

Uranium-bearing Carbonaceous Matter, McArthur River Uranium Deposit, Saskatchewan

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1. Introduction

Over the last 30 years, unconformity-type uranium deposits have been investigated extensively. Many of these deposits have common characteristics, such as: 1) their preferential location at the unconformities between siliciclastic sediments and older basement gneisses; 2) their primary age of formation (i.e. 1700 to 1300 Ma); 3) their spatial association with graphitic pelitic gneisses; 4) their association with variably reactivated shear/fault zones; 5) their overall high-grade ore of up to 15.9 percent U; 6) their primary and secondary mineralogy; 7) their extensive clay alteration and hydrothermal bleaching; 8) their multiple uranium remobilization ages ranging from 1300 Ma to Recent; and 9) their precipitation from warm (150° to 250°C) saline brines linked to basin diagenesis and fluid mixing.

Many theories have been proposed to explain the formation of unconformity-hosted uranium mineralization. Those in the early 1970s advocated paleoweathering or erosional origins for the mineralization. From 1978 onwards, most researchers have advocated a variant of the diagenetic-hydrothermal model proposed by Hoeve and Sibbald (1978). This model requires the mixing of highly saline basinal fluids with variably reduced basement fluids at temperatures near 200°C. Since 1984, modifications of the diagenetic-hydrothermal model show that transport and precipitation of uranium is coupled to basin paleohydrology, large-scale reactivated basement structures, fluid flow, and physiochemical traps (Hoeve and Quirt, 1984, 1987; Wilson and Kyser, 1987; Kotzer and Kyser, 1991, 1992, 1995; Fayek and Kyser, 1997; Quirt, 1997). Many constraints to the model remain unsolved, however, including: establishing the initial emplacement age of the uranium, the source(s) of uranium, the source(s) of the associated metals (e.g. Ni, Co, Cu, Pb, Zn, and Au), and the composition of the fluids transporting and precipitating the uranium.

Another unresolved question is the role of graphite and carbonaceous matter in the formation of an unconformity-type uranium deposit. Hoeve and Sibbald (1978) suggested that the destruction of graphite and the formation of hydrocarbons such as

bitumen buttons and methane was the main reducing mechanism. More recent work, on the basis of isotopic constraints (Kyser *et al.*, 1989) and geochemical modelling (Kominou and Sverjensky, 1996), suggested that graphite is not a necessary ingredient in the genesis of unconformity-type deposits. However, all of the larger, high-grade deposits in the Athabasca Basin (e.g. Key Lake, Cigar Lake, and McArthur River (P2 and P2 North), Figure 1) are spatially associated with graphitic conductors and contain carbonaceous matter, such as hydrocarbon buttons.

The purpose of this paper is to document the occurrence, petrography, chemistry, age, and formation of uranium-bearing carbonaceous matter from the McArthur River unconformity-type uranium deposit. An additional objective is to present the fluid-geochemical-uranium remobilization history recorded in the carbonaceous matter.

2. Local Geology

The McArthur River uranium deposit (P2 and P2 North) is situated in the southeastern part of the Athabasca Basin (Figure 1), approximately 70 km northeast of the Key Lake mine and 95 km southwest of the mined-out Rabbit Lake uranium deposit. The Archean/Paleoproterozoic basement comprises supracrustal and granitoid rocks of the western Wollaston Domain near the boundary with the Mudjatik Domain.

Recently, the geology and lithogeochemistry of the deposit has been documented by McGill *et al.* (1993) and McGill (1996). A southeast-dipping reverse fault with a vertical displacement of ca. 80 m is the main structural control of the deposit (Figure 2). The footwall basement rocks are composed of psammitic gneisses, psammopelitic gneisses, and meta-quartzites, whereas the hanging-wall basement rocks are composed mainly of sheared graphitic pelitic gneisses, and graphite-rich cataclasites and breccias. Within adjacent rocks of the overlying Athabasca Group, broad zones of fracturing and brecciation are developed. Most of the uranium mineralization is located at depths of 500 to 570 m adjacent to the thrust

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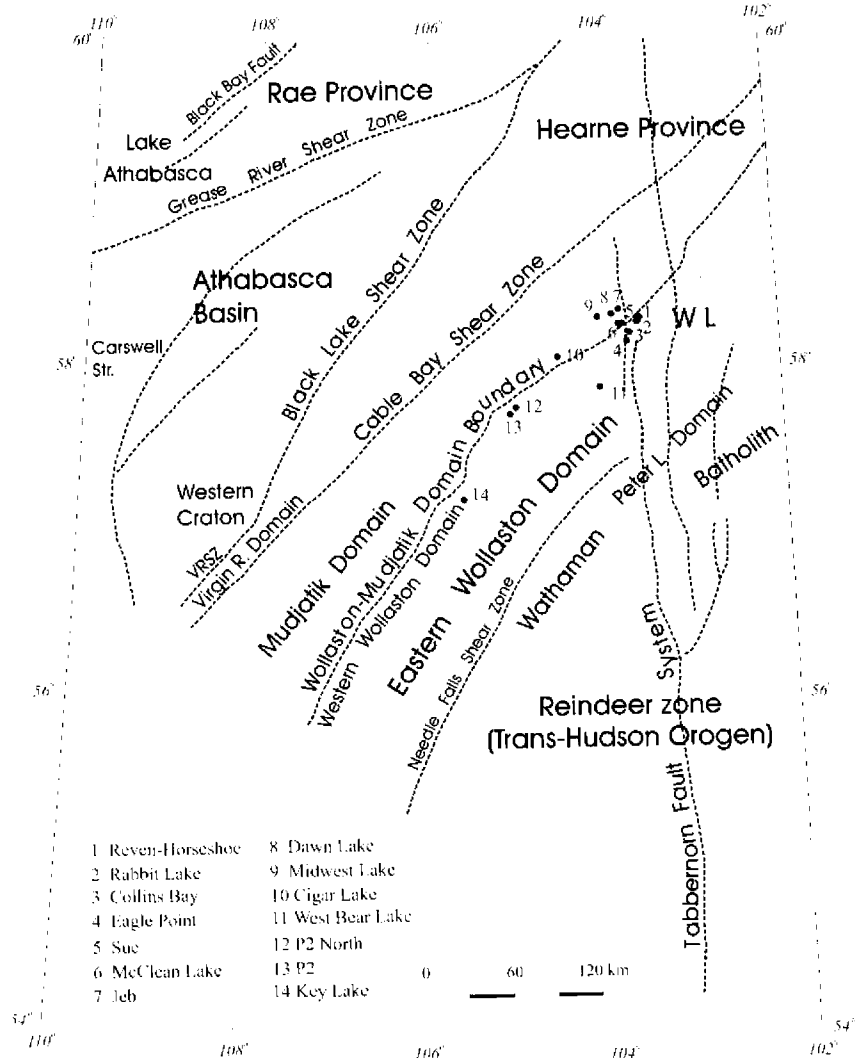


