Oxygen, U-Pb and Pb-Pb Isotope Systematics in Uraninite from Complex U-Au-PGE Vein-Type and Unconformity-type Uranium Deposits in Northern Saskatchewan[1]

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Stable isotopic, fluid inclusion and petrographic studies on alteration mineral assemblages occurring with high-grade unconformity-type uranium mineralization in the Athabasca Basin indicate that the early (ca. 1400 to 1100 Ma), high grade uranium ore formed as a result of interaction between high temperature basement and saline basin fluids in highly faulted areas (Kotzer and Kyser, 1990; Wallis *et al.*, 1983; Wilson and Kyser, 1987). Fluid inclusion studies on gangue minerals associated with mineralogically and chemically complex U±Ni±As±S±Au±PGE vein-type deposits in the Beaverlodge area (Rees, unpubl. data; Sassano *et al.*, 1972) yield temperatures and salinities similar to those of the fluids in the Athabasca Basin associated with unconformity-type uranium mineralization (Kotzer and Kyser, this volume; Pagel *et al.*, 1980). That similar fluids and structural controls are responsible for ore formation in the complex vein-type in the Beaverlodge area and the Athabasca unconformity-type uranium deposits has been suggested by numerous workers (Hoeve and Sibbald, 1978; Peiris and Parslow, 1988; Sibbald, 1988) on the basis of geochemical similarities of alteration associated with uranium mineralization, similar sulphide and arsenide mineralogies, proximity of uranium mineralization to the sub-Athabasca unconformity, and similarity of Pb-Pb and U-Pb ages of uranium minerals from both areas (Koeppel, 1968; Hoeve and Sibbald, 1978; Peiris and Parslow, 1988; Sibbald, 1988).

Since the initial suggestions that the complex vein-type and unconformity-type uranium deposits may have formed by the same mechanism and from the same fluid events, many fluid inclusion data have been acquired from the alteration minerals in both the Athabasca unconformity-type (Pagel *et al.*, 1980; Kotzer and Kyser, 1990 and this volume) and the Beaverlodge complex vein-type uranium deposits (Quirt and Rees, 1987; Rees, unpubl. data). These data indicate inclusions of similar paragenesis and microthermometric properties in both areas.

1. Objectives and Methodology

The present investigation is to determine (1) pitchblende and uraninite from both complex and simple vein-type deposits in the Beaverlodge area have had a fluid history similar to uraninites from unconformity-type deposits in the Athabasca Basin and, (2) to what extent oxygen, lead and uranium isotopic compositions of uraninites record the timing, origin, and expanse of fluids in the basin.

Uraninite and pitchblende samples from vein-type and unconformity-type uranium deposits (Figure 1) were examined by reflected light microscopy and with an electron microprobe. Areas showing minimal effects of later alteration were selected in the most pristine samples to determine the oxygen, lead, and uranium isotopic compositions and hence assess the type and timing of the fluid events associated with uranium formation. Pb-Pb and U-Pb isotopic systematics in the uraninites are also compared to the Pb-Pb isotopic systematics in paragenetically late Fe, Ni-As and Pb sulphide minerals occurring in the Athabasca Basin (Cumming *et al.*, 1984; Kotzer and Kyser, 1990) to determine if the Pb isotope ratios in the sulphides are the result of alteration by later fluids of the earlier-formed uranium mineralization.

2. Oxygen Isotope and Electron Microprobe Results

Uraninite and pitchblende samples from both the Beaverlodge and Athabasca Basin have $\delta^{18}O$ values from -27 to -2.3 per mil (Table 1). Samples which show the least petrographic alteration and have SiO_2 contents of less than 1 wt. percent have the lowest $\delta^{18}O$ values, from -27 to -22.3 per mil (Figure 2). Other samples having similar optical reflectivities, but exhibiting a greater degree of fracturing and chemical heterogeneity as shown by a general increase in Si and Ca contents and higher U/Pb ratios, have $\delta^{18}O$ values greater than -20 per mil (Figure 2). Those uraninites having similar $\delta^{18}O$ values of -27 to -23 per mil (Table 1) are the least petrographically altered in both the Beaverlodge and Athabasca areas and may have formed from similar fluids. The increase in $\delta^{18}O$ values with SiO_2 content of the more altered uraninites is exactly the behaviour expected from simple addition of SiO_2 (enriched in $\delta^{18}O$ relative to most fluids) to uraninite (depleted in $\delta^{18}O$ relative to most fluids).

