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Application of Organic Geochemistry in Determining the Hydrocarbon Potential of the Carbonaceous Shales of the Ecca Group (Main Karoo Basin) in Borehole KZF-1

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Abstract

South Africa's exploration priority for future energy resources has recently shifted to shale gas. The black shales of the lower Ecca Group in the southern Main Karoo Basin, in particular, are regarded as one of the most promising targets for shale gas development. Due to a paucity of exploration and a scarcity of current drill core data, evaluation of this potential resource has been limited. As a result, only a few previous geochemical data exist for these formations. In this research, the carbonaceous shales of the Ecca Group in the southern Main Karoo Basin were investigated for their hydrocarbon potential using the recently drilled borehole KZF-1. This study applied organic geochemistry through total organic carbon content (TOC) analysis and rock-eval pyrolysis to elucidate the hydrocarbon potential and organic matter characterization of the aforementioned shales. The TOC content of the shales ranges between 0,22 – 5,76 wt% and HI values are below 50 mg HC/ g TOC. The rock-eval pyrolysis values range between 0.02-1.38 mg/ g for S_1, S_2 and S_3. Moreover, Tmax varies from 304°C to 607°C. The organic geochemical assessment reveals that the organic matter of the shale samples is kerogen type III and IV. The shales have good to very good potential to generate dry gas and oil. In addition, most samples are over-mature, and a few are indicative of non-source rocks. The Whitehill Formation shows the best hydrocarbon potential and may present a significant exploration target. The organic geochemical assessment also suggests that the shales are indicative of secondary source rocks and the hydrocarbon generation occurred in-situ. Overall, the hydrocarbon potential of the shales is fair.

Keywords: *Main Karoo Basin; Ecca Group; Organic geochemistry; Shale gas; Rock-eval pyrolysis.*

1. Introduction

The Main Karoo Basin is a prominent foreland sedimentary basin which hosts majority of South Africa's fossil fuel resources. Recently, the basin has been receiving growing scientific attention due to the organic-matter rich shales of the Ecca Group which may serve as potential shale gas source rocks. However, the associated Karoo tectonic regimes including the Karoo Dolerite Suite which comprises of dykes and sills are likely to reduce the quality of shale gas resources [1]. For instance, sills or dykes may fracture the rocks of interest, promoting thermal degassing and fluid invasion which eventually influence the source rock potential [1]. Shale gas is a term used to define gas that is generated from organic-matter enriched shales [2]. However, shale gas can also be used to refer to natural gas that is hosted within other lithologies that include carbonates, mudrocks, silty mudrocks and siltstones [3]. The natural gas was derived from biological or thermal mechanisms or alternatively combined effects of both mechanisms; furthermore, the gas may also occur as free gas that is confined within natural fractures of the shales [4]. In addition, the gas may be trapped within intergranular pores wherein it is solvated in kerogen and bitumen or either absorbed or adsorbed into surface planes of kerogen or clay particles [4].

Based on the chemistry of the gas, it can be regarded as either dry or wet gas. Natural gas that is dominantly composed of methane is identified as dry gas and if the gas chemistry is dominated by long chains of hydrocarbons such as ethane it is considered as wet gas. Suitability for shale gas generation is dependent on several factors such as shale sedimentology, mechanical qualities, and permeability; moreover, shale gas exploration and exploitation may be controlled by shale bed thickness, areal extent, maturity, kerogen type, total organic carbon content (TOC) and mineralogy [5]. The natural gas hosted within the Main Karoo Basin is classified as unconventional gas which occurs as methane that is confined within poorly permeable shales and can only be released through hydro-fracturing (fracking) [6]. The fracking process may generate some environmental risks such as shallow ground water contamination, micro-seismicity induction and over-usage of water resources; as a result, this has raised some serious concerns regarding the recoverability of shale gas resources [7-8]. Presently, there are no substantial estimations on the economic recoverability of the Main Karoo Basin shale gas resources. Furthermore, there is considerable uncertainty on the characterization and assessment of the shale oil resources within the Ecca Group. However, organic matter rich and thermally mature black shales of the lower Ecca Whitehill Formation may present an important exploration target for shale gas resources [9-10].

In recent years, the alarming effects of global warming and climate change have caused a shift in the global energy policy which is now centred on the exploration of cleaner energy resources such as shale gas and oil. As a result, the carbonaceous shales of the Ecca Group are now an exploration target in South Africa. This could potentially be a game changer for the country's economy and energy security. Regardless of a number of authors suggesting the potential of Ecca shales as possible hydrocarbon source rocks [9,11], there is limited information on the detailed potential of the shales to generate natural gas and oil as well as the hydrocarbon reservoir characterization. Thus, there is a clear need to comprehensively evaluate the hydrocarbon potential of Ecca Group shales as possible source rocks. The investigated rock units in borehole KZF-1 are situated in the south-western coast of South Africa, specifically in the Tankwa Karoo Sub-basin which is found in the Western Cape Province. This study applied organic geochemistry in order to determine the total organic carbon content of the shales, organic matter type and quality as well as source rock potential. In essence, the study aims to validate or comprehensively define the potential of Ecca Group shales as significant hydrocarbon source rocks as well as provide findings to direct shale gas and oil exploration programmes and resource evaluation in the Main Karoo Basin.

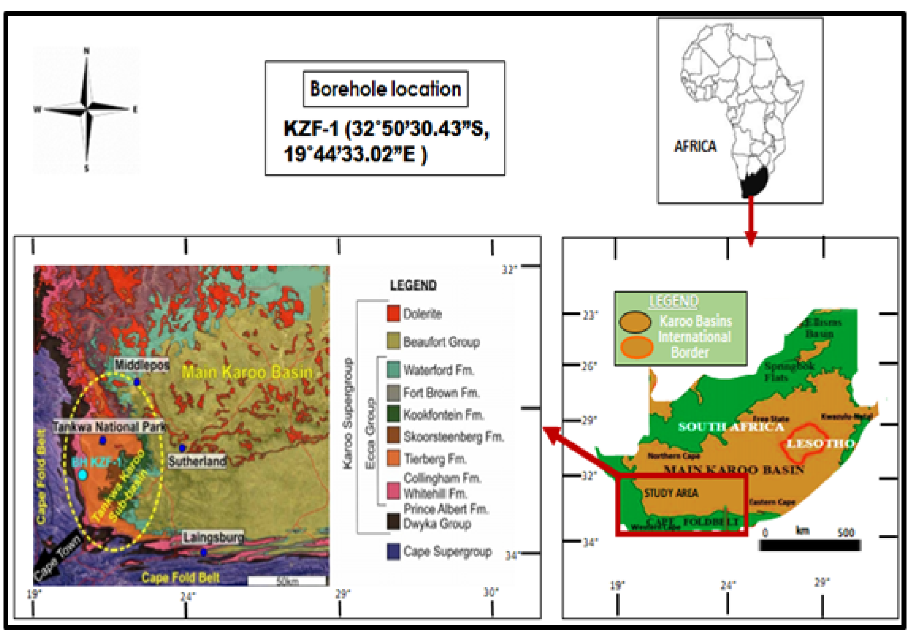

Figure 1. Location map of the study area (modified after [12]).

2. Geological setting

The Main Karoo Basin is a retroarc foreland basin which developed due to the subduction of the paleo-Pacific plate under the continental Gondwanan plate [13]. The event was accompanied by orogenic activities and the associated supracrustal weight promoted crustal sagging (Figure 2), thus forming the Main Karoo Basin including other Karoo basins [14]. The retroarc foreland system is defined by base level changes which are caused by the orogenic events of unloading and loading; moreover, the cyclic changes also gave rise to major marine transgressions and regressions together with transitions from marine to non-marine depositional environments throughout the basin [15]. According to [16], the cyclic changes are representative of the development of the basin through filled, underfilled and overfilled phases; additionally, the depositional settings associated with such phases range from fluvial to shallow or deep marine environments.

