

**UNDERSTANDING THE CONTROLS ON
FORMATION OF AUTHIGENIC CLAY MINERALS
IN MARGINAL MARINE SETTINGS: INSIGHTS
FROM HYDROTHERMAL-REACTOR
EXPERIMENTS**

BY

ANAS MUHAMMAD SALISU

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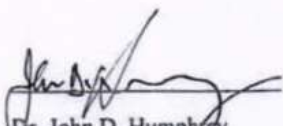
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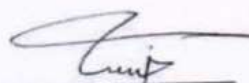
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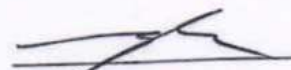
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Dr. John D. Humphrey
Department Chairman

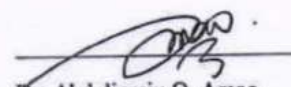

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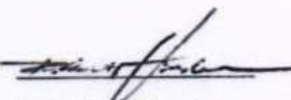
Date


Prof. Khalid A.H. Al-Ramadan
(Advisor)


Dr. Ardiansyah I.
Koeshidayatullah
(Co-Advisor)


Dr. Abdulwahab M. Bello
(Member)


Dr. Abduljamiu O. Amao
(Member)


Dr. Robert H. Lander
(External Member)



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“I finished my education as I started it, playing in a sand pit.”

Dedicated to my parents, wife, and daughter

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Table of Contents

ACKNOWLEDGMENTS	v
LIST OF TABLES	xvi
LIST OF FIGURES	xviii
LIST OF ABBREVIATIONS	xlii
ABSTRACT	xliv
ملخص الرسالة	xlvi
CHAPTER 1	1
INTRODUCTION	1
1.1. Background	1
1.2. Motivation	4
1.3. Problem Statement and Research Objectives	5
1.4. Study Areas	6
1.5. Methodology	11
1.6. Thesis Structure Overview	13
1.7. References	16
CHAPTER 2	22
LITERATURE REVIEW	22
2.1. Clay minerals and their impact on sandstone reservoir quality	22
Kaolinite	28

Smectite	30
Illite.....	32
Chlorite	35
2.2. Experimental simulation of clay minerals formation	37
References	42
CHAPTER 3	52
EXPERIMENTAL STUDY OF SMECTITE AUTHIGENESIS AND ITS SUBSEQUENT ILLITIZATION: INSIGHTS FROM MODERN ESTUARY SEDIMENTS	52
3.1. Abstract	52
3.2. Introduction	53
3.3. Materials and methods.....	57
3.3.1. Study area and sampling	57
3.3.2. Hydrothermal reactor experiments	60
3.3.3. Analytical Techniques	63
3.3.4. Grain coat coverage and grain-coating thickness.	69
3.4. Results	70
3.4.1. Composition of the Starting Material	70
3.4.2. Geochemical and Mineralogical Analysis of Post-reacted Samples.....	77
3.4.3. Mineralogical Evaluation of Post-reacted Samples and Synthesized Clay Minerals	

3.4.4.	Fluid Chemistry	91
3.4.5.	3D Analysis of Synthesized Grain-coat Thickness.....	95
3.4.6.	Chemistry of Synthesized Clay Minerals	97
3.5.	Discussion.....	101
3.5.1.	Controls and Mechanisms of Authigenic Smectite Formation	101
3.5.2.	Illitization of Smectite.....	104
3.5.3.	Impact of Fluid Chemistry on the Diagenetic Alteration of Modern Estuarine Sediments.....	107
3.5.4.	Implications for Reservoir Quality	110
3.5.5.	Limitations of the Study and Future Work	112
3.6.	Conclusions	114
3.7.	References	116
CHAPTER 4		128
THE ROLE OF FLUID CHEMISTRY ON THE DIAGENETIC TRANSFORMATION OF DETRITAL CLAY MINERALS: EXPERIMENTAL INSIGHTS FROM MODERN ESTUARINE SEDIMENTS.....		128
4.1.	Abstract	128
4.2.	Introduction	129
4.3.	Study area and geologic background of the sample.....	131
4.4.	Methods.....	134

4.4.1.	Hydrothermal experiments.....	134
4.4.2.	Analytical techniques.....	136
4.5.	Results	141
4.5.1.	Compositional evaluation of the starting material	141
4.5.2.	Geochemical and Mineralogical Evaluation of Post-Experiment Samples	147
4.5.3.	FIB-SEM observations.....	169
4.6.	Discussion	171
4.6.1.	Controls and mechanisms of authigenic illite formation	171
4.6.2.	Authigenic formation of chlorite	174
4.6.3.	Role of Fluid Chemistry on the Transformation Pathways of Modern Estuarine Sediments.....	175
4.6.4.	Relevance of hydrothermal experiments to natural sandstone diagenesis.....	178
4.7.	Conclusions	180
4.8.	References	182
CHAPTER 5		192
DEPOSITIONAL AND DIAGENETIC CONTROLS ON THE RESERVOIR QUALITY OF MARGINAL MARINE SANDSTONES: AN EXAMPLE FROM THE EARLY DEVONIAN SUBBAT MEMBER, JAUF FORMATION, NORTHWEST SAUDI ARABIA.....		192
5.1.	Abstract	192
5.2.	Introduction	193

5.3. Geological background	196
5.4. Methodology	198
5.4.1. Thin section petrography.....	198
5.4.2. Bulk and clay fraction XRD	200
5.4.3. XRF Analyses	201
5.4.4. SEM-EDS analyses.....	201
5.4.5. Porosity and permeability measurements	202
5.5. Results	203
5.5.1. Facies scheme	203
5.5.2. Facies association and interpretation	206
5.5.3. Petrography	209
5.5.4. Grain dissolution and secondary porosity.....	231
5.5.5. Petrophysical analysis.....	232
5.6. Discussion.....	235
5.6.1. Paragenetic Analyses	235
5.6.2. Early diagenesis	236
5.6.3. Burial diagenesis.....	237
5.6.4. Depositional controls on reservoir quality	238
5.6.5. Diagenetic controls on reservoir quality	243
5.7. Conclusion.....	248

5.8. References	250
CHAPTER 6	261
EXPERIMENTAL STUDY OF CHLORITE AUTHIGENESIS: INSIGHTS FROM K- FELDSPAR PRECURSOR	261
6.1. Abstract	261
6.2. Introduction	262
6.3. Geological Background of the Sample	264
6.4. Methodology	265
6.4.1. Hydrothermal reactor experiments	265
6.4.2. Analytical Techniques	268
6.5. Results	272
6.5.1. Composition of the Starting Material	272
6.5.2. Geochemical Analysis of pre-and post-reacted sample	274
6.5.3. Mineralogical Evaluation of Post-Reacted Samples.....	278
6.5.4. Mineralogical and porosity evolution	290
6.5.5. Chemistry of reaction fluids.....	293
6.6. Discussion.....	296
6.6.1. Controls and mechanisms of chlorite authigenesis	296
6.6.2. Smectite as an Intermediate Phase in Chlorite Authigenesis.....	298
6.6.3. Influence of fluid composition on chlorite formation.....	299

6.6.4. Implications for reservoir quality in arkosic aandstones	300
6.6.5. Limitations and Recommendations for Future Research.....	301
6.7. Conclusions	303
6.8. References	305
CHAPTER 7	313
CONCLUSIONS AND RECCOMENDATIOS	313
7.1. Conclusions	313
7.2. Recommendations	316
APENDIX	318
LIST OF PUBLICATIONS	323
VITAE.....	326

LIST OF TABLES

Table 3.1: Conditions for the hydrothermal experiments.....	62
Table 3.2: Results of the WDX-XRF analysis of the starting material and post-reacted samples [SM = Starting material]	71
Table 3.3: Bulk and clay fraction composition, percentage clay fraction, thickness, and coverage of clay coat in pre- and post-reacted samples.	76
Table 3.4: Results of the ICP-OES analysis showing the concentrations of major cations in solutions before and after the hydrothermal experiments. [Pre-Ex = Pre-Experiment, SF = Synthetic fluid, EW = Estuarine water, Na-SF = Na-rich synthetic fluid, ND = not detected]. Seawater is added for comparison with the composition of the synthetic fluid.....	94
Table 3.5: Mean structural formula of the synthesized smectite and Illite clays, calculated from EDS analyses based on 12 oxygen atoms.....	99
Table 4.1: Conditions for the hydrothermal experiments.....	137
Table 4.2: WDX-XRF analysis of the starting material and post-reacted sample. [SM = Starting material; SW=seawater; SF= synthetic fluid; EW= estuarine water]	143
Table 4.3: Bulk and clay fraction composition in pre- and post-reacted samples. [SM=starting material; Qtz=quartz; Orth=orthoclase; Pla=plagioclase; Cal=calcite; Mus=muscovite; CM=clay minerals; Hal= halite; Syl=sylvite; Ana= analcime; Kao=kaolinite; Sme=smectite; Ill=illite; Chl=chlorite]	150

Table 4.4: ICP-OES analysis showing the concentrations of major cations in solutions before and after the hydrothermal experiments.....	155
Table 5.1: Summary of the sedimentary facies descriptions and the assigned facies associations (modified after Algheryafi et al., 2022).....	204
Table 5.2: Petrographic point counts and permeability data for the Jauf Formation.....	210
Table 5.3: Results of the whole-rock XRD analysis for the Jauf Formation.....	216
Table 6.1: Conditions for the hydrothermal experiments.....	267
Table 6.2: Results of the WDX-XRF analysis of the starting material and post-reacted samples [SM = Starting material]	275
Table 6.3: TXRF analysis showing the concentrations of major cations in solutions before and after the hydrothermal experiments.....	294

LIST OF FIGURES

Figure 1.1. (A) Simplified geological map of the Anllóns Estuary catchment area, showing the distribution of various sedimentary environments (modified after Dowey et al., 2017). The red star indicates the location of the samples used in this study. (B) Regional view of the study area, with the yellow rectangle marking the approximate location of the Estuary.	7
Figure 1.2. Simplified facies map of the Gironde Estuary catchment (modified after Virolle et al., 2019) with the red square indicating the location of the samples analyzed in this study. The inset map provides a country-level view of the study area, with the red rectangle marking the approximate position of the estuary.	9
Figure 1.3. (A) Simplified geologic map of Saudi Arabia showing the distribution of the Early Devonian (Emsian) successions and location of the studied section (blue rectangle; redrawn after Konert et al., 2001; Algheryafi et al., 2022). The inset map is a regional view of the study area showing the approximate location of the study (red star). (B) Paleogeographic reconstruction of the Early Devonian showing the location of the Arabian Plate (red star; Stampfli & Borel, 2010). (C) Stratigraphic Column of the Devonian in Saudi Arabia (after Algheryafi et al., 2022). The red rectangle shows the studied Subbat Member.	10
Figure 2.1. Hierarchy of controls on clastic grains which governs sandstone reservoir quality: the “clastic factory”; eodiagenetic processes (early or shallow-burial diagenesis); mesodiagenetic processes (deep-burial diagenesis); and telogenetic influences related to uplift (Charlaftis, 2021; modified after Worden et al., 2018).	23

Figure 2.2. A model of porosity evolution with burial depth for a well-sorted, fine-grained, quartzofeldspathic aeolian sandstone bearing variable clay grain coatings. As clay-coat coverage increases, the extent of cement precipitation decreases. Curve A represents freshly deposited sand, while Curve B marks the onset of cementation at about 80 °C and 2 km of burial. In this hypothetical scenario, maximum porosities are retained at depth where both compaction and cement growth are inhibited by rigid grains enveloped in well-developed clay coats (Charfatis, 2021; modified after Ajdukiewicz and Lander, 2010).....24

Figure 2.3. (A) Thin-section micrograph showing chlorite (GCC) effectively coating detrital quartz grains (Qz) in the Lower Jurassic estuarine Tilje Formation sandstone, thereby preventing quartz overgrowths (Walderhaug & Porten, 2022). (B) SEM image of the Middle Jurassic shallow-marine Garn Formation sandstone reveals chlorite grain coatings with gaps between platelets exceeding approximately 5 µm, allowing quartz outgrowths (Qo) to penetrate and expand laterally through these coatings (Walderhaug & Porten, 2022). 25

Figure 2.4. Thin section photomicrograph (A) showing the occurrence of pore-filling kaolinite (PFK) between detrital quartz grains (Qz) filling pore-spaces. (B) SEM image showing the occurrence of pore-filling illite (PFI).....26

Figure 2.5. A schematic diagram illustrating the structural configuration of common clay minerals in sandstone reservoirs (adapted from Griffiths, 2018, modified after Worden and Morad, 2003). (A) kaolinite, (B) illite, (C) chlorite, and (D) dioctahedral smectite. Tetrahedral layers are represented by triangles, while octahedral layers are denoted by bars. 27

Figure 2.6. An image summarizing the diagenetic transformation pathways of clay minerals in sandstones (modified from Ulmer-Scholle et al., 2014).	28
Figure 2.7. (A) Thin-section photomicrograph showing the occurrence of microporous pore-filling kaolinite (mPFK) occupying pore space within detrital quartz grains (Qz). (B) SEM image showing intercrystalline microporosity (IcM) within vermicular pore-filling kaolinite (vPFK).	29
Figure 2.8. Scanning electron micrographs showing authigenic smectite in sandstone samples: (A) Detrital sand grains coated by dioctahedral montmorillonite. (B) Twinned calcite crystals accompanied by trioctahedral smectite grain coats (adapted from Taylor et al., 2022, reproduced from Clay Archive of the Mineralogical Society of Great Britain & Ireland).	31
Figure 2.9. Petrographic images displaying the type and mode of occurrence of authigenic illite in the Jauf Formation, Saudi Arabia. Thin section (A) and SEM (B) images showing radial grain-coating illite (CGI) on detrital quartz (Qtz) grains. Thin-section (C) and SEM (D) images showing fibrous to lath-like pore-filling illite (PFI).....	34
Figure 2.10. Schematic illustration of authigenic, grain-coating chlorite growth phases and how the site of precipitation controls platelet arrangement and microtexture (adapted from Charlaftis, 2021; modified from Worden et al., 2020; Billault et al., 2003). Before chlorite formation, the water–rock system must be highly supersaturated for chlorite. (A) Random three-dimensional nuclei of chlorite form indiscriminately on all available grain surfaces, producing an ultrathin coating. (B) As supersaturation declines after initial nucleation, fine chlorite sheets extend into the intergranular pore space. (C) Chlorite platelets thicken while retaining their original length and	

width. (D) Well-developed chlorite coats line grain contacts and pore walls; interruptions in the coating facilitate subsequent quartz overgrowth precipitation.....36

Figure 3.1. A) Simplified geological map of the Anllóns Estuary catchment area, showing the distribution of various sedimentary environments (modified after Dowey et al., 2017). The red star indicates the location of the samples used in this study. B) Regional view of the study area, with the yellow rectangle marking the approximate location of the Estuary.....58

Figure 3.2. Field photographs of the various sedimentary environments within the Anllóns Estuary, taken on November 22, 2023. A) Salt marsh in the northwestern part of the estuary, cut through by tidal creeks and channels that flow into the intertidal flat. B). Aeolian dunes formed on a sandy spit. C) Large sandy spit attached to the frontal part of the estuary. D) Estuary channels and tidal creeks. E) Terrace indicating the boundary between saltmarsh and intertidal flat. F) Vegetated muddy intertidal flat. G) Sandy intertidal flat. H) Partially vegetated muddy intertidal flat. Samples used in this study were taken from the sandy intertidal flat (G). 59

Figure 3.3. Photograph of the experimental setup used in this study. The system comprises four multi-position parallel reactors with kettles, each capable of holding up to 500 mL of solution. The reactors can be heated to a maximum temperature of 350°C and withstand pressures up to 160 bar.....61

Figure 3.4. Plots of WD-XRF concentrations for CaO, MgO, K₂O, Fe₂O, SrO, and pH versus experimental temperatures illustrating their evolution as temperature increases

during the hydrothermal experiments. Data points are color-coded according to the
brine compositions used in each experiment. 72

Figure 3.5. Petrographic images displaying the framework grains and detrital grain coat minerals of the starting material. A) Thin-section photomicrograph and (B) SEM image showing detrital quartz (Qtz) and K-feldspar (KF). C) SEM image and (D) EDS map illustrating the distribution of detrital quartz (Qtz), K-feldspar (KF), albite (Ab), carbonates (CB) and bioclast (BC) framework grains. E-F) SEM images showing detrital grain coats (DGC) on K-feldspar (KF) and quartz (Qtz) grains from the sandy intertidal flat. The G label shows the close-up view shown in G G) Close-up view of the detrital grain coat shown in F, revealing that the grain coatings are chiefly composed of detrital clay minerals and carbonate. The red X label indicates the point the EDS shown in H was obtained. H) EDS spectra of the grain coat in G, indicating the presence of kaolinite, illite, and carbonate. 74

Figure 3.6. XRD patterns of the clay (< 2 µm) minerals present in both the starting material (detrital) and those synthesized in the hydrothermal experiments (authigenic). D-spacing values are provided in parentheses. A) Diffractograms of the starting material revealing the presence of illite and kaolinite as the dominant clay minerals in the studied samples. Both kaolinite and illite are detrital and occur in minor amounts. B) Air-dried, ethylene glycol-solvated, and heated diffractograms from Experiment 4 (200 °C) showing the synthesized clay minerals. The overlaid patterns show the presence of smectite and mixed-layer illite/smectite as the synthesized clay minerals. Notably, there is a broadening of the illite primary peak in the heated diffractogram. C) Overlaid diffractograms from Experiment 5 (250

°C) indicating the presence of smectite and illite. There is a noticeable positional shift of the smectite primary peak from 15.00 Å in the air-dried XRD pattern to 16.99 Å after ethylene glycol solvation (Moore & Reynolds, 1998). Additionally, the smectite primary peak disappears after heating to 550 °C. D) Post-experiment XRD patterns from Experiment 7 (250 °C, using estuarine water) show smectite, illite/smectite, and illite as the primary synthesized clay minerals. Similar to Experiment 5, there is a positional shift in the smectite primary peak, as well as a broadening of the illite primary peak after heating. 79

Figure 3.7. SEM-EDS images showing diagenetic features observed in Experiment 3 (150 °C). A) SEM image depicting the early formation of a crenulated smectite coat (Sme) on the surface of a feldspar grain. B) SEM image illustrating the dissolution and alteration of K-feldspar (KF), accompanied by the development of smectite (Sme). C) SEM image showing authigenic quartz overgrowth (Qo) co-precipitated with poorly developed authigenic smectite (Sme) on a detrital quartz grain. D-E) SEM images displaying smectite coats covering the entire surface of a detrital quartz grain. The smectite flakes are curled upwards and flatly attached to the surface of the quartz grain. The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra of the smectite coat, indicating Mg-rich smectite.....82