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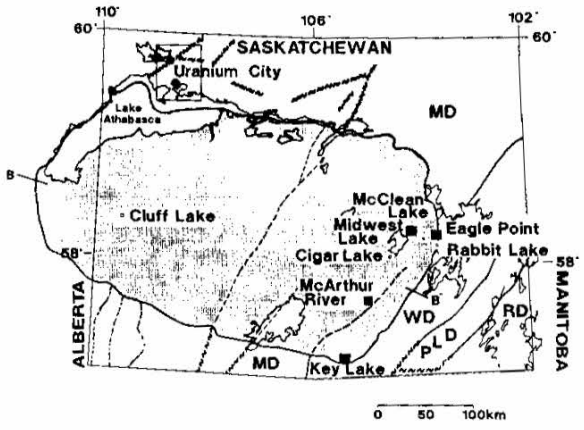

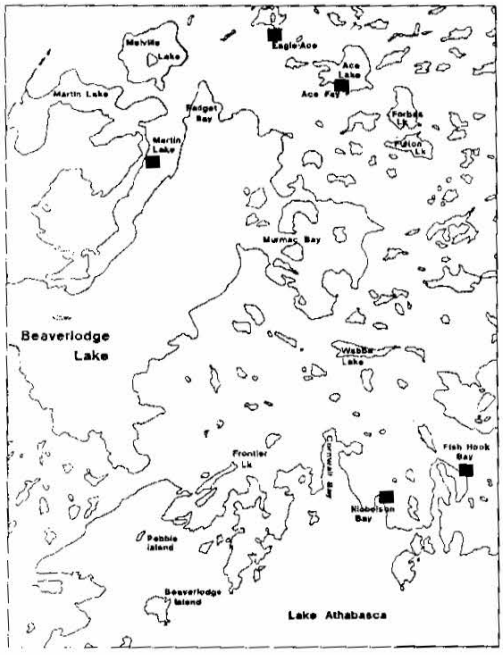

Figure 1 – Map of northern Saskatchewan showing lithostructural domains, the extent of the Athabasca Basin (shaded area), location of the uranium deposits, and uraninite samples used in this study (black squares). Enlargement for the Beaverlodge (Uranium City) area to show sample locations. MD, Mudjatik Domain; WD, Wollaston Domain; PLD, Peter Lake Domain; and RD, Rottenstone Domain.

Theoretical oxygen isotope fractionations between water and uraninite calculated by Hattori and Halas (1982) indicate that between temperatures of 25° to 200°C, uraninite will have $\delta^{18}O$ values which are 2 to 8 per mil lower than coexisting water. In the Athabasca Basin, the $\delta^{18}O$ values of co-existing quartz-illite assemblages and characteristics of fluid inclusions in euhedral quartz present in the alteration zones surrounding unconformity-type uranium deposits indicate formation at temperatures of 200°C from fluids having $\delta^{18}O$ values near 4 per mil. Fluids with similar temperatures and $\delta^{18}O$ values are suggested by analyses of gangue minerals associated with the complex, vein-type uranium

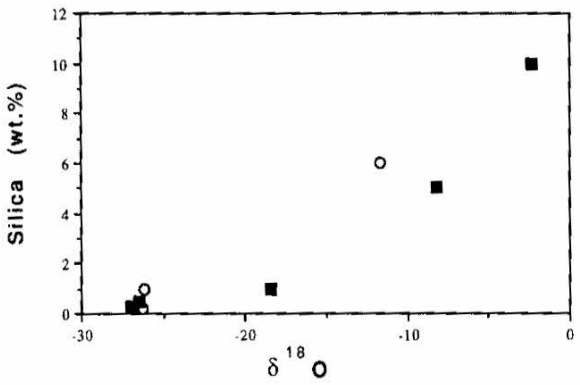

Figure 2 – Relation between $\delta^{18}O$ values of uraninites and silica content. Squares represent samples from Beaverlodge vein-type uranium deposits and open circles are samples from Athabasca unconformity-type uranium deposits. Data from Table 1.

deposits in the Nicholson-Fish Hook area. (Rees, unpubl. data).