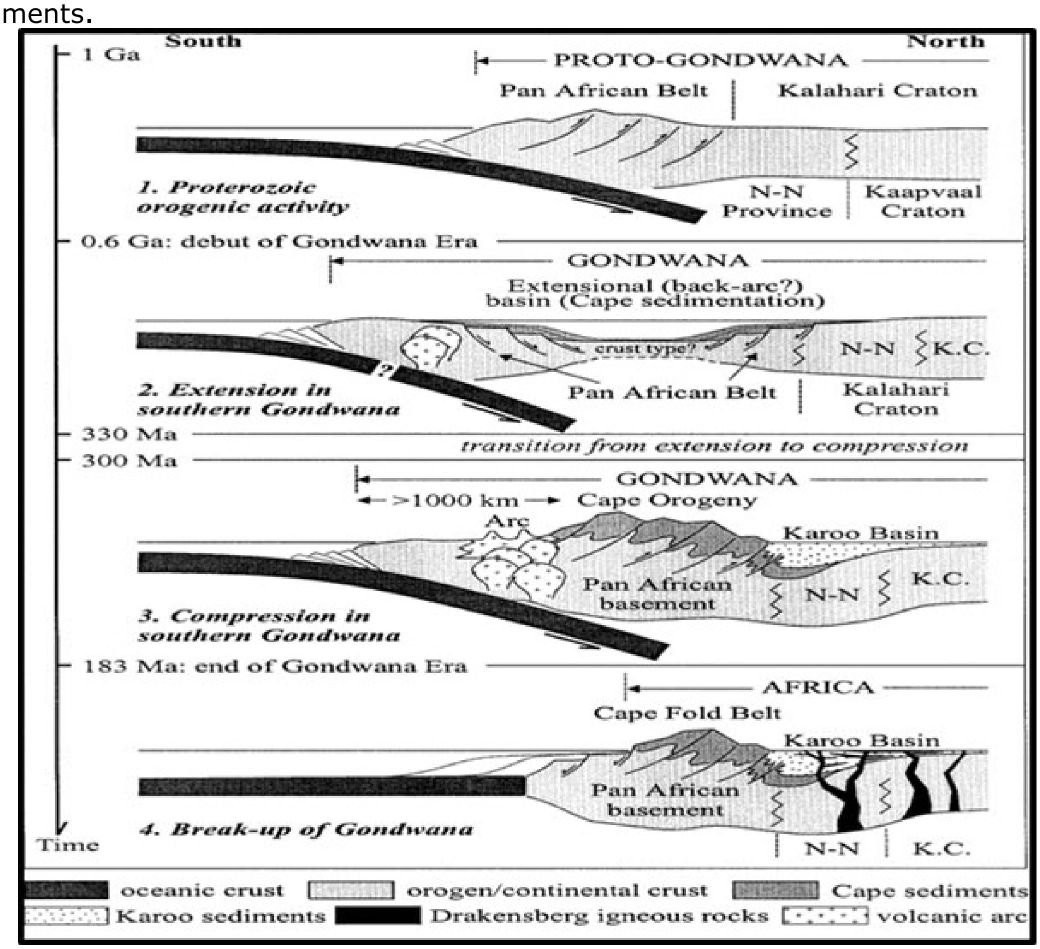

Figure 2. Overview of the Karoo tectonics (after [13]).

Sedimentation within the Main Karoo Basin occurred from Late Carboniferous to Early-Mid Jurassic (Figure 3), which is a period of about 130 million years, resulting in the formation of up to 6 km thick strata of the Karoo Supergroup [12 14]. During the early Karoo times, Southern Africa formed part of the ancient supercontinent of Gondwana which was in close proximity to the polar regions; as a result, the area experienced glaciation events and was covered in ice sheets [17]. According to [17], there was accumulation of glacial sediments which formed the stratigraphic sequences of the lowermost Dwyka Group. Ultimately, episodes of Dwyka deglaciation occurred as Gondwana drifted away from the pole and the events were accompanied by transgressions which formed an inland sea that served as a trap for fine-grained, organic-matter enriched sediments of the Whitehill, Prince Albert and Collingham formations which collectively make up the lower Ecca Group successions [18-19].

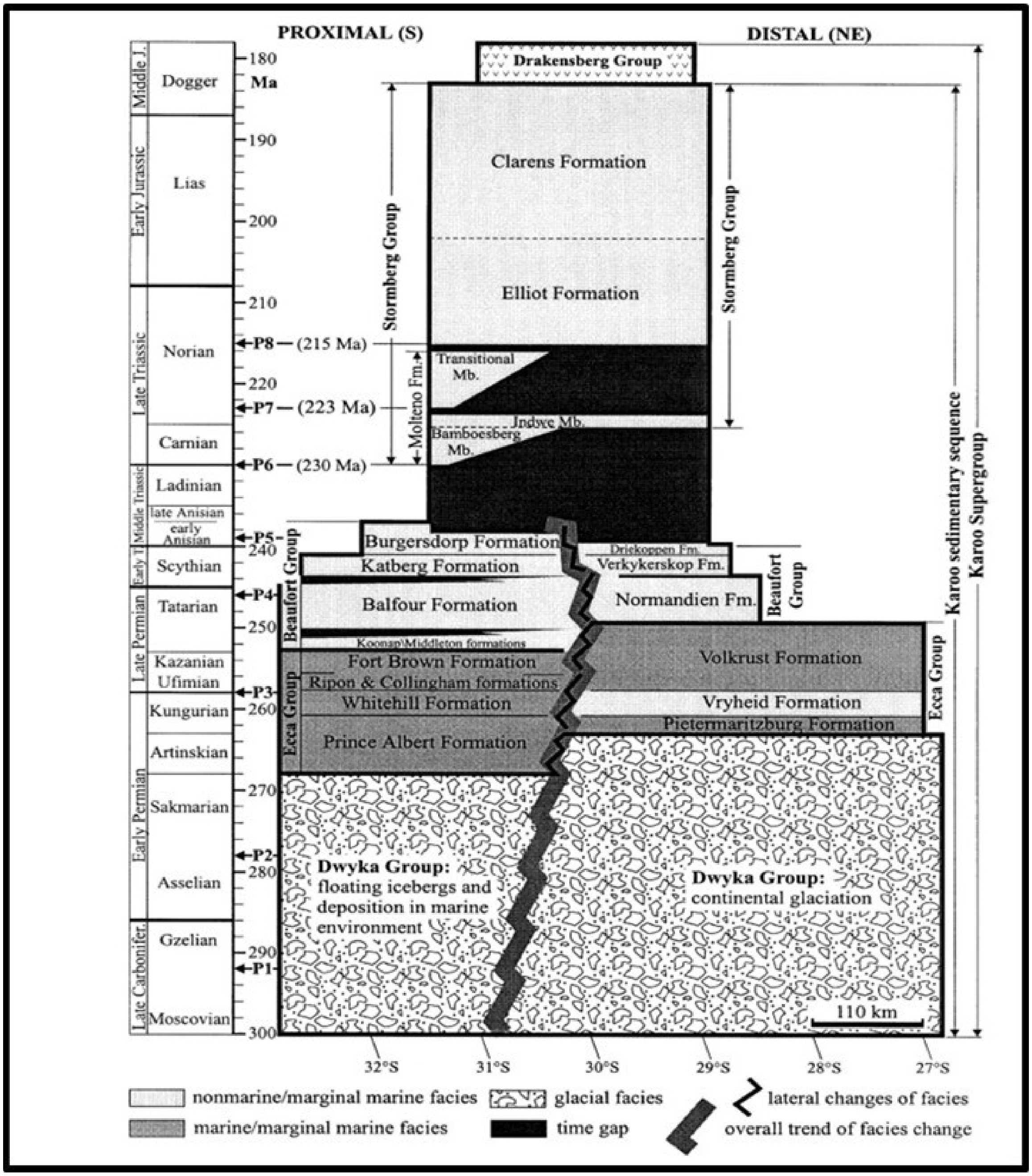

Figure 3. Lithostratigraphic units of the Karoo Supergroup, including Cape Fold Belt tectonic paroxysms P1-P8 (modified by [13] from [24-25]).

The upper Ecca Group was deposited in the Main Karoo Basin during the Permo-Triassic period; this was followed by the deposition of alluvial, fluvial, and lacustrine sediments of the overlying Beaufort Group and Upper Stormberg Group which is capped by desert/aeolian sediments [14,20]. Sedimentation within the basin was halted by continental flood basalts of the Drakensberg Group [12]. The Drakensberg flood basalts signalled the break-up of the ancient supercontinent of Gondwana [13]. The Karoo Supergroup successions were subjected to low-grade metamorphism and deformational events which were closely associated with the formation of the proximal Cape Fold Belt and its orogenic events [12]. Sedimentation within the Main Karoo Basin was mainly controlled by climatic transitions and tectonism, moreover, the sedimentation extended across Gondwana and was put to a halt when the supercontinent disassembled [14].

According to [21], the lowermost Dwyka Group is composed of seven lithofacies which are namely: basal massive diamictites, followed by stratified diamictites and carbonate-rich diamictites which are succeeded by conglomerate facies, sandstones, mudrocks with drop-stone successions and lastly, mudrock facies. The overlying Ecca Group is mainly dominated by clastic deposits such as sandstones, siltstones, mudstones, minor conglomerates, and coal seams in some regions [14]. Overall, the Ecca Group is representative of an Early to Mid-Permian succession of marine, continental, and fluvio deltaic clastic sediments which include coal seams, sandstones which are noted aquifers together with petroleum oil-related shales and organic carbon rich shales. The margin between the Ecca Group and the overlying Beaufort Group is indicative of a transition from deltaic settings to fluvial and lacustrine conditions [14,20,22]. Beaufort Group is characterized by dominant mudstones and siltstones with subordinate lenticular and tabular sandstones [14].

The upper Stormberg Group represents a period of increasingly hot and dry climatic conditions culminating in desert conditions [12]. The stratigraphic sequence begins with the basal Molteno Formation which is dominated by tabular sheets of medium to coarse grained sandstones representative of braided systems [13]. The overlying succession is the fluvial deposits of the Elliot Formation which are identified as red beds and exhibit a playa nature [23]. Finally, the end of Stormberg times is marked by the aeolian deposits of the Clarens Formation which reflect true desert settings [18]. The uppermost Drakensberg Group is the only igneous succession within the Karoo Supergroup which followed the Cape Fold Belt orogeny and is also characterized by extensional settings associated with the break-up of Gondwana [13].

