | 0.2 | 0.1 | 0.2 |
| Permeability (m²) | $5 \times 10^{-16}$ | $3 \times 10^{-13}$ | $3 \times 10^{-16}$ | $1 \times 10^{-12}$ |
| Thermal conductivity (W/(m°C)) | 2.5 | 3.5 | 2.5 | 4.0 |
3. Numerical Modeling Method

Numerical computations were performed by using the commercial software package TOUGHREACT (Xu et al., 2011), which is capable of simulating chemically reactive nonisothermal flow of fluids in porous and fractured media, as well as interactions between mineral assemblages and fluids.

Governing equations include coupled nonisothermal fluid flow, solute transport, and reactive geochemistry. The flow and transport equations can be derived from the principle of mass and energy conservation. The chemical transport equations are written in terms of total dissolved concentrations of chemical components that are concentrations of their primary species plus their associated aqueous secondary species (Steefel & Lasaga, 1994; Walter et al., 1994). Advection and diffusion processes are considered for chemical transport, and diffusion coefficients are assumed to be the same for all aqueous species. The fluid density and viscosity are calculated in TOUGHREACT through an Equation of State EOS1, which is particularly applicable to hydrothermal fluid flow problems. By choosing EOS1, all fluid properties (density, specific enthalpy, viscosity, and saturated vapor pressure) are calculated from the steam table equations as given by the International Formulation Committee (1967) (Pruess et al., 1999; Xu et al., 2004).

In this study, aqueous complexation, acid-base, redox, and cation exchange are assumed to be in local equilibrium. Mineral dissolution and precipitation are assumed to proceed under kinetic conditions, with the exception of anhydrite and calcite where an equilibrium approach is employed due to their fast reaction rate when reacting with aqueous species (Xu et al., 2011). The original chemical data in TOUGHREACT (Xu et al., 2011) did not include uranium aqueous species and minerals, so were modified by adding uranium aqueous species (e.g., UO₂²⁺, UO₂Cl⁺, and UO₂Cl₂⁻) and uranium minerals (e.g., uraninite and rutherfordite). Refer to Aghbelagh and Yang (2014, 2017) for the details of the modified thermodynamic data. More details on the numerical modeling approach and the geochemical system can be found in previous publications by Xu et al. (2004, 2011) and Aghbelagh and Yang (2014, 2017).

### Table 2

| Minerals            | Volume fractions |
|---------------------|------------------|
| Calcite             | 0.44             |
| Dolomite            | 0.013            |
| Hematite            | 0.0003           |
| Anhydrite           | 0.002            |
| Kaolinite           | 0.3              |
| Muscovite           | 0.001            |
| Quartz              | 0.095            |

| Aqueous components | Concentrations (mol/L) |
|--------------------|------------------------|
| AlO₂⁻               | 0.1                    |
| Ca²⁺                | 2.8 × 10⁻²              |
| CH₄(aq)             | 0.1                    |
| Cl⁻                 | 0.1                    |
| Fe²⁺                | 7.3 × 10⁻¹⁵            |
| HCO₃⁻               | 0.4                    |
| K⁺                  | 0.022                  |
| Mg²⁺                | 0.0026                 |
| Na⁺                 | 0.1                    |
| SiO₂(aq)            | 1.0                    |
| SO₄²⁻               | 1.5 × 10⁻²              |

*Note. Based on previous studies by Raffensperger and Garven (1995) and Aghbelagh and Yang (2017).*
To represent a geochemical system in TOUGHREACT, it is required to select a subset of aqueous species as primary species. All other species are called secondary species, including aqueous complexes and minerals. Secondary species are produced from primary species through chemical reactions (Xu et al., 2004). The aqueous uranium species in the Athabasca Basin are in the form of UO$_2^{2+}$ and uranyl chloride complexes (e.g., UO$_2$Cl$^+$, and UO$_2$Cl$_2^{0}$) (e.g., Migdisov et al., 2018). Notice that UO$_2$Cl$^+$ and UO$_2$Cl$_2^{0}$ are produced from UO$_2^{2+}$ via the following two reactions: UO$_2^{2+}$ + Cl$^-$ $\rightarrow$ UO$_2$Cl$^+$ and UO$_2^{2+}$ + 2Cl$^-$ $\rightarrow$ UO$_2$Cl$_2^{0}$ (Migdisov et al., 2018). Therefore, in this study UO$_2^{2+}$ is selected as the primary species, and UO$_2$Cl$^+$ and UO$_2$Cl$_2^{0}$ are selected as the secondary species that are considered as important forms in transporting oxidized uranium in ore-forming fluids via the above-mentioned two reactions, refer to Appendix 2 in Aghbelagh and Yang (2014).