Using the theoretical fractionation factor for uraninite-water and $\delta^{18}O$ values of 4 per mil and temperatures of 200°C for fluids associated with uranium mineralization, the $\delta^{18}O$ value of uraninite in both the Athabasca and Nicholson-Fish Hook areas could be from 2 to -4 per mil. None of the uraninites analyzed have $\delta^{18}O$ values this high, except for a sample of highly-fissile uraninite from the Ace-Fay mine. However, this sample also has a high SiO_2 content, which would suggest its initial chemical composition has been substantially altered. Accordingly, either the fractionation factor for uraninite is larger than has been originally calculated or the uraninites have undergone oxygen isotope exchange with fluids other than the high-temperature Athabasca fluids.

It is unlikely that the theoretical fractionation factors are in error, especially by the magnitude needed to produce uraninites having such low $\delta^{18}O$ values from high temperature Athabasca fluids with $\delta^{18}O$ values near 4 per mil. However, modern meteoric waters in the Athabasca Basin have $\delta^{18}O$ values of about -20 per mil, and recrystallization of uraninite with this meteoric water could produce the low $\delta^{18}O$ values of less than -20 per mil measured in the uraninites. That such meteoric waters have affected fault controlled uranium deposits in the Athabasca Basin is substantiated by the hydrogen isotopic compositions of clay minerals proximal to unconformity-type deposits, which indicate interaction between the clays and large quantities of low-temperature, meteoric water (Kotzer and Kyser, 1990 and this volume; Wilson and Kyser, 1987). Thus, the oxygen isotopic composition of the uraninites suggest that most samples have been extensively recrystallized in the presence of relatively modern meteoric waters.

3. U-Pb and Pb-Pb Ages of Uraninite

Chemical ages of the uraninites have been calculated using U and Pb contents measured with an electron

Table 1 – Petrologic Descriptions, Chemical and Isotopic Analyses, and Ages of Uranium for Uranium Minerals (see Figure 1 for locations). U/Pb chemical ages are determined by microprobe analysis (Cameron-Schimann, 1978).

Sample	Description	Remarks	U-Pb chemical age (Ma) electron microprobe	$^{207}Pb/^{206}Pb$ age (Ma)	^{18}O
8730-1	aniso. pitchblende + carbonate in vein Nicholson #4 (complex vein-type)	variable Si, Ca, Pb	802 - 1870	1214 ± 15	-8.2
8730-7	aniso. pitchblende intergrown with rammels+nicco. Nicholson #4 (complex vein-type)	homogenous Si, Ca, Pb	730 - 1120	1260 ± 10	-26.5
8730-24	weakly iso. pitchblende + quartz in vein Fish Hook 'B' (complex vein-type?)	variable Si, Ca, Pb	204 - 705.2	1018 ± 24	
Ea 26	massive, aniso.-iso. uraninite + carbonate + pyr./cpy/galena cubes Eagle Ace Mine (simple vein-type)	high Si, Ca, and homo. Pb - highly altered areas near fracs. (galena cubes)	252 - 312	----------	-18.6
Ea 24	----------same as Ea 26 ----------		261 - 282	393 ± 22	-18.5
ML 19	massive, aniso. uraninite + carbonate Martin Lake Mine (complex vein-type)	homo. Ca, Si, Pb v. little alteration	1050 - 1294	1144 ± 16	-27.0
Ace Fay 1	fissile, massive uraninite aniso. - iso. Ace Fay Mine (simple vein-type)	variable Si, Ca, Pb high SiO_2 contents appears v. heterogeneous	383 - 626	519 ± 29	-2.3
KL 478-14	massive, aniso. uraninite in vein x-cutting Athabasca Sst. Key Lake (uncon.-type)	v. homo. Si, Ca, Pb contents	1314	1207 ± 10	-26.3
M208-519.7	aniso. uraninite w/cpy. in silicified sst. x-cut by pyr. Bermuda Lake, McArthur River area (uncon.-type)	slightly variable Ca, Pb	~ 100 - 929	1371 ± 13 (possible qtz. contamination)	-11.7
M212-516.2	massive, botryoidal pitchblende Bermuda Lake, McArthur River area (uncon.-type)	----------	----------	1120 ± 6	-22.3
HL20-563.3	aniso., massive uraninite near unconformity, McArthur River area (uncon.-type)	v. homo. Si, Ca, Pb	~ 200 - 740	1428 ± 10	-26.2

