

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 $\delta^{18}\text{O}$ 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 ^{18}O -rich isotopic compositions. Pb-Pb ages of spatially associated S-bearing minerals in late-formed fractures are similar to those of uraninite. In contrast, $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ ages approximate those of formation for the U minerals. Large discrepancies between U/Pb ages and the $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $\delta^{18}\text{O}$ values that would have resulted from equilibration with fluids having $\delta^{18}\text{O}$ values of -20 to -11% . Such fluids are substantially ^{18}O -depleted relative to the O isotopic composition of $4 \pm 2\%$ 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 $\delta^{18}\text{O}$ values, which vary with chemical contents, variably reset U-Pb ages, and older $^{207}\text{Pb}/^{206}\text{Pb}$ 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 ($\text{UO}_2 + \text{Th}$ and REE; Steacy and Kaiman, 1978) and pitchblende ($\text{UO}_2 - \text{Th}$ 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 recrystal-

lization, 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, $^{235}\text{U}/^{207}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$, which, because of different decay rates of the two isotopes of U, yields three geochronometers: $^{207}\text{Pb}/^{235}\text{U}$, $^{206}\text{Pb}/^{238}\text{U}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ (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 (e.g.,

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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_2O and pitchblende- H_2O (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 $^{18}\text{O}/^{16}\text{O}$, $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, 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 $\text{U} \pm \text{Ni} \pm \text{Co} \pm \text{As} \pm \text{Cu} \pm \text{Zn}$ 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-Athabaskan 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 inter-

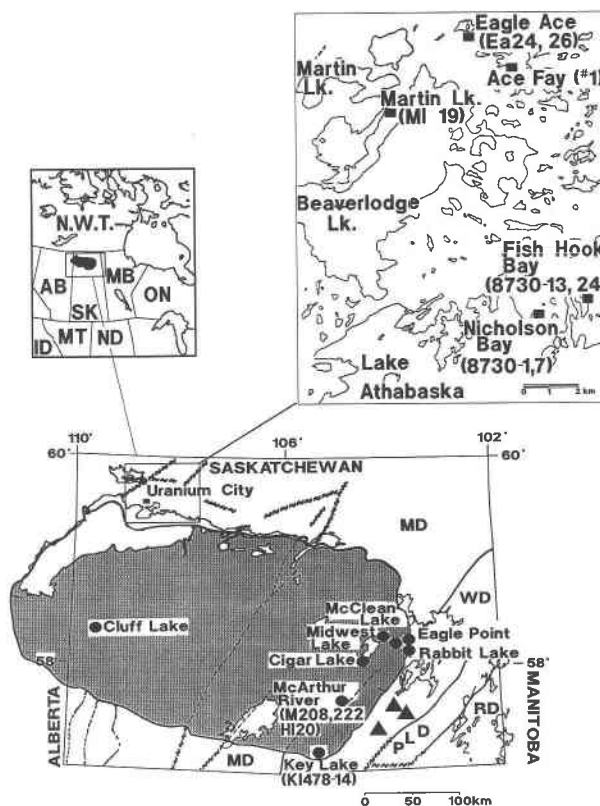


Fig. 1. Map of central North America and northern Saskatchewan showing present position and extent of Athabasca Basin, various lithostructural domains, locations of major U deposits of the unconformity type in Athabasca Basin (solid circles), and locations of U deposits of the complex vein type (solid squares) in the Beaverlodge area around Uranium City (inset). Solid triangles indicate the approximate positions of Pb-Zn deposits in Wollaston metasedimentary rocks at George Lake. Numbers in parentheses refer to drill hole and sample numbers in Tables 1 and 2. MD = Mudjatik Domain; WD = Wollaston Domain; PLD = Peter Lake Domain; and RD = Rottenstone Domain.

section 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 [$[\text{U}(\text{SiO}_4)_x(\text{OH})_{4-x}]$; 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 basal sandstone aquifers that were widespread throughout the entire Athabasca Basin (Kotzer, 1993). Stable isotopic compositions of magnesium chlorite 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 H_2O /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 $U \pm Ni \pm As \pm S \pm Au \pm PGE$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and δD values similar to the isotopic 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-Athabaskan 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 spa-

tially 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 BrF_3 technique of Clayton and Mayeda (1963). The isotopic compositions were determined on a MAT 251 mass spectrometer and are reported in units of permil (‰) relative to V-SMOW. The $\delta^{18}O$ value of NBS 28 quartz was 9.6‰, and replicate analyses of the U minerals are reproducible to ± 0.2 ‰. The theoretical U- H_2O O isotope fractionation factor of Hattori and Halas (1982), which generally agrees with that of Zheng (1991), was used to calculate the $\delta^{18}O$ 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 $HClO_4$. U and Pb contents were determined by isotope dilution. Sulfide minerals were treated with HF and subsequently leached in 8N HNO_3 at 80 °C for 4 h. Following this, both the leachate and residue from the samples were dissolved in concentrated HNO_3 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 PBDAT (Ludwig, 1987). Using these methods, the corrected $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, and $^{204}Pb/^{206}Pb$ ratios of the NBS 982 standard (eight samples) were 0.46711 ± 39 , 1.00039 ± 15 , and 0.02721 ± 8 , respectively, and $^{235}U/^{238}U$ ratios for the U500 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 SiO_2 contents generally < 1 wt% SiO_2 and $\delta^{18}O$ values between -28.0

TABLE 1. Mineralogical, chemical (wt%),* chemical U-Pb ages, and O isotopic compositions of U minerals