4. Results and Discussions

Richard et al. (2012, 2016) performed fluid inclusion analysis of quartz veins in barren samples coexisting with several uranium deposits in the Athabasca Basin, indicating that the concentration of aqueous uranium UO$_2^{2+}$ in the basement brines ranges from $1.0 \times 10^{-6}$ to $2.8 \times 10^{-3}$ mol/L and the average is $1.0 \times 10^{-4}$ mol/L. A recent analysis of fluid inclusions in barren sandstones in the Athabasca Basin (Chi et al., 2019) indicates that UO$_2^{2+}$ concentrations range from $2.2 \times 10^{-6}$ to $9.9 \times 10^{-5}$ mol/L, with an average of $2.5 \times 10^{-3}$ mol/L. Based on these data sets, this study assumes that the UO$_2^{2+}$ concentrations in the confining cover and fault zone are $1.0 \times 10^{-6}$ and $1.6 \times 10^{-6}$ mol/L, respectively. For the sandstone layer and basement unit, we consider the following four scenarios in order to address whether the basement-hosting uranium-rich brines or the sandstone-hosting brines favor the ore genesis based on the observed uranium concentrations.

In Scenario 1, the sandstone layer accommodates the uranium-rich brine with a UO$_2^{2+}$ concentration of $1.0 \times 10^{-4}$ mol/L, while the basement UO$_2^{2+}$ concentration is $2.5 \times 10^{-5}$ mol/L. Scenario 2 is the opposite of Scenario 1, using the measured average UO$_2^{2+}$ concentrations for the basement unit and sandstone layer. That is, the basement accommodates a UO$_2^{2+}$ concentration of $1.0 \times 10^{-4}$ mol/L, while the sandstone has a UO$_2^{2+}$ concentration of $2.5 \times 10^{-5}$ mol/L. In Scenario 3, the basement unit has a UO$_2^{2+}$ concentration of $2.8 \times 10^{-3}$ mol/L (the measured maximum basal concentration), and the sandstone UO$_2^{2+}$ concentration is

| Minerals        | Volume fractions |
|-----------------|------------------|
| Hematite        | 0.01             |
| Anhydrite       | 0.006            |
| K-feldspar      | 0.01             |
| Chlorite        | 0.0003           |
| Muscovite       | 0.02             |
| Quartz          | 0.75             |

| Aqueous components | Concentrations (mol/L) |
|--------------------|------------------------|
| AlO$_2^-$          | 0.1                    |
| Ca$^{2+}$          | 1.5                    |
| CH$_4$(aq)         | 1.0                    |
| Cl$^-$             | 5.0                    |
| Fe$^{3+}$          | $2.6 \times 10^{-11}$  |
| HCO$_3^-$          | $1.0 \times 10^{-4}$   |
| K$^+$              | 0.045                 |
| Mg$^{2+}$          | 0.48                  |
| Na$^+$             | 1.0                    |
| SiO$_2$(aq)        | 5.0                    |
| SO$_4^{2-}$        | $1.5 \times 10^{-3}$   |

*Note.* Based on previous studies by Raffensperger and Garven (1995) and Aghbelagh and Yang (2017).

Table 3

Initial Mineral Volume Fractions and Aqueous Component Concentrations for the Sandstone Layer
In Scenario 4, the sandstone layer accommodates a UO$_2^{2+}$ concentration of $2.8 \times 10^{-3}$ mol/L, and the basement UO$_2^{2+}$ concentration is $1.0 \times 10^{-6}$ mol/L (the measured minimum basal concentration). All other conditions remain the same in these four scenarios.

### 4.1. Scenario 1

Figure 2a illustrates the fluid flow vectors at 300,000 years. The max flow rates in the confining cover, sandstone layer, basement unit, and fault zone are equal to $1.83 \times 10^{-3}$, 1.50, $1.14 \times 10^{-3}$, and 1.52 m/year, respectively. Figure 2b shows an enlarged view surrounding the fault zone, indicating that the left half of the fault zone carries a downflow and the right half carries an upflow. Flow vectors in the cover and basement unit are too small to be identified. To better visualize them, the original flow vectors in Figure 2a are sparsely sampled. We also used a constant vector length to allow direction of flow to be seen and used a color scale to represent differences in the magnitude of flow velocity, as shown in Figure 2c. It can be seen from Figures 2a and 2c that there are four convection cells developed in the sandstone layer, with two upwelling flow zones along the side boundaries flanked by two downwelling zones. The dominant upwelling zone is shifted to the left by about 500 m from the fault zone, which is due to the “downslope” flow over the fault offset of the unconformity that is directed toward the left, see Figure 2b. As such, the clockwise convection cell on the right is greater in size than the anticlockwise convection cell on the left.

