

GEOCHEMISTRY OF URANIFEROUS BITUMEN IN THE SOUTHWEST ATHABASCA BASIN, SASKATCHEWAN, CANADA

P. ALEXANDRE[†] AND T. K. KYSER

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

Abstract

The sediment-hosted unconformity-type Southwest Athabasca uranium mineralization in northern Saskatchewan, Canada, contains uraniferous bitumen, as observed elsewhere in the Athabasca basin. Uraninite is present either as micron-sized grains dispersed in bitumen (uraniferous bitumen) or as larger grains situated in the pore space between bitumen globules. The spatial and textural relationships between uraninite and bitumen suggest that they were co-precipitated. LA-ICP-MS U/Pb dating of uraniferous bitumen yielded an age of 1575 ± 53 Ma, similar to that of other unconformity-type uranium mineralization in the Athabasca basin, indicating that the bitumen was formed early in the history of the basin. Nitrogen, carbon, and sulfur isotope analyses of uraniferous bitumen indicate that its source material was probably kerogen produced by cyanobacteria in a clastic environment.

Introduction

Solid, glassy, amorphous hydrocarbon or bitumen is present in most unconformity-related uranium deposits in the Paleoproterozoic Athabasca basin, Saskatchewan (Sibbald and Quirt, 1987; Kribek et al., 1999). Uraniferous bitumen is also present in uranium deposits elsewhere (e.g., the “natural fission reactors” at Oklo, Gabon; Mossman et al., 1993a; in uranium occurrences in Great Britain, Scandinavia, and South Africa: Eakin and Gize, 1992). In the Athabasca basin, the solid hydrocarbons occur in mineralized rock, immediately associated with uranium ore, and in unmineralized rocks of the alteration haloes (Sibbald and Quirt, 1987).

The intimate association of uranium with carbonaceous matter has been widely documented in a variety of settings (Dons, 1956; Welin, 1966; Leventhal et al., 1986; Landais, 1996) and accounts for the occurrences of uranium-enriched peat, lignite, coal, humite, bitumen, and kerogen, in addition to economic uranium deposits (Eakin and Gize, 1992). The significance of this relationship has been debated. In the Athabasca uranium deposits, it has been suggested that bitumen postdates uraninite (Leventhal et al., 1987), formed in response to graphite alteration (Landais et al., 1993), or had no role in uranium mineralization (Kyser et al., 1989; Wilson et al., 2002), whereas in other deposits a close association between bitumen and uranium mineralization has been suggested (Eakin and Gize, 1992; Mossman et al., 1993b). The debate is partly a consequence of uncertainties regarding the nature of the association between uranium and bitumen, their relative ages, and the form of the uranium. In order to advance that debate, this paper presents the results of geochemical and stable isotope analyses of uraniferous bitumen samples from the Southwest Athabasca basin.

Geologic Background and Samples Studied

The Southwest Athabasca exploration project, operated by Cameco Corporation, is situated on the south rim of the Athabasca basin, northern Saskatchewan, Canada (Fig. 1). Electromagnetic surveys and diamond core drilling have revealed the presence of subeconomic uranium mineralization

in the Athabasca Group sandstones, from which the samples for the present study were collected.

The basement of the Athabasca basin is composed of Archean and Aphebian rocks metamorphosed during the Hudsonian orogeny (Lewry and Sibbald, 1980). They are part of the Wollaston domain in the Cree Lake mobile zone, situated between the Rae province and the Trans-Hudson orogen (Lewry and Sibbald, 1980; Fig. 1). The Wollaston domain comprises mainly Archean continental crust and unfolded continental margin supracrustal rocks (Hoeve and Sibbald, 1978; Sibbald and Quirt, 1987).

The Athabasca basin formed at ca. 1700 to 1750 Ma (Kyser et al., 2000). Basin fill consists of thick clastic sequences of Paleoproterozoic age (Ramaekers, 1990) resulting from the rapid exhumation of the Trans-Hudson orogen (Kyser et al., 2000). The samples studied here are sandstones from the lowermost Manitou Falls Formation of the Athabasca Group,

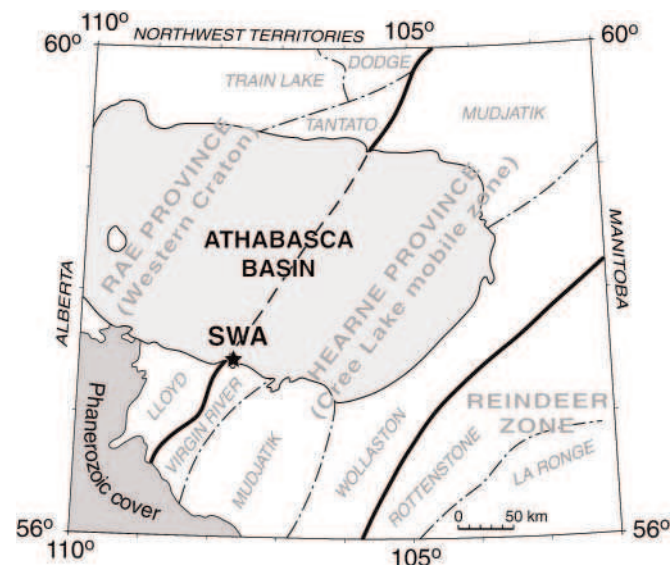


FIG. 1. Simplified geologic map of the Athabasca basin in northern Saskatchewan, Canada, and the major lithotectonic units. SWA - Southwest Athabasca. Modified from Hoeve and Sibbald (1978) and Sibbald and Quirt (1987).