aniso. = anisotropic; iso. = isotropic; pyr. = pyrite; cpy = chalcopyrite; homo. = homogeneous; fracs. = fractures; uncon. = unconformity; qtz. = quartz

microprobe (Cameron-Schimann, 1978), assuming that no Pb loss or gain has occurred and no thoranogenic Pb is present (Table 1). In some uraninite samples, a range of ages results from analyzing a number of areas which are only a few microns apart (Table 1). However, in nearly all cases, the U-Pb chemical age is younger than the $^{207}Pb/^{206}Pb$ age of the uraninites indicating Pb loss has occurred. The large range of chemical ages in some of the samples provides a qualitative indication of the amount of alteration by later fluids. The U-Pb chemical ages do not correlate well with $\delta^{18}O$ values because the $\delta^{18}O$ values are increased by the addition of SiO_2 to some of the samples.

The $^{207}Pb/^{206}Pb$ ages of the uranium minerals range from 393±22 to 1428±10 Ma (Table 1) with the bulk of the ages occurring between 1018±24 to 1428±10 Ma. Uraninite from the Beaverlodge complex vein-type uranium deposits have $^{207}Pb/^{206}Pb$ ages of 1018±24 to 1260±10 Ma, which overlap the $^{207}Pb/^{206}Pb$ ages of uraninites from the Athabasca unconformity-type deposits, suggesting that the complex vein-type uranium formed at the same time as did the high-grade uranium deposits in the Athabasca Basin.

Two samples from the Beaverlodge simple vein-type deposits, have $^{207}Pb/^{206}Pb$ ages of 393±22 and 519± 29 Ma (EA 24; Ace-Fay - Table 1). As these samples are fractured and contain chemical evidence for later alteration, they most likely represent a highly-altered, recrystallized early uraninite which has undergone complete lead loss. A comparison of the $^{207}Pb/^{206}Pb$ ages and $\delta^{18}O$ values of all the uraninites shows that some of the oldest ages are associated with the lowest $\delta^{18}O$ values (Figure 3). Inasmuch as low $\delta^{18}O$ values represent recrystallization of the uraninites by low-temperature meteoric waters, the $^{207}Pb/^{206}Pb$ ages indicate that this recrystallization event occurred relatively recently and that not all of the lead was removed from the uraninite during recrystallization. If the uraninite recrystallized completely and lead loss was complete, young $^{207}Pb/^{206}Pb$ ages would result, as is the case for the simple vein-type uraninites from the Beaverlodge area (EA 24; Ace-Fay - Table 1).

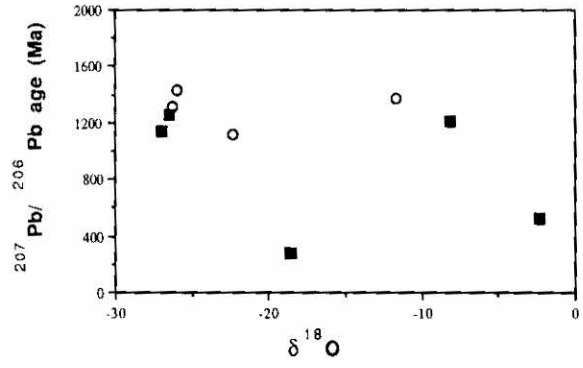

Figure 3 – Relation between $^{207}Pb/^{206}Pb$ age and $\delta^{18}O$ value of uraninites (squares represent samples from Beaverlodge complex and simple vein-type uranium deposits and open circles represent samples from Athabasca unconformity-type uranium deposits). Data from Table 1.

The U-Pb isotopic analyses of the uraninites from the Beaverlodge vein-type deposits yield a regression age of 1549±89 and a lower intercept age of 214±28 Ma from samples that are highly discordant (Figure 4a). As with many of the U-Pb ages previously reported for uraninites in the Athabasca Basin, the age obtained by regression of the Beaverlodge samples is probably not significant given the high degree of discordancy. Uraninite from the simple vein-type Eagle Ace Deposit (Ea 24) plots very close to the lower intercept with the concordia curve. As this sample has high Si, Ca, and low Pb contents and young $^{207}Pb/^{206}Pb$ and U/Pb chemical ages, it represents a sample of uraninite which has undergone complete lead loss during recrystallization by a later fluid event similar to what occurred at many of the unconformity-type deposits in the Athabasca Basin (Cumming and Rimsaite, 1978; Phillipe and Lancelot, 1988; Ruhlmann, 1985; Trocki *et al.*, 1984). Samples of petrographically and chemically unaltered uraninite from both the Athabasca and Beaverlodge areas yield a U-Pb regression line with intercepts of 1444±255 and 169±90 Ma (Figure 4b). Most samples are very discordant as a result of extensive recrystallization by a modern fluid, which is consonant with the oxygen isotopic compositions that indicate most uraninites have been recrystallized in the presence of relatively modern meteoric waters. Despite the extensive recrystallization reflected by the U-Pb ages and $\delta^{18}O$ values, most samples have retained an old age of formation in their $^{207}Pb/^{206}Pb$ ratios because not all of the lead was lost during recrystallization.

