

Petrography, Chemical Ages, Stable Isotopic Compositions, and REE Contents of Three Stages of Uranium Mineralization from the Athabasca Basin¹

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Uranium deposits of the Athabasca Basin are formed from the interaction between high salinity, metal-bearing basinal brines and reducing basement fluids at temperatures of 200°C (Pagel *et al.*, 1980; Bray *et al.*, 1988; Wallis *et al.*, 1983; Wilson and Kyser, 1987; Kotzer and Kyser, 1990b, 1993). The mixing of these two fluids,

and therefore the formation of the uranium deposits, occurred along subvertical fault zones at the unconformity between the Aphebian metasedimentary basement rocks and the overlying Helikian sandstones and conglomerates (Kotzer and Kyser, 1990b). Stable isotopic, fluid inclusion, and radiogenic studies of clay and other minerals in and around unconformity-type uranium deposits suggest that the Athabasca Basin has had a long and protracted fluid history (Powers and Stauffer, 1988; Wilson and Kyser, 1987; Kotzer and Kyser, 1990b, 1993). The long lasting nature of hydrothermal activity in the Athabasca Basin has also affected the mineralogical, isotopic and chemical composition of uranium mineralization (Kotzer and Kyser, 1990b).

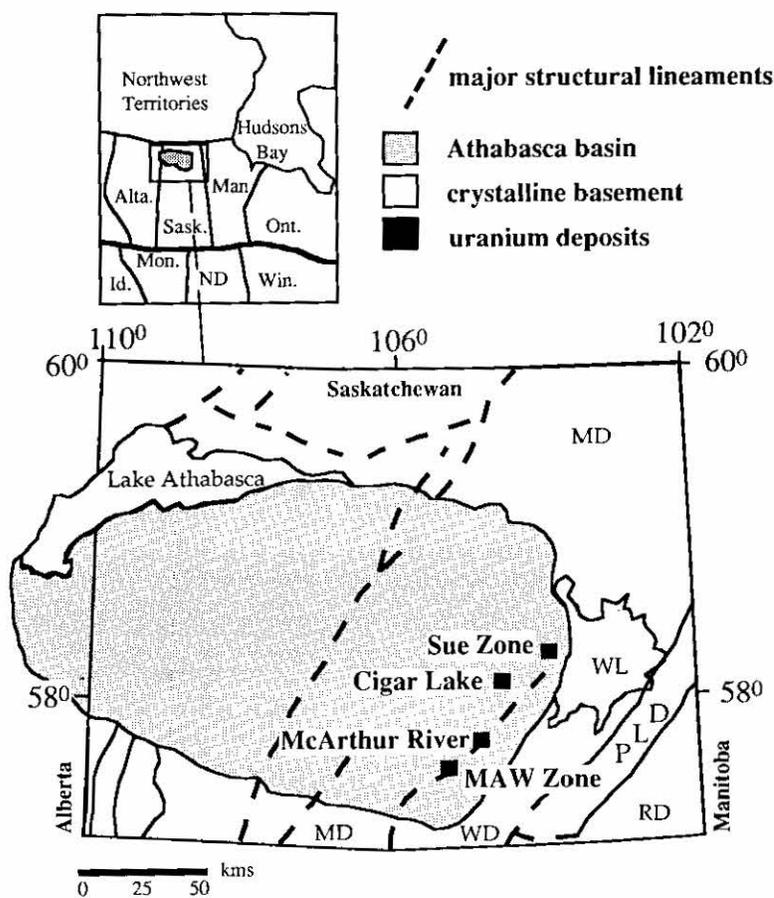


Figure 1 - Map showing the extent of the Athabasca Basin, location of the uranium deposits from which samples were collected for this report, and major lithostructural domains in the crystalline basement of Saskatchewan (after Hoeve and Sibbald, 1978). Abbreviations: MD=Mudjatik Domain; WD=Wollaston Domain; PLD=Peter Lake Domain; RD=Rottenstone Domain; and WL=Wollaston Lake.

Chemical analyses of Athabasca Group sandstones and conglomerates in the McArthur River–Wheeler River area and altered sandstones from the Maw Zone (Figure 1) indicate anomalously high abundances of incompatible-element rich minerals, especially phosphates enriched in rare earth elements (REE) (SEM Assessment files 74H-0006, -0010, -0011; MacDougall, 1990; Quirt *et al.*, 1991).

