

ORIGIN OF URANOUS AND URANYL MINERALS AT THE CENTENNIAL DEPOSIT, ATHABASCA BASIN, NORTHERN SASKATCHEWAN, CANADA

PAUL ALEXANDRE[§], YULIA UVAROVA, AND T. KURTIS KYSER

Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, ON, K7L 3N6, Canada

ABSTRACT

Both uranous and uranyl minerals are present in the Centennial unconformity-type U deposit situated in the SW Athabasca Basin, Canada. At least two generations of uraninite are present (disseminated and massive), often strongly altered to coffinite, followed by minor fibrous coffinite forming in veins. Uranyl minerals, mostly uranophane with minor haiweeite precipitating in veins and in hand sample-scaled breccias, are present in significant amounts (*ca.* 5% of the ore) not observed elsewhere in the Athabasca Basin. The multi-stage evolution of the Centennial deposit is explained by the existence of high permeability conduits, promoting the recurrent circulation of P-rich fluids that remobilized U locally. Stable isotopes composition of uranophane (δD of *ca.* -130 ‰ and $\delta^{18}O$ of *ca.* 6 ‰) suggests that recent oxidizing meteoric fluids penetrated to the unconformity (at a depth of *ca.* 800 m) via the major Dufferin lake fault.

Keywords: Uraninite, uranophane, coffinite, haiweeite, uranium deposits, Athabasca Basin

INTRODUCTION

The Paleoproterozoic Athabasca Basin, situated in northern Saskatchewan, Canada (Fig. 1A), is the host of several unconformity-related uranium deposits, some of which (McArthur River, Cigar Lake) represent a very significant source of uranium production today. The majority of the deposits are formed at or immediately below the unconformity that separates the clastic sediments of the Athabasca Basin from its metamorphic and igneous basement. They are situated predominantly on the eastern margin of the basin, with a few in the west, at the Carswell impact structure.

The only initial ore mineral in all Athabasca Basin deposits is uraninite, generally significantly altered and recrystallized by subsequent fluid circulation events to secondary uraninite, coffinite, becquerelite, and other uranium species. Minimal amounts of oxidized uranium minerals have been mentioned in the specialized literature, but never in any significant amount. This is in strong contrast with the Centennial deposit, a recent discovery by Cameco Corporation situated on the southwestern margin of the basin (Fig. 1A), where, in addition to uraninite, a large amount of oxidized uranium species is observed. The presence of large amounts of secondary oxidized uranium minerals is certainly unusual for the Athabasca Basin deposits and, given the depth at which these minerals are observed (*ca.* 800 m below the present day surface), clearly represents an

anomaly. The purpose of the present paper is to describe and characterize the ore mineralogy of the Centennial deposit using petrological and geochemical methods, suggest an explanation for the unusually high amount of oxidized uranium minerals there, and consider their significance for the metallogeny of this type of deposits.

GEOLOGICAL CONTEXT

The Centennial deposit is situated *ca.* 150 km due west of the major McArthur River deposit and *ca.* 120 km of the Key Lake mine and mill site (107.593°W, 57.591°N).

The Archean and Paleoproterozoic sub-Athabasca basement at Centennial belongs to the Virgin River Shear Zone, which separates the Lloyd domain of the Rae Province to the west from the Virgin River domain of the Hearne Province to the east (Fig. 1A). The shear zone is *ca.* 5 km wide and comprises highly mylonized rocks in addition to deformed and metamorphosed graphite and muscovite pelites and psamopelites with subordinate psammities, quartzite, mafic volcanics, amphibolites, and Hudsonian-aged granitoids, collectively termed the Virgin Schist group (VSG) (Johnson 1968, Chandler 1978, Card 2009). The major deformation affecting the VSG is S1 foliation parallel to that observed in the adjacent Lloyd and Virgin River domains, as well as a northeast trending D3 and a northwest trending D4, common to all these units (Card

[§] E-mail address: alexandre@geol.queensu.ca; phone: 613 533 6178; fax: 613 533 6592

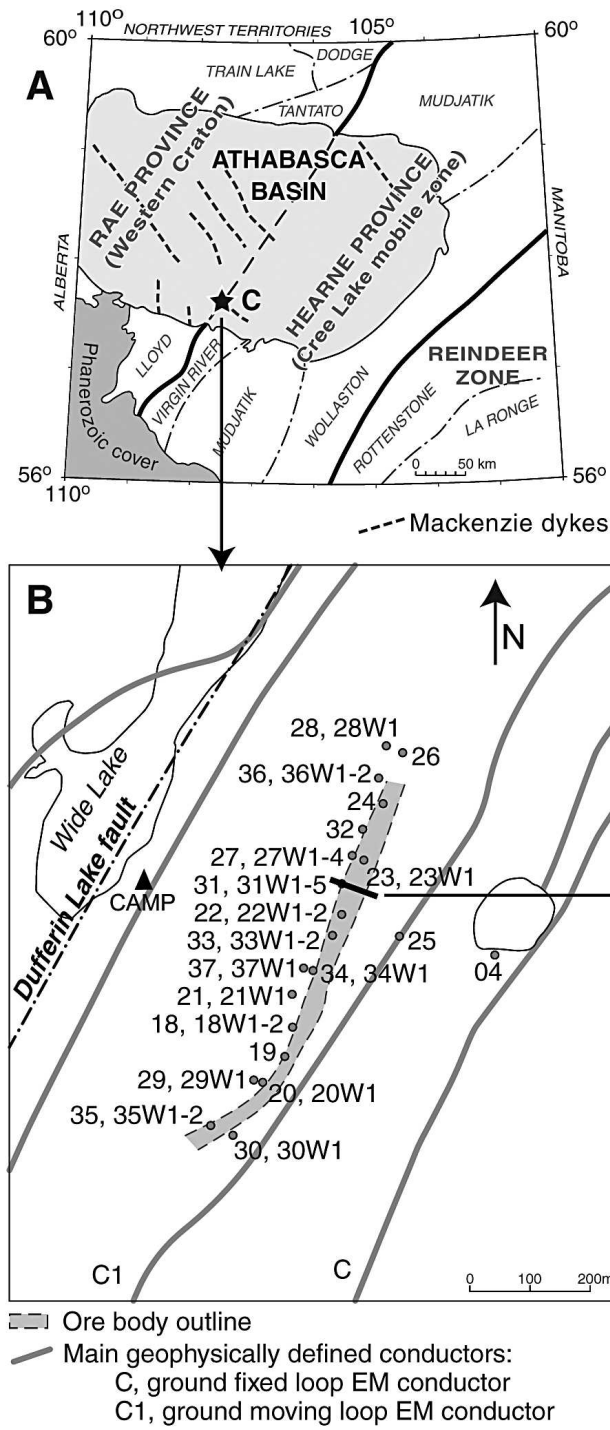
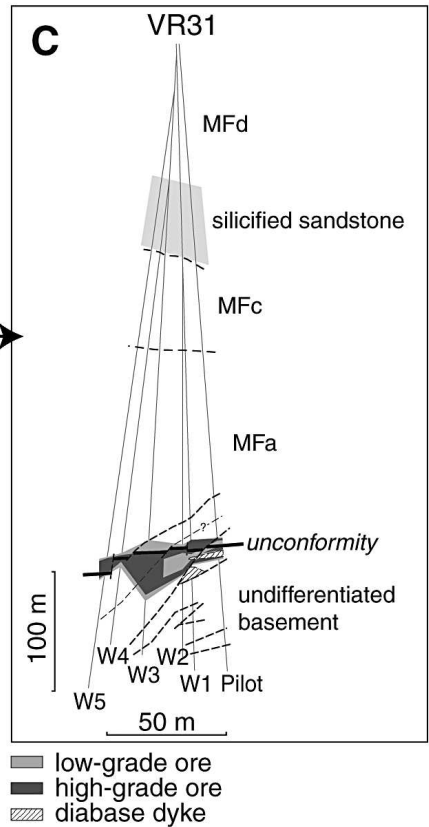