4. Implications of Pb-Pb Ages from Sulphides in the Athabasca Basin

The $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios from the late-stage sulphides occurring in the basement rocks and sandstones of the unconformity-type uranium deposits at Key Lake, McArthur River and Eagle Point (this study) and Midwest Lake (Cummings *et al.*, 1984) plot on secondary isochrons (Figure 5) which are discordant with a crustal Pb growth curve (Stacey and Kramers, 1975). Slopes of the secondary isochrons from sulphides in the Athabasca Basin indicate formation relatively late in the history of the basin. At Key Lake, late sulphides and sulphate minerals plot on a secondary isochron yielding an actual age of 444 Ma for the sulphides using a radiogenic Pb source age of 1406 Ma (Figure 5a). Late sulphides in the Athabasca Basin occur as pyrite and marcasite on re-activated high angle fractures at Eagle Point and McArthur River. The $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ isotopic compositions of lead in these sulphides plot on a secondary isochron yielding an actual age of 130 Ma for sulphide formation on the high angle fractures using a radiogenic Pb source age of 904 Ma (Figure 5b). These ages are similar to the galena ages associated with uranium at Midwest Lake (Cummings *et al.*, 1984) and to the lower intercept U-Pb age of uraninites. Such young ages suggest that the entire Athabasca Basin was affected by late stage fluids which mobilized lead from uranium mineralization into sulphides.

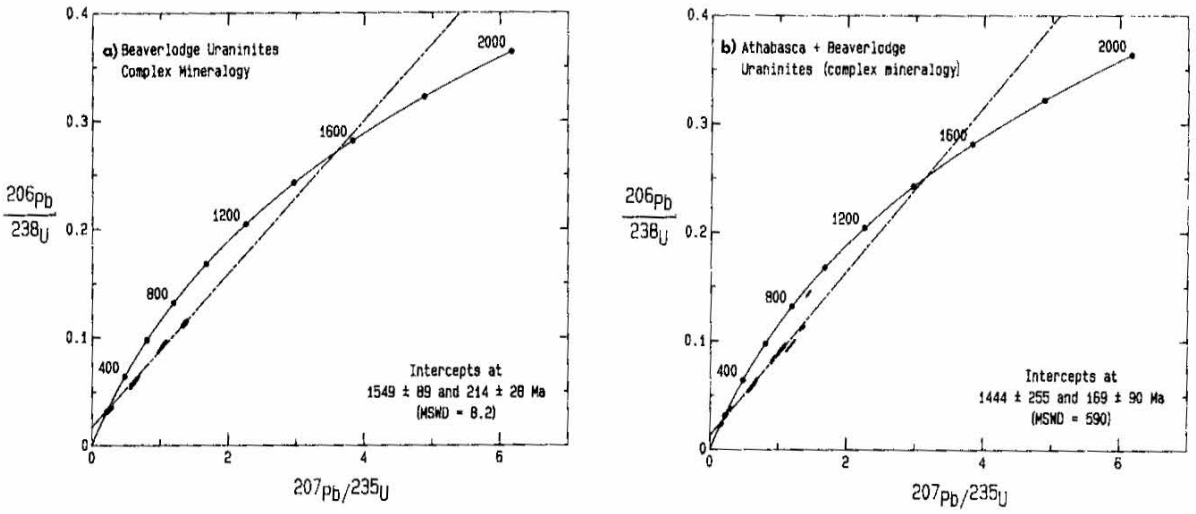

Figure 4 – a) U-Pb concordia plot of uraninite samples from the complex vein-type uranium deposits in the Beaverlodge area. Highly discordant points yield a regression line with intercepts at 1549±89 and 214±28 Ma. b) U-Pb concordia plot of uraninite from both the Beaverlodge vein-type and the Athabasca unconformity-type uranium deposits. Large MSWD indicates that all samples are not from the same fluids.