The basinal fluid travels upward through the three upwelling zones. When it reaches the top of the sandstone layer, most of it diverges to the left and right and then flows downward through the two downwelling zones. The rest of the basinal fluid penetrates across the sandstone-cover interface to mix with the cover fluid, which also moves upward but at a significantly lower rate (max $1.83 \times 10^{-3}$ m/year in the cover vs. 1.50 m/year in the sandstone). The cover fluid then diverges and flows downward to join the downwelling flow zones in the sandstone layer. On the other hand, as the basinal fluid descends through the downwelling zones to the bottom of the sandstone layer, most of it diverges and flows parallel to the unconformity interface and then merges with the upwelling zones. The rest seeps...
across the sandstone-basement interface to mix with the basement brine, which also moves downward but at a much lower rate (max $1.14 \times 10^{-3}$ m/year in the basement vs. 1.50 m/year in the sandstone). The basement brine then diverges and flows upward to join the upwelling zones in the sandstone layer. It is also noticed from Figure 2c that almost all basement brine of the entire basement is concentrated in the footwall of the fault zone below the unconformity, except for some shallow brine near the side boundaries that discharges to the sandstone layer. Figure 2d illustrates the temperature distribution at 300,000 years, which has an asymmetric mush-room shape due to the aforementioned fluid circulation within the sandstone layer. The fluid flow in the cover and basement has a negligible effect on the temperature distribution, as evidenced by the nearly evenly spaced isotherms in these two units. However, both the cover flow and basement flow are important for uranium mineralization, although their rates are nearly three orders of magnitude lower than the rate of the basinal flow.

Based on the oxygen fugacity $f_{O_2}$ assigned to each geologic unit in Section 2, two oxidation-reduction fronts occur. One is the sandstone-cover interface and the other is the sandstone-basement interface (i.e., the unconformity). At early time, uranium precipitation occurs along these two fronts when the basinal fluid percolates across the sandstone-cover interface and reacts with the more oxidizing cover fluid and when the basinal fluid infiltrates the basement and reacts with the reducing basement brine, respectively. Figure 3a shows the precipitated uraninite at 5,000 years, which is characterized by a horizontal sheet-like shape immediately above the sandstone-cover interface and below the unconformity. Note that the uraninite precipitation above the sandstone layer is stronger than that below the unconformity. The difference in amounts of uranium mineralization may be caused by the permeabilities assigned. As listed in Table 1, the cover is

Table 5
Initial Mineral Volume Fractions and Aqueous Component Concentrations for the Faulted Graphite Zone

| Minerals      | Volume fractions |
|---------------|------------------|
| Graphite      | 0.085            |
| Chlorite      | 0.001            |
| Kaolinite     | 0.0007           |
| Muscovite     | 0.42             |
| Pyrite        | 0.001            |
| Quartz        | 0.29             |

Aqueous components

| Components     | Concentrations (mol/L) |
|----------------|------------------------|
| $\text{AlO}_2^-$ | 0.1                    |
| $\text{Ca}^{2+}$ | 0.1                    |
| $\text{CH}_4\text{(aq)}$ | 4.0                  |
| $\text{Cl}^-$   | 3                      |
| $\text{Fe}^{3+}$ | 0.0005                 |
| $\text{HCO}_3^-$ | $1.2 \times 10^{-4}$  |
| $\text{K}^+$    | 0.038                  |
| $\text{Mg}^{2+}$ | 0.88                   |
| $\text{Na}^+$   | 1.0                    |
| $\text{SiO}_2\text{(aq)}$ | 0.5                  |
| $\text{SO}_4^{2-}$ | $1.0 \times 10^{-3}$  |

Note. Based on previous studies by Raffensperger and Garven (1995) and Aghbelagh and Yang (2017).

Table 6
Chemical Parameters of the Minerals Involved, Where $K_{25}$ Is Kinetic Rate Constant at 25°C, $E_a$ Is Activation Energy, and $A_m$ Is Reactive Surface Area