Figure 1 - Location of the main uranium deposits in the Athabasca Basin. VRSZ, Virgin River Shear Zone; WL, Wollaston Lake. Locations 12 and 13 are the McArthur River deposit.

fault contact between Athabasca Group and basement rocks (McGill *et al.*, 1993; McGill, 1996). A second pod of mineralization, known as the 'pelite mineralization', has been discovered recently along a deeper part of the fault structure, within pelitic gneisses thrust over meta-quartzites.

The McArthur River uranium deposit has characteristics different from other deposits in the basin. First, is the near absence of a hydrothermal clay alteration halo, which is typical in most other deposits (Marlatt *et al.*, 1992). Secondly, unlike many of the other major deposits, there is no significant Ni-Co mineralization associated with the uranium (Marlatt *et al.*, 1992). Thirdly, the deposit is situated at depths of 500 to 700 m, which is the deepest deposit found so far in the eastern Athabasca region (McGill *et al.*, 1993).

3. Megascopic Description of Carbonaceous Matter

The studied carbonaceous matter comes from the 8240 crosscut at the 530 m level below surface. It is found within the tectonic mobile zone of the overthrust basement hanging wall at McArthur River. The carbonaceous matter is black, dull, and uranium-bearing with a characteristic hydrocarbon smell. The volume of carbonaceous matter has not been ascertained as drilling has concentrated on delineating the extent of uranium mineralization.

4. Petrography of Carbonaceous Matter

The accumulations of carbonaceous matter are spherical to bulbous in shape and vary from 5 mm to 3 cm in size. Examination by scanning electron microscopy revealed most accumulations are a series of coalesced smaller nodule-like masses that are in the order of 500 μm in size (Figure 3). In contrast, at least one accumulation is not composed of coalesced nodules, but instead comprises a single nodule, which is zoned into a series of progressively younger shells, (which alternate between being uranium-rich and uranium-poor).

Similar to Phanerozoic bitumen nodules, the carbonaceous matter at McArthur River is commonly segregated into inclusion-poor and inclusion-rich domains.

The inclusions within a single accumulation, and in many examples within a single domain, of carbonaceous matter are not homogeneous in size. They vary from 1 to $\sim 50 \mu\text{m}$ in diameter and consist of a variety of minerals including both uranium-free and uranium-bearing varieties. These are described in detail within subsequent sections of this paper.

Three separate styles of inclusion-poor domains can be recognized: (1) those within the smaller nodule-like masses; (2) those surrounding the individual nodule masses; and (3) those that occur as cross-cutting veinlets, which generally are about 50 μm wide, and have razor sharp margins (Figure 4). The first type of domain is attributed to a later influx of hydrocarbon-type material along cracks within the older