3. Materials and methods

A geological investigation was carried out through core logging of the Karoo rock sequence, mainly the Ecca Group rock units that are intersected by borehole KZF-1. This was performed at the Council for Geosciences core library, which is situated in Pretoria, South Africa. Core logging was conducted in order to evaluate the lithology and establish the lithostratigraphic sequence of the Ecca Group in borehole KZF-1 (Figure 4).

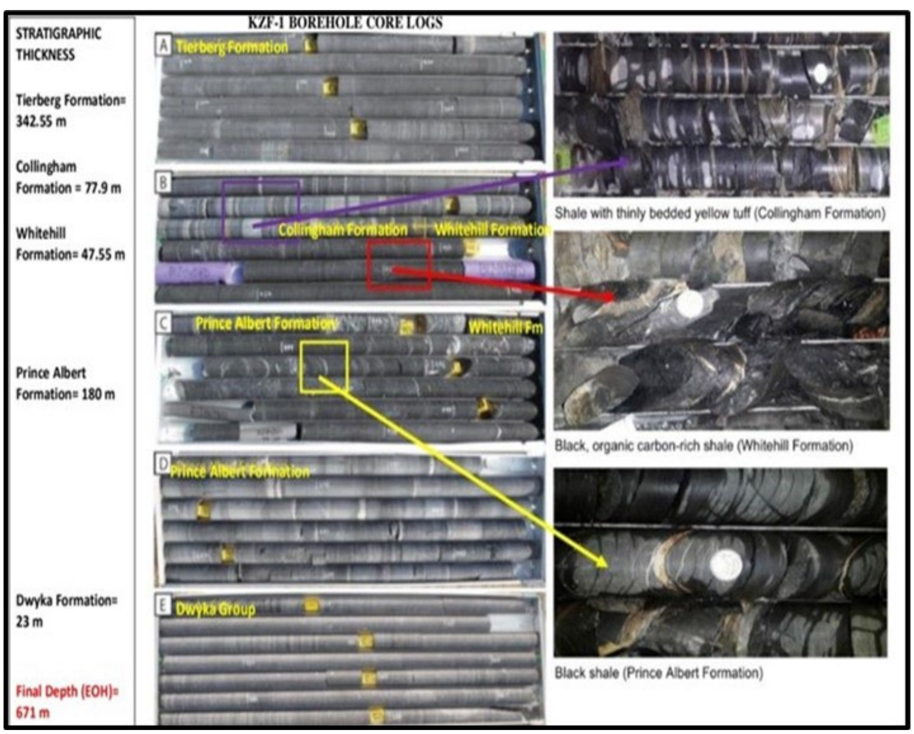

Figure 4. Image showing KZF-1 borehole drill cores at the Council for Geosciences core library, situated in Pretoria, South Africa.

Thirteen Ecca Group shale samples from the KZF-1 drill cores were collected. The samples were then subjected to petrographic studies and organic geochemical evaluation. At least three thin sections were prepared per sample and the thin sections were analysed using a petrographic microscope. X-ray diffraction analysis (XRD) was also performed to determine mineralogical composition of the shales. For organic geochemical evaluation, total organic carbon analysis and rock-eval pyrolysis were performed. To determine the TOC, samples were pulverized and filtered through a 60-mesh sieve. The samples were then de-mineralized by adding 10% hydrochloric acid and the acid was later filtered. This was then followed by drying the samples in an oven for 24 hours at 60°C, the dry weight of the samples was recorded once they dried up. The samples were later placed in a muffle furnace for combustion at 650°C. Ultimately, the samples were allowed to cool off and weighed again to determine the TOC. Samples with TOC content above 0.5 wt% were then taken for rock-eval pyrolysis whereby they were subjected to a specialized temperature program and those with a lower content were disregarded for further analysis. The rock-eval pyrolysis included heating the samples in order to determine fundamental variables at different temperature peaks, namely: S_1 which is indicative of the magnitude of hydrocarbons already contained within the source rock and hydrocarbons thermally extracted at temperatures below 300°C. S_2 which represents the remaining hydrocarbon potential and hydrocarbons subjected to temperatures between 300 and 650°C at the pace of 25°C /min (pyrolysis results in hydrogen generation at the temperature interval). Finally, S_3 which indicates the magnitude of organic carbon dioxide formed during thermal breakdown of kerogen at temperature interval of 300 and 390°C. The first peak was generated by heating the samples at 300°C for 3 minutes. Flame ionization detector was used to measure the first two peaks and the last peak was measured using thermal conductivity detector. The Tmax which is another important parameter that mainly defines maturity of the samples was determined using the rock-eval instrument. The variables and total organic carbon content results were collectively used to calculate the hydrogen or hydrocarbon potential (SP), hydrogen index (HI), oxygen index (OI) and production index (PI). The calculated variables were then used to plot binary plots which were used to interpret the organic matter characterization and hydrocarbon source rock potential of the investigated shale samples.

4. Results

4.1. Stratigraphy

Borehole KZF-1 intersects 671 m of the Karoo rock units. The 671 m thick Karoo Supergroup strata consist of 342 m thick rock units of the Tierberg Formation, underlain by roughly 80 m thick succession of the Collingham Formation, 47 m stratigraphic thickness of the Whitehill Formation, and 180 m thick rock units which form the Prince Albert Formation. Moreover, the Ecca Group strata in borehole KZF-1 is underlain by 23 m thick rock sequence of the Dwyka Formation. The uppermost Tierberg Formation is primarily composed of dark grey to black shales which are interbedded with light grey shales. The rock sequence also includes greyish shale rhythmites, sandstones with occasional soft sediment deformation and minor tuff horizons. Pyrite and calcite veins are also common, and the mineralisation also occurs along surface planes. Very few fractures are present and in places are infilled with pyrite. The underlying Collingham Formation is made up of dominant grey to black shales and subordinate breccias and sandstones. Tuff is also common, together with pyrite and calcite veins. The Collingham Formation is succeeded by the Whitehill Formation, which is characterized by dominant black carbonaceous shales. Occasional dark greyish to greyish shales also occur and minor breccia. The rock sequence is associated with angular quartz fragments, quartz veins, disseminated pyrite and calcite veins. The lowermost Ecca formation is the Prince Albert Formation which is marked by the presence of light to dark grey shales, black shales which are carbonaceous in places, minor breccia, and sandstones. Rhythmites that are defined by interbeds of black carbonaceous shales, black and grey shales are also present. Tuffaceous horizons are also common in the Prince Albert sequence and fractures which are more common in the basal rock units. The fracture planes have occasional traces of pyrite, additionally, the fractures are infilled with pyrite in places and artesian water. The stratigraphic succession is also associated with calcite and pyrite on bedding planes and some veins. The Karoo sequence also incorporates minor carbonate concretions in places. Lastly, the basal Dwyka Formation is primarily composed of greyish tillites and some tuff beds. The detailed lithostratigraphic sequence of the Karoo rock units that are intersected by borehole KZF-1 is shown in Figure 5.