The phosphates clearly indicate that the fluids which affected the Athabasca Basin and the uranium deposits therein were transporting REE as well as uranium. The purpose of this study is to determine the form and age of REE mineralization and assess the mobility of the REE in basinal fluids and their relation to uranium mineralization. Preliminary results reported here include details of the paragenesis, age, chemistry, and the $\delta^{18}\text{O}$ iso-

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topic composition of the various stages of uranium ore. REE contents of ore are compared to the REE patterns of HREE-, yttrium-rich phosphates from the Maw Zone. Samples for this study were collected from the Maw Zone REE showing, and McArthur River–Wheeler River area, Cigar Lake, and Sue Zone uranium deposits (Figure 1).

1. Geologic Consideration

Uranium mineralization at the McArthur River P2 North uranium deposit, which occurs in the Athabasca Group sandstone and basement graphite metasediment from 500 to 600 m depth, is structurally controlled by a regional, northeasterly trending thrust-fault cutting the graphitic basement rocks and overlying sandstones. Several stages of hydrothermal alteration involving silica, illite, kaolinite, chlorite, and dravite are associated with, predate or postdate initial uranium mineralization (Kotzer and Kyser, 1990a; Marlatt *et al.*, 1992).

The main ore body or "pod" at the Cigar Lake deposit, underlain by Aphebian metasediments, occurs at and immediately above the unconformity that separates these basement rocks and the overlying Helikian sandstones of the Athabasca Group. Lenses of "perched" mineralization are also present entirely within Helikian sandstones (Bruneton, 1993; Reyx and Ruhlmann, 1993). Hydrothermal alteration involving illite, kaolinite, sudoite, Fe-chlorite, and hematite is associated with, and followed, the initial uranium mineralizing event (Percival *et al.*, 1993).

The Sue Zone deposits are spatially related to the unconformity separating the Athabasca Group from the underlying graphitic metasedimentary rocks of the Wollaston Group, and are clustered on the western edge of a presumed Archean 'dome', along a 2.9 km north-south trend. The deposits occur at depths of 5 to 180 m below surface. Sue A and B deposits are entirely hosted by sandstones at and above the unconformity with little or no uranium mineralization occurring in the basement rocks. Sue C, CQ, D, and E deposits are basement-hosted ore bodies with limited uranium mineralization in the sandstone. Mineralization at the Sue C deposit forms a single lens, whereas mineralization at the Sue CQ, D, and E deposits occurs as multiple lenses. Alteration associated with the uranium mineralization in the Sue Zone deposits is typical of other Athabasca uranium deposits (Ey *et al.*, 1991; Baudemont *et al.*, 1993).

The Maw Zone is on the east side of a southeast dipping reverse fault. The fault is believed to occur at the contact between Archean granitic gneisses and Wollaston Group pelitic to psammopelitic graphitic gneisses (SEM Assessment files 74H-0006, -0010, and -0011). On surface, the Maw Zone appears as silicified, dravite, faulted, and anomalously radioactive sandstone. Diamond drilling by Agip Canada Ltd. intersected zones of highly brecciated sandstone down to a depth of 230 m. The fractures are locally open and lined with euhedral quartz, or healed by emerald green dravite and illite. The large vertical and restricted horizontal extent of the fracturing indicates that the process responsi-

ble for brecciation is one of intense hydrothermal activity (Quirt *et al.*, 1991).

2. Paragenesis of the Uranium Ore

Uranium mineralization from McArthur River, Cigar Lake, and Sue Zone is petrographically similar (Figure 2) and therefore will be discussed collectively. Three main ages of ore formation are observed in thin section and in back scatter electron (BSE) photographs (Figure 2). These are: stage 1 uraninite and pitchblende; stage 2 pitchblende and coffinite; and stage 3 pitchblende and coffinite.

a) Stage 1 Uranium Mineralization

Stage 1 uraninite occurs as homogeneous masses (Figure 2c) and uraninite cubes (Figure 2a) which exhibit the highest reflectivities and earliest paragenesis. Pitchblende occurs as nodular masses which range in size up to several centimetres across. Nodules are composed of many botryoids that exhibit radial textures in thin section as a result of uniformly distributed radial shrinkage cracks. Spaces between botryoids are filled with clay minerals and Ni-Cu arsenides.

