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Research Article

Multiple Controls on the Accumulation of Organic-Rich Sediments in the Besa River Formation of Liard Basin, British Columbia, Canada

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The Late Devonian Besa River Formation is an organic-rich shale sequence in Liard Basin, northeastern British Columbia, Canada, with significant natural gas reserves. High-resolution elemental geochemistry of three long continuous cored intervals of the Besa River Formation was used to better understand the paleodepositional environment of organic-rich intervals in this thick marine shale. The studied core intervals were divided into five chemostratigraphic units based on organic and inorganic geochemical proxies. The highest total organic carbon (TOC) content (up to 13 wt.%) was identified in the upper part of the Patry member (Unit III) within the Liard Basin. During the deposition of Unit III, low clastic influx and euxinic bottom conditions mostly contributed to the high accumulation of organic carbon. Moreover, a high productivity and organic influx may have increased organic-rich basinal sediments, which further depleted the seawater column oxygen content in the presence of a large amount of organic matter. This took place within the oxygen-deficient bottom water from the Patry–Exshaw stratigraphic units. This high TOC interval was most likely deposited through abundant biogenic silica production by radiolarians, thereby utilizing the supply of nutrients from the upwelling. Sea level change was also an important factor that controlled organic matter accumulation in the Besa River Formation. The transgression in sea level changed the residence time of the organic matter in oxic zones within the water column, which limited its supply in deeper water; this decreased the TOC content in Unit IV. Before the deposition, silica production collapsed and was replaced by terrestrial sedimentation of clay minerals in the upper part of the Exshaw member, which caused organic matter dilutions in Unit V (under 5 wt.%). These results provide new insights into the effects of relative sea level changes on redox conditions, productivity, and detrital flux, which are related to organic matter enrichment patterns and their geographic variations. Unit III is characterized by an organic-rich interval as well as an abundance of biogenic silica that is closely related to fracturing. Thus, Unit III is expected to have the highest shale gas potential in the Devonian Besa River Formation. The high-resolution geochemical data integrated with well log and/or seismic data can be used to determine the distribution of the perspective interval for shale gas production in the Liard Basin.

1. Introduction

The Liard Basin, one of the most significant shale gas reservoirs in Canada, has considerable gas resources in the Devonian-Mississippian strata and is expected to contain 219 trillion cubic feet (TCF) of marketable unconventional natural gas (Figure 1, [1]). Specifically, the Besa River Forma-

tion within the Liard Basin is stratigraphically located at a depth that can be economically developed for its shale gas resources [2]. The organic- and silica-rich Besa River shale intervals contain up to 92% quartz and 5 wt.% total organic carbon (TOC) content, respectively [3]. The high silica content makes the Besa River Formation a highly favorable target for shale gas exploration owing to the high brittleness of the
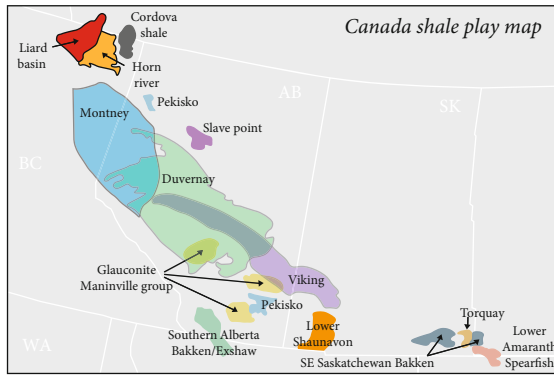
Figure 1: Map of Canada shale plays (modified from NGI, 2018).

organic- and silica-rich facies [3]. The upper Besa River Formation in the central Liard Basin contains sections of gas-saturated silica and organic-rich layers, which are found within the Exshaw member stratigraphic layers as well as the underlying units of the Patry member [4]. The underlying organic-rich Exshaw and Patry successions have recently been the focus of shale gas exploration, with the initial development well producing over 6.5 billion cubic feet (BCF) of natural gas in Canada since 2011 [1].

Organic-rich shale intervals are critical targets for shale gas exploration and development. The number of generated hydrocarbons is directly related to organic matter content and the resultant organic porosity comprises a major percentage of the storage capacity in the shale [5, 6]. Thus, organic matter content has a significant impact on both gas generation and storage potential of the shale gas reservoirs. The accumulation of organic matter in organic-rich sediments is mainly related to depositional conditions such as biological productivity [7–9], organic matter preservation [10, 11], and detrital sediment input [12, 13]. The depositional conditions can be reconstructed from geochemical properties. Ross and Bustin [9] revealed that the depositional process of anoxic conditions in bottom water are important for organic carbon sequestration in the Devonian–Mississippi shale of the western Canadian sedimentary basin through the application of a geochemical proxy.

The Liard Basin is separated from the Horn River Basin by the Bovie Fault [1, 2] (Figure 2). The Liard and Horn River basins share many of the same shales, including the Exshaw and Horn River shales [1] (Figure 2). Shale gas has been produced from the Devonian shales in the Horn River Basin. However, the lack of exploration shale gas exploration activity in the Besa River Formation is mainly due to limited information on deeper organic-rich shale intervals in the Liard Basin of BC. In this study, we provide detailed organic and inorganic geochemical data and then combine the TOC with inorganic geochemical proxies to clarify the accumulation mechanisms of organic matter in the Devonian Besa River Formation. Finally, based on this information, we subdivide the Devonian Besa River Formation into chemostratigraphic units and identify the prospective interval for shale gas exploration and development in Liard Basin. The rest of this paper is organized as follows. The Geological Setting is presented in Section 2, followed by Materials and Methods

in Section 3, Results in Section 4, Discussion in Section 5, and Summary and Conclusions in Section 6.

2. Geological Setting

The Liard Basin is located in the Western Canada Sedimentary Basin, straddling the BC, Yukon, and Northwest Territories boundary. The basin is defined based on its thick sections of Middle to Late Mississippian and Cretaceous clastic strata. Structurally, the area is dominated by the north-trending Bovie Lake Fault, which separates the Liard Basin in the west from the Horn River Basin in the east [14, 15] (Figure 2).

The Upper Devonian Besa River Formation is an organic-rich mudstone located along the southwestern margin of the Liard Basin, 80 km northwest of the Slave Point carbonate edge (Figure 2). The age of the Besa River Formation is mid-Middle Devonian to Early Carboniferous (Figure 2, [16]). In this study, the Besa River Formation is subdivided into the three members following Ferri et al. [17], which are the Fort Simpson, Patry, and Exshaw members (Figure 3). The Fort Simpson member is the low-level radioactive and resistive zone below the base of the Patry member. The Patry member is an organic-rich, radioactive, and high resistivity zone below the base of the Exshaw member. The Exshaw member is a less radioactive and lower resistivity organic-rich shale. The Exshaw–Patry intervals are the main target for shale gas production [18]. The Exshaw–Patry units are developed in central and western Liard Basin and are thicker than 200 m along the eastern boundary.

The Fort Simpson, Patry, and Exshaw members were formed at the late stage of the second-order Devonian transgression. The Fort Simpson member is represented by an offshore gray to dark gray shale. The overlying dark gray and black laminated mudstone of the Patry member was most likely formed in deep water conditions whereas the relatively abundant homogeneous mudstone in the Exshaw member was deposited within deeper anoxic water [17]. These Exshaw–Patry intervals are the main target for shale gas production [18].

3. Materials and Methods

The organic matter content is one of key factors affecting shale gas generation and storage potential. Thus, the understanding the accumulation mechanism of organic matter in shales can help to select the target area in shale gas exploration and development. The geochemical proxies related to accumulation of organic matter in shales are (1) biological productivity proxies (TOC, SiO_2, and Ba); (2) organic matter preservation proxies, associated with reducing conditions (Mo, U, and Th); and (3) detrital dilution proxies (Al_2O_3, K_2O, TiO_2, and Zr). In this study, to identify the mechanism of organic matter accumulation in the Devonian Besa River Formation, we analyzed the organic (TOC) and inorganic (SiO_2, Al_2O_3, K_2O, TiO_2, Zr, Mo, U, and Th) geochemical data in the organic-rich shales of wells distributed in the Liard Basin. The details for the well information and method will be discussed in the next section.
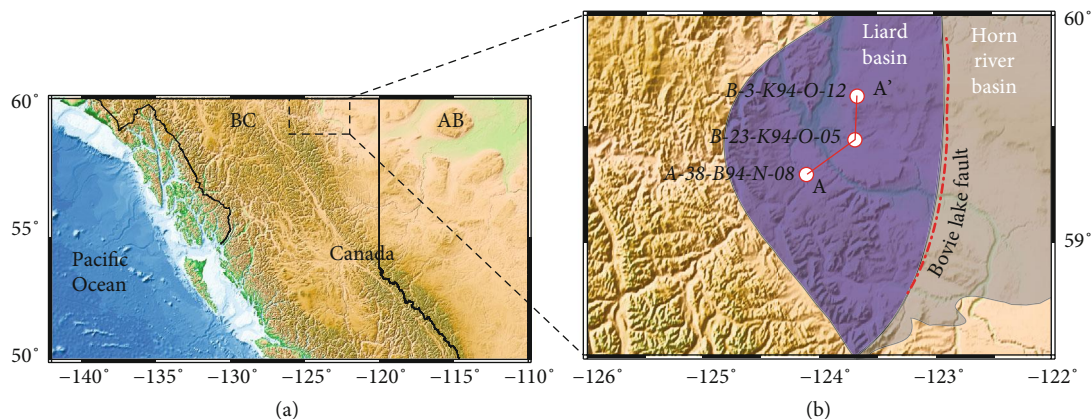
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FIGURE 2: (a) Map of Western Canada showing the location of the study area. (b) Location of the Liard Basin and the adjacent regions, showing well locations. (c) Time stratigraphic chart of the Middle Devonian to Early Carboniferous showing the stratigraphic units of the Liard and Horn River basins along the northwestern part of the Western Canada Sedimentary Basin in northeastern British Columbia.

