

Article

# Diagenesis and Reservoir Properties of the Permian Ecca Group Sandstones and Mudrocks in the Eastern Cape Province, South Africa

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**Abstract:** Diagenesis is one of the most important factors that affects reservoir rock property. Despite the fact that published data gives a vast amount of information on the geology, sedimentology, and lithostratigraphy of the Ecca Group in the Karoo Basin of South Africa, little is known about the diagenesis of the potentially feasible or economically viable sandstones and mudrocks of the Ecca Group. This study aims to provide an account of the diagenesis of sandstones and mudstones from the Ecca Group. Twenty-five diagenetic textures and structures were identified and grouped into three stages that include early diagenesis, burial diagenesis and uplift-related diagenesis. Clay minerals are the most common cementing materials in the sandstones. Smectite, kaolinite, and illite are the major clay minerals that act as pore lining rims and pore-filling materials. A part of the clay minerals and detrital grains was strongly replaced by calcite. Calcite precipitates locally in the pore spaces and partially or completely replaced clay matrix, feldspar, and quartz grains at or around their margins. Precipitation of cements and formation of pyrite and authigenic minerals occurred during the early diagenetic stage. This process was followed by lithification and compaction which brought about an increase in tightness of grain packing, loss of pore spaces, and thinning of bedding thickness due to overloading of sediments and selective dissolution of the framework grains. Mineral overgrowths, mineral replacement, clay-mineral transformation, dissolution, deformation, and pressure solution occurred during burial diagenetic stage. After rocks were uplifted, weathered and unroofed by erosion, this resulted in decementation and oxidation of iron-rich minerals. The rocks of the Ecca Group were subjected to moderate-intense mechanical and chemical compaction during their progressive burial. Intergranular pores, secondary dissolution, and fractured pores are well developed in the sediments of the Ecca Group. The presence of fractured and dissolution pores tend to enhance reservoir quality. However, the isolated nature of the pore linkage makes them unfavorable producers of hydrocarbons, which at best would require stimulation. The understanding of the space and time distribution of diagenetic processes in these rocks will allow the development of predictive models of their reservoir quality, which may contribute to the reduction of risks involved in hydrocarbon (oil and gas) exploration.

**Keywords:** diagenesis; reservoir rock properties; diagenetic textures; Ecca Group; Karoo Basin

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## 1. Introduction

The early search for oil and gas reservoirs focused on acquiring or knowing the regional tectonics, stratigraphy, and sedimentology of the reservoir rocks, followed by a more detailed assessment of diagenetic features, porosity, and permeability changes. During petroleum exploration, reservoir quality is one of the main controlling factors on prospectivity. Therefore, it is important to have a

detailed understanding of the factors that controls reservoir quality in order to assist with the appraisal of the economic feasibility of hydrocarbon discoveries. As documented by Selley [1], once petroleum has been discovered in a basin, it is very important to have detailed understanding of reservoir quality to help focus further exploration and appraisal efforts. Reservoir quality in clastic and fine grained rocks is controlled by several interconnected factors such as mineral composition, pore water chemistry, diagenetic events, temperature, fluid flow, depositional environment, tectonic setting, time, burial depth, uplift process, geothermal gradient, and subsurface pressure [2–4]. Diagenesis is the most crucial factor impacting reservoir property [5,6]. Hence, reconstruction of the diagenetic history is important in understanding reservoir porosity and permeability to predict the reservoir characteristics of clastic rocks.

In general term, diagenesis encompasses all of the changes that sediments undergo between the time of deposition and before the transition to metamorphism. These changes (i.e., physical, chemical and mineralogical) occurred as a result of several factors including compaction, deformation, dissolution, cementation, authigenesis, replacement, recrystallization, hydration, and bacterial actions [7]. The economic importance of certain shale and/or sandstone units as a source or reservoir rock for petroleum may ultimately depend on the diagenetic history of the units as well as their original depositional characteristics [7]. Diagenetic processes are continually active as the ambient environment changes in terms of temperature, pressure, and chemistry during deposition, burial and uplift cycle of the basin history [8]. These processes are thought to occur above the zone of metamorphism with temperatures below about 195–220 °C and at pressures  $\leq 5$  kb [7]. The lower and upper limits of diagenesis can be determined using certain minerals, for instance, Tucker [9] reported that the stable limit temperatures of limonite (195–220 °C) can be used as the highest temperature of diagenesis, whereas the stable limit temperatures of chlorastrolite and zonochlorite ( $\geq 250$  °C) are used as the lowest limiting temperature of metamorphism.

Several researchers including Curtis [10], Giles and Marshall [11], Wright [12], Bloch et al. [13], Burley and Worden [8], Mackenzie [14], and Milliken [15] have documented that diagenetic alterations in siliciclastic rocks have a significant influence on reservoir quality by modifying the rock's primary porosity, permeability and consequently, on reservoir quality. Petrographic studies are of key importance for characterizing the types, timing, and rate at which the diagenetic processes affect porosity and permeability of the sandstones and mudrocks [16]. The relationship between diagenesis and reservoir quality has been investigated and documented by several researchers (i.e., [17–21]).

In recent years, shale gas exploration has gained huge economic success in many countries, particularly in the United State of America, Canada, and China, which stimulate other countries to follow these examples. Thus the study of diagenesis on Ecca Group sandstones and mudrocks has not only theoretical significance, but also has potential economic importance. Presently, the lower Ecca Group formations of the Main Karoo Basin are attracting a great interest for hydrocarbon exploration in South Africa. The efficient exploitation of the Ecca Group reservoirs depends on several factors, including better understanding of the impact of diagenetic alterations on reservoir quality (porosity and permeability). However, there are very few published studies on the diagenesis of the clastic rocks from the Ecca Group within the study area. Despite the fact that such rocks may themselves constitute prospectable reservoirs, apart from providing vital palaeo-environmental information for the understanding of the detrital marine clastic reservoirs. The purpose of this research work is to examine if diagenesis has significantly altered the original petrologic characteristics of the Ecca sandstones and mudrocks after deposition. The study is also to add new information on the cement types, pore types, diagenetic sequence, as well as the impact of diagenesis on their quality as potential clastic reservoirs. The diagenetic study on the Ecca Group sandstones and mudrocks will contribute to reduce the exploration risks in this extensive area.

## 2. Geological Setting

The Karoo Supergroup in the study area is composed of the basal glaciogenic Dwyka Group (Westphalian-Early Permian), the marine Ecca Group (Permian) and the non-marine Beaufort Group (Permo-Triassic) [22,23]. The base of the Ecca Group is defined at the top of the glaciogenic succession of the Dwyka Group with varied sequences mainly of mudstones, siltstones, and sandstones, with occasional conglomerates and coal [24]. It is estimated that the group attained a thickness of about 3000 m in the southern part of the Main Karoo Basin and can be subdivided into five formations, namely, the Prince Albert Formation, Whitehill Formation, Collingham Formation, Ripon Formation, and Fort Brown Formation (Figure 1; Table 1) [25]. Catuneanu et al. [26] envisaged that the marine clays and mudstones of the Prince Albert Formation were deposited on the diamictites of the Dwyka Formation in the southern part of the basin. This was followed by the carbonaceous shale of the Whitehill Formation. Subsequently, the Collingham Formation that is made up of persistent grey shales alternating with yellow-claystones, as well as the sandstones and shales of the Ripon and Fort Brown Formations were deposited on the submarine fans and shelf, respectively [27].

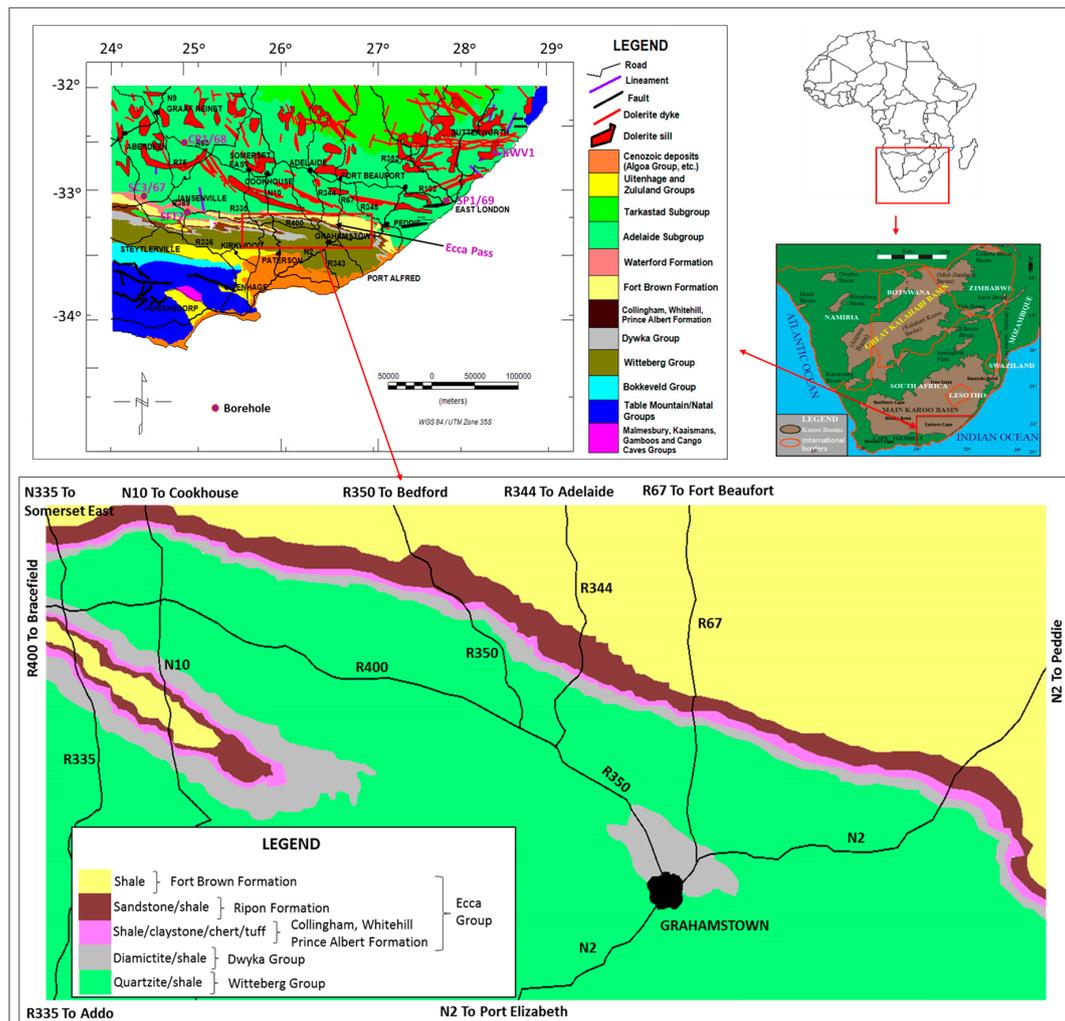


Figure 1. Location of the study area (Modified from [21]).

The Ecca Group is the main target of shale-gas exploration in South Africa and diagenetic research is the pre-requisite for the feasibility studies of the exploration. Reservoir quality in shales and sandstones is controlled by several interconnected factors such as mineral composition, sedimentary

facies, diagenetic events, and circulating basinal fluids [3,4]. Diagenesis is the most important factor that affects or impacts the reservoir property. Unconventional shale gas was identified in the Whitehill and Collingham Formations in the 1960s, but exploration stopped in the late 1970s due to technical problems [28,29]. Recently, South Africa has shown interest in recovering the natural gas resources that are hosted or trapped in the Ecca Groups shales of the Karoo Basin due to the recent global success in technological advancements in recovering petroleum from low permeability reservoirs (i.e., shale). Recent analysis by Decker and Marot [30] and Advanced Resources International [31] suggest that the southern Karoo has potential large gas reserves that range from 32–485 trillion cubic feet of technically recoverable shale gas resources and that the most conventional prediction or likelihood is still an important gas resource. Based on the report presented by Econometrix [32] and Advanced Resources International [31], the Lower Ecca Group hosts about 1559 Tcf of risked shale gas with 389.6 Tcf of technically recoverable shale gas resource (technically recoverable shale gas resource of 96.3 Tcf, 211.3 Tcf, and 82 Tcf, for the Prince Albert Formation, Whitehill Formation and Collingham Formation, respectively). The Upper Ecca Group (Ripon and Fort Brown Formations) host 95.4 Tcf technically recoverable shale gas resource. Kuuskraa et al. [33] initially suggested an optimistic prospective area of about 183,000 km<sup>2</sup> for shale gas exploration.