Stage 1 uraninite and pitchblende are characterized by high PbO contents (13.1 to 16.7 wt.%), low SiO₂ and CaO contents (<1 wt.%), and very low FeO contents (<0.2 wt.%) (Figure 3). Variation in PbO, SiO₂ and CaO contents, and chemical ages (see below) likely reflect cryptic alteration by subsequent fluids that affected virtually all stage 1 uranium mineralization.

b) Stage 2 Uranium Mineralization

Stage 2 uranium mineralization includes massive pitchblende, coffinite, disseminated coffinite, and alteration rims on stage 1 botryoids of pitchblende and uraninite (Figure 2d). Coffinite exhibits lower reflectivities relative to pitchblende. Locally, massive pitchblende appears as unaltered homogeneous masses with high reflectivities. Associated with the stage 2 uranium minerals are Ni-Cu sulpharsenides. Stage 2 uranium minerals are characterized by intermediate PbO contents (8.6 to 11.0 wt.%), intermediate SiO₂ and CaO contents (1 to 2 wt.%), relatively high FeO contents (~2 wt.%), and intermediate U-Pb chemical ages (Figure 3). The majority of stage 2 uranium mineralization appears to be an alteration product of the stage 1 uraninite and pitchblende, however, the occasional mass of unaltered highly reflective pitchblende may represent either the introduction of new ore or complete recrystallization and reprecipitation of stage 1 uranium mineralization by a fluid event at ca. 900 Ma.

c) Stage 3 Uranium Mineralization

Stage 3 uranium mineralization occurs as massive pitchblende and coffinite. The pitchblende generally appears unaltered and is highly reflective. The coffinite occurs as coliform bands along the edges of stage 1 and stage 2 ore and as feathery crystalline dark grey masses in carbonate veins (Figure 2b). Stage 3 coffinite and pitch-