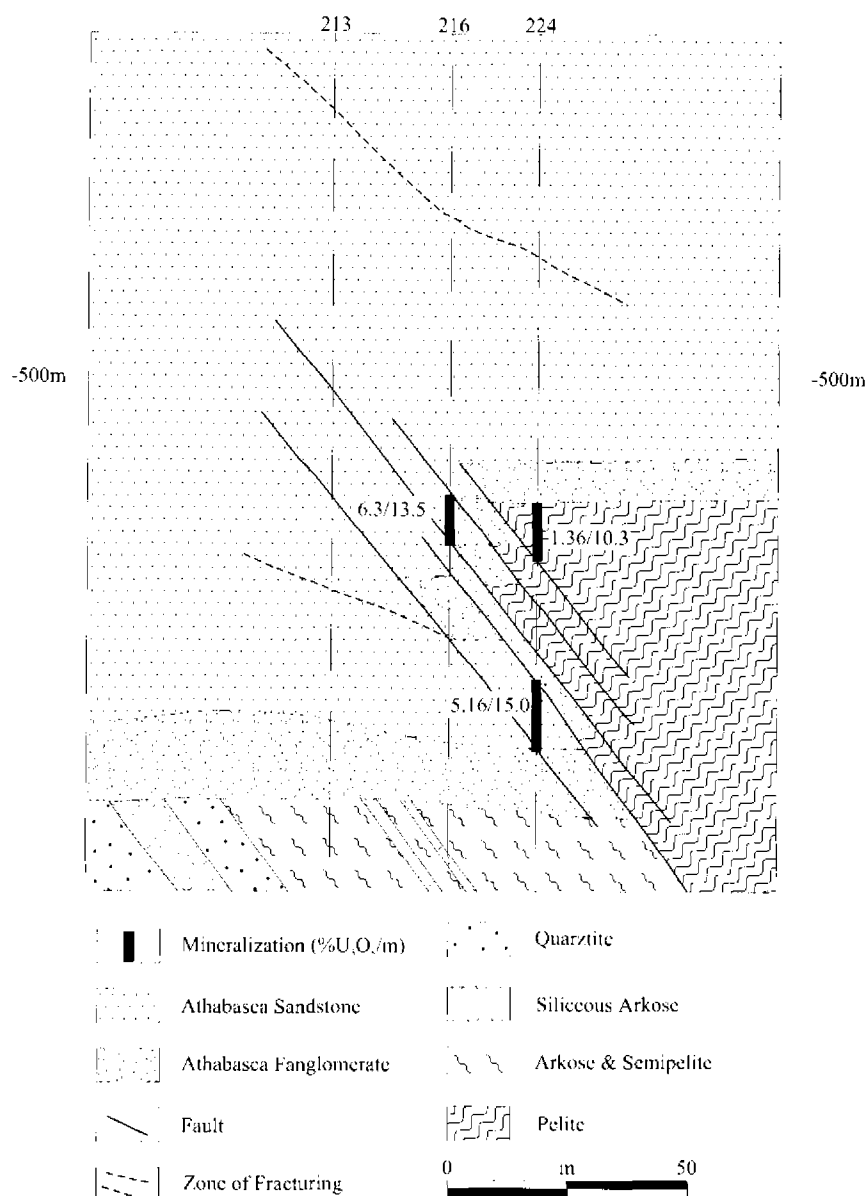


Figure 2 - Detailed cross-section of the McArthur River uranium deposit along line 78+50N (modified from Marlatt et al., 1992).

polymerized carbonaceous matter. The second is also attributed to a later influx of hydrocarbon-type material around each nodule into the void created by the contraction of the carbonaceous matter after initial swelling. These two domains may represent either the last vestige of material from the first migratory event or a second, unrelated event. This is in contrast to the third domain, which is envisaged, on the basis of the sharp/distinct margins and its linear plan, to be due to a later distinct veining event.

Many of the nodules are crosscut by large cracks or fissures. These are comparable to the cracks observed

within Phanerozoic thoriferous bitumen nodules (Monson, 1993; Veale and Parnell, 1996). These cracks represent shrinkage cracks, which are the result of the contraction of the hydrocarbon from a liquid through gel-like substances to solid bitumen (Rasmussen and Glover, 1990). Some cracks are filled by pyrite and kaolinite, whereas others are open and unfilled. The formation of cracks or widening of pre-existing ones during polishing cannot be precluded. Those that are infilled, however, cannot be explained as polishing artifacts, therefore are considered primary in origin.

In places, usually near the margin, the carbonaceous matter exhibits a 'flow-like pattern', with the carbonaceous matter engulfing rounded quartz grains. The latter are interpreted to represent remnants of the host rock. These flow-like patterns are interpreted to have formed prior to polymerization, while the carbonaceous matter was either in a liquid or in a semi-gelatinous state.

These relationships suggest there were at least two, or possibly three, separate hydrocarbon migration events, as well as a number of uranium precipitation/remobilization events. This provides the first indication of the deposit's complex fluid-geochemical history.

5. Uranium-free Inclusion Mineralogy

The carbonaceous matter from McArthur River contains a variety of non-radiogenic inclusions, including quartz, titanium dioxide, galena, pyrite, clay minerals, and gold.

a) Quartz

Quartz typically occurs as less than 10 µm-sized irregularly-shaped inclusions, which are located preferentially either in the center or near the edge of the nodule. The quartz inclusions in the center of the nodule rarely contain uranium-bearing micro-inclusions.

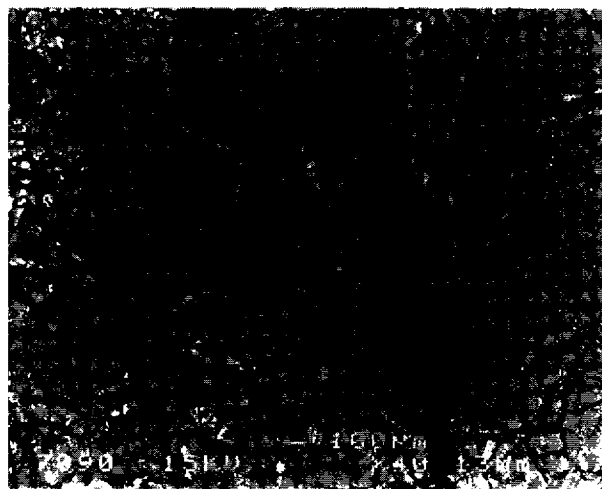


Figure 3 - Secondary electron micrograph of coalesced nodule-like masses of carbonaceous matter.

