O, U, and Pb isotopic and chemical variations in uraninite: Implications for determining the temporal and fluid history of ancient terrains

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ABSTRACT

Chemical and U, Pb, and O isotopic compositions have been measured on paragenetically well-characterized uraninite and pitchblende minerals from Proterozoic, high-grade U deposits of the unconformity type and complex vein type U deposits in northern Saskatchewan, Canada. Ca and Si contents in samples of pristine uraninite and pitchblende generally increase with increasing δ18O values in the U minerals, which span a range from -28 to -2.3‰. Discordant U-Pb and chemical U-Pb ages of the uraninite and pitchblende minerals vary from 142 to 940 and 252 to 1389 Ma, respectively, with the youngest ages in the uraninites and pitchblendes having the highest Si and Ca contents and most 18O-rich isotopic compositions. Pb-Pb ages of spatially associated S-bearing minerals in late-formed fractures are similar to those of uraninite. In contrast, 207Pb/206Pb ages for the uraninite and pitchblende minerals range between 1018 and 1428 Ma, which are comparable to a Rb-Sr isochron age of 1477 ± 57 Ma on illite coeval with the U minerals, and, hence, the 207Pb/206Pb ages approximate those of formation for the U minerals. Large discrepancies between U/Pb ages and the 207Pb/206Pb ages indicate the U minerals have variably recrystallized, resulting in recent Pb loss.

Illite and other silicate minerals coeval with the U minerals have formed at temperatures of 200 °C. At this temperature, the uraninite and pitchblende minerals have δ18O values that would have resulted from equilibration with fluids having δ18O values of -20 to -11‰. Such fluids are substantially 18O-depleted relative to the O isotopic composition of 4 ± 2‰ inferred from coeval silicates for the original fluids that formed the U ore but are similar to the isotopic compositions of Mesozoic and Cenozoic meteoric water in the area. The combination of low δ18O values, which vary with chemical contents, variably reset U-Pb ages, and older 207Pb/206Pb ages in the uraninite and pitchblende minerals are evidence that the minerals in the deposits of both the unconformity type and complex vein type have interacted extensively with meteoric water since original formation in the Proterozoic and demonstrate the utility of using U minerals for tracing fluid histories of complex terrains.

Chemical and isotopic systematics of U minerals

Uraninite (UO2 + Th and REE: Steacy and Kaiman, 1978) and pitchblende (UO2 - Th and REE: Steacy and Kaiman, 1978) are U minerals that commonly occur in relatively low abundances in many geologic terrains (Dyck, 1978; McMillan, 1978). However, because of their extreme solubilities in oxidizing fluids, these minerals are geochemically unstable in most surficial environments and are particularly susceptible to later alteration by meteoric fluids. This is evident in petrographic and isotopic studies on U minerals from near-surface and fault-controlled U deposits, where extensive alteration of uraninite and pitchblende by meteoric water has resulted in recrystallization, radiogenic Pb loss, and the resetting of U-Pb ages (Dyck, 1978; Baadsgaard et al., 1984). The dominant constituents of uraninite and pitchblende are U and O, varying amounts of Pb produced by decay of U, and Si and Ca. As these minerals contain O, U, and Pb in sufficient concentrations for stable and radiogenic isotopic analysis, they should be ideal for discerning the ages of crystallization and physiochemical conditions existing at the time of their formation. Radiogenic decay of U to Pb in U minerals results in two coupled isotopic systems, 235U/207Pb and 238U/206Pb, which, because of different decay rates of the two isotopes of U, yields three geochronometers: 207Pb/235U, 206Pb/238U, and 207Pb/206Pb (Faure, 1986). If the U minerals behaved as closed systems, allowing neither Pb loss nor U gain, U-Pb ages should be concordant. However, because of the geochemical behavior of uranium oxide minerals, most studies indicate that few have remained closed systems.
Carl et al., 1992; Cumming and Krstic, 1992). Isotopic compositions of trace amounts of Pb in sulfides, carbonate, and silicate gangue minerals spatially associated with U minerals are commonly anomalous and incongruent with a promordial Pb growth curve, indicating that these gangue minerals have incorporated varying amounts of radiogenic Pb (e.g., Kotzer and Kyser, 1990a; Carl et al., 1992). The $206\text{Pb}/204\text{Pb}$ and $207\text{Pb}/204\text{Pb}$ ratios in these minerals can be used to discern the timing of the alteration of associated U minerals.

Although theoretical O isotope fractionation factors have been calculated for the systems uraninite-H$_2$O and pitchblende-H$_2$O (Hattori and Halas, 1982; Zheng, 1991), there are very few systematic studies on the O isotopic compositions of uranium oxides. Those that have been reported are from Hattori et al. (1978). In sedimentary basins, which have had a protracted hydrogeologic history involving isotopically and chemically distinct fluids (e.g., Longstaffe and Ayalon, 1990; Kotzer, 1993), determination of U, Pb, and O isotopic ratios in uraninite and pitchblende minerals and in spatially associated gangue minerals of varying paragenesis can be used not only to trace the fluids from which these minerals originally formed and which have interacted with them since their crystallization, but, in addition, to determine the ages at which these fluid events occurred.