3.1. Core Samples. The studied wells are located in the interior of BC, and drill cores were collected from the BC Oil and Gas Commission. The core thickness was approximately 168 m (interval 3,907–4,075 m) for Well A-038-B/94-N-08, 160 m (interval 3,629–3,789 m) for Well B-023-K/94-O-05, and 286 m (interval 4,277–4,563 m) for Well B-003-K/94-O-12. Cutting samples were collected in a 1.0–2.0 m thick interval for organic-rich parts, which resulted in 84 samples from Well B-023-K/94-O-05 and 129 samples from Well B-003-K/94-O-12. The collected samples were analyzed for TOC content and elemental composition (Figure 2). In Well A-038-B/94-N-08, the geochemical data published by Hong et al. [19] was used.

Four mudstone and two siltstone lithofacies were identified in the measured cores of three wells (Figure 4). The upper part of the Fort Simpson member mostly comprises papery-fractured gray mudstone with convoluted lamination (Facies Mpf). The Patry member is dominated by gray to dark gray colored, thin to thickly laminated mudstone (Facies Ml) with minor thin-bedded massive siltstone layers (Facies Fl and Fb). This member thickens northward from 70 m to 200 m. The lower Exshaw member is represented by black laminated mudstone (Facies Mlb) with exceedingly thin cherty layers and the upper Exshaw member by homogeneous mudstone (Facies Mh) with massive or crudely stratified fine siltstone (Facies Fl). The lower Exshaw member

ranges from 20 m to 40 m in thickness, and the upper boundary of the Exshaw member is uncertain owing to a lack of core recovery.

3.2. Analysis Methods. TOC content was measured using Rock-Eval6. The samples were washed, dried, and crushed to powder and screened through a BSS (British standard screens) of 60-mesh size and were thoroughly homogenized. Approximately 60 to 70 mg of powder samples were used for the Rock-Eval6 analysis [20]. Free hydrocarbons (S_1) and potential hydrocarbons (S_2) were detected using a flame ionization detector (FID), and residual organic carbon (RC) was measured via an infrared cell (IR cell). Units are usually given as wt.% organic carbon per weight of dry rock (milligrams hydrocarbon per gram of rock). Vinci's IFP 160,000 was used as a standard, and the reproducibility of TOC was < 0.07 wt.%.

The major elements were analyzed using the X-ray fluorescence spectrometer owned by the Korea Institute of Geoscience and Mineral Resources. The X-ray fluorescence spectrometer used Shimadzu's MXF-2400 multichannel spectrometer, with the loss on ignition (LOI) weighed before and after 1-hour firing at 980 ± 20°C.

Trace elements (Mo, U, Th, and Zr) were analyzed using a PerkinElmer Optima 5300 DV inductively coupled plasma (ICP) optical emission spectrometer and a PerkinElmer Elan
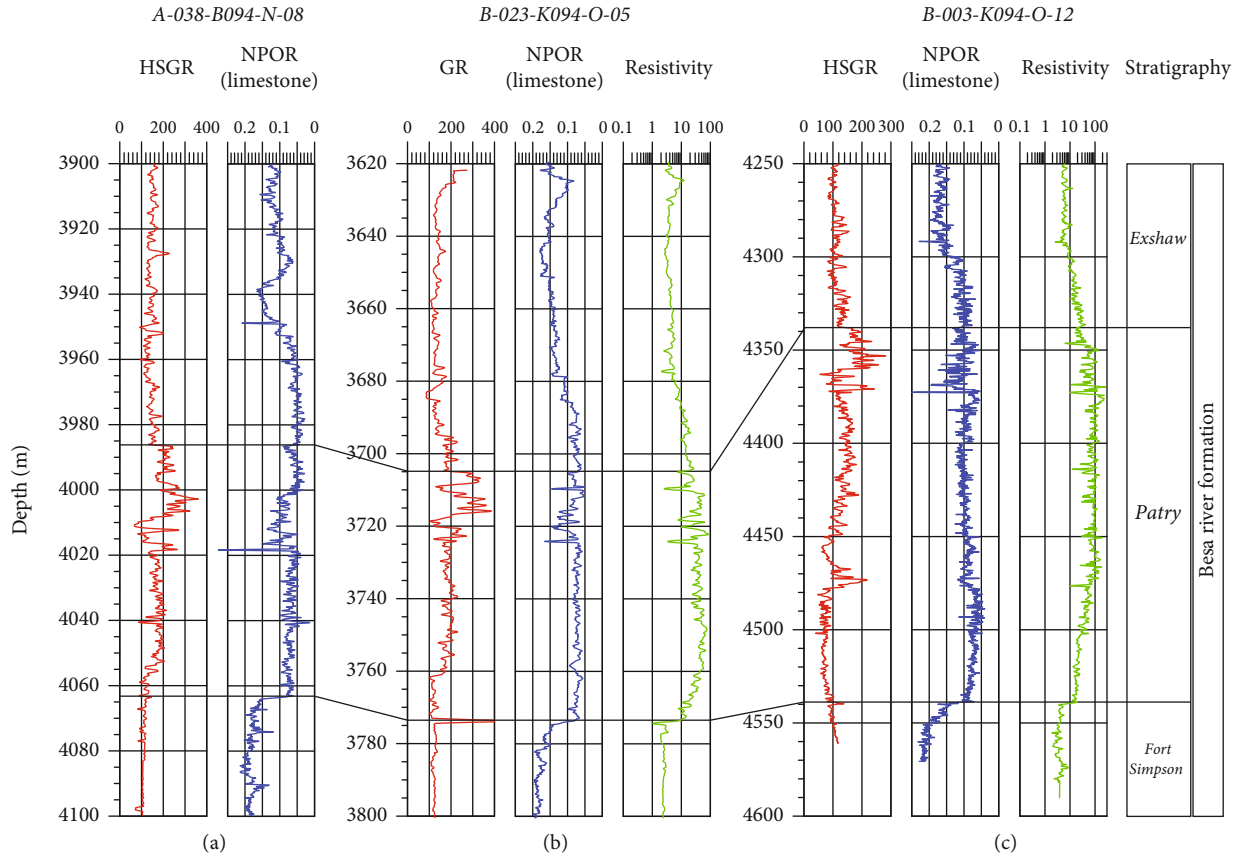
FIGURE 3: Well depth profiles of gamma ray, neutron porosity, and resistivity. The stratigraphic correlation of the Exshaw, Patry, and Fort Simpson members is shown across the study wells.

DRC-II ICP mass spectrometer based on the method of [21]. The US Geological Survey Standard MAG-1 was used for calibration. The analytical precision for the trace-element measurement is generally better than 5%. An average of three measurements was used for each sample.

4. Results

4.1. TOC Content Variations. The results for the TOC content in the studied wells are presented in Figure 5. The TOC content of Besa River shales ranged from 0.4 to 13.2 wt.% (mean = 4.6 ± 2.5 wt.%; $n = 143$) for Well A-038-B/94-N-08, 0.3–6.3 wt.% (mean = 2.8 ± 1.2 wt.%; $n = 84$) for Well B-023-K/94-O-05, and 0.3–12.1 wt.% (mean = 3.9 ± 1.9 wt.%; $n = 129$) for Well B-003-K/94-O-12. The TOC content was lower than 1 wt.% for the Fort Simpson, up to 13 wt.% for the Patry, and 1 to 5 wt.% for the Exshaw member. The highest organic-rich horizon in the study wells was the Patry member.

4.2. Major Elements. The distribution of major elements in the study wells is shown in Figure 6. Besa River shales are characterized by high SiO_2 content in the studied cores. The SiO_2 content ranges from 37.9 to 93.1% (mean = 74.7 ± 10%; $n = 143$) for Well A-038-B/94-N-08, 43.0–87.5% (mean = 69.7 ± 18%; $n = 53$) for Well B-023-K/94-O-05, and 43.7–94.1% (mean = 75.6 ± 9%; $n = 129$)

for Well B-003-K/94-O-12. In contrast, Al_2O_3 and CaO were low at 0.8–19.8% (mean = 7.6 ± 4.9%; $n = 143$) and 0.1–20.5% (mean = 2.0 ± 3.4%; $n = 143$) in Well A-038-B/94-N-08, respectively; the content was 3.1–18.6% (mean = 10.3 ± 4%; $n = 53$) and 0.2–15.4% (mean = 2.7 ± 4.0%; $n = 53$) in Well B-023-K/94-O-05, respectively, and 1.0–19.3% (mean = 5.1 ± 3.8%; $n = 129$) and 0.1–17.7% (mean = 4.5 ± 3.5%; n = 129) in Well B-003-K/94-O-12, respectively. The Al_2O_3 content was relatively higher than 10% in Fort Simpson, and CaO was higher than 5% in the Patry member. The K_2O and TiO_2 content showed significant correlation with Al_2O_3 (Figure 7). The positive correlations of K_2O and TiO_2 with Al_2O_3 indicate that these elements are associated entirely with clastic phases. The total sum percentage of Al_2O_3, K_2O, and TiO_2 was used as a proxy of the clastic influx [13]. The Fort Simpson member had $Al_2O_3 + K_2O + TiO_2$ content higher than 20%.