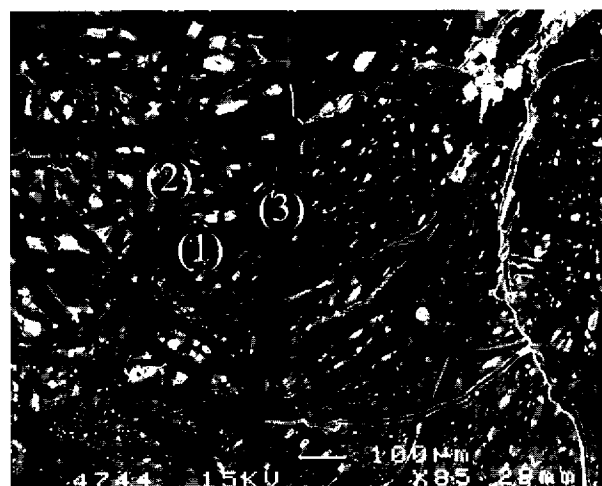


Figure 4 - Back-scattered electron micrograph showing the segregation of nodule-like masses into three distinct inclusion-free domains: (1) intra-nodule domain; (2) domain surrounding the nodule; and (3) cross-cutting veinlet domain.

The inclusions at the edge of the nodule are interpreted to represent the vestiges of the siliciclastic host rocks. The origin of quartz inclusions in the centre of the grains is more problematic. At least some, those that contain uraniferous micro-inclusions, are probably authigenic in origin. These interpretations for the quartz inclusions are consistent with observations of McGill *et al.* (1993) who noted the occurrence of both euhedral quartz grains (authigenic) and fragments of angular sandstone (detrital) within the uranium mineralization.

b) Titanium Dioxide

Titanium dioxide inclusions are generally less than 25 μm in size and tend to occur within the core of the carbonaceous accumulations. Some titanium dioxide inclusions contain a micro-inclusion assemblage of

uraninite, uranium titanite and galena (Figure 5). In addition, they are partially rimmed by pyrite.

Two theories concerning the origin of the titanium dioxide inclusions are considered: (1) they represent the vestiges of metasedimentary titanium dioxide grains; and (2) they represent small authigenic titanium dioxide grains, which are either the result of a distinct diagenetic event, or the selective dissolution and reprecipitation of an antecedent mineral e.g. ilmenite.

A metasedimentary origin for the titanium dioxide inclusions is precluded by the presence of uranium-bearing micro-inclusions within the grains. Consequently, an authigenic origin is favored.

If the individual titanium dioxide grains were the result of a distinct diagenetic event, then they would be expected to be distributed throughout the accumulations, rather than localized within specific domains, which is the case at McArthur River.

Their location within the nodule and spatial relationship to each other suggests they represent the remnants of the selective dissolution and reprecipitation of a precursor Fe-Ti mineral, whose constituent elements were only mobile over a small area, hence were only locally reprecipitated. Pyrite rims around titanium dioxide grains helps elucidate the remobilized site of the iron. By comparison, Hoeve and Quirt (1984) describe detrital Fe-Ti from the Manitou Falls Formation (MFa+b), in other parts of the basin, which have been altered in a similar way.

c) Galena

Galena occurs as either: (1) distinct individual micro-inclusions within the chlorite core present in some carbonaceous accumulations; (2) micro-inclusions within titanium dioxide inclusions; (3) euhedral cubic

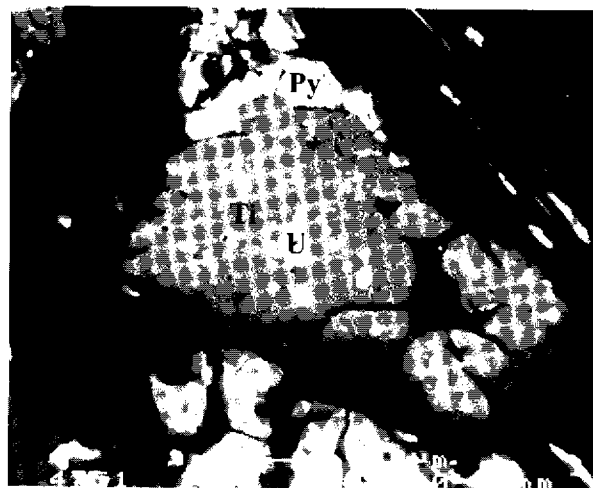


Figure 5 - Back-scattered electron micrograph of titanium dioxide grains (Ti) containing uranium-bearing inclusions (U), partially surrounded by pyrite (Py) within the chlorite core of a carbonaceous accumulation.

grains within the carbonaceous matter; and (4) irregular grains in association with the pyrite lattices. Based on morphology, the galena is interpreted to be authigenic in origin, the result of the remobilization of radiogenic Pb from paragenetically earlier uranium-bearing minerals, possibly primary uraninite.

d) Pyrite

Pyrite, the most common radioelement-free inclusion in the carbonaceous matter, occurs in a variety of morphologies: (1) as euhedral cubic or octahedral inclusions (5 to 10 μm in size) (Figure 6); (2) as lattice-like trellises which may reach up to 1mm in size and are intergrown with galena; (3) as irregularly-shaped grains that are interstitial to the carbonaceous matter; (4) as cross-cutting laths in clay minerals; (5) as rims around titanium dioxide grains (Figure 5); (6) as an accumulation that acts as a cement for quartz grains; and (7) as lath-like grains intergrown with radioelement-bearing inclusions.

e) Clay Minerals

Two different types of clay minerals are present in the carbonaceous matter. The first, kaolinite, usually forms veinlets that infill many of the shrinkage cracks. This suggests that they are not inclusions *sensu stricto*, but a post-bitumen phenomena. The second, chlorite, occurs within the central core of some accumulations, in association with quartz, pyrite, titanium dioxide, galena, and uraninite. This chlorite is interpreted to have formed early in the paragenetic sequence. Similarly, McGill *et al.* (1993) identified chlorite in the core of botryoidal uraninite at McArthur River.

