Elemental Composition and Organic Petrology of a Lower Carboniferous-Age Freshwater Oil Shale in Nova Scotia, Canada

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ABSTRACT: A 59 m-thick section of a freshwater oil shale interbedded with marlstone of Lower Carboniferous (Tournaisian) age from the Big Marsh area in Antigonish Basin, Nova Scotia, Canada, was examined using reflected light microscopy, Rock-Eval pyrolysis, X-ray diffractionmetry analysis, inductively coupled plasma-mass spectrometry for elemental analysis, and prompt γ for boron concentration. The oil shale was deposited in a lacustrine environment based on geology, sedimentology, variation in organic matter, and boron content (28–54 ppm). Organic petrology classified the oil shale into three broadly distinct types. Type A oil shale is a coastal facies shale containing terrestrially derived macerals, such as vitrinite and inertinite, sporinite, with some lamalginite, and amorphous bituminous matrix. Type B oil shale was deposited in a shallow-water facies and contains mostly lamalginite and some vitrinite and sporinite. Type C oil shale is a relatively deep-water facies, associated with open-water Torbanite-type oil shale and contains mostly Botryococcus colonial telaginate. The oil shale is therally mature (T+m is 441–443 °C). Total organic carbon (TOC) varies from 5.8 to 7.3 wt %, and the hydrogen index is between 507 and 557 mg HC/g TOC. The rate of sedimentation as determined by the Th/U ratio indicates possibility of three sedimentation periods: an irregular but mostly slow rate of sedimentation from the base of the section up to 68 m, followed by a regular and slow rate between 68 and 53 m, and a regular and fast rate between 53 m and the top of the section. The higher Th/U ratio during deposition of the shallow-water facies was due to the input of allochthonous U. The redox conditions, as reflected in the variation of Cr to Mo, U, and Ni + V, indicate that the oil shale was deposited under suboxic–dysoxic conditions. The high organic productivity by phytoplankton and bacteria is characterized by a low Cr and high V/Cr ratio and suboxic conditions. In contrast, the well-oxygenated and uniform, warm-temperature upper water level supports a dysoxic environment. Variation of Sr/Ca vs Mn/Ca ratios indicates that most samples have low values, a characteristic of colder water and high terrigenous influx. The post-Archean Australian shale (PAAS)-normalized rare earth elements (REEs) follow three trends. Type A oil shale has the highest concentration of total REEs (648 ppm) and light REEs (LREEs, 605 ppm) as compared with type C (269 and 233 ppm), which are less than half of type A. Type B oil shale has the lowest total REEs (184 ppm) and LREEs (152 ppm). The concentration of heavy REEs decreased from 43 ppm in type A oil shale to 36 ppm in type C oil shale. Comparison of PAAS-normalized REEs for the three oil shale types indicates a reduction of the negative Eu anomaly with depth, which is possibly related to sedimentary sorting as a result of accumulation of fine sediments in the deeper water zone of the lake. The concentration of most elements of environmental concern is similar to and/or lower than the world shale. However, there are instances of higher concentrations of hazardous elements (e.g., As, Cd, Mo, and Se).

1. INTRODUCTION

Oil shales are important sedimentary rocks because they are the immature precursors of hydrocarbon source rocks and are capable of producing liquid hydrocarbons under suitable geological conditions. Oil shale is generally a fine-grained rock containing hydrogen-rich organic matter, from which hydrocarbons can be extracted by thermal treatment processes. Oil shales are deposited mainly under anoxic conditions, where high algal input due to prolific planktonic growth in surface waters results in an abundance of sapropelic organic matter, which becomes preserved under anaerobic conditions.

Oil shale is divided broadly into continental and marine types based on kerogen composition and occurrence of organic and inorganic fossils. Continental oil shales are deposited under lacustrine and lagoonal conditions, in environments similar to coal but under more aquatic conditions. In fact,
Cannel coal and boghead coal are deposited under similar geological conditions to those of oil shale but contain terrestrial liptinite (cutinite-sporinite) and lacustrine telalginite (Botryococcus), respectively.