[†] Corresponding author: alexandre@geol.queensu.ca

which also hosts the majority of the sandstone-hosted deposits in the eastern Athabasca basin (Sibbald and Quirt, 1987). This formation is subdivided here into members A, C, and D, member B being absent from the area studied (MFA, MFC, MFD; Fig. 2). The MFA member is characterized by interbedded, matrix-supported quartz pebble conglomerate and well to poorly sorted, medium-grained sandstone (Ramaekers, 1990). Hematitic (red-colored) siltstone beds are a relatively typical but minor component of this member. The MFC member, which is only rarely present in the studied area, is dominated by medium-grained quartz sandstone along with a substantial component of poorly sorted and clast-supported conglomeratic sandstone. MFD is a relatively clean, medium- to coarse-grained sandstone with thin (<2 cm) granule and pebble beds. The thickness of the Athabasca Group in the studied area ranges from 360 to 400 m (Fig. 2). In the Southwest Athabasca prospect, uraniferous bitumen occurs in the MFA member near the unconformity. It cements the

otherwise friable sandstone forming a relatively firm yet malleable dense black mass with indistinct and irregular boundaries independent of any sedimentological features. These highly radioactive zones extend several centimeters vertically and have unknown horizontal dimensions. With the naked eye, bitumen is visible as densely disseminated globular grains, less than 1 mm in size, situated between quartz grains or, more rarely, in swarms of thin veins. In most cases, the bitumen globules have a chlorite rim (<100 μm), although this chlorite is sometimes absent or altered to kaolinite.

Mineral Paragenesis

Transmitted light microscopy and backscattered electron microscope (BSEM) images (Fig. 3) were used to determine the paragenesis of the minerals present in the samples studied (Fig. 4). The predominant mineral in the sandstone host rock is detrital quartz, with very minor detrital muscovite and corroded detrital zircon (Fig. 3). The latter are better preserved here than elsewhere in the sandstone of the Athabasca Group. Early diagenesis was characterized by hematite staining and quartz overgrowths (Fig. 3A), followed by fine and then coarser kaolinite (Fig. 3B) and spherulitic dravite. An intermediate stage of desilicification, visible because of the partial dissolution of quartz overgrowth rims, was followed by a late diagenetic stage of illite that replaced kaolinite (Fig. 3C) and by minor rutile and pyrite. This stage was followed by chlorite precipitation and chlorite alteration of kaolinite and illite (Fig. 4). The main mineralization event was characterized by the precipitation of uraninite and uraniferous bitumen (Fig. 3D-F), the latter commonly rimmed by chlorite (Fig. 3D). Finally, vein-filling spherulitic dravite, as well as rutile, pyrite, and copper and nickel sulfides were introduced during a late alteration event. At this time, early uraninite was commonly altered to coffinite or various Si- and Ca-rich uranyl minerals (Fig. 3E). Uraninite alteration was accompanied by the release of radiogenic lead, which precipitated as microscopic (1–10 μm across) grains of galena or migrated out of mineralized rock.

Morphology and Geochemistry of Uraniferous Bitumen

The uraniferous bitumen from the Southwest Athabasca basin typically displays rounded and globular, sometimes irregular, morphology (Fig. 3E, F), typical of other occurrences of uraniferous bitumen described in the literature (e.g., Eakin and Gize, 1992). Bitumen globules occur in the open space between quartz grains but do not fill it entirely (Fig. 3E). Dominant uraninite and minor coffinite and rutile grains are situated in the pore space between homogeneous and barren bitumen globules (Fig. 3E). Locally, a more complex texture is seen (Fig. 3F), where brighter areas within the bitumen are observed in backscattered electron imaging. Small spots with the highest brightness correspond to uraninite grains and small amounts of iron and lead sulfides. These spots are large enough to be resolvable under BSEM, the spatial resolution of which is less than 1 μm . The zones with variable brightness correspond to a uraninite-bitumen mixture wherein the uraninite grains are less than 1 μm in size; their concentration in the mixture determines its brightness.

Figure 3E shows uraninite grains situated in the pore space between bitumen globules. In similar occurrences elsewhere,

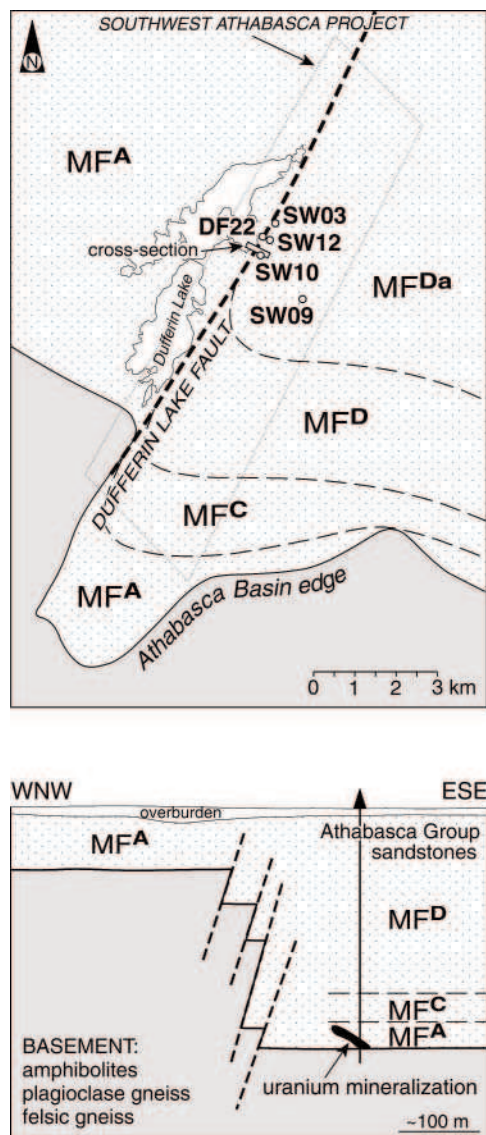


FIG. 2. Simplified geological sketch and cross section of the Southwest Athabasca prospect. The position of the sampled drill holes is indicated.