f) Apatite

Apatite crystals are rare inclusions in the carbonaceous matter. Where present, they occur as small (10 to 20 μm), euhedral, elongate, hexagonal crystals, or as elongate, tabular crystals (Figure 6). These crystals are normally associated with octahedral pyrite. Based on their euhedral morphology and occurrence, the apatite inclusions are interpreted to be authigenic in origin. This is the first recorded occurrence of authigenic apatite within the McArthur River deposit.

g) Gold

In one sample, three small (2 to 3 μm) grains of gold were observed. The grains were found close to pyrite in chlorite inclusions in the core of a carbonaceous accumulation. Based on its relationship with the pyrite, the gold is interpreted to be early authigenic in origin. Although rare, this occurrence of gold within the bitumen is not unique. Previously McGill *et al.* (1993) described gold grains in chlorite in a single polished thin section from McArthur River.

h) Absence of Ni-Co Sulpharsenides

Unlike the carbonaceous matter of the Key Lake and Cluff Lake deposits (Hoeve and Quirt, 1984), no Ni-Co sulpharsenide mineralization is present within the

carbonaceous matter from McArthur River. McGill *et al.* (1993) and Marlatt *et al.* (1992) suggested that such elements do not occur in sufficient quantities to allow for the formation of more than trace amounts of these minerals in the P2 North deposit.

6. Uranium-bearing Inclusions

a) Inclusion Varieties

Euhedral Inclusions

Euhedral cubic uranium-bearing inclusions of 30 to 50 μm width are commonly observed within the carbonaceous matter (Figure 7). The margins of the grains are typically corroded and scalloped. Internal

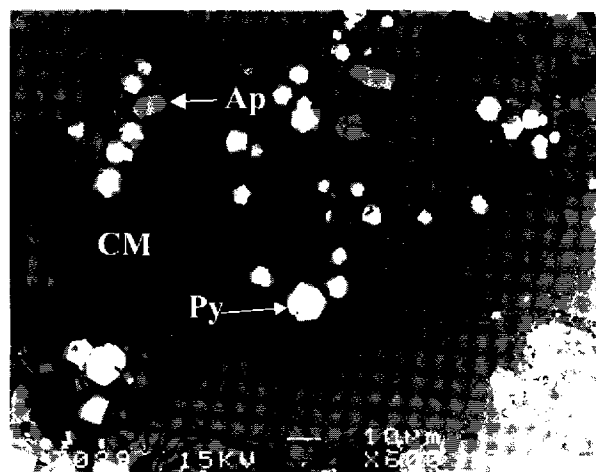


Figure 6 - Back-scattered electron micrograph of octahedral pyrite (Py) and apatite (Ap), associated with quartz (Q) and phyllosilicates (P), within carbonaceous matter (CM).

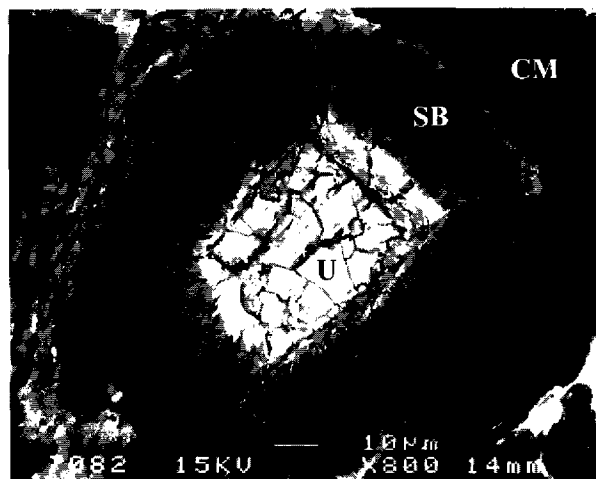


Figure 7 - Back-scattered electron micrograph of a shattered cubic uranium-rich inclusion (U), surrounded by a star-burst inclusion pattern (SB) within carbonaceous matter (CM).

cracking of many crystals is evident, with the cracks filled by carbonaceous matter. Some grains are completely shattered.

Fine-grained Inclusions

Fine-grained uranium-bearing inclusions form micron-sized specks (Figure 8), which, where present, tend to occur in great abundance, such that when viewed in the scanning electron microscope at low magnification ($\times 65$), they create a dust-like appearance. These grains are neither spatially related to any larger grain, nor are there any ghost-grains visible. These inclusions are similar in appearance to the micron-sized array of inclusions that are present in both uraniferous and thoriferous bitumen nodules from the Phanerozoic (Veale and Parnell, 1996; McCready and Parnell, 1998).

Two scenarios are plausible for the formation of these inclusions: (1) digestion/extreme fracturing of a former larger euhedral grain; and (2) precipitation from an urano-organic complex. A digestive origin is rejected on the basis of both the regularity in size of the inclusions and the lack of a ghost-grain. A precipitative origin has been suggested by a number of workers (e.g. Rouzaud *et al.*, 1981; Parnell, 1988; Eakin and Gize, 1992) as the formational mechanism for uraniferous hydrocarbons associated with a variety of deposits. Rouzaud *et al.* (1981) have shown that it is possible for uraninite crystals to precipitate out of urano-organic compounds with increasing time and temperature. Parnell (1988) contends that the annular array of uraninite crystals seen in hydrocarbons is more consistent with an exsolution process than one of replacement of a larger grain. Eakin and Gize (1992) suggest a two phase mechanism: (1) a pre-concentration stage involving the formation of urano-organic complexes; and (2) a concentration phase involving the reduction of mobile U^{6+} to immobile U^{4+} . This reduction is thought to be the result of the



Figure 8 - Back-scattered electron micrograph of a close-up view of fine-grained uranium-rich inclusions, creating a dusty appearance.

presence of sulphide species, which are abundant in systems studied, acting as reductants (Eakin and Gize, 1992). At McArthur River, either an earlier phase of pyrite or bitumen could have acted as the reductant.