Sample no. (location)	Description + remarks and associated minerals	SiO ₂	CaO	PbO	U ₃ O ₈	K ₂ O	Chemical U-Pb age (Ma)**	δ ¹⁸ O	δ ¹⁸ O _{H₂O} †
Athabasca unconformity type U deposits									
KL478-14 (Key Lk)	massive aniso pitchblende in sandstones	0.17–0.19	0.56–0.80	16.34–16.45	82.79–82.84	—	1334–1352	–26.3	–19
HL20-563.3 (Hughes Lk)	massive, aniso pitchblende near unconformity	1.30	1.11	9.55	87.60	—	740	–26.2	–19
M208-519.7(P2)	aniso pitchblende + cpy in silicified sandstones	0.07	0.72	11.71	85.58	—	929	–11.7‡	–4
M222-517.7(P2)	aniso pitchblende	0.09–0.34	0.73–1.53	10.61–15.60	83.27–88.34	—	852–1183	–28.0	–20
M222-531.4(P2)	aniso-iso botryoidal pitchblende + galena in fractures	0.17–0.47	0.67–0.88	9.72–10.54	84.36–87.76	—	719–808	–23.8	–16
M222-536.6(P2)	aniso, brecciated euhedral uraninite	0.18–0.31	0.50–0.51	10.07–10.67	87.95–88.31	—	749–796	–25.4	–18
M222-537(P2)	aniso, brecciated uraninite + galena in fractures	0.38–0.45	0.67–0.77	9.50–10.76	87.80–88.60	—	704–800	–22.4	–15
Complex vein type U (Beaverlodge area)									
8730-1 (Nicholson)	aniso pitchblende + CaCO ₃ in vein	0.54–6.80	0.9–2.21	10.45–18.09	65.49–88.57	0.10–0.13	1084–1389	–8.2	–1
8730-7 (Nicholson)	aniso pitchblende + nicco + rammels	0.23–0.28	0.95–1.57	9.37–15.87	83.47–87.24	—	730–1120	–26.5	–19
8730-13 (Fish Hook)	radially textured aniso pitchblende	0.07–0.27	—	11.89–14.46	82.48–85.80	0.00–0.17	978–1145		
8730-24 (Fish Hook)	weakly iso pitchblende + qtz in vein	0.68–1.25	2.10–2.84	7.49–8.82	84.84–85.04	0.13–0.17	204–705	–26.0	–19
Ea24 (Eagle Ace)	massive, aniso-iso uraninite + CaCO ₃ + qtz	0.69–1.14	4.68–6.66	3.43–3.98	87.08–89.45	—	261–282	–18.4	–11
Ea26 (Eagle Ace)	same as Ea24	0.55–2.83	4.42–6.73	3.21–3.99	86.73–86.78	—	252–312	–18.6	–11
ML19 (Martin Lake)	massive aniso pitchblende + CaCO ₃ in vein	0.15–0.29	4.75–5.34	12.93–15.2	79.70–82.93	—	1050–1294	–27	–20
Ace Fay 1 (Ace Fay)	massive, aniso-iso fissile uraninite	2.26–5.36	2.90–3.57	6.84–7.96	79.93–84.82	0.12–0.14	383–626	–2.3	+5

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

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

** Ages calculated using the equation $t = (Pb \times 10^{10} \text{ yr}) / (1.612 \text{ U})$ (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 δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O 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 relative to the Athabasca U 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% U₃O₈ 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 pitchblendes and coffinite from the Midwest Lake Uranium deposit (Fig. 1).

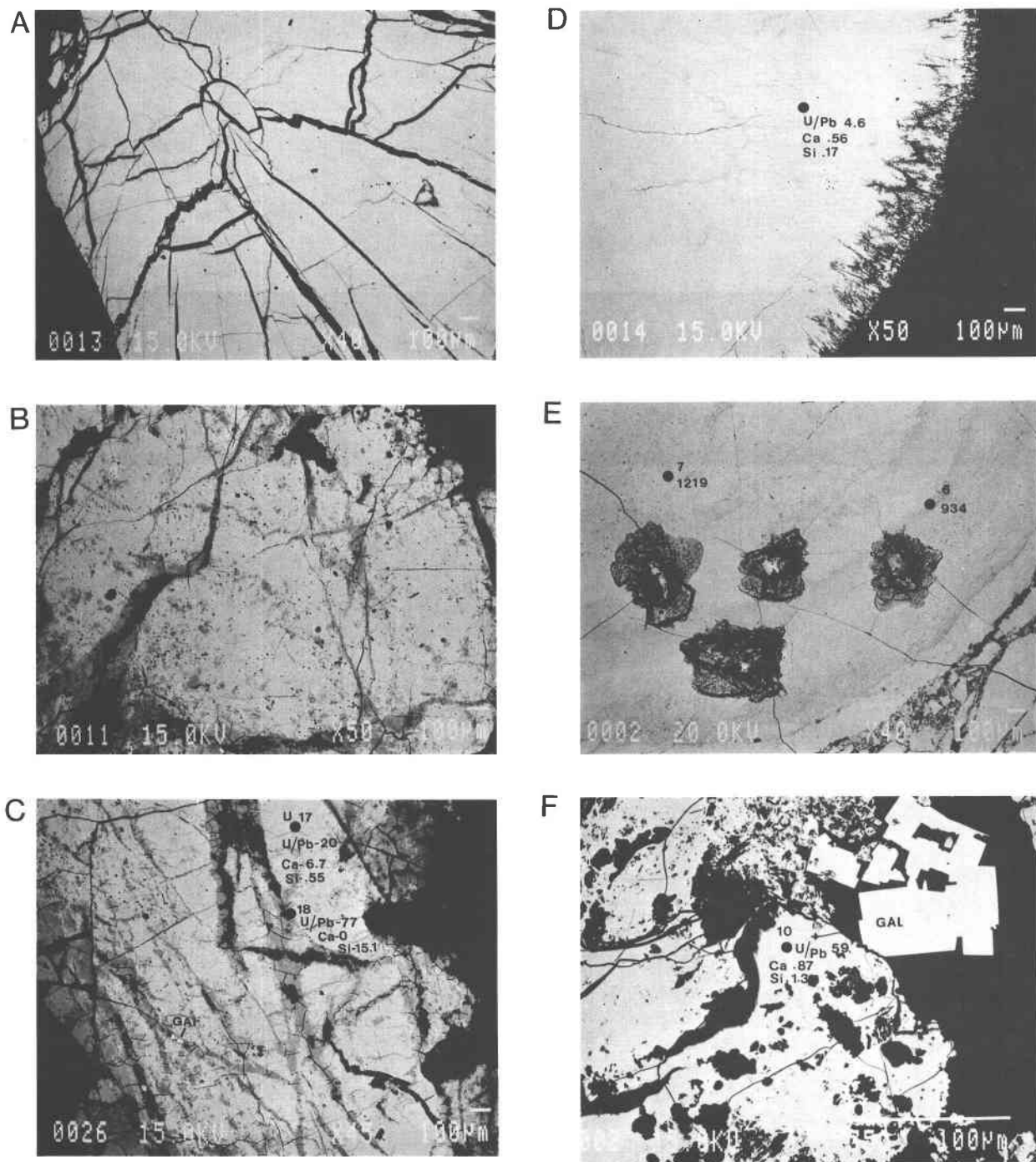


Fig. 2. SEM photographs of uraninite and pitchblende samples used in this study (Table 1): (A) sample of petrographically pristine, unaltered pitchblende (8730-13); (B) uraninite sample showing characteristic alteration near microfractures, although the majority of area is petrographically unaltered (Ea 24); (C) fractured and chemically altered uraninite (gray areas) and less altered massive uraninite (Ea 26), GAL = galena; (D) petrograph-

ically 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.