Figure 3.8. Diagenetic characteristics of authigenic clays observed in Experiment 4 (200 °C): A) SEM image showing the formation of grain-replacive smectite (GRS) adjacent to pervasively dissolved K-feldspar (pKF). B) SEM-EDS map and C) SEM image illustrating the development of grain-coating smectite (GCS) on detrital quartz (Qtz) and K-feldspar (KF). Note the uniform and continuous nature of the coat

coverage in B. D) SEM image showing the formation of honeycomb-textured grain-coating smectite (GCS) and mixed-layer illite-smectite (I/S), indicating the initial stages of the illitization process in the authigenic smectite. The clay flakes are strongly curled upward. E) SEM image displaying mixed-layer illite-smectite (I/S) fully coating the surface of a detrital quartz grain. The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra confirming the presence of mixed-layer illite-smectite. 84

Figure 3.9. Diagenetic illitization of smectite during Experiment 5 (250 °C): A-B) SEM images displaying mixed-layer illite-smectite (I/S) and illite morphologies, from aggregated plates (A) to crenulated (B), resulting from the complete illitization of smectite. C) The authigenic illite retained the honeycomb morphology characteristic of the illitized smectite. The red X label indicates the point the EDS shown in D was obtained. D) EDS spectra indicating the presence of illite. E) SEM image showing authigenic grain-coating illite (GCI) covering adjacent detrital grains. Note the presence of pore-bridging radial illite (PBI) between the grains. F) EDS map illustrating the degree of clay coat coverage on the detrital grains.....86

Figure 3.10. Diagenetic features observed in Experiment 7 (250 °C, using estuarine water): A) SEM image showing the partial dissolution of K-feldspar (KFD) and the formation of grain-replacive smectite (GRS). B) SEM image depicting the formation of grain-replacive smectite (GRS) adjacent to pervasively dissolved K-feldspar (pKF). Note the occurrence of mixed-layer illite-smectite (I/S) due to the smectite illitization process. C) Continuous illitization of authigenic smectite led to the development of

radial illite adjacent to mixed-layer illite-smectite (I/S). D) Authigenic grain-coating illite-smectite (GC I/S) covering the surface of a detrital quartz grain. E) SEM image showing the complete development of illite transformed from smectite. The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra showing the elemental composition of the identified illite in E. 88

Figure 3.11. Main diagenetic features observed in Experiment 8 (250 °C), using highly alkaline Na₂CO₃ solution (pH = 11.2). A) SEM image showing the pervasive dissolution of K-feldspar (pKF) and the early development of halite and acicular chabazite (zeolite) minerals. B) Formation of fully developed cubic crystals of halite. C-D) SEM images showing the formation of well-developed acicular (C) and rosette-like (D) chabazite (zeolite) mineral. E) SEM image showing the formation of chabazite at the edge of a dissolving K-feldspar (KFD). The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra showing the elemental composition of identified chabazite in E. Note the absence of smectite and illite, which were observed in previous experiments, highlighting the impact of fluid chemistry on the diagenetic formation of clay minerals.....90

Figure 3.12. Plots of ICP-OES concentrations of Al, Ca, Mg, Fe, Na, and K (in mg/L) versus experimental temperatures in °C, illustrating their evolution with increasing temperature and changes in fluid chemistry. Data points are color-coded according to the brine compositions used in each experiment. 93

Figure 3.13. Thickness and coverage of the synthesized clay mineral coatings in the hydrothermal experiments. A-B) SEM images showing well-developed and continuous grain-coating clays on detrital grains. Grain-coating clays (GCC) completely cover

detrital quartz (Qtz) and inhibit the development of quartz overgrowth. The missing part of the coating in (B) was likely removed during sample preparation. C-F) FIB-SEM images illustrating the three-dimensional thickness of grain-coating clays across the hydrothermal experiments. The thickness of the grain coatings increases with rising experimental temperatures. 96

Figure 3.14. Mg-Al-Fe ternary diagram showing the composition and classification of authigenic smectite synthesized during the hydrothermal experiments (adapted from Weaver and Pollard, 1973). The plot reveals that smectite formed from synthetic fluid (Experiments 3–6) predominantly exhibits an intermediate to Mg-rich (saponite) composition, whereas smectite synthesized from estuarine solution (Experiment 8) is mainly Al-rich (montmorillonite-beidellite). As temperature increases, the smectites generally trend from the Mg-rich (trioctahedral) pole toward the Al-rich (dioctahedral) pole. 98

Figure 3.15. $MR^{3+}-2R^{3+}-3R^{2+}$ ternary diagram (adapted from Velde, 1985) showing the transformation of synthesized smectite into mixed-layer illite/smectite and illite clays. [MLm = mixed-layer montmorillonite series; MLb = mixed-layer beidellite series]. MR^{3+} represents trivalent octahedral cations (e.g., Al^{3+} , Fe^{3+}), while $2R^{3+}$ and $3R^{2+}$ denote the sums of normalized octahedral cations. The diagram highlights the balance between Al^{3+} , Mg^{2+} , Fe^{2+} , and Fe^{3+} in octahedral sheets, aiding in clay mineral classification. 100

Figure 4.1. (A) Simplified facies map of the Gironde Estuary catchment (modified after (Virolle et al., 2019b)) with the red square indicating the location of the samples analyzed in this study. The inset map provides a country-level view of the study area, with

the red rectangle marking the approximate position of the estuary. (B) Google Earth aerial image showing the sample collection area (red square). (C) Field photograph depicting the muddy estuarine sediments utilized in this study.....133

Figure 4.2. Photograph of the experimental setup employed in this study, highlighting the key components of the hydrothermal reactors. 136

Figure 4.3. A 2D stacked column plot of XRF analysis illustrating the normalized concentration and distribution of major oxides in the sediments before and after the hydrothermal experiments. Note the relative abundance and evolution of CaO, MgO, Fe₂O₃, and K₂O across the different experiments. 142

Figure 4.4. A stacked plot of the bulk XRD analysis presenting the diffractograms of the major minerals identified in the starting material (SM) and selected experiments conducted using seawater (SW), estuarine water (EW), Mg-rich synthetic fluids (Mg), K-rich synthetic fluids (KCl), and Na-rich synthetic fluids (Na). Notably, a broad analcime peak is observed in Na_250 (Exp. 12), while it is absent in all other experiments. 145

Figure 4.5. SEM and EDS images illustrating detrital framework grains and clay coatings. (A) SEM image showing detrital quartz (Qtz), K-feldspar (KF), and calcite, with clay drapes (CD) coating the K-feldspar. (B) SEM image highlighting detrital albite (Ab), muscovite (Musc), and clay aggregates (CA) coating a quartz grain. (C) SEM image and (D) corresponding EDS spectra depicting a diatom embedded within detrital clay coats, with the red square in (C) marking the point of the EDS analysis shown in (D). (E) High-resolution SEM image of a detrital clay drape (CD), with

the red square indicating the point of the EDS analysis displayed in (F). (F) EDS spectra of the clay drape in (E) revealing the presence of kaolinite, smectite, and illite. 146

Figure 4.6. XRD patterns of the oriented clay fraction (< 2 μm) from the starting material and selected experiments. (A) Overlaid diffractograms of the starting material reveal the presence of smectite, illite, and kaolinite as the primary detrital clays in the sediments. (B) Diffractograms of air-dried, ethylene glycol-solvated, and heated clay fractions from Exp. 5 show the presence of smectite, kaolinite, and illite. Notably, the kaolinite peaks exhibit a decrease in intensity and the primary smectite peak shifts from 14.90 Å in the air-dried pattern to 16.99 Å following ethylene glycol solvation. (C) Air-dried, ethylene glycol-solvated, and heated diffractograms from Exp. 6 reveal the presence of illite and kaolinite. Smectite peaks are absent, kaolinite peaks are significantly weakened, and an increase in the intensity of the illite peak is observed, alongside the appearance of sylvite. (D, E) Overlaid diffractograms from Experiments 10 and 11 indicate the authigenic formation of chlorite along with the presence of illite and kaolinite. (F) Diffractograms from Exp. 12 confirm the presence of illite, smectite, and kaolinite. 148

Figure 4.7. SEM and SEM-EDS images illustrating the diagenetic features in seawater-based experiments (1–5). (A) SEM image depicting the onset of clay disaggregation and dissolution in Exp. 2. (B) SEM image showing the authigenic formation of honeycomb smectite (Sme) adjacent to kaolinite (Kaol) in Exp.3. (C) SEM image highlighting the formation of mixed-layer illite/smectite (I/S) with initial crenulated to honeycomb morphologies in Exp. 4. (D) SEM image showing the formation of

illite adjacent to mixed-layer I/S in Exp. 5, where the illite retains the honeycomb morphology of smectite. (E) Fully developed illite with honeycomb morphology and spiny terminations. (F) EDS spectra confirming the presence of illite. The location of the EDS point is shown in E (red square).....156

Figure 4.8. Diagenetic features of post-experiment clay minerals from STEM and STEM-EDS analyses. (A) STEM image showing hexagonal kaolinite aggregates during Exp. 3. The red square indicates the location of EDS analysis shown in B. (B) EDS spectra confirming the presence of kaolinite. (C) STEM image illustrating the polycrystalline nature of clays in Exp. 5, where illite developed adjacent to illite/smectite (I/S), smectite, and pseudo-hexagonal kaolinite. (D) Elemental analysis (EDS) highlighting authigenic illite. The location of the EDS point is shown in C (red square). (E) STEM image showing authigenic chlorite and mixed-layer chlorite/smectite (C/S) in Exp. 11. (F) Close-up view of an elongated chlorite crystal in Exp. 11. 157

Figure 4.9. Diagenetic features observed in Exp. 6. (A) SEM image showing kaolinite dissolution (KD). B) SEM image revealing the occurrence of illite with a rugged honeycomb morphology, alongside mixed-layer illite/smectite (I/S) and newly formed sylvite. (C) Newly formed illite. The illite displayed lath-like to radial flakes morphology. The red square marks the EDS point shown in D. D) EDS spectra of the observed illite. 158

Figure 4.10. Clustered histogram displaying the concentrations of Al, Ca, Fe, Mg, Na, and K in pre-experiment solutions and their subsequent evolution post-experiments.....161

Figure 4.11. Main diagenetic features observed in Experiments 7–10 (conducted using Mg-rich synthetic fluid). (A) SEM image illustrating the onset of detrital clay aggregate dissolution in Exp. 7. (B) SEM image showing the initial transformation of smectite in Exp. 8. (C) SEM image highlighting the formation of mixed-layer chlorite/smectite (C/S) with rugged honeycomb morphology adjacent to kaolinite (Kaol). (D) SEM image depicting the formation of microcrystalline quartz (Crs) crystal aggregates alongside transforming chlorite/smectite (C/S). (E) SEM image showing the development of chlorite with mixed honeycomb-to-rosette morphology. The red square marks the location of the EDS spectra shown in F. (F) EDS spectra indicating the Mg-rich nature of the newly formed chlorite.....161

Figure 4.12. Diagenetic features observed in the estuarine water experiment (Exp. 11). (A) SEM showing acicular crystals of neoformed Fe-oxides (Fe-O). (B) SEM image illustrating the initial transformation of kaolinite (Kaol). (C) SEM image depicting the formation of microcrystalline quartz (mQ) near transforming chlorite/smectite (C/S), which exhibits honeycomb to web-like morphologies. (D–E) SEM images showing the formation of chlorite with rosette morphology. (F) EDS spectra indicating that the chlorite formed in this experiment is Fe-rich. The location of the EDS analysis is marked by the red square in (E). 165

Figure 4.13. Main diagenetic features in Exp. 12 (conducted with Na-rich synthetic fluid). (A) SEM image showing the onset of detrital clay disaggregation (DCA). (B) SEM image showing detrital clay dissolution (DC). (C) SEM image highlighting the formation of cubic halite crystals. (D–E) SEM images depicting the development of massive aggregates (D) and acicular-to-botryoidal (E) authigenic analcime. (F)

EDS spectra of the newly formed analcime, indicating its high Na content. The red square in (E) marks the location of the EDS analysis. 168

Figure 4.14. FIB-SEM and EDS images illustrating the internal structure of clay minerals and their relationships with detrital framework grains. (A) FIB-SEM image showing microporous pore-filling clay minerals (PFC) cementing detrital quartz (Qz), K-feldspar (KF), and albite (Ab) in Exp. 3. (B) EDS map of (A). (C) SEM image showing less microporous pore-filling clays (PFC) cementing quartz (Qtz) and K-feldspar (KF) in Exp. 5. Quartz overgrowths (Qo) are observed at the edges of detrital quartz. (D) EDS spectra of the quartz overgrowth, indicating Si and O as the main constituents. The red square in (C) marks the EDS analysis location. (E) FIB-SEM image showing grain-coating chlorite (GCC) on detrital grains in Exp. 11. (F) EDS spectra of the GCC, showing its Fe-rich content. The red square in (E) marks the EDS analysis location.....170

Figure 5.1. (A) Simplified geologic map of Saudi Arabia showing the distribution of the Early Devonian (Emsian) successions and location of the studied section (blue rectangle; redrawn after Konert et al., 2001; Algheryafi et al., 2022). The inset map is a regional view of the study area showing the approximate location of the study (red star). (B) Paleogeographic reconstruction of the Early Devonian showing the location of the Arabian Plate (red star; Stampfli & Borel, 2010). (C) Stratigraphic Column of the Devonian in Saudi Arabia (after Algheryafi et al., 2022). The red rectangle shows the studied Subbat Member. 197

Figure 5.2. Measured outcrop sections of Jabal Al Helwat 2 as described in Algheryafi et al., (2022) and this study. The logged section in this study is around 50 meters away

from the previously logged section. Minor variations in the sand distribution of the lower part are caused by the covered sections in each side of the outcrop.....199

Figure 5.3. Outcrop photographs showing the studied section and the established lithofacies in the Subbat sandstones, Jauf Formation. (A) Studied Jebal Helwat 2 section of the Subbat Member overlaid by the carbonate Hammaiyat Member (B) Stratified to structureless mudstone (F3). (C) Wave-rippled sandstone (F4). (D) Moderately bioturbated sandstone (F7). Note the presence of *Zoophycus* (*Zo*) dominated trace fossil assemblage. Additionally, *Spirophyton* (*Sp*) traces were identified for the first time in these outcrops. (E) Deformed sandstone and mudstone (F8). (F) Cross-bedded sandstone (F10). (G) Rooted and variegated sandstone (F14). (H) Fine argillaceous sandstone (F16). (I) Sigmoidal sandstone (F17). (J) Continuous thin layers of anhydrite within mudstone and localized marlstone facies.....205

Figure 5.4. Histogram showing the grain size distribution of studied samples. 209

Figure 5.5. Photomicrographs of the main type of framework grains within the studied samples (A) Cross-polarized light (XPL) thin-section image showing detrital, monocrystalline quartz (mQ). (B) XPL image showing detrital polycrystalline quartz (pQ). (C) Pane-polarized (PPL) thin-section image showing detrital k-feldspar grains (Kfs). (D) PPL photomicrograph showing plagioclase (Pla). (E) XPL image showing sandstone rock fragment (SRF). (F) PPL image showing detrital biotite (Bio). 212

Figure 5.6. Sandstone classification for the studied Subbat Member, Jauf Formation, according to Folk’s classification (1980). 213

Figure 5.7. Mean elemental (A), oxides (B), and trace elements (C) plot with depositional environments derived from WD-XRF. Note the relative abundance of Ca and K within the different depositional facies in relation to the distribution of carbonates and clay cements.	215
Figure 5.8. Bulk XRD pattern of framework minerals from representative samples of the studied sandstones.	217
Figure 5.9. Variation in grain contact showing the degree in mechanical and chemical compaction. (A) Thin-section photomicrograph showing point contact and long grain contact (B) Thin-section image showing concavo-convex contact with the red arrow showing long-grain contact. (C) PPL image showing poorly developed sutured contact, noting the onset of pressure dissolution. (D) Thin-section image showing slightly deformed biotite grains suggesting a low impact of mechanical compaction.....	218
Figure 5.10. Cross-plot porosity reduction due to compaction (COPL) versus porosity loss due to cementation (CEPL) showing that porosity is dominantly reduced by mechanical compaction than cementation.	219
Figure 5.11. Thin-section photomicrographs and SEM-EDS images showing the occurrence and distribution of authigenic kaolinite in the Subbat sandstones. (A) Thin section photomicrograph pore-filling kaolinite. (B) SEM image showing the stacked booklet to vermicular nature of the pore-filling kaolinite. (C) Dense, stacked booklet pore-filling kaolinite. Note the intense micropores within kaolinite (D) EDS spectra for the measured composition of kaolinite in C (red X). (E) SEM image	

showing grain replacive kaolinite (GRK) adjacent to partially dissolved detrital k-feldspar (PDF). (F) SEM image showing pore-filling, grain replacive kaolinite (GRK) adjacent to pervasively dissolved K-feldspar (PvDF). (G) EDS spectra showing the measured composition of k-feldspar in F (red X). (H) Sem image showing partially dissolved detrital muscovite (Musc) and grain replacive kaolinite (GRK). 221

Figure 5.12. XRD patterns of the clay fraction (< 2 µm) showing the dominant clay minerals in the Jauf Formation sandstones. 222

Figure 5.13. Petrographic images displaying the type and mode of occurrence of authigenic illite in the Jauf Formation. Thin section (A), and SEM (B) images showing radial grain-coating illite (CGI) on detrital quartz (Qtz) grains. Thin-section (C) and SEM (D) images showing fibrous to lath-like pore-filling illite (PFI). (E) Honeycomb grain-coating illite on detrital grains. The honeycomb morphology is preserved from the precursor illitized smectite. (F) EDS spectra for the measured composition of illite in E (red X). Thin-section (G) and SEM (H) images showing the occurrence of illite mixed with kaolinite indicating illitization of kaolinite. 224

Figure 5.14. Thin-section and SEM-EDS showing authigenic chlorite and quartz cement. Thin-section (A) and SEM (C-D) images showing quartz overgrowth (Qo) growing where grain-coating chlorite (GCC) is absent. (D-E) Sem images showing the rosette morphology of grain-coating chlorite. (F) EDS spectra showing the composition of the measured chlorite in E (red X). 226

Figure 5.15. Petrographic images displaying authigenic carbonate cements. (A) Thin-in section photomicrograph showing nodular poikilitopic pore-filling Fe-dolomite. Note the floating detrital grains (PDF) that engulf and replace patchy remnants of pore-filling calcite (PC). (B) XPL image pore-filling Fe-dolomite (PDF) encasing k-feldspar overgrowth. (C) SEM image showing the blocky nature of pore-filling Fe-dolomite (PDF). (D) EDS spectra showing the composition of the Fe-dolomite. Note the Mg/Fe ration. (E) SEM image showing the remnants of subhedral to euhedral crystals of pore-filling calcite in PFD. (F) thin-section image showing pore-filling ankerite (Ank) replacing Fe-dolomite pore-filling (PDF). (G) SEM image showing euhedral ankerite (Ank) over (PFD). The ankerite is encased by anhydrite (Anh). (H) EDS spectra showing the measured composition of ankerite. Note the presence of Mn and the Mg/Fe ratio as compared to D. 228

Figure 5.16. Thin-section and SEM-EDS images showing minor authigenic cements within the studied sandstones. (A) Thin-section image showing nodular, poikilitopic, pore-filling anhydrite (PFA). (B-C) SEM images showing the occurrence of euhedral needle to prismatic crystals of anhydrite (Anh) occurring above Fe-dolomite (Fe-dol). (D) EDS spectra showing the measured composition of anhydrite in C (red X). (E) thin-section image showing pore-filling hematite replacing dissolved Fe-dolomite. (F) Thin-section photomicrograph showing pore-filling hematite filling secondary porosity created by Fe-dolomite dissolution. (G) SEM image showing pore-filling k-feldspar overgrowth (PFKfs) encased by kaolinite and illite. (H) EDS spectra showing the measured composition of k-feldspar overgrowth in G (red X).....230

- Figure 5.17.** Thin-section photomicrographs showing secondary porosity created by the dissolution of detrital feldspar grains and carbonate cements. (A-B) PPL image partial to pervasive dissolution of k-feldspar creating feldspar dissolution porosity (FDP). (C) Moldic porosity (MP) created by the complete dissolution of k-feldspar grain. (D) Carbonate dissolution porosity (CDP). Note the remnants of the carbonate cements from the dissolved poikilitopic crystal. 232
- Figure 5.18.** (A) Cross plot of thin-section porosity with Helium porosity of selected samples showing excellent correlation. (B) Cross-plot of Thin-section porosity and permeability, permeability increases with increasing porosity. (C) cross-plot of He permeability with spot permeability showing good correlation.....234
- Figure 5.19.** Simplified Paragenetic analyses showing the sequence of diagenetic events in the Jauf Formation and their impacts on porosity. 236
- Figure 5.20.** Cross-plots of depositional processes with porosity and permeability showing their impact on reservoir quality. Plot of mean grain size with porosity (A) and permeability (B) showing an irregular relationship. Reservoir quality increases with increasing grain size except in fluvial and estuarine facies where porosity and permeability increase are independent of grain size. Cross plots of detrital matrix with porosity (C) and permeability (D) show that porosity and permeability increase with decreasing detrital matrix content in the sandstones. (E-F) Plot of sorting versus porosity (E) and permeability (F) show that sorting reservoir quality increases with better sorting. 240

Figure 5.21. Interpreted stratigraphic chart of the studied section showing the relationship between porosity and permeability, detrital matrix, and pore-filling authigenic cements.