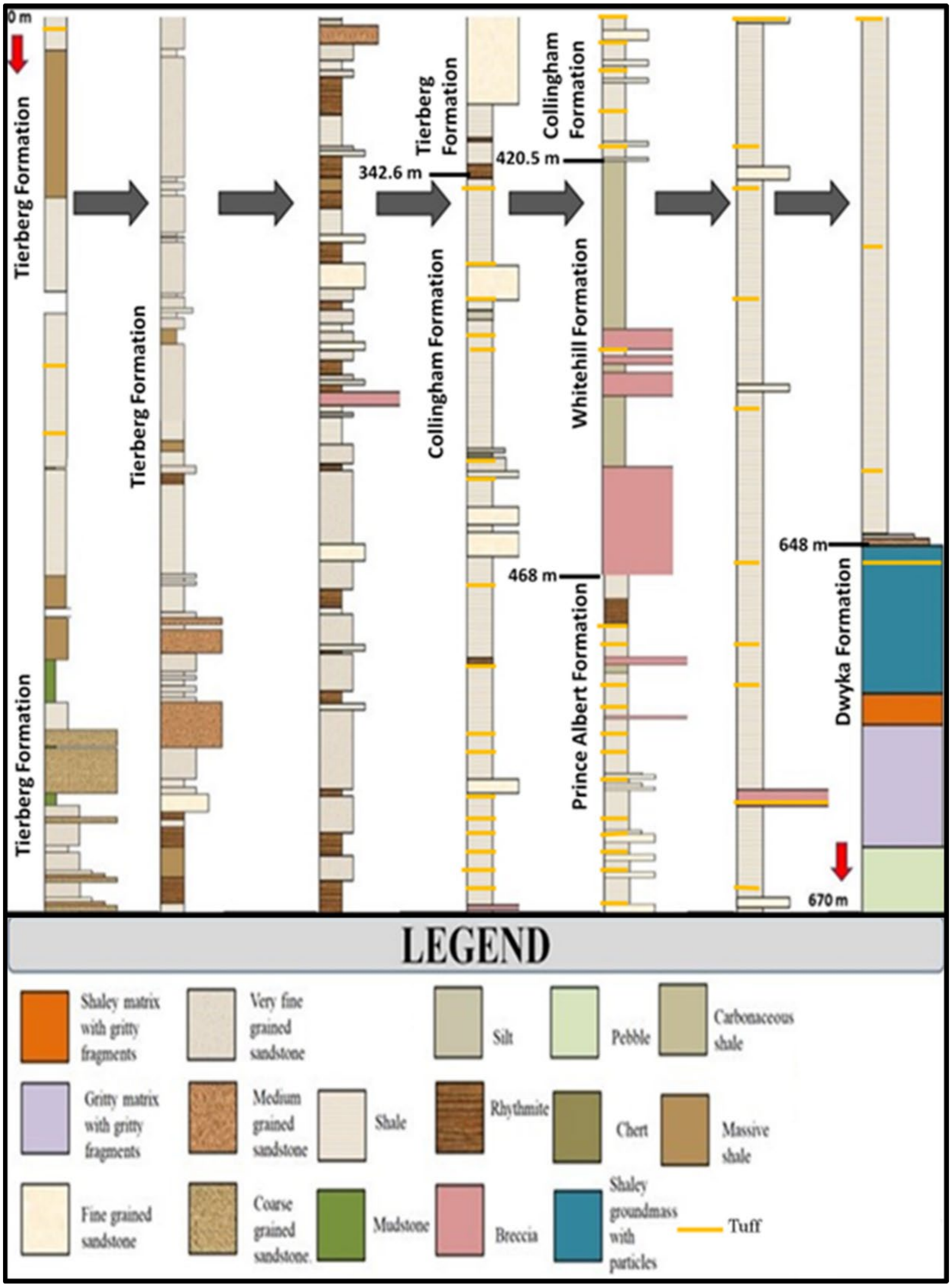

Figure 5. Lithostratigraphic column of the Karoo strata intersected in borehole KZF-1.

4.2. Mineralogy

The XRD results show that the studied shale samples (Figure 6) are composed of quartz, clay minerals, mica, plagioclase, minor contents of pyrite and dolomite, and traces of heavy minerals such as hematite, zeolite, zircon and garnet (Table 1). The detected clay minerals include smectite, kaolinite, chlorite, illite, sericite and microcline.

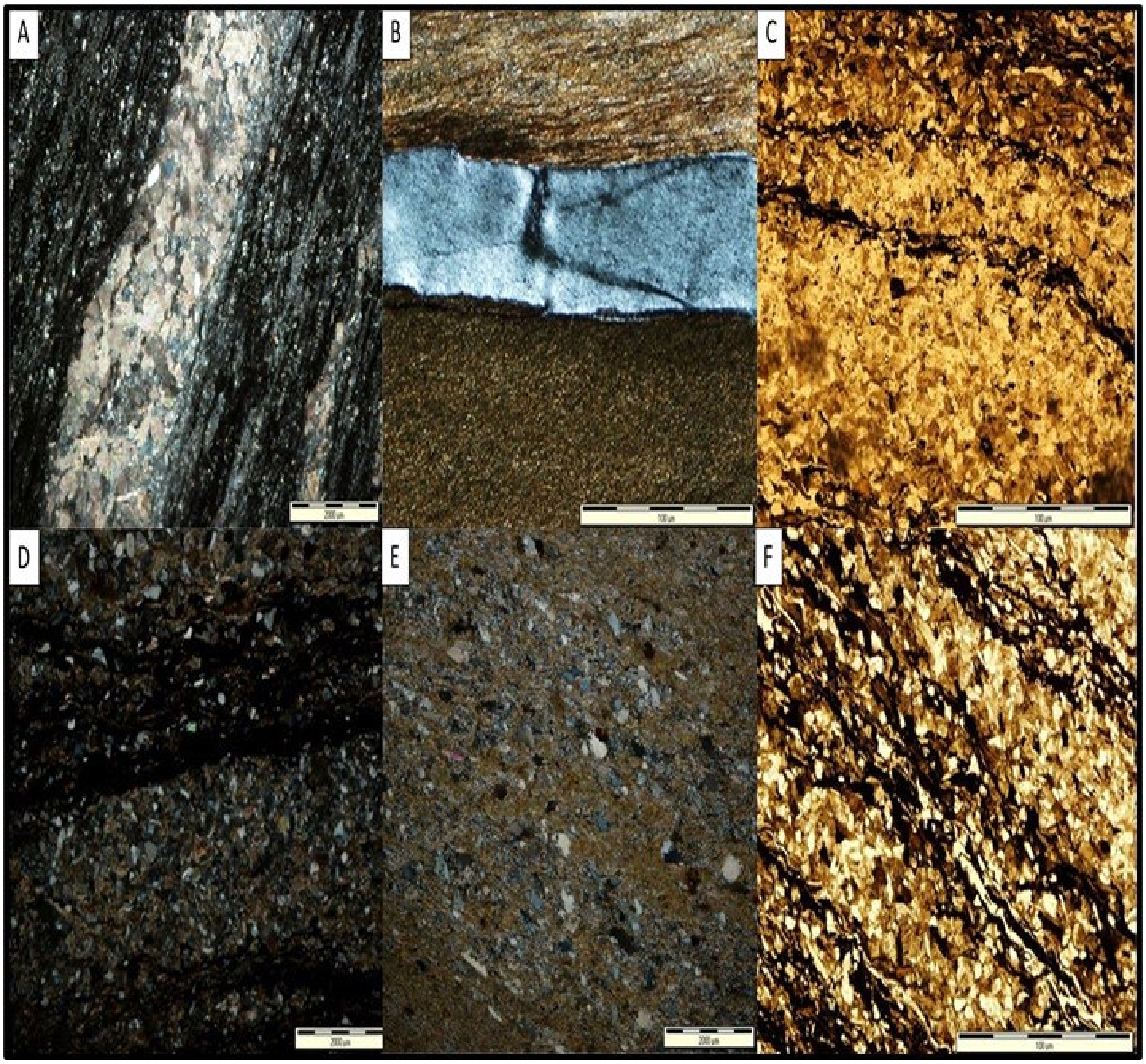

Figure 6. Photomicrographs showing: A. Carbonaceous shale dominated by organic matter, clay minerals and some quartz grains. B. Silty shale with quartz vein, pyrite, and organic matter. C. Carbonaceous shale characterized by pyrite and hematite staining. D. Carbonaceous siltstone with quartz grains that are primarily supported by a clay rich matrix. E. Siltstone with angular to sub-rounded quartz grains embedded within a clay rich matrix. F. Mudrock characterized by pyrite and quartz veins, hematite staining, and rounded to sub-rounded quartz grains within clay matrix.

Table 1. XRD data showing the detected minerals within the investigated shale samples.

Depth (m)	Formation	Plagioclase (%)	Microcline (%)	Quartz (%)	Kaolinite (%)	Chlorite (%)	Mica (%)	Smectite (%)	Illite (%)	Sericite (%)	Hematite (%)	Pyrite (%)	Dolomite (%)	Garnet (%)	Zircon (%)	Zeolite (%)
164	Ripon	20	3	38	7	3	5	17	6	-	-	-	-	-	tc	tc
231	Ripon	16	tc	21	30	10	8	12	2	-	-	tc	-	tc	tc	tc
276	Ripon	17	tc	18	28	9	6	18	3	-	-	-	-	tc	-	-
280	Ripon	12	tc	25	26	11	4	20	1	-	-	-	-	tc	-	tc
299	Ripon	10	2	32	25	14	17	tc	-	-	-	-	-	-	-	-
323	Ripon	10	tc	36	18	9	26	-	-	-	-	-	-	tc	-	-
377	Collingham	12	4	32	13	10	5	23	-	-	-	tc	-	tc	tc	-
386	Collingham	13	-	30	11	13	4	28	-	-	-	tc	-	tc	-	-
425	Whitehill	14	-	23	16	7	17	15	-	tc	tc	7	-	-	-	-
431	Whitehill	19	-	30	17	10	13	6	-	tc	-	4	-	-	-	-
438	Whitehill	12	-	32	26	-	2	tc	-	tc	-	5	22	-	-	-
518	Prince Albert	11	tc	26	12	9	3	33	-	6	tc	tc	-	tc	tc	-
568	Prince Albert	10	2	25	18	6	3	30	-	5	tc	tc	-	tc	tc	-

Note: tc in the table represents minerals detected in traces and dash (-) represents minerals not detected.

4.4. Organic geochemistry

The TOC content analyses and rock-eval pyrolysis yielded results that are shown in Table 2. The results were collectively used to calculate fundamental variables and create binary plots for further organic geochemical evaluation in order to define the hydrocarbon potential of the investigated shale samples.

Table 2. Rock-eval pyrolysis and TOC content results.