In general, SiO_2 is most commonly found in nature as quartz and within various living organisms. To determine the temporal variability of biogenic silica (BSi) content from total SiO_2, excess SiO_2 (Ex-SiO_2) was calculated using the following equation [9]:

$$Ex\text{-}SiO_2 = SiO_{2total} - Al_2O_{3total} \times \left(\frac{SiO_2}{Al_2O_3}\right)_{detrital}, \quad (1)$$
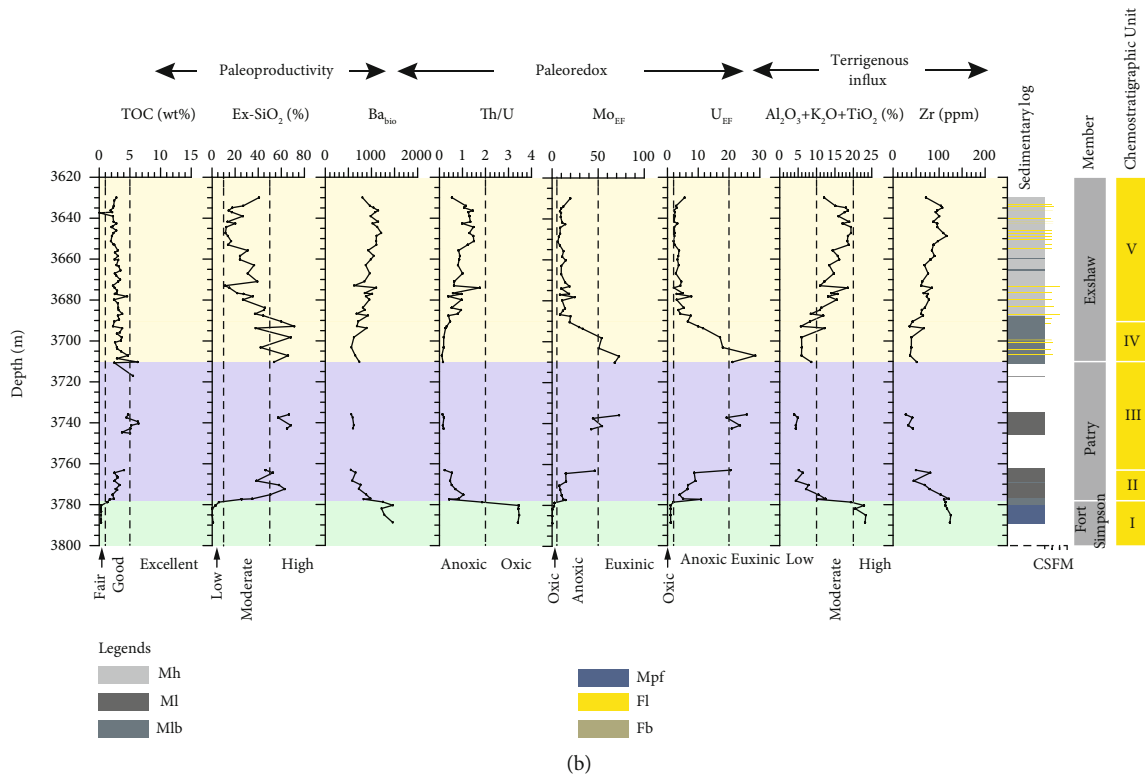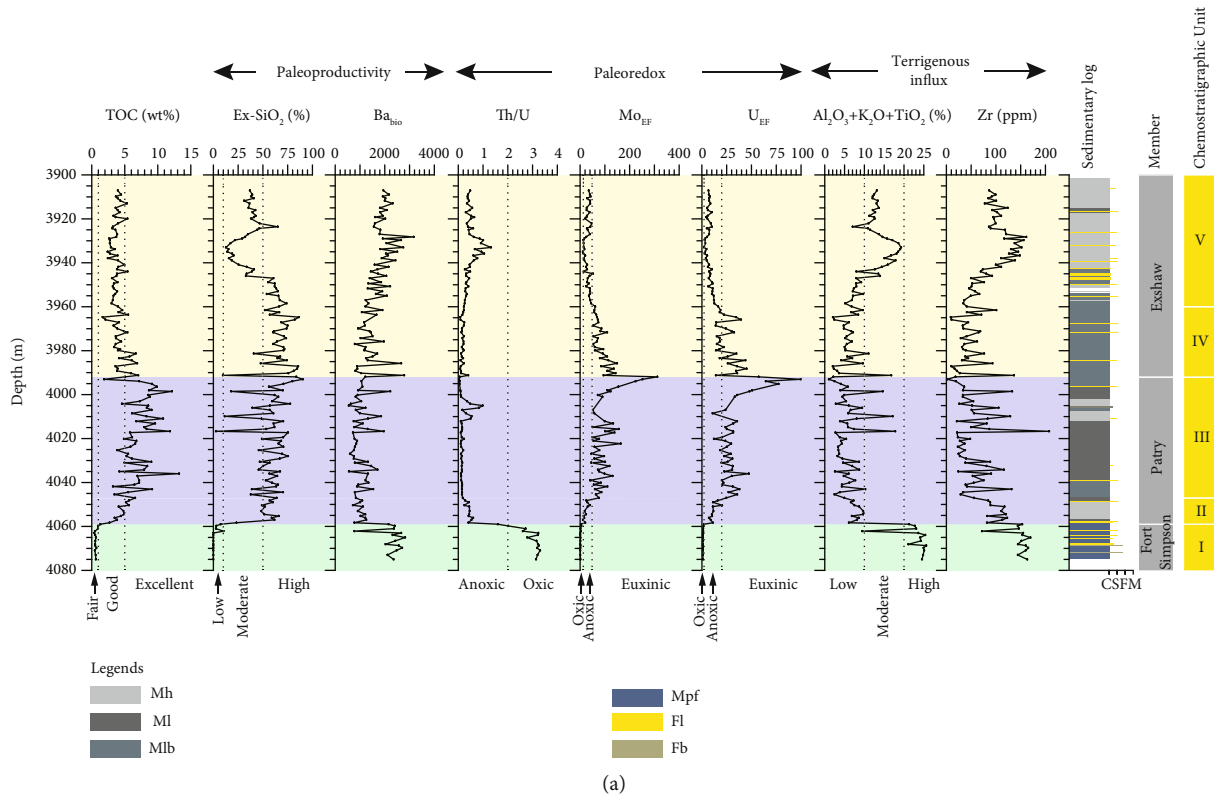
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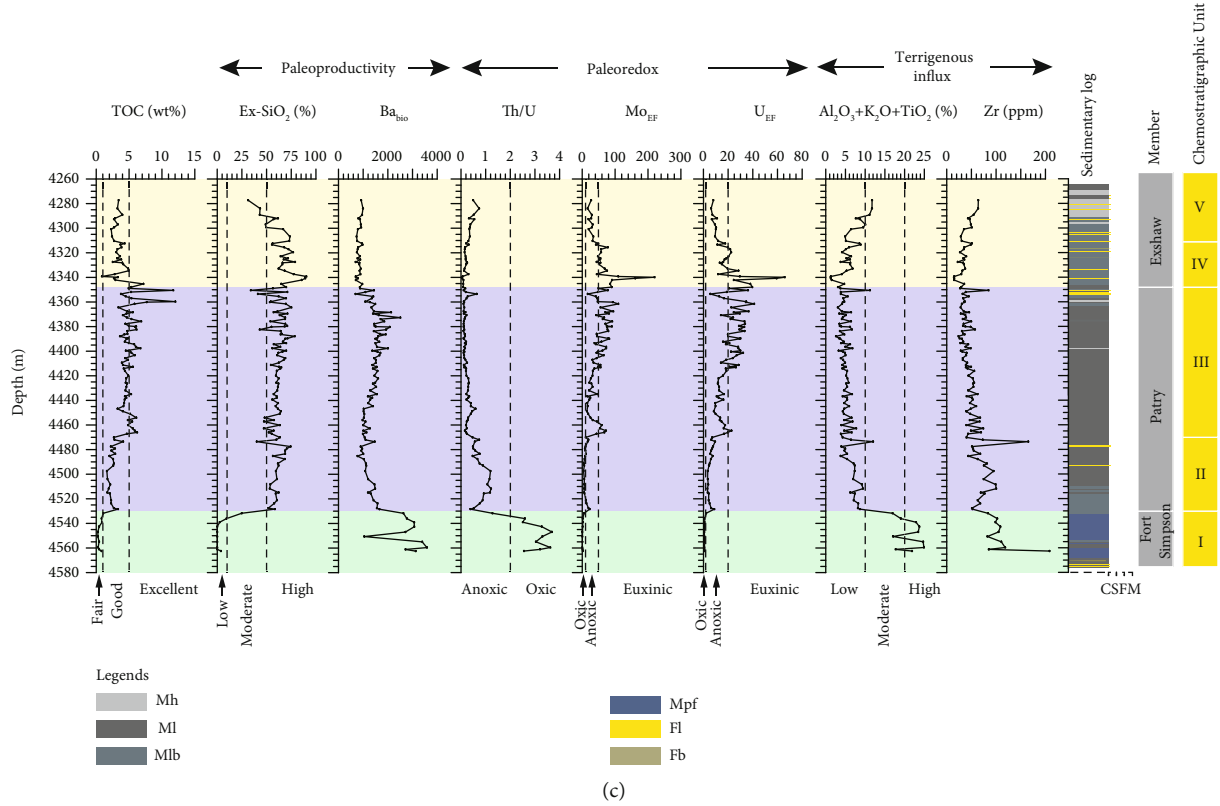
Figure 4: Stratigraphic distribution of paleoproductivity (Ex-SiO$_2$, Cu/Al, and Ni/Al), terrigenous influx (Al$_2$O$_3$+K$_2$O+Na$_2$O+TiO$_2$, Zr), paleoredox (Th/U, Mo$_{EF}$, and U$_{EF}$), and δ^{13}C$_{org}$ with TOC content in wells (a) A-038-B/94-N-08, (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12. Legends indicate simplified 6 lithofacies, which are Mh (homogeneous mudstone), Ml (laminated mudstone), Mlb (black laminated mudstone), Mpf (papery fractured mudstone), Fl (laminated siltstone), and Fb (bioturbated fine siltstone).

where $(SiO_2/Al_2O_3)_{detrital}$ of 3.53 is used for average shale [22]. The content of Ex-SiO$_2$ is higher than 50% in both the Patry and Exshaw members, but lower than 5% in the Fort Simpson member.