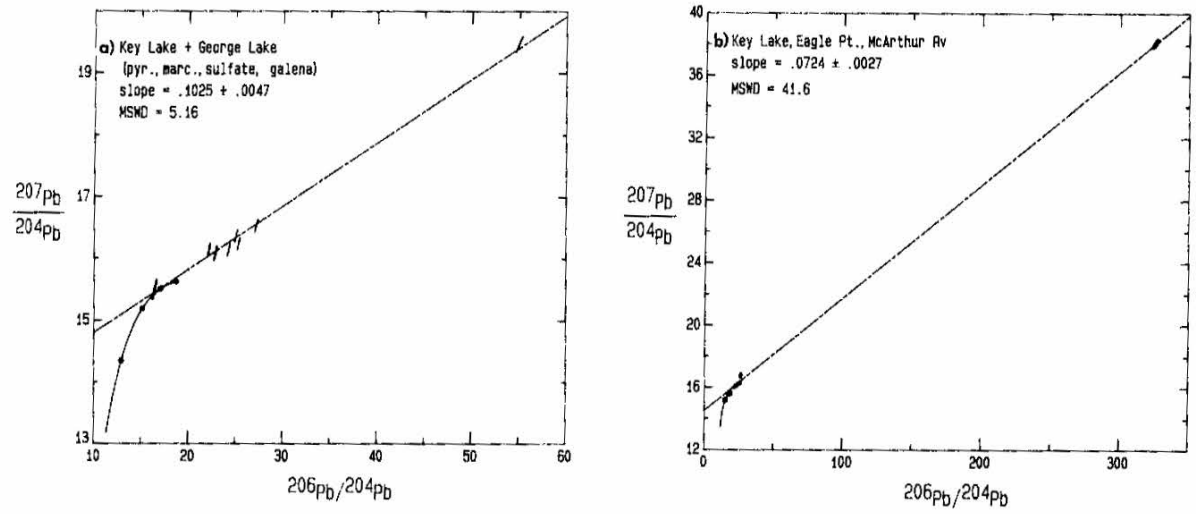

Figure 5 – Pb isotopic compositions of sulphides and sulphates of varying paragenesis in the Athabasca Basin. a) $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ secondary isochron plot of sulphides and sulphates having a similar paragenesis at the Key Lake deposit and nearby George Lake. b) $^{207}Pb/^{204}Pb$ and $^{204}Pb/^{204}Pb$ secondary isochron plot of late Fe-sulphides from Key Lake, McArthur River, and Eagle Point.

5. Conclusions

1) The $\delta^{18}O$ values and Pb-Pb isotope systematics of the most pristine uraninites (generally those with $\delta^{18}O$ values below -22 per mil) from both the Athabasca unconformity-type and vein-type Beaverlodge uranium deposits are similar and indicate that both areas have been affected by similar fluid events.

2) $^{207}Pb/^{206}Pb$ ages of uraninites from both the complex vein-type deposits in the Beaverlodge area and unconformity-type deposits in the Athabasca Basin are older than the U-Pb ages of the uraninites indicating that various degrees of Pb loss have recently occurred. On the basis of the $^{207}Pb/^{206}Pb$ ages, uranium mineralization in both the Beaverlodge complex vein-type and Athabasca unconformity-type deposits is temporally related.

3) Using the oxygen isotope fractionation factor calculated for the system uraninite-water (Hattori and Halas, 1982), most uraninites have equilibrated with

a fluid having a $\delta^{18}O$ value similar to modern meteoric water. Obvious petrographic alteration of uraninites affected by this fluid event are absent, but the Pb-Pb isotope systematics suggest that uraninite can recrystallize and retain some of the $^{207}Pb/^{206}Pb$ isotope systematics.

4) The general agreement between the lower intercept ages from the U-Pb concordia plots (Figures 4a and b) and the Pb-Pb ages of sulphide formation (Figures 5a and b) indicates that the U-Pb and Pb-Pb systematics in the uranium minerals and sulphides in both the Athabasca Basin and the Beaverlodge areas are coupled systems that reflect large scale fluid processes.

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