Formation	S1 - (mg/g)	S2 - (mg/g)	Tmax(°C)	S3 - (mg/g)	TOC (%)	HI	OI	S1/S2	S1/TOC	PG=(S1+S2)	PI= (S1/(S1+S2)
Tieberg	0,06	0,18	604	0,61	1,5	12	41	0,33	0,04	0,24	0,25
Tieberg	0,08	0,18	603	0,55	1,41	13	39	0,44	0,06	0,26	0,31
Tieberg	0,05	0,12	607	0,59	0,78	15	76	0,42	0,06	0,17	0,29
Tieberg	0,08	0,22	604	0,84	1,97	11	43	0,36	0,04	0,30	0,27
Tieberg	0,08	0,19	605	1,38	1,98	10	70	0,42	0,04	0,27	0,30
Tieberg	0,06	0,23	604	1,13	2,77	8	41	0,26	0,02	0,29	0,21
Tieberg	0,05	0,16	605	0,62	2,07	8	30	0,31	0,02	0,21	0,24
Tieberg	0,05	0,14	606	0,45	2,3	6	20	0,36	0,02	0,19	0,26
Tieberg	0,07	0,14	605	0,56	2,77	5	20	0,50	0,03	0,21	0,33
Tieberg	0,08	0,19	605	0,8	2,45	8	33	0,42	0,03	0,27	0,30
Collingham	0,05	0,14	605	0,12	2,13	7	6	0,36	0,02	0,19	0,26
Collingham	0,04	0,1	604	0,16	1,63	6	10	0,40	0,02	0,14	0,29
Collingham	0,04	0,09	602	0,65	1,1	8	59	0,44	0,04	0,13	0,31
Whitehill	0,08	0,12	388	0,2	5,46	2	4	0,67	0,01	0,20	0,40
Whitehill	0,08	0,1	322	0,17	4,37	2	4	0,80	0,02	0,18	0,44
Whitehill	0,05	0,13	396	0,1	5,33	2	2	0,38	0,01	0,18	0,28
Whitehill	0,06	0,21	607	0,25	4,06	5	6	0,29	0,01	0,27	0,22
Whitehill	0,06	0,17	392	0,17	4,06	4	4	0,35	0,01	0,23	0,26
Whitehill	0,07	0,12	382	0,1	5,11	2	2	0,58	0,01	0,19	0,37
Whitehill	0,04	0,13	605	0,14	3,92	3	4	0,31	0,01	0,17	0,24
Prince Albert	0,08	0,36	392	0,23	5,76	6	4	0,22	0,01	0,44	0,18
Prince Albert	0,03	0,09	488	0,05	0,22	41	23	0,33	0,14	0,12	0,25
Prince Albert	0,02	0,08	491	0,1	0,4	20	25	0,25	0,05	0,10	0,20
Prince Albert	0,03	0,07	503	0,06	0,3	23	20	0,43	0,10	0,10	0,30
Prince Albert	0,05	0,13	344	0,06	0,71	18	8	0,38	0,07	0,18	0,28
Prince Albert	0,06	0,16	304	0,09	1,93	8	5	0,38	0,03	0,22	0,27

5. Interpretations and discussion

5.1. Petrography and mineralogy

The XRD data shows that major minerals are clay mineral, smectite (7-32%) and quartz (25-31%). Considerable quantities of plagioclase feldspar (10-15%), mica (3-11%), including other clay minerals kaolinite (12-23%) and chlorite (5-12%) were also detected in the shales. Subordinate amounts of microcline (0.8-2%) were noted, however, the mineral is absent in the Whitehill Formation. Minor content of mica-type clay minerals illite and sericite range between 2-5.5% in the Rippon and Prince Albert formations. Traces of sericite and pyrite mineralisation occur within the Whitehill Formation. Dolomite is also present and is associated with carbonate concretions. Some of the studied samples contain traces of heavy minerals which include zircon, hematite, garnet, and zeolite. The quartz grains are mostly angular, subrounded and rounded. Quartz veins were also identified and some minor mica minerals. The shale samples are mostly characterized by mineral grains that are embedded within a clay rich matrix.

5.2. Organic geochemistry

5.2.1. Total organic carbon (TOC) content

The TOC content can be applied to deduce some information on the source rock potential as it determines the quantity of organic matter, which is indicative of the hydrocarbon generation potential of the investigated source rocks.The criteria for the evaluation of hydrocarbon source rock potential based on TOC content (Table 3) was suggested by [26]. Based on the criteria, the Tierberg Formation shale samples are likely to present good to very good quality source rocks as their TOC content ranges between 0.78- 2.77 wt%. Given the results, the Tierberg Formation is associated with fairly low TOC values. Studies conducted by [9] also suggested low TOC values for the Tierberg (0.44-2.54 wt%) and Collingham (0.91-2.87 wt%) formations. On the basis of this study and application of the aforementioned criteria, TOC content of the Collingham Formation classifies the investigated shales from the formation as potentially good quality source rocks. The content range is 1.1- 2.13 wt% and is similarly low. TOC content results for Whitehill Formation range between 3.92 and 5.46 wt%, this implies that the source rock quality is likely to be very good to excellent. TOC estimations made by [27] indicate that the Whitehill Formation contains TOC average of 4.35 wt%. The results obtained from this study infer that the average TOC of the formation is 4.62 wt% and the content is notably higher than all Ecca formations. The individual results are nearly the same. The Prince Albert Formation TOC content is between 0.22 and 5.76 wt% and based on the criteria the source rock quality is highly variable, but mostly poor. However, studies conducted by [10] revealed that the TOC content for the Prince Albert Formation ranges between 0.2 to 4.9 wt% which is a minor difference. The minor difference may be due to different quantitative analyses. According to [9], the TOC content contained within the Prince Albert Formation is highly variable and varies between 0.47 to 3.64 wt%. The three separate results are slightly different; however, they all indicate high variability of TOC content for the Prince Albert samples in borehole KZF-1.

Table 3. Criteria for hydrocarbon source rock quality based on TOC content (after [26]).

Quality	TOC (wt. %)	S_1 (mg HC/ g rock)	S_2 (mg HC/g rock)	$S_1 + S_2$ (mg HC/g rock)
Poor	< 0.5	< 0.5	< 2.5	< 2
Fair	0.5 - 1	0.5 - 1	2.5 - 5	2 - 5
Good	1 - 2	1 - 2	5 - 10	5 - 10
Very Good	2 - 4	2- 4	10 - 20	> 10
Excellent	> 4	> 4	> 20	-

5.2.2. Organic matter type and quality

The characterization of organic matter type (kerogen type) is fundamental in hydrocarbon potential evaluation studies, this is simply because the organic matter type closely influences the hydrocarbon products that can be generated by source rocks [28]. Hence, comprehension of organic matter characterization can be used to predict the hydrocarbon products of the assessed shale samples.

The binary plot of hydrogen index against oxygen index (Figure 7) which applied the framework that was suggested by [29] indicate that the organic matter within the investigated shale samples is mostly classified as kerogen type III and a few samples from Tierberg and Collingham formations are indicative of kerogen type IV. A different framework proposed by [29] was applied using the same parameters for the binary plot in Figure 8 which characterized the organic matter as only kerogen type III. Additionally, the binary plot also reflects that the hydrocarbon product that may be generated by the samples is gas. Another important information that can be inferred from Figure 7 and 8 is that the shale samples exhibit low hydrogen index (HI) values. Studies conducted by [9] similarly suggest that the Ecca Group shales in borehole KZF-1 are associated with low HI values. The low HI values imply that most of the organic matter that is contained within the shales is not hydrogen bound and the kerogen is over-mature or 'dead'. Binary plot of the remaining hydrocarbon potential (S_2) and total organic carbon (Figure 9) on the background proposed by [30] indicate that the studied shale samples contain kerogen type IV, and the source rocks are likely to generate dry gas. However, the plot also indicates that the samples have low remaining hydrocarbon potential. The poor remaining hydrocarbon generation potential was most likely influenced by the associated tectonic episodes which promoted over-maturity of the shales. Collectively, the figures mainly suggest that shales are representative of kerogen type III and IV. This implies that the samples are of poor or low kerogen quality and are likely to present poor source rock quality. Moreover, source rocks associated with kerogen type III and IV are likely to generate gas and this is supported by Figure 8 and 9. The results also correspond with those obtained by [9], wherein the organic matter in borehole KZF-1 was also identified as kerogen type III and IV.