FIG. 1. Geological situation of the Centennial deposit, with (A) its position within the Athabasca Basin in northern Saskatchewan; (B) an outline of the deposit and drill holes (W for wedged hole with the number of wedges); and (C) a cross section of fence VR31, which was sampled for the present work.



et al. 2008). Metamorphism grade ranges from upper greenschist to lower amphibolite; retrograde greenschist assemblages are widespread. Intensive paleoweathering, consisting of kaolinite in the upper portions and of illite and chlorite in the lower portions of the weathered zone, affected the basement rocks prior to the deposition of the Athabasca Group sediments.

The Athabasca Basin formed at *ca.* 1730 Ma as a series of three NE-SW oriented sub-basins (Armstrong & Ramaekers 1985, Kyser *et al.* 2000). Basin fill, up to 2 km thick, consists of thick clastic sequences of Paleoproterozoic age resulting from the rapid exhumation of the Trans-Hudson Orogenic Belt (Ramaekers 1990). At Centennial, the Athabasca Group is 800 to 900 m thick and consists only of the Read Formation and the Manitou Falls Formation (MF). The Read Formation is represented by interbedded matrix-supported quartz pebble conglomerate and poorly sorted medium grained sandstone. The MFb member, only rarely present in the area, is a poorly sorted and clast-supported conglomeratic sandstone. The MFw member is dominated by medium-grained quartz sandstone with lower amounts of conglomeratic layers than in the MFb member. The MFc member is a relatively clean, medium to coarse-grained sandstone with narrow (<2 cm) granule and pebble beds. The MFd member is also a relatively clean, medium to coarse-grained sandstone, but contains a significant amount of clay interclasts.

The Athabasca Group sedimentary rocks and the basement complex are intruded by a series of north-westly trending mafic dikes known as the Mackenzie dike swarms (Cumming & Kristic 1992; Fig. 1A). The dike trend corresponds to tensional directions associated with left-lateral movement along the ancient Hudsonian faults (Hoeve & Sibbald 1978, Sibbald & Quirt 1987). These intrusives range in size from one meter to several hundred meters wide and have a U-Pb age of 1267 ± 2 Ma (Le Cheminant & Heaman 1989). At Centennial, several dikes and sills of diabase are observed (Fig. 1C) and are probably related to the same magmatic event.

The major structural feature at Centennial is the major NE-SW oriented dextral oblique and NW-plunging Dufferin Lake thrust fault, which extends to more than 50 km from north to south and affects all lithologies present (Fig. 1B), with a significant (*ca.* 250 m) post-Athabasca displacement (Reid *et al.* 2010) thrusting the western side up. This structure represents a major fluid flow conduit that may have been active during deposit formation (Jiricka 2010).

The sub-Athabasca basement and the Athabasca Group sediments were affected by several episodes of diagenetic and hydrothermal alteration (detailed paragenesis in Alexandre *et al.* 2012). Early diagenesis during initial burial is characterized by hematite staining (indicative of oxidizing fluids) preceding quartz overgrowths and the precipitation of fine-grained kaolinite and minor spherulitic dravite, followed by desilicification and minor coarse-grained kaolinite.

Illite and chlorite, as well as minor pyrite and rutile, form near the Centennial orebody. The diabase dikes are strongly altered (illite and chlorite), as well, with locally total loss of primary minerals. Initial mineralization at Centennial, dated at *ca.* 1.6 Ga (Alexandre *et al.* 2012), consists of uraninite grains not exceeding 0.5 mm across disseminated in the Athabasca Group sandstones. The main ore stage, possibly formed shortly after the disseminated ore (Alexandre *et al.* 2012), consists of massive uraninite and hematite (Fig. 2) and is situated at the basal unconformity. Large amounts of secondary uranyl minerals are present, locally forming up to 30% of the ore (Fig. 2). Uranyl minerals have rarely been observed elsewhere in the Athabasca Basin (*e.g.*, Thomas *et al.* 1998, Jefferson *et al.* 2007).

ANALYTICAL METHODS

Thin sections were prepared from high-grade ore samples from the Centennial ore zone intersected by drill hole fence VR31, consisting of a pilot hole and five wedged holes (Fig. 1C). Pure ore minerals were manually separated under binoculars from the same samples, for stable isotope analyses and X-ray diffraction analyses. The thin sections were observed under transmitted and reflected light optical microscopes and using a scanning electron microscope (SEM) at Queen's University and the University of Manitoba, Canada.

X-ray diffraction (XRD) analyses were performed on powdered separates using a Panalytical X'pert Pro MPD system at Queen's University, Canada, equipped with an X'celerator (high-speed) detector, copper target, 0.02° Söller slits on both incident and diffracted beams, a divergence slit of 0.5° , and an anti-scatter slit of 1° . The analytical conditions were: step of 0.1° and counting time of 10 s. In all cases, the scan was performed between 5 and $70^\circ 2\theta$, the accelerating voltage was 40 kV, and the current was 45 mA.

Chemical compositions of the uranium ore minerals were obtained by electron-microprobe analyses (EMPA) at the University of Manitoba, Canada, using a Cameca SX100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 2 μ m and counting times on peak and background of 20-50 and 10 s, respectively. The following standards were used for K, L, or M X-ray lines: diopside (Si, Ca); UO_2 (U); fayalite (Fe); titanite (Ti); chromite (Cr); PbTe (Pb); ThO_2 (Th); VP_2O_7 (V); apatite (P); barite (Ba); cuprite (Cu); orthoclase (Al, K); TbPO_4 (Tb); YAG (Y). Data were reduced using the X-PHI procedure (Merlet 1992).