In this study, petrographically and paragenetically characterized uraninite and pitchblende and spatially associated sulfide and sulfate minerals were selected from a number of high-grade U deposits of the unconformity type in the Proterozoic Athabasca Basin and from vein-type U deposits in the Beaverlodge area of northern Saskatchewan (Fig. 1). The $18\text{O}/16\text{O}$, $206\text{Pb}/238\text{U}$, $207\text{Pb}/235\text{U}$, $207\text{Pb}/206\text{Pb}$, $206\text{Pb}/204\text{Pb}$, and $207\text{Pb}/206\text{Pb}$ ratios and chemical compositions are used to assess whether the U- and S-bearing minerals indicate a time-fluid history in the Athabasca Basin comparable to that already established by stable and radiogenic isotope analysis on coeval clay, silicate, and hematite minerals (Kotzer and Kyser, 1992; Rees, 1992; Kotzer, 1993).

**Geologic constraints and fluid characteristics of Athabasca and Beaverlodge areas**

Stable isotopic, fluid inclusion, and petrographic studies on clay and silicate gangue mineral assemblages associated with the middle-Proterozoic unconformity-type U ± Ni ± Co ± As ± Cu ± Zn ore deposits in the Athabasca Basin, northern Saskatchewan, Canada (Fig. 1), indicate the U ore formed as a result of mixing between isotopically and chemically distinct basement and basinal fluids at temperatures of 200 °C in basement-rooted fault zones that intersect a pre-Athabasca unconformity and project into the overlying sandstones (Hoeve and Sibbald, 1978; Wallis et al., 1983; Wilson and Kyser, 1987; Kotzer and Kyser, 1990a; Kotzer and Kyser, 1992). Substantial accumulations of high-grade U ore are located within diagenetically altered sandstones at the intersection of the faults, the unconformity, and the overlying sandstones. Textural relationships in the U ore indicate a complex fluid history of these deposits, as early euhedral uraninite is commonly replaced by botryoidal and fractured pitchblende and later-formed coffinite [U(SiO$_4$)$_r$·(OH)$_r$]$_x$: Steacy and Kaiman, 1978).

Field relationships and petrographic evidence indicate that illite is coeval with the high-grade U minerals in the basin (Hoeve and Quirt, 1984; Wilson and Kyser, 1987; Kotzer, 1993). The illites have Rb-Sr isochron and model ages of 1477 ± 57 and 957 Ma, respectively. Similarly, ages of approximately 900 and 1450–1600 Ma have been determined on diagenetic hematite that are coeval with the illites (Fig. 3 in Kotzer et al., 1992). Both the radiometric and paleomagnetic ages represent the timing of high-temperature basinal fluid migration and hydrothermal alteration associated with formation of the U ore.
deposits (Kotzer and Kyser, 1992; Kotzer, 1993). In contrast, K-Ar ages on illites coeval with the U ore have been variably reset and range between approximately 400 and 1500 Ma. Those illites with the youngest K-Ar ages have the lowest δD values, which approach the δD values of post-Cretaceous waters in the area, suggesting the illites have also been affected by a relatively late-stage fluid event (Wilson and Kyser, 1987; Wilson et al., 1987; Kotzer and Kyser, 1991, 1992).

Stable and radiogenic isotopic compositions of diagenetic illite and dravite and microthermometric analyses on diagenetic quartz in altered sandstones distal and proximal to the U deposits indicate that the diagenetic basin fluids flowed laterally in basin sandstone aquifers that were widespread throughout the entire Athabasca Basin (Kotzer, 1993). Stable isotopic compositions of magnesium chloride that formed from interactions between the basement fluids and rocks in the vicinity of the faults imply that the basement fluids in the faults were rock dominated, with H2O/rock ratios between approximately 0.3 and 0.6 (Wilson and Kyser, 1987; Kotzer and Kyser, 1992). Since the initial formation of the U ores at 1400–1500 Ma, incursion of substantial amounts of meteoric water along faults that were periodically reactivated from late-Precambrian onward has resulted in recrystallization of many of the ore-forming minerals and contemporaneous silicate and clay minerals near the faults (Wilson et al., 1987; Kotzer and Kyser, 1991, 1992).