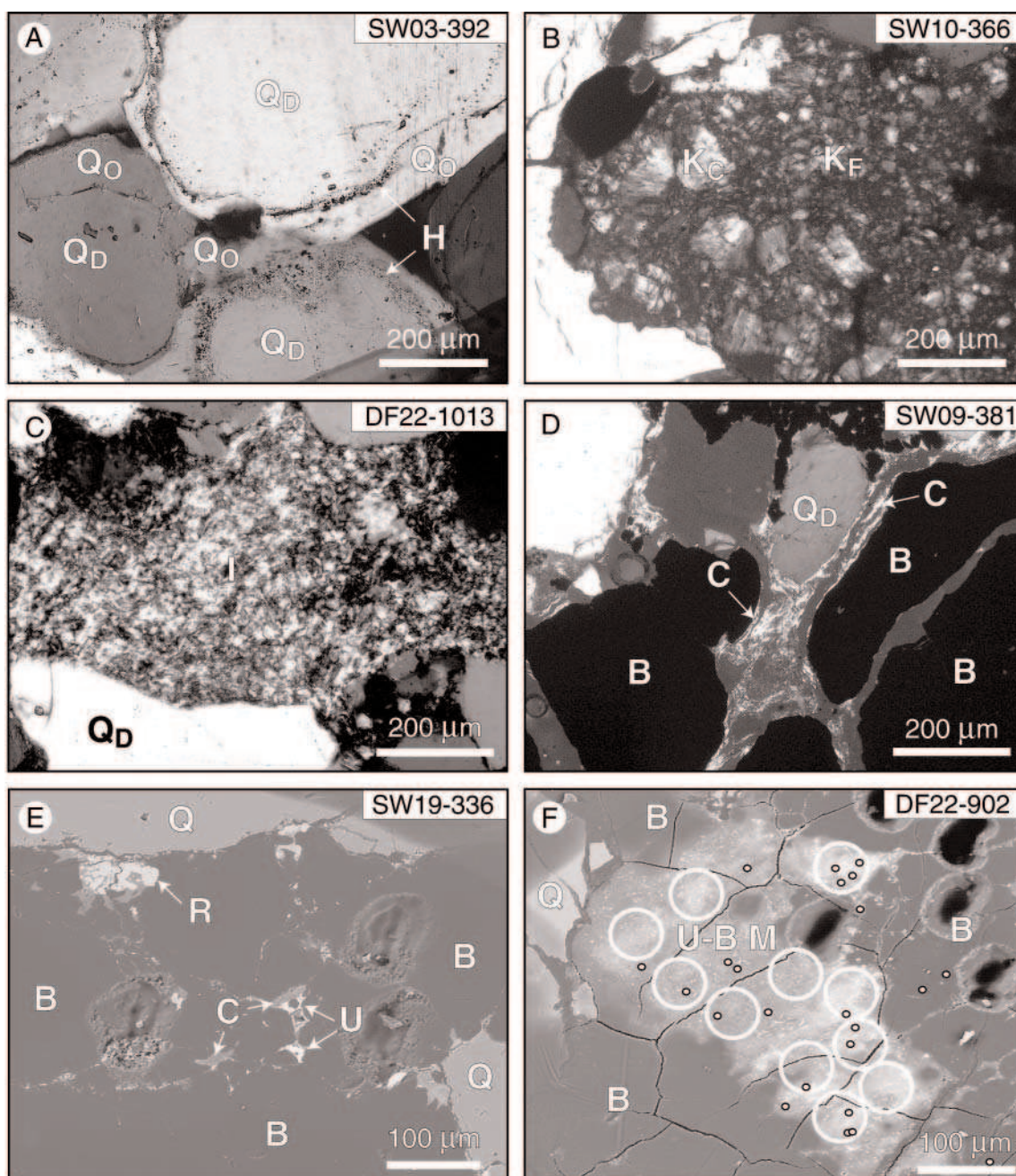


FIG. 3. Transmitted light microscopy (A-D) and backscattered electron microscope (BSEM) (E, F) images of alteration assemblage and of uraniferous bitumen from the Southwest Athabasca. A. Quartz overgrowth (Q_o) separated from detrital quartz (Q_d) by a hematite rim (H). B. Fine- and coarse-grained kaolinite (K_c and K_f). C. Illite alteration of kaolinite (I). D. Uraniferous bitumen globules (B) rimmed by chlorite (C). E. Typically globular bitumen (B) surrounded by quartz (Q), with uraninite (U), coffinite (C), and rutile (R) situated in the pore spaces left between the bitumen globules. F. Mixture of less than micrometer-sized uraninite grains and bitumen (uraninite-bitumen mixture, or U-B M), surrounded by barren bitumen (B); the areas analyzed by LA-ICP-MS (large white-rimmed circles) and by electron microprobe (small black-rimmed circles) are indicated.

this texture has been interpreted as uraninite forming after bitumen (e.g., Eakin and Gize, 1992), with the bitumen acting as a reductant for uraninite precipitation (Mossman et al., 1993b; Nagy et al., 1993). Others have interpreted the relatively sharp transition between bitumen and the uraninite-bitumen mixture (Fig. 3F) as indicating the alteration and replacement of a preexisting uranium mineral by later bitumen

(Abdel-Gawad and Kerr, 1961; Nagy et al. 1991; Eakin and Gize, 1992; Janeczek and Ewing, 1992). On the basis of our observations, we suggest that the uraninite and bitumen formed contemporaneously.

Quantitative analyses were made on an automated 4 spectrometer Camebax MBX electron probe by the wavelength dispersive X-ray analysis method (WDX) at Carleton University

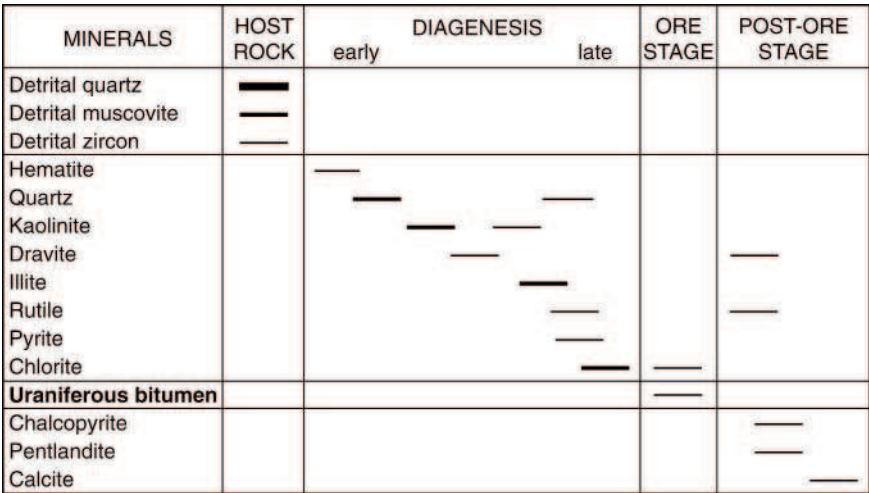


FIG. 4. Proposed paragenetic sequence for the Southwest Athabasca uranium mineralization. The thickness of the lines indicates the relative abundance.