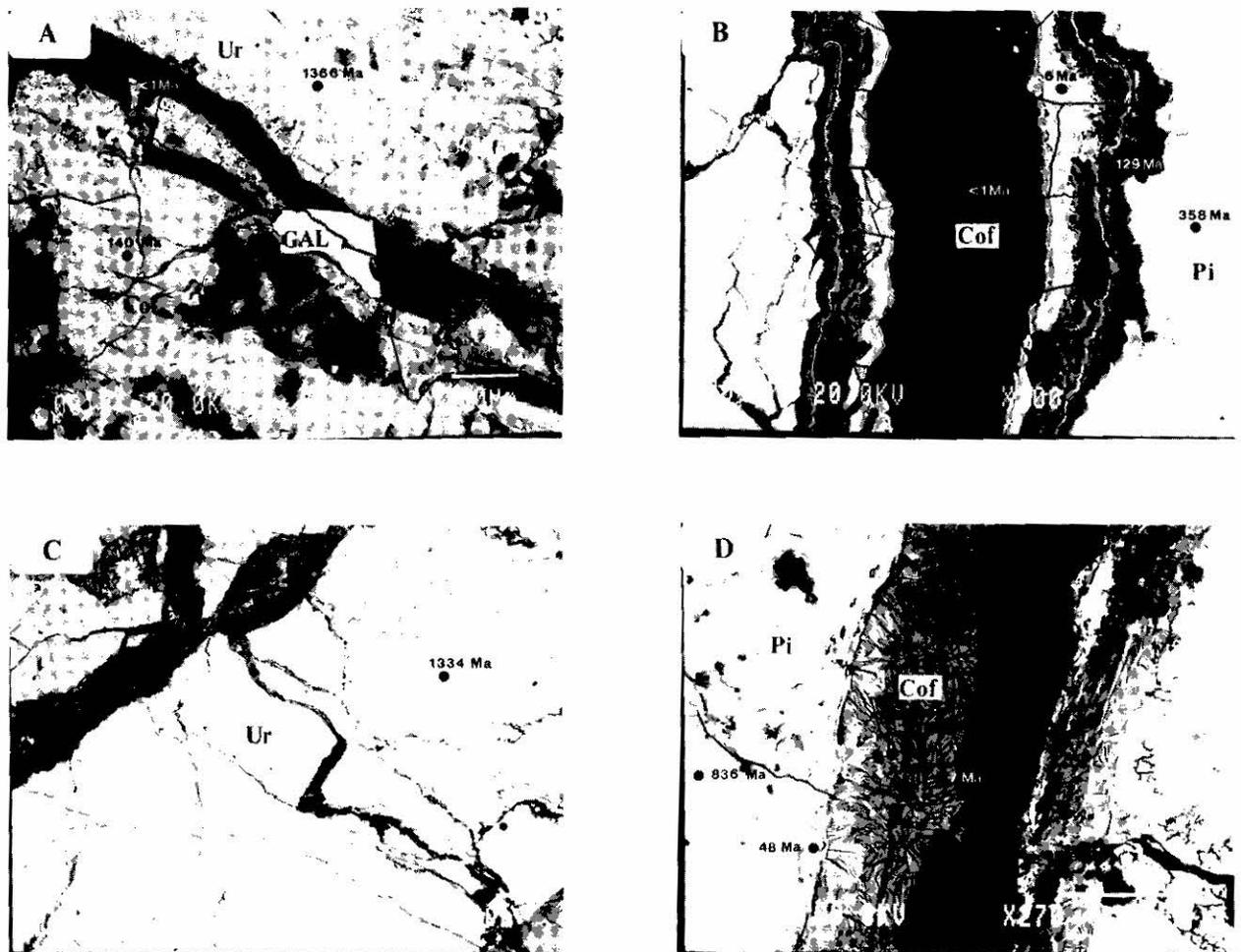


Figure 2 - Back scatter electron photographs of the three dominant stages of uranium mineralization from deposits of the Athabasca Basin with chemical ages indicated: a) sample from the Sue C zone (Sue C-247) basement hosted deposit showing characteristic alteration of stage 1 uraninite; b) sample from Cigar Lake (480-170) showing stage 2 and 3 uranium mineralization near a carbonate microvein (black); c) sample from McArthur River (204-503.5) of optically pristine unaltered stage 1 uraninite; d) sample from McArthur River (236-515) showing typical stage 2 and 3 uranium mineralization proximal to carbonate microveinlet (black). Ages shown are chemical ages. Abbreviations: Ur=uraninite; Pi=pitchblende; Cof=coffinite; and GAL=galena.

blende are characterized by low to moderate PbO contents (0.08 to 5.2 wt.%), variable SiO₂, CaO, and FeO contents, and chemical ages less than 500 Ma (Figure 3). The majority of stage 3 coffinite appears to be an alteration product of stage 1 and 2 ore; however, the massive pitchblende with high reflectivities may represent the introduction of new ore, or again may be the product of complete recrystallization of previously deposited ore.

3. Chemical Ages of Uranium Mineralization

Chemical ages of the three stages of uranium mineralization were calculated based on their uranium and lead contents determined by the electron microprobe. Stage 1 uraninite, as expected, has the oldest ages ranging from 1057 to 1366 Ma. Stage 2 pitchblende has ages ranging from 667 to 903 Ma, whereas stage 3 coffinite

has ages that range from <1 to 452 Ma (Figure 3). Uranium minerals from each stage of mineralization exhibit a wide range of ages. Those with the highest reflectivities and least alteration are generally older. Clay minerals associated with, and post dating uranium mineralization from uranium deposits throughout the Athabasca Basin, indicate three main hydrothermal events (Wilson and Kyser, 1987; Kotzer and Kyser, 1990b). The first hydrothermal event occurred at approximately 1500 Ma and is considered to be responsible for the transportation and deposition of the majority of the uranium ore. The second hydrothermal event occurred at approximately 900 Ma and is considered to have altered and remobilized the uranium ore forming some of the "perched" mineralization. The third hydrothermal event occurred at approximately 300 Ma precipitating coffinite and altering previously deposited uranium ore. The increase in SiO₂ and CaO with decreasing age of uranium minerals is further evidence that later fluids affected the initial uranium mineralization (Figure 3).