Irregular Inclusions

This term is employed as a 'catch-all' grouping for all the inclusions that are neither euhedral or fine-grained. These exhibit a variety of shapes, ranging from elongate rectangular inclusions to irregular chunky inclusions. Many of these grains exhibit exterior surface corrosion, to form what Veale (1997) terms 'karstic weathering'. The 'karstic weathering' of these exterior areas is thought to provide at least some of the uranium that is incorporated into the proposed urano-organic complexes.

b) Textures

Relict Colloform Textures

Some nodules consist of concentrically arranged layers, that are typically ~ 0.5 to 1.0 mm thick. Three main types of banding are distinguished: (1) fine-grained bands, (2) coarse-grained bands, and (3) radially-patterned bands. More than one set of bands may be present in the same area. The interstice between each group of bands is filled by pyrite. This feature is interpreted to be a relict colloform or botryoidal texture, which is still preserved despite the introduction of hydrocarbon/bitumen. The occurrence of more than one set of layers suggests that several nucleation sites are present in the same area. This relict structure is interpreted to be comparable, in paragenetic terms, to the early colloform uraninite/pitchblende described by McGill *et al.* (1993).

Blasenblende Textures

Some, or parts of some, bitumen nodules consist of a series of circular to lobate-shaped uraniferous blobs or pods. The pods range in size, reaching a maximum of ~ 200 μm in diameter. The individual pods are typically spherical in outline, although there are many deviations from this shape. These pods are interpreted as the remains of small botryoidal uraninites, also referred to as 'blasenblendes'. Fracturing of the pods was probably caused by the migration, polymerization, and subsequent swelling of carbonaceous matter in internal cracks.

Volcano-like Structure

In one nodule, inclusions are arranged in a radial strip-like configuration about what appears to be a central 'vent'. Each strip ranges from 50 μm to more than 200 μm long and 10 to 30 μm wide; many of the individual strips have coalesced to form larger strips. These uranium-bearing inclusions are intergrown with pyrite. This style of inclusion assemblage is termed a

'volcano-like structure', due to its resemblance to an aerial photograph of an active volcano, with the 'central vent' being filled by carbonaceous matter.

Star-burst Pattern

Many inclusions are surrounded by a series of micron-scale specks that are arranged in a 'star-burst pattern' (Figure 7), that extends up to 30 μm away from the core inclusion. This feature is not restricted to any particular variety of inclusion.

7. Geochemistry

The inclusions are composed of varying amounts of U, Pb, Ca, Si, Fe, P, and REEs. Representative analyses of the minerals are displayed in Table 1. The term $\Sigma\text{REE}_2\text{O}_3$ represents the total of La_2O_3 , Ce_2O_3 , Y_2O_3 , and Nd_2O_3 . Correlation of the various oxides highlights some interesting chemical associations: (1) UO_2 clearly shows a highly inverse relationship with P_2O_5 ($r = -0.88$), $\Sigma\text{REE}_2\text{O}_3$ (-0.85) and CaO (-0.81); and (2) P_2O_5 clearly shows a highly positive relationship to $\Sigma\text{REE}_2\text{O}_3$ ($+0.83$) and CaO ($+0.67$).

8. Discussion

Based on the euhedral morphology of many inclusions, and the presence of both colloform and blasenblende textures, the initial uranium mineralization is undoubtedly authigenic in origin. The occurrence of the fine-grained inclusions, the star-burst pattern, and karstic weathering textures are interpreted to have formed from the dissolution and remobilization of uranium.

Based on the chemistry of the inclusions and their associations, it is proposed that the inclusions represent a progressive chemical alteration from a U-O-Pb-bearing phase to a U-Pb-REE-Ca-P-Si-O-bearing

phase. This alteration is due to the introduction of Ca-REE-P-bearing fluid(s) and the removal of uranium and possibly lead from the system. The highly inverse relationship (r value of -0.94) between $\text{UO}_2 + \text{PbO}$ and $\text{CaO} + \Sigma\text{REE}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{SiO}_2$ is interpreted to be a good indication of the process involved (Figure 9); the difference between -0.94 and an ideal value of -1.00 is due to the presence of H_2O and minor quantities of other elements (e.g. Al_2O_3 and FeO). The U-O-Pb-bearing phase is interpreted as primary uraninite. The U-Ca-REE-P-O-bearing phase is interpreted as a secondary uranyl phosphate mineral. This mineral group constitutes, by far, the most diverse group of uranyl minerals, with over 45 species described (along with the structurally related uranyl arsenates, the total approaches 80) (Dahlkamp, 1993). The uranyl phosphates are interpreted as an autunite-like mineral.