Canada hosts numerous oil shale deposits, which are found in most provinces and territories (Figure 1a). Oil shales in Nova Scotia, eastern Canada, were first discovered in 1868. Nova Scotia has nine confirmed oil shale deposits, all of which occur in Upper Paleozoic-age strata that fill the Maritimes Basin (Figure 1a). The Late Carboniferous–Devonian Maritimes Basin formed as a major depocenter during the Acadian Orogeny. This large basin comprises various smaller, northeast-trending, intermontane basins. Two of the largest oil shale deposits are found in the Stellarton Formation (Stellarton Basin, in Pictou coalfield) and in the Rights River Formation (also known as the South Lake Creek Formation) in the Antigonish Basin (Figure 1b). The present study focuses on a freshwater oil shale deposit, which is located approximately 11 km north of Antigonish. This deposit (shown by the red circle in Figure 1a) has been the focus of significant exploration with over 9 cored wells drilled based on surface exposures of the oil shale near the Big Marsh settlement.

This study is part of a research and development program on Canadian oil shale deposits to characterize their potential for hydrocarbon extraction and possible environmental impact during extraction of hydrocarbon in ex situ (mining/retorting) and in situ (underground) operation. As part of this large program, the current study focuses specifically on the organic petrology and elemental composition of the lacustrine Big Marsh oil shale as related to its variation to the paleo shoreline and depth. The hydrocarbon potential and variation of elements of environmental concern will also be discussed in detail.
2. STRATIGRAPHY

The Antigonish Basin contains some of the earliest sediments deposited in the Maritimes Basin, which are of alluvial fan, lacustrine, and coal swamp origin.\(^7\)-\(^10\) The formation of interest in terms of the highest hydrocarbon potential is the Tournaisian-aged Rights River Formation of the Horton group (Figure 2a). The Rights River Formation is a red conglomerate interbedded with mudstones, sandstones, oil shale, and coal beds. The oil shale deposits occur in two major areas, the Beaver settlement (average thickness 61.6 m) and the Big Marsh (average thickness 117.5 m). The two lithologies associated with the oil shale, in order of abundance, are (a) Marsh (average thickness 117.5 m). The two lithologies Beaver settlement (average thickness 61.6 m) and the Big interbedded with mudstones, sandstones, oil shale, and coal formation in the Moncton Basin of New Brunswick.\(^11\) The equivalent of the Albert Formation, an economically important having a low hydrocarbon yield; and (b) massive, bituminous drilling mud center of the cores to avoid possible contamination with hydrocarbon yield.

3. ANALYTICAL PROCEDURES

3.1. Sampling. The lacustrine oil shale deposits in the study area have been described from outcrops along the nearby shoreline.\(^7\) In the Big Marsh #4 well (Figure 2b), the oil shale succession is 65 m thick\(^7\) and comprises gray sandstones overlain by a thick, relatively monotonous succession of interbedded dark and light-gray mudstones with only minor interbedded siltstones and concretions. These, in turn, are sharply overlain by reddish to gray medium-grained sandstones. A total of 24 samples were collected, approximately one sample every 3 m (10 ft).\(^3\) Samples were collected from the center of the cores to avoid possible contamination with drilling mud fluids. Of the original 24 samples, 13 were selected to be analyzed further geochemically [by Rock-Eval pyrolysis/total organic carbon (TOC)], petrographically (maceral composition), and elementally (major, trace, and rare earth elements). The 13 samples were collected from the organic-rich light to dark-gray mudstone intervals. They were selected based on the following criteria: (a) their characteristics to represent different depositional facies, and (b) their hydrocarbon yield.

3.2. Optical Microscopy. Organic petrology, including fluorescence analysis, was carried out on selected polished whole-rock samples that were prepared according to the ISO 7404-2 (2009) standard.\(^1\) Reflectance measurements followed the ASTM standard D7708-14 (2014)\(^14\) and the ISO 7404-5 (2009) standard.\(^15\) A reflected light Zeiss Axio Imager A2m microscope system equipped with fluorescent light sources was used for petrological observation under standard conditions (filters: excitation 450—490, beam splitter S10, and barrier S20 nm). Maceral analysis was performed using the point-counting method (300 points of organic matter were counted in each sample; mineral matter was excluded) under both white and UV light. The ICCP (1994) classification of the liptinite group macerals was followed, as described in ref.\(^16\).