Fluid inclusion and stable isotopic studies also have been done on silicate, oxide, and carbonate gangue minerals associated with complex U ± Ni ± As ± S ± Au ± PGE vein type deposits in the Beaverlodge area near Uranium City (Sassano et al., 1972; Rees, 1992; Fig. 1). Rees (1992) documented the occurrence of U intergrown with euhedral quartz and carbonate in veins similar to those in the Athabasca Basin. The δ18O values of the quartz and carbonate and salinities and δD values of fluids in three-phase fluid inclusions in the euhedral quartz and carbonate indicate that the quartz and carbonate formed from a saline fluid having δ18O and δD values similar to the isotope compositions of the basinal fluids involved with formation of the Athabasca U deposits of the unconformity type (Rees, 1992). Peiris and Parslow (1988) and Sibbald (1988) noted the close proximity of the complex vein type U mineralization to a pre-Athabasca unconformity and, on the basis of these observations, suggested similar fluid compositions and structural controls for U ore formation of the unconformity type and vein type.

**Analytical procedures and methodology**

Fifteen uraninite and pitchblende samples from the Athabasca unconformity type and Beaverlodge complex vein type U deposits were collected for stable and radiogenic isotopic and chemical analysis (Fig. 1, Table 1). Late-formed pyrite, marcasite, and anglesite, which occur in fractures and hydrothermally altered sandstones spatially associated with the Athabasca unconformity type U ore, were also collected.

The mineralogical characteristics of the U samples were examined using reflected light microscopy and SEM. Chemical compositions of the uranium oxides were determined using a Jeol 8600 electron microprobe at operating voltages of 20 kV, a beam diameter of 2 μm, and counting times of 50 s per element. Detection limits of the elements were on the order of 0.1 wt%. Data reduction for the various elements was done by taking into account the matrix corrections between the standards and samples and the analytical parameters (i.e., take-off angle and operating voltage) of the microprobe. On the basis of their petrologic and alteration characteristics, areas in the U minerals with minimal alteration effects were selected for O, U, and Pb isotopic analysis. O isotopic compositions of the uranium oxide minerals were determined using the BrF5 technique of Clayton and Mayeda (1963). The isotopic compositions were determined on a MAT 251 mass spectrometer and are reported in units of per mil (‰) relative to V-SMOW. The δ18O value of NBS 28 quartz was 9.6‰, and replicate analyses of the U minerals are reproducible to ±0.2‰. The theoretical U-H2O O isotope fractionation factor of Hattori and Halas (1982), which generally agrees with that of Zheng (1991), was used to calculate the δ18O values of the fluids with which the uranium oxide minerals interacted.

U and Pb were separated from uranium oxides using standard column separation techniques, as described by Parrish et al. (1987), following dissolution in HF and HClO4. U and Pb contents were determined by isotope dilution. Sulfide minerals were treated with HF and subsequently leached in 8N HNO3 at 80 °C for 4 h. Following this, both the leachate and residue from the samples were dissolved in concentrated HNO3 and separated using standard column-separation techniques. U and Pb isotopic compositions of the U- and S-bearing minerals were measured with a MAT 261 thermal ionization mass spectrometer at temperatures of 1200–1300 °C at the University of Saskatchewan. The resulting data were corrected for Pb and U mass fractionations of 0.10 and 0.11%/AMU, respectively and were reduced using the program PBDAI (Ludwig, 1987). Using these methods, the corrected 207Pb/206Pb, 208Pb/206Pb, and 204Pb/206Pb ratios of the NBS 982 standard (eight samples) were 0.4671 ± 39, 1.0003 ± 15, and 0.0272 ± 8, respectively, and 235U/238U ratios for the USO standard (five samples) were 0.9992 ± 48.

**Results and Discussion**

Chemical and stable isotopic compositions of uraninite and pitchblende

Uraninite and pitchblende from the unconformity type U deposits in the Athabasca Basin and vein type U deposits from the Beaverlodge area with the highest reflectivities and least alteration (Fig. 2A) have SiO2 contents generally <1 wt% SiO2 and δ18O values between −28.0
Table 1. Mineralogical, chemical (wt%), chemical U-Pb ages, and O isotopic compositions of U minerals