For oxygen isotopes analyses, approximately 5 mg of powdered mineral separate sample were dissolved in BrF_5 at 650°C overnight. The extracted oxygen was converted to CO_2 in contact with a heated graphite rod and the CO_2 was then analyzed off-line using a Finnigan MAT 252 isotope ratio mass spectrometer (IRMS) at Queen's University, Canada. For hydrogen isotope anal-

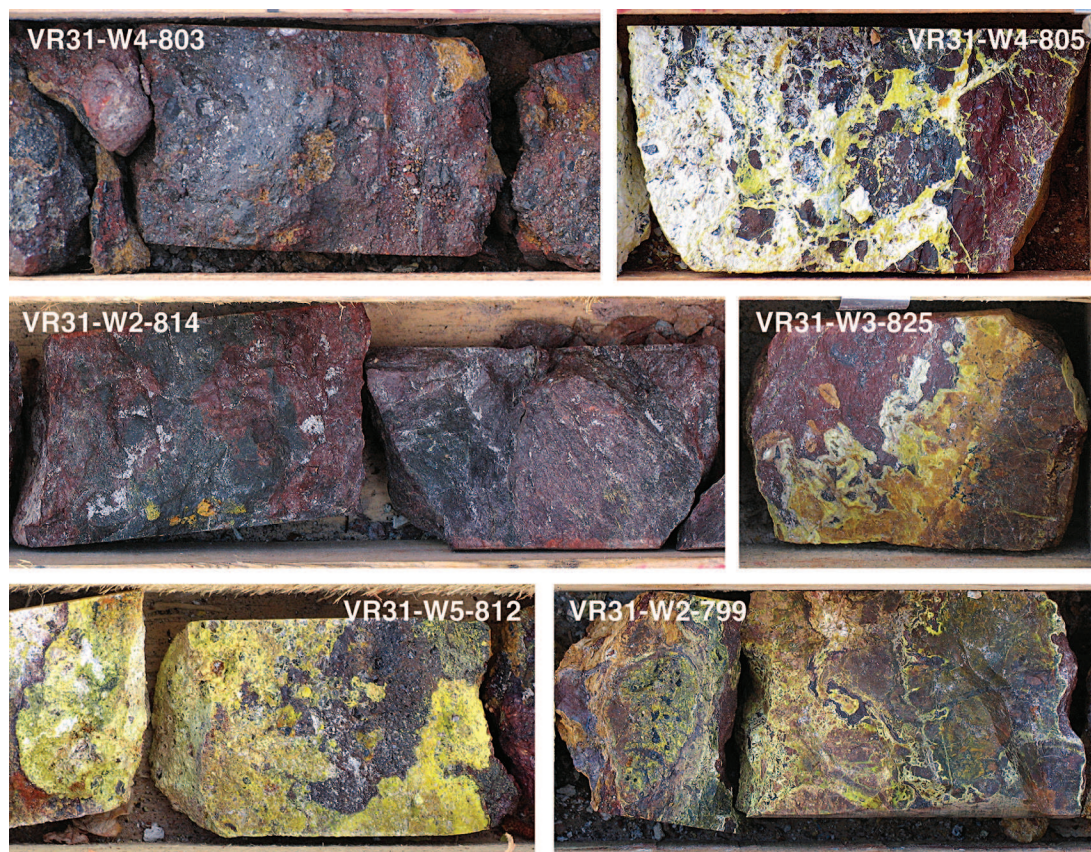


FIG. 2. Drill core photographs showing typical high-grade ore and the two types of U mineralization: reduced (massive uraninite associated with hematite) and oxidized (bright yellow and orange). The diameter of the drill core is *ca.* 5 cm.

yses, encapsulated powdered sample was introduced in an automated thermal combustion–element analyzer device where hydrogen was separated and then analyzed online using a Delta^{plus}XP IRMS at Queen's University, Canada. The results are given in the customary δ (δD and $\delta^{18}O$) notation, relative to Vienna standard mean ocean water (V-SMOW).

URANIUM MINERALS PRESENT

Macroscopic observation of drill-hole samples reveals the presence of two types of U ore minerals in the main ore zone of fence VR31 at the Centennial deposit: massive uraninite, accompanied by hematite, and bright yellow secondary U minerals, their color varying between pale yellow and orange with, in some cases, greenish hues (Fig. 2). The secondary U minerals most commonly fill millimetric fractures or, more rarely, form the matrix of hand-sample-sized hydraulic breccia (Fig. 2).

Microscopic observation using optical microscope and SEM reveals the presence of two distinct types of massive uraninite. The volumetrically predominant uraninite is strongly altered, with a mottled appearance, porosity and cracks, and variation in reflectance, locally strong (Fig. 3A–D). A second generation of uraninite forms an overgrowth over the massive uraninite and is characterized by the absence of any visible alteration and by a colloform texture (Fig. 3B). This late uraninite rarely exceeds 0.5 mm in thickness and individual grains are typically 100 to 200 μm across (Fig. 3B).

The main secondary U mineral present at Centennial, identified by SEM, is uranophane, crystallizing in fine fractures (between 1 and 200 μm in width) and in some cases forming limited stockworks (Fig. 3E). In larger fractures, uranophane forms well-defined needle-shaped crystals, typical of this mineral (Fig. 3F), suggesting that it was formed from a fluid rather than as an *in situ* product of alteration of uraninite. X-ray diffraction analyses of hand-picked and powdered

yellow U mineral confirm that it is uranophane with traces of calcite (Fig. 4).

A minor amount of fibrous coffinite was detected by SEM (Fig. 3G). It seems to have formed at the same time or shortly before uranophane.

Apart from the U minerals described above, euhedral goyazite (Al-Sr phosphate) was also observed within a groundmass of uranophane (Fig. 3H). It is invariably euhedral and rarely exceeds 10 μm in size. Its chemical formula, defined from semiquantitative analyses, is $(\text{Sr}_{0.8}\text{Ca}_{0.2})(\text{Al}_{2.3}\text{Fe}^{3+}_{0.7})(\text{PO}_4)(\text{OH})_5(\text{H}_2\text{O})$.

COMPOSITION OF THE URANIUM MINERALS

The two generations of uraninite, massive altered and late colloform, have distinct chemical compositions, with differences in most elements analyzed (Table 1). Both display very high Ca contents (4.55 and 4.98 wt.% CaO, respectively). Previously reported calcium contents in magmatic uraninite are rather low, up to 0.5 wt.% CaO (Förster 1999), however, in some examples of low-temperature uraninite Ca content is up to 2.28 wt.% CaO (Janeczek & Ewing 1992) or up to 9.55 wt.% CaO (Kempe 2003). Microprobe analyses of uraninite grains from the Centennial deposit show that Ca concentrations are very homogeneous within grains and thus not attributable to inclusions of calcite or apatite. Rather, the incorporation of Ca in the uraninite structure compensates for the charge difference due to the presence of U^{6+} (Janeczek & Ewing 1992). The low totals observed (*ca.* 98 wt.%, Table 1) can be explained by the presence of limited amount of water and the presence of U^{6+} and U^{5+} .

Other elements typical of uraninite, such as Si, Fe, Ti, V, P, and Y, are present in amounts of less than 1 wt.% (Table 1). The Pb and U contents of two generations of uraninite are significantly different, with 4.96 and 0.16 wt.% PbO, and 79.24 and 85.06 wt.% UO_2 , respectively, indicating that the two minerals formed at different times. A very limited amount of relatively fresh massive uraninite was also observed, with all elements other than U accounting for less than 4 wt.%. When plotted on a CaO-SiO₂-UO₂ diagram (Fig. 5), this relatively fresh uraninite plots near the U end-member as expected, whereas the compositions of altered massive uraninite and late colloform uraninite overlap each other and plot in the direction of high Ca contents (Fig. 5). The late colloform uraninite thus formed from elements mobilized from the massive uraninite; in other words, all elements for the formation of the late colloform uraninite were locally derived.