(Ottawa, Canada). Operating conditions were 15kV accelerating potential and 20 nA beam current. Peak counting times for each element were either 30 seconds or 40,000 accumulated counts, while background counting times on each side of the analyzed peak were one half that of the peak counting time. Raw X-ray data were corrected for peak interference, dead time, and background, and converted to oxide weight percent by the standard Cameca PAP matrix correction program. A suite of well-characterized natural and synthetic minerals and compounds were used as calibration standards. Analyses are precise to 1 to 2 percent relative for major elements and 3 to 5 percent relative for minor elements (<1 wt %). The calibration and validation material standards were chosen so that they can have a composition range similar to that of the analyzed samples.

The chemical composition of the uraniferous bitumen is highly variable (Table 1). The brightest spots in BSE (Fig. 3F) have the highest concentrations of U, Pb, Fe, S, and P (Table 1), reflecting the presence of uraninite with minor galena and pyrite. The relative amounts of U and C, indicated by the Energy Dispersion Spectrum analysis (EDS; Fig. 5), vary between the zones, suggesting that fine uraninite grains are finely dispersed in the bitumen matrix. Spot analyses of the dark areas of the bitumen (Fig. 3F) have the lowest totals (Table 1), and this material is interpreted to be composed mainly of C, N, O, and H (Fig. 6A). Bright spots have the highest measured concentrations of UO₂ (Table 1) and are interpreted to reflect abundant submicroscopic uraninite in the bitumen (Finch and Murakami, 1999).

Stable Isotope Composition and Origin of Uraniferous Bitumen

Grains of uraniferous bitumen were crushed to less than 0.3 mm in size and washed in 10 percent hydrochloric acid for two to three hours in order to remove any carbonate phases. CO₂ for the mass-spectrometric analysis was generated by flash combustion in O₂ at 1020°C, while nitrogen oxides were reduced to N₂ at 650°C. CO₂, N₂, H₂O, and SO₂ were separated using a 2 m gas chromatographic column at 80°C, and

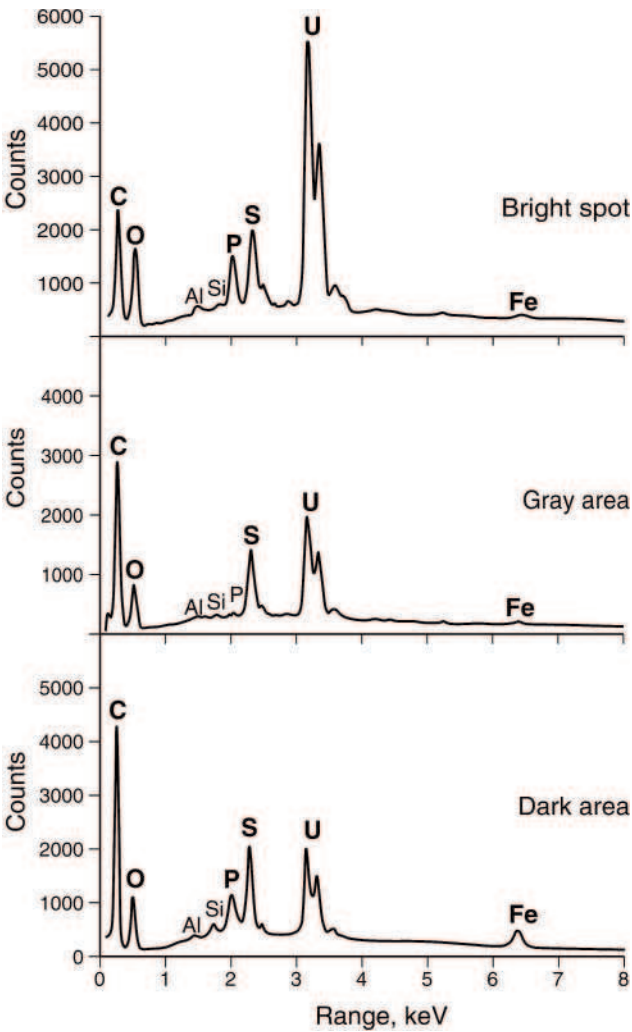


FIG. 5. Energy dispersion spectra (EDS) for different brightness zones in the bitumen-uraninite mixture in Figure 3F, showing the presence of carbon, oxygen, and phosphorus, typical for bitumen, as well of uranium, corresponding to uraninite.