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Description + remarks and associated minerals</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{CaO} )</th>
<th>( \text{PbO} )</th>
<th>( \text{U}_2\text{O}_5 )</th>
<th>( \text{K}_2\text{O} )</th>
<th>( \text{Chemical U-Pb age (Ma)} )</th>
<th>( \delta^18\text{O} )</th>
<th>( \delta^18\text{O}_{\text{H}_2\text{O}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KL478-14 (Key Lk)</td>
<td>massive aniso pitchblende in sandstones</td>
<td>0.17-0.19</td>
<td>0.56-0.80</td>
<td>18.34-16.45</td>
<td>82.79-82.84</td>
<td>—</td>
<td>1334-1352</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HL20-563.3 (Hughes Lk)</td>
<td>massive, aniso pitchblende near unconformity</td>
<td>1.30</td>
<td>1.11</td>
<td>9.55</td>
<td>87.60</td>
<td>—</td>
<td>740</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>M208-519.7 (P2)</td>
<td>aniso pitchblende + cpy in silicified sandstones</td>
<td>0.07</td>
<td>0.72</td>
<td>11.71</td>
<td>85.58</td>
<td>—</td>
<td>929</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>M222-517.7 (P2)</td>
<td>aniso-iso botryoidal pitchblende + galena in fractures</td>
<td>0.09-0.34</td>
<td>0.73-1.53</td>
<td>10.61-15.60</td>
<td>83.27-88.34</td>
<td>—</td>
<td>852-1183</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>M222-531.4 (P2)</td>
<td>aniso, brecciated euhedral uraninite</td>
<td>0.17-0.47</td>
<td>0.67-0.88</td>
<td>9.72-10.54</td>
<td>84.36-87.76</td>
<td>—</td>
<td>719-808</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>M222-536.8 (P2)</td>
<td>aniso, brecciated uraninite + galena in fractures</td>
<td>0.18-0.31</td>
<td>0.50-0.51</td>
<td>10.07-10.67</td>
<td>85.97-88.51</td>
<td>—</td>
<td>749-796</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>M222-537 (P2)</td>
<td>aniso, brecciated uraninite + galena in fractures</td>
<td>0.38-0.45</td>
<td>0.67-0.77</td>
<td>9.50-10.76</td>
<td>87.80-88.60</td>
<td>—</td>
<td>704-800</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Note: abbreviations used are: aniso = anisotropic; iso = isotropic; qtz = quartz; nicco = niccolite; rammels = rammelsbergite; cpy = chalcopyrite.

* Range in chemical compositions in samples analyzed for O, U, and Pb isotopic compositions.

** Ages calculated using the equation \( t = \frac{\text{Pb} \times 10^{10} \text{yr}}{1.612 \text{U}} \) (Powers, 1985).

† The value of \( \delta^18\text{O}_{\text{H}_2\text{O}} \) calculated using uraninite-H2O fractionation factor of Hattori and Halas (1982) at temperatures of 200°C.

‡ Sample contained quartz contamination that could not be removed.

and -22.4‰ (Table 1). Conversely, uraninite and pitchblende that contain abundant microfractures (Fig. 2B) are more chemically heterogeneous, with SiO₂ contents between 1.14 and 6.80 wt% (Table 1) and have \( \delta^18\text{O} \) values that are > -20‰ and increase with increasing silica contents (Fig. 3a, Table 1). K₂O contents in all of the U minerals are low (<1.0 wt% K₂O) and do not correlate with silica contents (Table 1). Ca concentrations in uraninite and pitchblende from the Athabasca unconformity type deposits are generally low and do not correlate with \( \delta^18\text{O} \) values (Fig. 3b, Table 1). In contrast, Ca contents in uraninite and pitchblende from the Beaverlodge complex vein type deposits are higher and more variable, and in several of these deposits (8730-1, Ea24, Ea26, Ace Fay 1), minerals with higher CaO and SiO₂ contents have the highest \( \delta^18\text{O} \) values, from -18.6 to -2.3‰ (Table 1, Fig. 3a, 3b). The main reason for higher Ca contents in the U minerals from the Beaverlodge complex vein type deposits is the differences in the lithologies of the host rocks, with the Beaverlodge complex vein type hosted by carbonate-rich basement rocks, whereas quartz-rich rocks host the Athabasca unconformity type deposits.

U and Pb contents of the uraninite and pitchblende minerals from both the Athabasca and Beaverlodge areas are highly variable at the scale of the electron microprobe, ranging from 65.49 to 89.45 wt% U₂O₅ and 3.43 to 16.45 wt% PbO (Table 1). Because of alteration of the U minerals, a poorly defined correlation is apparent among Pb, Ca, and silica in the U minerals, as U samples showing the greatest degree of microfracturing also generally have the highest and most variable SiO₂ and CaO contents and among the lowest and most variable PbO concentrations (Fig. 4). These results suggest that recrystallization of the uranium oxide minerals, which involves incorporation of silica and Ca into the U structure, has resulted in Pb loss. Similar, although more well-defined, correlations among silica, Ca, U, and Pb contents in the uranium oxide minerals have been observed at other U deposits in the Athabasca Basin. For example, both Baadsgaard et al. (1984) and Powers and Stauffer (1988) documented a correlation between increasing As and silica and decreasing Pb concentrations in pitchblende and coffinite from the Midwest Lake Uranium deposit (Fig. 1).
Fig. 2. SEM photographs of uraninite and pitchblende samples used in this study (Table 1): (A) sample of petrographically pristine, unaltered pitchblende (8730-13); (B) uraninite sample showing characteristic alteration near microfractures, although the majority of area is petrographically unaltered (Ea 24); (C) fractured and chemically altered uraninite (gray areas) and less altered massive uraninite (Ea 26), GAL = galena; (D) petrographically pristine, unaltered pitchblende showing little evidence of fracturing (KL478-14); (E) unaltered, pristine uraninite with variable chemical U-Pb ages (M222-517.7); (F) fracture in pitchblende sample containing large galena cube of radiogenic Pb juxtaposed against uraninite with a U-Pb ratio of 59 and a U-Pb chemical age of 740 Ma (H120-563.3), GAL = galena.
Fig. 3. Relationship between (a) $\delta^{18}$O values and Si contents; (b) $\delta^{18}$O values and Ca contents (fields 1 and 2 represent highly altered and relatively unaltered uraninite and pitchblende, respectively); (c) $\delta^{18}$O values and U contents; and (d) $\delta^{18}$O values and Pb contents in uraninite and pitchblende. Squares represent samples from Beaverlodge vein type U deposits, and circles are samples from Athabasca unconformity type U deposits. Shaded vertical line represents the calculated $\delta^{18}$O values for uraninite and pitchblende minerals that would have formed from fluids with $\delta^{18}$O values of 4 ± 2‰ and temperatures of approximately 200 °C that formed diagenetic clay and silicate minerals associated with the U ores. Data from Table 1.