3.3. Rock-Eval Pyrolysis Analysis. A Rock-Eval 6 (Vinci Technologies, France) instrument\(^17\) was used on the 13 samples to determine parameters of total organic carbon (TOC, wt %), \(T_{\text{max}}\) (°C), the amount of in situ hydrocarbons (\(S_1\)), and those generated upon heating to 650 °C (\(S_2\)) (mg HC/g rock). Simultaneously, the amount of CO and CO\(_2\) released during pyrolysis and oxidation was measured to quantify the portion of oxygen-containing organic matter (\(S_1\) and \(S_4\) peaks; mg CO\(_2\)/g rock). Other parameters reported include the hydrogen index (HI, mg HC/g TOC), the oxygen index (OI, mg CO\(_2\)/g TOC), the production index [PI, (\(S_1\)/\(S_1 + S_2\))], mineral carbon (MINC, wt %), and yield (L/t).

4. RESULTS

4.1. Petrology. Based on organic matter composition as revealed by point-counting and supported by elemental composition, the oil shale samples in the oil shale deposit can be classified broadly into three distinct types, namely, types A, B, and C. Representative photomicrographs of each type are shown in Figures 3–5.

Type A oil shale contains large fragments of vitrinite (part of type III gas-prone kerogen) and inertinite (part of type IV kerogen) (Figure 3a–c). Also present are remnants of...
lamalginite (part of type II oil-prone kerogen), which are partially assimilated into the amorphous bituminous matrix (bituminite) (Figure 3b,d). Type A oil shale was deposited in coastal facies. Type B oil shale has a matrix of lamalginite and bituminite and contains sporinite (part of type II kerogen) and inertinite fragments (Figure 4a–c). Type B oil shale was deposited in shallow-water facies. Type C oil shale contains abundant Botryococcus (Pila-type) telalginite (part of type I oil-prone kerogen) that fluoresces with bluish-green to brown colors depending on the degree of weathering (Figure 5a,b).

Type C oil shale was deposited in deep-water facies (near the center of the lake). The maceral composition of each individual sample from the three facies analyzed in this study and the average composition of each facies are shown in Table 1.

### 4.2. Rock-Eval Pyrolysis/TOC

The Rock-Eval pyrolysis and TOC data for each of the 13 samples are shown in Table 2. The average values of the three facies (coastal, shallow, and deep) are shown at the bottom of Table 2. The average TOC content in the three distinct facies ranges from 5.8 to 7.3 wt %. $S_1$ values are less than 1 mg HC/g rock, and the $S_2$ values range from 32.6 to 40.9 mg HC/g rock. HI values range between 507 and 557 mg HC/g TOC. The $T_{max}$ values range from 441 to 443 °C. The very low PI values (0.01–0.02) are an artifact of the high $S_2$ compared with $S_1$. Figure 6 shows the hydrocarbon yield (L/t) calculated from the Rock-Eval parameters (yield = $S_2 \times 1.1$).

### 4.3. Mineralogy and Elemental Composition

The mineralogical composition of the lacustrine oil shale has been studied extensively and reported in ref 11. Since mineralogy is not the focus of the present study, only the average composition of the minerals will be presented. The mineral composition is as follows: quartz (53 wt %), clay minerals (38 wt %), and feldspar and siderite occur in small quantities. Carbonates are rare to absent.

![Figure 4](image1.png)

**Figure 4.** (a–c) Type B oil shale contains sporinite displaying zonation with bright rims, inertinite fragments, lamalginite, and matrix bituminite (a), sporinite, and inertinite (b). There is some microlayering of algae in sections perpendicular to the bedding, indicating underwater deposition of organic matter. Lamalginite, matrix bituminite, vitrinite, and inertinite are present (c).

![Figure 5](image2.png)

**Figure 5.** (a, b) Organic matter in type II oil shale consists mostly of Botryococcus (Pila-type) telalginite showing serrated margins and various stages of maturation, as evidenced by the intensity of fluorescent light. Sporinite grains fluorescing light-brown are also present.

| facies | depth (m) | Botryococcus telalginite | filamentous algae | bituminite matrix | vitrinite + inertinite | mineral matter (%) |
|--------|-----------|--------------------------|-------------------|-------------------|-----------------------|--------------------|
| coastal| 31.7      | 1                        | 1                 | 10                | 16                    | 73                 |
| deep   | 40.8      | 13                       | 4                 | 40                | 2                     | 41                 |
| shallow| 46.9      | 8                        | 8                 | 17                | 11                    | 64                 |
| shallow| 50        | 9                        | 9                 | 15                | 15                    | 61                 |
| shallow| 53        | 5                        | 5                 | 13                | 13                    | 69                 |
| deep   | 59.1      | 8                        | 5                 | 37                | 4                     | 46                 |
| shallow| 65.2      | 7                        | 7                 | 19                | 11                    | 63                 |
| shallow| 68.3      | 1                        | 9                 | 20                | 11                    | 59                 |
| deep   | 71.3      | 11                       | 7                 | 33                | 4                     | 45                 |
| shallow| 77.4      | 10                       | 10                | 17                | 10                    | 63                 |
| shallow| 83.4      | 8                        | 8                 | 18                | 14                    | 60                 |
| deep   | 89.6      | 14                       | 6                 | 34                | 3                     | 43                 |
| deep   | 96.7      | 9                        | 8                 | 32                | 3                     | 48                 |