**Table 1.** Lithostratigraphy of the Ecca Group in the Eastern Cape Province compiled by the Council for Geoscience [21].

Supergroup	Group	Formation	Lithology	Max. Thickness (m)
Karoo	Beaufort	Koonap	Grey Sandstone Shale	1300
		Waterford (Not present in Ecca Pass)	Sandstone Shale	800
	Ecca	Fort Brown	Shale Sandstone	1500
		Ripon	Sandstone Shale	1000
		Collingham	Grey Shale Yellow Claystone	30
		Whitehill	Black Shale Chert	70
		Prince Albert	Khaki Shale	120
		Dwyka	Dwyka	Diamictite, Tillite, Shale

### 3. Methodology

Thin sections of 152 rock and core samples (104 sandstones and 48 mudrocks) were prepared and studied under optical microscope in order to determine mineral compositions, rock textures, shape and size of grains, and cements. The core samples were taken from borehole KVV 1, SC 3/67 and SP 1/69 (Figure 1). In addition, a total of 30 samples (20 sandstones and 10 mudrocks) were properly cleaned and glued on a glass microscope slide using Struers specifix resin mixed with Struers specifix-40 curing agent in the ratio 5:2 by weight (the mounted samples were left for 24 h). After the samples had been stuck to the microscope slide, they were carbon coated using Cressington Carbon Coater 108 Carbon/A machine combined with a pumping system and thickness monitor into a space of approximately 42 cm × 60 cm. The coated samples were analyzed using a scanning electron microscopy (SEM) instrument (Model: JSM-6390LV, JEOL, Tokyo, Japan) in the working condition of 15 KV, and equipped with a link system Energy Dispersive X-ray microanalyzer (EDX, JSM-6390LVSEM, Tokyo, Japan). The diagenetic study reported in this paper focuses more on the sandstones, with less emphasis on the mudrocks. The studied samples were examined in secondary electron imaging (SEI) and backscattered electron (BSE) modes of imaging. The description of cementation textures, primary and authigenic mineralogy of the shales and sandstones were described based on petrographic study of thin sections, SEM, and EDX analyses. In addition, clay minerals, dissolution effect, quartz overgrowth, diagenetic textures, pore geometry, and other related diagenetic textures were investigated using SEM. Both SEM and petrographic microscopy were carried out at the University of Fort Hare, South Africa. Mineral compositions of the shales, mudstones, and sandstones were determined by X-ray diffraction

(XRD) at the Council for Geoscience laboratory in Pretoria. The XRD measurements were performed on a Bruker XRD D8 Advance (Model: V22.0.28, Bruker, Madison, WI, USA) at a room temperature of 25 °C and the samples were scanned at 2° 2θ per minute from 2° to 70° (wavelength of 1.5406). Thirty five representative thin sections of the sandstones and mudrocks were studied under optical microscope and applied to modal composition analysis. Comparative abundance of the main mineral constituents was determined by counting at least 500 points per thin section using the methods of Dickinson and Suczek [34] and Dickinson et al. [35]. Each thin section was analyzed in accordance with the Gazzi-Dickinson's traditional point-counting method using an Olympus BX51 microscope equipped with an Olympus DP72 digital camera. An evenly spaced counting grid was employed to traverse the thin section, and mineral grains under the grid nodes were counted. The grids were equally spaced in such a way that each grid exceeded the average grain size in order to avoid counting an individual grain more than once. Constituent minerals of the sandstones were classified into monocrystalline quartz, polycrystalline quartz, K-feldspar, plagioclase, lithic fragments, accessory minerals, and matrix. The Whitehill Formation of the Eccca Group is mainly made up of shale and chert. Therefore, the formation was not studied for modal compositional analysis.

#### 4. Result

Detrital framework grains of the Eccca Group sandstones include quartz, feldspars, rock fragments, matrix, and accessory minerals (Table 2). The matrix is made of clay minerals and minor detrital silts. Quartz is the most dominant mineral in the sandstones, and it ranges from about 18.4–31.8%, averaging 25.1% of the overall composition. The quartz minerals exist as monocrystalline grains, polycrystalline grains, and quartz cement. The monocrystalline quartz grains make up to 81.33% of the total quartz grains in the samples. Alkali feldspar (orthoclase and microcline) and plagioclase feldspar (albite) are the feldspar minerals present in the sandstones, with alkali feldspar and albite being the most dominant. The amount of feldspar grains range from 10.6 to 34.4%, averaging 19.41% of the total grains in the samples. Rock fragments constitute an average of about 19.51% of the total grains. The framework grains are bound together by both cement and matrix. The matrix is mostly clay minerals and they are either detrital or diagenetic in form. The diagenetic matrix minerals were formed as a result of framework grains alteration and precipitation, as well as recrystallization of other matrix minerals. Muscovite and biotite are the mica in the sandstones, with muscovite occurring more frequently than biotite. This could be due to the fact that muscovite is chemically more stable than biotite in the depositional environment. Heavy minerals in the rocks occur as accessory minerals of detrital garnet, rutile, and zircon, and they constitute less than 1% of the total grains.

**Table 2.** Modal compositions of the sandstones from the Eccca Group.

SAMPLE	Qt (%)	Qm (%)	Qp (%)	F (%)	L (%)	Lt (%)	Mx (%)	Acc (%)	Normalized (100%)					
									Qm-F-Lt (%)			Qt-F-L (%)		
									Qm	F	Lt	Qt	F	L
FB 6	27.4	21.6	5.8	32.0	17.6	23.4	18.6	4.4	28.05	41.6	30.4	35.6	41.6	22.9
FB 5	24.2	20.6	3.6	34.4	18.6	22.2	20.2	2.6	26.7	44.6	28.8	31.4	44.6	24.1
FB 4	31.8	27.8	4.0	26.4	20.4	24.4	17.2	4.2	35.4	33.6	31.0	40.5	33.6	26.0
FB 3	29.2	27.4	1.8	26.2	29.2	31.0	13.6	1.8	32.4	30.8	36.6	34.5	31.0	34.5
FB 2	30.6	26.2	4.4	26.2	16.8	21.2	21.4	5.0	35.6	35.6	28.8	41.6	35.6	22.8
FB 1	28.4	23.8	4.6	32.8	14.8	19.4	20.8	3.2	31.3	43.1	25.5	37.4	43.2	19.5
RP 19	18.6	15.8	2.8	17.2	26.2	29.0	31.2	6.8	25.5	27.7	46.8	30	27.7	42.3
RP 18	17.8	15.2	2.6	12.8	18.2	20.8	33.6	17.6	31.1	26.2	42.6	36.5	26.2	37.3
RP 17	23.0	19	4.0	20.6	29.6	33.6	23.4	3.4	26.0	28.1	45.9	31.4	28.1	40.4
RP 16	23.0	14.2	8.8	20.8	24.0	32.8	25.6	6.6	20.9	30.7	48.4	33.9	30.7	35.4
RP 15	21.4	20.2	1.2	23.2	16.6	17.8	34.0	4.8	33.0	37.9	29.1	35.0	37.9	27.1
RP 14	24.4	20.0	4.4	18.4	26.4	30.8	24.8	6.0	28.9	26.6	44.5	35.3	26.6	38.2
RP 13	27.2	20.4	6.8	19.2	18.6	25.4	30.4	4.6	31.4	29.5	39.0	41.9	29.5	28.6
RP 12	30.0	25.4	4.6	16.8	20.8	25.4	26.8	5.6	37.6	24.9	37.6	44.4	24.9	30.8
RP 11	24.8	21.6	3.2	17.2	23.2	26.4	32.4	2.4	33.1	26.4	40.5	38.0	26.4	35.6

Table 2. Cont.

SAMPLE	Qt (%)	Qm (%)	Qp (%)	F (%)	L (%)	Lt (%)	Mx (%)	Acc (%)	Normalized (100%)					
									Qm-F-Lt (%)			Qt-F-L (%)		
									Qm	F	Lt	Qt	F	L
RP 10	21.6	15.6	6.0	16.4	25.4	31.4	32.2	4.4	24.6	26.0	49.5	34.1	25.9	40.1
RP 9	20.8	15.2	5.6	11.4	17.2	22.8	42.2	8.4	30.8	23.1	46.2	42.1	23.1	34.8
RP 8	19.6	15.0	4.6	14.8	29.6	34.2	34.0	2.0	23.4	23.1	53.4	30.6	23.1	46.3
RP 7	25.6	17.6	8.0	23.0	31.6	39.6	16.8	3.0	21.9	28.7	49.4	31.9	28.7	39.4
RP 6	18.4	11.2	7.2	20.0	22.4	29.6	32.4	6.8	18.4	32.9	48.7	30.3	32.9	36.8
RP 5	27.4	22.0	5.4	21.2	32.0	37.4	17.2	2.2	27.3	26.3	46.4	34	26.3	39.7
RP 4	29.0	25.0	4.0	20.6	25.6	29.6	21.4	3.4	33.2	27.4	39.4	38.6	27.4	34.0
RP 3	23.0	18.2	4.8	11.8	20	24.8	41.2	4.0	33.2	21.5	45.3	42.0	21.5	36.5
RP 2	30.2	23.8	6.4	23.2	24.8	31.2	16.2	5.6	30.4	29.7	39.9	38.6	29.7	31.7
RP 1	26.8	21.8	5.0	19	16.4	21.4	30.6	7.2	35.0	30.6	34.4	43.1	30.6	26.4
CH 5	31.6	26.4	5.2	16.8	19.6	24.8	25.6	6.4	38.8	24.7	36.5	46.5	24.7	28.8
CH 4	24.6	19.2	5.4	19	17.8	23.2	35.2	3.4	31.2	30.9	37.8	40.1	30.9	29.0
CH 3	28.6	26.2	2.4	20.4	18.0	20.4	28.4	4.6	39.1	30.5	30.5	42.7	30.5	26.9
CH 2	30.4	24.8	5.6	15.8	21.4	27.0	20.8	11.6	36.7	23.4	39.9	45.0	23.4	31.7
CH 1	27.8	21.2	6.6	12.8	20.6	27.2	32.0	6.8	34.6	20.9	44.4	45.4	20.9	33.7
PA 5	19.4	15.8	3.6	10.8	18	21.6	42.6	9.2	32.8	22.4	44.8	40.3	22.4	37.3
PA 4	23.2	20.4	2.8	13.8	18.6	21.4	34.0	10.4	36.7	24.8	38.5	41.7	24.8	33.5
PA 3	20.4	16.8	3.6	10.6	21.0	24.6	42.2	5.8	32.3	20.4	47.3	39.2	20.4	40.4
PA 2	23.8	19.2	4.6	12.8	16.0	20.6	35.0	12.4	36.5	24.3	39.2	45.3	24.3	30.4
PA 1	18.4	17.2	1.2	15.6	17.0	18.2	41.2	7.8	33.7	30.6	35.7	36.1	30.6	33.3

Qt, Qp, Qm, F, Lt, L, Mx, Acc, PA, CH, RP and FB represent total quartzose grains, polycrystalline quartz, monocrystalline quartz, feldspar grains, total siliciclastic lithic fragments, unstable (siliciclastic) lithic fragments, matrix minerals, accessory minerals, Prince Albert Formation, Collingham Formation, Ripon Formation, and Fort Brown Formation, respectively.