4.3. Trace Elements. The abundance of major paleoredox (Th, U, and Mo), primary productivity (Ba), and detrital (Zr) proxies is presented in the supplementary materials (available here).

Ba is mainly divided into the biological origin associated with the barite and the detrital origin associated with the aluminosilicates. The biogenic Ba (Ba$_{bio}$) as a paleoproductivity proxy was calculated using the following equation [23]:

$$Ba_{bio} = Ba_{total} - \left(Al_{total} \times \frac{Ba}{Al_{aluminosilicate}} \right).$$ (2)

Ba$_{total}$ and Al$_{total}$ represent the total amounts of those elements, respectively. Ba/Al$_{aluminosilicate}$ is the Ba/Al ratio of aluminosilicate fraction in the continental crust. Ba/Al$_{aluminosilicate}$ can vary between 0.005 and 0.01, where a median value of 0.0075 is used for the calculation [23]. The values of Ba$_{bio}$ are higher than 1,300 ppm in the Fort Simpson member.

To minimize dilution effects from biogenic mineral phases (such as silica and calcium), we normalized Mo and U content to aluminum, which is an indicator of the aluminosilicate fraction of sediments and has negligible remobili-

zation during diagenesis [24]. Enrichment factors were estimated using the following equation [8]:

$$EF_{element} = \frac{(X/Al)_{sample}}{(X/Al)_{average\,shale}},$$ (3)

where X and Al represent the amounts of the elements X and Al, respectively. This estimation is performed by normalizing the content of the element (X) relative to Al in the sediments and comparing these ratios to the same ratio in average shale from [22]. Enrichment factors > 10 are considered authigenic enrichment relative to the average shale, whereas when EF is <1, the elemental content is depleted [8]. Mo$_{EF}$ and U$_{EF}$ displayed the same trend in all study sites. Based on EF values, the average values of Mo and U were higher than 10 in the Patry and Exshaw members and lower than 1 in the Fort Simpson member in all study sites. High Mo$_{EF}$ and U$_{EF}$ suggest that the sediment was probably O$_2$-deficient. Similar trends are followed by the Th/U ratio, which was considered as a reliable redox proxy.

5. Discussion

5.1. Depositional Environment

5.1.1. Dilution Effect. Organic carbon content dilutes as a result of enhanced clastic flux in sedimentary environment
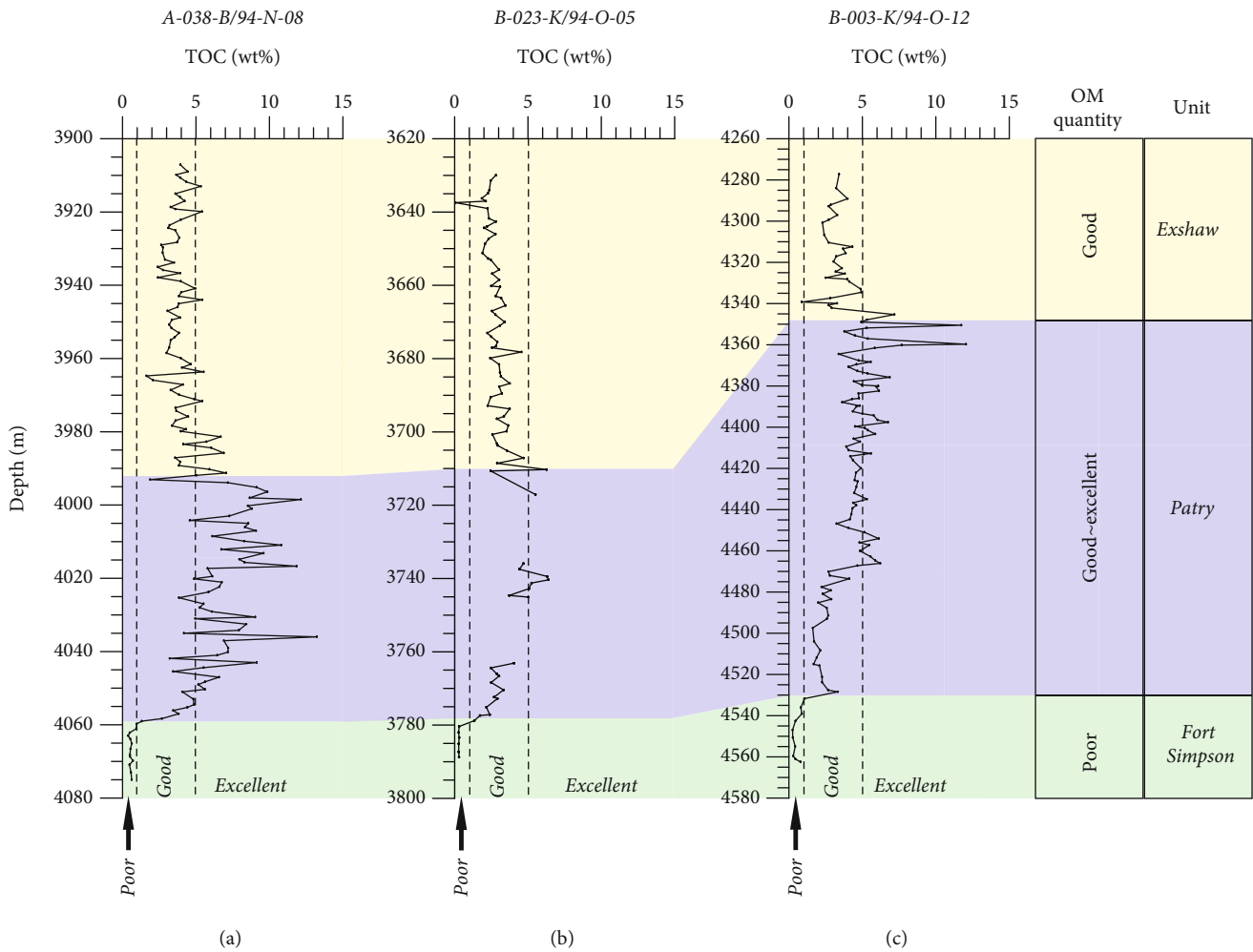
FIGURE 5: Depth profiles of TOC content in wells (a) A-038-B/94-N-08, (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12.

[12, 13, 25]. The K_2O and TiO_2 content shows a positive correlation with Al_2O_3 (Figure 7), which indicates that the K_2O and TiO_2 abundances are controlled by clay minerals [13]. The $Al_2O_3+K_2O+TiO_2$ value, an indicator of clastic influx, is higher in the Fort Simpson member, lower in the Patry, and increased in the Exshaw member (Figure 4). The Fort Simpson member with the highest clastic influx has the lowest TOC content, whereas the Exshaw member with an increased clastic influx decreased the TOC content. The Zr is a reliable proxy for the clastic influx because it is weakly affected by weathering and diagenesis during deposition [12]. The Zr content also shows a significant relationship with $Al_2O_3+K_2O+TiO_2$ (Figure 7). In the Fort Simpson member, Zr was relatively high, indicating a relatively high clastic supply during this period. The low content in the Patry member reflects a relatively stable environment and less clastic supply during this period.

5.1.2. Paleoredox Conditions. Samples from the Besa River shale exhibit a wide range of Th/U ratios, ranging from 0.26 to 3.18; this suggests frequent fluctuations in the paleodepositional condition because Th/U is a reflection of the

reducing conditions during deposition [26, 27]. Th/U varies from 0 to 2 in an anoxic environment and from 2 to 8 in a strongly oxidizing environment [28]. The Th/U ratios are lower than 2 in samples from the Patry to Exshaw members but higher than 2 in the samples from the Fort Simpson member. This suggests the development of anoxic conditions in the Patry to Exshaw members and oxic conditions in the Fort Simpson member. The Th/U ratio versus TOC shows the negative exponential distribution in the Besa River Formation samples ($R^2 = 0.44$) (Figure 8). When the Th/U ratio decreases to 0.2–0.3, the TOC increases rapidly and slowly increases with a further decrease of Th/U.