| facies | Botryococcus telalginite | filamentous algae | bituminite matrix | vitrinite + inertinite | mineral matter (%) |
|--------|--------------------------|-------------------|-------------------|-----------------------|--------------------|
| coastal| 1                        | 10                | 16                | 73                    |
| shallow| 8                        | 17                | 12                | 63                    |
| deep   | 11                       | 6                 | 35                | 3                     | 45                 |

*Average values apply to the shallow and deep facies only.*

![Table 1](image3.png)

**Table 1. Kerogen Composition of the Studied Samples**
Based on Swaine (1990), the variation of elemental composition of the oil shale samples is presented here as a grouping of elements, such as major elements, elements of environmental concern, other elements, and REEs and their ratios (Table 3). The variation of selected elements vs depth and TOC content is shown in Figure 7a,b. The rate of sedimentation, which is based on the ratio of Th/U, is shown in Figure 8.

Redox-sensitive trace elements, such as Cr, Mo, Ni, and V, and their ratios and relationship to TOC, HI, and organic facies of oil shales provide information about the position of the sedimentary redox boundary at the time of deposition and variation of redox with depth (Figures 9a,b, 10a,b, and 11). The relationship in the Mn/Ca vs Sr/Ca ratios was used to estimate the rate of terrigenous input and relative water temperature (Figure 12).

The concentration of the REEs in each sample and the total amount of LREEs (light REEs), HREEs (heavy REEs), and...
their ratio for oil shales deposited in the coastal, shallow, and deep facies of the lake are presented in Table 6 and Figure 13. The variation in the average PAAS-normalized REEs values for each distinct oil shale facies is shown in Figure 14. The variation of elements of environmental concern with depth in the oil shales, along with their concentration in world shale, is presented in Figure 15.

5. DISCUSSION

5.1. Organic Matter Assemblages and Rock-Eval Pyrolysis/TOC. As stated earlier, three types of oil shales
are broadly recognized based on their organic matter assemblages: type A oil shale is similar to lamosite and contains terrestrial macerals, remnants of lamalginite, and amorphous bituminous matrix (Table 1 and Figure 3a−c). Vitrinite in the coastal facies shale shows a granular surface due to leaching of hydrocarbons. Inertinite displays a cellular morphology, which indicates that it was deposited close to its source and was not subjected to fragmentation as a result of long transportation (Figure 3c). Type B oil shale, which occurs in a transitional shallow facies, contains transported sporinite displaying zonation with bright rims and pollen grains in a matrix of lamalginite and matrix bituminite (Figure 4a,b). Inertinite in this facies consists of small angular fragments, the result of their transportation (Figure 4a,c). Microlayering of lamalginite in sections perpendicular to the bedding was also observed, indicating subaqueous deposition of organic matter, which includes layering of lamalginite, matrix bituminite, vitrinite, and inertinite (Figure 4c). Type C oil shale is mostly associated with deep facies (open-water), a Torbanite-type environment, and contains mostly Botryococcus (Pila-type) algae and some wind-blown sporinite grains (Table 1 and Figure 5a,b).

Although the average hydrogen index (HI) values of the shale facies vary from 507 to 557 mg HC/g TOC (Table 2), the original HI (HI_o) values were probably 600−700 at immaturity (T_max ∼ 430−435 °C) based on the following equation developed for the Barnett Shale.23 This method is based on maceral percentages determined by visual kerogen assessment and is expressed as

\[
HI_o = \left( \frac{\text{type I}}{100} \times 750 \right) + \left( \frac{\text{type II}}{100} \times 450 \right) + \left( \frac{\text{type III}}{100} \times 125 \right) + \left( \frac{\text{type IV}}{100} \times 50 \right)
\]

The S_i values indicate that the hydrocarbon generating potential is high. The average T_max values of the three facies have a tight range, from 441 to 443 °C, which points to the middle stage of the oil window (thermally mature organic matter). The average TOC, HI, and hydrocarbon yields of the three oil shale facies (Table 2) show that oil shale from the shallow facies has the lowest hydrocarbon yield and that the oil shale from the coastal facies has the highest. Based solely on the hydrocarbon yield economic threshold and the TOC content proposed by Yen and Chilingarian (1976)24 (34 L/t and 6 wt %, respectively), the majority of the oil shale is considered to be suitable for ex situ extraction (Figure 6).