#### 4.1. Diagenesis of Sandstones

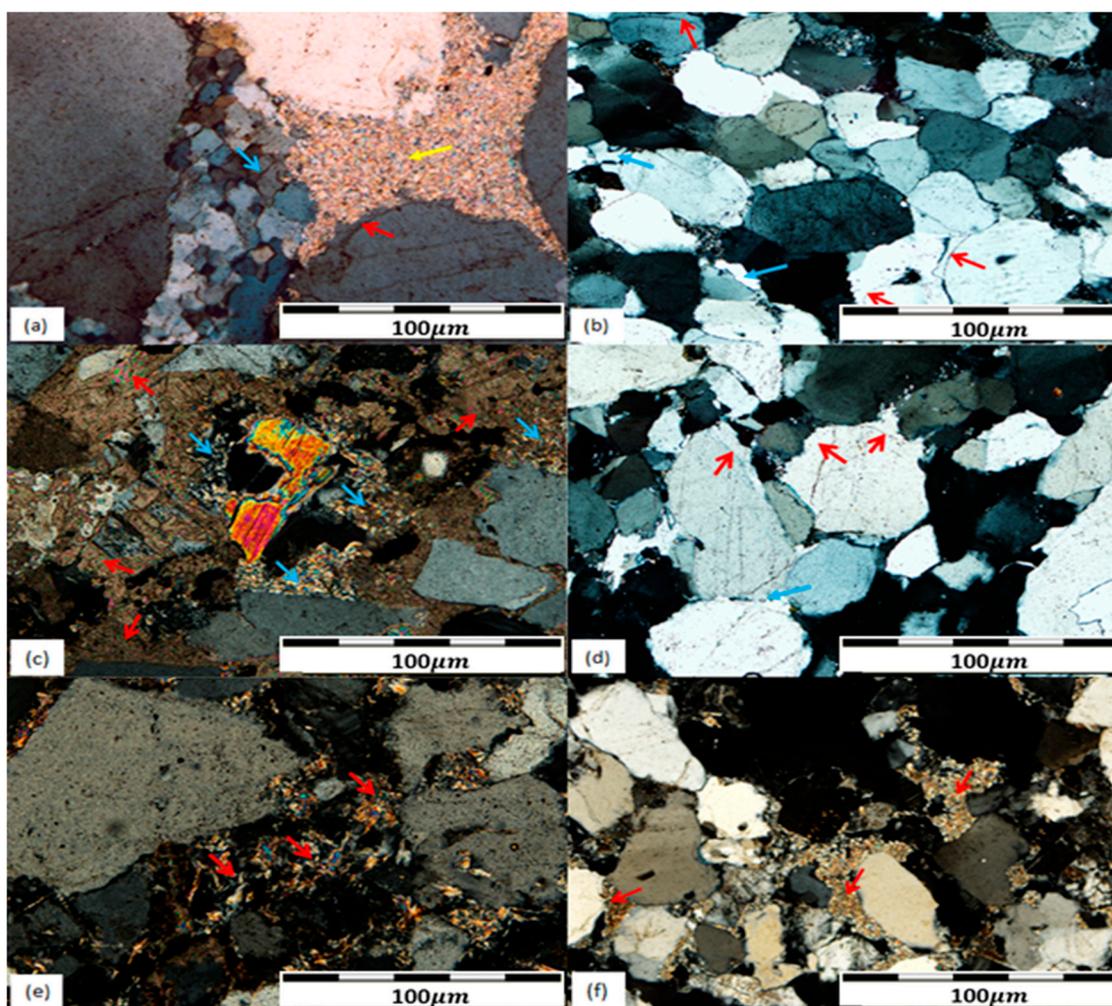
##### 4.1.1. Description of Sandstone Diagenesis

The main diagenetic processes that have strongly affected the sandstones of the Eccca Group are cementation, mechanical compaction, dissolution, grain replacement, and recrystallization.

##### Cementation

Cementation is one of the most important processes leading to the loose sediments forming a consolidated rock, thus resulting in porosity reduction. Four types of cements were identified in the sandstones of Eccca Group, which are quartz cement, calcite cement, feldspar cement, and authigenic clay mineral cements.

**Quartz Cementation.** Quartz cement exists in the rocks as a result of precipitation of silica into the pore spaces between grains. Quartz cement occurs as both pore-filling and overgrowths in the rocks. This type of cement was formed early in the shallow marine diagenetic environment and in the early diagenetic stage. Quartz overgrowths occur as syntaxial overgrowth, growing outwardly from detrital quartz grain surface. The overgrowths have the same optical properties as the original detrital quartz grains. In some cases, the boundaries between the detrital quartz and overgrowths are marked by clay coatings and dust lines. The result of overgrowths commonly gives the grain more euhedral crystal faces. The dissolution of feldspars and micas led to the release of silica, thus providing the silica source for the formation of quartz cement and authigenic quartz. Quartz cement exists in the rocks as fine granular quartz (Figure 2a) as well as quartz overgrowths (Figure 2b). Quartz cements were formed due to silica precipitation in pore spaces.



**Figure 2.** Thin section photomicrographs of sandstones showing: (a) fine granular quartz cement (blue arrow) and clay matrix (red-brownish area; yellow arrow) and overgrowth part (red arrow); (b) quartz overgrowths (red arrows) and quartz cement (blue arrows); (c) calcite replacement of feldspar grains (red arrows) and clay matrix (illite and sericite, blue arrows); (d) feldspar overgrowths (red arrows) and feldspar cement (blue arrow); (e) recrystallization of kaolinite to illite (red arrow); (f) clay (illitized smectite) matrix around feldspar and quartz grains (red arrows).

**Calcite Cementation.** Calcite cementation is another type of cement in the Eccca Group. It occurs mainly as a pore-filling and replacement mineral of clay matrix and detrital grains. This possibly points to precipitation in different diagenetic stages. Calcite precipitates locally in pore spaces and partly or completely replaced feldspar and quartz grains, commonly at their margins. Most of the clay minerals (matrix) and detrital grains were seriously attacked and replaced by calcite (Figure 2c). In some cases, the replacement even penetrated into the cores of grains. Calcite cementation replaces quartz overgrowths. Calcite filled most of the secondary pores after dissolution of feldspar.

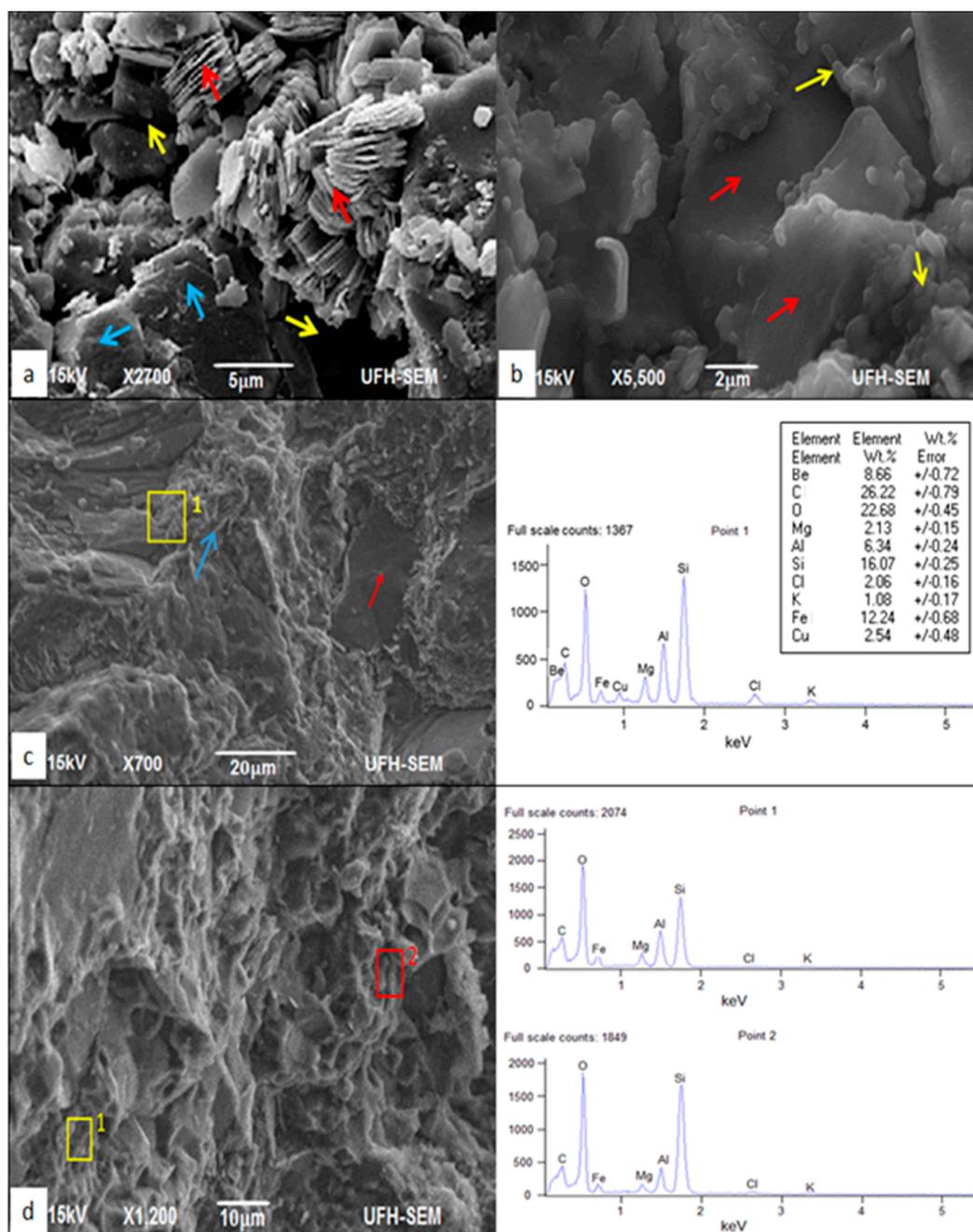
**Feldspar Cementation.** Feldspar cement is a minor cement type in the sandstones and siltstones. It occurs as pore-filling feldspar and as overgrowths around detrital K-feldspar grains (Figure 2d). In a few cases, the feldspar overgrowth shows hematite rims (dust rim) around the original detrital grain. Feldspar overgrowths behave as an authigenic feldspar pore-filling cement and represents early diagenetic mineral. Most of feldspar syntaxial overgrowths are associated with quartz overgrowths. This cement was formed after quartz cementation.

**Clay minerals Cementation.** Clay minerals are the most common cementing materials in the Eccca sandstones. These minerals act as pore lining rim cement and pore-filling matrix. Smectite, kaolinite,

and illite are the major clay minerals that act as cementing agent in the rocks. These authigenic clay minerals are formed through recrystallization of fine matrix and dissolution of K-feldspars. In addition, they may also have been formed due to modification or alteration of one kind of clay mineral to another, for instance, both smectite and kaolinite were transformed into illite. Other clay minerals that occurred as minor constituent in the rocks are sericite and chlorite. Smectite recrystallized into illite and chlorite, kaolinite recrystallized into illite. Illite also further changed to sericite, which later recrystallized to muscovite.

*Kaolinite clay.* Kaolinite occurs as both pore filling and lining clay matrix or cement. In addition, kaolinite clay also occurs as common replacement mineral, replacing weak detrital K-feldspar after weathering and muscovite grains. Kaolinite can either be detrital or authigenic in origin. Detrital kaolinite is deposited in the depositional basin by erosion and transportation, whereas authigenic kaolinite is formed in situ in the depositional basin. The former shows erosion and transportation effects such as angular and broken grain shapes, while the latter shows fibrous or euhedral crystalline shape, or booklet crystalline shape under SEM. SEM studies revealed that accordion-shaped clay flakes occur as euhedral crystals in the intergranular pores (Figure 3a). Kaolinitized intraclasts occur as relatively large, irregular, scattered patches of kaolinite. On the other hand, partially kaolinitized mica sometimes has thin, thread-like remnants of the muscovite. Thus some kaolinite resembles fragments of detrital mud or silt-size lithic grains. In some cases, kaolinite patches, which are squeezed and deformed between the grains, fill nearby intergranular pores. This possibly points to kaolinitized pseudomatrix. Completely kaolinitized feldspars occur as patches of kaolinite with well-defined relic outlines, similar in size to the original detrital feldspar grains. However, partially kaolinitized feldspars have detrital feldspar remnants. In some cases, the kaolinite is engulfed by quartz overgrowth, and thus pre-dates the quartz overgrowths. The kaolinite was formed in the early diagenetic stage and uplift stage. Hence, the presence of altered K-feldspar and muscovite serves as sources of silica and aluminum resulting in the formation of kaolinite.

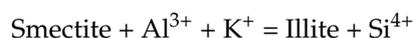
*Illite Clay.* Illite clay occurs as pore filling and lining of clay minerals. It also occurs as booklets and vermicular stacked platelets that resemble kaolinite, and thus were likely formed as a result of partial to complete alteration or recrystallization of kaolinite and smectite (Figure 2e). Illitization usually occurred after the precipitation of kaolinite and smectite and requires influx of potassium under a higher temperature. Despite the fact that illitic clays are often associated with the decomposition of kaolinite, kaolinite decomposition is not always accompanied by illitization nor does kaolinite always decompose when illitic cements form [36]. Illite commonly retains the shape of its predecessors especially when it is formed due to dissolution of kaolinite. Authigenesis of illite clay depends on the presentation and alteration of smectite/kaolinite and other labile detrital minerals that are easily altered and require alkaline (illite) and acidic (kaolinite) pore fluid. Illite is usually formed in shallow burial diagenesis under increased temperature. Smectite changed to illite at temperatures ranging from 55–200 °C [36]. As temperature increases, smectite changes to illite, starting with the growth of single illite pellets on smectite for their nucleation (Figure 3b). The observed smectite generally has honey-comb shape and curved flake or platy box-work shapes with illite growing from its surfaces, resulting in the formation of a mixed illite-smectite layers. As temperatures continued to increase, illite is transformed into sericite. Afterwards, the sericite are altered to muscovite. The formation of illite requires a growth medium (pore fluid and space) with high potassium (K), silica (Si) and aluminum (Al) compositions. The EDX graph (Figure 3c; right hand side) shows that the mineral is mainly composed of silica and aluminum, whereas potassium, iron and magnesium elements only occur in small quantity. This agrees with the chemical formula or composition of illite  $((K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)])$ . Therefore, the occurrence of illite or illite-smectite mixed layers lies merely on the transformation/conversion of smectite clay mineral during a shallow burial diagenetic process at increased temperature between 90 °C and 130 °C [37].