| Minerals     | $K_{25}$ (mol/m²s) | $E_a$ (kJ/mol) | $A_m$ (cm²/g) |
|--------------|--------------------|---------------|---------------|
| Calcite      | at equilibrium     | at equilibrium| at equilibrium|
| Dolomite     | $2.95 \times 10^{-8}$ | 52.2 | 9.8            |
| Hematite     | $2.514 \times 10^{-15}$ | 66.2 | 12.87          |
| Anhydrite    | at equilibrium     | at equilibrium| at equilibrium|
| Kaolinite    | $1.0 \times 10^{-13}$ | 62.76 | 151.6          |
| Muscovite    | $1.0 \times 10^{-13}$ | 62.76 | 151.6          |
| Chlorite     | $1.0 \times 10^{-13}$ | 62.76 | 151.6          |
| K-feldspar   | $1.0 \times 10^{-12}$ | 67.83 | 9.8             |
| Pyrite       | $1.0 \times 10^{-11}$ | 67.83 | 12.87          |
| Rutherfordine| $1.0 \times 10^{-13}$ | 67.83 | 9.8             |
| Uraninite    | $1.0 \times 10^{-13}$ | 67.83 | 9.8             |
| Graphite     | $1.0 \times 10^{-12}$ | 67.83 | 9.8             |
| Quartz       | $1.258 \times 10^{-14}$ | 87.5 | 9.8             |

Note. Based on previous studies by Raffensperger and Garven (1995) and Aghbelagh and Yang (2017).
assigned a permeability that is slightly higher than that of the basement, which facilitates more basinal fluid percolation into the cover. Figures 3b, 3c and 3d illustrates the precipitated uraninite at 100,000 years, 200,000 years, and 300,000 years, respectively. As time progresses, more basinal uranium-rich fluid seeps into the overlying cover and the underlying basement, resulting in increased uranium deposition. The max volume fractions of the precipitated uraninite in Figures 3b, 3c and 3d are $3.73 \times 10^{-6}$, $3.75 \times 10^{-6}$, and $4.05 \times 10^{-6}$, respectively. Starting from 100,000 years, the precipitated uraninite in the confining cover is mainly distributed just above the sandstone-cover interface between the upwelling and downwelling zones, and it is also distributed along narrow bands in the downwelling zones close to the side boundaries, representing the converging belts of the percolated basinal fluid with the more oxidizing cover fluid, see Figure 2c. As mentioned above, most of the basement brine is focused in the footwall region of the fault zone below the unconformity. As a result, starting from 100,000 years the uranium deposition in the basement is concentrated in the footwall. Again, the precipitated uraninite in the basement grows over time, see Figures 3a–3d. However, because the uranium-rich brine is hosted in the sandstone layer, the volume fraction and size of the precipitated uraninite in the basement are always smaller than in the cover.

4.2. Scenario 2

Figure 4a shows the precipitated uraninite at 5,000 years, indicating that a wide range of uraninite precipitation occurs immediately below the unconformity with a max volume fraction of $2.52 \times 10^{-7}$. Uraninite mineralization also occurs above the sandstone-cover interface but at a much lower volume fraction because the uranium-rich
brine is now hosted in the basement. The depletion of UO$_2^{2+}$ from uraninite precipitation results in a decrease in its concentration in the basement near the unconformity. Thus, at late time the basement brine becomes more important as it drives deep aqueous uranium to the shallow region. As shown in Figure 2c, the basement brine is focused dominantly in the footwall region of the fault zone, allowing deep aqueous uranium to rise and react with shallow oxidizing fluid that seeps into the basement from the overlying sandstone layer. Figure 4b illustrates the precipitated uraninite at 100,000 years. Now uranium deposition is concentrated in the footwall with a max volume fraction of $3.17 \times 10^{-6}$. Thus, the footwall region seems to represent a favorable structural trap for uranium deposition. As time increases, more of the basement brine is concentrated into the structural trap, bringing more aqueous uranium from the depths. This increases the size and volume fraction of the precipitated uraninite. Figure 4c shows the precipitated uraninite at 200,000 years with a max volume fraction of $8.99 \times 10^{-6}$, and Figure 4d illustrates the precipitated uraninite at 300,000 years with a max fraction of $1.08 \times 10^{-5}$. The uranium deposit is located in the same structural trap but the size and volume fractions increase slightly from 200,000 to 300,000 years.

Comparing Scenario 2 with Scenario 1 reveals that the basement-bearing uranium-rich brine enables the formation of more concentrated, higher grade uranium deposits in the footwall region. In contrast, the sandstone-bearing uranium-rich brine leads to sheet-like uranium mineralization above the sandstone-cover interface but at a much lower grade.

4.3. Scenario 3

Figures 5a and 5b illustrates the precipitated uraninite at 200,000 and 300,000 years, with max volume fractions of $2.75 \times 10^{-4}$ and $3.06 \times 10^{-4}$, respectively. As in Scenario 2, the uranium deposit is again formed in the same...
structural trap but the volume fraction of precipitated uraninite is increased by about 30 times, as evidenced by comparing Figures 5a and 5b with Figures 4c and 4d. This is because the $\text{UO}_2^{2+}$ concentration in the basement fluid is now 28 times higher than in Scenario 2. The precipitated uraninite in the confining cover has a negligible volume fraction in comparison with that in the basement unit because the sandstone layer has a lower $\text{UO}_2^{2+}$ concentration of $2.2 \times 10^{-6}$ mol/L in this scenario compared with Scenario 2.