Fig. 4. Relationship between PbO and CaO and SiO$_2$ concentrations in uraninite and pitchblende. Symbols as in Fig. 3; data from Table 1; error bars indicate the total chemical variation in samples. Fields labeled a and b represent relatively unaltered and highly altered uraninite and pitchblende, respectively.

Chemical and isotopic alteration of U minerals in this study can be extremely subtle, as areas on the U minerals appearing to be petrographically pristine exhibit substantial variation in chemical and isotopic compositions. However, much of the variation in the chemical and isotopic compositions of these minerals is due to the presence of numerous small fractures that were hard to detect optically (Fig. 2B, 2C). In contrast, uranium oxides exhibiting very little fracturing at the scale of the electron microprobe display the least variation in their U, Pb, and SiO$_2$ contents (Fig. 2D).

O isotope systematics of uraninite and pitchblende

The $\delta^{18}$O values of uraninite and pitchblende vary between −28 and −2.3‰ and normally correlate with the degree of chemical heterogeneity at the scale of the electron microprobe (Table 1, Fig. 3a–3d). Evidence for increasing $\delta^{18}$O values and increasing SiO$_2$ and Ca contents in uraninite and pitchblende minerals is expected as incorporation of SiO$_2$ or CaO into the U mineral structure should result in overall $^{18}$O enrichment in the absence of substantial temperature variations during formation of the minerals, which are not evident from fluid inclusion homogenization temperatures and O-isotope geother-
The Athabasca Basin should have δ18O values comparable to those in uraninite and pitchblende from the Beaverlodge area. The δ18O values of hematite calculated by Hattori and Halas (1982), the pitchblende from the Athabasca and Beaverlodge areas, has similarly low δ18O values as those in uraninite and pitchblende minerals from the Athabasca Basin, and also the Beaverlodge U deposits, have been affected by isotopically distinct fluids since their formation. The O isotope fractionation between U and H2O is between 3 and 8‰ at temperatures <100 °C (Hattori and Halas, 1982; Zheng, 1991), and so recrystallization of the uraninite and pitchblende with relatively recent, low-temperature meteoric fluids, which in the Athabasca area have δ18O values of approximately −20 to −16‰, could explain the low δ18O values observed. The lack of petrographically observable alteration in many of the uraninite and pitchblende samples having low δ18O values requires that uranium oxide minerals may exchange O isotopes with fluids with only minor disturbances in their chemical compositions and original textures.

Uraninite from other geologic environments, having similarly low δ18O values as those in uraninite and pitchblende from the Athabasca and Beaverlodge areas, has been documented by Hattori et al. (1978). It is unclear whether their U samples had experienced postcrystallization alteration because no petrographic information is available, although interaction of the U minerals with modern meteoric water in each area, which are similar in isotopic composition to those in the Athabasca region, could result in some of the low δ18O values reported by Hattori et al. (1978).

**U-Pb and Pb-Pb isotope systematics**

The 207Pb/206Pb ages of the uraninite and pitchblende minerals range between 393 and 1428 Ma, although most of the 207Pb/206Pb ages occur between 1018 and 1428 Ma (Table 2). The δ18O values for these uraninite and pitchblende samples range substantially, although, with excep-
Fig. 5. Relationship between δ¹⁸O values and ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²⁰⁶Pb, and chemical U-Pb ages. Shaded vertical line represents the calculated δ¹⁸O values for uraninite and pitchblende minerals that would have formed from fluids with δ¹⁸O values of 4 ± 2‰ and temperatures of approximately 200 °C, similar to the fluids that formed diagenetic clay and silicate minerals and U ores in the Athabasca and Beaverlodge areas. Symbols as in Fig. 3; data from Tables 1 and 2.