The Mo_{EF}-U_{EF} crossplot can be used to explain the redox conditions and the degree of bottom water restriction [10, 11, 24, 29]. Almost all the Mo_{EF}-U_{EF} values are plotted in the unrestricted marine zone, thereby supporting the deposition of Besa River sediments in an open marine system during the Devonian (Figure 9). In unrestricted marine systems such as continental margin upwelling systems, the change from suboxic to sulfidic redox conditions enhances the accumulation of both Mo and U, but the strong Mo enrichment results in a gradual increase of the Mo_{EF}/U_{EF} ratio from 0.3 to 1.0 to
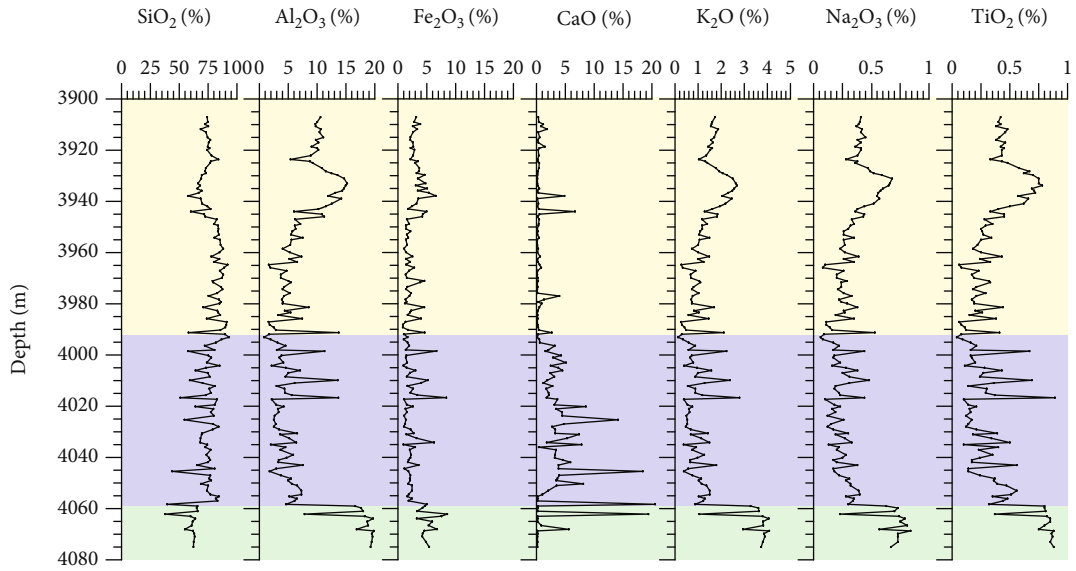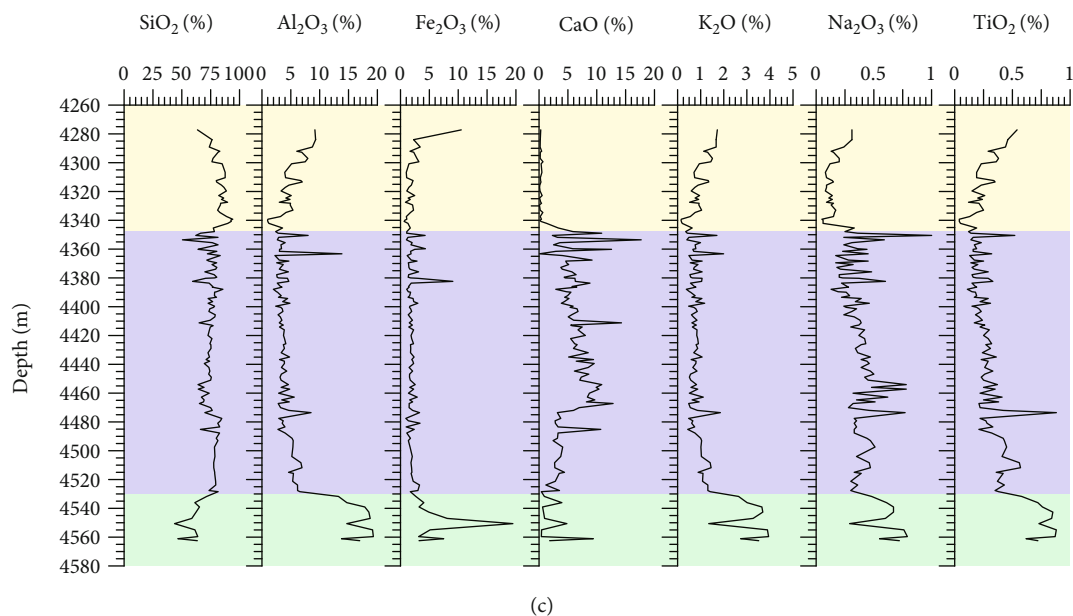
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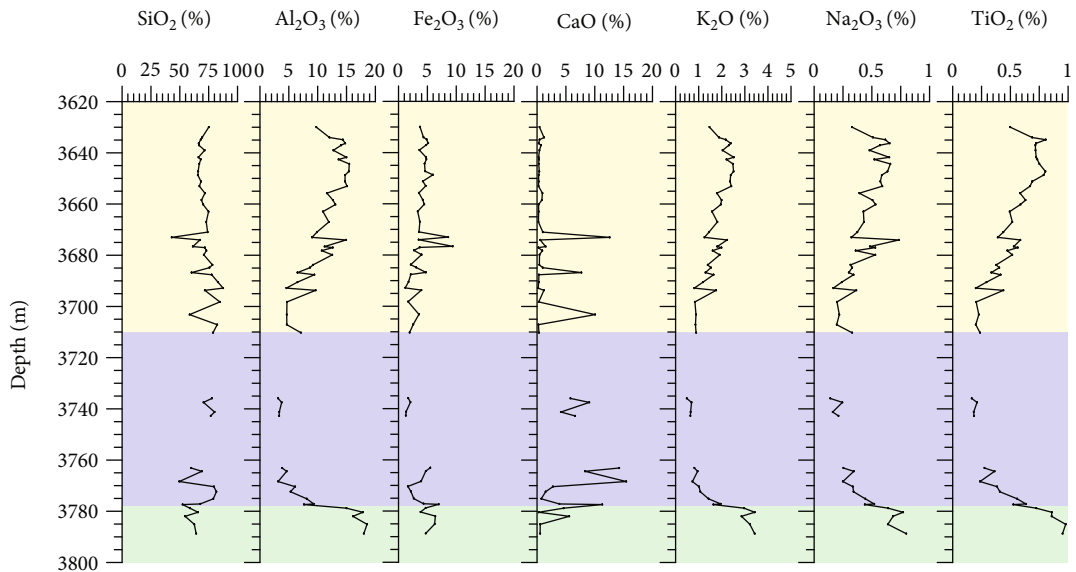
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FIGURE 6: Depth profiles showing the distributions of major elements in wells (a) A-038-B/94-N-08, (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12.

3.0 times that of modern seawater [24]. During the accumulation of the Fort Simpson member, Mo_{EF} and U_{EF} were low, and the Mo_{EF}/U_{EF} ratios are mostly lower than 0.3–1.0 times that of modern seawater (Figure 9). Thus, the Fort Simpson member was deposited under oxic-suboxic conditions, which is consistent with higher Th/U ratios. The Patry member displays enrichment for Mo and U as well as high Mo_{EF}/U_{EF} ratios of over 1.0 times that of modern seawater (Figures 4 and 9). The data of the Patry member was divided into two subgroups, which indicated that the anoxic conditions changed into euxinic conditions. The Exshaw member shows decreases of Mo_{EF} and U_{EF} but high Mo_{EF}/U_{EF} ratios of over 1 times that of modern seawater (Figures 4 and 9). The data of the Exshaw member indicates that the euxinic conditions changed to anoxic conditions. This suggests that redox conditions of the Besa River Formation during the Devonian gradually changed from oxic/suboxic (within the Fort Simpson member) to anoxic (lower part of the Patry member) to euxinic (upper part of the Patry and lower part of the Exshaw) to anoxic conditions (upper part of the Exshaw)(Figure 9).

5.1.3. Paleoproductivity. A variety of geochemical proxies have been used to reconstruct paleoproductivity, including Ex-SiO_2 and Ba_{bio}; these methods have been widely used in paleoproductivity studies [23, 30]. Nevertheless, Ba_{bio} in Besa River shales shows a negative correlation with the TOC content, as it is high in the Fort Simpson member with a low TOC (Figure 10). Schroeder et al. [31] suggest that Ba content was derived from different sources and can be influenced by redox conditions. Notably, Ba content cannot be used as a paleoproductivity proxy in anoxic sediments. Barite ($BaSO_4$), the domain Ba-bearing mineral, generally forms under oxic conditions, but it dissolves under reducing conditions. This means the Ba was thoroughly preserved in the Fort Simpson

member under oxic and suboxic conditions, but less Ba accumulated in the Patry and Exshaw members under anoxic conditions. The lack of correspondence between Ba_{bio} and TOC (Figure 10) suggests that the abundance of Ba was affected by environmental factors other than primary productivity, such as barite dissolution owing to elevated rates of bacterial sulfate reduction [32–34].

Ross and Bustin [9] suggested that biogenic silica content is a useful proxy for paleoproductivity, especially where other elemental proxies, such as Ba, cannot be used. The Ex-SiO_2 content can be related to detrital quartz and/or biogenic silica. In this study, the Ex-SiO_2 is negatively correlated with Zr as a detrital input proxy (Figure 10). This indicates that the Ex-SiO_2 mainly originated from biogenic silica rather than detrital quartz. The presence of Radiolaria in the Besa River shales further confirms that Ex-SiO_2 is associated with biogenic silica (e.g., [9]). Thus, Ex-SiO_2 can be taken as a reliable indicator of paleoproductivity. In this study, Ex-SiO_2 is relatively high, above 50% in the Patry member to the lower part of the Exshaw member (Figure 4).