Coffinite, ideally $\text{U}[\text{SiO}_4](\text{H}_2\text{O})_n$, and uranophane, ideally $\text{Ca}(\text{UO}_2)_2[\text{SiO}_3(\text{OH})_2](\text{H}_2\text{O})_5$, at the Centennial deposit have low Pb, Fe, and V contents. Concentrations of P in both minerals are relatively high, with 0.66 and 0.79 wt.% P_2O_5 in coffinite and uranophane, respectively (Table 1). Plotted on a CaO-SiO₂-UO₂ diagram, coffinite and uranophane from Centennial form two

distinct populations falling in the respective fields of concentrations reported in the literature (Fig. 5); they have the same Si:U ratio of nearly 1 and 0.95, respectively, very close to the theoretical ratio of 1 (Stohl & Smith 1981). The amount of Ca in coffinite (*ca.* 3 wt.% CaO, Table 1) cannot be explained by contamination by some Ca-rich inclusions, as electron microscopy did not reveal the presence of such phases.

Haiweeite, ideally $\text{Ca}(\text{UO}_2)_2[\text{Si}_5\text{O}_{12}(\text{OH})_2](\text{H}_2\text{O})_5$, was not detected by optical or secondary electron microscopy, but electron microprobe analyses revealed its presence in the Centennial high-grade ore samples, in close association with uranophane. It is characterized by low U and high Si contents (49.63 wt.% UO_2 and 19.73 wt.% SiO_2). The concentration of P is relatively high (Table 1) as in the case of coffinite and uranophane. Haiweeite plots closest to the SiO₂ corner on a the CaO-SiO₂-UO₂ diagram, with a Si:U ratio of 1.89, slightly lower than the theoretical ratio of 2.5 (Fig. 5).

STABLE ISOTOPE COMPOSITION OF THE U ORE MINERALS

Hand-picked grains of massive uraninite give $\delta^{18}\text{O}$ values of *ca.* -20‰, whereas uranophane samples give $\delta^{18}\text{O}$ values of *ca.* 3 to 9‰ and δD values of -135 to -125‰ (Table 2). In a plot of δD versus $\delta^{18}\text{O}$, the O composition of uranophane is very similar to that of fluids in equilibrium with alteration clay minerals from this area, but the H composition is much lower (Fig. 6). The fractionation factor between uranophane and aqueous fluid is not known, so it is difficult to know or speculate about the isotopic composition of the fluids in equilibrium with uranophane from the Centennial deposit; therefore only the mineral values will be discussed here.

DISCUSSION

The formation of uranous phases

The two uranous phases present at Centennial, uraninite and coffinite, contain relatively high amounts of P (Table 1), suggesting that they precipitated from a fluid in which U was transported mainly as a phosphate complex, but possibly as C, F, and Cl complexes as well. The amount of Pb and the spatial association of main-stage massive uraninite with the diabase dikes suggest that this uraninite formed some time after the initial disseminated uraninite, which formed at *ca.* 1600 Ma (Alexandre *et al.* 2009). It can be argued that the massive uraninite formed as a local re-mobilization and re-concentration of the initial disseminated uraninite, without the introduction of U from outside of the ore zone. The late colloform uraninite may have formed by an analogous process, as it has a comparably high amount of P (Table 1). It has more U and less Pb than the main-stage massive uraninite, indicating that it formed

TABLE 1. CHEMICAL COMPOSITION OF THE U MINERALS IDENTIFIED AT CENTENNIAL (MEDIAN VALUES AND STANDARD DEVIATIONS, WT.%) OBTAINED BY ELECTRON MICROPROBE ANALYSES*. THE AVERAGE CALCULATED STRUCTURAL FORMULA** FOR EACH MINERAL ALSO GIVEN.

Mineral (sample number)	UO ₂ ***	SiO ₂	CaO	PbO	Fe ₂ O ₃	TiO ₂	V ₂ O ₅	P ₂ O ₅	Y ₂ O ₃	K ₂ O	H ₂ O****	Total
Massive altered uraninite (W1-796m, W1-807m, W3-803m, W5-808m)												
	79.24 ± 4.70	0.64 ± 0.27	4.55 ± .75	4.96 ± 2.56	0.72 ± 0.32	0.33 ± 0.72	0.16 ± 0.12	0.59 ± 0.33	0.20 ± 0.14	bdl	6.77	97.83
(U _{0.78} Ca _{0.22} Pb _{0.06} Si _{0.03} Fe ³⁺ _{0.02} P _{0.02}) _{1.13} O ₂ (H ₂ O)												
Late colloform uraninite (W1-796m)												
	85.06 ± 0.86	0.62 ± 0.12	4.98 ± 0.47	0.16 ± 0.10	0.17 ± 0.04	bdl	0.12 ± 0.03	0.20 ± 0.04	bdl	bdl	6.79	98.10
(U _{0.84} Ca _{0.24} Si _{0.03}) _{1.11} O ₂ (H ₂ O)												
Coffinite (W1-807m, W3-803m, W4-804m)												
	66.87 ± 1.37	14.15 ± 0.76	3.01 ± 2.31	0.14 ± 0.54	0.12 ± 0.22	bdl	0.15 ± 0.11	0.66 ± 0.55	bdl	0.52 ± 0.36	14.26	99.88
(U _{0.94} Ca _{0.20} K _{0.04}) _{1.18} [(Si _{0.89} P _{0.04}) _{0.93} O ₄](H ₂ O) ₃												
Uranophane (W1-807m, W3-803m, W4-804m)												
	66.24 ± 1.33	13.91 ± 0.99	6.17 ± 0.73	0.07 ± 0.28	0.15 ± 0.20	bdl	0.17 ± 0.23	0.79 ± 0.75	bdl	0.11 ± 0.29	12.82	100.43
(Ca _{0.93} K _{0.02} Fe ³⁺ _{0.02}) _{0.97} (UO ₂) _{1.95} [(Si _{1.95} P _{0.09})O ₃ (OH)] ₂ (H ₂ O) ₅												
Haiweeite (W4-804m)												
	49.63 ± 2.76	19.73 ± 0.96	4.75 ± 0.35	bdl	bdl	bdl	0.09 ± 0.03	0.48 ± 0.09	bdl	0.21 ± 0.21	8.16	83.05
Ca _{1.12} (UO ₂) _{2.30} [(Si _{4.35} P _{0.09})O _{11.4}](OH) ₂ (H ₂ O) ₅												

* Th, Cr, S, Cu, and Tb (as proxy for REE) were also analyzed, but were always below detection limit.

Energy dispersive spectroscopy (EDS) analyses did not reveal the presence of any other element.