.....242

Figure 5.22. Impacts of authigenic cements on reservoir properties of the Jauf sandstones. Cross-plot of pore-filling carbonate cements with porosity (A) and permeability bimodal relationship depositional facies. Reservoir properties increase with decreasing pore-filling carbonate cements except in the shoreface-to-offshore transition where reservoir properties are independent of pore-filling carbonate cements. Plots of pore-filling clay cements versus porosity (C) and permeability (D) showing general increase in porosity and permeability with decreasing pore-filling clay cements. Cross-plots of quartz cements with porosity (E) and permeability (F) showing inverse relationships. Porosity and permeability increase with decreasing quartz cements. 245

Figure 5.23. Controls of authigenic cements on reservoir quality. Cross-plots of total pore-filling cements with porosity (A) and permeability (B). Overall, reservoir properties increase with decreasing pore-filling cements. Cross plots of grain-coating clays with porosity (C) and permeability (D) show a positive correlation. Porosity and permeability increase with increasing grain-coating clays. 246

Figure 6.1. Photograph of the experimental setup employed in this study, highlighting the key components of the hydrothermal reactors. 267

Figure 6.2. Petrographic images showing the framework grains and cements of the pre-experimental Subbat sandstone sample. A-B) Thin-section photomicrographs

showing the quartz (Qz) and K-feldspar (KF) dominated nature of the sandstone and the occurrence of pore-filling kaolinite (PFK) and pore-filling hematite cements within the pores. C) SEM image of a partially dissolved K-feldspar (PDKF). D) SEM image displaying a booklet pore-filling kaolinite. E) SEM image showing the occurrence of well-developed pore-filling K-feldspar overgrowth enclosed by kaolinite (Kaol.). The red X label indicates the point at which the EDS shown in F was obtained. F) EDS spectra of the K-feldspar overgrowth in E. 273

Figure 6.3. Plots of WD-XRF concentrations for SiO₂, CaO, Fe₂O, and MgO versus experimental temperatures illustrating their evolution as temperature increases during the hydrothermal experiments. Data points are color-coded according to the brine compositions used in each experiment. 276

Figure 6.4. A stacked plot of the bulk XRD analysis presenting the diffractograms of the major minerals identified in the starting material (J_0) and experiments conducted using seawater (SW), synthetic fluid (SF), and deionized water (DI). 277

Figure 6.5. XRD patterns of the oriented clay fraction (< 2 μm) from the starting material and selected experiments. (A) Overlaid diffractograms of the starting material reveal the presence of kaolinite, smectite, and illite as the clay minerals in the starting material. The kaolinite peaks were absent in the heated diffractogram. B-D) Diffractograms of air-dried, ethylene glycol-solvated, and heated clay fractions from Exp. 5-7 showing the presence of smectite, kaolinite, illite, and the authigenic formation of chlorite. Notably, the kaolinite/chlorite peaks are still present after heating, confirming the presence of chlorite. 278

Figure 6.6. SEM images showing the early diagenetic features observed in Exp.1-2. A) Initial kaolinite dissolution in Exp. 1. B) early disintegration of detrital K-feldspar (DKF). C-D) Feldspar-dissolution pits and cracks indicating the dissolution of detrital K-feldspar (DKF). E) Initial dissolution of pore-filling K-feldspar (PFKF). F) Authigenic formation of quartz overgrowth in Exp. 2. 280

Figure 6.7. SEM images displaying the diagenetic features observed in Exp. 3, conducted at 150 °C. Pervasive dissolution of kaolinite (A) and K-feldspar (B). Authigenic precipitation of smectite encasing kaolinite. D) Incipient precipitation of smectite coats on detrital K-feldspar (KF). (E-F) Authigenic smectite platelets engulfing detrital pore-filling kaolinite. 282

Figure 6.8. Main diagenetic characteristic of the authigenic clays observed in Experiment 4 (200 °C): A-B) SEM images showing the formation of grain-replacive honeycomb smectite adjacent to pervasively dissolved pore-filling K-feldspar (KF) overgrowth. C) SEM image illustrating the development of grain-coating smectite on detrital K-feldspar grain (red arrow). D) High-resolution SEM image showing the authigenic formation of rosette to cabbage-head chlorite adjacent to smectite (green arrow). (E) SEM image displaying the occurrence of rosette chlorite entirely coating a detrital feldspar grain, and occurring adjacent to partially dissolved smectite. F) EDS map indicating the dominance of Fe over Mg in the newly formed chlorite. 283

Figure 6.9. Diagenetic features observed in Experiment 5 (seawater, 2 weeks @ 250 °C): A) SEM image showing the incipient development of authigenic smectite (green arrow) on the surface of feldspar (KF) dissolution pits. B-C) SEM images showing the

continuous development of authigenic clays with chlorite (blue arrow) forming adjacent to honeycomb authigenic smectite (blue arrow), which encases partially dissolved K-feldspar (red arrow). D) SEM image showing authigenic quartz overgrowth co-precipitating with authigenic smectite. E) SEM image illustrating the formation of a continuous rosette chlorite coat on detrital K-feldspar. F) EDS map of authigenic smectite and chlorite. The map illustrates that authigenic smectite is Mg-rich, while the synthesized chlorite is Fe-rich. 285

Figure 6.10. SEM images showing the main diagenetic characteristics observed in Experiment 6 (seawater, 1 month @ 250 °C): A-B) Rosette-like aggregates of chlorite developing adjacent to detrital K-feldspar (KF). C-D) Rosette to cabbage head like chlorite (blue arrow) co-existing with authigenic honeycomb smectite (green arrow) adjacent to pervasively dissolved K-feldspar (red arrow). E-F) Fully developed authigenic chlorite crystal. 287

Figure 6.11. Main diagenetic features observed in Experiment 7 (synthetic fluid, 2 weeks @ 250 °C): A-B) SEM images indicating the pervasive dissolution of K-feldspar and the incipient development of authigenic smectite crystals. C-E) SEM images showing the formation of chlorite adjacent to honeycomb smectite. The red X label indicates the point at which the EDS shown in F was obtained. F) EDS spectra of the chlorite shown in E. Note the Mg richness of the chlorite. 289

Figure 6.12. QEMSCAN mineralogical maps displaying the occurrence and distribution of detrital grains and clay mineral cements in the starting material (A) and selected experiments (B-D). Note the increasing amount of clay minerals replacing K-feldspar grains across the experiments. 291

Figure 6.13. Micro-CT images and pore network of the sample before and after experiment 6 (seawater, 1 month @ 250 °C). A) 2D grayscale tomographic image from a 2 cm cylindrical core before experiment (A) and after experiment 6 (B), scanned at 3.3 µm resolution. (C-D) 2D segmented slice of (A-B). (E-F) 3D voxelized rendering of the total resolved porosity. The total resolved microporosity value is 0.6 mD in the starting material and 0.5 mD in Experiment 6. 292

Figure 6.14. Plots of TXRF concentrations of Fe, Mg, Ca (mg/L), and pH versus the experimental temperatures in °C, illustrating their evolution with increasing temperature and changes in fluid chemistry. Data points are color-coded according to the brine compositions used in each experiment.....295

LIST OF ABBREVIATIONS

BSE	:	Backscattered Electron
EDS	:	Energy Dispersive X-ray Spectroscopy
EW	:	Estuarine Water
FIB-SEM:		Focused Ion Beam Scanning Electron Microscopy
ICCD	:	International Centre for Diffraction Data
ICP-OES:		Inductively Coupled Plasma-Optical Emission Spectroscopy
XCT	:	Microcomputed Tomography
QEMSCAN	:	Quantitative Evaluation of Minerals by Scanning Electron Microscopy
RIR	:	Relative Intensity Ratio
SE	:	Secondary Electron
SEM	:	Scanning Electron Microscopy
SF	:	Synthetic Fluid
SF	:	Synthetic Fluid
SM	:	Starting Material
STEM	:	Scanning Transmission Electron Microscopy
SW	:	Seawater
TDS	:	Total Dissolved Solids

TXRF : Transmission X-ray Fluorescence

WD-XRF: Wavelength-dispersive X-ray Fluorescence

XRD : X-ray diffraction

XRF : X-ray Fluorescence

ABSTRACT

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The storage capacity, deliverability, and effectiveness of hydrocarbon exploitation, CO₂ sequestration, and hydrogen storage in sandstone reservoirs are largely controlled by variations in reservoir quality (porosity and permeability). In marginal marine sandstones, the diagenetic transformation of detrital clay minerals plays a critical role in influencing reservoir quality. The detrital texture and composition of these sandstones vary across depositional sub-environments, creating heterogeneities that significantly affect diagenesis and, consequently, reservoir quality, posing significant challenges for accurate prediction. While recent studies have investigated the factors controlling the occurrence and distribution of detrital clay coatings in modern marginal marine settings, the diagenetic alteration of these sediments and the role of detrital precursors in forming authigenic clay coatings remain underexplored. This gap often leads to empirical models that inaccurately predict the quality of ancient marginal marine sandstone reservoirs. This research integrates field observations, hydrothermal experiments, petrography, geochemistry, and petrophysical analyses to investigate the controls on authigenic clay formation in modern and ancient marginal marine systems. Hydrothermal experiments simulating burial diagenesis were conducted using sediments from the Anllóns (Spain) and Gironde (France) estuaries, as well as Devonian sandstones from the Subbat Member of the Jauf Formation (Saudi Arabia). These

experiments were performed at temperatures ranging from 50°C to 250°C for up to 30 days, using a variety of natural and synthetic fluids. The findings reveal that detrital composition, fluid chemistry, temperature, and time are key controls on the formation of smectite, illite, and chlorite. Initial dissolution of detrital kaolinite and K-feldspar triggered smectite precipitation at 150–250°C via dissolution–crystallization processes, followed by illitization above 200°C in K-rich fluids. Mg- and Fe-bearing chlorites developed through smectite transformation in Mg- and Fe-rich solutions. In contrast, highly alkaline and Na-rich fluids produced zeolites and halite, reflecting divergent diagenetic pathways. The hydrothermal experiments yielded clay morphologies and compositions comparable to those found in natural sandstone reservoirs. Petrographic and petrophysical analyses of the Subbat sandstones demonstrated that depositional settings and diagenetic processes significantly influence reservoir quality. Well-sorted fluvial–estuarine sandstones exhibited higher porosity and permeability due to low detrital matrix content and limited cementation, unlike the poorly sorted shoreface–offshore facies. The findings of this research provide critical insights into the mechanisms controlling authigenic clay minerals formation and highlight their implications for predicting reservoir quality in marginal marine sandstones, critical for hydrocarbon exploration and the transition to sustainable energy.

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التخصص: جيولوجيا

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تتأثر السعة التخزينية، والقدرة على التسليم، وكفاءة استغلال الهيدروكربونات، وتخزين ثاني أكسيد الكربون، والتخزين الحديث للهيدروجين في الخزانات الرملية بشكل كبير بتغيرات جودة الخزان، التي تُعرف بالمسامية والنفاذية. في الصخور الرملية الهامشية البحرية، تلعب التحولات الدياجينية للمعادن الطينية المتكونة دورًا حاسمًا في التأثير على جودة الخزان. تختلف التركيبة النسيجية والتكوينية لهذه الصخور الرملية عبر البيئات الترسيبية الفرعية، مما يُولد تفاوتات كبيرة تؤثر بشكل ملحوظ على العمليات الدياجينية وجودة الخزان، مما يشكل تحديات كبيرة للتنبؤ الدقيق. وعلى الرغم من أن الدراسات الحديثة قد بحثت في العوامل التي تتحكم في وجود وتوزيع الطلاءات الطينية المتكونة في البيئات الهامشية البحرية الحديثة، إلا أن التغيرات الدياجينية لهذه الرواسب ودور المواد الأولية المتكونة في تكوين الطلاءات الطينية الأوثيجينية لا تزال غير مدروسة بشكل كافٍ. يؤدي هذا النقص غالبًا إلى نماذج تجريبية غير دقيقة في التنبؤ بجودة خزانات الصخور الرملية الهامشية البحرية القديمة. يدمج هذا البحث بين الملاحظات الميدانية، والتجارب الهيدروحرارية، والتحليلات البتروغرافية، والجيوكيميائية، والفيزيائية للخزان لدراسة العوامل المتحكممة في تكوين المعادن الطينية الأوثيجينية في الأنظمة الهامشية البحرية الحديثة والقديمة. أُجريت تجارب هيدروحرارية لمحاكاة الدياجينيز الدفني باستخدام رواسب من مصبات أنليونس (إسبانيا) وجيرون (فرنسا)، إلى جانب صخور رملية ديفونية من عضو سوبات، تكوين جاف (المملكة العربية السعودية). أُجريت هذه التجارب عند درجات حرارة تتراوح بين 50 و250 درجة مئوية لمدة تصل إلى 30 يومًا، باستخدام مجموعة متنوعة من السوائل الطبيعية والاصطناعية. تكشف النتائج أن التركيبة المتكونة، والكيمياء السائلة، ودرجة الحرارة، والزمن هي العوامل الرئيسية المتحكممة في تكوين السيمكتايت، والإليت، والكلوريت. أدى الذوبان الأولي للكاولينايت والبوتاسيوم-فلسبار إلى ترسيب السيمكتايت عند 150-250 درجة مئوية من خلال عمليات الذوبان-التبلور، تلاها الإليتيزيشن فوق 200 درجة مئوية في السوائل الغنية بالبوتاسيوم. تطورت الكلوريتات الغنية بالمغنيسيوم والحديد من خلال تحول السيمكتايت في محاليل غنية بالمغنيسيوم والحديد. في المقابل، أنتجت

السوائل القلوية العالية والغنية بالصوديوم زيوليتات وهاليت، مما يعكس مسارات دياجنينية متباينة. أنتجت التجارب الهيدروحرارية مورفولوجيات وتركيبات طينية مماثلة لتلك الموجودة في خزانات الصخور الرملية الطبيعية. أظهرت التحليلات البتروغرافية والفيزيائية للخزان لصخور سوبات الرملية أن الإعدادات الترسيبية والعمليات الدياجينية تؤثر بشكل كبير على جودة الخزان. تُظهر الصخور الرملية النهرية-المصبية جيدة الفرز مسامية ونفاذية أعلى بسبب المحتوى المنخفض من المصفوفة المتكونة والتسميت المحدود، على عكس الفاسيس الساحلية-البحرية ضعيفة الفرز. توفر نتائج هذا البحث رؤى حاسمة حول الآليات المتحكممة في تكوين المعادن الطينية الأوثيجينية وتبرز آثارها في التنبؤ بجودة الخزانات في الصخور الرملية الهامشية البحرية، وهو أمر حيوي لاستكشاف الهيدروكربونات والانتقال إلى الطاقة المستدامة.

CHAPTER 1

INTRODUCTION

1.1. Background

The rise in global population growth and technological advancements has led to an increasing demand for energy. Despite efforts to transition away from fossil fuels, oil and gas still contribute to more than half of the world's energy supply (Litvenenko, 2020). Sandstones represent approximately half of the world's identified hydrocarbon reservoirs (Bjørlykke and Jahren, 2010). The quality of a sandstone reservoir is gauged by its hydrocarbon storage capacity and deliverability (Bello et al., 2021). Storage capacity is delineated by porosity and the reservoir size, while deliverability is closely tied to its permeability. Therefore, porosity and permeability are pivotal parameters for assessing the quality of sandstone reservoirs (Worden et al., 2018; Virolle et al., 2019a). These parameters dictate the volume of hydrocarbons a sandstone can accommodate and the pace of their extraction. As energy consumption rises and hydrocarbon exploration extends to more challenging and frontier areas, it becomes increasingly vital to conduct pre-drill evaluations of reservoir quality (Ajdukiewicz and Lander, 2010). The global drive towards net-zero emissions and addressing climate change repercussions has also led to intensive research into sustainable and low-carbon energy alternatives. These alternatives include carbon capture and storage (CCS), hydrogen storage, and geothermal energy (Burruss, 2004; Hassanpouryouzband et al., 2022). Recently, sandstone reservoirs have been considered potential sites for CO₂ storage (Kordi, 2013) and, more recently, hydrogen storage (Barshep and Worden, 2021). The quality of these reservoirs critically influences their capacity, efficiency, and safety as subsurface media for

underground storage of CO₂ and hydrogen (Kordi, 2013; Hassanpouryouzband et al., 2022). Thus, proper characterization of sandstone reservoir quality is essential to the success and sustainability of CO₂ sequestration and hydrogen storage, an area that continues to gain significant attention from both industry and academia (Kordi, 2013; Flesh et al., 2018; Yekta et al., 2018; Hassanpouryouzband et al., 2022).