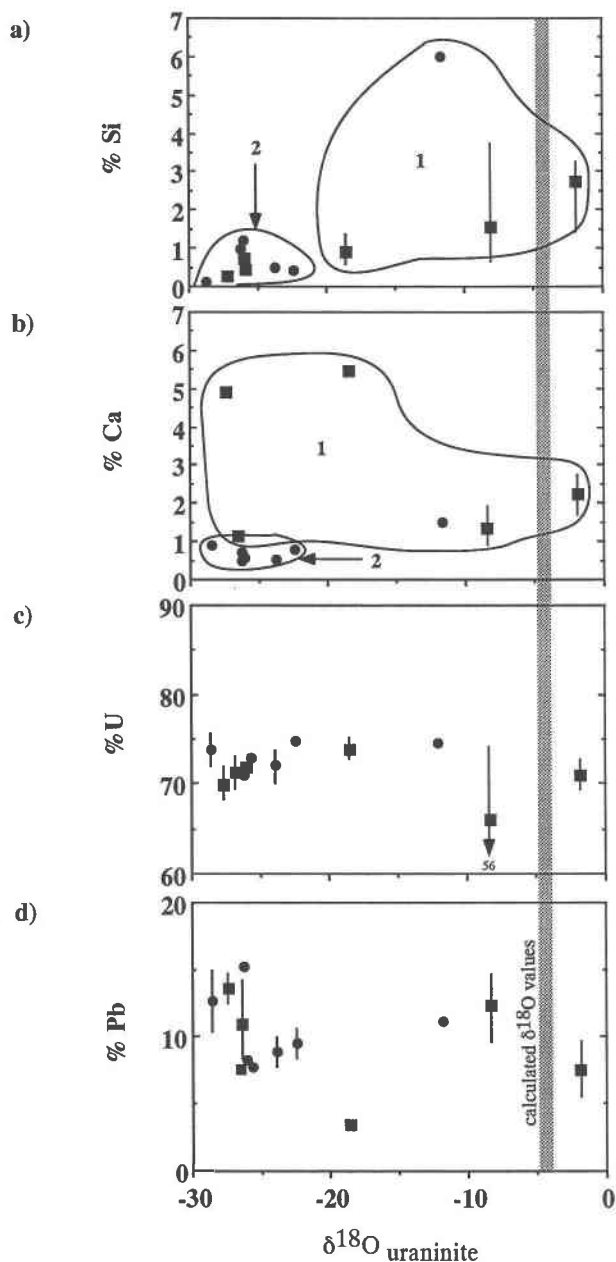


Fig. 3. Relationship between (a) $\delta^{18}\text{O}$ values and Si contents; (b) $\delta^{18}\text{O}$ values and Ca contents (fields 1 and 2 represent highly altered and relatively unaltered uraninite and pitchblende, respectively); (c) $\delta^{18}\text{O}$ values and U contents; and (d) $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values for uraninite and pitchblende minerals that would have formed from fluids with $\delta^{18}\text{O}$ values of $4 \pm 2\text{‰}$ and temperatures of approximately $200\text{ }^\circ\text{C}$ that formed diagenetic clay and silicate minerals associated with the U ores. Data from Table 1.

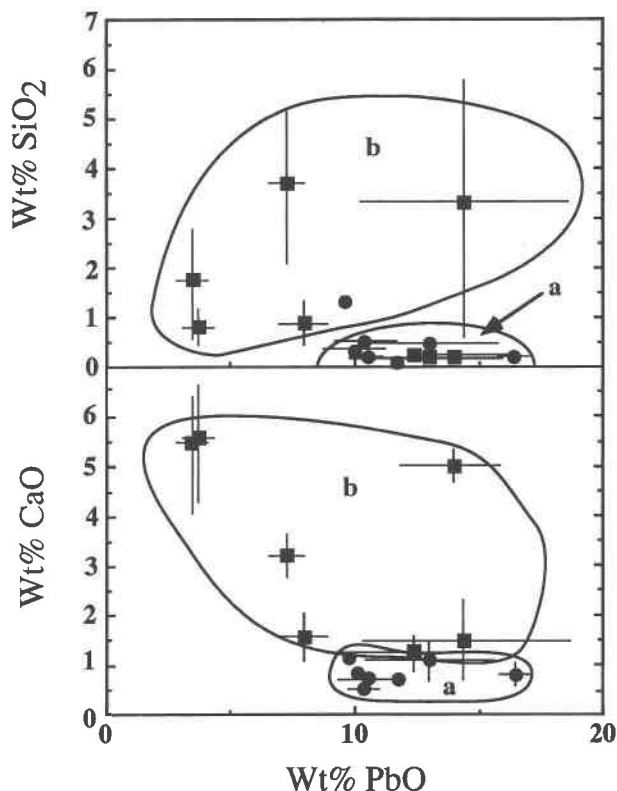


Fig. 4. Relationship between PbO and CaO and SiO_2 concentrations in uraninite and pitchblende. Symbols as in Fig. 3; data from Table 1; error bars indicate the total chemical variation in samples. Fields labeled a and b represent relatively unaltered and highly altered uraninite and pitchblende, respectively.

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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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-

TABLE 2. U and Pb isotopic compositions and U-Pb chemical, * $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ ages on selected uraninite samples from Table 1

Sample no.	Unspiked ratios			Spiked ratios			Ages (Ma)			
	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{204}\text{Pb}/^{207}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{233}\text{U}/^{235}\text{U}$	$^{233}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	U-Pb chemical	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{207}\text{Pb}/^{206}\text{Pb}$
KL478-14**	0.00016 (93)	0.00292 (17)	0.07978 (20)	28.61831 (476)	0.23421 (72)	0.00819 (29)	1334–1352	513	661	1207 ± 10
HL20-563.3**	0.00019 (38)	0.00201 (42)	0.09014 (94)	11.47610 (101)	0.08758 (76)	0.00763 (30)	740	—	—	1428 ± 10
M208/519.7**	0.00009 (27)	0.00113 (31)	0.08747 (65)	16.55287 (848)	0.13143 (16)	0.00795 (17)	929	142	156	1371 ± 13
8730-1†	0.00018 (43)	0.00219 (52)	0.08069 (65)	19.33008 (465)	0.15771 (53)	0.00816 (24)	1084–1329	371	491	1214 ± 15
8730-7†	0.00010 (18)	0.00125 (21)	0.08259 (43)	14.98860 (899)	0.11685 (81)	0.00781 (14)	730–1120	562	717	1260 ± 1
8730-24†	0.00002 (37)	0.00032 (50)	0.07316 (49)	19.26035 (347)	0.15864 (36)	0.00825 (11)	204–705	865	904	1018 ± 14
ML19†	0.00001 (51)	0.00003 (39)	0.07787 (61)	21.59612 (964)	0.17307 (19)	0.00800 (15)	1050–1294	684	865	1144 ± 16
Ea24†	0.00002 (72)	0.00033 (75)	0.05453 (69)	11.97040 (384)	0.09136 (18)	0.00768 (22)	261–282	223	231	393 ± 22
Ace Fay 1†	0.00018 (70)	0.00318 (12)	0.05776 (78)	11.20692 (570)	0.08558 (69)	0.00763 (49)	383–626	589	790	519 ± 29

Note: numbers in parentheses indicate errors in ratios (2σ).