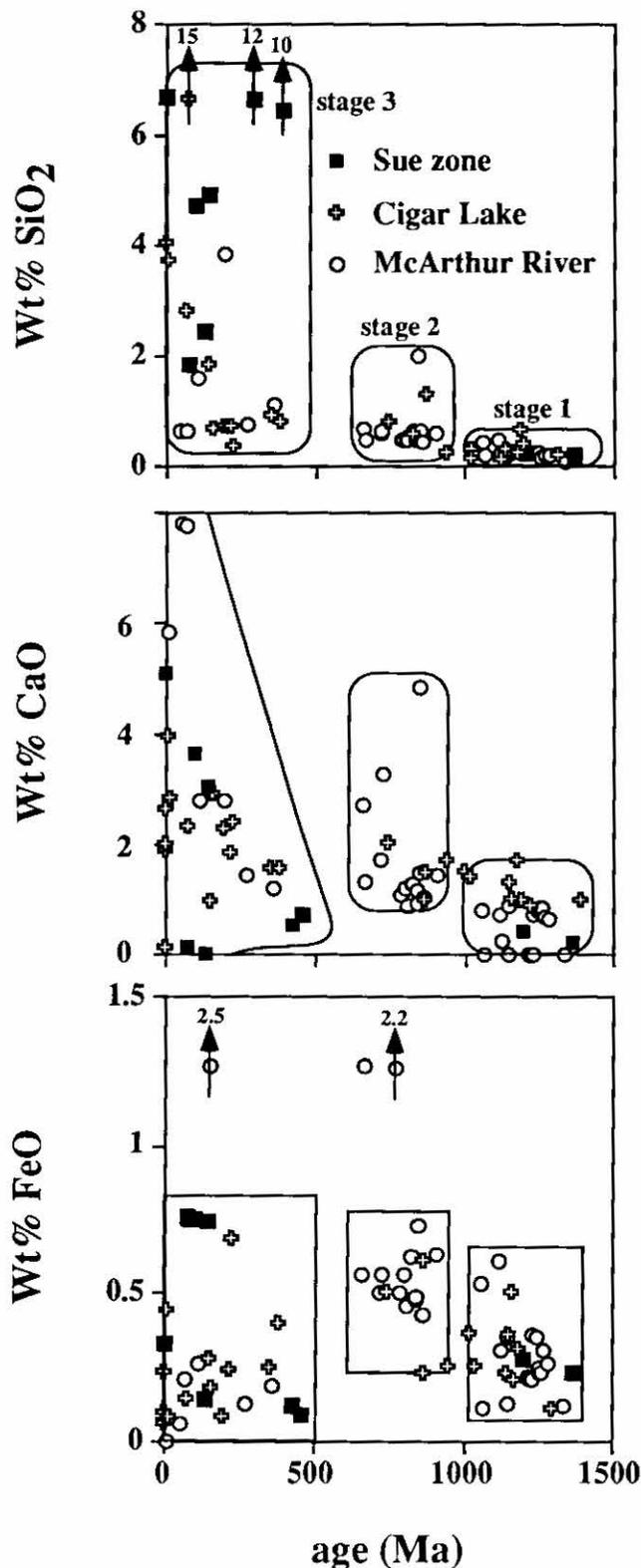


Figure 3 - Relationship between SiO_2 , CaO , FeO , and chemical age of uranium minerals from the Sue Zone, Cigar Lake, and McArthur River uranium deposits (data is from this study and Janeczek and Ewing, in press).

These later fluids either totally recrystallized previous uranium minerals *in situ* or precipitated as new mineralization. However, at present it is difficult to distinguish altered or recrystallized stage 1 uranium from new uranium mineralization.

4. Oxygen Isotope Systematics of Uranium Mineralization

Uranium minerals from the McArthur River, Cigar Lake, and Sue Zone deposits were analyzed for their $\delta^{18}\text{O}$ values. Stage 1 and 2 uraninite and pitchblende have $\delta^{18}\text{O}$ values that range from -26.5‰ to -19.5‰, whereas stage 3 pitchblende have $\delta^{18}\text{O}$ values near -10.0‰ and stage 3 coffinite has $\delta^{18}\text{O}$ values near 0‰ (Figure 4). There is positive correlation between increasing $\delta^{18}\text{O}$ values and increasing SiO_2 and CaO contents of uraninite, pitchblende, and coffinite (Figure 5), as is expected from the incorporation of $\delta^{18}\text{O}$ -rich SiO_2 and CaO during formation or alteration of uranium minerals (Kotzer and Kyser, 1992). Consequently, there is negative correlation between increasing PbO content and increasing $\delta^{18}\text{O}$ because the uranium mineralization with the highest SiO_2 and CaO contents are the most altered and paragenetically late. Based on the fractionation factor of Hattori and Hales (1982), the stage 1 uranium minerals should have $\delta^{18}\text{O}$ values near -5‰, as the dominant fluids that equilibrated with silicate and clay minerals associated with primary uranium mineralization are saline fluids having $\delta^{18}\text{O}$ values of approximately 4 ± 2 ‰ and temperatures between 150° and 220°C (Kyser *et al.*, 1990; Kotzer and Kyser, 1993; Rees, 1992). The anomalously low $\delta^{18}\text{O}$ values of stage 1 uranium mineralization, therefore, must have resulted from the interaction between uranium minerals and relatively recent, low temperature meteoric fluids which have $\delta^{18}\text{O}$ values of approximately -20‰ to -16‰. The high reflectivities and lack of alteration (i.e. low SiO_2 and CaO) of stage 1 uranium minerals indicate that uranium minerals can exchange oxygen isotopes with fluids with only minor disturbances to their chemical composition and texture. Similar observations from other uranium deposits in the Athabasca Basin have been reported by Hattori *et al.* (1978) and Kyser *et al.* (1990).

5. REE Geochemistry of Uranium Ore

REE contents of the various stages of uranium minerals were analyzed by electron microprobe, and ranged from 8.0 to 12.5 wt.%. Stage 1 uranium minerals have the highest REE contents (11.0 to 12.5 wt.%) whereas stage 3 coffinite has the lowest totals (8.0 to 9.5 wt.%). Normalized REE patterns from all three deposits and from the three stages of uranium minerals are similar and indicate HREE-enrichment (Figure 6). Xenotime from the Maw Zone has a similar pattern whereas illite, goyazite, and dravite from the alteration halo surrounding unconformity-type uranium mineralization at McArthur River, Key Lake, and Midwest Lake, and dravite intergrown with xenotime at the Maw Zone have lower REE contents and LREE-enriched patterns (Quirt *et al.*, 1991).