**Figure 3.** (a) Scanning electron microscopy (SEM) backscattered electron (BSE) photomicrograph showing accordion or book-page shaped kaolinite (red arrows) and quartz cements (blue arrows) partly filling the intergranular pores (yellow arrows); (b) SEM (BSE) photomicrograph showing illite growth (yellow arrows) from smectite flakes (red arrows); (c) SEM (BSE) photomicrograph showing fabric shaped illite (blue arrow), detrital quartz (red arrow), and energy dispersive X-ray (EDX) graph on the right hand side showing elemental composition of illite at point 1 (yellow area); (d) SEM (BSE) photomicrograph on the left hand side showing honey-comb shaped smectite, and EDX graphs on the right hand side showing elemental compositions of smectite at point 1 (yellow area) and point 2 (red area).

*Smectite Clay.* Smectite occurs as grain coatings and microcrystalline matrix aggregates (Figure 2f). SEM examinations revealed that smectite clay has a cornflake-shaped texture and sometimes appears to have honey-comb morphology (Figure 3d; left hand side). In some cases, illite grows from the

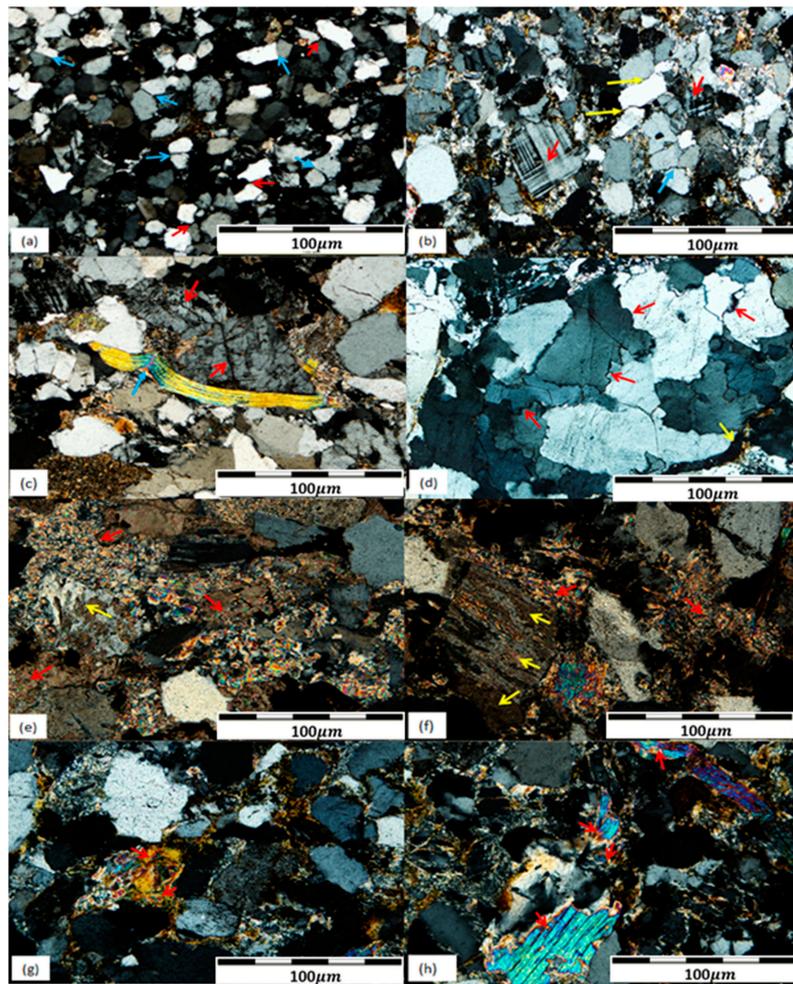
surface of the cornflake-shaped smectite or forms the mixed illite-smectite interlayers. The smectite flakes also recrystallized to pelletic and fibrous illite. Smectite can be transformed to illite through the process of illitization. Smectite can contain substantial amounts of Fe and Mg. Thus, destruction of smectite layers during illitization can release significant amounts of these elements, depending on the initial composition of the rock. Pollastro (1985) [37] documented that, for smectite to be converted to illite, it is essential that  $K^+$  must be added in the interlayer space and the amount of tetrahedral  $Al^{3+}$  must be increased. The mathematical expression is shown below:



The released silica ( $Si^{4+}$ ) is believed to form or add to the quartz cement in rocks, whereas the Fe and Mg (Figure 3d; EDX images) are believed to form as part of reaction products that are more stable under the increased burial temperature conditions. Smectite in the studied samples does not uniformly change to illite. Al-rich layers are more susceptible to illitization than those containing Fe and Mg. Alteration of smectite to illite also led to the increase of sodium (Na) in the Ecca sediments. At uplift-related diagenesis, weathering, dissolution, and oxidation may result in the alteration of smectite to chlorite. In addition, it may also cause the rocks and minerals to break down, decompose, and become weathered.

### Compaction

During the initial stages where diagenesis took place under oxidizing pore waters, mechanical compaction start to influence the soft sediment when it was buried by overloading deposits. The higher the overburden, the more intense is the compaction. The overburden pressure results in bed thinning in sedimentary rocks, expelling intergranular fluids (dewatering), closer packing of the grains, and porosity reduction. The sandstones of Ecca Group are subjected to moderate-intense physical and chemical compaction during their progressive burial. This is revealed by the change in grain contacts, with long, concavo-convex and sutured contacts of neighboring framework grains (Figure 4a,b). The grain contact patterns progressively changed from non-contact to point contacts, to long contact, then to concavo-convex contact. In a more advanced stage, the concavo-convex contacts become sutured. The overburden that compacts the sediments also resulted in the fracturing of some of the grains, particularly the feldspar and muscovite grains (Figure 4c). Some muscovite grains were completely deformed in shape. In a few cases, mica flakes are cracked or bent (Figure 4c). Long contacts are common in the examined samples and their existence points to a moderate degree of compaction (Figure 4a). Concavo-convex and sutured contacts are also common and they can be attributed to deep burial diagenesis. Progressive burial resulted in increasing compaction and porosity loss either by grain rotation or slippage, leading to eventual fracturing of resistant minerals. This resulted in pressure dissolution, which is a deformation mechanism that involves the dissolution of minerals at grain to grain contacts (boundaries) into an aqueous pore fluid in areas of relatively high stress. Quartz and muscovite grains are occasionally deformed due to pressure dissolution. Stylolites structures are present in some of the siliciclastic sandstones. Fracturing is generally uncommon, but when present it is mostly observed as minor fractures on detrital quartz grains. Grain fracturing in the rocks also points to burial compaction.



**Figure 4.** Thin section photomicrographs of sandstones showing: (a) point contacts (red arrows) and long contacts (blue arrows) between detrital grains; (b) concavo-convex grain contacts (yellow arrows), sutured grain contacts (blue arrow), and partial recrystallization of microcline to albite (red arrows); (c) fractured feldspar grains (red arrows) and deformed mica (blue arrow); (d) dissolution crack (yellow arrow) and sutured grain contacts formed by pressure solution along grain boundaries (red arrows); (e) calcite replacement of clay matrix (red arrows) and detrital grains (yellow arrows); (f) feldspar grains replaced by clay mineral along the cleavage (yellow arrows) and clay matrix (red arrows); (g) transformation of clay matrix to sericite (yellowish crystals); (h) alteration of mica to clay mineral (kaolinite) along its boundary.

### Dissolution

Dissolution generally involves the removal in solution of all or part of previously existing minerals, leaving pore spaces in the rocks [7]. It provides silica source for quartz cement and quartz overgrowths. High temperature under deep burial depth led to the dissolution of some mineral grains at their boundaries (Figure 4d). SEM observation revealed that some kaolinite and albite grains were formed due to dissolution of weak detrital K-feldspars. In addition, the dissolution of feldspars and micas resulted in the release of silica, thus providing a silica source for the formation of authigenic quartz. The dissolution and replacement of feldspar to illite also favored the formation of authigenic quartz.

### Mineral Replacement

Mineral replacement encompasses dissolution of one mineral and simultaneous precipitation of another mineral in situ. This dissolution and re-precipitation may take place over a period of time,

with new minerals progressively replacing the host or existing minerals. Replacement is a relatively common diagenetic process in the rocks of Ecca Group and is possibly due to the fact that K-feldspars are liable to alteration in burial diagenesis. When temperature increases as a result of increase in burial depth, some minerals become weak and unstable, subsequently, these minerals are replaced by more stable minerals in a new diagenetic environment. The observed mineral replacements in the studied rocks are calcite replacing quartz, feldspar and clay matrix, as well as albitization and kaolinitization/illitization.

**Replacement with Calcite.** Calcite is the most abundant replacement mineral in the rocks. Calcite replaced both the clay matrix and framework grains (Figures 2c and 4e), i.e., the detrital feldspars, quartz, and volcanic fragments are replaced by calcite. The most affected feldspars were the K-feldspar (microcline) and minor plagioclase. Mineral replacement of the feldspars by calcite also resulted in the formation of pores in sediments.

**Replacement with Albite.** Feldspars are easily susceptible to alteration whenever their diagenetic environmental conditions are changed. The K- or Ca-feldspar framework grains were either partially or completely replaced by albite. In the rocks of Ecca Group, albitization of K- and Ca-feldspar is one of the major diagenetic changes during burial diagenesis. Albite replaced particularly the K-feldspar mineral grains. However, in some cases, albite grain precipitated out after partial dissolution of weak detrital feldspar grain (i.e., calcite first replace K-feldspar, and it was subsequently replaced by albite). Albite formed through replacement was revealed by the blocky to tabular sector extinction patterns where incomplete replacement occurred (Figure 4b). Albitization occurred preferentially along microfractures, cleavages, and grain contact margins.

**Authigenic Clay Minerals.** K-feldspar grains are also commonly altered to kaolinite and sericite (Figure 4f). The sericite grains appear as scattered fine flakes along cleavage planes or on the entire feldspar grain. SEM observation shows that fibrous kaolinite partially to completely replaces both the matrix and framework grains of K-feldspar and muscovite. In a few instances, illite and sericite replaced some of the feldspar grains.

## Recrystallization

Mineral recrystallization is a common phenomenon in the rocks of Ecca Group. Recrystallization involves the change in shape or size of crystals of a given mineral, without subsequent change in the mineralogy or chemical composition. As temperature and pressure increases with burial depth, micro-granular and fine minerals can transform into coarse textures. Existing minerals can also retain their chemical composition, while only changing in size. On the other hand, some existing minerals may be completely transformed or changed into a new mineral. Petrographic and SEM observations revealed that authigenic quartz, muscovite, chlorite, illite, sericite, and feldspars are the transformed silica or silicate minerals in the rocks. With regard to clay minerals, smectite transform into illite and chlorite, kaolinite transformed into illite. As temperature increases, illite further changed to sericite (Figure 4g) and muscovite. The mica was further altered to clay mineral (kaolinite), usually around the edges or along the boundary as depicted in Figure 4h. Some quartz cements were formed through transformation of fine matrix minerals. Furthermore, detrital grains, such as quartz and feldspar were observed to gradually transformed and increase their crystalline size. Through progressive recrystallization, the crystalline grain size is increased, which tends to reduce the pore space between the grains as well as the pore interconnectivity.