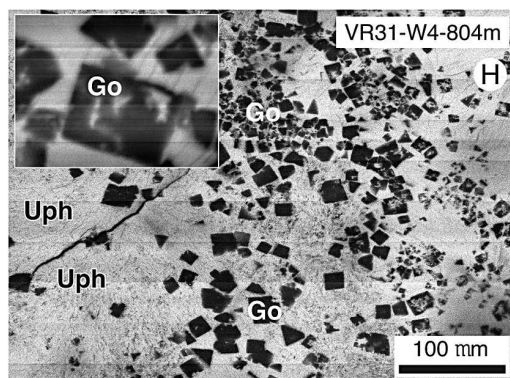
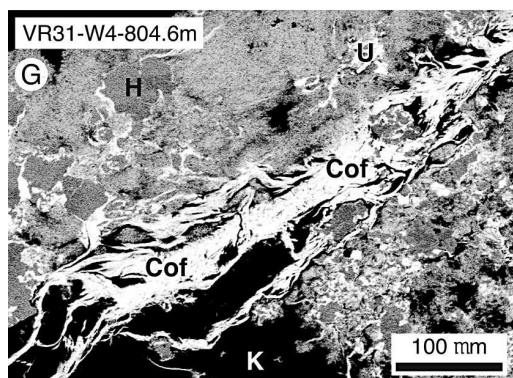
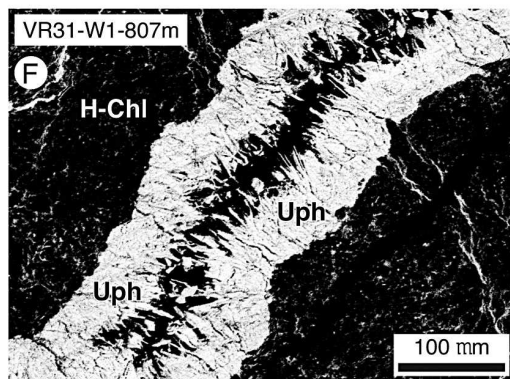
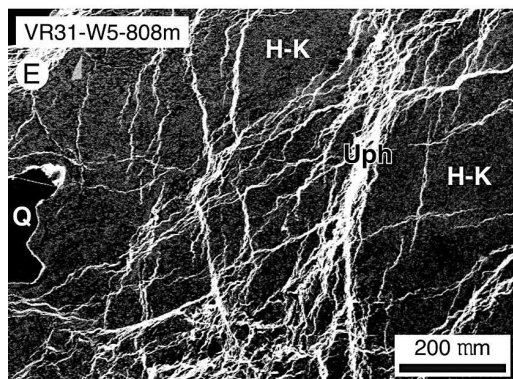
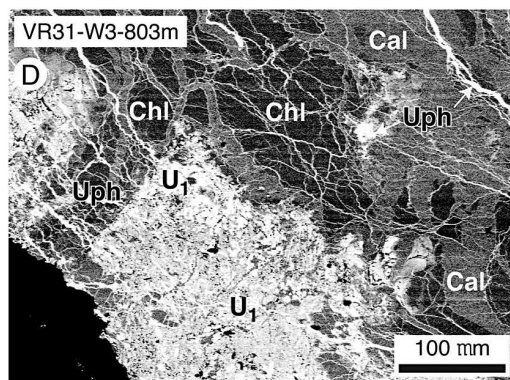
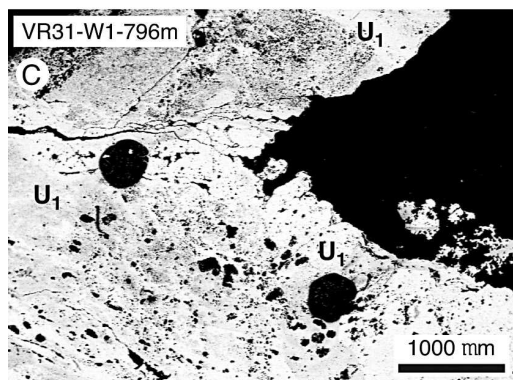
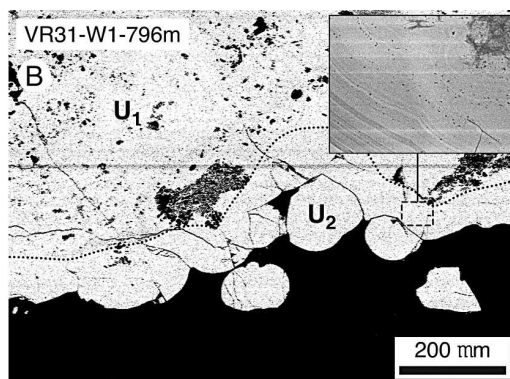
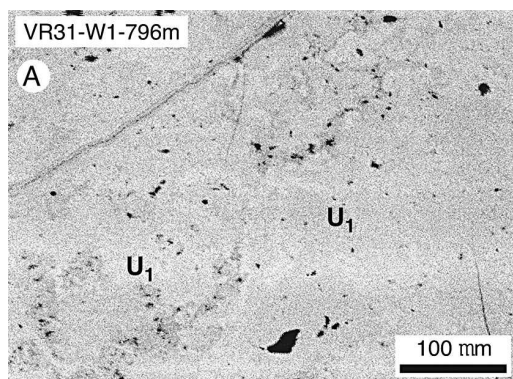
** Chemical formulae for the minerals analyzed were calculated on the anion basis, with O = 3 and (H₂O) = 1 for uraninite, O = 7 and (H₂O) = 3 for coffinite, O = 17, (OH) = 2, and (H₂O) = 5 for uranophane, and O = 23, (OH) = 2 and (H₂O) = 5 for haiweeite.

*** UO₃ for uranophane and haiweeite

**** determined by stoichiometry

bdl = below detection limit

Fig. 3. Scanning electron microscope images of uranous and uranyl minerals observed at the Centennial deposit: (A) massive altered uraninite and late colloform uraninite (U₁); (B) massive altered uraninite; (C) massive altered uraninite; (D) uranophane veins (Uph) cutting through massive uraninite (U₁), chlorite (Chl), and calcite (Cal); (E) a stockwork of uranophane veins cutting through a mixture of hematite and kaolinite (H-K); (F) A large uranophane vein showing well-crystallized individual crystals, and cutting through a mixture of hematite and chlorite (H-Chl); (G) a vein of late fibrous coffinite (Cof), cutting through hematite (H) and uraninite (U); (H) late goyazite (Go) in an uranophane matrix (Uph).



much later, but has the same concentration of other elements, with the exception of Fe (Table 1), further suggesting that it originated by local remobilization of massive uraninite. This remobilization of the main-stage massive uraninite may account for the very low $\delta^{18}\text{O}$ values observed (*ca.* -20‰ ; Table 2), if fluids with very low $\delta^{18}\text{O}$, such as present-day meteoric water, participated in this remobilization. This hypothesis has been suggested for the very low $\delta^{18}\text{O}$ values obtained from uraninite from Cigar Lake in the Athabasca Basin (-32 to -20‰ ; Fayek *et al.* 2002).

On the basis of petrographic observations (Alexandre *et al.* 2012), coffinite formed shortly before the late vein uranophane and, in some cases, possibly at the same time. Its low Pb concentration, comparable to that of uranophane (Table 1) also indicates that coffinite formed relatively recently, its amount of Pb being mainly function of time. Considering that coffinite forms in reducing conditions and uranophane in oxidizing conditions, the shift in $f\text{O}_2$ of the mineralizing fluid is given by the formation of these two minerals. Uranophane formed at *ca.* 2 Ma (Alexandre *et al.* 2012), indicating that reducing fluids were predominant at Centennial until that time, underlining that the deposit was isolated from the surficial oxidizing fluids for most of its history.