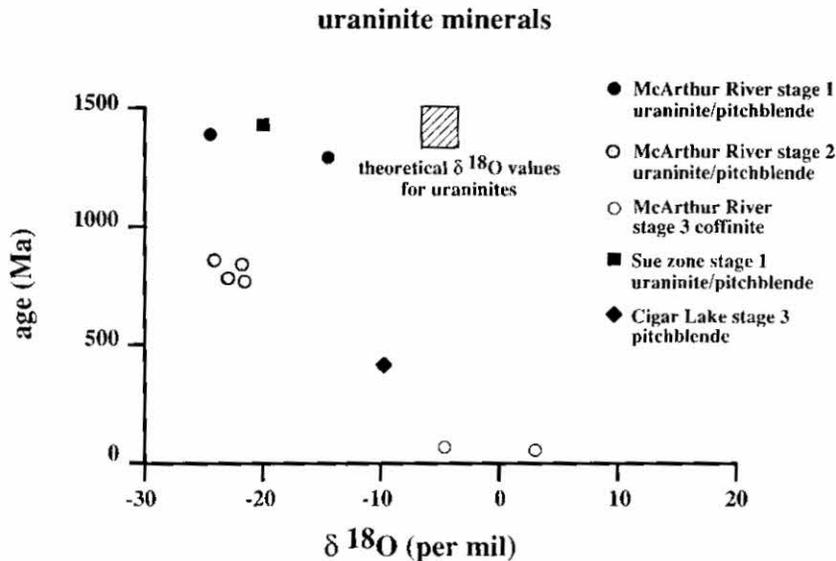


Figure 4 - Relationship between the $\delta^{18}\text{O}$ isotopic composition and relative ages of uranium minerals from McArthur River, Sue Zone, and Cigar Lake. The shaded box represents the calculated $\delta^{18}\text{O}$ value for uraninite and pitchblende minerals which would have formed from fluids with $\delta^{18}\text{O}$ values of $4 \pm 2\%$ and temperatures of approximately 200°C that formed diagenetic clay and silicate minerals associated with uranium ore (data is from this study and Kotzer and Kyser, 1993).

REE contents of stage 2 and 3 uranium minerals normalized relative to stage 1 uraninite and pitchblende indicate that there is no appreciable fractionation, loss or gain of REE during subsequent hydrothermal activity, except for Ce (Figure 7). Subsequent fluid events which clearly have altered the stage 1 uranium mineralization appear not to have remobilized the REE. These results thus imply either that later fluid events had similar chemical compositions to that associated with stage 1 uranium mineralization, despite distinct isotopic differences (Wilson and Kyser, 1987; Kotzer and Kyser, 1990b), or minerals were recrystallized by subsequent fluids with only limited removal or addition of uranium and REE.

6. Conclusions

Three stages of uranium mineralization are observed in thin section. Stage 1 uraninite and pitchblende have chemical ages of 1057 to 1366 Ma and have $\delta^{18}\text{O}$ values that range from -26.5 to -19.5‰. Stage 2 pitchblende have younger ages, 667 to 903 Ma, and $\delta^{18}\text{O}$ values near -20‰, whereas the latest stage of uranium mineralization have young ages of <1 Ma to 452 Ma and $\delta^{18}\text{O}$ values near 0.0‰. These three stages of uranium mineralization coincide with three major fluid events that have precipitated clay and silicate minerals throughout the entire Athabasca Basin. Stage 1 uraninite and pitchblende appear to have concentrated the HREE whereas the associated gangue minerals concentrated the LREE. Subsequent fluid events did not affect the REE contents of the uranium minerals. Although the majority of stage 2 and 3 uranium mineralization appears to be an alteration product of stage 1 uraninite and pitchblende, the similarities in REE pat-

terns, the high reflectivities, and unaltered appearance of some stage 2 and 3 pitchblende implies that new uranium mineralization most likely represents complete recrystallization of earlier-formed minerals by subsequent fluid events.