* U-Pb chemical ages from Table 1.

** Athabasca unconformity type U deposits.

† Beaverlodge complex vein type U deposits.

metry on contemporaneous gangue minerals (Kotzer and Kyser, 1992; Rees, 1992).

Previous isotopic and microthermometric studies on clay, silicate, carbonate, and oxide gangue minerals in textural equilibrium with the uranium oxide minerals from the Athabasca Basin and Beaverlodge area indicate that the dominant fluids involved with formation of unconformity-type and complex vein-type U mineralization were saline fluids having $\delta^{18}\text{O}$ values of approximately $4 \pm 2\text{‰}$ and temperatures between 150 and 220 °C (Kotzer and Kyser, 1990b, 1992; Rees, 1992). Using these results, in conjunction with the fractionation factor of uraninite- H_2O calculated by Hattori and Halas (1982), the pitchblende and uraninite minerals should have $\delta^{18}\text{O}$ values of near -5‰ . However, at temperatures of 200 °C, the $\delta^{18}\text{O}$ values of the uraninite and pitchblende indicate they would have been in equilibrium with fluids having calculated $\delta^{18}\text{O}$ values of $< -11\text{‰}$ (Table 1). These fluids are substantially ^{18}O -depleted relative to those of the ore-forming fluids ($\delta^{18}\text{O} \sim 4\text{‰}$), determined from the silicate and clay gangue minerals coeval with the U minerals.

It is unlikely that the theoretical O isotope fractionation factor of Hattori and Halas (1982) is in error, especially by the amount needed to produce uraninite and pitchblende with such low $\delta^{18}\text{O}$ values from the high-temperature saline fluids of the Athabasca Basin and Beaverlodge area. The $\delta^{18}\text{O}$ values of hematite contemporaneous with high-grade U ore in the Athabasca Basin are -7.4 to -6.4‰ (Kotzer et al., 1992), and, since the theoretical O isotope fractionations for hematite- H_2O and uraninite- H_2O are similar at temperatures between 150 and 200 °C (Zheng, 1991), pitchblende and uraninite from the Athabasca Basin should have $\delta^{18}\text{O}$ values comparable with those of the coeval hematite. The low $\delta^{18}\text{O}$ values

measured in the U minerals indicate that 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 H_2O 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 $\delta^{18}\text{O}$ values of approximately -20 to -16‰ , could explain the low $\delta^{18}\text{O}$ values observed. The lack of petrographically observable alteration in many of the uraninite and pitchblende samples having low $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values reported by Hattori et al. (1978).

U-Pb and Pb-Pb isotope systematics

The $^{207}\text{Pb}/^{206}\text{Pb}$ ages of the uraninite and pitchblende minerals range between 393 and 1428 Ma, although most of the $^{207}\text{Pb}/^{206}\text{Pb}$ ages occur between 1018 and 1428 Ma (Table 2). The $\delta^{18}\text{O}$ values for these uraninite and pitchblende samples range substantially, although, with excep-

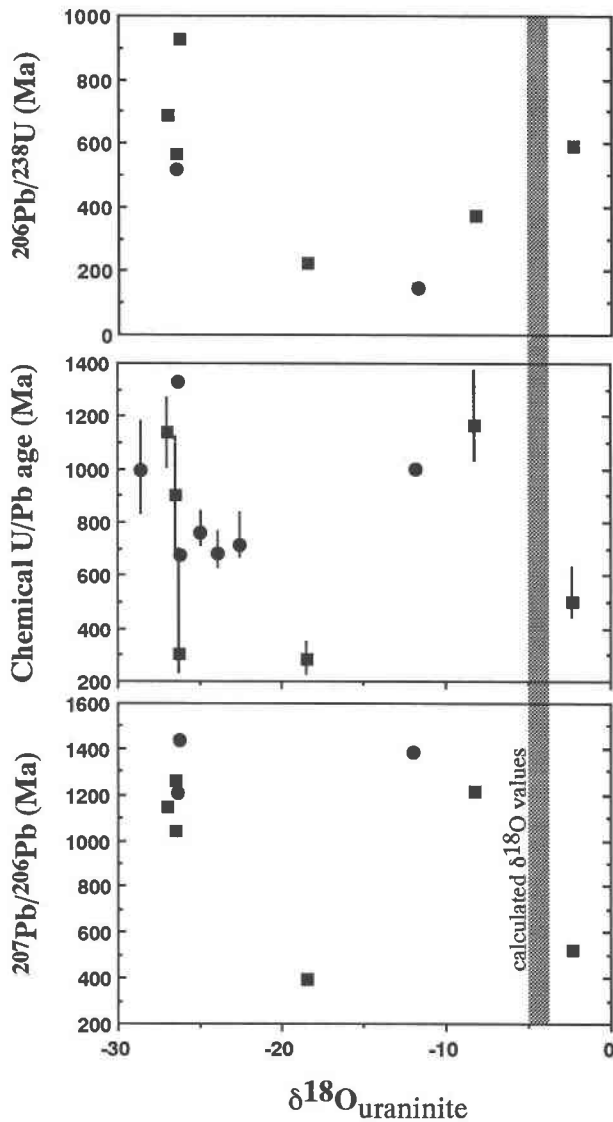


Fig. 5. Relationship between $\delta^{18}\text{O}$ values and $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and chemical U-Pb ages. Shaded vertical line represents the calculated $\delta^{18}\text{O}$ values for uraninite and pitchblende minerals that would have formed from fluids with $\delta^{18}\text{O}$ values of $4 \pm 2\text{‰}$ 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.

tions, those with the oldest ages generally have among the lowest $\delta^{18}\text{O}$ values (Fig. 5). The $^{207}\text{Pb}/^{206}\text{Pb}$ ages for uraninite and pitchblende from the Athabasca Basin range between 1120 and 1428, which are comparable to the discordant U-Pb ages of 1250–1521 Ma previously reported for presumed primary pitchblende and uraninite from unconformity type U deposits in the Athabasca Basin (e.g., Hohndorf et al., 1985; Carl et al., 1988; Ruhrmann and von Pechmann, 1989; Cumming and Krstic, 1992; Carl et al., 1992). Uraninite and pitchblende from