## 4.2. Diagenesis of Mudrocks

### 4.2.1. Description of Mudrock Diagenesis

The main diagenetic processes that have affected the mudrocks are mechanical compaction, authigenic minerals, and replacement by calcite. The mudrocks are mostly composed of detritus clay, mudstones (Figure 5a), and silt-sized nodules (Figure 5g,h and Figure 6a) with some chemically

precipitated and authigenic minerals, and carbonaceous or organic materials (Figure 5b). Manganese iron rich nodules, dark micrite, and chalcedony nodules are present in some of the mudrock (Figure 5g,h). The dolomite concretions and lenses occurred near the base of the Whitehill Formation and are often laminated and have a physical texture that looks like microbial mats and/or stromatolite-like features. SEM observation shows spherical “holes” that are enclosed within the dolomite crystals which may possibly enhance porosity in the mudrock. The micrite consists of chemically precipitated calcite mud, whose crystals are generally 1–4 micrometers in diameter. Chalcedony is a cryptocrystalline form of silica, composed of very fine intergrowths of quartz and are observed to have whitish-grey color. Most marine micrites started as soft carbonate mud on the sea floor. Carbonate mud is much like regular mud. The mud particles are generally thought to have originated with coralline algae. Coralline algae are little green crunchy plant-like organisms that use microscopic grains of calcium carbonate to give their tissues some support. When these plants die, the tissues rot and the tiny grains add to the local mud. In addition, some of the micrites may have originated when calcium carbonate precipitated as tiny grains in the water column and settled to the sea floor. Quartz, feldspar, and a few micromicas (muscovite) are surrounded by abundant clay minerals (kaolinite, smectite), organic matters, and glauconite pellets. The observed detrital and authigenic minerals include smectite, kaolinite, illite, sericite, feldspar, and quartz silts and chlorite.

#### Physical Compaction

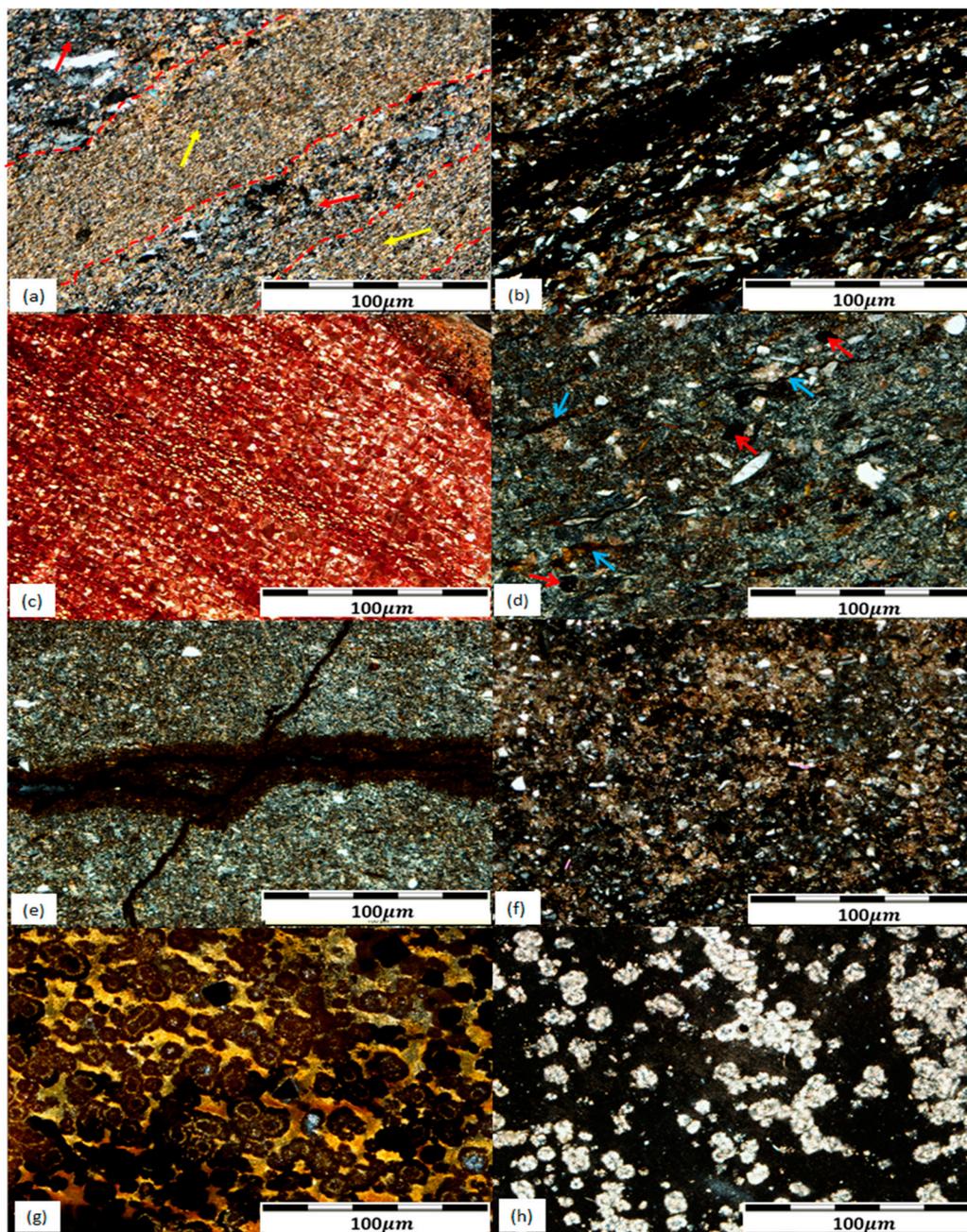
Some of the mudrocks have fissility texture allowing the rocks to break along laminae planes. The fissility of the shale is as a result of the high organic content, the alignment of clay particles, and the presence of laminae. The texture was affected by compaction allowing the clay and silt grains to lie parallel to the lamination of the rocks as shown in Figure 5a–c. The detrital muscovite has been deformed and the deformation is possibly due to compaction of the sediments by the overburden. The mudrocks of Ecca Group are subjected to moderate-intense physical compaction during their progressive burial. This is revealed by cracks or fractures in the rock (Figure 5d,e).

#### Mineral Replacement

Calcite is the most abundant replacement mineral in the mudrocks. Calcite replaced both the clay matrix and silt-grains (Figure 5f), i.e., the detrital feldspars, quartz, and volcanic fragments are replaced by calcite. The most affected feldspars were the K-feldspar (microcline) and minor plagioclase. Mineral replacement of the feldspars by calcite also resulted in the formation of micropores in sediments. In a few cases, the detrital muscovite were recrystallized and chloritized. The recrystallization of the minerals is due to the high temperature as burial depth increases.

#### Mineral Compositions

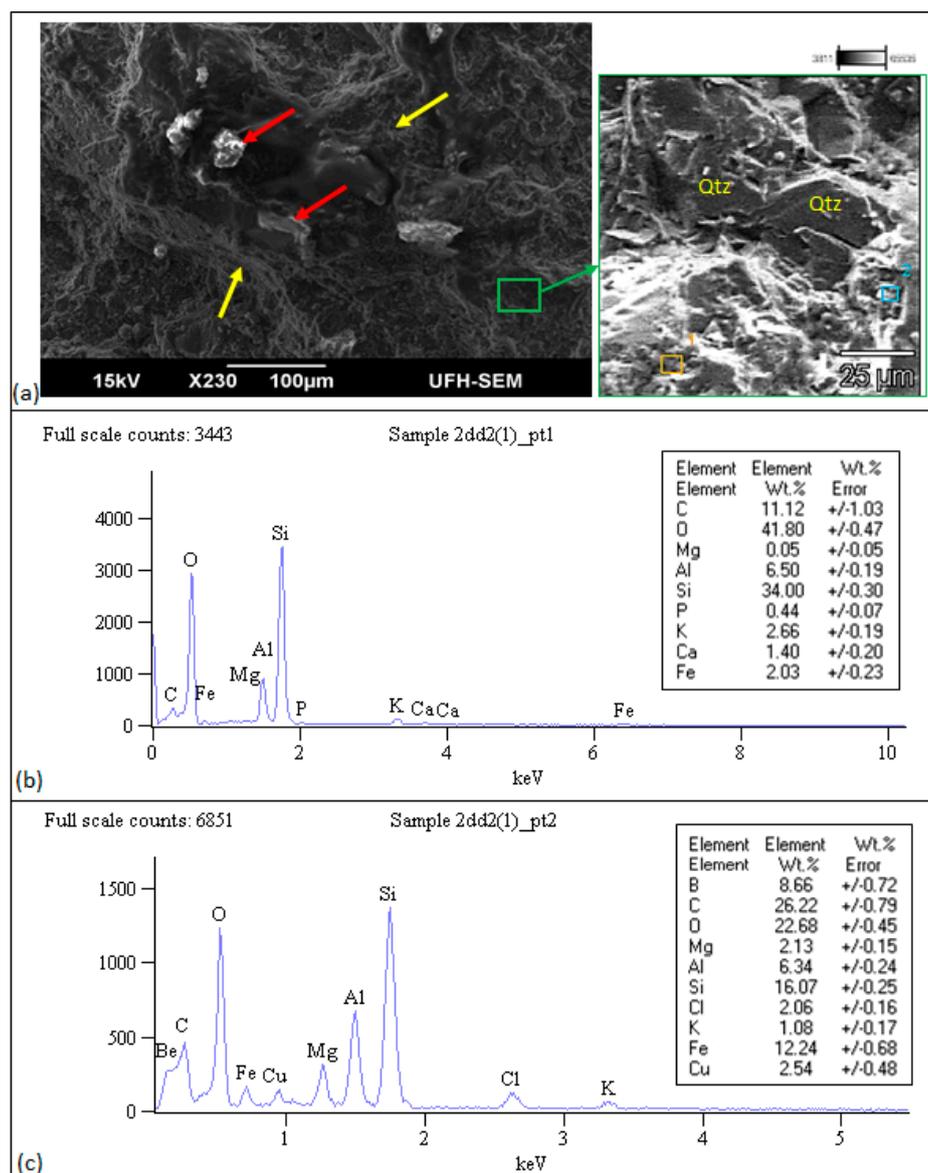
Kaolinite, illite, smectite clay minerals, and hematite are present in the mudrocks. These minerals formed from both the dissolution of potassium feldspars and through the recrystallization of fine sediments. The minerals also formed through the modification of one clay mineral to another; for instance, both kaolinite and smectite were transformed into illite. In addition, illite and sericite recrystallized from both smectite and kaolinite. Hematite is also a common type of authigenic mineral in the mudrocks. It is recognized for its red-brownish staining color, and it stains the detrital grains and clay minerals with a red brownish color (Figure 5c). This iron oxide in the form of reddish-brown crypto-to microcrystalline mineral occurs as a thin coating around detrital grains, within mica flakes and along the boundary of cracks (Figure 5d,e). This suggests that the formation of these iron-oxide minerals occurred in early diagenesis under oxidizing conditions. In this stage, the chemistry of the interstitial waters was mainly controlled by the depositional environment. The abundant of biotite and other iron-bearing minerals in the mudstones could possibly be the source of iron for the formation of hematite mineral. The SEM-EDX results for the mudstone sample shows that the dominant minerals in rock are clay minerals (Figure 6b,c).



**Figure 5.** Thin section photomicrographs of mudrocks showing: (a) claystone (yellow arrow) and siltstone (red arrows, more than half are clays) layers; (b) carbonaceous siltstone of the Whitehill Formation with mineral grains lying parallel to the lamination planes; (c) iron stained (hematite) mudrock of the Prince Albert Formation; (d) siltstone with pyrite (dark area, red arrows) and also hematite staining (blue arrow); (e) mudstone with secondary cracks; hematite filled the cracks (iron staining); (f) calcite replacement of clay matrix and framework grains (brownish area); (g) manganese-iron rich nodules in mudrock of the Collingham Formation; (h) dark micrite and white chalcidony nodules in the Whitehill Formation.

The XRD result of the analyses mudrocks and sandstones are presented in Table 3. The most abundant minerals include quartz (16–40%) and plagioclase (7–30%), while the dominant clay minerals are illite (5–30%), smectite (<1–35%) and chlorite (1–14%). The identified heavy minerals are hematite, garnet, and zircon and they all exist in traces. It is observed that the percentages of quartz and feldspar for some of the mudstone/shales are high or over estimated. This could be an over estimation caused

as a result of authigenic silicification which was recorded as quartz. Actually, most mudstone/shale contains more clay minerals than detrital minerals like quartz and feldspar (cf. Table 3), only a part of the studied samples contain near a half of detrital mineral. Furthermore, some of the quartz and feldspar are authigenic minerals, other than detrital minerals; therefore the total percentage of quartz and feldspar is basically still normal. Talc/pyrophyllite were identified in most of the samples indicating low grade metamorphism, which takes place at temperatures between about 200 and 320 °C, and relatively low pressure. The low grade metamorphic rocks are generally characterized by an abundance of hydrous minerals. With increasing grade of metamorphism, the hydrous minerals begin to react with other minerals and/or break down to less hydrous minerals.