The formation of uranyl phases

Uranophane, a U^{6+} silicate, is one of the most common uranyl minerals (Stohl & Smith 1981, Viswanathan & Harnet 1986); it forms at $E_h > 0.2$ and at a pH above 7 (Langmuir 1978). It is commonly observed as the alteration product of primary uranous minerals (predominantly uraninite and coffinite; Read *et al.* 2008, El-Naby 2009), but has also been described as newly formed mineral (Brookins 1981).

The predominant U species observed and described in other unconformity-type deposits in the Athabasca Basin are invariably uraninite and coffinite, the latter in every case an alteration product of the former. Secondary uraninite, as an alteration of primary uraninite or as a newly formed mineral, is also common (McGill *et al.* 1993, Thomas *et al.* 1998, Jefferson *et al.* 2007). Uranyl species have been very rarely described in the Athabasca Basin, and only as an alteration product of uraninite (*e.g.*, Fayek *et al.* 1997). This preponderance of uranous species is explained by the reducing conditions typically prevalent at the deposition sites (*e.g.*, Langmuir 1978, Parks & Pohl 1988), which underlines the uniqueness of the U mineralogy observed at the Centennial deposit, where both uranous (uraninite and coffinite) and uranyl (uranophane and haiweeite) species are present. The presence of newly formed uranyl species at Centennial indicates that oxidizing conditions were prevailing at the corresponding time; it is important to understand what factors contributed to the establishment of these conditions.

Uranophane and haiweeite formed last; they occur late in the paragenetic sequence established for Centennial and crosscut all other minerals present (Fig. 3). Their low age is reflected by the low amount of Pb in their structure (near or below detection limit; Table 1), suggesting that very little time elapsed since their formation, probably only a few million years (Alexandre *et al.* 2012). The δD values of -135 to -125‰ for uranophane samples (Table 2) correspond to that of modern meteoric water for northern Saskatchewan (Canadian Network for Isotopes in Precipitation), suggesting that recent meteoric waters mobilized U from pre-existing U phases and participated in the formation of uranophane (comparing mineral data, as for uranophane, with fluid data can be challenging because of the mineral-water fractionation, but, in the absence of fractionation data, it can be done as an approximation and recognizing its limitations.) On the other hand, the oxygen isotopic composition of uranophane is much higher (*ca.* 3 to 9 ‰ ; Table 2) than that of present-day northern Saskatchewan precipitations (-18 to -16‰ ; Fig. 6). This can be explained by the preferential equilibration of oxygen isotopes in meteoric water with the host rock and the clay alteration phases associated with the deposit, which have the same range of $\delta^{18}\text{O}$ values (Fig. 6). On the basis of the values obtained and disregarding fluid-mineral isotopic fractionation, it is possible to suggest that the meteoric water is fully equilibrated with the deposit host-rock with regards to O, but much less for H (Fig. 6), which can be explained by the relative amounts of H and O in water and in the predominant host-rocks at Centennial.

An important factor to consider is the depth at which the uranyl phases are found, which is typically around 800 m below the present-day surface. The fact that oxidizing fluids of probably superegene origin are found at this depth can be explained by their large amount and the permeability of the conduits used by them. The most obvious choice for a fluid circulation

TABLE 2. HYDROGEN AND OXYGEN ISOTOPIC COMPOSITIONS FOR U MINERALS FROM THE CENTENNIAL DEPOSIT

	$\delta\text{D}_{\text{VSMOW}}\text{‰}$	$\delta^{18}\text{O}_{\text{VSMOW}}\text{‰}$
Main stage uraninite		
W1-796		-19.8
W1-797		-20.3
Late vein uranophane		
W3-803	-130	2.8
W3-803.7	-125	4.1
W4-804	-135	8.9
W4-804.6	-130	8.3
W4-804.7	-129	8.1
W3-819.1	-133	3.3
W3-826.5	-132	5.9

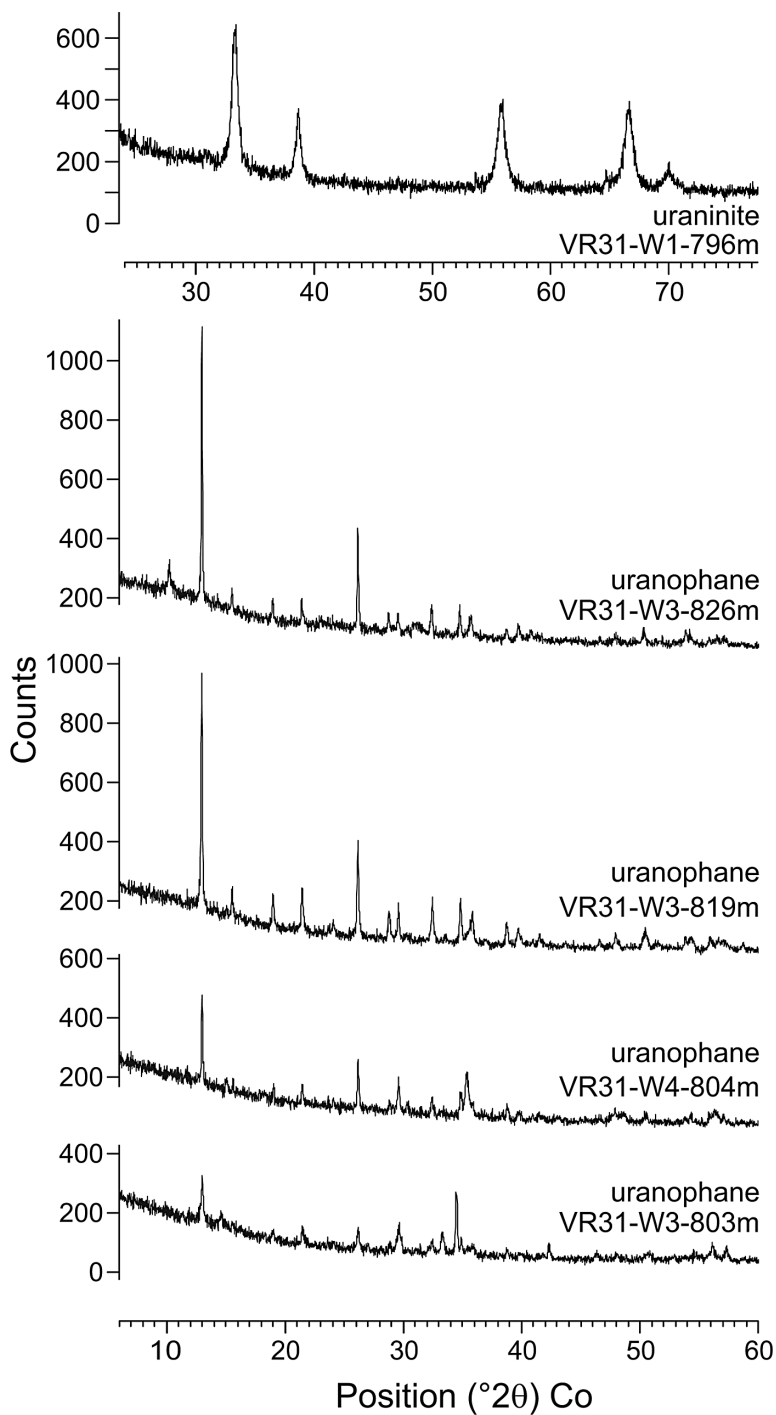


FIG. 4. X-ray diffraction spectra of hand-picked U minerals from Centennial. The main U mineral as seen in hand sample is uraninite (top spectrum), whereas the only U^{6+} mineral detected is uranophane (bottom four spectra); minor calcite is also present with uranophane.