Fig. 6. U-Pb concordia diagrams of uraninite and pitchblende samples from both the Beaverlodge complex vein type and Athabasca unconformity type U deposits. Data from Table 2 and symbols as in Fig. 3a–3d; (a) U-Pb ratios of uraninite and pitchblende from both the Athabasca unconformity type and the Beaverlodge complex vein type U deposits. MSWD = 5.90. (b) U-Pb ratios of uraninite and pitchblende from the Beaverlodge complex vein type deposits. MSWD = 8.2.

The Beaverlodge complex vein type deposits have ²⁰⁷Pb/²⁰⁶Pb ages of 1018–1260 Ma, which partially overlap the ²⁰⁷Pb/²⁰⁶Pb ages of uraninite and pitchblende from the Athabasca unconformity type U deposits. Similarities in the ²⁰⁷Pb/²⁰⁶Pb ages of U minerals from the Athabasca and Beaverlodge areas are consistent with the petrographic observations and geochemical and stable isotope data on gangue minerals and fluid inclusions of comparable paragenesis, which suggests that the unconformity type and complex vein type U minerals formed at approximately the same times and from chemically and isotopically similar fluids.

Two samples of uraninite and pitchblende from the complex vein type deposits, Ea24 and Ace Fay 1, have distinctly younger ²⁰⁷Pb/²⁰⁶Pb ages of 393 and 519 Ma (Table 2). On the basis of their field and petrographic relationships, these two samples should have the same ²⁰⁷Pb/²⁰⁶Pb ages as other U minerals in the Beaverlodge area. These samples contain numerous microfractures.
the Beaverlodge uraninite and pitchblende are similarly discordant and yield a regression line with intercepts of 1549 ± 89 and 214 ± 28 Ma (Table 2, Fig. 6b). The high MSWD values (mean square of weighted deviates) indicate that the scatter of the sample points along the regression is considerably more than the analytical errors, suggesting that the minerals were not similarly affected by the same fluid events or possibly were affected by different fluid events. This is substantiated by large variations in both the δ18O values and corresponding U-Pb isotope ages for these minerals (Fig. 5).

The U-Pb isotopic compositions of U minerals from this study are similar to those from previous radiogenic isotope studies on uranium oxide minerals from the Athabasca and Beaverlodge areas (Table 3), wherein samples that were selected on the basis of their petrographic and chemical compositions have highly discordant U-Pb ages because of varying degrees of radiogenic Pb loss (Koeppel, 1968; Cumming and Rimsait, 1979; Baadsgaard et al., 1984; Trocki et al., 1984; Phillip and Lancelot, 1988; Cumming and Kröst, 1992; Carl et al., 1992). Many of the U-Pb ages previously reported for U minerals from the Athabasca Beaverlodge areas, obtained by regression of the U-Pb isotope ratios, probably are not significant because of their variable and high degree of discordancy.

U-Pb ages of 400 Ma and less for some of the U minerals, as defined by the lower discordia intercept ages and concordant U-Pb ages (Fig. 6), approximate the timing of the latest fluid events that are most likely responsible
for lowering their original $\delta^{18}O$ values. A sample of highly fractured pitchblende from the Beaverlodge complex vein type deposits, Ea24, has $^{206}Pb/^{238}U$ and $^{206}Pb/^{236}U$ ratios that are nearly concordant at 230 Ma (Table 2, Fig. 6b). As this sample has high Si and Ca and low Pb contents, a low $\delta^{18}O$ value of $-18.4\%$o, and similarly young $^{207}Pb/^{206}Pb$ and chemical U-Pb ages (Tables 1 and 2), it represents a sample that has recrystallized during a relatively recent incursion of meteoric water along faults that host the U mineralization. Similarly, pitchblende from an Athabasca unconformity type U deposit, M208-519.7, has a comparably low $\delta^{18}O$ value of $-11.7\%$o and concordant U-Pb ratios at approximately 140 Ma (Tables 1 and 2, Fig. 6a). However, this pitchblende has older $^{207}Pb/^{206}Pb$ and chemical U-Pb ages, indicating that it was subjected to a lesser degree of H$_2$O/rock interaction than was the Beaverlodge U mineral.

Pb isotopic compositions and Pb isochron ages of S-bearing minerals

Evidence for substantial migration of radiogenic Pb out of U minerals from the Athabasca and Beaverlodge areas is recorded by the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios in late-formed S-bearing minerals. Sulfides and sulfates in proximity to the U ore in both the Athabasca and Beaverlodge U deposits have highly anomalous and uranogenic $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios (Koeppel, 1968; Cumming et al., 1984; Kotzer and Kyser, 1990a; Carl et al., 1992). The $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios (Table 4) in late-stage pyrite, marcasite, and anglesite are highly radiogenic relative to an average crustal Pb growth curve (Fig. 7). Pb-Zn deposits, which are hosted by Aphebian-age metasedimentary rocks adjacent to the Athabasca Basin (Fig. 1), contain galena that has $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios that are concordant with a crustal Pb growth curve at approximately 1600–1700 Ma (Fig. 7a). A linear correlation between the isotopic compositions of the Pb in the late sulfides and sulfates and in galena from the nearby Pb-Zn mineralization is compatible with a process wherein Pb in the late-formed sulfides and sulfates has formed from mixing between uranogenic Pb from U minerals in the basin and single-stage Pb from the detrital sulfides from Pb-Zn deposits that were eroded into the basin (Fig. 7a).