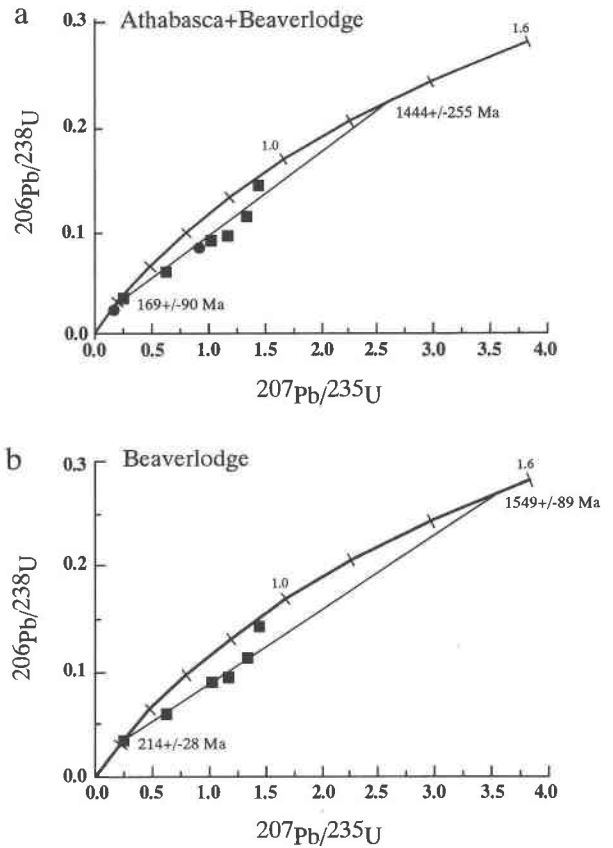


Fig. 6. U-Pb concordia diagrams of uraninite and pitchblende samples from both the Beaverlodge complex vein type and Athabasca unconformity type U deposits. Data from Table 2 and symbols as in Fig. 3a–3d; (a) U-Pb ratios of uraninite and pitchblende from both the Athabasca unconformity type and the Beaverlodge complex vein type U deposits. MSWD = 590. (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 $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1018–1260 Ma, which partially overlap the $^{207}\text{Pb}/^{206}\text{Pb}$ ages of uraninite and pitchblende from the Athabasca unconformity type U deposits. Similarities in the $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 393 and 519 Ma (Table 2). On the basis of their field and petrographic relationships, these two samples should have the same $^{207}\text{Pb}/^{206}\text{Pb}$ ages as other U minerals in the Beaverlodge area. These samples contain numerous microfractures

TABLE 3. U/Pb and ²⁰⁷Pb/²⁰⁶Pb ages of uraninite and pitchblende and Pb/Pb secondary isochron ages for sulfide and sulfate minerals from Athabasca and Beaverlodge areas

Deposit	Mineral dated (no. of samples from Tables 2 and 4)	U-Pb age (Ma)		²⁰⁷ Pb/ ²⁰⁶ Pb age (Ma)	Pb-Pb model age (Ma)	Reference
		Upper intercept	Lower intercept			
McArthur River	uran. (3)	1444 ± 255	169 ± 90	1120 ± 6 to 1428 ± 1		a
McArthur River	uran.	1521 ± 8	713 ± 14			
McArthur River	uran.	1401 ± 18	749 ± 24			2
McArthur River	cubic pyrite (2)				~130	b
Key Lake	uran. (1)	1444 ± 255	169 ± 90	1207 ± 10		a
Key Lake	uran.	1421 ± 49	671 ± 67			
Key Lake	uran.	1350 ± 4	300 ± 6			3
Key Lake	uran.	1250 ± 34	282 ± 13			4
Key Lake	pyrite, marcasite anglesite (8)				~370	b
Eagle Point	uran.	1400 ± 25				5
Eagle Point	uran.	1242 ± 2				6
Eagle Point	uran.	1153	340			6
Eagle point	cubic pyrite (1)				~130	b
Cigar Lake	uran.	1341 ± 26	323 ± 33			7
Midwest Lake	uran.	1328 ± 17	330 ± 120			8
Midwest Lake	galena				50 to 260	9
Beaverlodge complex vein type U (Fish- hook, Nicholson, Eagle, Martin Lk— 6)	uran. + pitch	1549 ± 89	214 ± 28	393 ± 22 to 1260 ± 1		a
Fishhook, Eagle	uran. + pitch.	1110 ± 50	270 ± 20			10
Nicholson		1125 ± 25	290 ± 15			10
	galena				1110 ± 50	10

Note: abbreviations used are: uran. = uraninite, pitch. = pitchblende, references are 1 = Cumming and Krstic (1992), 2 = Carl et al. (1992), 3 = Trocki et al. (1984), 4 = Hohndorf et al. (1985), 5 = Eldorado Resources (1987), 6 = Andrade (1989), 7 = Phillippe and Lancelot (1988), 8 = Baadsgaard et al. (1984), 9 = Cumming et al. (1984), 10 = Koeppel (1968), a = U/Pb and ²⁰⁷Pb/²⁰⁶Pb ages from Table 2, b = model Pb/Pb ages determined from ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios in Table 4.

(Fig. 2C) and have silica and Ca contents of 0.69–5.36 wt% SiO₂ and 2.90–6.66 wt% CaO, respectively (Table 1), and therefore most likely represent uraninite that has started to transform to coffinite and has experienced complete Pb loss. The δ¹⁸O values for these samples, which are as low as –18.4‰, indicate they probably have recrystallized with relatively modern-day meteoric water.

U-Pb chemical ages for uraninite and pitchblende minerals have been calculated based on U and Pb contents determined by electron microprobe (Table 1). Calculation of the ages assumes that Pb loss, U gain, or addition of thoranogenic Pb has not occurred (Cameron-Schimmann, 1978; Powers, 1985). Chemical U-Pb ages of uraninite and pitchblende from U deposits in the Beaverlodge and Athabasca U deposits range from 204 to 1389 Ma (Table 1, Fig. 5) and, in many cases, are substantially younger than their corresponding ²⁰⁷Pb/²⁰⁶Pb ages (Table 2). At the scale of the electron microprobe, the chemical U-Pb ages range considerably over distances of tens to hundreds of micrometers (Fig. 2E). Because variations in the chemical and stable isotopic compositions in the same areas are due to a late-stage alteration process, no temporal significance can be attributed to the chemical U-Pb ages.