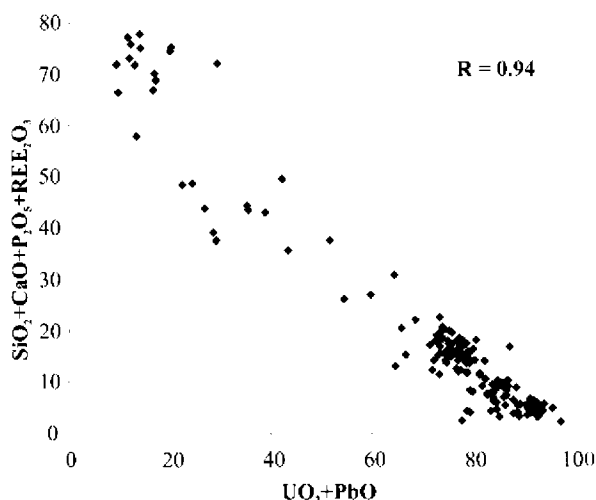


Figure 9 - Bivariate plot of $\text{UO}_2 + \text{PbO}$ versus $\text{SiO}_2 + \text{CaO} + \text{P}_2\text{O}_5 + \text{REE}_2\text{O}_3$ for inclusions within carbonaceous matter.

Table 1 - Representative electron-microprobe analysis (wt %) of uranium-bearing inclusions in carbonaceous matter from McArthur River. H_2O is assumed to account for most of the balance; ND, not detected.

	Analysis 1: euhedral cubic inclusion (immature alteration stage)	Analysis 2: irregular inclusion (immature alteration stage) includes 0.64% Al_2O_3 , and 3.07% FeO	Analysis 3: euhedral cubic inclusions (intermediate alteration stage) includes 0.78% TiO_2	Analysis 4: autunite-like rim around a primary core of uraninite (mature alteration stage) includes 0.49% Al_2O_3 and 1.34% TiO_2	Analysis 5: irregular inclusion (intermediate alteration stage) includes 0.71% SO_3	Analysis 6: autunite-like rim around a primary core of uraninite (very mature alteration stage) includes 1.32% SO_3 and 1.23% FeO
SiO_2	3.65	2.70	0.80	ND	0.98	ND
P_2O_5	ND	1.87	7.58	22.8	8.75	42.69
CaO	3.31	3.26	2.84	6.93	3.80	10.37
Ce_2O_3	ND	ND	1.52	6.59	0.90	6.34
La_2O_3	0.54	ND	ND	1.17	0.90	1.02
Nd_2O_3	ND	0.63	2.19	7.12	1.82	10.11
Y_2O_3	1.53	0.67	2.03	4.05	ND	6.81
ThO_2	ND	ND	ND	ND	ND	ND
UO_2	81.23	79.35	69.76	24.12	78.17	11.59
PbO	4.9	2.71	3.68	0.36	1.13	0.00
Total	95.14	94.90	91.18	74.97	97.16	91.48

One problem with understanding the alteration process is the REE content, as autunite does not generally contain REEs (Roberts *et al.*, 1987). Hence the use of the term autunite-like.

Based on the variety of inclusion chemistries, alteration of primary uraninite was irregular. In some instances, alteration is apparent as either a subtle difference in brightness and contrast within one grain, or as a distinct rim of autunite surrounding a core of uraninite. These varieties are interpreted to represent examples of immature and mature stages of alteration, respectively. In the majority of cases, however, the alteration is cryptic in nature, only distinguishable by means of electron microprobe analysis.

The autunite-like alteration of uraninite in carbonaceous matter at McArthur River is unique on a mine-, basin-, and global-scale. The alteration of uraninite, not within carbonaceous matter, to various secondary uranium minerals, including autunite, however, has been described by various workers (e.g. Wronkiewicz *et al.*, 1992; Finch and Ewing, 1992; Fayek and Kyser, 1997).

One problem with the proposed alteration process is the mobility of REEs. Some workers (e.g. Fleet, 1984; Howard, 1985) report that REEs are essentially immobile during diagenesis and metamorphism. However, the observations made in this study and those made by other workers (e.g. Rasmussen and Glover, 1994; Morton and Hurst 1995; Lev *et al.*, 1998) suggest that REEs are mobile during diagenesis and metamorphism.

There is little evidence as to the source of the REEs. The dominant controls on the remobilization and redistribution of REEs, however, are related to mineralogical changes in monazite and rhabdophane, crandallite-group minerals, xenotime and churchite, apatite, and uraninite (McCready, 1999; McCready *et al.*, 1999). Such precursor minerals are present within leucogranites and pegmatites in the basement (Annesley and Madore, 1999; Annesley *et al.*, 1999). This suggests that the REEs are possibly extra-basinal in origin (i.e. basement-derived).

Concerning the transport of REEs during diagenesis or metamorphism; trivalent REE and Y exhibit strong, predominantly electrostatic complexing with 'hard' ligands such as fluoride, sulphate, phosphate, carbonate, and hydroxide. Complexation with chloride and nitrate is moderately weak, and with ammonia and bisulphide is extremely weak (Wood, 1990). Based on thermodynamic data, where *Ln* signifies: the REE; sulphate complexes $LnSO_4^+$ and $Ln(SO_4)_2^-$; the fluoride complexes LnF_3^0 , LnF_2^+ , and LnF_4^- ; the nitrate complex $LnNO_3^{2+}$; the chloride complex $LnCl^{2+}$; the carbonate complexes $LnCO_3^+$, $Ln(CO_3)_2^-$, and $LnHCO_3^{2+}$; and the phosphate complex $LnH_2PO_4^{2+}$; have all been demonstrated to exist (Wood, 1990). The REE complexing ligand is dependent on pH: the simple ion and sulphate complexes dominate at acidic pH; and carbonate complexes are predominant at near-neutral conditions to basic pH (Wood, 1990).