**Figure 6.** (a) SEM (BSE) photomicrograph of mudrocks showing silt-sized calcareous nodules (red arrow) amongst clayey matrix (yellow arrow); (b) SEM-EDX graph showing elemental composition of clay matrix (smectite) at point 1 (yellow area); (c) SEM-EDX graphs showing elemental composition of clay matrix at point 2 (blue area). The SEM-EDX results for mudstone sample shows clay minerals (Al, Si, Mg, Fe, and K) as the dominant minerals in the rock.

**Table 3.** Results of X-ray diffraction (XRD).

Formation	Sample ID	Plagioclase (%)	Microcline (%)	Quartz (%)	Illite (%)	Chlorite (%)	Mica (%)	Smectite (%)	Talc/pyrophyllite (%)	Sericite (%)	Hematite (%)	Pyrite (%)	Dolomite (%)	Garnet (%)	Zircon (%)	Zeolite (%)
Fort Brown	Sandstone	26	1	31	4	4	1	24	8	-	tc	-	-	tc	tc	tc
Fort Brown	Sandstone	30	2	29	6	5	2	20	5	-	tc	-	-	tc	tc	tc
Fort Brown	Mudstone	28	2	30	6	6	2	18	7	-	tc	-	-	tc	tc	tc
Ripon	Sandstone	20	3	38	7	3	5	17	6	-	-	-	-	-	tc	tc
Ripon	Sandstone	16	tc	21	30	10	8	12	2	-	-	tc	-	tc	tc	tc
Ripon	Sandstone	17	tc	18	28	9	6	18	3	-	-	-	-	tc	-	-
Ripon	Sandstone	12	tc	25	26	11	4	20	1	-	-	-	-	tc	-	tc
Ripon	Sandstone	10	2	32	25	14	17	tc	-	-	-	-	-	-	-	-
Ripon	Sandstone	10	tc	36	18	9	26	-	-	-	-	-	-	tc	-	-
Ripon	Mudstone	20	-	27	6	11	tc	35	tc	-	tc	tc	-	tc	tc	-
Ripon	Shale	19	tc	16	26	9	8	16	5	-	-	-	-	tc	-	-
Ripon	Shale	28	4	40	7	3	5	2	11	-	-	-	-	-	-	-
Ripon	Sandstone	25	tc	30	6	4	6	28	-	tc	tc	-	-	-	-	-
Ripon	Sandstone	18	3	34	6	1	9	23	5	-	-	-	-	-	tc	tc
Ripon	Mudstone	25	tc	32	5	8	2	25	2	tc	tc	tc	-	tc	tc	tc
Ripon	Mudstone	19	-	28	7	10	1	34	tc	-	tc	tc	-	tc	tc	-
Ripon	Mudstone	23	3	34	7	6	11	13	tc	2	-	-	7	tc	-	-
Collingham	Shale	12	4	32	13	10	5	23	-	-	-	tc	-	tc	tc	-
Collingham	Shale	13	-	30	11	13	4	28	-	-	-	tc	-	tc	-	-
Collingham	Shale	11	-	40	12	8	16	12	-	-	-	-	-	tc	tc	-
Whitehill	Shale	23	-	37	9	6	14	8	-	tc	-	2	-	-	-	-
Whitehill	Shale	9	-	28	14	4	18	12	-	-	-	9	6	-	-	-
Whitehill	Shale	12	-	32	26	-	2	tc	-	tc	-	5	22	-	-	-
Whitehill	Shale	7	tc	30	16	8	15	6	-	tc	tc	7	9	-	-	-
Prince Albert	Mudstone	10	2	25	18	6	3	30	-	5	tc	tc	-	tc	tc	-
Prince Albert	Mudstone	15	tc	20	14	8	4	31	-	7	tc	tc	-	tc	tc	-
Prince Albert	Mudstone	13	tc	23	16	4	6	33	-	3	tc	tc	-	tc	tc	-

tc and - represent minerals identified in traces and not detected, respectively.

## 5. Discussion of the Diagenesis of Mudrocks and Sandstones

Thin section study, SEM-EDX, and XRD analyses revealed that the minerals in the Ecca Group include detrital minerals of quartz, orthoclase, microcline, plagioclase (i.e., albite), biotite, muscovite, and clay minerals (kaolinite, illite, smectite, sericite, and chlorite). These minerals constitute the rock framework grains with some occurring as cements, whereas the authigenic minerals of pyrite, hematite, glauconite, calcite, and vitrinite (organic maceral) were formed during diagenesis. Petrology study shows that the Ecca Group rocks are mostly terrigenous sandstones and mudrocks. The sandstones are dominated by feldspathic graywackes with minor quartz-wackes, while the mudstones are dominated by dark or greyish mudstones and siltstones, black shales, and yellow claystones.

### 5.1. Diagenetic Stages

The diagenetic features in the rocks of Ecca Group can be divided into three stages that include early diagenesis, burial diagenesis, and uplift-related diagenesis. The time is relative, with the earliest diagenetic event occurring shortly after deposition and the latest occurring up to the present time. The early diagenesis covers all processes that happened at or near the sediment's surface where the chemistry of the interstitial water is primarily controlled by the depositional environment [38]. In this stage, the effect of original depositional pore water dominates, and thus includes bacterially mediated redox reactions in marine environments [8]. The early diagenetic realm may extend to only a few meters below the sediment surface at shallow burial but still be influenced by the depositional system. Burial diagenesis encompasses those diagenetic processes that happened during burial, just after the sediments were cemented and passed from the influence of depositional environment until metamorphism. On the

other hand, uplift-related diagenesis happens in uplifted and exhumed rocks. These rocks have been exposed to the inflow of surface (meteoric) water which is not linked or related to the depositional environment of the host sediments. Uplift-related diagenesis differs from burial diagenesis basically because the rocks are in contact with low salinity, high oxygen, and high carbon dioxide-charged waters. Despite the waters having low ionic strength; they can still result in significant geochemical changes, such as alteration feldspars to clay minerals (usually kaolinite) and ferric mineral oxidations.

#### 5.1.1. Early Diagenetic Stage

Early diagenesis covers all the changes that the Ecca sediments changed from the soft loose state until it became a consolidated hard rock. The main factors that affect early diagenesis are time–temperature history, primary mineralogy, and fabric, geochemistry of the pore water, and presence of petroleum-related fluids (i.e., oil and shale gas). The observed processes in the early diagenetic stage include precipitation of authigenic clay minerals, development of minor quartz and hematite coatings, pyrite formation, and lithification. Minor quartz cementation due to the remobilization of biogenic silica as well as compaction starts forming at the early diagenetic stage. However, quartz syntaxial overgrowths occur at about 70 to 80 °C, at several kilometers depth, well beyond the realms of early diagenesis and after most compaction. In fact, it is grain compaction and dissolution that supplies much of the quartz and feldspar cements. Lewin [39] documented that the early occurrence of quartz cements in marine sandstones and mudstones possibly points to the decomposition of biogenic siliceous organisms just after the sediments were deposited. Cementation almost began immediately and precipitation of different cement types was initiated. The first minerals that precipitated out of pore-spaces between framework detrital grains are the clay matrix. Authigenic smectite and kaolinite cements are the second group of cement that were formed in the Ecca Group. Quartz, feldspar and hematite cements are the third group of cement. Illite, kaolinite and smectite are the most common clays in the Ecca sandstones and mudstones. They occur as pore-filling and pore-lining cements and clay rims around grains. Alkaline pore fluids with sufficient K, Si, and Al are required for illite formation whereas kaolinite requires more acid pore waters. The ions for kaolinite and illite precipitation are largely derived from the alteration of detrital minerals, in particular clay minerals and feldspars. Hematite directly precipitates on some quartz and feldspar grain surfaces, visible as reddish-brown rims on grain surfaces. This reveals that the formation of these grain coatings occurred during early diagenesis through iron oxide rich pore-water. At this stage, oxidizing conditions in the interstitial waters must have existed to allow for the formation of iron cement since the chemistry of the interstitial waters was primarily controlled by the depositional environment as documented by Schmidt and McDonald [40,41].

Despite the fact that iron oxide (hematite cement) is not a common cement type in sandstones and siltstones, the presence of iron oxide allowed the red staining of the Prince Albert siltstone and mudstone. The iron was released during the breakdown of unstable iron-rich clay minerals in the mudstones under surface temperature and pressure conditions. Also, iron may have been transported into the basin by meteoric waters from weathering of the adjacent hinterland and precipitated under favorable oxic conditions. Walker [42] reported that the interstitial dissolution of hornblende, magnetite, biotite, and pyroxene grains are usually the most probable source of iron. As the depth gradually increases, the fine organic matter preserved in the mudstones becomes involved in diagenetic reactions, contributing reaction products to the pore waters. With time, the oxic condition becomes reducing as oxygen is used up in bacterial processes (due to the reaction of hydrogen sulfide with iron bearing minerals), thus pyrite is precipitated. Glauconite is another clay mineral that precipitates at the early diagenetic stage. The process of glauconite precipitation must have occurred at the interface between reducing and oxidizing zones in muddy sediments and in the presence of Si, Fe, Al, and K containing pore fluids [43]. Silica content is one of the controlling factors in the precipitation of glauconite. With regard to this, the organic material content in the mudstones is more than those of the sandstones. This possibly led to the higher amounts of glauconite in the clayey sediments than in the sandy sediments. Lithification of the soft sediments occurred due to cementation and mechanical compaction. The compaction which involves dewatering and a closer packing of grains is the result of increased burial depth as well as

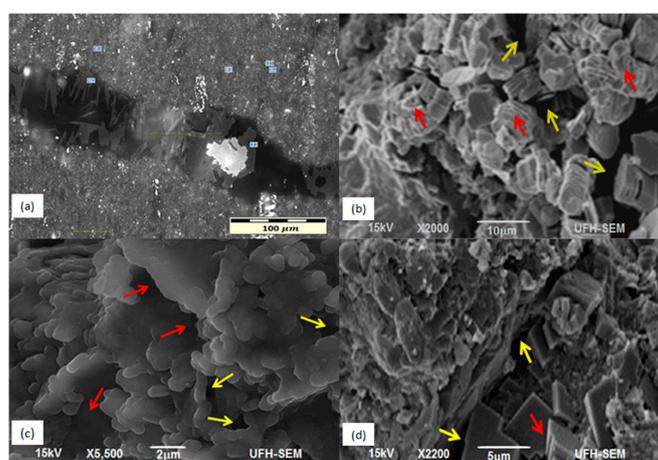
overburden pressure. In summary, the early diagenetic processes were characterized by matrix and cement precipitation, authigenic mineral formation, compaction, and minor cementation.

### 5.1.2. Burial Diagenetic Stage

Burial diagenesis covers all the changes that may happen to the rocks after consolidation and before metamorphism. The main factors that affect diagenesis in the burial diagenetic stage are increased temperature and pressure, as well as a change in pore-water compositions [44]. These factors result in both physical (i.e., compaction and porosity loss) and chemical/mineralogical changes (i.e., mineral replacement, dissolution of minerals and precipitation of new cements) that tend to get the sediments into equilibrium with the diagenetic environment. During deeper burial, pore waters were further modified or changed by reactions with clay minerals. In addition, dissolution of unstable grains occurred. Diagenesis in the burial diagenetic environment is not complete without considering the influence of organic matter [7]. During burial, organic matter is originally changed chiefly by microbial activity, but as burial depth increases, it further undergoes chemical changes due to chemical processes like polymerization, polycondensation, and insolubilization. These processes convert the organic matter into a highly complex geopolymer (kerogen) which may be a predecessor to petroleum generation [45]. Kerogen has carboxylic and phenolic functional groups that undergo thermal cracking at high temperature (about 80 °C) to form soluble organic acids in associated shales and mudstones [7]. These organic acids are forced out of the shales during clay-mineral dewatering into the related sandstones. As burial depth increases with further increase in temperature in the range of 120–200 °C, the carboxylic acid anions are destroyed by thermal decarboxylation [7]. In addition, dissolution of both carbonates (i.e., calcite cements) and some silicate minerals (i.e., feldspar) may occur in reaction to the organic–inorganic interactions. The diagenetic processes that occurred in burial diagenetic stage are cementation, physical and chemical compaction, dissolution, recrystallization, precipitation, and replacement of minerals (i.e., albitization, sericitization, and chloritization), pressure-solution, grain-deformation and fracturing. Compaction of the Ecca Group sediments continues during burial diagenesis due to the increase in overburden pressure. This brought about an increase in tightness of grain packing and partial loss of pore spaces. Likewise, the increase in temperature and pressure as a result of compaction also led to partial dissolution of silicate grains and recrystallization of fine minerals. Subsequently, quartz and feldspar overgrowths, as well as mineral replacement and clay mineral alteration (i.e., alteration of smectite to illite, sericite or chlorite, kaolinite to illite or sericite) dominate the burial diagenetic changes. Albite and illite are formed through replacement of K- and Ca-feldspars, particularly the K-feldspars. Some K-feldspars are replaced by calcite, with authigenic quartz being released as a by-product. Unstable detrital grains release cations to pore-waters, allowing the calcite cements to precipitate in the pore-space or replace detrital grains and matrix. Some of the calcium carbonate ions moved towards a center in pore-solution within the sandstones and mudstones, which resulted in the formation of calcareous concretions or nodules that is commonly found in the sandstones of Ripon Formation and mudrock of the Collingham and Whitehill Formations (Figure 5g,h). These calcareous concretions are usually related to the original depositional environment such as marine sediments, and also could be linked with later diagenesis due to leaching and evaporation of pore-water (caliche). Solutions rich in  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are capable of destroying the potash feldspar lattice, possibly by causing the silica tetrahedral units to go into solution under high pH burial environment [46].