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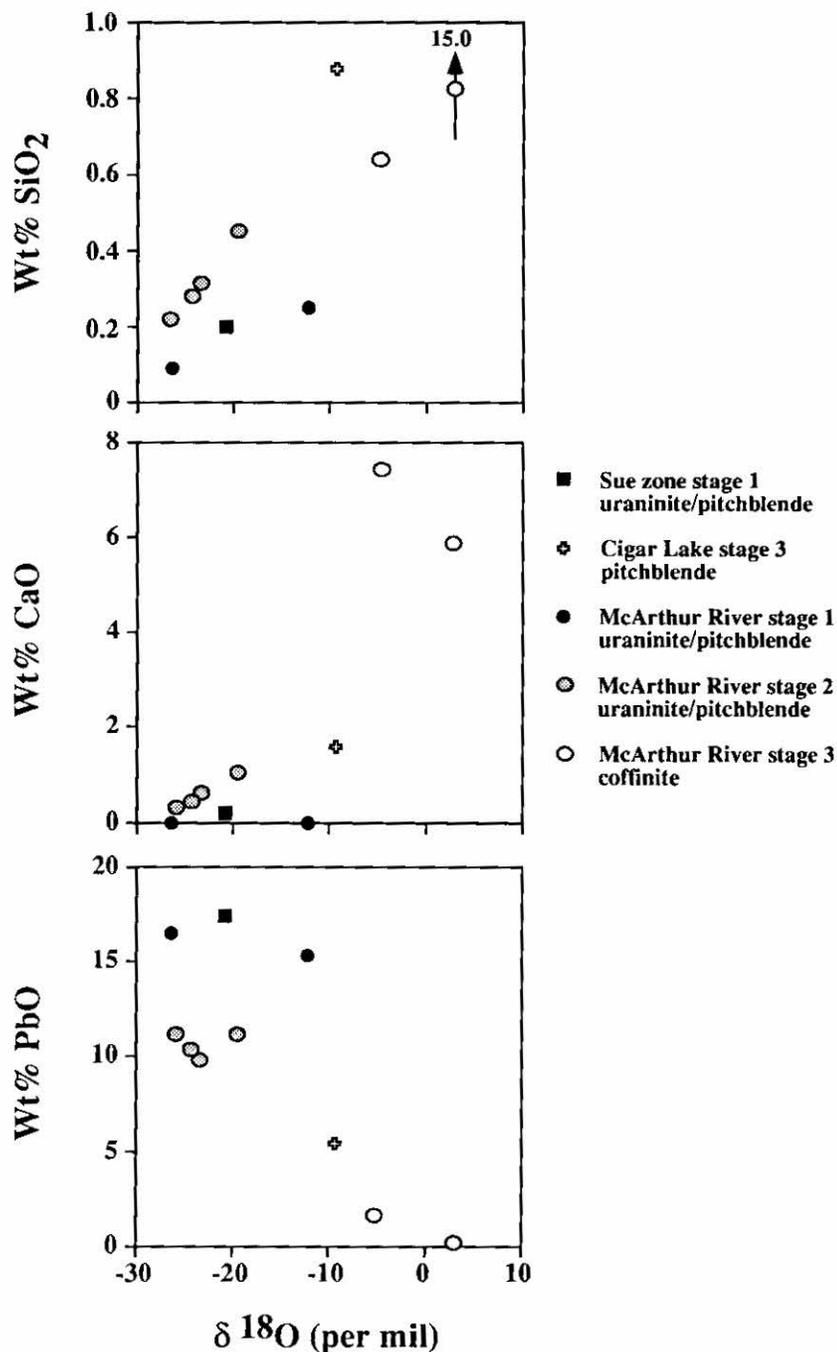


Figure 5 - The relationship between $\delta^{18}\text{O}$ values and SiO_2 , CaO , and PbO contents in uranium minerals from the Sue Zone, Cigar Lake, and McArthur River uranium deposits (data is from this study and Kotzer and Kyser, 1993).