### 4.4. Scenario 4

Figures 6a and 6b illustrate the precipitated uraninite at 200,000 and 300,000 years, respectively, with a max volume fraction of $1.03 \times 10^{-4}$. As in Scenario 1, the predominant uraninite precipitation occurs immediately above the sandstone-cover interface and along the converging belts in the downwelling zones in the cover. The max volume fraction is increased by about 30 times, and this is because the $\text{UO}_2^{2+}$ concentration in the sandstone layer is 28 times higher than in Scenario 1. The volume fraction of the precipitated uraninite in the footwall region is reduced substantially because the basement brine is now assigned a lower $\text{UO}_2^{2+}$ concentration of $1.0 \times 10^{-6}$ mol/L in comparison with $2.5 \times 10^{-5}$ mol/L in Scenario 1.

### 5. Conclusions

Reactive mass transport modeling has been conducted to evaluate the role of the source location of uranium-bearing brines in controlling uranium ore genesis. Our results from four numerical case studies show that the fluid circulation in each geological unit is important for temperature distribution, transport of aqueous components, and uranium deposition. Flow rates in the confining cover and the basement unit are about three orders of magnitude lower than those in the sandstone layer and fault zone. However, fluid flow in the cover and basement is critical
to the genesis of uranium deposits. At early time, uraninite precipitation initially occurs immediately above the sandstone-cover interface and below the unconformity, but at a very low volume fraction. At later time, different locations of uranium-rich brines result in different distributions and grades of precipitated uraninite. When the sandstone layer accommodates the uranium-rich brine, the predominant uranium precipitation occurs in the confining cover rather than in the basement unit since it is relatively easier for the basinal fluid to percolate across the sandstone-cover interface than across the sandstone-basement interface. As a result, the precipitated uraninite takes on a sheet-like shape directly above the sandstone layer and between the upwelling and downwelling zones in the cover. When the basement unit holds the uranium-rich brine, the predominant uranium precipitation occurs in the footwall of the fault zone below the unconformity because the basement reducing brine is mainly focused in such a favorite trap to react with the basinal oxidizing fluid being percolated from the overlying sandstone layer. As a result, uraninite deposition is concentrated in the footwall region with a much higher volume fraction. Therefore, our numerical results reveal that the scenarios with the basement unit serving as the main uranium source favor the formation of unconformity-related uranium deposits, while the scenarios

Figure 5. Numerical results of the precipitated uraninite and volume fraction for Scenario 3: (a) at 200,000 years, and (b) at 300,000 years.
with the sandstone layer as the main uranium source do not support the formation of unconformity-related uranium deposits because the precipitated uraninite is in the confining cover and has no spatial relation with the unconformity interface.

Data Availability Statement

Reactive flow modeling was conducted by using the commercial software package TOUGHREACT. Details of the software and modeling methodology can be found in published journal articles by Xu et al. (2011) and Aghbelagh and Yang (2014, 2017). All data used in this research are tabulated in Tables 1–6. No other data were used nor created for this research. The data tables are also available at Xu et al. (2022).
Acknowledgments
This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Discovery Grant to Jianwen Yang. Constructive reviews and comments from two anonymous reviewers and Dr. John Molson and Dr. Xiangchong Liu greatly improved the paper.