In the rocks of Ecca Group, mineral replacement was not only confined to the K-feldspars. Clay matrix and quartz grains also underwent partial replacement. Precipitation of calcite inside clay minerals can be linked to the crystalline structures of minerals consisting of  $\text{Ca}^{2+}$  ions, which occupy less interstitial space thus, allowing the remainder to be filled by the precipitated carbonate [46]. Some of the calcite precipitation could have been due to clay mineral replacement in burial environment with pH of >8 in addition to a high concentration of  $\text{Ca}^{2+}$  ions, a condition that rendered clay minerals unstable. Furthermore, the  $\text{CO}_2$  released when organic materials decayed during diagenetic processes, may also be an additional source of carbonate ion for the precipitation of calcite cements. High temperatures and pressure resulted in the dissolution of silicate materials from which some of the silicate minerals recrystallized. For example,

smectite recrystallized into illite and chlorite, whereas kaolinite changed into illite. Illite also further recrystallized to sericite, which later changed into muscovite. Partial to complete replacement of some detrital grains and clay matrix by new minerals is a common phenomenon in this stage. Albitization of feldspar possibly occurred during fracturing of the detrital K-feldspar grains. As a result of the progressive increase in burial depth, detrital grains started to pack more tightly resulting in thinning of the beds as well as porosity reduction. The effects of compaction are evidenced in both the sandstones and mudrocks. In the sandstones, point and line contacts are formed between the grains, whereas in the mudrocks, the grains developed an alignment parallel to lamination and show signs of bed thinning. Due to further compaction, the initial point and line contacts changed to convex–concave grain contacts and finally to suture contacts. Furthermore, muscovite flakes became bent and deformed due to over compaction. Secondary porosity was created when the detrital feldspar, rock fragments, and muscovite grains were also fractured. As a result of high temperatures, organic materials in the sediments were altered to vitrinite. Thin section examination of the argillaceous rocks also revealed the existence of plant fossils in the rocks. The vitrinite is thought to have formed from the lignin and cellulose of the plant materials (Figure 7a).



**Figure 7.** (a) Woody fragments in a mudstone sample from the Ecca Group, which has been partially decayed and some of the wood tissue remained, or was replaced by illite; (b) SEM (BSE) photomicrograph showing secondary pores (yellow arrows) occurring between vermicular kaolinite crystals (red arrows); (c) SEM (BSE) photomicrograph showing elongated (red arrows) and rounded pores (yellow arrows) between the smectite and illite crystals; (d) SEM (BSE) photomicrograph showing rhomboid calcite cement (red arrow) blocking pore (yellow arrows).

### 5.1.3. Uplift-Related Diagenetic Stage

Uplift and exposure of marine Ecca Group rocks to influx of surface water takes the rock into an uplift-related diagenetic environment. Hurst and Irwin [36] reported that marine deposited materials are never invaded by large quantities of meteoric or surface waters unless they are uplifted and subjected to weathering. In general, oxidizing and meteoric pore waters as well as lowered temperatures and pressures characterize the uplift-related diagenetic stage. Mineral assemblages that were initially formed under high temperature and pressure in the burial diagenetic stage become unstable in the uplift-related diagenetic stage. This could result in alteration or dissolution of unstable minerals. Furthermore, the original detrital mineral assemblages may undergo additional diagenesis. Diagenetic alteration in the Ecca Group rocks took place at some depth below the Earth's surface, but still within the region of meteoric water circulation. It continued at the surface as a result of uplift and weathering processes. At uplift, the rocks were exposed to acidic rain water, which led to dissolution of previously formed carbonate cements (decementation), thus resulting in porosity increase.

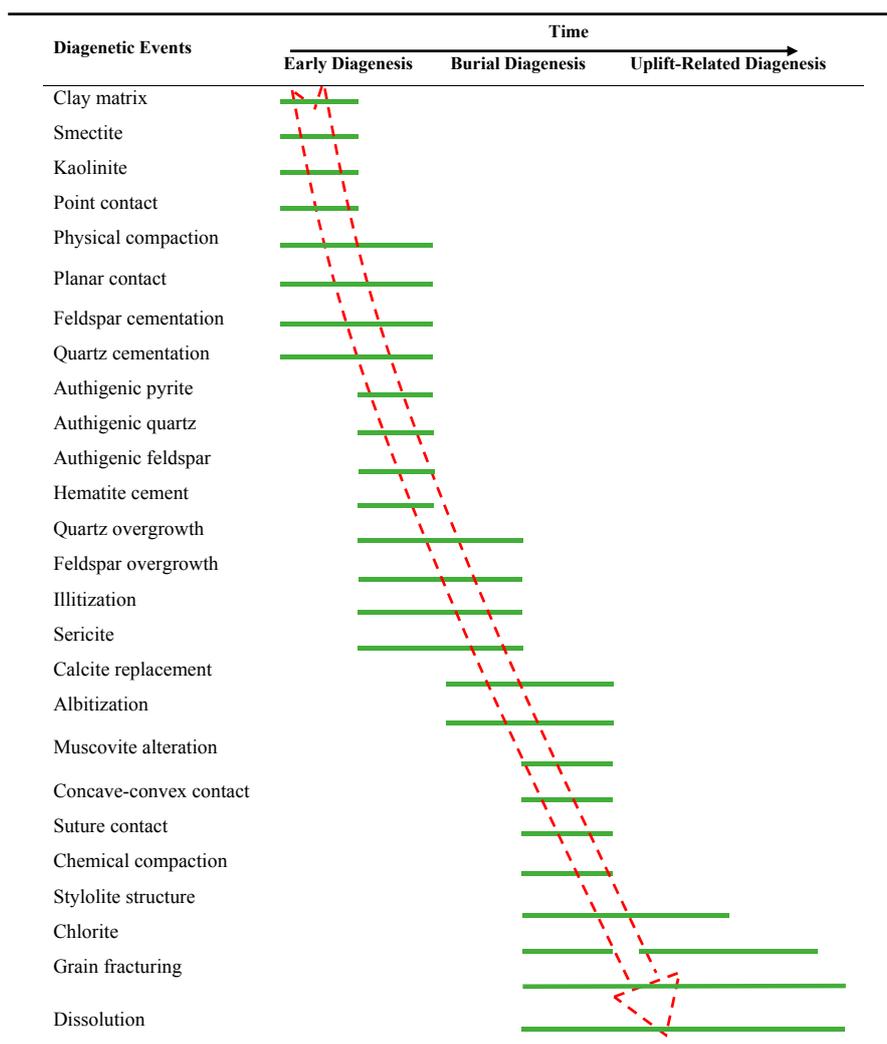
Mudstones of the Prince Albert Formation also underwent changes after being exposed on the surface. The changes may have included in situ alteration of framework grains to clay minerals (weathering), which tends to occlude or block porosity. Most of the clay minerals were stained by iron oxide thus resulting

in the red or brownish color. The red pigmentation in the mudstones of the Prince Albert Formation can be related to the change that took place when the rocks were exposed to surface or meteoric waters. The leaching/oxidation of iron-rich minerals (i.e., illite and pyrite) resulted in red coloration or staining in the mudstones (Figure 5c). Apart from the clay minerals, the dissolution of hornblende and weathering of pyrite could be another source of iron that stained the Prince Albert Formation shales to red brownish. The red color is secondary in nature because it was not the original color of the sediment. Parts of detrital feldspars are altered to illite and chlorite. Also, some of the observed kaolinites are formed due to weathering and alteration of feldspar. This type of kaolinite is found in minor quantities possibly due to the fact that argillaceous rocks are mainly made up of smectite clay rather than kaolinite in the Eccca Group. The kaolinization of feldspars was due to the presence of fresh surface-water at uplift. Flushing of sediments by fresh water is generally thought to be a vital process in kaolinization, especially in the kaolinization of sandstones [47]. Calcite and kaolinite were also partially dissolved and leached, which created pore-space. In summary, the uplifted related diagenetic processes were characterized by chloritization, grain fracturing, and dissolution.

### 6. Diagenetic Sequence

A series of diagenetic changes in the Eccca Group are associated with each other and can constitute a diagenetic pathway and sequence. The diagenetic processes and pathway for the development of different minerals in the rocks of the Eccca Group are tabulated in Table 4.

**Table 4.** Diagenetic events and pathway of the Eccca Group in the study area.



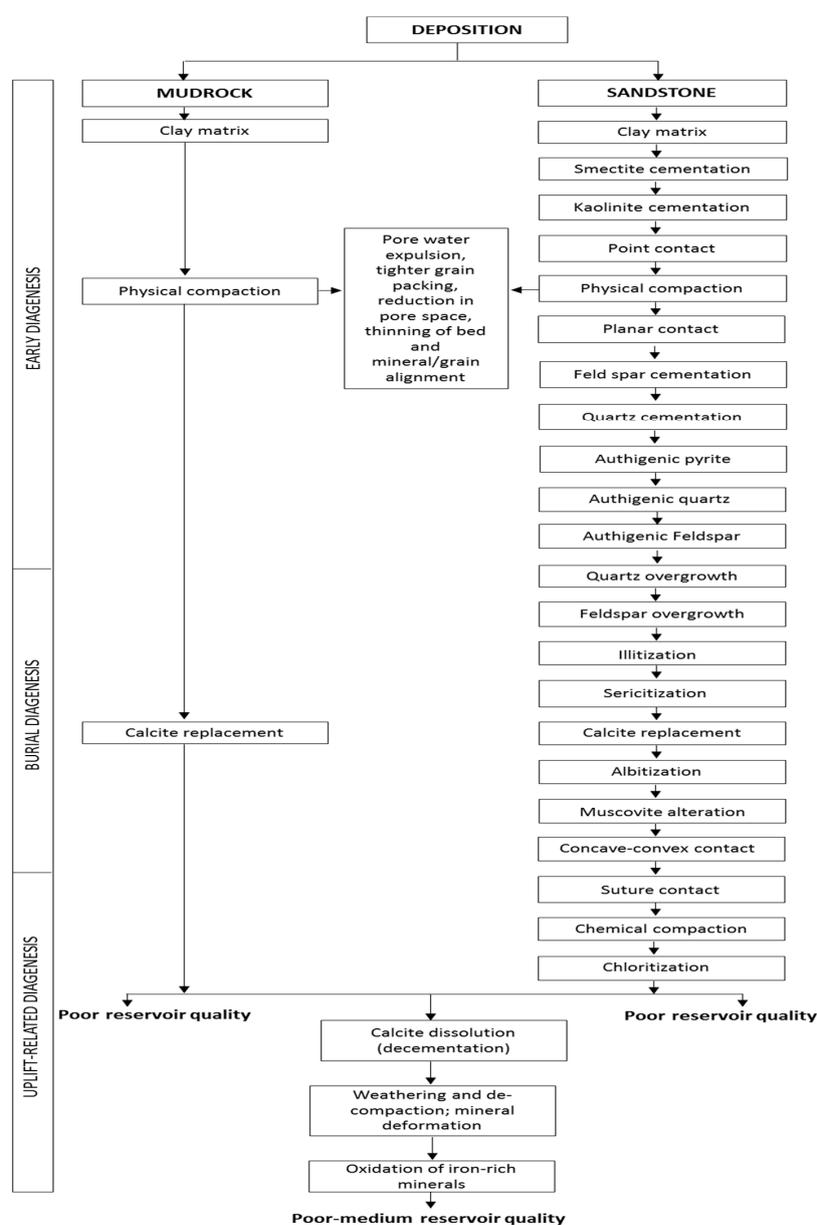
## 7. Implications of Diagenesis for Reservoir Properties

Reservoir quality mainly depends on the relationship between porosity and permeability, which may be of different types. Porosity and permeability are two vital properties of sedimentary rocks that are partially influenced by the textural characteristics of grain size, shape, packing, and arrangement. In addition, they play a very crucial role in the diagenesis of sediments by controlling the flow of fluids through rocks. The fluid that flows in the rock causes dissolution, cementation, and authigenesis of minerals. Petrographic and SEM examination of the Ecca Group rocks revealed both primary and secondary porosity. Primary porosity is the pore space that existed in the sediment just after deposition before diagenetic modification. It is comprised of intergranular (pore space between grains) and micro porosity (matrix micro pores). Diagenesis may cause a change of porosity types, for instance, precipitation of authigenic clay minerals in pores causing the pore throats to decrease.