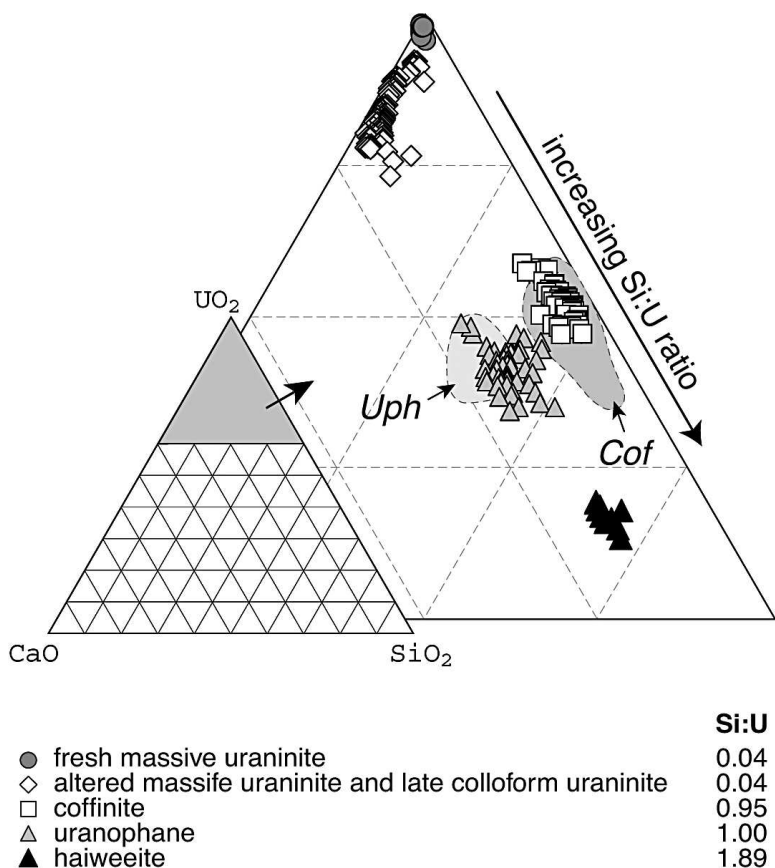


FIG. 5. Chemical composition of the U minerals present at Centennial. The fields of typical uranophane and coffinite are also given.

conduit is the major Dufferin Lake fault (Fig. 1B) and the high-permeability zone that is formed by its repeated reactivation, combined with the high-permeability Read Formation at the basis of the Athabasca Group (Jiricka 2010). The oxidizing fluids probably mobilized U from the pre-existing uranous phases and transported it by phosphate complexes, suggested by the relatively high P contents in uranophane and haiweeite (Table 1). The precipitation of uranophane was probably provoked by an increase of pH, as it is typically stable at pH above 6 (Langmuir 1978).

SUMMARY

The great rarity of uranyl minerals in the unconformity-related U deposits in the Athabasca Basin is explained by the prevailing and lasting reducing conditions there. The presence of oxidizing fluids is usually seen as a challenge to the preservation of the

initial uranous ore, which underlines the particularity of the Centennial deposit. Here, the presence of a large concentration of U is the result of a particular sequence of events, the most important being the repeated remobilization of U from pre-existing uranous phases by P-rich fluids and its reprecipitation locally as either uranous or uranyl phases. The most important factor for this successive reconcentration of U was the existence of high-permeability conduits in the area, combined with the presence of P, probably derived from the alteration of P-rich detrital phases such as apatite. High-permeability zones are observed in most deposits in the Athabasca Basin and are indeed one of the prerequisites for the formation of an unconformity-related U deposit. However, it would seem that at Centennial the presence of the Dufferin Lake fault created a high-permeability conduit, which allowed for meteoric fluids to penetrate to more than 800 m in depth and form a relatively large amount of uranyl phases.

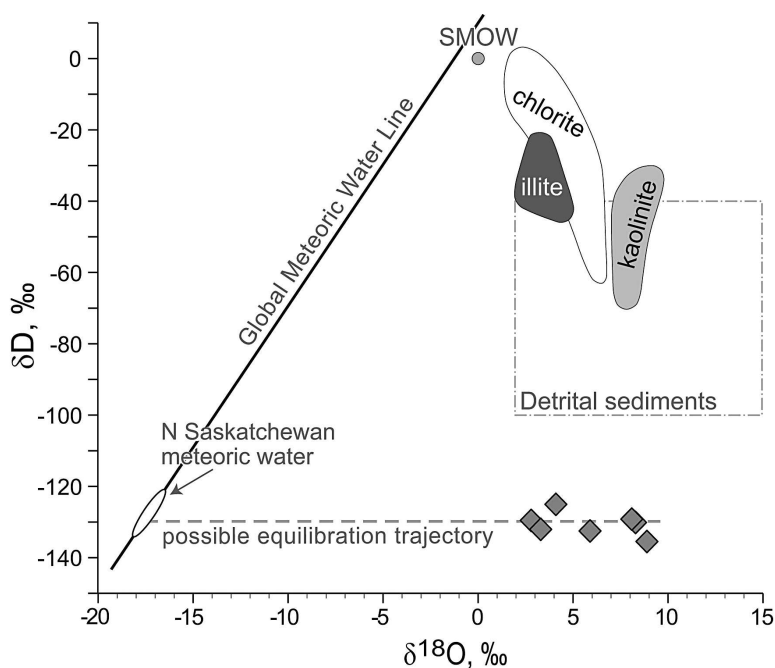


FIG. 6. Stable isotope analyses of uranophane from Centennial (grey diamonds). For comparison, the fields of fluids in equilibrium with alteration clay minerals in the same alteration system are given, as well as the fluids present in typical detrital sediments. The Northern Saskatchewan meteoric waters and its possible evolution by interaction with the deposit host rocks are indicated as well.

ACKNOWLEDGEMENTS

G. Witt and D. Jiricka (Cameco Corporation) are thanked for the sampling logistics support. R. Sidhu and A. Camacho (University of Manitoba) provided help with EMPA and SEM, K. Klassen (Queen's University) conducted stable isotopes analyses, and A. Grant (Queen's University) performed X-ray diffraction analyses. This work benefited from financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) via Discovery, Major Facility Access, and Collaborative and Research Development grants. R. Martin, associated Editor R. Linnen, reviewer A. Deditius, and an anonymous reviewer are thanked for their contribution.