5.2. Variation of Elements. Numerous studies have focused on the reconstruction of paleo-environmental conditions in Devonian-Mississippian black shales in the central-eastern and southern United States using inorganic geochemical studies, including major and redox-sensitive elements and other indicators based on proxies. Other studies used sedimentological or organic geochemistry (biomarker) approaches.25−28

The trends of major elements (e.g., Al, Na, Fe, and Ti) with depth of burial for the lacustrine oil shale (Table 3 and Figure 7a) indicate a variation in input from the surrounding land and possibly the rate of recharge/discharge. Most notable is the variation in Ca, which shows two peaks at 59 and 77 m (Figure 7b), which possibly indicates a higher rate of discharge to
In general, higher and sedimentary recycling result in the loss of U and increase in the Th/U ratio in sedimentary rocks.39 In general, higher and sedimentary recycling result in the loss of U and increase in the Th/U ratio in sedimentary rocks. The higher Th/U ratio in periods I and II also supports slower rate of sedimentation due to the input of allochthonous U. Interestingly, the other alkali metal elements, such as Cs, Li, and Rb, follow almost a similar pattern (not shown) to that of Th/K.

The Th/U ratio can be used as an indicator of the rate of sedimentation, weathering, and transportation. The variations of Th/U in the oil shale (Figure 8) are very informative and indicate three sedimentation periods: an irregular but slow rate of sedimentation (I) from the base of the section up to 68 m, followed by a relatively regular and slow sedimentation (II) in the interval between 68 and 53 m, and, finally, a faster rate of sedimentation (III) in the upper part between 53 and 31.7 m (Figure 8). The higher Th/U ratio in periods I and II also supports slower rate of sedimentation due to the input of allochthonous U.

### 5.2.2. Paleo-Redox Conditions.
Redox conditions occur at the sediment–water interface, as well as in the water column. They consist of dysoxic condition with low oxygen concentration (2.0–0.2 mg/L), suboxic condition with very low oxygen content (0.2–0.0 mg/L), and anoxic condition with no oxygen.42 Redox-sensitive trace elements provide information about the position of the sedimentary redox boundary at the time of deposition. The bottom-water oxygen levels in marine settings were evaluated by their elemental composition such as As, Co, Cr, Mo, Ni, Pb, V, and U.43,44