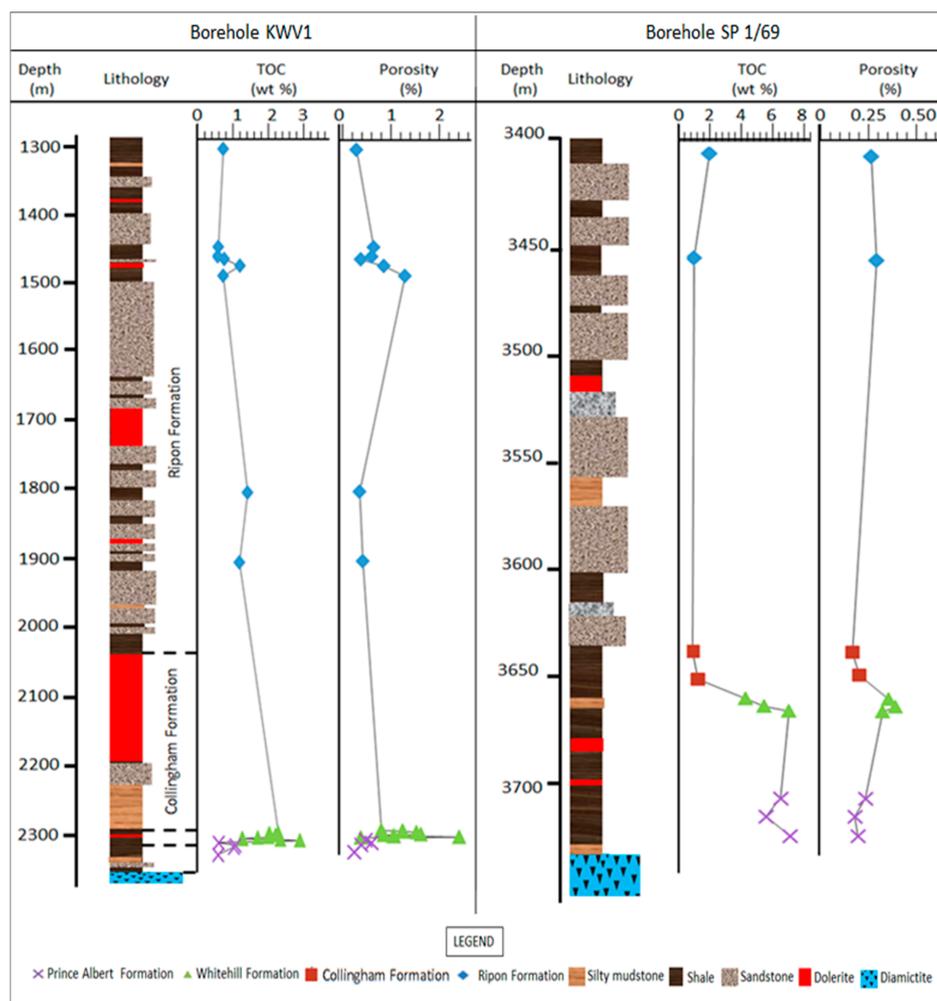
Reservoir quality of Ecca sandstones and mudrocks is largely determined by diagenetic processes that either reduce or enhance porosity and permeability. The most important diagenetic processes in the rocks of Ecca Group are compaction, cementation by calcite, quartz, feldspar, clays, and iron oxide. The observed primary porosities are primary intergranular and matrix micro pores. As sediments become compacted due to overburden, point and line contacts are formed. The progressive burial was responsible for primary porosity reduction due to compaction as indicated by long and sutured contact between neighboring clastic grains. Primary intergranular porosity and pore radii were reduced due to changes in grain contacts. In some samples, the carbonate cement reduced or prevented further compaction and the resulting close packing of clastic grains. Authigenic kaolinite, and iron oxide also played an important role in the preservation of porosity. Kaolinite and mixed layer clays caused reduction in primary porosity, but can form and preserve porosity between kaolinite crystals (Figure 7b). Generally, the pores in the matrix are very small in size, possibly due to the high percentage of smectite-illite minerals. However, a few, relatively big and elongated pores were observed in the rocks (Figure 7c). Since quartz cements are known to be destructive on primary porosity, the existence of quartz cements could possibly limit the preservation of primary porosity in the rocks. In some samples, quartz overgrowth coats the detrital quartz grains resulting in the decrease of pore radii and consequently reducing porosity and permeability. In a few cases, chlorite rims surround the overgrowths thus preserving the ineffective matrix micro pores (micro-porosity). Calcite cement in the mudrock and sandstones appears as patches and partially occupies the intergranular pores (Figure 7d).

Primary intergranular pores are reduced as a result of intense compaction and cementation. Most of the primary pores were destroyed by the same process that resulted in generation of the epimatrix of wackes (epimatrix is a matrix that is composed of clays that grow during diagenesis (authigenic), sometimes from the alteration of feldspars). However, a small amount of secondary porosity occurred in the rocks. During burial diagenesis, preferential destruction of less stable minerals or clastic grains by pore fluids produced pore spaces for secondary cementation. Another episode of dissolution which occurred during uplift-related diagenesis and involved partial removal or dissolution of earlier formed carbonate cements also created secondary porosity. The observed secondary porosities in the rocks are secondary intragranular, dissolution and fractured pores. Secondary intragranular and dissolution pores resulted from the dissolution of unstable feldspar grains, from dissolution of clay minerals formed by alteration of the pseudomatrix and from the dissolution of carbonate materials (i.e., calcite cement). Conversely, the fractured pores are due to structural forces and differential compaction. Some of the detrital feldspar and muscovite grains are cracked probably due to compaction as burial depth increases. Fracturing also points to over-compaction which in some case resulted in porosity reduction. With regard to reservoir quality, the initial porosity was decreased by compaction and cementation and then increased by dissolution of unstable minerals and calcite cement (decementation). Most of the secondary pores are very small and isolated, resulting in very low porosity and permeability, resulting in poor-medium potential reservoir quality (Figure 8). The low porosity and permeability of most of the Ecca rocks make them unfavorable producers of hydrocarbons, which at best would require stimulation or fracking. A summary of the petrophysical properties measured by the authors

for the Ecca Group rocks is presented in Figure 9 and Table 5. The measured thin section porosity for the outcrop samples (shale and sandstones) from the Prince Albert, Whitehill, Collingham, Ripon, and Fort Brown Formations vary between 0.2–2.6%, 1–3.2%, 0.4–2.0%, 1–5.1%, and 0.3–3.5% (Table 5), respectively. Due to the development of cracks, joints, and faults in the outcrops of the Ecca Group, the actual or real porosity of the rocks in the field could be much higher than the observed or measured thin section porosity. The size of pores in the mudrocks are predominantly <1 μm (nanopores), thus providing evidence that the formations as a whole are characterized by low permeability values. The shales (core samples) of the lower Ecca Group formations (Prince Albert, Whitehill, and Collingham Formations) have average porosities that are lower than those determined for active shale gas plays (Marcellus shale in Appalachian Basin and Barnett shale in Fort Worth Basin) in the United States. Productive, organic rich units of the Marcellus and Barnett Shale play have average porosities of ranging between 3% and 6% [48] and permeabilities of ≤0.1 mD [49], which are slightly higher than those measured in the potentially gas bearing shales of the Whitehill Formation (Table 5).



**Figure 8.** Flow chart of the main diagenetic processes in mudrocks and sandstones of the Ecca Group as well as their impact on the potential reservoir quality.



**Figure 9.** Downhole TOC and mercury intrusion porosimetry porosity for boreholes KVV 1 and SP1/69.

**Table 5.** Measured petrophysical properties of the Eccca Group rocks in the study area.

Formation	Lithology	Average Thickness (m)	Average Density (kg/m <sup>3</sup> )	Average Porosity (%)
Fort Brown	Sandstone	892	2.774	2.444
	Shale		2.656	1.574
Ripon	Sandstone	700	2.721	3.241
	Shale		2.662	1.595
Collingham	Shale	65	2.598	1.188
Whitehill	Shale	21	2.526	2.710
Prince Albert	Shale	87	2.641	1.260

### 8. Conclusions

This study revealed that the rocks of the Eccca Group were subjected to moderate-intense mechanical and chemical compaction during their progressive burial and the diagenetic processes passed through early, burial and uplift-related diagenetic stages. The main diagenetic processes that affected the rocks are cementation, mechanical compaction, dissolution crystallization, and replacement of framework grains and cements. During early diagenesis, sediments mainly undergo cementation and minor lithification. Mechanical compaction, pressure solution, dissolution by pore fluids, mineral replacement, clay-minerals authigenesis, and mineral deformation are the major diagenetic processes during burial

diagenesis. Uplift-related diagenesis is comprised of decementation, mineral replacement, oxidation of ferromagnesian minerals, and destruction of detrital grains by oxidation. The identified cements are quartz cement, calcite cement, hematite cement, feldspar cement, and authigenic clay minerals. Quartz and feldspar cements occur as both pore-filling and overgrowths in the rocks. The authigenic clays are mostly smectite, kaolinite, illite, and illite/smectite. Calcite cements occur as replacement mineral of detrital grains as well as pore-filling and pore-lining clays in the rocks. Deformation and alteration of labile grains due to compaction create clays in the pseudomatrix.

The primary porosities (intercrystalline pores, intergranular pores, and matrix micro pores) are reduced due to intense mechanical compaction and filling of early authigenic cements such as carbonate, quartz, clay minerals, and iron oxides. The dissolution of carbonates and feldspars after diagenetic modification as well as the effects of tectonic forces and differential compaction led to the formation of secondary pores. These diagenetic processes that resulted in secondary porosities (solution pores, secondary intragranular pores, and fracture pores) occurred during both burial diagenesis and uplift-related diagenesis when meteoric water influx was significant. Conversely, the diagenetic process also resulted in the production of some diagenetic products, for example, clay cements (i.e., smectite filling and lining) which reduce porosity. Mechanical compaction and authigenic cements also reduce porosity and permeability. Grain-coating rims of iron oxide in some cases prevented the formation of quartz overgrowths and thus preserved porosity. Generally, there is no single diagenetic process that mainly or solely controls the pattern of porosity evolution in the rocks. Instead, it appears that the main types of cements (carbonates, clay minerals, and quartz) as well as compaction collectively controlled the reservoir quality of the rocks. Petrophysically, potential reservoir quality of the Ecca Group is poor-medium. Porosity types are dominated by primary intergranular pores and secondary intragranular, solution and fracture pores. However, both inter- and intra-granular porosity decreases systematically with increasing burial depth. The presence of fractured and dissolution pores tend to enhance reservoir quality. However, the low porosity as well as the isolated nature of the pores (low permeability) makes them unfavorable producers of hydrocarbons, which at best would require stimulation and fracking.

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**Author Contributions:** Kuiwu Liu conceived the research within the framework of Christopher Baiyegunhi's PhD research project. Christopher Baiyegunhi and Kuiwu Liu collected the samples, analyzed and interpreted the data. Christopher Baiyegunhi wrote the paper with contributions from Kuiwu Liu and Oswald Gwavava. In addition, Oswald Gwavava co-supervised the research work.

**Conflicts of Interest:** The authors declare no conflict of interest.

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