Sandstone reservoir quality (Porosity and permeability) typically decreases with increasing burial depth (Wooldridge et al., 2017a). After compaction, the predominant factor for porosity and permeability reduction in sandstone reservoirs during deep burial and heating is the emergence of quartz cementation (McBride, 1989; Walderhaug, 1996). Yet, a notable percentage of these deeply buried reservoirs exhibit unexpectedly high levels of porosity and permeability (Bloch et al., 2002). The preservation of such unusual porosity and permeability is often attributed to the presence of grain-coating clays, which prevent the formation of porosity-decreasing cements (Ehrenberg 1993; Anjos et al., 2003; Ajdukiewicz and Larese 2012).

In many deeply buried sandstone reservoirs worldwide, chlorite has been commonly identified as the predominant clay coat that prevents the nucleation and growth of quartz cement (Stricker and Jones, 2018; Worden et al., 2020). While illite and mixed-layer clay coatings have been identified as agents of porosity preservation in such reservoirs, they are noted less frequently than chlorite (Al-Ramadan et al., 2017). The emergence of diagenetic clay coatings in sandstones can either originate from the heat-induced recrystallization of detrital clay coatings or from in situ development resulting from the authigenic transformation of precursor minerals when they interact with pore fluids during burial (Worden and Morad, 2003; Ajdukiewicz and Larese, 2012).

Consequently, in the pursuit of improved reservoir quality prediction models, there has been a growing emphasis on using modern analogs to understand the occurrence, spatial distribution, and varying extents of clay coatings in siliciclastic reservoirs (Daneshvar, 2011; Dowey et al., 2017; Wooldridge et al., 2017a; Griffiths et al., 2018; Virolle et al., 2018).

Over the past decades, there has been a lot of research conducted on the factors that affect the reservoir quality of sandstones as well as the occurrence and distribution of clay coats within deeply buried reservoirs (Heald and Larese, 1974; Curtis 1983; Worden and Morad, 2003; Morad et al., 2010; Al-Ramadan et al., 2017; Bello et al., 2023). Multiple models for pre-drill sandstone reservoir quality prediction have been developed (Wood and Byrnes, 1994; Lander and Walderhaug, 1999; Lander et al., 2008; Taylor et al., 2010). Yet, despite the acknowledged impacts of clay coatings in preserving the porosity of deeply buried sandstone reservoirs and their broad applications in the exploration, development, and storage of various energy sources, there remains a dearth of quantitative data on clay coat authigenesis to develop reliable predictive models for sandstone reservoir quality (Charlaftis et al., 2021).

Experimentally simulating diagenesis is essential for generating data on the evolution of sandstone reservoir quality throughout the diagenetic process. This information is vital for developing more reliable reservoir quality prediction models and comprehensive basin simulations (Charlaftis et al., 2022). Temperature-controlled laboratory experiments have been widely employed to investigate the formation and transformation of quartz and clay mineral cements (Aagaard et al., 2000; Small et al., 2002; Ajdukiewicz and Larese, 2012; Haile et al., 2015; Charlaftis et al., 2021; Bello et al., 2022). While these studies provide valuable insights into the influence of quartz and clay minerals on petrophysical properties, few studies have simulated the diagenetic alteration of detrital clay coatings from modern sedimentary environments (Bello et al., 2022), despite their importance in

revealing the key factors controlling their diagenetic transformation. Thus, the primary aim of this research is to conduct a series of hydrothermal-reactor experiments that simulate burial diagenesis using modern sediments and ancient sandstones from various marginal marine settings. In addition, an integrated approach combining field observations, petrography, geochemical and hydrochemical analyses is employed to investigate the role of detrital composition, temperature, fluid chemistry, mineralogical alterations, and time in controlling the transformation pathways of clay minerals during diagenesis. These findings are expected to provide critical insights into the mechanisms governing the evolution of clay minerals and significantly improve the accuracy of modeling the reservoir quality of shallow and deeply buried sandstones in marginal marine environments.

1.2. Motivation

The ability to predict the evolution of sandstone reservoir quality is essential for sustainable energy exploration and transition. As exploration ventures into more challenging and frontier areas, precise pre-drill reservoir quality assessments are becoming increasingly important. As such, constraining the factors that affect the quality of deeply buried reservoirs is crucial for global energy security and climate change mitigation. The preservation of porosity in deeply buried sandstones is often linked to the presence of grain-coating clays such as chlorite, illite, and mixed-layer clays (Ehrenberg, 1993; Bloch, 2002; Al-Ramadan et al., 2004; Taylor et al., 2010; Ajdukiewicz and Larese, 2012). While porosity and permeability-preserving factors like grain-coating clays are generally known to geologists, there are misconceptions about their formation and development. To date, most experimental diagenesis research works have concentrated on core and outcrop studies of ancient sandstones. However, while core-based studies are often challenged by the limited spatial resolution of samples, stemming from the scarcity of core data in

many fields, outcrop investigations are skewed by weathering-induced alterations of clay minerals (Wooldridge et al., 2017b). This research, therefore, aims to produce new insight into how temperature, precursor minerals, time, and variations in fluid chemistry impact the formation and transformation of clay minerals within sandstones during burial. This will be achieved through experimental simulation of diagenesis by utilizing modern estuarine sediments as analogs for ancient marginal marine sandstone reservoirs.

1.3. Problem Statement and Research Objectives

The accurate prediction of reservoir quality in sandstones remains a major challenge in subsurface energy exploration and storage, particularly in marginal marine settings. These environments exhibit significant sediment composition and texture heterogeneity across depositional sub-environments, strongly influencing subsequent diagenetic alterations. A key but underexplored aspect of this diagenesis is the transformation of detrital clay minerals and the formation of authigenic clay coatings, which critically impact porosity and permeability. Despite recent efforts to understand the occurrence and distribution of detrital clay coatings in modern estuarine sediments (Wooldridge et al., 2017a, 2017b, 2018, 2019; Griffiths et al., 2018, 2019a, 2019b; Virolle et al., 2019a, 2019b, 2020, 2021, 2022; McGhee et al., 2022; Muhammed et al., 2022), the diagenetic pathways of these coatings and their transformation into authigenic clays such as smectite, illite, and chlorite remain poorly constrained. Moreover, few studies (Bello et al., 2022) have experimentally simulated the diagenetic evolution of detrital clays under controlled physicochemical conditions that mirror burial processes. This limited the understanding of how factors like temperature, fluid composition, and time influence mineralogical transformations and reservoir properties. Thus, there is a critical need for experimental and integrated analytical

approaches that bridge the gap between modern depositional processes and ancient diagenetic outcomes in marginal marine sandstones.

Therefore, the main objectives of this research are:

- (1) To experimentally simulate the diagenetic formation of clay minerals in modern estuary sediments as analogs for deep burial diagenesis.
- (2) To constrain the controlling factors and the mechanisms of formation for these clay minerals
- (3) To evaluate the impact of fluid chemistry on the diagenetic alteration of modern estuarine sediments.
- (4) To assess the role of authigenic grain coatings on the reservoir quality of marginal marine sediments
- (5) To examine the depositional and diagenetic processes that influenced the quality of marginal marine sandstone reservoirs

1.4. Study Areas

This study analyzes samples from both modern and ancient marginal marine sedimentary environments, specifically the Anllóns Estuary (Spain), the Gironde Estuary (France), and the Devonian Subbat sandstones of the Jauf Formation in Saudi Arabia.

Located in Galicia, northwestern Spain, the Anllóns Estuary (Fig. 1.1) was selected for several compelling reasons. Foremost is its quartzo–feldsparthic-rich mineralogical source, which closely resembles the composition of many ancient sandstone reservoirs worldwide. Additionally, the

estuary encompasses a diverse array of sedimentary sub-environments (Fig. 1.1), making it an invaluable natural laboratory for investigating the complex controls on reservoir quality in coastal systems. Furthermore, the estuary remains accessible during most of the tidal cycle, and the occurrence and distribution of detrital clay coatings within it are well-documented (Dowey et al., 2017).

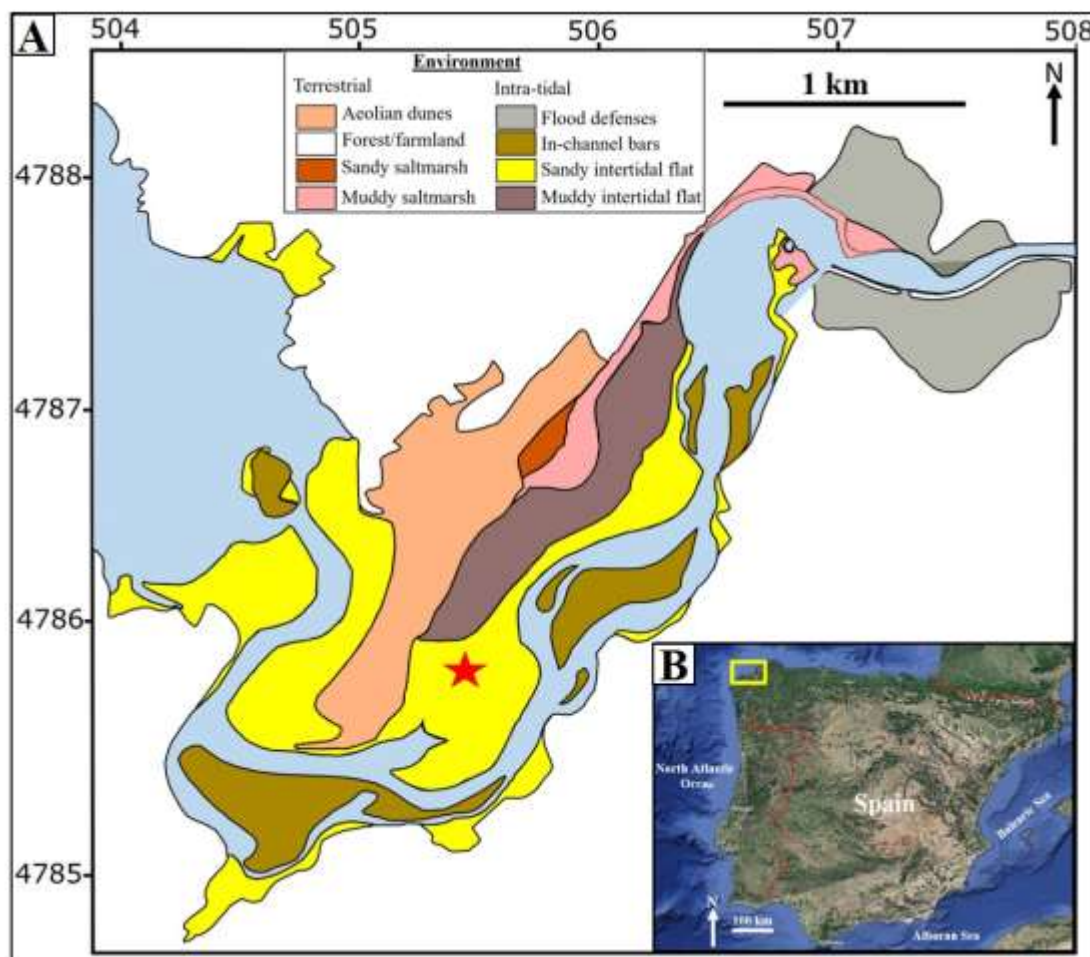


Figure 1.1 A) Simplified geological map of the Anllóns Estuary catchment area, showing the distribution of various sedimentary environments (modified after Dowey et al., 2017). The red star indicates the location of the samples used in this study. B) Regional view of the study area, with the yellow rectangle marking the approximate location of the Estuary

The Gironde Estuary, located near Bordeaux in southwestern France, is one of the largest estuarine systems in Europe, covering an area of approximately 630 km² (Fig. 1.2; Sottolichio et al., 2011; Virolle et al., 2021). It is topographically divided into three principal zones: (1) the Dordogne–Garonne estuarine channels, known for their sandy heterolithic point bars; (2) the inner estuary funnel, which hosts tidal bars within a bay-head delta system; and (3) the expansive outer estuary funnel, characterized by a muddy central basin with tidal bars, terminating in a well-defined tidal inlet at the marine boundary (Fig. 1.2; Allen and Posamentier, 1993; Billy et al., 2012; Virolle et al., 2019b). Integrating the depositional variability of the Gironde with insights from the Anllóns Estuary offers a comprehensive framework for understanding clay mineral formation in modern analogs of ancient marginal marine sandstone reservoirs worldwide. Examples of such reservoirs include the Crystal Field in Canada (Clark and Reinson, 1990), the Tilje Formation in Norway (Martinius et al., 2001), the Sacha Field in Ecuador (Shanmugam et al., 2000), the Cape Hay Formation in Australia (Saiag et al., 2016), the Kalpingtage Formation in China (Zhang and Zhang, 2008), and the El-Basant Gas Field in Egypt (Selim and Abdel Baset, 2020). These coastal environments are not only vital hydrocarbon reservoirs but also have growing potential for CO₂ and hydrogen storage.

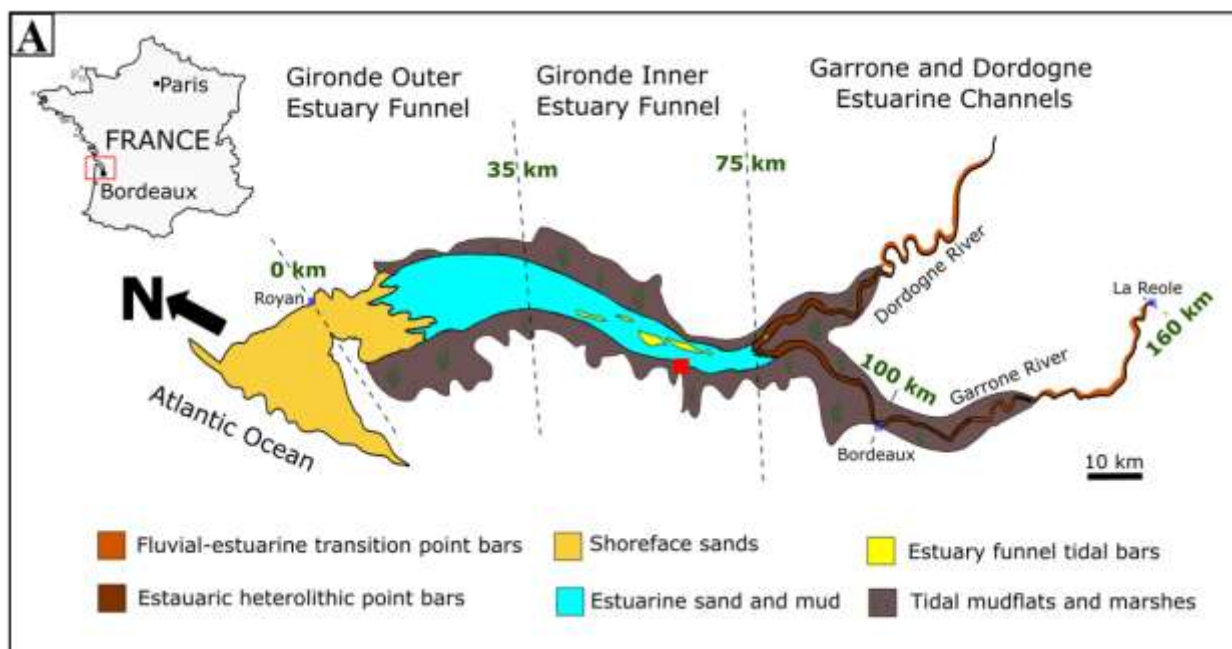


Figure 1.2 (A) Simplified facies map of the Gironde Estuary catchment (modified after Virolle et al., 2019a) with the red square indicating the location of the samples analyzed in this study. The inset map provides a country-level view of the study area, with the red rectangle marking the approximate position of the estuary.

For comparative analysis, the reservoir quality of the Subbat Member of the Early Devonian Jauf Formation, located in Al Huj, northwestern Saudi Arabia (Fig. 1.3), was also investigated. This unit was selected due to its significance as an analogue for subsurface gas reservoirs and its potential for CO₂ sequestration. A kaolinite- and feldspar-rich sample from the Subbat sandstone was also used in hydrothermal reactor experiments to further explore its diagenetic evolution.

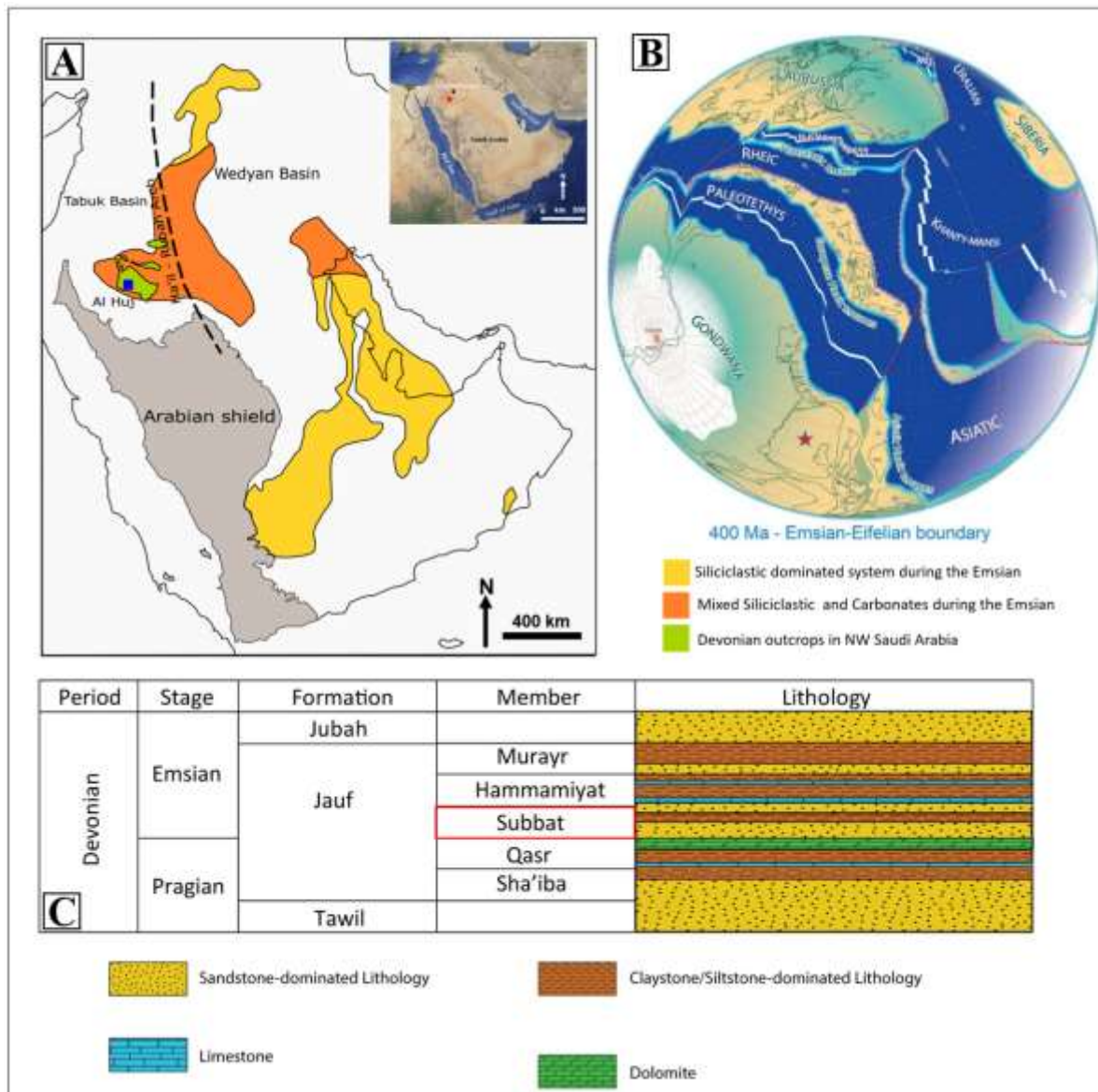


Figure 1.3. (A) Simplified geologic map of Saudi Arabia showing the distribution of the Early Devonian (Emsian) successions and location of the studied section (blue rectangle; redrawn after Konert et al., 2001; Algheryafi et al., 2022). The inset map is a regional view of the study area showing the approximate location of the study (red star). (B) Paleogeographic reconstruction of the Early Devonian showing the location of the Arabian Plate (red star; Stampfli & Borel, 2010). (C) Stratigraphic Column of the Devonian in Saudi Arabia (after Algheryafi et al., 2022). The red rectangle shows the studied Subbat Member.