| facies | depth (m) | As | B | Ba | Cd | Cr | Co | Cu | Mn | Mo | Ni | Pb | Se | Sr | Th | U | V | Zn |
|--------|----------|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| coastal | 31.7 | 7.8 | 30 | 1236 | 0.59 | 60 | 29 | 46.5 | 588 | 3.74 | 50.4 | 34.88 | 0.5 | 103 | 14.4 | 5.7 | 121 | 124.1 |
| deep   | 40.8 | 45.9 | 45 | 231 | 0.12 | 11.6 | 65 | 28.67 | 2060 | 1.76 | 29.2 | 21 | 0.5 | 82 | 12.6 | 5.3 | 116 | 47 |
| shallow | 46.9 | 8.3 | 40 | 275 | 0.13 | 57 | 14.1 | 48.6 | 3053 | 2.74 | 33.4 | 27.72 | 0.6 | 97 | 14.9 | 5.9 | 115 | 76.2 |
| shallow | 50 | 4.1 | 45 | 228 | 0.22 | 61 | 13.4 | 52.3 | 1972 | 1.81 | 33.4 | 19.37 | 0.6 | 76 | 13.6 | 7.2 | 126 | 77.5 |
| shallow | 53 | 21 | 38 | 217 | 0.18 | 41 | 65 | 40.2 | 1506 | 3.98 | 33.5 | 44.46 | 1.2 | 80 | 10.3 | 3.1 | 124 | 86.3 |
| deep   | 59.1 | 4.6 | 32 | 189 | 1.13 | 17.9 | 12 | 37.3 | 594 | 1.86 | 19.5 | 20.17 | 0.7 | 170 | 13.8 | 3.7 | 78 | 247.2 |
| shallow | 65.2 | 3.5 | 29 | 187 | 0.14 | 43 | 15.2 | 24 | 2854 | 1.22 | 19.4 | 21.9 | 0.3 | 95 | 12.7 | 3.5 | 91 | 73.2 |
| shallow | 68 | 10.2 | 28 | 232 | 0.23 | 47 | 25 | 43.05 | 673 | 2.5 | 20.4 | 14.56 | 1 | 65 | 7.2 | 4.9 | 119 | 54 |
| deep   | 71.3 | 6.7 | 32 | 205 | 0.2 | 10 | 18.3 | 33.2 | 5000 | 2.86 | 34.28 | 32.48 | 1 | 88 | 16.6 | 5.8 | 94 | 135.2 |
| shallow | 77.4 | 6.9 | 28 | 278 | 0.74 | 44 | 17.4 | 24.2 | 1779 | 4 | 31.5 | 37.38 | 1 | 111 | 13.2 | 3.8 | 79 | 215.1 |
| shallow | 83.4 | 5.2 | 49 | 281 | 0.76 | 56 | 50 | 61.38 | 3317 | 5.44 | 33.8 | 34.24 | 1.5 | 78 | 19.5 | 4.3 | 79 | 311.8 |
| deep   | 89.6 | 5.7 | 54 | 278 | 0.39 | 14.2 | 51 | 107.16 | 815 | 3.99 | 37.5 | 26.49 | 1.5 | 56 | 20.4 | 6.1 | 98 | 207.4 |
| shallow | 96.7 | 13.2 | 43 | 258 | 0.28 | 11.7 | 20.4 | 48.6 | 895 | 3.33 | 39.3 | 37.72 | 0.5 | 114 | 15.7 | 9.1 | 105 | 117.1 |
| world  | 13 | 100 | 580 | 0.3 | 90 | 19 | 45 | 850 | 2.6 | 68 | 20 | 0.6 | 300 | 12 | 3.7 | 130 | 95 |

**Table 4. Variation of Elements of Environmental Concern (Parts per Million or ppm; 10 000 ppm = 1.0 wt %) in the Oil Shale with Depth**

*“After ref 20.*
Therefore, U water or pore water into the anoxic horizons, forming variation of the V/Cr ratio with HI and TOC (Figure 10a, b) also shows a similar pattern to that of the V/Cr ratio vs Ni + V (Figure 9b).

5.2.2.1. Uranium. Uranium in mudrock successions is partially terrestrial.\textsuperscript{59} Uranium is mostly associated with the organic fraction (organic ligands).\textsuperscript{60,61} Anoxic bottom waters, combined with high organic productivity of the aerated upper part of the water column, promote uranium diffusion out of the water or pore water into the anoxic horizons, forming organometallic and/or metallic complexes.\textsuperscript{62} Therefore, U concentrations can be used as an index for bottom-water anoxia.\textsuperscript{63} In this study, the variation of Cr with U was used to determine the redox conditions of the oil shale (Figure 11). The samples from the deep facies have low Cr (<20 ppm), which indicates their suboxic conditions. However, the coastal-shallow facies appear to consist of two groups; one group includes samples from the coastal and three shallow facies (samples 1, 3, 4, and 11), while the other group includes only the shallow facies (samples 5, 7, 8, and 10) (Figure 11).

5.2.2.2. Sr/Ca Ratio. The Sr and Mn concentrations are used to determine the paleo-temperature and salinity/brackishness of the depositional environment.\textsuperscript{64,65} The variation of Sr/Ca and Mn/Ca ratios was also used to determine the temperature and rate of recycling of terrigenous input in the marine Second White Specks oil shales in Manitoba, Canada.\textsuperscript{65} The high Mn/Ca ratio is an indication of high terrigenous input in the marine Second White Specks oil shales.\textsuperscript{65} In this study, the associations of Mn and Sr with Ca (carbonate) and Mn/Ca vs Sr/Ca ratios in the oil shale (Figure 12) were used to estimate the paleo-temperature and sedimentary influx.