Phosphate ligands attain importance where the concentration of phosphorus is somewhat anomalous compared to Wood's (1990) model ground water ($\Sigma PO_4^{2-} = 10^{-6}$). The possibility of a phosphate ligand is enhanced through the nature of mineralogical transformations; most, if not all, of the important REE-bearing minerals contain significant amounts of phosphorus, thus any mineralogical breakdown would release anomalous amounts of dissolved phosphate into the system. This suggests that phosphate is likely to have been the dominant complexing agent in the case of the McArthur River deposit, with the phosphate ligand being incorporated into the autunite-like mineral as phosphorus.

The relative timing of the P-Ca-REE alteration must be prior to or coeval with the introduction of hydrocarbon. The latest date for the alteration event is immediately prior to the polymerization of the bitumen. If the alteration event was post-hydrocarbon polymerization in age, the bitumen would have shielded the uraninite from later chemical alteration. This was the case in the Witwatersrand, where the uraninite inclusions within the carbon were not subjected to the branneritization alteration event, which occurred after the introduction of the carbon.

9. Chemical Age Dating

Aggregate chemical age dating for a number of inclusions, calculated by the method of Bowles (1990), are summarized in Figure 10. The calculations yielded ages, ranging from 80 to 1997 Ma, with a mean of 435 Ma. This age is markedly younger than the available primary isotopic ages for McArthur River of 1521 and 1348 Ma (Cameco Corporation, 1990, internal rep.), 1514 Ma (Cumming and Krstic, 1992), and 1444 Ma (Kotzer and Kyser, 1992). All the chemical ages, except seven, are younger than the primary isotopic ages, thus suggesting that the dates may be too erroneous for use. However, in addition to the primary ages, a number of secondary ages have been defined, the main two of which are 512 ± 26 Ma and 210 ± 6 Ma (Cumming and Krstic, 1992).

The spread of the data suggests that several sub-groups, some of which are more evident than others, can be identified: (1) 50 to 349 Ma, average of 189 Ma; (2) 350 to 700 Ma, average of 488 Ma; (3) 750 to 1200 Ma, average of 988 Ma; (4) 1450 to 1500 Ma, average of 1471 Ma; and (5) greater than 1600 Ma.

Comparison of the chemical age dates with the available isotopic dates suggests that the two averages of 189 and 488 Ma, correspond to the 210 and 512 Ma events respectively. This suggests that chemical ages of the inclusions within carbonaceous matter record the age of the secondary mineralization/alteration, rather than the primary age of mineralization. The application of chemical age dating to the deposit further attests to its complex fluid-geochemical-uranium remobilization history.

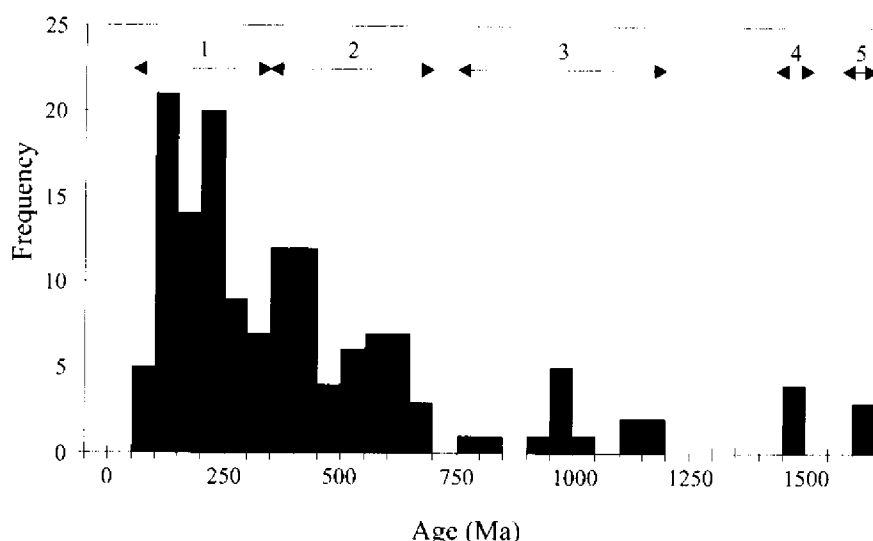


Figure 10 - Frequency histogram of chemical ages calculated from electron microprobe analyses of uranium-rich inclusions.

The ages, both chemical and isotopic, for the McArthur River deposit are not unique to the Athabasca Basin. Many of the events correspond to recognized events in many other deposits, compatible with the results of Fayek and Kyser (1997).

10. Conclusions

The carbonaceous matter accumulations at McArthur River record a previously undocumented part of a complex fluid-geochemical-uranium remobilization history. The petrography of the accumulations suggests that there has been at least two separate hydrocarbon migration events. The non-uranium-bearing inclusions indicate the mobility of several elements (e.g. Fe, Pb, Ti, P, Ca) prior to the formation of the accumulations. Some uranium-bearing inclusions display textures indicative of an early authigenic (*sensu lato*) origin; others display textures that indicate younger uranium remobilization events. The geochemistry of the inclusions indicates that the primary uraninite has been altered by P-Ca-REE-bearing fluid(s) to uranyl phosphates, prior to the accretion of the carbonaceous matter. Chemical age dating of the inclusions yields the dates of the younger alteration/remobilization events rather than the primary mineralization events.

This work suggests that additional studies of carbonaceous matter may yield information on the genesis of other uranium deposits within the Athabasca Basin, which is not recorded elsewhere in the rock history.

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