REFERENCES

- ALEXANDRE, P., KYSER, T.K., JIRICKA, D., & WITT, G. (2012) Formation and evolution of the Centennial unconformity-related uranium deposit in the south-central Athabasca Basin, Canada. *Economic Geology*, in press.
- ALEXANDRE, P., KYSER, K., THOMAS, D., & MARLATT, J. (2009) Geochronology of unconformity-related uranium deposits in the Athabasca Basin, Saskatchewan, Canada, and their integration in the evolution of the basin. *Mineralium Deposita* **44**, 41-59.
- ARMSTRONG, R.L. & RAMAEKERS, P. (1985) Sr isotopic study of the Helikian sediment and diabase dikes in the Athabasca Basin, northern Saskatchewan. *Canadian Journal of Earth Sciences* **22**, 399-407.
- BROOKINS, D.G. (1981) Primary uranophane from the Ambrosia Lake uranium district, Grants Mineral Belt, USA. *Mineralium Deposita* **16**, 3-5.
- CARD, C.D. (2009) Cree South Project 2009: Reconnaissance Bedrock Mapping in the Lloyd Domain and Virgin River Shear Zone. In Summary of Investigations 2009, Volume 2. Saskatchewan Geological Survey, Miscellaneous Report 2009-4.2, paper A-7, 21 pp.
- CARD, C.D., MCEWAN, B., & BOSMAN, S.A. (2008) The Cree Lake South Project 2008: Regional Implications of Bedrock mapping along the Virgin River Transect. In Summary of Investigations 2008, Volume 2. Saskatchewan Geological Survey, Saskatchewan Ministry of Energy and Resources, Miscellaneous Report 2008-4.2, CD-ROM, Paper A-2, 23pp.
- CHANDLER F.W. (1978) Geology of part of the Wollaston Lake fold belt, northern Wollaston Lake, Saskatchewan. *Geological Survey of Canada Bulletin* **277**, 57 pp.

- CUMMING G.I. & KRISTIC, D. (1992) The age of unconformity uranium mineralization in the Athabasca Basin, northern Saskatchewan. *Canadian Journal of Earth Sciences* **29**, 1623-1639.
- EL-NABY, H.H.A. (2009) High and low temperature alteration of uranium and thorium minerals, Um Ara granites, south Eastern Desert, Egypt. *Ore Geology Reviews* **25**, 436-446.
- FAYEK, M. & KYSER, K. (1997) Characterization of multiple fluid-flow events and rare-earth elements mobility associated with formation of unconformity uranium deposits in the Athabasca Basin, Saskatchewan. *Canadian Mineralogist* **35**, 627-658.
- FAYEK, M., JANECEK, J., & EWING, R.C. (1997) Mineral chemistry and oxygen isotopic analyses of uraninite, pitchblende, and uranium alteration minerals from the Cigar Lake deposit, Saskatchewan, Canada. *Applied Geochemistry* **12**, 549-565.
- FAYEK, M., HARRISON, T.M., EWING, R.C., GROVE, M., & COATH, C.D. (2002) O and Pb isotopic analyses of uranium minerals by ion microprobe and U-Pb ages from the Cigar Lake deposit. *Chemical Geology* **185**, 205-225.
- FÖRSTER, H.-J. (1999) The chemical composition of uraninite in Variscan granites of the Erzgebirge, Germany. *Mineralogical Magazine* **63**(2), 239-252.
- HOEVE, J. & 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.
- JANECEK, J. & EWING, R.C. (1992) Dissolution and alteration of uraninite under reducing conditions. *Journal of Nuclear Materials* **190**, 157-173.
- JEFFERSON, C.W., THOMAS, D.J., GANDHI, S.S., RAMAEKERS, P., DELANEY, G., BRISBIN, D., CUTTS, C., PORTELLA, P., & OLSON, R.A. (2007) Unconformity-associated uranium deposits of the Athabasca Basin, Saskatchewan and Alberta. In EXTECH IV: Geology and uranium exploration technology of the Proterozoic Athabasca Basin (C.W. Jefferson and G. Delaney eds.). *Geological Survey of Canada Bulletin* **588**, 23-68.
- JIRICKA, D. (2010) The Centennial deposit – an atypical unconformity-related uranium deposit – an update. *13th quadrennial IAGOD symposium*, Adelaide, Australia, 6-9 April 2010.
- JOHNSON, R.L. (1968) The geology of the Nyberg Lake area, Saskatchewan. Saskatchewan Energy and Resources, Report 118, 1-15p.
- KEMPE, U. (2003) Precise electron microprobe age determination in altered uraninite: consequences on the intrusion age and the metallogenic significance of the Kirchberg granite (Erzgebirge, Germany). *Contributions to Mineralogy and Petrology* **145**, 107-118.
- KYSER, K., HIATT, E., RENAC, C., DUROCHER, K., HOLK, G., & DECKART, K. (2000) Diagenetic fluids in Paleoand Mesoproterozoic sedimentary basins and their implications for long protracted fluid histories. In *Fluids and Basin Evolution* (T.K. Kyser, ed.). *Mineralogical Association of Canada Short Course* **28**, 225-262.
- LANGMUIR, D. (1978) Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits. *Geochimica et Cosmochimica Acta* **42**, 547-569.
- LE CHEMINANT, A.N. & HEAMAN, L.M. (1989) Mackenzie igneous events, Canada: middle Proterozoic hotspot magmatism associated with ocean opening. *Earth and Planetary Science Letters* **96**, 38-48.
- MERLET, C. (1992) Quantitative electron probe microanalysis. New accurate f(rZ) description. *Microchimica Acta* **12**, 107-115.
- MCGILL, B.D., MARLAT, J.L., MATTHEWS, R.B., SOPUK, V.J., HOMENIUK, L.A., & HUBREGTSE, J.J. (1993) The P2 North uranium deposit, Saskatchewan, Canada. *Exploration and Mining Geology* **2**, 321-331.
- PARKS, G.A. & POHL D. (1988) Hydrothermal solubility of uraninite. *Geochimica et Cosmochimica Acta* **52**(4) 863-875.
- RAMAEKERS, P. (1990) Geology of the Athabasca Group (Helikian) in Northern Saskatchewan. *Saskatchewan Energy and Mines, Saskatchewan Geological Survey Report* 195, 48pp.
- READ, D., BLACK, S., BUCKBY T., HELLMUTH, K.-H., MARCOS, N., & SIITARI-KAUPPI, M. (2008) Secondary uranium mineralization in southern Finland and its relationship to recent glacial events. *Global and Planetary Change* **60**, 235-249.
- REID, K., ANSDELL, K., JIRICKA, D., WITT, G., & CARD, C. (2010) Regional setting and general characteristics of the Centennial unconformity-related uranium deposit, Athabasca Basin, Saskatchewan. *GeoCanada 2010 conference*, Calgary, May 10-14 2010.
- SIBBALD, T.I.I. & QUIRT, D. (1987) Uranium deposits of the Athabasca Basin. *Geological Association of Canada, Fieldtrip guidebook, Trip 9*, Saskatchewan Research Council Publication R-855-1-G-87, 79 pp.
- STOHL, F.V. & SMITH, D.K. (1981) The crystal chemistry of uranyl silicate minerals. *American Mineralogist* **66**, 610-625.
- THOMAS, D.J., MATTHEWS, R.B., & SUPUCK, V.J. (1998) Athabasca Basin unconformity-type uranium deposits: a synopsis of the empirical model and review of exploration and production trends. *Proceedings, Canadian Institute of Mining, Metallurgy and Petroleum meeting*, Montreal 1998, May 3-7.
- VISWANATHAN, K., & HARNET, O. (1986) Refined crystal structure of beta-uranophane, $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$. *American Mineralogist* **71**, 1489-1493.

Received September 27, 2011, revised manuscript accepted June 13, 2012.