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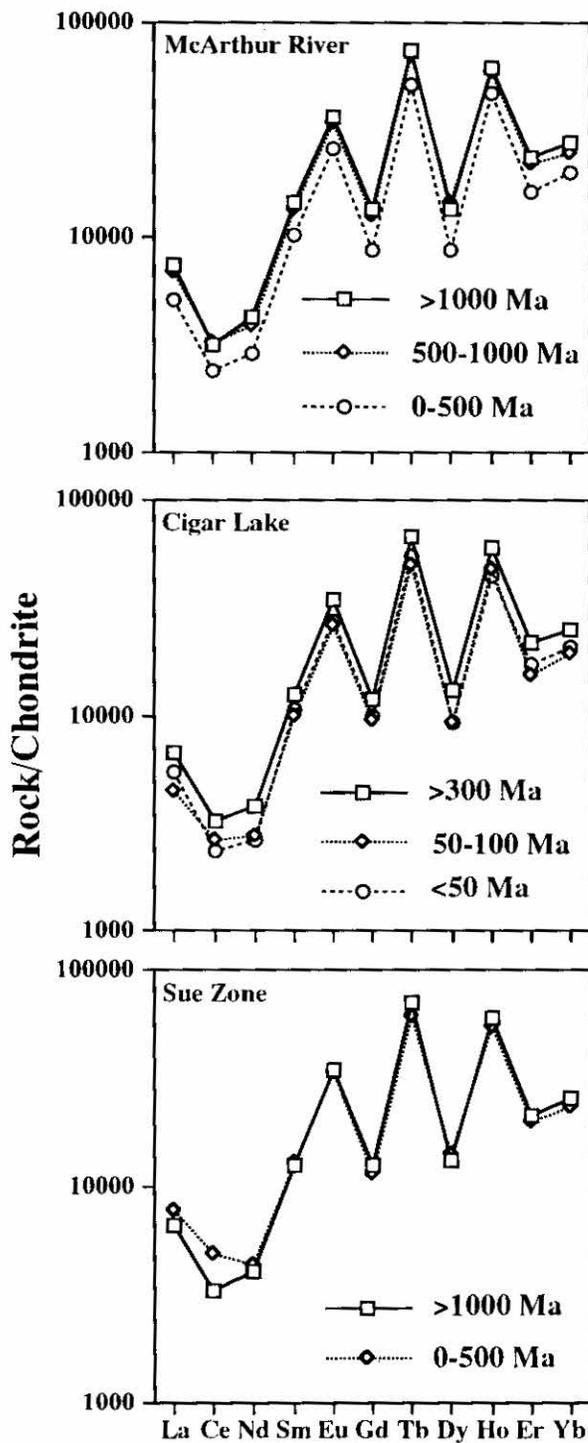


Figure 6 - Chondrite normalized REE patterns for stage 1, 2, and 3 uranium minerals from McArthur River, Cigar Lake, and Sue Zone deposits.

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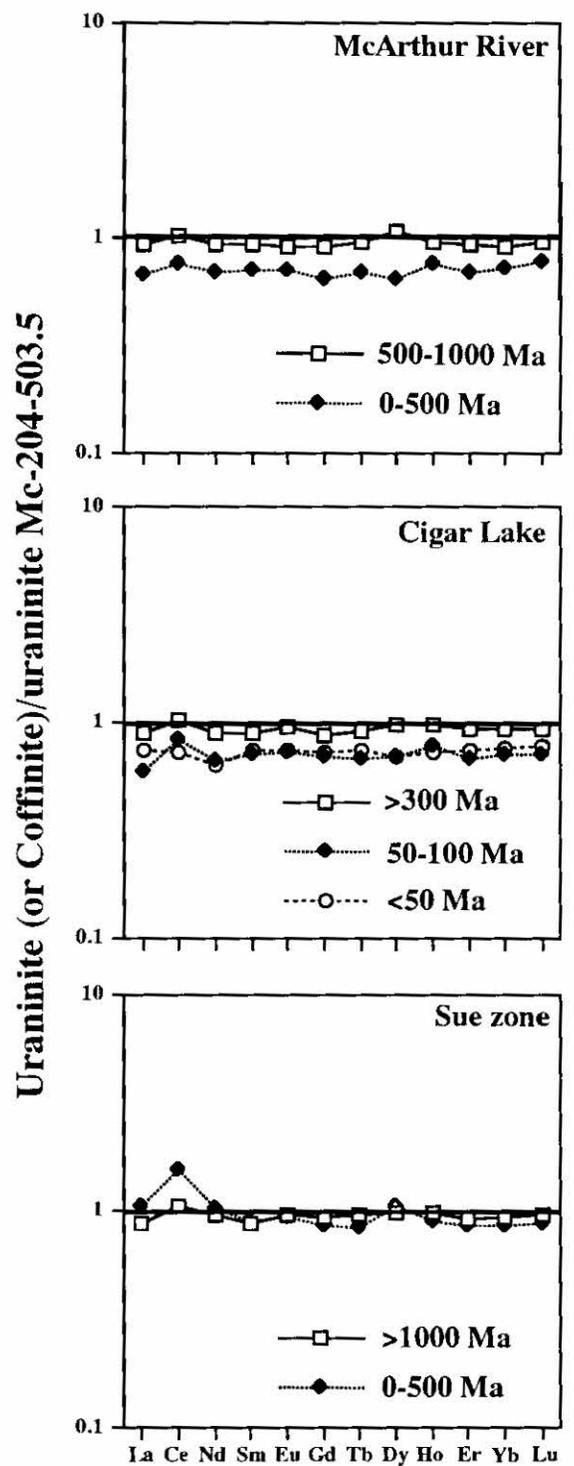


Figure 7 - Stage 1 uraninite/pitchblende normalized REE patterns for stage 2 and 3 uranium minerals from McArthur River, Cigar Lake, and Sue Zone deposits.

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