5.2.3. Paleo-Temperature. The Sr and Mn concentrations are used to determine the paleo-temperature and salinity/brackishness of the depositional environment.\textsuperscript{64,65} The variation of Sr/Ca and Mn/Ca ratios was also used to determine the temperature and rate of recycling of terrigenous input in the marine Second White Specks oil shales in Manitoba, Canada.\textsuperscript{65} The high Sr/Ca ratio is an indication of high terrigenous input in the marine Second White Specks oil shales.\textsuperscript{65} In this study, the associations of Mn and Sr with Ca (carbonate) and Mn/Ca vs Sr/Ca ratios in the oil shale (Figure 12) were used to estimate the paleo-temperature and sedimentary influx.

5.2.4. Rare Earth Elements. Rare earth elements (REEs) have similar chemical and physical properties due to their specific electronic configurations and are divided into two subgroups: the light rare earth elements (LREEs) from La–Sm...
and the heavy rare earth elements (HREEs) from Eu to Lu. REEs have received considerable attention due to the systematic variation of their behavior known as the “lanthanide contraction”. REEs have been used to explain a number of geochemical events/processes in the environment, such as origin of certain sediments, paleo-environmental and paleoceanic changes, weathering, and impact of anthropogenic sources.

The variation of REEs in sedimentary rocks has been studied by a number of authors. The REEs are often associated with clay minerals in coal and are likely to be absorbed on the surface of the clay−size fraction and on minerals such as rutile (Ti), zircon (Zr), monazite (Th), xenotime (Y), and chromite (Cr). The abundance of REEs in coal seams has been examined by numerous researchers. However, there is very little information on the abundance and behavior of REEs in oil shales (Table 5).

REEs are in high demand due to their use in various industrial applications, which have increased in the past several decades, particularly for some of the REEs such as Nd, Ho, and Yb. China has most of the REE reserves and produces over 95% of the world’s rare earth supply. Therefore, it is important to find new sources of REEs. Hydrocarbons from oil shales are extracted by retorting at temperatures of <500 °C. The heat-treated byproduct of oil shale could be a good source of REEs. Therefore, it is very important to characterize an oil shale deposit and determine its REE content. Based on a comparison with coal, the REEs in oil shale are primarily associated with the inorganic fraction. In general, the controls on REEs distribution and occurrence in organic-rich sedimentary rocks such as coal appear to be related to the mineralogical composition of the country rock and to the weathering process.

5.2.4.1. REEs in the Oil Shale. The concentration of REEs in the lacustrine oil shale is summarized in Table 6. For comparative purposes, the REEs and their total concentrations in each of the three facies are presented in Table 6 and Figure 13. The concentration of REEs in the oil shale is heterogeneous and depends on their depositional location and water depth. The total LREEs (La−Sm) are remarkably more concentrated in the coastal oil shale facies, which has the highest concentration of LREEs (605 ppm) out of a total REEs of 648 ppm (Table 6 and Figure 13). This trend indicates a possible association with a higher input of aluminosilicates and accessory minerals in the coastal facies. The oil shale deposited in the shallow-water facies has total REEs of 184 ppm and LREEs of 152 ppm, which is less than that found in the shallow facies (Table 6 and Figure 13). The oil shale deposited in the deep-water facies at the center of the lake also has low total REEs (269 ppm) and LREEs (233 ppm). This relationship between REEs for the various depositional settings/depths indicates an association of LREE with sedimentary input, and possibly quartz and accessory minerals, which are depleted/reduced in the oil shale deposited in the shallow facies of the lake. The latter zone contains mostly fine clay-marl and a higher carbonate content compared with the other zones (even though the oil shale is very poor in carbonates). The LREEs also follow a similar trend to that of concentration of both REEs and HREEs (Table 6 and Figure 13) The LREEs/HREEs ratio is very informative as it is related to the depositional facies. It is the highest in the coastal facies (Table 6 and Figure 13), indicative of sedimentary sorting and progressive deposition of fine clay and carbonates toward the deep facies although the latter group is rarely registering in the above figure because of the absence of carbonate minerals in the oil shale.