U-Pb isotope ratios in samples of petrographically pristine uraninite and pitchblende from the Athabasca and Beaverlodge areas are highly discordant and yield a regression line having upper and lower intercepts of 1444 ± 255 and 169 ± 90 Ma (Fig. 6a). U-Pb ratios of only

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 Rimsaite, 1979; Baadsgaard et al., 1984; Trocki et al., 1984; Phillippe and Lancelot, 1988; Cumming and Krstic, 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

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

Sample no.	Description and remarks	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Sulfates in Pb dispersion halo from Key Lake				
D482-5	Pb dispersion halo (4680 ppm Pb)	22.858	16.101	42.118
D490-31	Pb dispersion halo (202 ppm Pb)	22.880	16.066	42.057
D490-16b	Pb dispersion halo (212 ppm Pb)	25.059	16.363	42.687
D482-36	Pb dispersion halo (824 ppm Pb)	54.959	19.470	44.109
D482-14	Pb dispersion halo (824 ppm Pb)	27.182	16.526	44.034
Late-formed sulfide minerals				
Ep226/811 (r)	pyrite	325.153	38.061	47.889
M162/493.7 (r)	pyrite	299.928	27.294	56.733
D458-34 (r)	pyrite and marcasite	25.327	16.232	45.954
D458-34 (l)		25.829	16.302	44.113
D482-61	pyrite	24.266	16.132	43.219
PR-2	pyrite	26.239	16.769	44.676
D474-46 (r)	pyrite and marcasite	22.843	16.063	40.257
D474-46 (l)		31.347	16.629	46.260
Sandstone-hosted galena (Key Lake)				
D466-14G	galena	22.175	16.121	41.865
D466-13G	galena	22.144	16.141	41.881

Note: Pb contents in parts per million were determined by ICP-AES in commercial laboratory; l = leach, r = residue.

for lowering their original $\delta^{18}\text{O}$ values. A sample of highly fractured pitchblende from the Beaverlodge complex vein type deposits, Ea24, has $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ 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 $\delta^{18}\text{O}$ value of -18.4‰ , and similarly young $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $\delta^{18}\text{O}$ value of -11.7‰ and concordant U-Pb ratios at approximately 140 Ma (Tables 1 and 2, Fig. 6a). However, this pitchblende has older $^{207}\text{Pb}/^{206}\text{Pb}$ and chemical U-Pb ages, indicating that it was subjected to a lesser degree of $\text{H}_2\text{O}/\text{rock}$ 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 $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ 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 uraniumogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios (Koepfel, 1968; Cumming et al., 1984; Kotzer and Kyser, 1990a). Late-formed pyrite, marcasite, galena, and anglesite, which occur in the faulted metasedimentary rocks and sandstones hosting the unconformity type U deposits at Key Lake, Midwest Lake, McArthur River, and Eagle Point, have $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios as high as 400 and 50, respectively, which suggests they have formed as a result of at least a two-stage Pb evolution process, whereby radiogenic Pb from the U minerals mixed with a primordial

Pb source (Cumming et al., 1984; Kotzer and Kyser, 1990a; Carl et al., 1992). The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ 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 $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ 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 uraniumogenic 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 $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ 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 uraniumogenic 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 $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of spatially associated late sulfide minerals in the faults that host the U minerals have resulted from large-

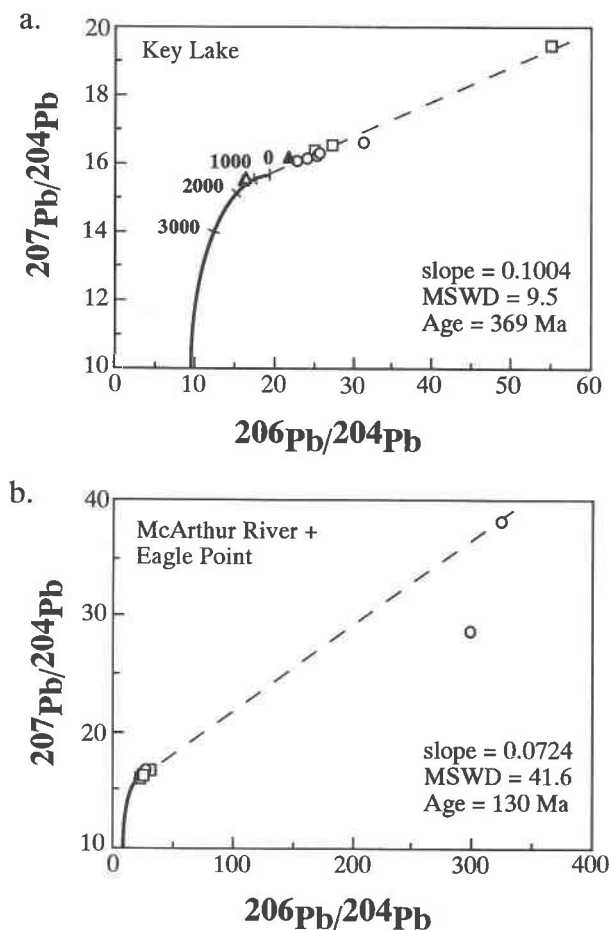


Fig. 7. Secondary isochron plots of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in sulfide and sulfate minerals of varying paragenesis from the Athabasca Basin. Data from Table 4 and from Bjorlykke and Sangster (1981). Symbols represent Pb ratios determined in galena from Pb-Zn deposits at George Lake (open triangles = data from Bjorlykke and Sangster, 1981), massive galena in sandstones near Key Lake U ore deposits (solid triangles), pyrite and marcasite in sandstones and fractures at Key Lake, McArthur River, and Eagle Point (open circles), anglesite in altered sandstones proximal to Key Lake U ore deposits (open squares). Stacey-Kramers growth curve shown for reference (Stacey and Kramers, 1975). (a) Secondary isochron plot comprising Pb ratios from galena at George Lake and from pyrite, marcasite, galena, and anglesite at Key Lake. Age calculated using secondary isochron equations (e.g., Cumming et al., 1984), assuming an age of 1400 Ma for the radiogenic Pb source. (b) Secondary isochron plot comprising Pb ratios from pyrite, marcasite, and anglesite at Key Lake (lower left) and from fracture-related cubic pyrite at McArthur River and Eagle Point. Age calculated using secondary isochron equations (e.g., Cumming et al., 1984), assuming the age of the radiogenic Pb source was 900 Ma, similar to the age of fracture-controlled coffinite formation in the basin (Hohndorf et al., 1985).

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 aqwi-

fers surrounding the U ore at the Cigar Lake U deposit (Fig. 1). The groundwater has distinct ^{206}Pb anomalies and contains relatively little dissolved U (Cramer and Vilks, 1989; Toulhoat and Beaucaire, 1989). Apparently, relatively modern meteoric water that has low $\delta^{18}\text{O}$ 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 $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ 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 $\delta^{18}\text{O}$ values (Fig. 5). Because the low $\delta^{18}\text{O}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 concordant chemical and isotopic U-Pb ages and young $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $\delta^{18}\text{O}$ value of -26.2‰ , indicating it has exchanged O isotopes with relatively modern meteoric water, it has a $^{207}\text{Pb}/^{206}\text{Pb}$ 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 Athabasca 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 $\delta^{18}\text{O}$ 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 $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in spatially associated sulfide and sulfate minerals.