References
Aghbelagh, Y. B., & Yang, J. (2014). Effect of graphite zone in the formation of unconformity-related uranium deposits: Insights from reactive mass transport modeling. Journal of Geochemical Exploration, 144, 12–27. https://doi.org/10.1016/j.jgeoex.2014.01.020
Aghbelagh, Y. B., & Yang, J. (2017). Role of hydrodynamie factors in controlling the formation and location of unconformity-related uranium deposits: Insights from reactive-flow modeling. Hydrogeology Journal, 25(2), 465–486. https://doi.org/10.1007/s10040-016-1485-9
Bishop, C., Mainville, A., & Yesniki, L. (2016). Cigar Lake operation Northern Saskatchewan, Canada. Cameco Technical Report. (pp. 1–164).
Bruce, M., Kreuzer, O., Wilde, A., Buckingham, A., Butera, K., & Bierlein, F. (2020). Unconformity-type uranium systems: A comparative review and predictive modelling of critical genetic factors. Minerals, 10(9), 738–793. https://doi.org/10.3390/min10090738
Bruneton, P. (1993). Geological environment of the Cigar Lake uranium deposit. Canadian Journal of Earth Sciences, 30(4), 653–673. https://doi.org/10.1139/e93-054
Chi, G., Chu, H., Pettis, D., Potter, E., Jackson, S., & Williams-Jones, A. (2019). Uranium-rich diagenetic fluids provide the key to unconformity-related uranium mineralization in the Athabasca Basin. Scientific Reports, 9, 1–10. https://doi.org/10.1038/s41598-019-42052-0
Cui, T., Yang, J., & Samson, I. M. (2012a). Solve transport across basement/cover interfaces by buoyancy-driven theromhaline convection: Implications for the formation of unconformity-related uranium deposits. American Journal of Science, 312(9), 994–1027. https://doi.org/10.2475/09.2012.02
Cui, T., Yang, J., & Samson, I. M. (2012b). Tectonic deformation and fluid flow: Implications for the formation of unconformity-related uranium deposits. Economic Geology, 107(1), 147–163. https://doi.org/10.2113/gsecongeo.107.1.147
Cuney, M. (2009). The extreme diversity of uranium deposits. Mineralium Deposita, 44(1), 3–9. https://doi.org/10.1007/s00126-008-0223-1
Deronde, D., Cathelineau, M., Cuney, M., Fabre, C., Lhomme, T., & 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(8), 1529–1545. https://doi.org/10.2113/gsecongeo.100.8.1529
Eldursi, K., Chi, G., Bethune, K., Li, Z., Ledru, P., & Quiet, D. (2020). New insights from 2- and 3-D numerical modelling on fluid flow mechanisms and geological factors responsible for the formation of the world-class Cigar Lake uranium deposit, eastern Athabasca Basin, Canada. Mineralium Deposita, 56(7), 1365–1388. https://doi.org/10.1007/s00126-020-00799-5
Fayek, M., & Kyser, T. K. (1997). Characterization of multiple fluid events and rare-Earth-element mobility associated with formation of unconformity-type uranium deposits in the Athabasca Basin, Saskatchewan. The Canadian Mineralogist, 35, 627–658.
Feltrin, L., McLelland, J. G., & Oliver, N. H. S. (2009). Modelling the giant, Zn–Pb–Ag Century deposit, Queensland, Australia. Computers & Geosciences, 35(1), 108–133. https://doi.org/10.1016/j.cageo.2007.09.002
Finch, W. (1996). Uranium provinces of North America: Their definition, distribution, and models. US Geological Survey Bulletin, 2141, 1–15.
Hajnal, Z., Györfi, I., Annesley, I. R., White, D. J., Powell, B., & Koch, R. (2005). Seismic reflections outline complex structural setting of the uranium in the Athabasca Basin. In Uranium production and raw materials for the nuclear fuel cycle: Supply and demand, economics, the environment and energy security. Extended synopses, report IAEA-CN-128, proceedings of an international symposium held in Vienna, Austria, 20–24 June 2005.
Harvey, S. E., & Bethune, K. M. (2007). Context of the Deilmann orebody, Key Lake mine, Saskatchewan. In EXTECH IV: Geology and uranium exploration technology of the protoreczic Athabasca Basin, Saskatchewan and Alberta (Vol. 588, pp. 249–66). Geological Survey of Canada Bulletin.