5.2.4.2. PAAS-Corrected REEs. The PAAS-normalized REEs in the oil shale fall into three different trends (Figure 14). As noted earlier, type A oil shale was deposited in the coastal facies of the lake and contains terrestrial organic matter and some lamalginite (Figure 3) and has an average TOC content of 7.3 wt % (Table 2). The PAAS-corrected patterns of REEs display a strong negative Eu anomaly and enrichment of LREE (La−Sm) as compared with HREE (Eu−Lu) (Figure 14). Type B oil shale was deposited nearshore in the shallow facies, contains some allochthonous terrestrial kerogen (Figure 4), and has lower TOC (5.8 wt %) (Table 2) and coarser sediments. Type C oil shale displays an enrichment of HREE compared with LREE and also shows a moderate negative Eu anomaly (Figure 14), which is similar to that documented for the upper continental crust and for sediments from Lake Baikal, Russia. Type B oil shale also has a much lower concentration of LREE (La−Sm) than type A oil shale and almost a similar HREE (Eu−Lu) content to type A (Figure 14). Type C oil shale was deposited in the deep facies near the center of the lake, contains Botryococcus algae (Figure 5), and has low terrestrial kerogen and higher carbonate content (relatively speaking) compared with the other two groups. The PAAS-corrected REEs pattern displays a weak to very weak Eu anomaly, and the concentration of PAAS-normalized REEs increases continuously from LREE toward HREE (Figure 14). Furthermore, a reduction in the negative Eu anomaly with increasing depth of deposition is apparent, possibly being related to the sedimentary sorting that results in the accumulation of finer sediments such as clays in the deeper water/central part of the lake.

5.2.5. Economic Feasibility and Elements of Environmental Concern. In general, the concentration of most elements in this group for some of the oil shale samples is similar to and/or lower than the world shale values (Table 4). However, there are some samples with a higher concentration of hazardous elements (e.g., As, Cd, Mo, and Se) (Figure 15), which indicates that there is a possibility that some of these elements may be released into the environment during the hydrocarbon extraction process, particularly during ex situ extraction. Most of the hazardous elements are mobilized at much higher temperatures, particularly those associated with pyrite/sulfides (As, Cd, Se). Decomposition of pyrite into pyrrhotite (FeS) and elemental sulfur starts at 540 °C, which is a higher temperature than the temperature used for extraction of hydrocarbons during ex situ operations (generally less than 500 °C). So, it is unlikely that extraction of the oil shale will release elemental sulfur from the decomposition of sulfides or sulfates. However, a detailed study of the mode of occurrence and speciation of these elements is required if this lacustrine oil shale is to be considered as feedstock for the extraction of hydrocarbons.

6. CONCLUSIONS
The present study indicates the following:

- The oil shale studied was deposited in a lacustrine environment with boron content in the range from 28 to 54 ppm, which is typical of a freshwater depositional environment.
There are three diﬀerent trends for PAAS-normalized REEs. Type A oil shale was deposited in the coastal facies of the lake and displays a moderate negative Eu anomaly. There is enrichment of LREE compared with HREE. Type B oil shale was deposited near the shore in coastal-shallow facies and displays an enrichment of HREE. Type C oil shale was deposited in the coastal-shallow facies of the lake and contains mostly Botryococcus colonial algae.

The concentrations of LREEs change very little and contain mostly Botryococcus colonial algae.

The redox conditions determined using the V/Cr ratio, TOC, and HI are mirror images of the following: oil shale that was deposited under coastal-shallow facies was deposited in dysoxic conditions and having a low V/Cr ratio, while those deposited in deep facies are characterized by a high V/Cr ratio.

The redox conditions determined using the V/Cr ratio to the V + Ni ratio, TOC, and HI are mirror images of Cr, with the coastal-shallow facies deposited under oxic–dysoxic conditions and having a low V/Cr ratio, while those deposited in deep facies are characterized by a high V/Cr ratio.

The Sr/Ca and Mn/Ca ratios indicate that the oil shale was deposited under colder water with high terrigenous influx.

There are three different trends for PAAS-normalized REEs. Type A oil shale was deposited in the coastal facies of the lake and displays a moderate negative Eu anomaly. There is enrichment of LREE compared with HREE. Type B oil shale was deposited near the shore in the shallow facies and displays an enrichment of HREE compared with LREE and a strong negative Eu anomaly similar to that in the upper continental crust. Type C oil shale was deposited in deeper water facies near the center of the lake and displays a weak to very weak Eu anomaly. The concentration of REEs increases continuously from LREE toward HREE.

Type A oil shale has the highest concentration of total REEs (648 ppm) and LREEs (605 ppm) compared with type C, which has 269 ppm and 233 ppm, respectively. Type 2 oil shale has the lowest total REEs at 184 ppm and LREEs at 152 ppm.

The concentration of HREEs changes very little and decreases from 43 ppm in type A oil shale to 36 ppm in type C oil shale.

Elements of environmental concern in the oil shale have similar and/or lower concentration to that of the world shale. However, there are instances of higher concentra-

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