1.5. Methodology

To achieve the research objectives, this study integrated geological fieldwork and sample collection with a multi-technique analytical approach, utilizing state-of-the-science equipment and facilities at the Center for Integrative Petroleum Research (CIPR), College of Petroleum and Geosciences (CPG), King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia. The general methodological workflow is outlined below, while detailed explanations of each method are provided in the subsequent chapters of the thesis.

- ❖ Data were collected during field trips to the study areas through detailed observations and the collection of sediment samples for laboratory analysis.
- ❖ Samples were prepared for pre-experimental analyses at the CIPR laboratories.
- ❖ Hydrothermal reactor experiments simulating burial diagenesis were conducted using an Ollital OLT-HP-500 multi-position parallel reactor autoclave system and LABE Instrument's advanced hydrothermal reactors connected to a nitrogen gas cylinder, located at the Experimental Diagenesis Laboratory, CIPR.
- ❖ After the experiments, samples were air-dried in fume hoods in preparation for subsequent laboratory analyses.
- ❖ Samples were further prepared for post-experimental analytical procedures.
- ❖ Thin-section petrographic analysis was performed using an Olympus BX53F petrographic microscope to examine the occurrence and distribution of framework grains and detrital clay coatings in the starting material, as well as the authigenic clay minerals synthesized during the experiments.

- ❖ Elemental analysis of sediment samples, both before and after the experiments, was carried out using wavelength-dispersive X-ray fluorescence (WD-XRF) spectroscopy with a PANalytical Zetium spectrometer (Malvern PANalytical).
- ❖ Detailed analysis of the bulk and clay fraction (<2 µm) mineralogy of the initial and post-experiment samples was conducted using X-ray diffraction (XRD) with a Malvern Empyrean PANalytical diffractometer equipped with Ni-filtered Cu K α radiation (PANalytical, Almelo, Netherlands).
- ❖ Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) was performed on selected samples to quantify and map sediment mineral distributions.
- ❖ The morphology, composition, and mode of occurrence of detrital minerals in the starting material, as well as any authigenic minerals formed during the experiments, were examined using a Zeiss Gemini 550 scanning electron microscope (SEM; Oberkochen, Germany), coupled with energy-dispersive X-ray spectrometry (EDS). The SEM was equipped with a backscattered electron (BSE) detector and an Aztec EDS system (Oxford Instruments, UK).
- ❖ Structural formulas of the synthesized clay minerals were calculated based on EDS analyses.
- ❖ High-resolution morphological and structural characterization of clay minerals was conducted using scanning transmission electron microscopy (STEM) on a Dual Beam Laser FIB-SEM system (Zeiss 550).
- ❖ Grain-coating coverage and two-dimensional (2D) grain coat thickness were measured using Petrog software (Conwy Valley Systems Ltd, UK). For more complex three-

dimensional (3D) analysis, focused ion beam scanning electron microscopy (FIB-SEM) was employed.

- ❖ Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Total Reflection X-ray Fluorescence (TXRF) were used to analyze the elemental composition (major cations) of experimental fluids before and after the hydrothermal treatments. Analyses were conducted using an ICPE-9820 Spectrometer (Shimadzu Inc., Kyoto, Japan) and an S4 Tstar-800 TXRF benchtop spectrometer (Bruker, Massachusetts, USA), respectively.
- ❖ For petrophysical analysis of the Subbat sandstones, porosity measurements were conducted on 1.5-inch core samples using a helium gas expansion porosimeter (AP-128-003-0; Vinci Technologies, France). Permeability was assessed using the TinyPerm© handheld air permeameter (New England Research, USA) and the 1.5-inch gas permeameter GP-101AE (Porous Materials, Inc., USA).

1.6. Thesis Structure Overview

This PhD thesis is organized into seven chapters and adopts an alternate, journal-style format. As such, the four core chapters are either already published or have been submitted for publication.

Chapter 1 introduces the research by establishing its motivation, context, and significance. It outlines the primary objectives of the study and provides an overview of the methodological approach adopted.

Chapter 2 presents a comprehensive literature review, focusing on the occurrence of clay minerals in sandstones, the influence of clay coatings on reservoir quality, and previous experimental studies simulating the authigenesis of clay minerals.

The core of the thesis consists of four independent chapters (Chapters 3-6), each representing a standalone manuscript containing original contributions. These chapters are structured with their abstract, introduction, geological background, methodology, results, discussion, and conclusions. A summary of these contributions is provided below. While some content overlap may exist, such repetition is unavoidable due to the self-contained nature of each chapter.

Chapter 3 explores the authigenic formation of smectite grain coatings and their subsequent illitization through a series of hydrothermal experiments. The experiments utilized modern quartzo-feldspathic sediments from the sandy intertidal flat of the Anllóns Estuary, NW Spain. High-resolution petrographic and geochemical analyses revealed smectite formation via a dissolution–crystallization process, with progressive illitization occurring through a mixed-layer illite/smectite intermediate phase as temperature increased. This transformation followed the dissolution of detrital kaolinite and K-feldspar at lower temperatures. The resulting authigenic grain coatings closely resembled those found in natural sandstone reservoirs. Additionally, this chapter introduces a novel methodology for three-dimensional quantification of grain coatings using FIB-SEM.

Chapter 4 investigates the influence of fluid composition on the diagenetic transformation of modern estuarine sediments, using sediments from the Gironde Estuary, SW France. Hydrothermal experiments with various natural and synthetic solutions demonstrated that fluid chemistry

significantly controls authigenic mineral formation, leading to the development of smectite, chlorite, zeolites, and halite.

Chapter 5 examines the roles of depositional and diagenetic processes in controlling the reservoir quality evolution of ancient marginal marine sandstones, focusing on the Subbat Member of the Devonian Jauf Formation. Variations in reservoir quality across different depositional facies are primarily attributed to sedimentary parameters (such as sorting and detrital clay matrix) and burial diagenetic alterations (compaction and cementation).

Chapter 6 presents the experimental synthesis of authigenic chlorite through the initial dissolution of detrital K-feldspar, using Subbat Member sandstones in hydrothermal reactor experiments. The study emphasizes the critical role of reaction time in the formation and development of authigenic clay minerals under diagenetic conditions.

Chapter 7 concludes the thesis by summarizing the key findings, addressing the original research objectives, and providing recommendations for future research directions in the field of clay mineral diagenesis and reservoir quality evolution.

1.7. References

- Aagaard, P., Jahren, J.S., Harstad, A.O., Nilsen, O., and Ramm, M., 2000. Formation of grain-coating chlorite in sandstones. Laboratory synthesized vs. natural occurrences. *Clay Miner.* 35, 261–269. <https://doi.org/10.1180/000985500546639>.
- Ajdukiewicz, J.M., and Lander, R.H., 2010. Sandstone reservoir quality prediction: The state of the art. *Am. Assoc. Pet. Geol. Bull.* 94, 1083–1091. <https://doi.org/10.1306/intro060110>.
- Ajdukiewicz, J.M., and Larese, R.E., 2012. How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments. *Am. Assoc. Pet. Geol. Bull.* 96, 2091–2119. <https://doi.org/10.1306/02211211075>.
- Algheryafi, H., Viseras, C., Polo, C., & Al-Ramadan, K. (2022). Facies architecture and paleogeography evolution of regressive wave-dominated shorelines transitioning into tide-dominated estuaries: Early Devonian Subbat Member, Jauf Formation, Saudi Arabia. *Journal of Sedimentary Research*, 92(10), 955–987. <https://doi.org/10.2110/jsr.2021.112>
- Allen, G.P., and Posamentier, H.W., 1993, Sequence stratigraphy and facies model of an incised valley fill: the Gironde estuary, France: *Journal of Sedimentary Petrology*, v. 63, doi:10.1306/D4267B09-2B26-11D7-8648000102C1865D.
- Al-Ramadan, K., Franks, S.G., Al-Shammari, S., Rees, A., Koeshidayatullah, A., and Abu-Khamsin, S., 2017, Depositional and Diagenetic Barriers, Baffles and Conduits: Permian – Carboniferous Unayzah Reservoir, Nuayyim Field, Central Saudi Arabia: *Journal of Petroleum Geology*, v. 40, p. 85–103, doi:10.1111/jpg.12665.
- Al-Ramadan, K.A., Hussain, M., Imam, B., and Saner, S., 2004. Lithologic characteristics and diagenesis of the Devonian Jauf sandstone at Ghawar Field, Eastern Saudi Arabia: *Marine and Petroleum Geology*, v. 21, p. 1221–1234, doi: 10.1016/j.marpetgeo.2004.09.002
- Anjos, S.M.C., De Ros, L.F., and Silva, C.M.A., 2003. Chlorite Authigenesis and Porosity Preservation in the Upper Cretaceous Marine Sandstones of the Santos Basin, Offshore Eastern Brazil, in: Worden, R. H. and Morad, S. (Ed.), *Clay Mineral Cements in Sandstones*. International Association of Sedimentologists Special Publications, pp. 289–316. <https://doi.org/10.1002/9781444304336.ch13>.
- Barshep, D. V., and Worden, R. H., 2021. Reservoir Quality of Upper Jurassic Corallian Sandstones, Weald Basin, UK. *Geosciences*, 11(11), 446. MDPI AG. Retrieved from <http://dx.doi.org/10.3390/geosciences11110446>
- Bello, A. M., Charlaftis, D., Jones, S. J., Gluyas, J., Acikalin, S., Cartigny, M., and Al-Ramadan, K., 2022. Experimental diagenesis using present-day submarine turbidite sands. *Frontiers in Earth Science*, 10(August), 1–20. <https://doi.org/10.3389/feart.2022.952690>
- Bello, A., Jones, S., Gluyas, J., Açıkalın, S., and Cartigny, M., 2021. Role played by clay content in controlling reservoir quality of submarine fan system, Forties Sandstone Member, Central Graben, North Sea. *Marine and Petroleum Geology*, 128, 105058. <https://doi.org/10.1016/j.marpetgeo.2021.105058>
- Bello, A.M., Butt, M.N., Hussain, A., Amao, A.O., Olariu, C., Koeshidayatullah, A.I., Malik, M.H., Al-Hashem, M., and Al-Ramadan, K., 2023. Impact of Depositional and Diagenetic

- Controls on Reservoir Quality of Syn-rift Sedimentary Systems: An example from Oligocene-Miocene Al Wajh Formation, Northwest Saudi Arabia: *Sedimentary Geology*, p. 106342, doi: 10.1016/j.sedgeo.2023.106342.
- Billy, J., Chaumillon, E., Fe'Nie` S, H., and Poirier, C., 2012, Tidal and fluvial controls on the morphological evolution of a lobate estuarine tidal bar: the Plassac tidal bar in the Gironde Estuary (France): *Geomorphology*, v. 169–170, p. 86–97, doi: 10.1016/j.geomorph.2012.04.015.
- Bjørlykke, K., Jahren, J., 2010. Sandstones and sandstone reservoirs. In: *Petroleum Geoscience*. Springer, Berlin, Heidelberg, pp. 113–140.
- Bloch, S., Lander, and R.H., Bonnell, L., 2002. Anomalously high porosity and permeability in deeply buried sandstone reservoirs: Origin and predictability. *Am. Assoc. Pet. Geol. Bull.* 86, 301–328. <https://doi.org/10.1306/61eedabc-173e-11d7-8645000102c1865d>.
- Burruss, R., 2004, *Geologic Sequestration of Carbon Dioxide in the Next 10 to 50 Years: An Energy Resource Perspective*, Prepared for the 10-50 Solution: Technologies and Policies for a Low-Carbon Future, Pew Center on Global Climate Change and the National Commission on Energy Policy, March 25-26, Washington, DC
- Charlaftis, D., 2021. Assessing sandstone reservoir quality: identifying the reality. Durham University, U.K.
- Charlaftis, D., Dobson, K. J., Jones, S. J., Lakshtanov, D., Crouch, J., and Cook, J., 2022. Experimental simulation of burial diagenesis and subsequent 2D-3D characterization of sandstone reservoir quality. *Front. Earth Sci.* 10, 766145. doi:10.3389/feart.2022.766145
- Charlaftis, D., Jones, S. J., Dobson, K. J., Crouch, J., and Acikalin, S., 2021. Experimental study of chlorite authigenesis and influence on porosity maintenance in sandstones. *J. Sediment. Res.* 91, 197–212. doi:10.2110/JSR.2020.122
- Clark, J.E., and Reinson, G.E., 1990. Continuity and Performance of an Estuarine Reservoir, Crystal Field, Alberta, Canada. In: *Sandstone Petroleum Reservoirs*. Springer. pp. 343-361.
- Curtis, C.D., 1983. Geochemistry of porosity enhancement and reduction in clastic sediments, in: Brooks, J. (Ed.), *Petroleum Geochemistry and Exploration of Europe*. Blackwells, Oxford, pp. 113–125. <https://doi.org/10.1144/GSL.SP.1983.012.01.12>.
- Daneshvar, E., 2011. Role of provenance on clay minerals and their distribution in modern estuaries. The University of Liverpool (United Kingdom).
- Dowey, P.J., Worden, R.H., Utley, J., Hodgson, D.M., 2017. Sedimentary controls on modern sand grain coat formation. *Sediment. Geol.* 353, 46–63. <https://doi.org/10.1016/j.sedgeo.2017.03.001>.
- Ehrenberg, S.N., 1993. Preservation of anomalously high porosity in deeply buried sandstones by grain-coating chlorite: examples from the Norwegian Continental Shelf. *AAPG Bulletin*, 77, 1260–1286.
- Flesch, S., Pudlo, D., Albrecht, D.; Jacob, A., Enzmann, F., 2018. Hydrogen underground storage- Petrographic and petrophysical variations in reservoir sandstones from laboratory

- experiments under simulated reservoir conditions. *Int. J. Hydrogen Energy*, 43, 20822–20835.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., and Duller, R.A., 2019a, Compositional variation in modern estuarine sands: Predicting major controls on sandstone reservoir quality: *AAPG Bulletin*, v. 103, p. 797–833.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., and Duller, R.A., 2018, Detrital clay coats, clay minerals, and pyrite: A modern shallow-core analogue for ancient and deeply buried estuarine sandstones: *Journal of Sedimentary Research*, v. 88, p. 1205–1237.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., Duller, R.A., and Edge, R.L., 2019b, Estuarine clay mineral distribution: Modern analogue for ancient sandstone reservoir quality prediction: *Sedimentology*, v. 66, p. 2011–2047.
- Haile, B. G., Hellevang, H., Aagaard, P., and Jahren, J., 2015. Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces. *Mar. Petroleum Geol.* 68, 664–674. doi: 10.1016/j.marpetgeo. 2015.02.006
- Hassanpouryouzband, A., Adie, K., Cowen, T., Thaysen, E. M., Heinemann, N., Butler, I. B., Wilkinson, M., Edlmann, K., 2022. Geological Hydrogen Storage: Geochemical Reactivity of Hydrogen with Sandstone Reservoirs. *ACS Energy Letters* 7, 2203–2210, DOI: 10.1021/acsenergylett.2c01024
- Heald, M.T., and Larese, R.E., 1974. Influence of Coatings on Quartz Cementation. *SEPM J. Sediment. Res.* Vol. 44, 1269–1274. <https://doi.org/10.1306/212f6c94-2b24-11d7-8648000102c1865d>.
- Kordi, M., 2013. Characterization and prediction of reservoir quality in chlorite-coated sandstones: evidence from the Late Cretaceous Lower Tuscaloosa Formation at Cranfield Field, Mississippi, U.S.A. The University of Texas at Austin, pp. 27-172.
- Lander, R. H., and O. Walderhaug, 1999, Porosity prediction through simulation of sandstone compaction and quartz cementation: *AAPG Bulletin*, v. 83, p. 433–449
- Lander, R. H., R. E. Larese, and L. M. Bonnell, 2008, Toward more accurate quartz cement models: The importance of euhedral versus noneuhedral growth rates: *AAPG Bulletin*, v. 92, p. 1537–1563, doi:10.1306/07160808037
- Litvinenko, V.S., 2020. The Role of Hydrocarbons in the Global Energy Agenda: The Focus on Liquefied Natural Gas. *Resources*.
- Martinius, A.W., Kaas, I., Naess, A., Helgesen, G., Kjaerefjord, J.M. and Leith, D.A., 2001. Sedimentology of the heterolithic and tide-dominated Tilje Formation (Early Jurassic, Halten Terrace, offshore mid-Norway). *NPF Spec. Publ.*, 10, 103–144.
- McBride, Earle F., 1989. Quartz cement in sandstones: a review. *Earth Sci. Rev.* 26, 69–112. [https://doi.org/10.1016/0012-8252\(89\)90019-6](https://doi.org/10.1016/0012-8252(89)90019-6).
- McGhee, C., Muhammed, D., Simon, N., Acikalin, S., Utley, J.E.P., Griffiths, J., Wooldridge, L., Verhagen, I.T.E., van der Land, C., and Worden, R.H., 2022, Stratigraphy and sedimentary