Hecht, L., & Cuney, M. (2000). Hydrothermal alteration of monazite in the Precambrian crystalline basement of the Athabasca Basin (Saskatchewan, Canada): Implications for the formation of unconformity-related uranium deposits. Mineralium Deposita, 35(8), 791–795. https://doi.org/10.1007/s001260050280
Hoeve, J., & Quiet, D. H. (1984). Mineralization and host rock alteration in relation to clay mineral diagenesis and evolution of the middle Proterozoic, Athabasca Basin, Northern Saskatchewan, Canada. Saskatchewan Research Council Technical Publication, 22, 76–89.
Hoeve, J., & Sibbald, T. I. (1978). On the Genesis of Rabbit Lake and other unconformity-type uranium deposits in Northern Saskatchewan, Canada. Economic Geology, 73(8), 1450–1473. https://doi.org/10.2113/gsecongeo.73.8.1450
International Formulation Committee. (1967). A formulation of the thermodynamic properties of ordinary water substance. IFC Secretariat.
Jefferson, C. W., Thomas, D. J., Gandhi, S. S., Ramakers, P., Delaney, G., Brisbin, D., et al. (2007). Unconformity associated uranium deposits of the Athabasca Basin, Saskatchewan and Alberta. In W. D. Goodfellow (Ed.), Mineral deposits of Canada: A Synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods (Vol. 5, pp. 273–305). Geological Association of Canada, Mineral, Division, Deposits Division, Special Publication.
Ju, M., & Yang, J. (2011). Numerical modeling of coupled fluid flow, heat transport and mechanic deformation: An example from the Chanchping ore district, South China. Geoscience Frontiers, 2, 577–582.
King, M. S., Stauffer, M. R., Yang, H. J. P., & Zhajnal, Z. (1988). Elastic-wave and related properties of clastic rocks from the Athabasca Basin, Western Canada. Canadian Journal of Exploration Geophysics, 24, 110–116.
Kotzer, T. G., & Kyser, T. K. (1990). The use of stable and radiogenic isotopes in the identification of fluids and processes associated with unconformity-type uranium ore deposits. Geological Society of Canada Special Publication, 10, 115–131.
Kotzer, T. G., & Kyser, T. K. (1995). Petrogenesis of the Proterozoic Athabasca Basin, northern Saskatchewan, Canada, and its relation to diagenesis, hydrothermal uranium mineralization and paleohydrology. Chemical Geology, 120(1–2), 45–89. https://doi.org/10.1016/0009-2541(94)00114-n
Kyser, T. K., Wilson, M. R., & Ruhrmann, G. (1989). Stable isotope constraints on the role of graphite in the Genesis of unconformity-type uranium deposits. Canadian Journal of Earth Sciences, 26, 490–498.
Li, Z., Chi, G., & Bethune, K. (2016). The effects of basement faults on thermal convection and implications for the formation of unconformity-related uranium deposits in the Athabasca Basin. Canada. Geofluids, 4(4), 729–751. https://doi.org/10.1111/gef.12180
Li, Z., Chi, G., Bethune, K., Thomas, D., & Zaluski, G. (2017). Structural controls on fluid flow during compressional reactivation of basement faults: Insights from numerical modeling for the formation of unconformity-related uranium deposits in the Athabasca Basin, Canada. Economic Geology, 112(2), 451–466. https://doi.org/10.2113/econgeo.112.2.451
Li, Z., Chi, G., Bethune, K. M., Eldursi, K., Quiet, D., Ledru, P., & Gudmundsson, G. (2018). Numerical simulation of strain localization and its relationship to formation of the Sue unconformity-related uranium deposits, Eastern Athabasca Basin, Canada. Ore Geology Reviews, 101, 17–31. https://doi.org/10.1016/j.oregeorev.2018.07.004
Li, Z., Chi, G., Bethune, K. M., Eldursi, K., Quiet, D., Ledru, P., & Thomas, D. (2021). Interplay between thermal convection and compressional fault reactivation in the formation of unconformity-related uranium deposits. Mineralium Deposita, 56(7), 1389–1404. https://doi.org/10.1007/s10114-020-01111-6
Liu, X. C., Ma, Y., Xing, H., & Zhang, D. H. (2018). Chemical responses to hydraulic fracturing and wolframite precipitation in the vein-type tungsten deposits of southern China. *Ore Geology Reviews, 102*, 44–58. [https://doi.org/10.1016/j.oregeorev.2018.08.027](https://doi.org/10.1016/j.oregeorev.2018.08.027)