TABLE 1. Chemical Composition of the Uraninite-Bitumen Mixture from the Southwest Mineralization, as Determined Using the Electron Microprobe

Sample Description	SiO ₂ (wt %)	PbO ₂ (wt %)	UO ₂ (wt %)	FeO (wt %)	ThO ₂ (wt %)	CaO (wt %)	Y ₂ O ₃ (wt %)	SO ₃ (wt %)	TiO ₂ (wt %)	P ₂ O ₅ (wt %)	Total (wt %)
DF22-902											
Bright spot	0.64 ± 0.03	8.20 ± 0.20	36.39 ± 0.33	1.11 ± 0.06	0.52 ± 0.11	0.18 ± 0.01	<DL	8.06 ± 0.17	0.49 ± 0.02	3.19 ± 0.05	58.80
	0.86 ± 0.03	2.41 ± 0.11	20.02 ± 0.22	0.74 ± 0.05	0.12 ± 0.08	0.17 ± 0.01	<DL	4.91 ± 0.13	0.35 ± 0.02	0.92 ± 0.03	30.54
	1.11 ± 0.04	0.95 ± 0.09	49.92 ± 0.40	0.38 ± 0.04	0.20 ± 0.09	0.26 ± 0.01	0.28 ± 0.04	5.61 ± 0.13	0.53 ± 0.02	1.91 ± 0.04	61.14
	0.41 ± 0.03	3.77 ± 0.14	31.62 ± 0.28	2.48 ± 0.08	0.28 ± 0.09	0.25 ± 0.01	<DL	6.41 ± 0.15	0.74 ± 0.02	2.60 ± 0.05	48.59
	1.67 ± 0.05	5.16 ± 0.16	33.20 ± 0.30	2.94 ± 0.09	0.26 ± 0.10	0.32 ± 0.02	<DL	9.37 ± 0.18	0.91 ± 0.03	1.77 ± 0.05	55.67
	0.66 ± 0.04	1.79 ± 0.11	62.09 ± 0.43	0.78 ± 0.05	0.38 ± 0.12	1.37 ± 0.03	<DL	2.84 ± 0.10	0.76 ± 0.03	1.37 ± 0.04	72.05
	0.68 ± 0.04	4.04 ± 0.15	44.37 ± 0.35	0.51 ± 0.05	0.46 ± 0.11	0.26 ± 0.01	<DL	8.57 ± 0.17	1.00 ± 0.03	2.42 ± 0.05	62.33
	0.08 ± 0.03	0.11 ± 0.04	35.94 ± 0.32	0.56 ± 0.04	0.20 ± 0.10	0.29 ± 0.01	<DL	5.20 ± 0.13	0.40 ± 0.02	2.93 ± 0.05	45.73
	<DL	1.67 ± 0.10	17.46 ± 0.21	0.34 ± 0.04	<DL	0.07 ± 0.01	<DL	4.38 ± 0.12	0.07 ± 0.01	0.38 ± 0.03	24.37
	<DL	0.21 ± 0.06	15.58 ± 0.19	0.28 ± 0.03	0.06 ± 0.00	0.10 ± 0.01	<DL	3.63 ± 0.11	0.08 ± 0.01	0.41 ± 0.03	20.40
	<DL	<DL	17.71 ± 0.21	0.25 ± 0.03	<DL	0.06 ± 0.01	<DL	4.08 ± 0.11	0.07 ± 0.01	0.28 ± 0.02	22.49
	1.25 ± 0.04	0.19 ± 0.06	23.48 ± 0.23	0.47 ± 0.04	0.23 ± 0.09	0.20 ± 0.01	<DL	6.07 ± 0.14	0.57 ± 0.02	0.85 ± 0.03	33.37
Bright area	0.07 ± 0.02	0.71 ± 0.07	15.47 ± 0.19	0.12 ± 0.03	0.11 ± 0.07	0.25 ± 0.01	<DL	4.37 ± 0.12	<DL	0.17 ± 0.02	21.32
	<DL	<DL	5.79 ± 0.12	1.07 ± 0.05	<DL	<DL	<DL	3.42 ± 0.11	0.10 ± 0.01	0.26 ± 0.02	10.79
	0.20 ± 0.02	0.23 ± 0.06	6.34 ± 0.12	1.16 ± 0.05	0.19 ± 0.08	0.12 ± 0.01	<DL	3.91 ± 0.12	0.51 ± 0.02	1.07 ± 0.03	13.77
	<DL	0.08 ± 0.05	8.18 ± 0.14	0.91 ± 0.05	<DL	<DL	<DL	3.53 ± 0.11	0.01 ± 0.01	0.08 ± 0.02	12.83
	0.08 ± 0.02	<DL	6.41 ± 0.12	1.20 ± 0.06	<DL	0.08 ± 0.01	<DL	3.90 ± 0.11	0.08 ± 0.01	0.25 ± 0.02	12.02
Dark area	<DL	0.53 ± 0.07	6.69 ± 0.13	1.28 ± 0.06	<DL	0.08 ± 0.01	<DL	4.07 ± 0.12	0.14 ± 0.01	0.55 ± 0.03	13.41
	<DL	<DL	0.07 ± 0.03	<DL	0.06 ± 0.00	<DL	<DL	3.31 ± 0.11	<DL	<DL	3.50