5.2. Chemostratigraphic Units of the Besa River Formation. The Besa River Formation was subdivided into five chemostratigraphic units based on TOC content and geochemical data, which are related to productivity, clastic sediment input, and oxygen content in the bottom water during deposition (Table 1). The chemostratigraphic units are shown in Figure 4. The certain values of each property for defining the chemostratigraphic unit are as follows. Each value was classified into fair (<1 wt.%), good (1~5 wt.%), and excellent (>5 wt.%) for TOC; low (<10%), moderate (10~50%), and high (>50%) for Ex-SiO_2; and low (<10%), moderate (10~20%), and high (>20%) for detrital index. The proxies for redox condition are oxic (>2) and anoxic (<2) for Th/U; oxic (<5 ppm), anoxic (5~50 ppm), and euxinic (>50 ppm)
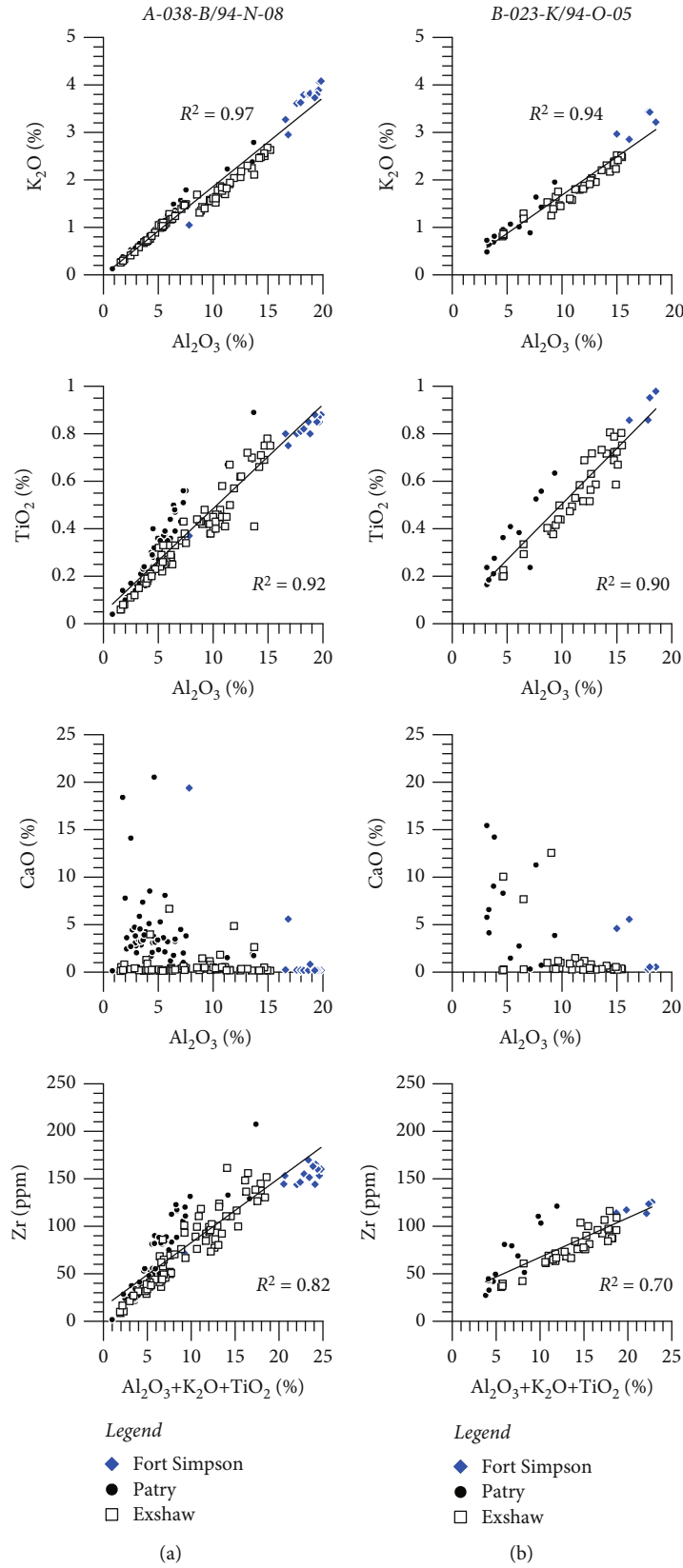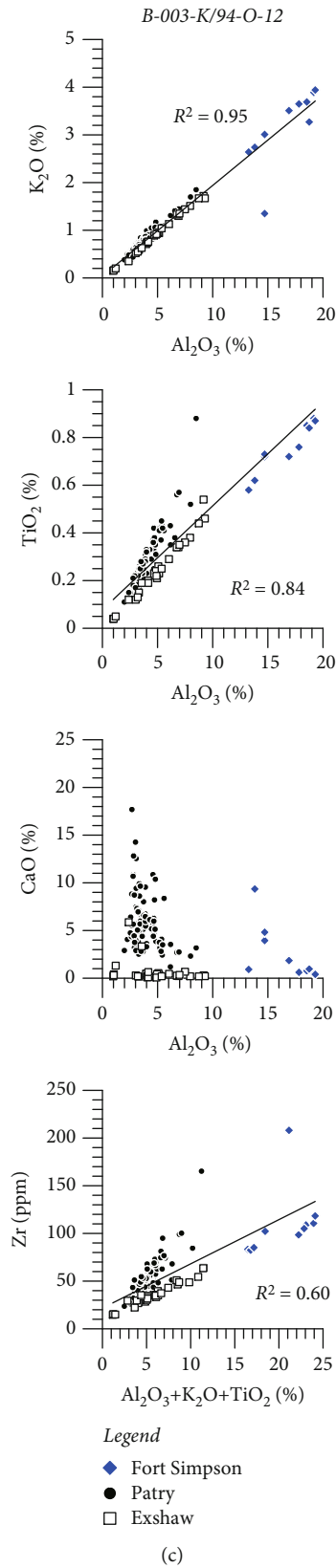
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FIGURE 7: Major elemental distributions of Al_2O_3 versus K_2O, TiO_2, and CaO, and Zr versus $Al_2O_3+K_2O+TiO_2$ in wells (a) A-038-B/94-N-08, (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12.
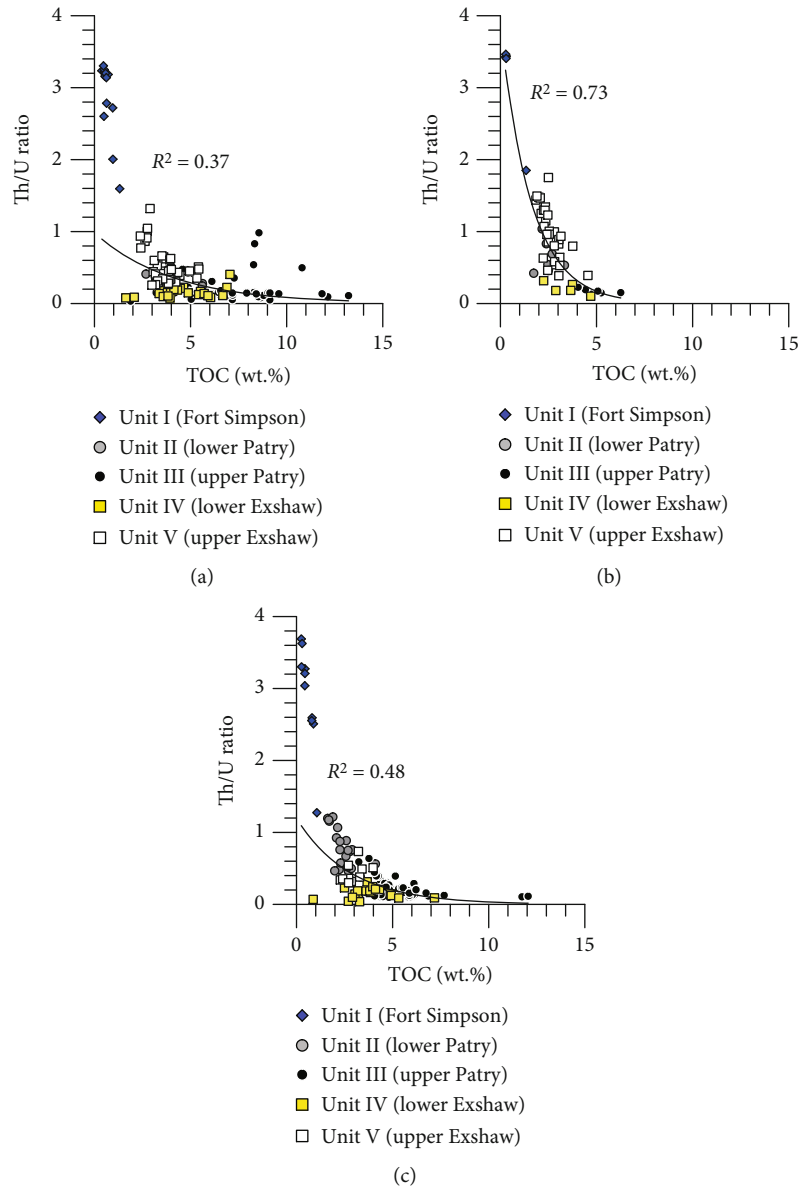
(a)

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FIGURE 8: Crossplots of the Th/U ratio versus TOC in wells (a) A-038-B/94-N-08, (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12.

for Mo_{EF}; and oxic (<2 ppm), anoxic (2~20 ppm), and euxinic (>20 ppm) for U_{EF}.