The isotopic compositions of Pb in sulfate and sulfide minerals from the Athabasca Basin plot on secondary isochrons having ages of approximately 130–370 Ma (Fig. 7), which are similar to the youngest concordant U/Pb ages in spatially associated uraninite and pitchblende minerals (Table 2). These age correlations suggest that the high $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios in the sulfide and sulfate minerals have resulted from formation of these minerals from fluids that have interacted with the U ores and transported uranogenic Pb. Petrographic evidence for Pb loss from the crystalline uranium oxide minerals occurs as formation of galena, which is found in fractures crosscutting chemically altered areas on the uranium oxides that have anomalously high U-Pb ratios (Fig. 2F). Such petrographic relationships, although at a small scale, indicate alteration of the U minerals with ensuing Pb loss and suggest that the high $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios of spatially associated late sulfide minerals in the faults that host the U minerals have resulted from large-

### Table 4. Sample no., description, and Pb isotope ratios in sulfide and sulfate minerals from Athabasca Basin

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Description and remarks</th>
<th>$^{206}Pb/^{204}Pb$</th>
<th>$^{207}Pb/^{204}Pb$</th>
<th>$^{208}Pb/^{204}Pb$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D482-5</td>
<td>Pb dispersion halo (4680 ppm Pb)</td>
<td>22.658</td>
<td>16.101</td>
<td>42.118</td>
</tr>
<tr>
<td>D490-31</td>
<td>Pb dispersion halo (202 ppm Pb)</td>
<td>22.880</td>
<td>16.066</td>
<td>42.057</td>
</tr>
<tr>
<td>D490-16b</td>
<td>Pb dispersion halo (212 ppm Pb)</td>
<td>25.059</td>
<td>16.363</td>
<td>42.887</td>
</tr>
<tr>
<td>D482-36</td>
<td>Pb dispersion halo (824 ppm Pb)</td>
<td>54.959</td>
<td>19.470</td>
<td>44.109</td>
</tr>
<tr>
<td>D482-14</td>
<td>Pb dispersion halo (824 ppm Pb)</td>
<td>27.182</td>
<td>16.526</td>
<td>44.034</td>
</tr>
<tr>
<td>Ep226/811</td>
<td>pyrite</td>
<td>325.153</td>
<td>38.061</td>
<td>47.869</td>
</tr>
<tr>
<td>M162/493.7</td>
<td>pyrite</td>
<td>299.928</td>
<td>27.294</td>
<td>56.733</td>
</tr>
<tr>
<td>D458-34</td>
<td>pyrite and marcasite</td>
<td>25.327</td>
<td>16.232</td>
<td>45.954</td>
</tr>
<tr>
<td>D458-35</td>
<td>pyrite</td>
<td>25.829</td>
<td>16.302</td>
<td>44.113</td>
</tr>
<tr>
<td>D482-61</td>
<td>pyrite</td>
<td>24.266</td>
<td>16.132</td>
<td>43.219</td>
</tr>
<tr>
<td>Pb-2</td>
<td>pyrite</td>
<td>25.239</td>
<td>16.769</td>
<td>45.867</td>
</tr>
<tr>
<td>D474-46</td>
<td>pyrite and marcasite</td>
<td>22.843</td>
<td>16.063</td>
<td>40.257</td>
</tr>
<tr>
<td>D474-46</td>
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<td>31.347</td>
<td>16.629</td>
<td>46.260</td>
</tr>
<tr>
<td>D466-14G</td>
<td>galena</td>
<td>22.175</td>
<td>16.121</td>
<td>41.865</td>
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<tr>
<td>D466-13G</td>
<td>galena</td>
<td>22.144</td>
<td>16.141</td>
<td>41.881</td>
</tr>
</tbody>
</table>

Note: Pb contents in parts per million were determined by ICP-AES in commercial laboratory; l: leach, r: residue.
scale radiogenic Pb migration from the U minerals by means of meteoric fluids in the fault zones that transect these deposits (Fig. 8).

That this process operates even today is substantiated by chemical analyses of groundwater in sandstone aquifers surrounding the U ore at the Cigar Lake U deposit (Fig. 1). The groundwater has distinct 206Pb anomalies and contains relatively little dissolved U (Cramer and Vilks, 1989; Touhoal and Beaucaire, 1989). Apparently, relatively modern meteoric water that has low δ18O values has interacted with the U ores, which has resulted in substantial late-stage Pb migration by meteoric fluids into the fractured sandstones (Fig. 8).