- evolution of a modern macro-tidal incised valley: An analogue for reservoir facies and architecture: *Sedimentology*, v. 69, p. 696–723.
- Morad, S., Al-Ramadan, K., Ketzer, J.M., De Ros, L.F., 2010. The impact of diagenesis on the heterogeneity of sandstone reservoirs: A review of the role of depositional fades and sequence stratigraphy. *Am. Assoc. Pet. Geol. Bull.* 94, 1267–1309. <https://doi.org/10.1306/04211009178>.
- Muhammed, D.D., Simon, N., Utley, J.E.P., Verhagen, I.T.E., Duller, R.A., Griffiths, J., Wooldridge, L.J., and Worden, R.H., 2022, *Geochemistry of Sub-Depositional Environments in Estuarine Sediments: Development of an Approach to Predict Palaeo-Environments from Holocene Cores: Geosciences (Switzerland)*, v. 12, p. 23.
- Saiag, J., Brigaud, B., Portier, E., Desaubliaux, G., Bucherie, A., Miska, S. and Pagel, M., 2016. Sedimentological control on the diagenesis and reservoir quality of tidal sandstones of the Upper Cape Hay Formation (Permian, Bonaparte Basin, Australia). *Mar. Pet. Geol.*, 77, 597–624.
- Selim, S.S., and Abdel Baset, A.A., 2020. Sedimentological analysis and reservoir characterization of an estuarine bar: An example from the El-Basant Gas field, Nile Delta. Egypt. J. Nat. Gas Sci. Eng. 84, 103548. <https://doi.org/10.1016/j.jngse.2020.103548>
- Shanmugam, G., Poffenberger, M., and Toro Alava, J., 2000. Tide-dominated estuarine facies in the Hollin and Napo (“T” and ‘U’) formations (Cretaceous), Sacha field, Oriente basin. Ecuador. *AAPG Bulletin*, 84, 652–682.
- Small, J.S., Hamilton, D.L., and Habesch, S., 1992, Experimental simulation of clay precipitation within reservoir sandstones 1: techniques and examples: *Journal of Sedimentary Petrology*, v. 62, p. 508-519.
- Sottolichio, A., Castaing, P., Etcheber, H., Maneux, E., Schmeltz, M., and Schmidt, S., 2011, Observations of suspended sediment dynamics in a highly turbid macrotidal estuary, derived from continuous monitoring: *Journal of Coastal Research*, v. 64, p. 1579–1583
- Stampfli, G. M., & Borel, G. D. (2002). A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrons. *Earth and Planetary Science Letters*, 196(1), 17–33. [https://doi.org/10.1016/S0012-821X\(01\)00588-X](https://doi.org/10.1016/S0012-821X(01)00588-X)
- Stricker, S., Jones, S.J., 2018. Enhanced porosity preservation by pore fluid overpressure and chlorite grain coatings in the Triassic Skagerrak, Central Graben, North Sea, UK. *Geol. Soc. Spec. Publ.* 435, 321–341. <https://doi.org/10.1144/SP435.4>
- Taylor, T. R., M. R. Giles, L. A. Hathorn, T. N. Diggs, N. R. Braunsdorf, G. V. Birbiglia, M. G. Kittridge, C. I. Macaulay, and I. S. Espejo, 2010, Sandstone diagenesis and reservoir quality prediction: Models, myths, and reality: *AAPG Bulletin*, v. 94, p. 1093–1132, doi:10.1306/04211009123

- Virolle, M., Brigaud, B., Beaufort, D., Patrier, P., Abdelrahman, E., Thomas, H., Portier, E., Samson, Y., Bourillot, R., and Féliès, H., 2022, Authigenic berthierine and incipient chloritization in shallowly buried sandstone reservoirs: Key role of the source-to-sink context: *GSA Bulletin*, v. 134, p. 739–761.
- Virolle, M., Brigaud, B., Bourillot, R., Féliès, H., Portier, E., Duteil, T., Nouet, J., Patrier, P., and Beaufort, D., 2019a, Detrital clay grain coats in estuarine clastic deposits: origin and spatial distribution within a modern sedimentary system, the Gironde Estuary (south-west France): *Sedimentology*, v. 66, p. 859–894.
- Virolle, M., Brigaud, B., Féliès, H., Bourillot, R., Portier, E., Patrier, P., Derriennic, H., and Beaufort, D., 2021, Preservation and distribution of detrital clay coats in a modern estuarine heterolithic point bar in the Gironde estuary (Bordeaux, France): *Journal of Sedimentary Research*, v. 91, p. 812–832.
- Virolle, M., Brigaud, B., Luby, S., Portier, E., Féliès, H., Bourillot, R., Patrier, P., and Beaufort, D., 2019b, Influence of sedimentation and detrital clay grain coats on chloritized sandstone reservoir qualities: Insights from comparisons between ancient tidal heterolithic sandstones and a modern estuarine system: *Marine and Petroleum Geology*, v. 107, p. 163–184.
- Virolle, M., Féliès, H., Brigaud, B., Bourillot, R., Portier, E., Patrier, P., Beaufort, D., Jalon-Rojas, I., Derriennic, H., and Miska, S., 2020, Facies associations, detrital clay grain coats and mineralogical characterization of the Gironde estuary tidal bars: A modern analogue for deeply buried estuarine sandstone reservoirs: *Marine and Petroleum Geology*, v. 114, p. 104225.
- Walderhaug, O., 1996. Kinetic modeling of quartz cementation and porosity loss in deeply buried sandstone reservoirs. *Am. Assoc. Pet. Geol. Bull.* 80, 731–745.
- Wood, J. R., and A. P. Byrnes, 1994, Alternate and emerging methodologies in geochemical and empirical modeling, in M. D. Wilson, ed., *Reservoir quality assessment and prediction in clastic rocks: SEPM Short Course 30*, p. 395–400
- Worden, R. H., Griffiths, J., Wooldridge, L. J., Utley, J. E. P., Lawan, A. Y., Muhammed, D. D., Simon, N., and Armitage, P. J., 2020. Chlorite in sandstones. *Earth-Science Reviews*, 204(August 2019), 103105. <https://doi.org/10.1016/j.earscirev.2020.103105>
- Worden, R.H., Armitage, P.J., Butcher, A.R., Churchill, J.M., Csoma, A.E., Hollis, C., Lander, R.H., Omma, J.E., 2018. Petroleum reservoir quality prediction: Overview and contrasting approaches from sandstone and carbonate communities, in: P.J. Armitage, A. Butcher, J. Churchill, A. Csoma, C. Hollis, R.H. Lander, J.O. and R.H.W. (Ed.), *Geological Society Special Publication*. Geological Society, London, Special Publications, pp. 1–31. <https://doi.org/10.1144/SP435.21>.

- Worden, R.H., Morad, S., 2003. Clay Minerals in Sandstones: Controls on Formation, Distribution and Evolution, in: Clay Mineral Cements in Sandstones. Blackwell Publishing Ltd., Oxford, UK, pp. 1–41. <https://doi.org/10.1002/9781444304336.ch1>.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., Thompson, A., and Chung, P., 2017a, Biofilm origin of clay-coated sand grains: *Geology*, v. 45, p. 875–878.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., and Utley, J.E.P., 2017b, Clay-coated sand grains in petroleum reservoirs: Understanding their distribution via a modern analogue: *Journal of Sedimentary Research*, v. 87, p. 338–352.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., and Utley, J.E.P., 2019, How to quantify clay-coat grain coverage in modern and ancient sediments: *Journal of Sedimentary Research*, v. 89, p. 135–146.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., Utley, J.E.P., and Thompson, A., 2018, The origin of clay-coated sand grains and sediment heterogeneity in tidal flats: *Sedimentary Geology*, v. 373, p. 191–209.
- Yekta, A. E., Pichavant, M., Audigane, P., 2018. Evaluation of geochemical reactivity of hydrogen in sandstone: Application to geological storage. *Appl. Geochem.* 2018,95, 182–194
- Zhang, J., and Zhang, Z., 2008. Sedimentary facies of the Silurian tide-dominated paleoestuary of the Tazhong area in the Tarim basin. *Pet. Sci.* 5 (2), 95–104.

CHAPTER 2

LITERATURE REVIEW

2.1. Clay minerals and their impact on sandstone reservoir quality

The reservoir quality of sandstones is a function of both depositional attributes and subsequent diagenetic processes. While initial porosity and permeability are largely dictated by depositional factors such as grain size, sorting, and mineralogy (Worden et al., 2018a; Payton et al., 2022; Khan et al., 2023; El-Ghali et al., 2024; Naveed Butt et al., 2024), diagenesis, comprising eodiagenesis, mesodiagenesis, and telodiagenesis (Fig. 2.1), plays a central role in the post-depositional modification of these properties (Worden and Morad, 2009). After compaction, the predominant factor for porosity and permeability reduction in sandstone reservoirs during deep burial and heating is the emergence of quartz cementation (McBride, 1989; Ehrenberg, 1993; Walderhaug, 1996; Lander and Walderhaug, 1999; Walderhaug and Porten, 2022). Yet, a notable percentage of these deeply buried reservoirs exhibit unexpectedly high levels of porosity and permeability (Bloch and McGowen, 1994; Bello et al., 2023b). The preservation of such unusual porosity and permeability is often attributed to the presence of grain-coating clays (Fig. 2.2), which prevent the formation of porosity-decreasing cement (Ehrenberg, 1993; Anjos et al., 1999; Ajdukiewicz and Larese, 2012a; Al-Ramadan et al., 2013b, 2013a; Al-Ramadan, 2014b, 2014a). Clay minerals, a group of hydrous aluminosilicate minerals with particle diameters lower than 2 μm , are present as detrital and diagenetic cements in sandstone (Deer et al., 2013). Although clay minerals occupy a small volume relative to other minerals within sandstones, clay mineral cements significantly influence sandstone reservoir quality (Heald and Larese, 1974; Wilson and Pittman, 1977; Imam and Shaw, 1985; Pittman et al., 1992; Lander and Walderhaug, 1999; Worden and Morad, 2000,

2009; Ajdukiewicz and Lander, 2010; Taylor et al., 2010; Morad et al., 2010; Al-Ramadan et al., 2013a, 2013b; Tang et al., 2018; Worden et al., 2018; Bello et al., 2021; Taylor et al., 2022; Bello et al., 2023c, 2023a, 2024b, 2024a; Hussain et al., 2024; Naveed Butt et al., 2024; Salisu et al., 2024).

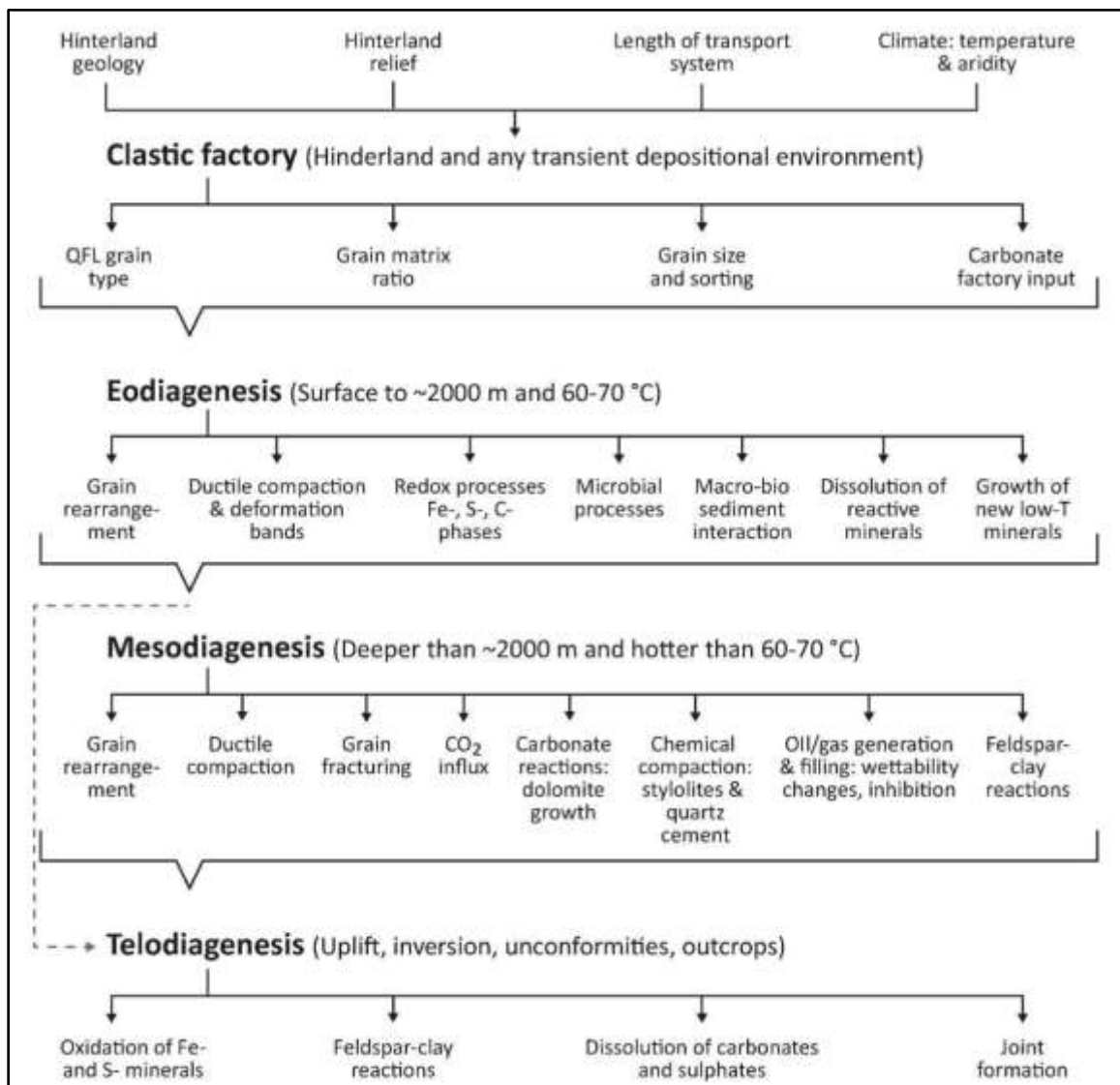


Figure 2.1. Hierarchy of controls on clastic grains which governs sandstone reservoir quality: the “clastic factory”; eodiagenetic processes (early or shallow-burial diagenesis); mesodiagenetic

processes (deep-burial diagenesis); and telogenetic influences related to uplift (Charlaftis, 2021; modified after Worden et al., 2018).

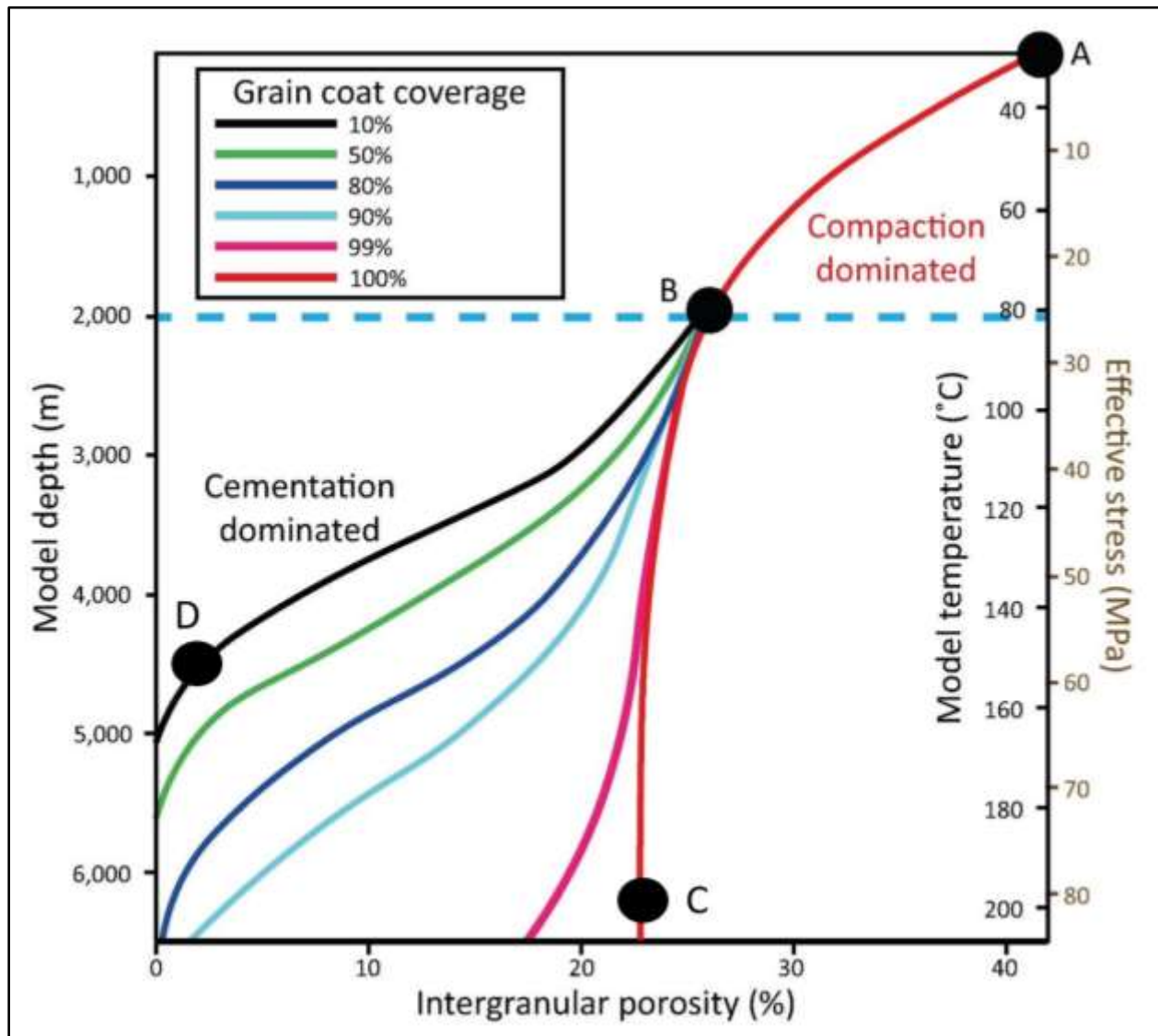


Figure 2.2. A model of porosity evolution with burial depth for a well-sorted, fine-grained, quartzofeldspathic aeolian sandstone bearing variable clay grain coatings. As clay-coat coverage increases, the extent of cement precipitation decreases. Curve A represents freshly deposited sand, while Curve B marks the onset of cementation at about 80 °C and 2 km of burial. In this hypothetical scenario, maximum porosities are retained at depth, where both compaction and

cement growth are inhibited by rigid grains enveloped in well-developed clay coats (Charlaftis, 2021; modified after Ajdukiewicz and Lander, 2010)

Their impact on porosity and permeability varies based on their type, mode of occurrence, and abundance (Bello et al., 2021). Numerous studies indicate that, based on these factors, clay mineral cements can either preserve or degrade the porosity and permeability of sandstone reservoirs (Pittman 1992; Ehrenberg 1993; Imam and Shaw 1995; Ajdukiewicz and Larese 2012; Al-Ramadan et al., 2004; Worden and Morad, 2009). Grain-coating clays, such as chlorite, illite, and mixed-layer clays, have been shown to inhibit authigenic quartz cementation in deeply buried reservoirs (Fig. 2.3), thereby preserving reservoir quality (Heald and Anderegg, 1960; Ehrenberg, 1993; Bloch and McGowen, 1994; Lander and Walderhaug, 1999; Anjos et al., 1999; Bloch et al., 2002; Storvoll et al., 2002; Al-Ramadan et al., 2004, 2005; Saner et al., 2006; Mansurbeg et al., 2008; Ajdukiewicz and Larese, 2012; Al-Ramadan, 2014; Stricker and Jones, 2018; Hussain et al., 2022a, 2022b; Walderhaug and Porten, 2022; El-Ghali et al., 2024).