	<DL	<DL	<DL	<DL	<DL	0.31 ± 0.01	<DL	3.06 ± 0.10	<DL	<DL	3.46
	<DL	<DL	<DL	<DL	<DL	<DL	<DL	3.23 ± 0.11	<DL	<DL	3.36
Black zone	<DL	<DL	<DL	<DL	<DL	<DL	<DL	3.18 ± 0.11	<DL	<DL	3.24
SW12-336											
Bright area	14.07 ± 0.13	0.27 ± 0.07	24.71 ± 0.25	2.98 ± 0.09	2.35 ± 0.16	0.95 ± 0.02	0.18 ± 0.05	3.89 ± 0.12	2.28 ± 0.04	2.99 ± 0.07	54.67
	12.94 ± 0.13	0.35 ± 0.08	23.14 ± 0.23	3.16 ± 0.09	2.69 ± 0.17	0.81 ± 0.02	0.27 ± 0.05	5.16 ± 0.14	2.18 ± 0.04	2.83 ± 0.07	53.53
	5.65 ± 0.07		24.48 ± 0.24	3.52 ± 0.09	1.66 ± 0.13	0.75 ± 0.02	0.11 ± 0.03	2.83 ± 0.10	1.49 ± 0.03	1.35 ± 0.04	41.87
	8.14 ± 0.09		22.33 ± 0.25	2.46 ± 0.08	1.68 ± 0.14	1.24 ± 0.02	0.14 ± 0.04	3.92 ± 0.12	1.60 ± 0.03	1.90 ± 0.05	43.45
	12.68 ± 0.13	0.12 ± 0.05	23.48 ± 0.23	2.56 ± 0.08	2.11 ± 0.16	0.84 ± 0.02	0.23 ± 0.04	3.54 ± 0.11	2.23 ± 0.04	2.80 ± 0.06	50.61
Gray area	0.55 ± 0.03	0.32 ± 0.06	6.88 ± 0.12	8.22 ± 0.15	0.13 ± 0.08	0.20 ± 0.01	<DL	5.68 ± 0.14	1.47 ± 0.03	0.39 ± 0.03	23.82
	0.65 ± 0.03	1.16 ± 0.09	9.27 ± 0.14	10.68 ± 0.16	0.33 ± 0.09	0.30 ± 0.01	<DL	8.00 ± 0.17	1.50 ± 0.03	0.48 ± 0.03	32.39
	0.58 ± 0.03	0.20 ± 0.06	6.84 ± 0.12	5.21 ± 0.11	0.37 ± 0.08	0.19 ± 0.01	<DL	5.55 ± 0.14	0.95 ± 0.02	0.33 ± 0.02	20.26
	0.37 ± 0.03	0.18 ± 0.05	6.04 ± 0.11	4.31 ± 0.10	0.33 ± 0.08	0.38 ± 0.01	<DL	2.93 ± 0.10	1.12 ± 0.03	0.34 ± 0.02	16.07
	0.38 ± 0.02	0.17 ± 0.06	6.90 ± 0.12	2.96 ± 0.08	0.27 ± 0.09	0.30 ± 0.01	<DL	4.01 ± 0.12	2.24 ± 0.04	0.25 ± 0.02	17.53
	0.32 ± 0.02	0.14 ± 0.05	8.90 ± 0.14	3.38 ± 0.09	0.37 ± 0.08	0.50 ± 0.02	<DL	5.22 ± 0.14	1.55 ± 0.03	0.30 ± 0.02	20.72
	<DL	0.10 ± 0.06	<DL	<DL	<DL	<DL	<DL	1.23 ± 0.07	<DL	<DL	1.40
Dark area	<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.17 ± 0.07	<DL	<DL	1.25
	<DL	<DL	<DL	<DL	0.06 ± 0.01	<DL	<DL	1.33 ± 0.07	<DL	<DL	1.48
SW03-389											
Bright area	<DL	0.32 ± 0.06	20.94 ± 0.23	0.58 ± 0.04	<DL	0.08 ± 0.01	<DL	3.50 ± 0.10	0.07 ± 0.01	0.41 ± 0.02	25.96
	<DL	0.10 ± 0.03	18.20 ± 0.20	0.22 ± 0.03	<DL	<DL	<DL	1.84 ± 0.08	0.12 ± 0.02	0.34 ± 0.02	20.94
	0.07 ± 0.02	0.52 ± 0.06	20.44 ± 0.22	0.17 ± 0.03	<DL	0.07 ± 0.01	0.06 ± 0.02	0.92 ± 0.05	0.12 ± 0.01	0.24 ± 0.02	22.62
Dark area	<DL	0.22 ± 0.05	23.72 ± 0.24	0.14 ± 0.03	<DL	0.14 ± 0.01	<DL	3.41 ± 0.11	0.07 ± 0.01	0.58 ± 0.03	28.27
	<DL	0.21 ± 0.06	23.90 ± 0.24	0.23 ± 0.03	<DL	<DL	<DL	4.04 ± 0.11	0.10 ± 0.02	0.74 ± 0.03	29.26
	<DL	0.40 ± 0.06	19.88 ± 0.22	0.17 ± 0.03	<DL	0.06 ± 0.01	<DL	1.87 ± 0.08	<DL	0.34 ± 0.02	22.83