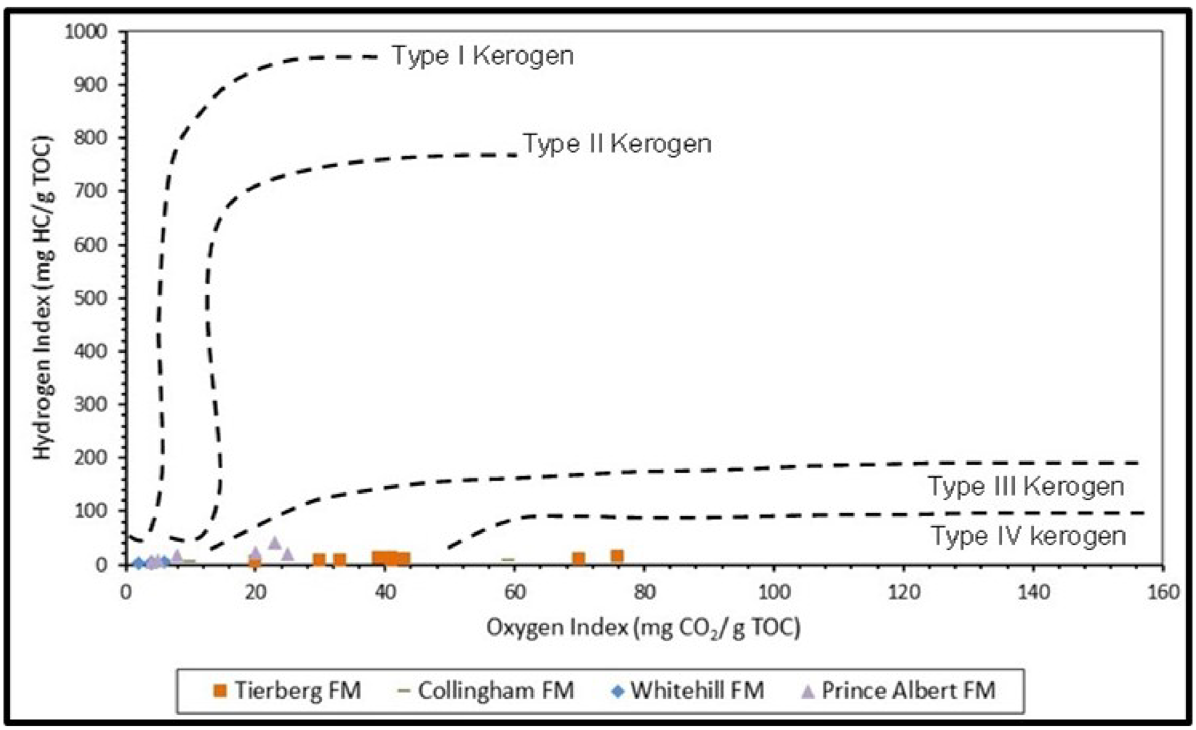

Figure 7. Hydrogen Index against Oxygen Index plot for kerogen type characterization of the carbonaceous shales of the Ecca Group in borehole KZF-1 (Framework after [29]). Hydrogen index (HI) is given by the formula: HI= $\left(\frac{S_2}{TOC}\right) \times 100$, the variable is indicative of hydrogen content within kerogen and higher values are associated with oil prone source rocks [31]. Oxygen index (OI) is defined by OI= $\left(\frac{S_3}{TOC}\right) \times 100$ and it represents the oxygen shield within the kerogen, additionally, it can be used to deduce important information on the maturation path of the organic matter [31].

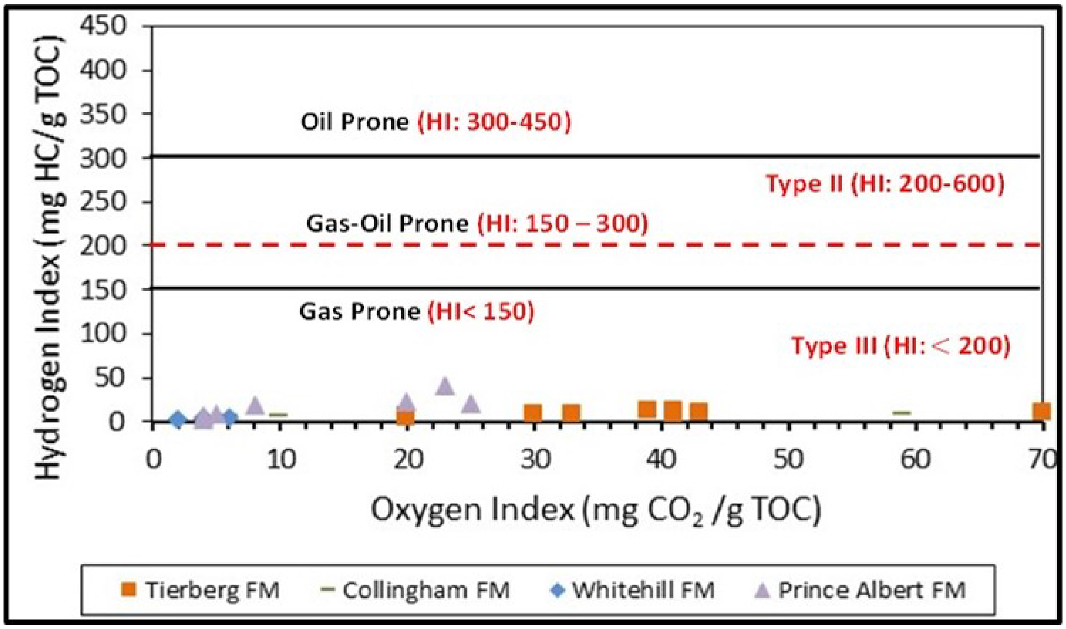

Figure 8. Hydrogen Index against Oxygen Index graphical plot indicative of the kerogen type and hydrocarbon product of the carbonaceous Ecca Group shales in borehole KZF-1 (framework after [29]).

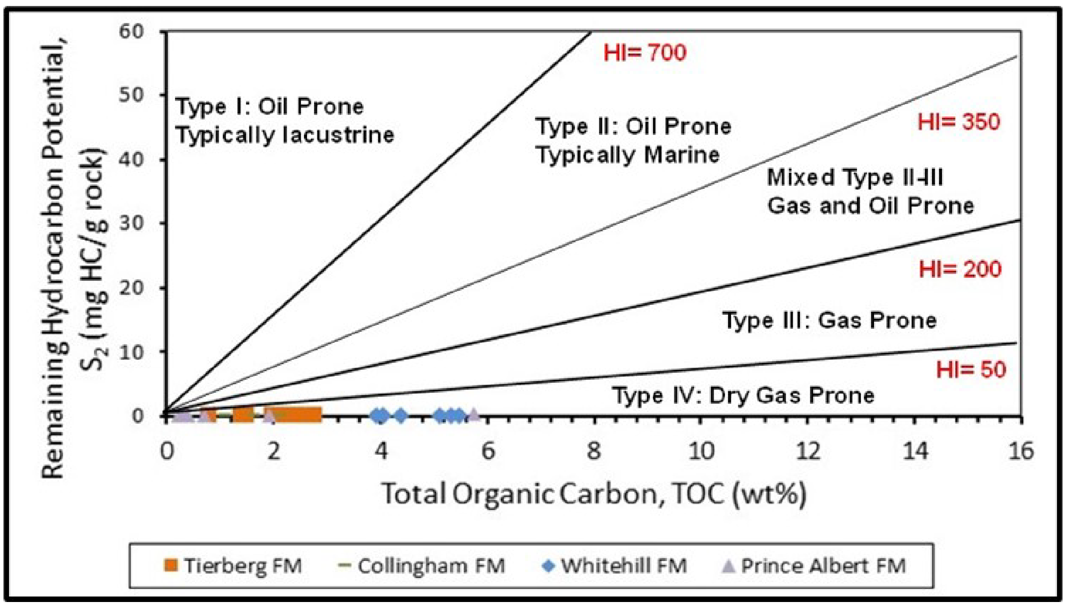

Figure 9. Remaining hydrocarbon potential (S_2) against TOC binary plot indicating the kerogen type and the associated hydrocarbon product of the carbonaceous Ecca Group shales in borehole KZF-1 (framework [30]).

According to [32], the Tmax that is obtained during pyrolysis is indicative of the maximum heat energy required to break any kerogen chemical bonds which plays a vital role in the generation of hydrocarbon products. Source rocks that are mature need high energy to break kerogen bonds and this consequently promotes hydrocarbon generation [33]. Binary plot of hydrogen index against Tmax (Figure 10) on frame-work that was proposed by [36] shows that a few shale samples from the Whitehill and Prince Albert formations are immature. This implies that the samples have not yet generated any hydrocarbons. Given the high TOC content of the Whitehill shales, thermal maturity of the rocks may promote significant hydrocarbon generation and prompt their classification as potential source rocks. Prince Albert shales may also generate hydrocarbons, however the rocks are likely to show poor source rock potential as they are not enriched in organic matter. Most of the Ecca Group shales in KZF-1 are highly over-mature and have already generated petroleum gas. This implies that they have already reached their maximum hydrocarbon generation potential and their remaining hydrocarbon potential is extremely low. Given the highly over-mature nature of the shales, their organic matter is of poor quality.

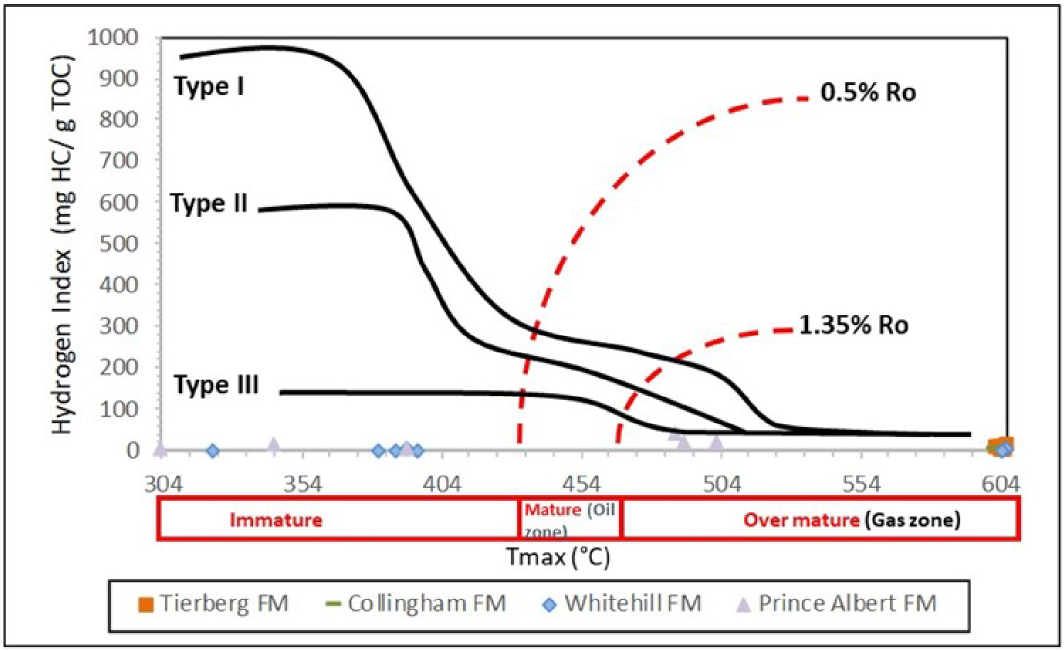

Figure 10. Hydrogen index VS Tmax graphical representation indicating the maturity as well as the hydrocarbon products of the shale samples from Prince Albert and Whitehill formations in borehole KZF-1 (framework after [34]).