Unit I (Fort Simpson) has the lowest Ex-SiO$_2$ content (less than 5%) and the highest Al$_2$O$_3$+K$_2$O+TiO$_2$ content (more than 20%). Its Th/U ratios are higher than 2, and Mo_{EF} (~5 ppm) and U_{EF} (~2 ppm) content is extremely low. The highest Ba$_{bio}$ is only observed in this interval. Based on geochemical proxies, the dilution of organic matter was enhanced by increased clastic flux, and the supply of organic matter was reduced owing to low primary productivity. In addition, preservation of organic matter was limited owing to the oxic conditions in the bottom water. The TOC content is lower than 1 wt.%.

In Unit II (lower part of the Patry member), the Ex-SiO$_2$ content begins to increase, whereas the Al$_2$O$_3$+K$_2$O+TiO$_2$ content decreased. This indicates that primary productivity increased and the clastic influx reduced. The low Th/U (less

than 2) and the moderate Mo_{EF} (~39 ppm) and U_{EF} (~20 ppm) content reflect development of anoxic conditions that prohibited the aerobic degradation of organic matter. The TOC content can increase up to 5 wt.%.

Unit III (upper part of the Patry member) is characterized by higher TOC content (more than 5 wt.% up to 13 wt.%) relative to other intervals. The Ex-SiO$_2$ content is higher than in Unit II, and the Al$_2$O$_3$+K$_2$O+TiO$_2$ content is lowest, thereby suggesting an enhanced primary productivity and limited clastic sediment influx. The Th/U ratios are lower than 2 and the Mo_{EF} (~312 ppm) and the U_{EF} (~100 ppm) content are elevated, indicating enhanced anoxic conditions through intense water column stratification. In addition, the high Mo_{EF}/U_{EF} ratio reflects euxinic conditions in the bottom water.

In Unit IV (lower part of the Exshaw member), the Ex-SiO$_2$ and the Al$_2$O$_3$+K$_2$O+TiO$_2$ content are similar to Unit
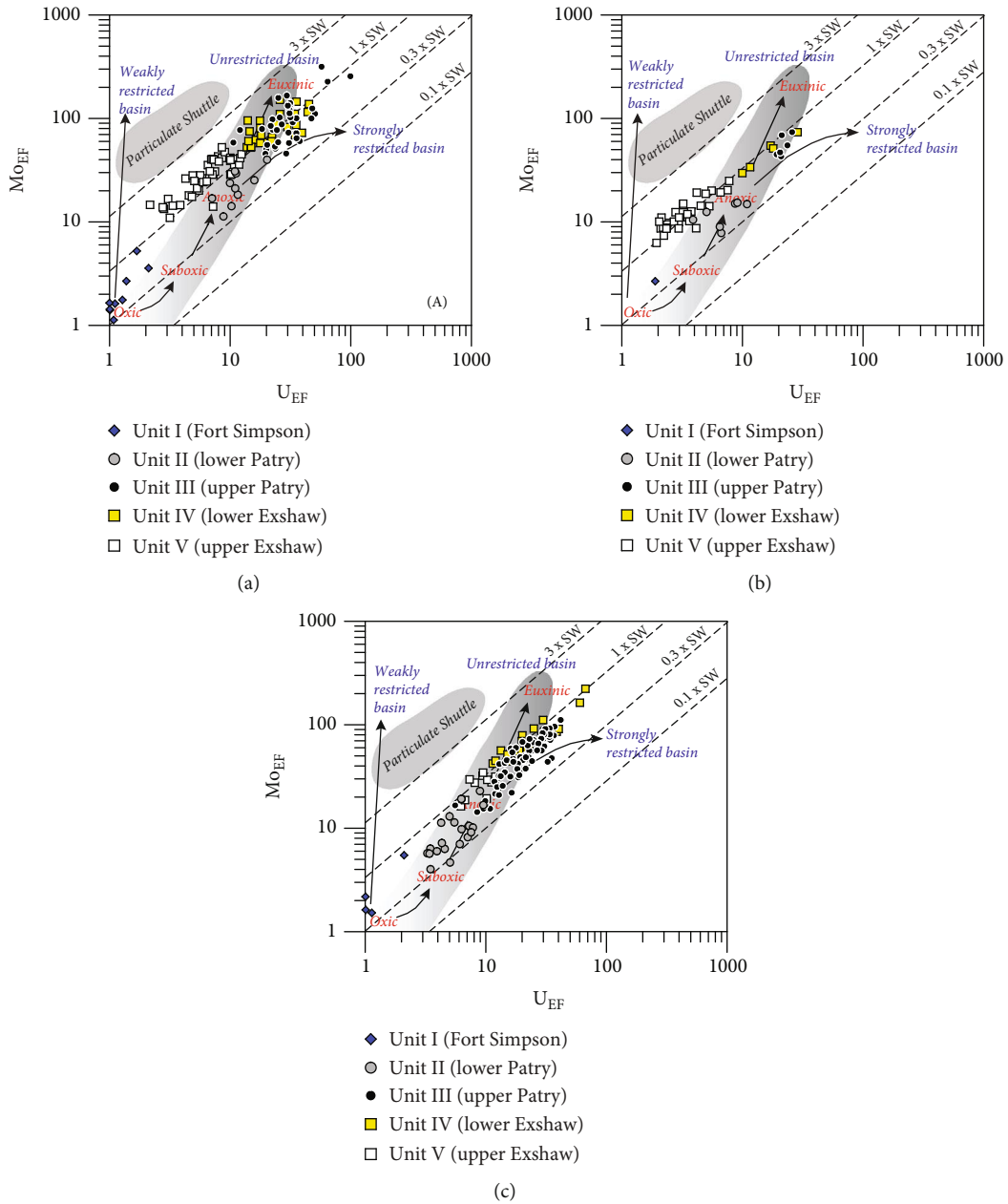
FIGURE 9: Mo_{EF} versus U_{EF} in wells (a) A-038-B/94-N-08, (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12. Dotted lines indicate Mo/U molar ratios as multiples of the seawater value (3x SW, 1x SW, 0.3x SW, and 0.1x SW) (modified from Algeo and Tribovillard [24]).

III. This indicates that the enhanced primary productivity and limited clastic sediment influx were maintained within Unit IV. Consistently high Mo_{EF} (~220 ppm) and U_{EF} (~66 ppm) content indicates that the euxinic conditions in the bottom water remained. Nevertheless, its TOC content (~7 wt.%) is lower than that of Unit III.

In Unit V (upper part of the Exshaw member), the Ex-SiO_2 content decreased, and the $Al_2O_3+K_2O+TiO_2$ content increased, thereby suggesting that the primary productivity decreased and the influx of terrigenous sources increased. The moderate Mo_{EF} (~52 ppm) and U_{EF} (~12 ppm) content reveals that anoxic conditions were dominant in Unit V. The TOC content (~5 wt.%) slightly decreased compared to Unit IV.

5.3. Factors Controlling Organic Matter Accumulation. The mechanisms of organic matter accumulation reflect the interplay of various oceanographic and sedimentological conditions, including productivity, redox conditions, and organic matter dilution effects via clastic influx [7, 35, 36]. All these mechanisms are influenced by sea level changes.