Notes: For each sample, the zones with different brightness as seen in the SEM images, have been analyzed separately, as indicated; the uncertainty margins indicated correspond to analytical counting statistic; DL = detection limit

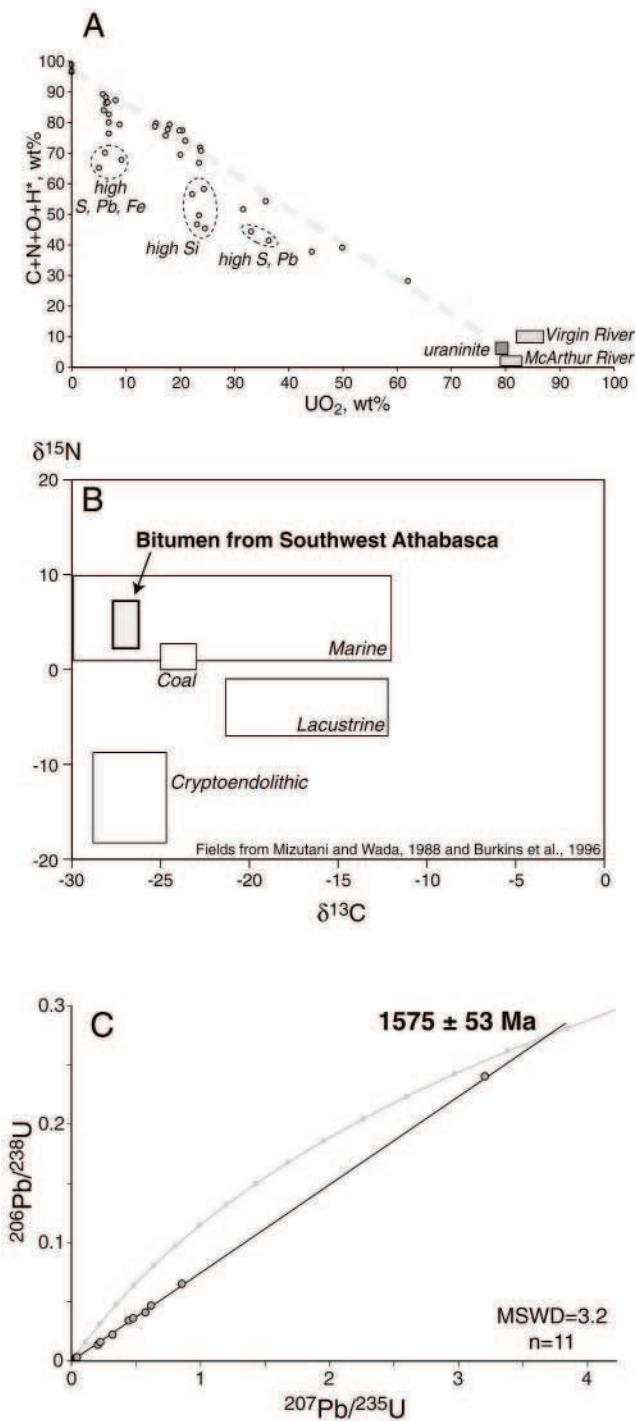


FIG. 6. Chemical and isotopic compositions of uraniferous bitumen from the Southwest Athabasca. (A) Mixing line between a “bitumen” and a “uraninite” end-members, the latter corresponding to uraninite from the sandstone-hosted Virgin River mineralization situated ~30 km to the north of the Southwest area, and to an average uraninite composition from various environments (Eakin and Gize, 1992; Janeczek and Ewing, 1992; Fayek et al., 1997). (*calculated assuming that the oxides plus C, N, O, and H total 100%). (B) Stable isotope composition, with fields corresponding to particular environments indicated for comparison. (C) Concordia diagram showing the results of LA-ICP-MS U-Pb dating of uraniferous bitumen from the Southwest Athabasca uranium mineralization, with upper intercept age and statistical information.

analyzed using the Continuous Flow Isotope Ratio Mass Spectrometer (ConFlow IR-MS) ThermoFinnigan Delta^{PLUS} XP. The δ¹³C values are reported relative to the international PDB standard, and the δ¹⁵N values are reported relative to atmospheric N₂. SO₂ for the mass-spectrometric analysis was generated by flash combustion in O₂ at 1,000°C. CO₂, N₂, H₂O, and SO₂ were separated using a gas chromatographic column at 90°C, and SO₂ was analyzed by a IR-MS Finnigan MAT 252. The δ³⁴S values are reported relative to the international V-CDT standard.

The δ¹³C values for uraniferous bitumen in the Southwest Athabasca project fall in a narrow range between -27.6 and -26.3 per mil, with an average value of -26.8 ± 0.6 per mil (Table 2; Fig. 6B). They are close to the δ¹³C values of barren bitumen from Cigar Lake (-28.2 to -27.5‰; Landais et al., 1993) and very similar to the values for uranium-rich bitumen from the Key Lake deposit (-25‰; Kyser et al., 1989) but lower than those for graphite in the basement at Key Lake (-20‰; Kyser et al., 1989).

The nitrogen isotope composition of the bitumen ranges from 2.2 to 7.1 per mil, with an average δ¹⁵N value of 4.0 ± 2.7 per mil (Table 2) and is comparable with that of organic matter found in modern marine sediments (Fig. 6B; Mizutani and Wada, 1988; Burkins et al., 1998). The sulfur isotope composition of uraniferous bitumen varies from -4.2 to -2.7 per mil, with an average of -3.3 ± 0.6 per mil (Table 2).

The C and N isotope compositions of uraniferous bitumen from Southwest Athabasca do not appear to be indicative of a particular source. However, the isotopic data are similar to that of bitumen in the Lower Proterozoic Huronian Supergroup in Canada, which has very similar petrographic characteristics and δ¹³C values of about -33 to -25

TABLE 2. Carbon, Nitrogen, and Sulfur Isotope Composition of Uraniferous Bitumen from Southwest Athabasca Project

Sample	Isotopic composition
	<u>$\delta^{13}\text{C}, \text{‰ vs. PDB}$</u>
DF22-902	
No. 1	-27.57
No. 2	-27.61
SW09-381	
No. 1	-26.32
No. 2	-26.35
No. 3	-26.67
No. 4	-26.41
Average	-26.8 ± 0.6
	<u>$\delta^{15}\text{N}, \text{‰ v. N}_2^{\text{ATM}}$</u>
DF22-902	
No. 1	2.8
No. 2	2.2
No. 3	7.1
Average	4.0 ± 2.7
	<u>$\delta^{34}\text{S}, \text{‰ v. VCDT}$</u>
DF22-902	
No. 1	-4.19
No. 2	-3.12
No. 3	-2.74
No. 4	-3.12
Average	-3.3 ± 0.6

per mil (Mossman et al., 1993b). The latter is thought to have been derived from kerogen that originated from cyanobacteria. Cyanobacteria were locally abundant in Paleoproterozoic and Archean intertidal carbonates and fine-grained clastic sediments to high-energy braided streams, alluvial fans, and fan deltas containing quartz pebble conglomerates (Willingham et al., 1985; Goodarzi et al., 1993). The latter is thought to have been the depositional environment of the Manitou Falls Formation in the Athabasca basin, which is characterized by interbedded, matrix-supported quartz pebble conglomerate and medium-grained sandstone (Ramaekers, 1990).

Age of Formation of Uraniferous Bitumen and Timing of Mineralization Events

On the basis of the BSEM images, the brightest areas of the uraniferous bitumen were selected for U-Pb dating using the laser ablation ICP-MS method. The laser used is the Mercaitek® LUV213 Laser Ablation System with a frequency quintupled Nd-YAG (213 nm) used in spot mode. The analytical conditions were as follows: laser power output of 30 to 40 percent ($<1\text{ mJ/cm}^2$), pulses of 50 msec with repetition rate of 2 Hz, and spot size of 25 to 35 μm . The HR-ICP-MS instrument used was the Finnigan MAT Element® with a double (magnetic and electrostatic) analyzer. The installation was used in medium resolution (~ 4500), which permits the resolution of all molecular interferences, including those of ^{31}P on U and Pb. The isotopes measured were ^{201}Hg , ^{202}Hg (used for correction for unresolved interferences of ^{204}Hg on ^{204}Pb), ^{204}Pb (used for common Pb correction, following the Stacy-Krammers' model), ^{206}Pb , ^{207}Pb , ^{235}U , and ^{238}U (used for age calculations). The measuring time was 1.1 msec (for ^{201}Hg , ^{202}Hg , ^{206}Pb , and ^{238}U), 20 msec (for ^{204}Pb), 4 msec (for ^{207}Pb and ^{208}Pb), and 6 msec (for ^{235}U). The analytical procedure used here follows Kyser et al. (2003). The size of the laser beam (25–35 μm) did not permit analysis of the small uraninite grains. Eleven ablation points were analyzed (Fig. 3F) and the results are shown in Table 3 and Figure 6D.