5.2.3. Source rock potential

According to [35], the total organic carbon content cannot be solely applied to determine the source rock potential as different organic matter may exhibit the same TOC quantity. Based on the criteria proposed in Table 3, S_1, S_2 , and $S_1 + S_2$ can also be applied to predict the source rock potential. Given the results shown in Table 2, the proposed assessment criteria classify the source rock quality of the investigated shales as poor.

The binary plot of hydrogen index and total organic carbon (Figure 11) which is displayed on the frame-work proposed by [26] indicates that the investigated shales are gas prone. Based on Figure 11, shale samples from the Whitehill Formation show excellent source rock potential. The source rock potential of samples from Collingham Formation ranges between good and very good. On the other hand, Prince Albert Formation is indicative of mostly poor source rocks and very few samples exhibit fair, good or excellent potential. Tierberg Formation source rock potential varies from fair to very good, but mostly very good. Binary plot of genetic potential and total organic carbon (Figure 12) on the frame-work that was proposed by [26] shows results that are comparable with Figure 11. Overall, Whitehill Formation shale samples exhibit excellent source rock potential. Collingham and Tierberg formations are mostly indicative of good source rock potential and the Prince Albert Formation exhibit poor potential. The poor source rock potential is most likely associated with the over-mature nature that is supported by Figure 10. Collectively, all frameworks proposed by [26,28-29,33], specifically Figure 8-12 suggest that the Ecca Group shales show potential for petroleum gas generation. However, given their over-maturity the associated shale gas generation potential is slim.

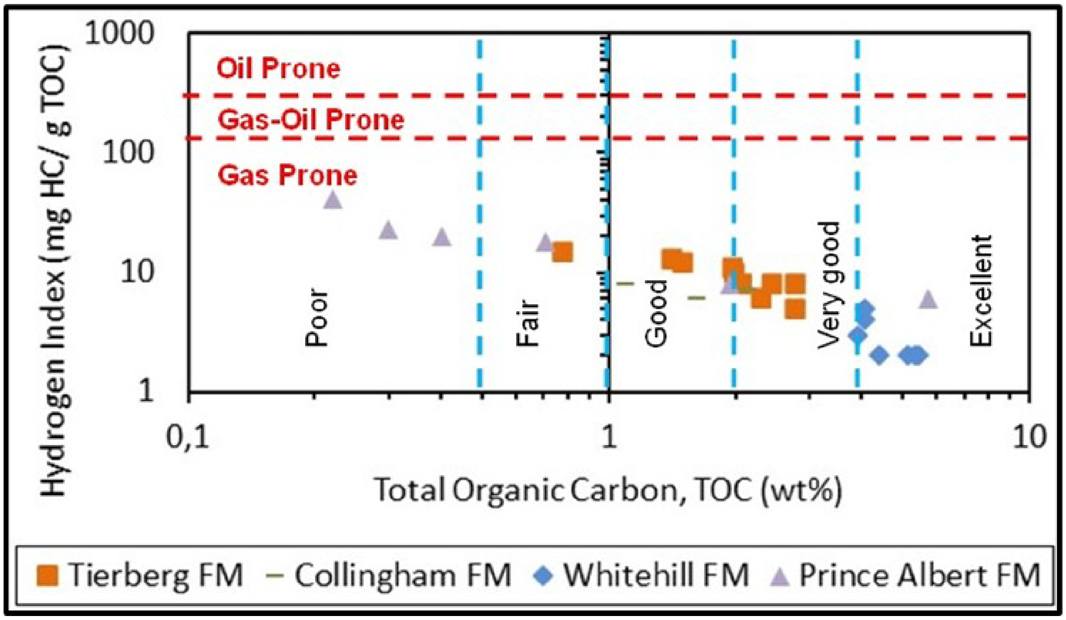

Figure 11. Hydrogen Index VS TOC binary plot representing the source rock potential and the associated hydrocarbon products that could possibly be generated by the carbonaceous shales of the Ecca Group in borehole KZF-1 (framework after [26]).

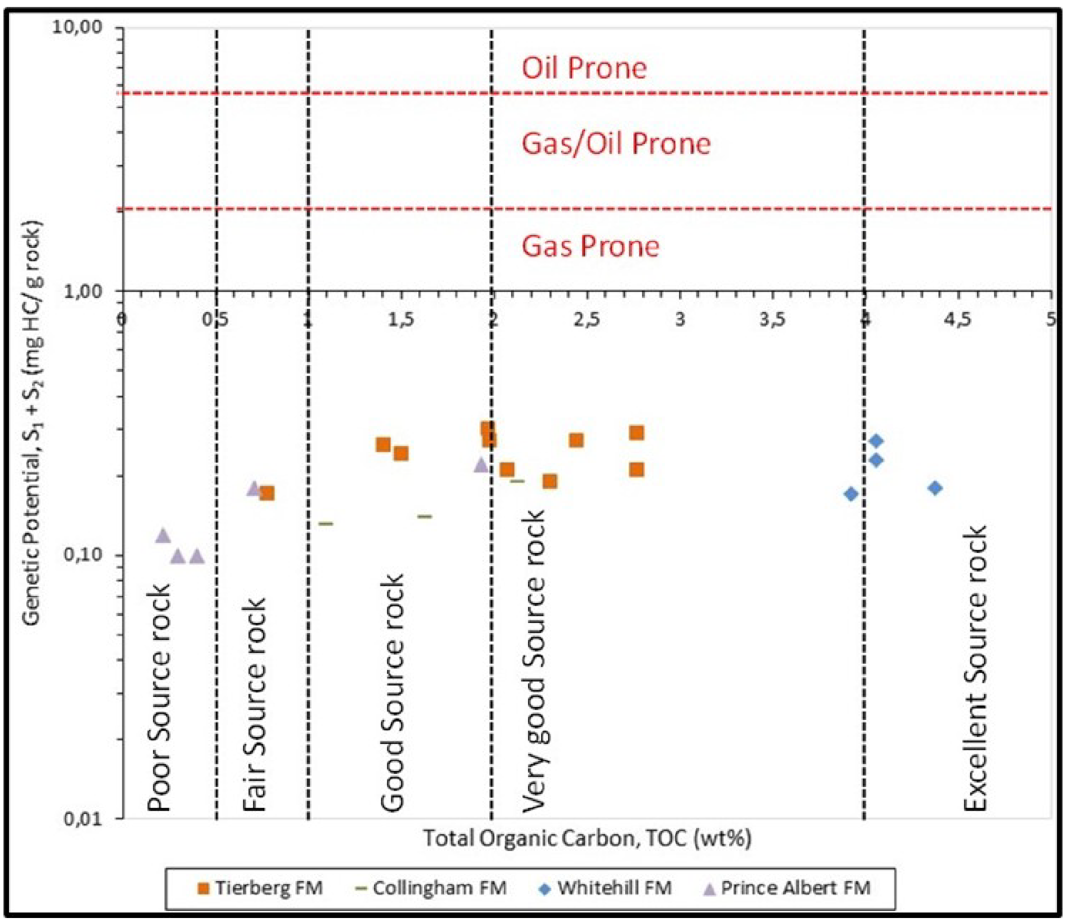

Figure 12. Genetic potential VS TOC binary plot showing the source rock potential of the carbonaceous shales of the Ecca Group in borehole KZF-1 (framework after [26]).

On the contrary, binary plot of the hydrogen index and total organic carbon (Figure 13) on the framework proposed by [36] show that a few shale samples from the Prince Albert and Tierberg formations are non-source rocks which means they cannot generate any hydrocarbons; and other studied samples from the Ecca formations contain gas and oil.