Liu, X. C., & Xiao, C. H. (2020). Wolframite solubility and precipitation in hydrothermal fluids: Insight from thermodynamic modeling. *Ore Geology Reviews, 117*, 103289. [https://doi.org/10.1016/j.oregeorev.2019.103289](https://doi.org/10.1016/j.oregeorev.2019.103289)

Liu, X. C., Xiao, C. H., Zhang, S., & Chen, B. (2021). Numerical modeling of deformation at the Baiyun gold deposit, Northeastern China: Insights into the structural controls on mineralization. *Journal of Earth Sciences, 32*(11), 174–184. [https://doi.org/10.1007/s12583-020-1388-5](https://doi.org/10.1007/s12583-020-1388-5)

McGill, B., Marlatt, J., Matthews, R., Sopuck, V., Homeniuk, L., & Hubregtse, J. (1993). The P2 North uranium deposit Saskatchewan, Canada. *Exploration And Mining Geology*, 2, 321–331.

Mercadier, J., Richard, A., Boiron, M. C., Cathelineau, M., & Cuney, M. (2010). Migration of brines in the basement rocks of the Athabasca Basin through microfracture networks (P-Patch U deposit, Canada). *Lithos*, 115, 121–136.

Migdisov, A. A., Boukhalfa, H., Timofeev, A., Runde, W., Roback, R., & Williams-Jones, A. E. (2018). A spectroscopic study of the Athabasca Basin through microfracture networks. *P-Patch U deposit, Canada*. [https://doi.org/10.2113/gsecongeo.101.1.1](https://doi.org/10.2113/gsecongeo.101.1.1)

Pek, A. A., & Malkovsky, V. I. (2016). Linked thermal convection of the basement and basal fluids in formation of the unconformity-related uranium deposits in the Athabasca Basin, Saskatchewan, Canada. *Geofluids, 16*(5), 925–940. [https://doi.org/10.1111/gfl.12196](https://doi.org/10.1111/gfl.12196)

Pruess, K., Olsenburg, C., & Morigi, G. (1999). TOUGH2 user’s guide, version 2.0: Lawrence Berkeley laboratory report LBL-43134.

Raffensperger, J. P., & Garven, G. (1995). The formation of unconformity-type uranium ore deposits 2. coupled hydrochemical modeling. *American Journal of Science, 295*(5), 639–696. [https://doi.org/10.2475/ajs.295.6.639](https://doi.org/10.2475/ajs.295.6.639)

Richard, A., Banks, D. A., Mercadier, J., Boiron, M. C., Cuney, M., & Cathelineau, M. (2011). An evaporated seawater origin for the ore-forming brines in unconformity-related uranium deposits (Athabasca Basin, Canada): Cl/Br and δ37Cl analysis of fluid inclusions. *Geochimica et Cosmochimica Acta, 295*(10), 2792–2810. [https://doi.org/10.1016/j.gca.2011.02.026](https://doi.org/10.1016/j.gca.2011.02.026)

Richard, A., Cathelineau, M., Boiron, M. C., Mercadier, J., Banks, D. A., & Cuney, M. (2016). Metal-rich fluid inclusions provide new insights into unconformity-related U deposits (Athabasca Basin and Basement, Canada). *Mineral Deposition, 51*(2), 249–270. [https://doi.org/10.1007/s00126-015-0601-4](https://doi.org/10.1007/s00126-015-0601-4)

Richard, A., Rozzypal, C., Mercadier, J., Cuney, M., Boiron, M. C., Cathelineau, M., & Banks, D. A. (2012). Giant uranium deposits formed from exceptionally uranium-rich acidic brines. *Nature Geoscience, 5*(2), 142–146. [https://doi.org/10.1038/ngeo1338](https://doi.org/10.1038/ngeo1338)

Steele, C. I., & Lasaga, A. C. (1994). A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with applications to reactive flow in single phase hydrothermal system. *American Journal of Science, 294*(5), 529–592. [https://doi.org/10.2475/ajs.294.5.529](https://doi.org/10.2475/ajs.294.5.529)

Walter, A. L., Frind, E. O., Blows, D. W., Pteck, C. J., & Molson, J. W. (1994). Modeling of multicomponent reactive transport in groundwater: 1. Model development and evaluation. *Water Resources Research, 30*(11), 3137–3148. [https://doi.org/10.1029/94wr00955](https://doi.org/10.1029/94wr00955)

Wang, Y., Chi, G., Li, Z., & Bosman, S. (2021). Large-scale thermal convection in sedimentary basins revealed by coupled quartz cementation-dissolution distribution pattern and reactive transport modeling A case study of the Proterozoic Athabasca Basin (Canada). *Earth and Planetary Science Letters, 574*, 117168. [https://doi.org/10.1016/j.epsl.2021.117168](https://doi.org/10.1016/j.epsl.2021.117168)

Xu, T., Sonnenthal, E., Spycher, N., & Pruess, K. (2004). TOUGHREACT user's guide: A simulation program for nonisothermal multiphase reactive geochemical transport in variably saturated geologic media: Earth Sciences Division. Lawrence Berkeley National Laboratory.

Xu, T., Spycher, N., Sonnenthal, E., Zhang, G., Zheng, L., & Pruess, K. (2011). TOUGHREACT version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions. *Computers & Geosciences, 37*(6), 763–774. [https://doi.org/10.1016/j.cageo.2010.10.007](https://doi.org/10.1016/j.cageo.2010.10.007)

Xu, X., Lin, H., & Yang, J. (2022). Location of uranium-rich brines determines the distribution and grade of unconformity-related uranium deposits. *Earth and Space Science* [Dataset]. Zenodo. [https://doi.org/10.5281/zenodo.6611439](https://doi.org/10.5281/zenodo.6611439)

Yang, J., Feng, Z., Luo, X., & Chen, Y. (2010). Three-dimensional numerical modeling of salinity variations in driving basin scale ore-forming fluid flow: Example from Mount Isa Basin, northern Australia. *Journal of Geochemical Exploration, 106*(1–3), 236–243. [https://doi.org/10.1016/j.jgeexplo.2009.12.004](https://doi.org/10.1016/j.jgeexplo.2009.12.004)