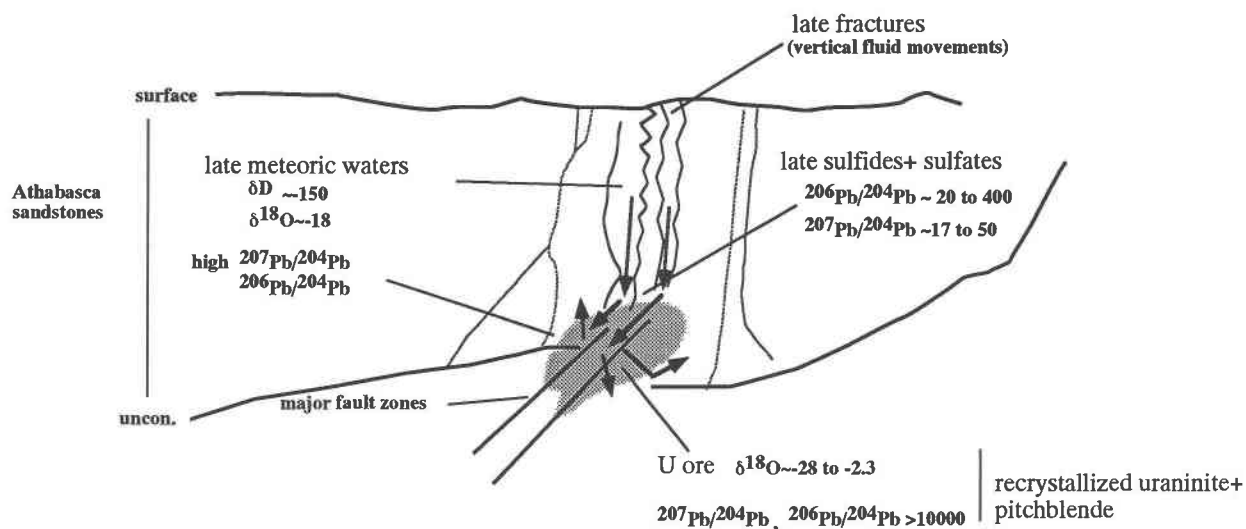


Fig. 8. Circulation patterns for late-stage ^{18}O - and D-depleted meteoric water along reactivated faults that host U mineralization in the Athabasca Basin based on O, U-Pb, and Pb isotope ratios in uraninite, pitchblende, and S minerals (this study, Tables 1, 2, 4), and H and O isotope ratios in clay and silicate minerals coeval with the U minerals from previous studies (Wil-

son and Kyser, 1987; Kotzer and Kyser, 1991, 1992). Shown are the $\delta^{18}\text{O}$ values and $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for U minerals, late-formed sulfate and sulfide minerals, and the $\delta^{18}\text{O}$ and δD 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 $\delta^{18}\text{O}$ 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_2O contents, increasing H_2O contents, and δD 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 δD and $\delta^{18}\text{O}$ 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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REFERENCES CITED

- Andrade, N. (1989) The Eagle Point uranium deposits, northern Saskatchewan, Canada. In *Uranium resources and geology of North America*. International Atomic Energy Agency Technical Document, 500, 455–490.
- Baadsgaard, H., Cumming, G.L., and Worden, J.M. (1984) U-Pb geochronology of minerals from the Midwest uranium deposit, northern Saskatchewan. *Canadian Journal of Earth Sciences*, 21, 642–648.
- Bjorlykke, A., and Sangster, D.F. (1981) Comparison of sandstone lead deposits and their relation to red-bed copper and carbonate-hosted lead-zinc deposits. *Economic Geology*, 75th Anniversary Volume, 179–213.
- Cameron-Schimann, M. (1978) Electron microprobe study of uranium minerals and its applications to some Canadian deposits, 229 p. Ph.D. thesis, University of Alberta, Edmonton, Alberta.
- Carl, C., Hochtendorf, F., Pechmann, E.V., Strnad, J.G., and Ruhmann, G. (1988) Geochronology of the Key Lake uranium deposit, Saskatchewan, Canada (abs.). *Journal of Chemical Geology*, 70, 133.
- Carl, C., von Pechmann, E., Hochtendorf, A., and Ruhmann, G. (1992) Mineralogy and U/Pb, Pb/Pb and Sm/Nd geochronology of the Key Lake uranium deposit, Athabasca Basin, Saskatchewan, Canada. *Canadian Journal of Earth Sciences*, 29, 879–895.
- Clayton, R., and Mayeda, T.K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, 27, 43–52.
- Cramer, V.V., and Vilks, P. (1989) Hydrogeochemistry and uranium fixation in Cigar Lake uranium deposit, northern Saskatchewan. In: *Uranium resources and geology of North America*. International Atomic Energy Agency Technical Document, 500, 359 p.
- Cumming, D.B., and Rimsaite, J. (1979) Isotopic studies of lead-depleted