The average TOC content in Unit I is the lowest at less than 1 wt.% (Figure 4). The rise in detrital silicate flux increased the dilution of organic matter, and the low primary productivity limited the supply of organic matter. In addition, oxic conditions in the bottom water driven by the decline in the primary productivity limited the preservation of organic matter. The supply of clastic sediment likely increased because of the closer proximity to the coastline,
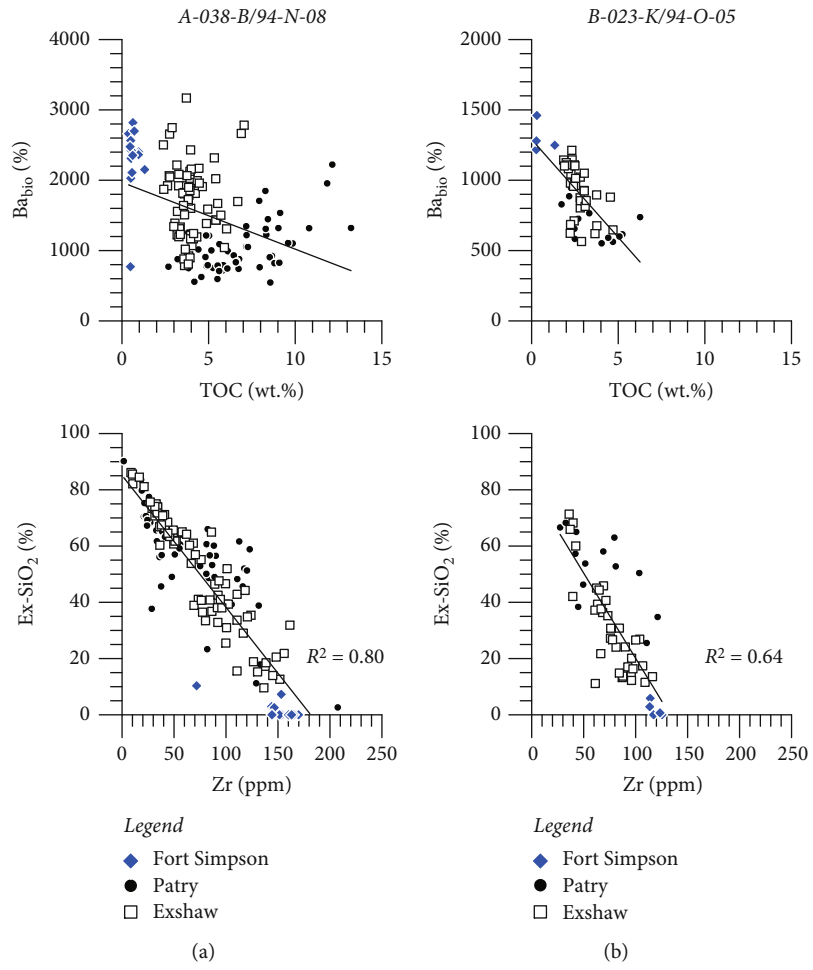
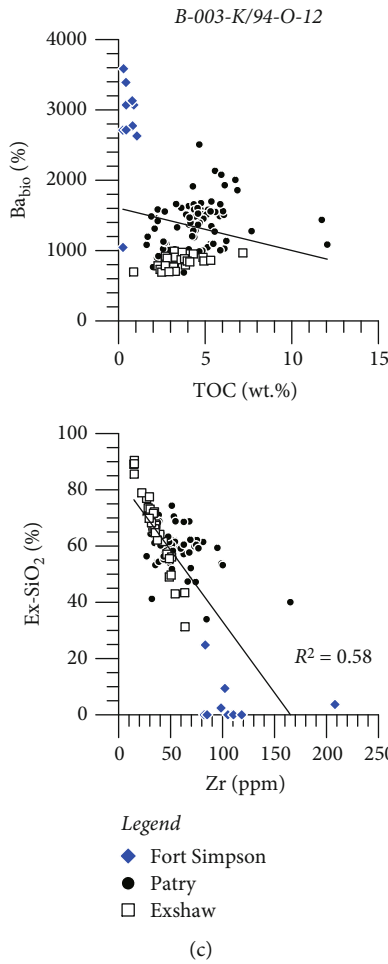FIGURE 10: Crossplots of Ba_{bio} and TOC, as well as $Ex-SiO_2$ and Zr, in the wells (a) A-038-B/94-N-08 (Hong et al. [19]), (b) B-023-K/94-O-05, and (c) B-003-K/94-O-12.

TABLE 1: Chemostratigraphic units with the status of TOC, paleoproductivity, redox condition, and terrigenous influx.

| Chemostratigraphic units | Interval (m) | | | TOC (wt.%) | Paleoproductivity Ex-SiO$_2$ | Redox condition | Terrigenous influx |
	A-038-B/94-N-08	B-023-K/094-O-05	B-003-K/94-O-12				
I	4059–4075	3778–3789	4530–4563	<1	Low	Oxic	High
II	4047–4059	3763–3778	4470–4530	1~5	High	Anoxic	Low
III	3992–4047	3710–3763	4348–4470	>5	High	Euxinic	Low
IV	3960–3992	3690.5–3710	4311–4348	1~5	High	Euxinic	Low
V	3907–3960	3629–3690.5	4277–4311	1~5	Moderate	Anoxic	Moderate

and nutrient supply was reduced by decreased upwelling, as sea level fell during deposition of Unit I. In summary, the low accumulation of organic matter was caused by decreased primary productivity, oxic conditions in the bottom water, and elevated detrital siliciclastic influx as a consequence of marine regression.

TOC content begins to increase in Unit II and rose to 13 wt.% in Unit III (Figure 4). The enhanced productivity is related to increased nutrient supply. Nutrients are supplied by the upwelling of deep, nutrient-rich waters, riverine sources, and/or aeolian dust. Because the clastic influx was reduced during the deposition of Units II and III, the supply of nutrients was primarily caused by the upwelling of deep water. Rising sea levels from Unit II would have brought in nutrient-rich water through upwelling. With high productivity, an oxygen minimum zone (OMZ) associated with degradation of particulate organic matter was formed. This would have made the bottom water oxygen-deficient. Thus, within Units II and III, abundant organic matter supplied from enhanced productivity might have been thoroughly

preserved in anoxic bottom water [37]. In addition, because clastic flux was reduced during the marine transgression, the dilution of organic matter was limited. The interplay between productivity and preservation associated with high sea level was caused by the high accumulation of organic matter.

Despite the relatively reduced TOC content in Unit IV, the primary productivity was still high, and anoxic conditions remained in Unit IV. In addition, based on low clastic sediment influx, TOC was not reduced by the change in the dilution effect. The integrated response to the rising sea level was the development of anoxia and enhanced productivity, which was favorable for increased organic matter accumulation and preservation [37]. However, increasing the exposure time of organic matter to the effects of oxidation in the water column negatively affected organic matter accumulation [37]. The Exshaw member represents the beginning of a significant, continent-wide transgression [38, 39], and the maximum flooding surface likely occurred within the deposition of the lower part of the Exshaw member [18]. The deepening sea level might have led to an increase in primary productivity and development of anoxic conditions, and residence time in oxic zones of the water column might have also increased, which may have resulted in less accumulation of organic matter relative to Unit III.

Although the anoxic conditions were dominant in Unit V, productivity decreased, and clastic sediment influx increased relative to Unit VI. These conditions might have led to moderate levels of organic matter accumulation in Unit V.

5.4. Evaluation of Shale Gas Reservoir Quality. In general, the TOC is one of the major determinants of a shale gas reservoir quality. Ferri et al. [17] compared gas saturation to TOC, porosity, and clay content using Well B-023-K/94-O-05. In this study, gas saturation showed no correlation between porosity and clay content, but a positive correlation with TOC content was observed. This suggests that the variation of gas saturation in the Besa River Formation is primarily related to the TOC content. Based on the TOC content [40, 41], the Devonian shale in the Besa River Formation is classified as poor source rock quality in the Fort Simpson member, good to excellent in the Patry member, and good in the Exshaw member (Figure 5). The highest TOC content is observed in the upper part of the Party member (Unit III). The TOC content in Unit III ranges from 1.9 to 13.2 wt.% in Well A-038-B/94-N-08, 2.5 to 6.4 wt.% in Well B-023-K/94-O-05, and 2.4 to 12.1 wt.% in Well B-003-K/94-O-12; these values designate a good-to-excellent source rock (Figure 5). In addition, Unit III shows relatively high biogenic silica content and low clay content, indicating that this interval is favorable for fracturing, which is essential for shale gas production. Therefore, Unit III may provide the most substantial shale gas production potential within the Besa River Formation. The Unit III depth ranges from 3,992 to 4,047 m (net 55 m) in Well A-038-B/94-N-08, 3,710 to 3,763 m (net 53 m) in Well B-023-K/94-O-05, and 4,348 to 4,470 m (net 122 m) in Well B-003-K/94-O-12, indicating that Unit III is thicker from south to north in the Liard Basin.

6. Summary and Conclusions

Based on the high-resolution geochemical data of three studied wells, the mechanism of organic matter accumulation during the deposition of the Besa River Formation in the Liard Basin was studied. In addition, we distinguished five chemostratigraphic units considering variations of the high-resolution geochemical proxies and then suggested the most favorable unit for shale gas production in the Devonian Besa River Formation.

(1) The lowest TOC interval at under 1 wt.% was equivalent to the Fort Simpson member, which was deposited in oxic bottom conditions, a high detrital flux, and low bioproductivity (Unit I).

(2) The highest TOC intervals, up to 13 wt.%, were identified in the upper part of the Patry member (Unit III). This highest TOC interval most likely formed by abundant biogenic production of radiolarians related to the nutrient supply by upwelling. The siliceous sediments were settled with abundant organic matter under the stable euxinic conditions and a limited terrestrial supply

(3) The low TOC interval, ranging from 1 to 5 wt.%, occurred in the Exshaw member. Sea level rise affected the reduction of organic matter accumulation in the Exshaw member (Units IV and V). Moreover, there was more detrital input during the deposition of the upper Exshaw member, which likely diluted the organic matter

(4) Sea level change and productivity played an important role in forming a high TOC interval in the Devonian Besa River Formation

(5) The most promising interval for shale gas production in the Devonian Besa River Formation is likely Unit III, which is composed of organic and biogenic silica-rich shales

(6) Although the target interval for shale gas production in the Devonian Besa River was identified by the high-resolution geochemical data in the three wells, there is a limit to determining the distribution of a favorable unit for shale gas production in the Liard Basin. Therefore, further research is required to better understand the regional distribution of favorable units such as the integrated analysis of the well log and/or seismic data with the high resolution geochemical data suggested in this study

Nomenclature

Parameter and name

S_1:   Free hydrocarbons
S_2:   Kerogen
RC: Residual organic carbon
TOC: Total organic carbon

SiO$_2$: Silicon dioxide
Al$_2$O$_3$: Aluminum oxide
Fe$_2$O: Iron oxide
CaO: Calcium oxide
K$_2$O: Potassium oxide
Na$_2$O: Sodium oxide
TiO$_2$: Titanium dioxide
Mo: Molybdenum
U: Uranium
Th: Thorium
Zr: Zirconium
Ba: Barium.

Data Availability

The data used to support the findings of this study are included within the manuscript and supplementary materials.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

Supplementary Materials

Table S1: geochemical data from the Well A-038-B/94-N-08 (Hong et al., submitted). Table S2: geochemical data from the Well B-023-K/94-O-05. Table S3: geochemical data from the Well B-003-K/94-O-12. (Supplementary Materials)

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