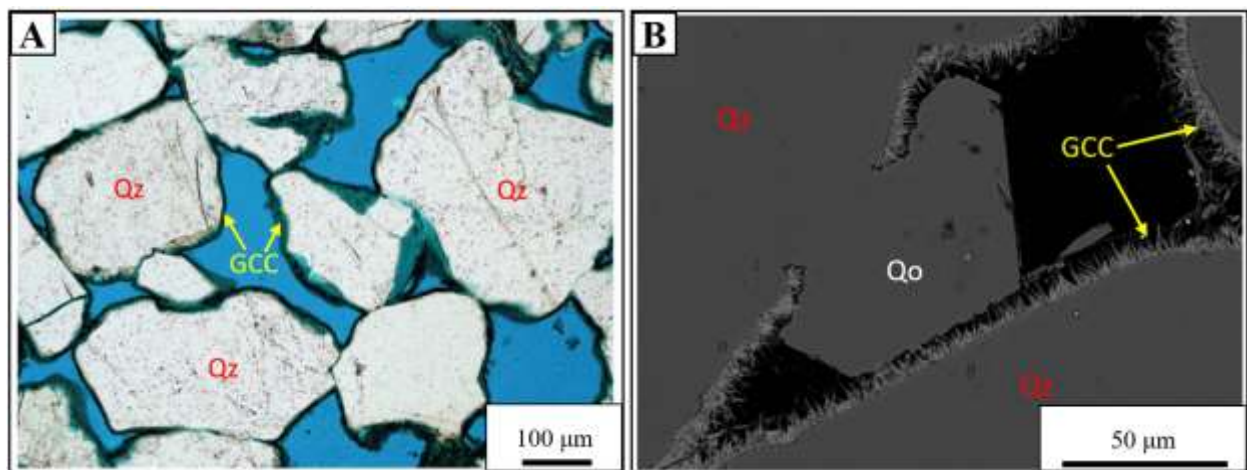


Figure 2.3. (A)Thin-section micrograph showing chlorite effectively coating detrital quartz grains in the Lower Jurassic estuarine Tilje Formation sandstone, thereby preventing quartz overgrowths.

(B) SEM image of the Middle Jurassic shallow-marine Garn Formation sandstone reveals chlorite grain coatings with gaps between platelets exceeding approximately 5 μm , allowing quartz outgrowths to penetrate and expand laterally through these coatings (Walderhaug and Porten, 2022).

Conversely, pore-filling clays, including smectite, kaolinite, and illite, occupy pore spaces (Fig. 2.4) and obstruct fluid flow, significantly reducing reservoir porosity and permeability (Nadeau et al., 1985; McKinley et al., 1999; Franks and Zwingmann, 2010; Ulmer-Scholle et al., 2015; Bello et al., 2022c; Khan et al., 2023; Salisu et al., 2023).

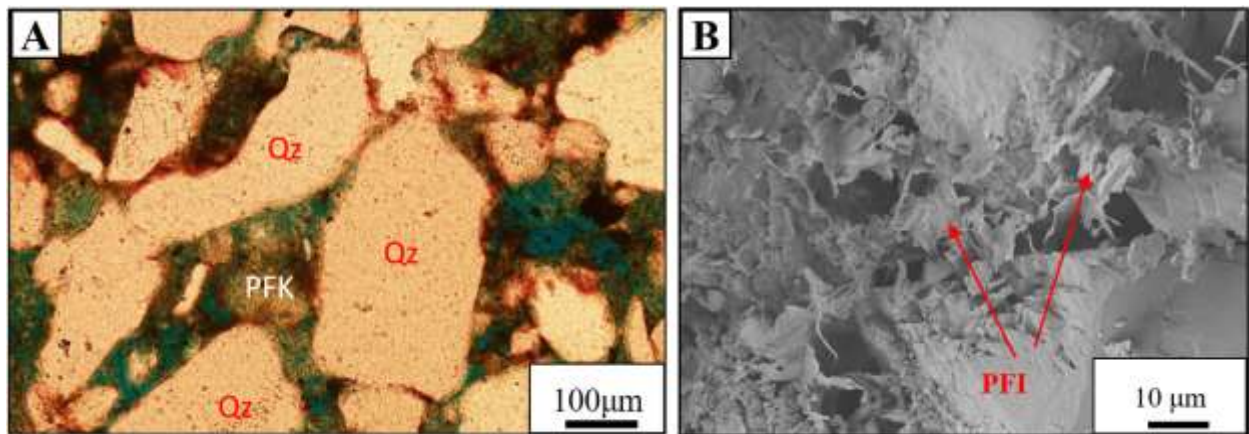


Figure 2.4. Thin section photomicrograph (A) showing the occurrence of pore-filling kaolinite (PFK) between detrital quartz grains (Qz) filling pore-spaces. (B) SEM image showing the occurrence of pore-filling illite (PFI).

The primary clay mineral groups in sandstone encompass kaolinite, smectite, illite, chlorite, and mixed-layer clays (Fig. 2.5). These clay minerals may either be derived from detrital origins or emerge due to diagenetic (authigenic) activities (Ajdukiewicz and Larese, 2012). Allogenic clays are formed before deposition, integrated with the sand during or immediately after deposition

(McKinley et al., 1999; Worden and Burley, 2009). Mechanisms such as mechanical infiltration (Worden and Morad, 2009), bioturbation (Needham et al., 2005), sediment dewatering (Houseknecht, 1987), and biofilm formation (Wooldridge et al., 2017) contribute to the placement of detrital clay coatings in sandstones. Authigenic clays emerge after burial, precipitating either directly from the formation fluids or due to interactions between precursor minerals and pore fluids (Fig. 2.6; Ajdukiewicz and Larese, 2012).

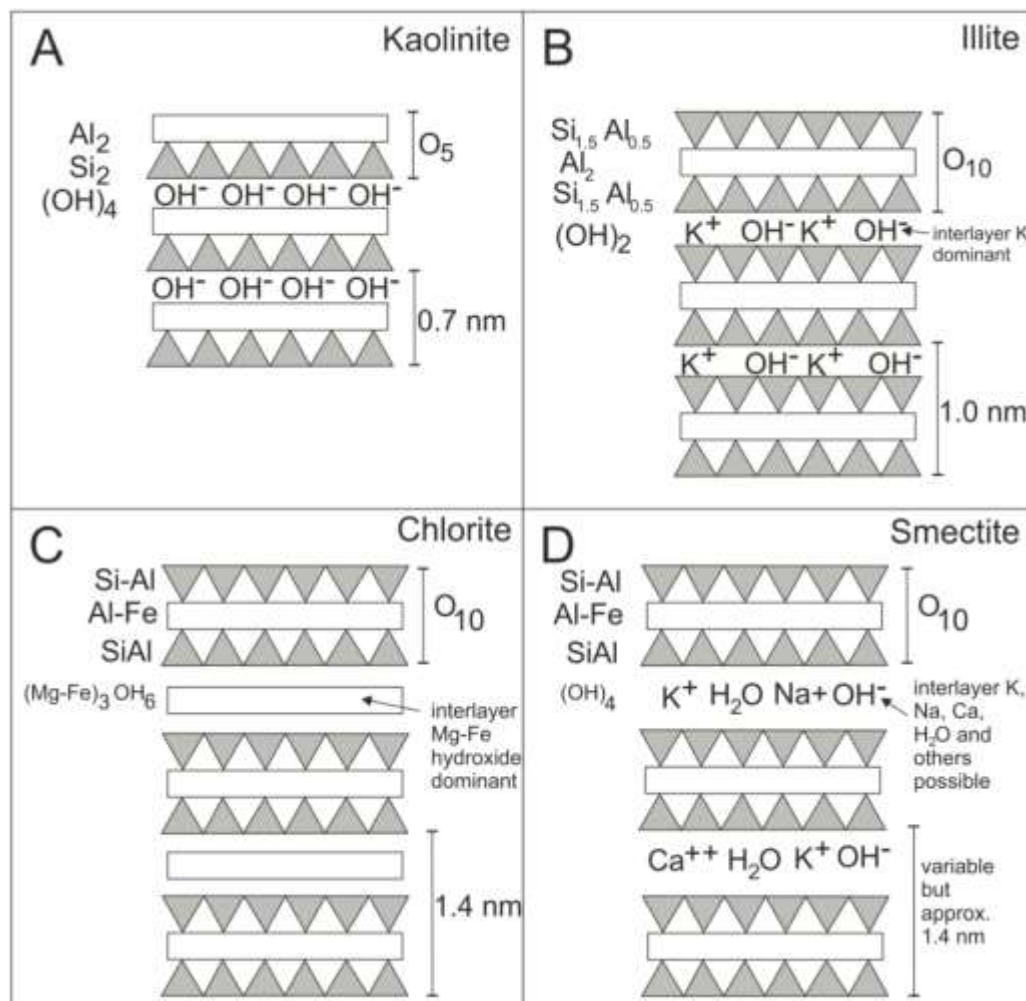


Figure 2.5. A schematic diagram illustrating the structural configuration of common clay minerals in sandstone reservoirs (adapted from Griffiths, 2018; modified after Worden and Morad, 2003).

(A) kaolinite, (B) illite, (C) chlorite, and (D) dioctahedral smectite. Tetrahedral layers are represented by triangles, while octahedral layers are denoted by bars.

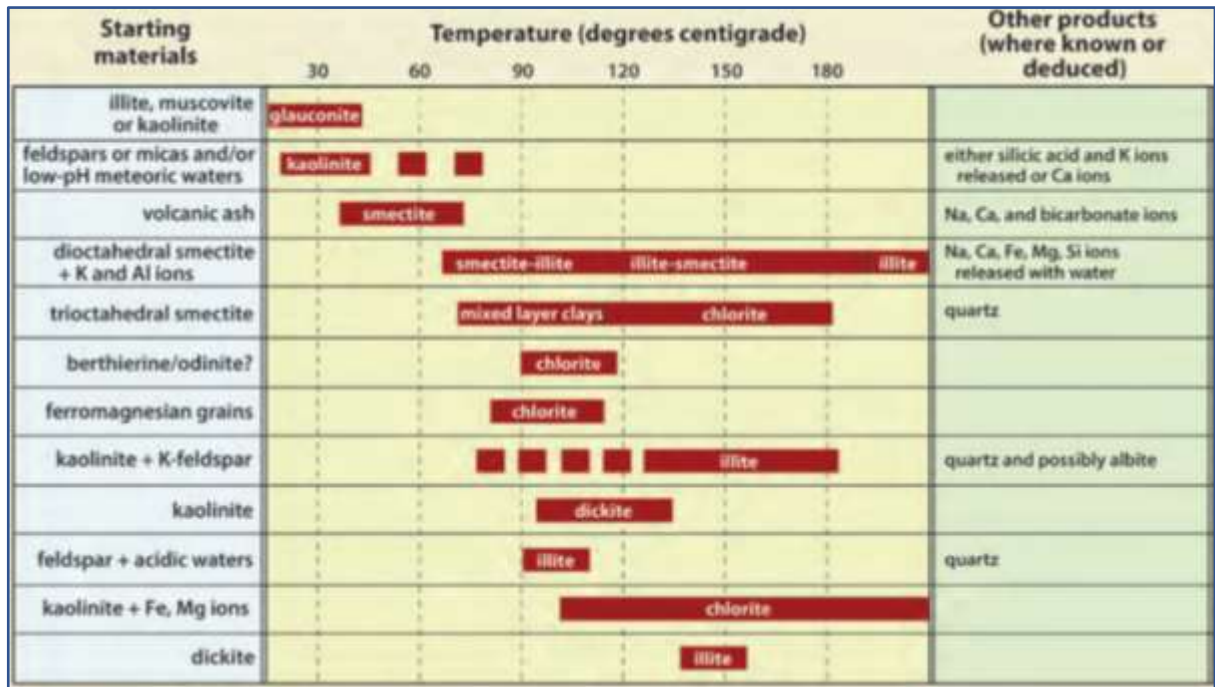


Figure 2.6. An image summarizing the diagenetic transformation pathways of clay minerals in sandstones (adapted from (Ulmer-Scholle et al., 2015))

Kaolinite

Kaolinite is a significant 1:1 clay mineral in sandstone reservoirs, with a general chemical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Fig. 2.5A; Worden and Morad, 2003). Its crystal structure comprises a single tetrahedral silica sheet bonded to a single octahedral alumina sheet, resulting in a neutral layer that lacks significant interlayer cation exchange capacity (Worden and Morad, 2003; Ulmer-Scholle et al., 2015). Kaolinite forms pseudo-hexagonal plates that often exhibit vermicular or book-like

habits (Fig. 2.7). As the low-temperature polymorph of kaolin minerals, kaolinite typically forms under surface or near-surface conditions, whereas dickite represents the high-temperature polymorph associated with deeper burial and elevated thermal regimes (Marfil et al., 1999). In sandstones, kaolinite may occur as either a detrital or authigenic phase. Detrital kaolinite is sourced from the erosion of older, weathered rocks rich in kaolin, whereas authigenic kaolinite forms mainly through feldspar and mica dissolution during early diagenesis (Marfil et al., 1999). Formation typically occurs under humid climatic conditions where meteoric water infiltration introduces low-pH fluids into sediments, promoting chemical weathering and the release of aluminosilicates necessary for kaolinite precipitation (Lanson et al., 2002; Worden and Morad, 2009)

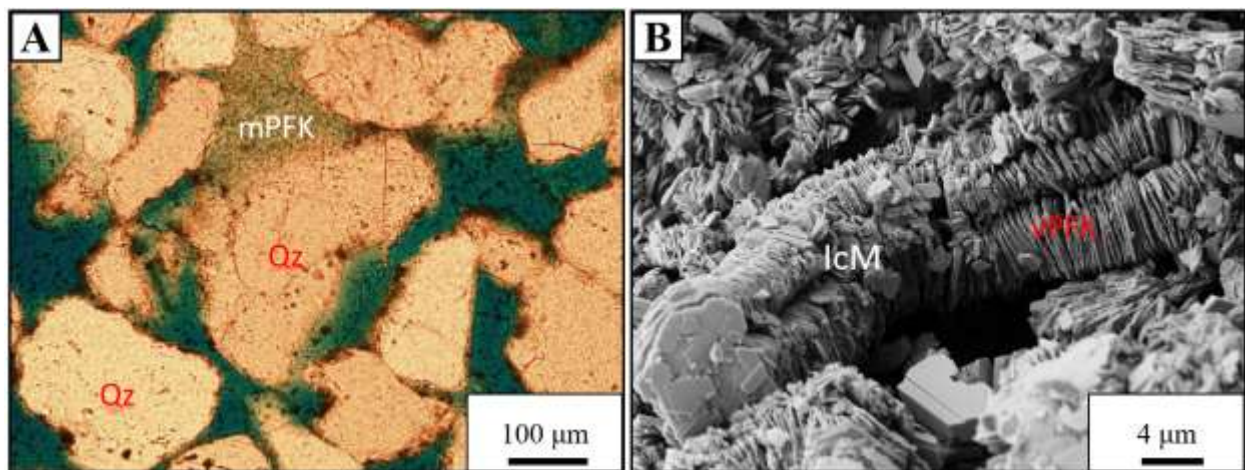


Figure 2.7. (A) Thin-section photomicrograph showing the occurrence of microporous pore-filling kaolinite (mPFK) occupying pore space within detrital quartz grains (Qz). (B) SEM image showing intercrystalline microporosity (IcM) within vermicular pore-filling kaolinite (vPFK).

As burial depth and temperature increase, kaolinite undergoes progressive diagenetic transformation. Vermicular, fine-grained kaolinite recrystallizes into thicker, blocky dickite at

temperatures between 70–90 °C, typically at depths of 2–3 km (Beaufort et al., 1998). This transformation is promoted in high porosity and permeability sandstones but may be inhibited in heavily compacted or hydrocarbon-charged reservoirs (Beaufort et al., 1998; Lanson et al., 2002). Under mesodiagenetic conditions (temperatures above 120 °C), kaolinite can react with potassium, often sourced from K-feldspar dissolution, to form illite, accompanied by quartz precipitation (Bjørlykke et al., 1989; Bjørlykke, 1998, 2014). Further burial into Fe- and Mg-rich environments at depths exceeding 3.5 km can transform kaolinite into chlorite (Chen et al., 2011).

The presence and diagenetic alteration of kaolinite significantly affect sandstone reservoir quality. Pore-filling vermicular kaolinite tends to occlude pore throats (Fig. 2.7), reducing both porosity and permeability (Marfil et al., 1999). Conversely, grain-replacive kaolinite may partially preserve primary porosity by stabilizing grain frameworks (Milliken, 2003). Feldspar dissolution during kaolinitization may initially enhance secondary porosity; however, subsequent transformation of kaolinite to illite often deteriorates permeability due to the fibrous, pore-bridging nature of illite crystals (Worden and Morad, 2009). Deep burial formation of dickite stabilizes pore structures but generally does not improve reservoir quality.

Smectite

Smectites, a 2:1 expandable clay mineral (Fig. 2.5D), chemically more complex than other clay minerals (McKinley et al., 1999), occur in various geological settings (Chamley, 1994; Taylor et al., 2022) and have broad industrial and environmental applications (García-Romero et al., 2021). In sandstones, smectites occur as both detrital and diagenetic materials (Primmer et al., 1997; Ulmer-Scholle et al., 2015). The formation of diagenetic smectite in sandstones occurs early during shallow burial via several authigenic processes (Fig. 2.8), including the replacement of detrital

framework grains such as K-feldspar, the transformation of precursor detrital clays, and direct neomorphic precipitation from pore water (McKinley et al., 1999; Ryu and Niem, 1999; Taylor et al., 2022). The structure and composition of smectite minerals are complex, and their authigenic formation is influenced by factors such as pH, pore water chemistry, and the availability of cations (Chamley, 1994; McKinley et al., 1999; Deer et al., 2013; Taylor et al., 2022). Additionally, authigenic smectite coatings are unstable during deeper burial and are transformed into illite or chlorite through mixed-layer phases, depending on the composition of the precursor smectite and the chemistry of the pore fluid (McKinley et al., 1999). The presence of mixed-layer illite-smectite or chlorite-smectite clays in sandstones is thus indicative of progressive diagenesis and often correlates with decreasing reservoir quality unless accompanied by early grain coatings.