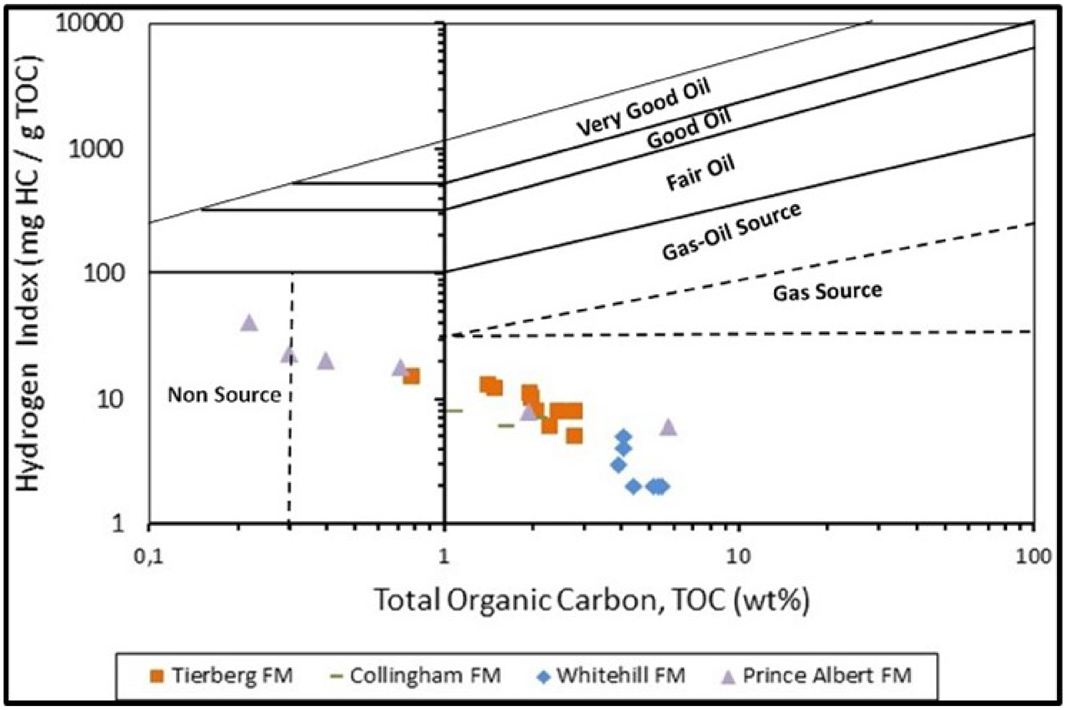

Figure 13. Hydrogen index against TOC graphical representation indicating the hydrocarbon potential of the carbonaceous Ecca Group shales in borehole KZF-1 (framework after [36]).

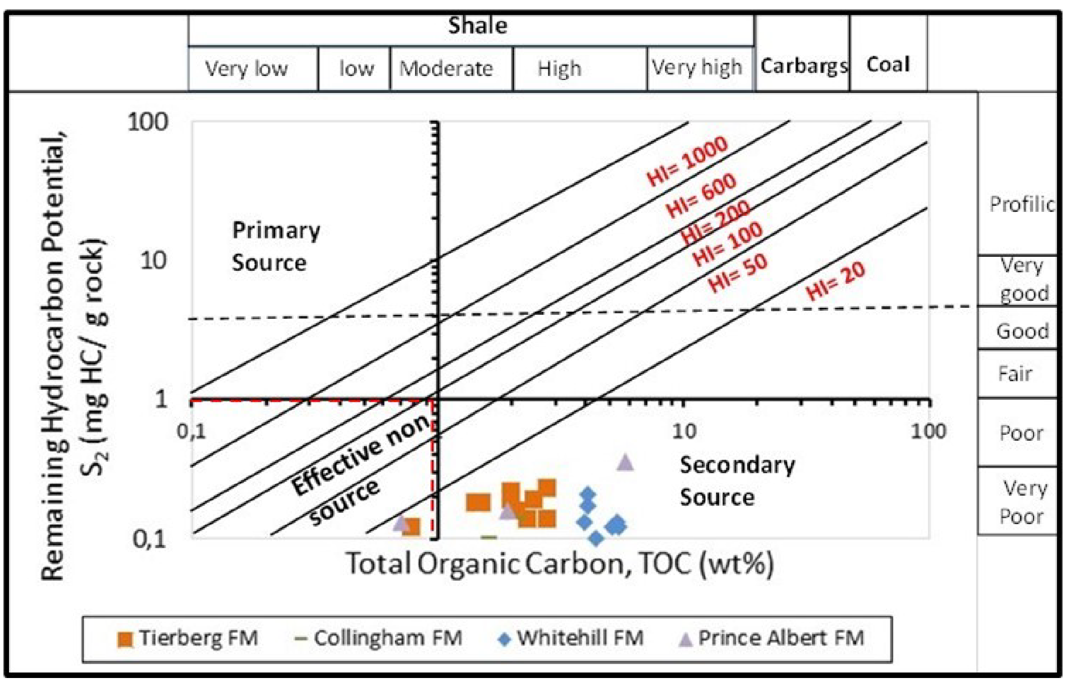

Figure 14. The remaining hydrocarbon potential (S_2) against TOC graphical plot showing the source rock classification of carbonaceous Ecca Group shales in borehole KZF-1 (framework after [37]).

For further source rock characterization, binary plot of the remaining hydrocarbon potential (S_2) against TOC (Figure 14) on the background proposed by [37] indicates that the studied carbonaceous shales are secondary source rocks. Additionally, very few investigated samples from the Prince Albert and Tierberg formations are effective non-source rocks. Binary plot of S_1 and TOC (Figure 15) reveals that the studied carbonaceous Ecca Group shales are associated with autochthonous/indigenous accumulation of the hydrocarbons. This implies that the hydrocarbon products were not derived from another source, but their generation occurred in-situ.

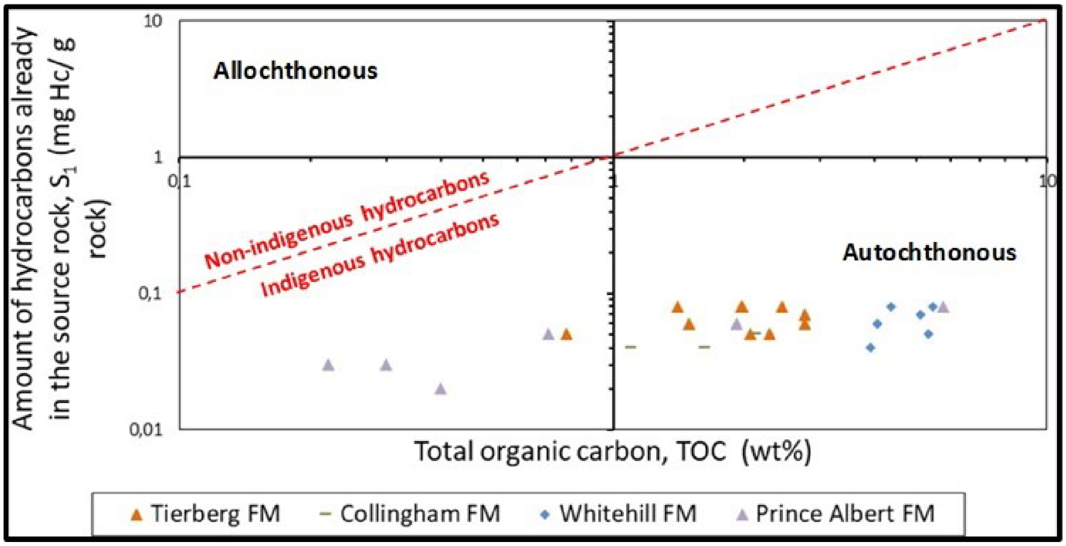

Figure 15. The graphical representation of the amount of hydrocarbon already in the source rock (S_1) against TOC showing the hydrocarbons origin of the carbonaceous Ecca Group shales in borehole KZF-1 (framework after [36]).

6. Conclusions

The studied Ecca Group shales in borehole KZF-1 may represent prominent source rocks and thus, show potential to elevate the existing petroleum resources of the Main Karoo Basin. The Karoo stratigraphic units that are intersected by the borehole are mainly dominated by shales that are carbonaceous and rhythmically bedded in places, sandstones and minor silt, breccia and tillites. Tuffaceous horizons are also common. The shales are predominantly composed of smectite and quartz. Other clay minerals such as chlorite, kaolinite, minor quantities of illite, sericite and microcline also make up the mineralogical composition, including plagioclase feldspar. The samples also contain traces of pyrite and heavy minerals such as zircon, hematite, zeolite, and garnet. The samples are defined by low HI index values that are below 50 mg HC/ g TOC. This implies that most of the organic matter that contained within the shales is not bound to hydrogen. The organic geochemistry of the shales is also mostly defined by TOC content that is above 1 wt% and a good proportion of the rocks show good hydrocarbon generation potential. Organic geochemistry further revealed that the organic matter contained within the studied samples is kerogen type III and IV. The associated kerogen types are identified as low-quality kerogen. The Whitehill Formation possess the highest organic carbon content and shows the best source rock potential. Moreover, the samples are associated with Tmax range of 302-607^{o}C. Based on the Tmax, a few samples are immature and have not generated any hydrocarbons yet. Majority of the samples are over-mature and associated with poor quality organic matter. The studied carbonaceous shales are dry gas and oil prone, however non-source rocks mainly occur in the Tierberg and Prince Albert formations. In essence, the carbonaceous shales of the Ecca Group in borehole KZF-1 represent over-mature hydrocarbon source rocks with low remaining hydrocarbon generation potential. Additionally, the investigated shales represent secondary source rocks associated with in-situ hydrocarbon generation.

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