All analytical points define a single discordia line, situated between the origin and an upper intercept age of 1575 ± 53 Ma (MSWD = 3.2, $n = 11$) (Fig. 6D). If the discordia is calculated excluding the oldest analytical point, the upper intercept age would be 1577 ± 59 Ma (MSWD = 3.5, $n = 10$). Most of the points are close to the origin, with $^{207}\text{Pb}/^{235}\text{U}$ ratios of

less than 0.9 and $^{206}\text{Pb}/^{238}\text{U}$ ratios of less than 0.07 (Fig. 6C), which indicates a significant loss of radiogenic Pb and is consistent with the presence of galena in the samples studied. However, the average $^{207}\text{Pb}/^{206}\text{Pb}$ ratio is ~ 0.0975 , which corresponds to an age of 1577 Ma (i.e., the same as the upper intercept age). This age is similar to the mineralization age of ca. 1590 Ma for unconformity-related uraninite elsewhere in the Athabasca basin (Alexandre and Kyser, 2003). If the analyses of the uraniferous bitumen can be assumed to represent only the isotopic composition of uraninite, then the calculated age suggests that uraninite precipitation in Southwest Athabasca was part of the major Athabasca uranium mineralization event and formed much earlier than previously proposed (e.g., Wilson et al., 2002). Radiogenic lead may have been retained in the uraniferous bitumen by the protective coating of bitumen (cf. Oklo and Elliot Lake uranium deposits: Nagy et al., 1991) and was precipitated in situ as galena, as indicated by the chemical analyses (Table 1).

Conclusions

The Southwest Athabasca uranium mineralization is distinct from most other deposits in the Athabasca basin. Although bitumen has been reported elsewhere in deposits of the Athabasca basin, in the Southwest Athabasca project it appears to be much older. The present study suggests that, at least in this case, bitumen precipitated before or contemporaneously with uraninite and served as a reductant for uranium precipitation. As a result, uraninite is present either as micro-sized grains disseminated in the mass of the bitumen, or as larger grains situated in the pore space between bitumen globules (Fig. 3).

The Southwest Athabasca mineralization was formed during the same major uraninite precipitation event at ~ 1590 Ma, observed throughout the Athabasca basin (Alexandre and Kyser, 2003), and has other characteristics in common with all deposits in this basin, such as the origins of uranium and of the alteration and precipitation fluids (Alexandre et al., 2005). The main difference is that the reductant for uraninite precipitation is bitumen, which could potentially result in deposits forming far above the unconformity where most other deposits are located. However, the distribution of the bitumen could also result in numerous small occurrences of uranium mineralization that are unfavorable for exploration.

TABLE 3. Analytical Data of the U/Pb Laser Ablation ICP-MS Analyses of Uraninite-Bitumen Mixture in the Southwest Athabasca Uranium Mineralization

Spot no.	Corrected Ratios					Calculated Ages		
	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{206}\text{Pb}$ (Ma)	$^{207}\text{Pb}/^{235}\text{U}$ (Ma)	$^{206}\text{Pb}/^{238}\text{U}$ (Ma)
1	616	62	0.10101 ± 0.00303	0.57113 ± 0.01713	0.04101 ± 0.00123	1642.7 ± 30.7	460.1 ± 15.5	259.1 ± 5.6
2	558	54	0.09658 ± 0.00290	0.47927 ± 0.01438	0.03599 ± 0.00108	1559.2 ± 50.6	415.7 ± 4.4	227.9 ± 3.2
3	1179	114	0.09703 ± 0.00291	0.03836 ± 0.00115	0.00287 ± 0.00009	1567.9 ± 69.1	39.4 ± 9.9	18.5 ± 5.1
4	646	60	0.09313 ± 0.00279	0.44166 ± 0.01325	0.03440 ± 0.00103	1490.4 ± 44.9	367.7 ± 17.3	218.0 ± 7.7
5	-	-	0.10058 ± 0.00302	0.22417 ± 0.00673	0.01616 ± 0.00048	1634.8 ± 48.6	215.9 ± 3.3	103.4 ± 1.9
6	1069	102	0.09550 ± 0.00287	0.61395 ± 0.01842	0.04662 ± 0.00140	1538.0 ± 11.7	478.8 ± 17.5	293.8 ± 11.2
7	18	2	0.09091 ± 0.00273	0.03425 ± 0.00103	0.00273 ± 0.00008	1444.7 ± 14.3	34.1 ± 4.9	17.6 ± 6.7
8	784	81	0.10358 ± 0.00311	0.20605 ± 0.00618	0.01443 ± 0.00043	1689.3 ± 67.8	192.4 ± 5.4	92.3 ± 3.0
9	513	49	0.09636 ± 0.00289	3.19828 ± 0.09595	0.24073 ± 0.00722	1554.8 ± 75.6	1502.9 ± 42.0	1390.5 ± 5.7
10	546	52	0.09451 ± 0.00284	0.85387 ± 0.02562	0.06552 ± 0.00197	1518.4 ± 19.9	650.9 ± 9.8	409.1 ± 4.5
11	996	102	0.10284 ± 0.00309	0.31252 ± 0.00938	0.02204 ± 0.00066	1676.0 ± 10.1	283.6 ± 9.4	140.5 ± 6.5

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