- pitchblende in secondary radioactive minerals and sulphides from the Rabbit Lake uranium deposit, Saskatchewan. *Canadian Journal of Earth Sciences*, 16, 1702–1715.
- Cumming, G.L., and Krstic, D. (1992) The age of unconformity-related uranium mineralization in the Athabasca Basin, northern Saskatchewan. *Canadian Journal of Earth Sciences*, 29, 1623–1639.
- Cumming, G.L., Krstic, D., Worden, J., and Baadsgaard, H. (1984) Isotopic composition of lead in galenas and Ni-arsenides of the Midwest Deposit, northern Saskatchewan. *Canadian Journal of Earth Sciences*, 21, 649–656.
- Dyck, W. (1978) The mobility and concentration of uranium and its decay products in temperate surficial environments. In *Mineralogical Association of Canada Short Course in Uranium Deposits: Their Mineralogy and Origin*, 3, 57–92.
- Eldorado Resources Ltd. (1987) The Eagle Point uranium deposits, northern Saskatchewan. Saskatchewan Geological Society Special Publication, 8, 78–99.
- Faure, G. (1986) *Principles of isotope geology* (2nd edition), 589 p. Wiley, New York.
- Hattori, K., and Halas, S. (1982) Calculation of oxygen isotope fractionation between uranium dioxide, uranium trioxide and water. *Geochimica et Cosmochimica Acta*, 46, 1863–1868.
- Hattori, K., Muehlenbachs, K., and Morton, D. (1978) Oxygen isotope geochemistry of uraninites. *Geological Society of America—Geological Society of Canada Program with Abstracts*, 10, A417.
- Hoeve, J., and Quirt, D. (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 Report, 187, 187 p.
- Hoeve, J., and Sibbald, T.I.I. (1978) On the genesis of Rabbit Lake and other unconformity-type uranium deposits in northern Saskatchewan, Canada. *Economic Geology*, 73, 1450–1473.
- Hohendorf, F., Lenz, H., von Pechmann, E., and Voultsidis, V. (1985) Radiometric age determinations on samples of Key Lake uranium deposits. In *Geology of Uranium Deposits*, Canadian Institute of Mining and Metallurgy, special volume 32, 48–53.
- Koepfel, V. (1968) Age and history of the uranium mineralization of the Beaverlodge area, Saskatchewan. *Geological Survey of Canada Paper*, 67-31, 111 p.
- Kotzer, T.G. (1993) Fluid history of the Proterozoic Athabasca Basin, 304 p. Ph.D. thesis, University of Saskatchewan, Saskatoon, Saskatchewan.
- Kotzer, T.G., and Kyser, T.K. (1990a) The use of stable and radiogenic isotopes in the identification of fluids and processes associated with unconformity-type uranium deposits. In *Modern Exploration Techniques*, Saskatchewan Geological Society Special Publication, 10, 115–131.
- (1990b) Fluid history of the Athabasca Basin and its relation to uranium deposits. In *Summary of Investigations 1990*, Saskatchewan Energy and Mines, Saskatchewan Geological Survey, Miscellaneous Report, 90-4, 153–157.
- (1991) Retrograde alteration of clay minerals in uranium deposits: Radiation-catalysed or simply low-temperature exchange? *Isotope Geoscience*, 86, 307–321.
- (1992) Isotopic, mineralogic and chemical evidence for multiple episodes of fluid movement during prograde and retrograde diagenesis in a Proterozoic Basin. *Proceedings of the 7th International Symposium on Water-Rock Interaction*, Park City, Utah, 13–18 July, 1177–1181.
- Kotzer, T.G., Kyser, T.K., and Irving, E. (1992) Paleomagnetism and the evolution of fluids in the Proterozoic Athabasca Basin, northern Saskatchewan, Canada. *Canadian Journal of Earth Sciences*, 29, 1474–1491.
- Longstaffe, F., and Ayalon, A. (1990) Hydrogen isotope geochemistry of diagenetic clay minerals from Cretaceous sandstones, Alberta: Evidence for exchange. *Applied Geochemistry*, 5, 657–668.
- Ludwig, K.R. (1987) PBDAT: A computing program for processing raw Pb-U-Th isotope data. U.S. Geological Survey Open File Report, 85-547, 34 p.
- McMillan, R.H. (1978) Genetic aspects and classification of important Canadian uranium deposits. In *Mineralogical Association of Canada Short Course in Uranium Deposits: Their Mineralogy and Origin*, 3, 187–203.
- Parrish, R.R., Roddick, J.C., Loveridge, W.D., and Sullivan, R.W. (1987) Uranium-lead analytical techniques at the geochronology laboratory, Geological Survey of Canada. In *Radiogenic age and isotopic studies: Report 1*. Geological Survey of Canada Paper, 87-2, 3–7.
- Peiris, E., and Parslow, G. (1988) Geology and geochemistry of the uranium-gold mineralization in the Nicholson Bay-Fish Hook Bay Area. In *Summary of Investigations*, Saskatchewan Geological Survey Miscellaneous Report, 88-4, 70–77.
- Phillips, S., and Lancelot, J. (1988) U-Pb geochronological investigation of the Cigar Lake uranium deposit, Saskatchewan (abs.). *Chemical Geology*, 70, 135.
- Powers, L. (1985) Ore mineralogy and paragenesis of the Midwest deposit, northern Saskatchewan, 156 p. MSc. thesis, University of Saskatchewan, Saskatoon, Saskatchewan.
- Powers, L., and Stauffer, M. (1988) Multiple generations of pitchblende from the Midwest uranium-nickel deposit, northern Saskatchewan. *Canadian Journal of Earth Sciences*, 25, 1945–1954.
- Rees, M.I. (1992) History of the fluids associated with the lode-gold deposits, and complex U-PGE-Au vein-type deposits, Goldfields Peninsula, northern Saskatchewan, Canada, 209 p. MSc. thesis, University of Saskatchewan, Saskatoon, Saskatchewan.
- Ruhrmann, G., and von Pechmann, E. (1989) Structural and hydrothermal modification of the Gaertner uranium deposit, Key Lake, Saskatchewan, Canada. In *Uranium resources and geology of North America*. International Atomic Energy Agency Technical Document, 500, 363–379.
- Sassano, G., Fritz, P., and Morton, R. (1972) Paragenesis and isotopic composition of some gangue minerals from the uranium deposits of Eldorado, Saskatchewan. *Canadian Journal of Earth Sciences*, 9, 141–157.
- Sibbald, T.I.I. (1988) Nicholson Bay uranium-gold-platinum group element deposit studies. In *Summary of Investigations 1988*, Saskatchewan Geological Survey, Saskatchewan Energy and Mines Miscellaneous Report, 88-4, 77–81.
- Stacey, J., and Kramers, J. (1975) Approximation of terrestrial lead isotopic evolution by a two-stage model. *Earth and Planetary Science Letters*, 26, 207–221.
- Stacey, H.R., and Kaiman, S. (1978) Uranium minerals in Canada: Their description, identification and field guides. In *Mineralogical Association of Canada Short Course in Uranium Deposits: Their Mineralogy and Origin*, 3, 107–140.
- Toulhoat, P., and Beaucaire, C. (1989) Lead and uranium isotopes in groundwaters around the Cigar Lake uranium deposit, northern Saskatchewan. In *Uranium resources and geology of North America*. International Atomic Energy Agency Technical Document, 500, 361–362.
- Trocki, L., Curtis, D., Gancarz, J., and Banar, J. (1984) Ages of major uranium mineralization and lead loss in the Key Lake uranium deposit, northern Saskatchewan, Canada. *Economic Geology*, 79, 1378–1386.
- Wallis, R.H., Saracoglu, N., Brummer, J.J., and Golightly, J.R. (1983) Geology of the McClean uranium deposits. *Geological Survey of Canada Paper*, 82-11, 71–110.
- Wilson, M.R., and Kyser, T.K. (1987) Stable isotope geochemistry of alteration associated with the Key Lake uranium deposit, Canada. *Economic Geology*, 82, 1540–1557.
- Wilson, M.R., Kyser, T.K., Mehnert, H.H., and Hoeve, J. (1987) Changes in the H-O-Ar isotopic composition of clays during retrograde alteration. *Geochimica et Cosmochimica Acta*, 51, 869–878.
- Zheng, Y.F. (1991) Calculation of oxygen isotope fractionation in metal oxides. *Geochimica et Cosmochimica Acta*, 55, 2299–2307.