CONCLUSIONS

1. The 206Pb/235U and 207Pb/235U ratios measured in the uraninite and pitchblende from both U deposits of the unconformity type and vein type are highly discordant and may yield inaccurate ages, but, when combined with stable isotope and chemical data, they do provide unique information regarding their fluid petrogenesis since crystallization. U-bearing minerals from both unconformity type and vein type U deposits with the oldest ages also have the lowest δ18O values (Fig. 5). Because the low δ18O values require exchange of the O in the U minerals with relatively modern meteoric water, not all of the uranogenic Pb that accumulated since the formation of these uraninite and pitchblende samples was lost during late recrystallization. Therefore, despite recent recrystallization of the U minerals, the 207Pb/206Pb ages of the uraninite and pitchblende, which range between 1018 and 1428 Ma, probably represent the original crystallization ages of these minerals. In contrast, completely recrystallized uraninite and pitchblende minerals from the Athabasca and Beaverlodge deposits have discordant chemical and isotopic U-Pb ages and young 207Pb/206Pb ages of <500 Ma (Fig. 6a, 6b). Hence, these U minerals record a relatively accurate age for the timing of late meteoric water incursion responsible for destruction of some of these ore deposits (Kotzer and Kyser, 1990a).

2. Many of the 207Pb/206Pb ages of the uraninite and pitchblende from the Athabasca Basin are comparable with ages obtained from Rb-Sr isotope systematics of the coeval clay minerals. For example, the oldest 207Pb/206Pb age of 1428 Ma (Table 2) for an Athabasca U mineral from this study is comparable to an Rb-Sr isochron age of 1477 ± 57 Ma, determined from petrographically and isotopically pristine illite contemporaneous with formation of the U ore (Kotzer and Kyser, 1992). Although this uraninite has an extremely low δ18O value of −26.2‰, indicating it has exchanged O isotopes with relatively modern meteoric water, it has a 207Pb/206Pb age that reflects the timing of high-temperature basinal fluid flow and basin-basement fluid mixing responsible for both the formation of diagenetic clay minerals and generation of the Athabascan U ore deposits. Uraninite and pitchblende from the Athabasca and Beaverlodge areas predominantly record the effects of interaction with late-stage meteoric water, as evidenced by their low δ18O values, chemical compositions, and discordant U-Pb ages (Figs. 3–6). Further evidence for recrystallization of the U minerals and late-stage Pb losses are the anomalously variable and high 206Pb/204Pb and 207Pb/204Pb ratios in spatially associated sulfide and sulfate minerals.
Fig. 8. Circulation patterns for late-stage $^{18}$O and D-depleted meteoric water along reactivated faults that host U mineralization in the Athabasca Basin based on O, U-Pb, and Pb isotope ratios in uraninite, pitchblende, and S minerals (this study, Tables 1, 2, 4), and H and O isotope ratios in clay and silicate minerals coeval with the U minerals from previous studies (Wilson and Kyser, 1987; Kotzer and Kyser, 1991, 1992). Shown are the $\delta^{18}$O values and $^{207}$Pb/$^{204}$Pb and $^{207}$Pb/$^{204}$Pb ratios for U minerals, late-formed sulfate and sulfide minerals, and the $\delta^D$ and $\delta^1$H values of relatively modern meteoric water that have affected the clay minerals.

3. In the Athabasca Basin, recrystallization of uraninite and pitchblende has been facilitated by incursion of meteoric water into the reactivated fault structures that host the U deposits (Fig. 8; Wilson et al., 1987; Kotzer and Kyser, 1991, 1992). U minerals that have been completely recrystallized by severe meteoric water alteration have increasing silica contents and $\delta^1$H values and concordant U/Pb and Pb/Pb ages of 200–500 Ma. Similarly, illite within these reactivated faults and contemporaneous with the U ore has reset K-Ar ages to as young as 400 Ma, with K-Ar ages decreasing with decreasing K$_2$O contents, increasing H$_2$O contents, and $\delta^D$ values decreasing to as low as $-180\%$ (Wilson and Kyser, 1987; Kotzer and Kyser, 1991, 1992). For both the U and illitic clay minerals from the Athabasca Basin and U minerals from the Beaverlodge areas, all of which occur within or in proximity to reactivated faults, U-Pb, Pb-Pb, and K-Ar ages of <600 Ma clearly indicate that late-stage incursion of meteoric water into the basin and surrounding supracrustals by re-activated fault and fracture systems was dominant in the Phanerozoic. Overall, comparison of $\delta^D$ and $\delta^{18}$O values and U-Pb, Pb-Pb, Rb-Sr, and K-Ar ages in coeval clay and U minerals from many of the Athabasca unconformity type U deposits indicates they have been affected by similar fluid events and suggests that O and Pb isotope systematics in uranium oxide minerals can be highly sensitive indicators of specific fluid events.

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