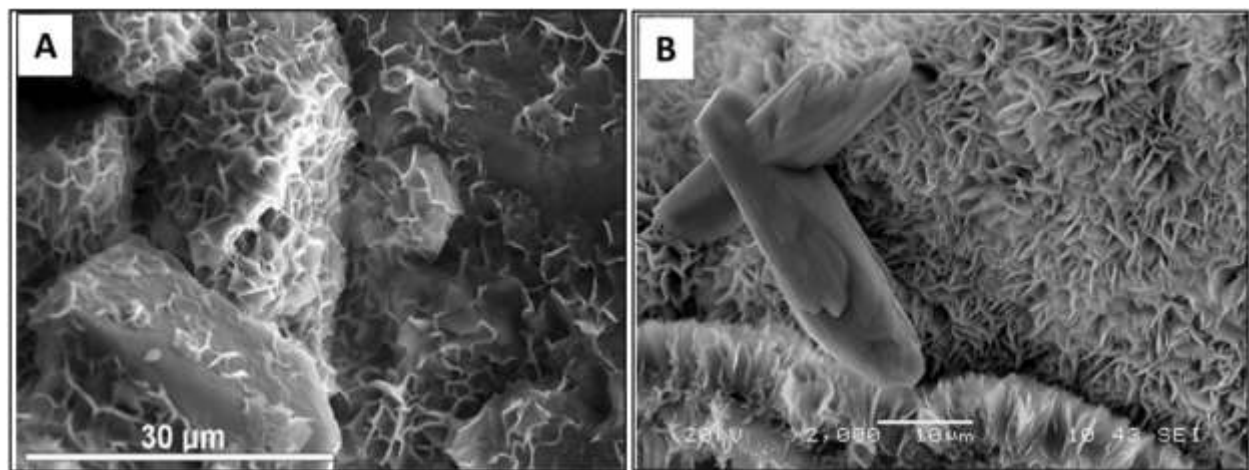


Figure 2.8. Scanning electron micrographs showing authigenic smectite in sandstone samples: (A) Detrital sand grains coated by dioctahedral montmorillonite. (B) Twinned calcite crystals accompanied by trioctahedral smectite grain coats (adapted from Taylor et al., 2022; reproduced from Clay Archive of the Mineralogical Society of Great Britain & Ireland)

Authigenic smectites are highly unstable under elevated temperatures and transform into illite or chlorite through intermediate stages during progressive burial. The smectite-to-illite transformation initiates at temperatures above 70 °C and becomes widespread with increasing temperature in natural diagenetic systems, reaching near-completion at temperatures above 200 °C (Eberl and Hower, 1977; Klopogge et al., 1999). Additionally, the transformation of smectite into illite is strongly influenced by the availability of K^+ , which plays a crucial role in the process. However, this transformation is only possible when the layer charge increases, principally in the tetrahedral layer, due to the loss of silica. The increased layer charge allows K^+ to replace Ca^{2+} and Na^+ in the interlayer spaces of smectite, stabilizing the structure and facilitating the formation of illite (Boles and Franks, 1979; Huang et al., 1993; Wise et al., 2001; Mosser-Ruck and Cathelineau, 2004; Ferrage et al., 2011). In natural sedimentary systems, the required K^+ is often sourced from migrating fluids or the dissolution of potassium-rich minerals like K-feldspars (Lanson et al., 2002; Franks and Zwingmann, 2010; Bjørlykke, 2014; Khan et al., 2023; Bello et al., 2024b).

Illite

Illite, a dioctahedral 2:1 layered sheet silicate (Fig. 2.5B) with the general formula $K_{1.5-1.0}Al_4Si_{6.5-7.0}Al_{1.5-1.0}O_{204}$ consists of an octahedral alumina layer sandwiched between two tetrahedral silica layers, with potassium ions in the interlayer space maintaining charge balance (Deer et al., 1992). It is one of the most abundant clay minerals in sandstone reservoirs, predominantly forming through diagenetic processes (Worden and Morad, 2003). Illite occurs as grain-coating cements (Fig. 2.9A-B), grain-replacive phases, and pore-filling cements (Fig. 2.9C-D), with morphologies ranging from platy flakes to fibrous strands observable under scanning electron microscopy (SEM) (Franks and Zwingmann, 2010). Grain-coating illite is particularly significant, as it inhibits quartz overgrowths, preserving porosity in deeply buried sandstones

(Pittman et al., 1992). However, its presence as pore-filling or pore-bridging cement, often replacing kaolinite or feldspar, can significantly reduce permeability by blocking pore throats (Oluwadebi et al., 2018). Illite forms through three primary diagenetic mechanisms in sandstones: replacement of kaolinite, replacement of K-feldspar, and illitization of smectite (Worden and Morad, 2003). The conversion of kaolinite to illite, requiring a source of K^+ often derived from K-feldspar dissolution, begins at temperatures around 70°C but becomes prevalent between 120–140°C, making it more common in arkosic sandstones than quartz arenites (Bjørlykke, 1998; Lanson et al., 2002). The reaction releases silica that may precipitate as quartz cement (Franks and Zwingmann, 2010). Illitization of smectite, a dioctahedral clay with low Al/Si ratios, occurs with increasing burial depth and temperature, transforming through mixed-layer illite-smectite phases (Nadeau et al., 1985; Inoue et al., 1987, 2005; Lander et al., 1991; Storvoll et al., 2002; Lanson et al., 2009; Tang et al., 2018; Mills et al., 2023). This process involves a loss of silicon in tetrahedral sites, a gain of K^+ in interlayer sites, and the release of cations like Ca^{2+} , Mg^{2+} , and Fe^{2+} , which may contribute to carbonate cementation or albitization. Illite also forms through direct replacement of K-feldspar or muscovite, particularly in feldspathic sands, where the availability of K^+ and Al^{3+} drives neomorphic crystallization (Lanson et al., 2002).

The net effect of illite on reservoir quality depends on its morphology, abundance, and paragenesis. Thin, grain-coating illite can preserve porosity by inhibiting quartz cementation, whereas pervasive, pore-filling illite and fibrous illite aggregates reduce permeability by increasing surface area, generating microporosity, and bridging pore throats, often lowering permeability by one to two orders of magnitude (Howard, 1985; Nadeau, 2004; Bello et al., 2023b). Moreover, illitization reactions release silica, promoting secondary quartz cementation and water, which can contribute to overpressure development (Lynch, 1996). Consequently, accurate petrophysical assessment of

sandstone reservoirs must consider not only total illite content but also its spatial distribution, polytype ordering, and timing relative to other diagenetic events.

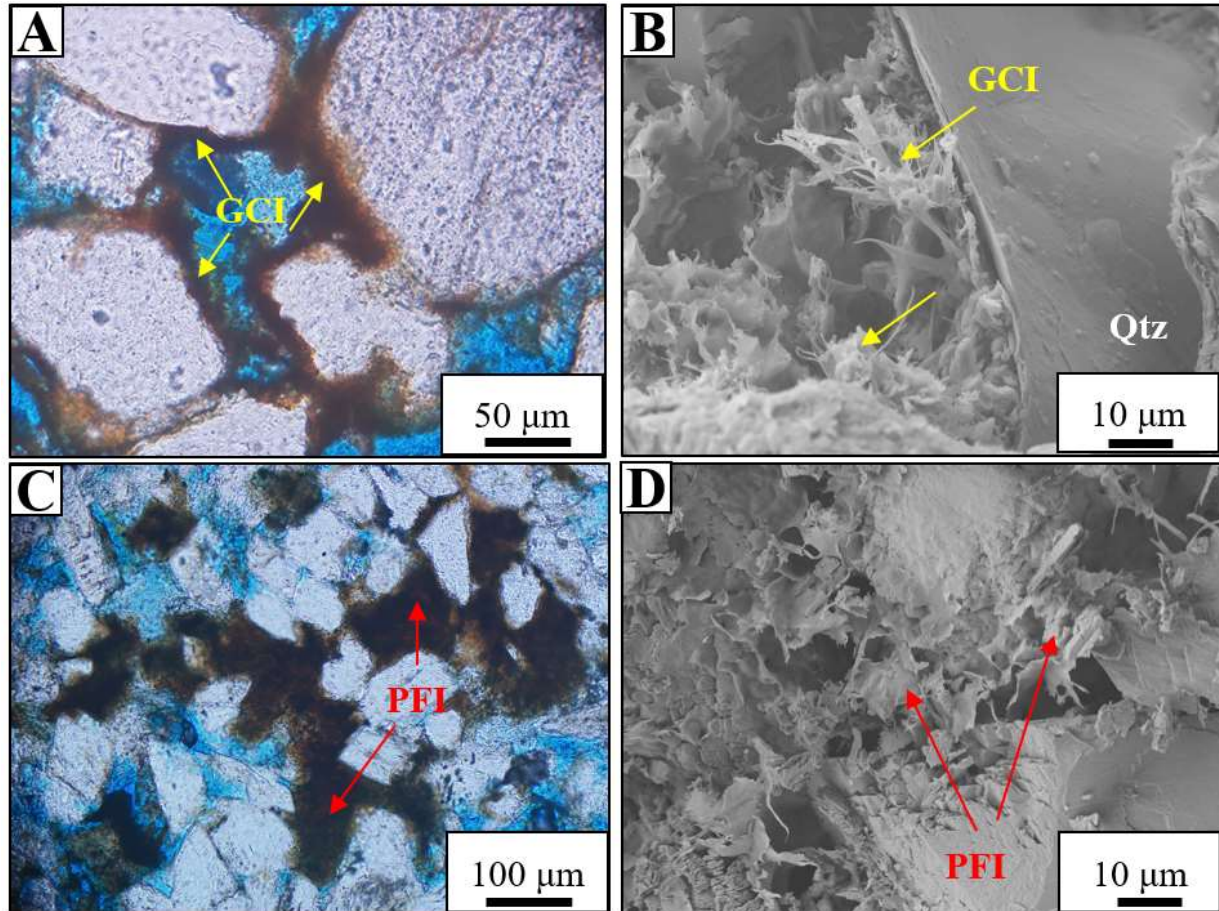


Figure 2.9. Petrographic images displaying the type and mode of occurrence of authigenic illite in the Jauf Formation, Saudi Arabia. Thin section (A) and SEM (B) images showing radial grain-coating illite (CGI) on detrital quartz (Qtz) grains. Thin-section (C) and SEM (D) images showing fibrous to lath-like pore-filling illite (PFI).

Chlorite

Chlorite, a 2:1:1 trioctahedral clay (Fig. 2.5C), is an important clay mineral that forms across a wide range of geological settings and temperatures, from approximately 80°C up to 800°C, making it one of the most abundant minerals in siliciclastic, hydrothermal, and metamorphic environments (Hillier, 1999; Worden and Morad, 2009; Beaufort et al., 2015; Charlaftis et al., 2021). Chlorite typically forms as grain coatings during early diagenesis in reducing, Fe-Mg-rich pore waters (Dowey et al., 2012). These coatings can inhibit quartz overgrowths by providing a physical barrier (Fig. 2.10), thus preserving primary porosity at great depths (Pittman et al., 1992; Bloch et al., 2002; Worden et al., 2020). However, excessive chlorite precipitation within pore bodies rather than as coatings can block pore throats and reduce permeability. The effectiveness of chlorite coatings is therefore governed by their completeness and spatial distribution around detrital grains (Ajdukiewicz and Larese, 2012). Due to its importance in retarding quartz cementation and preserving reservoir quality in deeply buried sandstones, grain-coating chlorite has been the focus of many diagenetic studies over the past decades (Heald and Larese, 1974; Ehrenberg, 1993; Anjos et al., 1999; Aagaard et al., 2000; Ajdukiewicz and Lander, 2010; Chen et al., 2011; Stricker and Jones, 2018; Charlaftis et al., 2021; Aro et al., 2023). The formation of authigenic chlorite in sandstones largely depends on its precursor mineral, and chlorite is characterized by a diverse mineral precursors, including berthierine (Aagaard et al., 2000; Charlaftis et al., 2021), odinite (Worden et al., 2020), trioctahedral smectites (McKinley et al., 2003; Worden et al., 2020), and kaolinite (Beaufort et al., 2015).

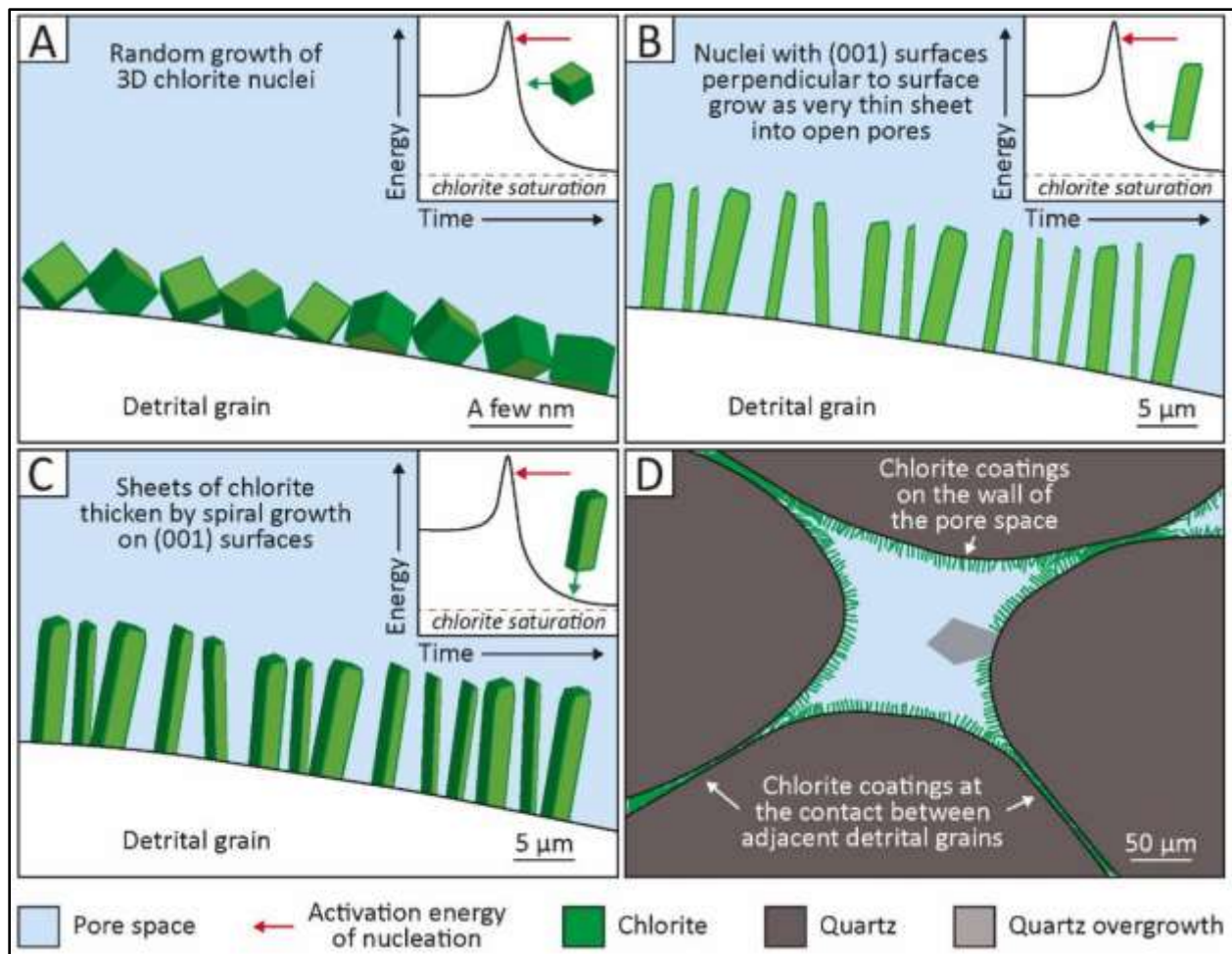


Figure 2.10. Schematic illustration of authigenic, grain-coating chlorite growth phases and how the site of precipitation controls platelet arrangement and microtexture (adapted from Charlaftis, 2021; modified from Worden et al., 2020). Before chlorite formation, the water–rock system must be highly supersaturated for chlorite. (A) Random three-dimensional nuclei of chlorite form indiscriminately on all available grain surfaces, producing an ultrathin coating. (B) As supersaturation declines after initial nucleation, fine chlorite sheets extend into the intergranular pore space. (C) Chlorite platelets thicken while retaining their original length and width. (D) Well-developed chlorite coats line grain contacts and pore walls; interruptions in the coating facilitate subsequent quartz overgrowth precipitation.

2.2. Experimental simulation of clay minerals formation

The occurrence of clay minerals can profoundly influence reservoir quality in sandstones. To this effect, a number of hydrothermal experiments have been carried out to document the nucleation and crystallization of quartz and clay minerals cements (Pittman et al., 1992; Small et al., 1992; Ajdukiewicz and Larese, 2012b; Haile et al., 2015a, 2015b; Murphy, 2016; Birkle et al., 2019; Charlaftis et al., 2021, 2022; Bello et al., 2022a).

In the initial experiment by Pittman et al. (1992), it was demonstrated that clay minerals, specifically illite in this case, effectively block quartz nucleation sites, inhibiting the development of quartz overgrowths. In their subsequent experiment, a sample of chlorite-coated sandstone was artificially compacted, leading to fractures in the quartz grains. This sample was then placed in an autoclave, where experimental precipitation of quartz overgrowths occurred, indicating that such overgrowths develop where fractures breach the chlorite coating. In their last experiment, they utilized a hydrothermal reactor to precipitate chlorite, smectite, and illite coatings on rounded sand-sized fragments of quartz and serpentinite. This experiment underscored the significance of root zones (especially, the connection between detrital and diagenetic grain coats) in the growth of authigenic clay coats. Root zones arise from clay platelets oriented tangentially to the surface of the detrital grain. They're often concealed by subsequent crystal structures, such as honeycombs, commonly linked to authigenic clay coats. The authors compared the experimentally simulated smectite coats with those that formed naturally and deduced that established root zones can comprehensively envelop the detrital grain, acting as a barrier against the nucleation of syntaxial quartz overgrowths.

Small et al. (1992) tested the precipitation of clay minerals with clay-free sandstones, quartz sand substrates, aqueous solutions, and solid minerals in a closed-system experiment. They

employed a wide range of temperature (150-500⁰ C) and pressure (75-100 MPa) which facilitated the precipitation of varied clay minerals on sand grains after the initial dissolution of the starting material. While their efforts to produce 14 Å chlorite did not succeed, they managed to precipitate a magnesium-rich 7Å-phase coat, such as berthierine, characterized by a platy boxwork structure. The distinct morphologies observed between 14 Å authigenic chlorites and the berthierine produced in this experiment indicate that authigenic chlorites precipitate directly and don't necessitate any pre-existing precursors, as per the findings of Small et al. (1992).

Almost a decade later, Aagaard et al. (2000) conducted hydrothermal experiments on sandstones coated with berthierine from the Veslefrikk and Oseberg Fields, offshore Norway. The primary objectives of these experiments were to determine whether grain coats such as chlorite could be experimentally precipitated and to understand the diagenetic formation of chlorite coats in sandstone reservoirs. Samples were subjected to temperatures of 200-250°C in a hydrothermal reactor for up to 28 days. The results revealed that thin and broken grains of berthierine precursor coatings when exposed to conditions resembling early-stage diagenesis, recrystallize around 100°C. This process results in the formation of thick, unbroken coats of authigenic chlorite that resembles the morphology of naturally occurring chlorite. Nonetheless, this study did not delve into the precise processes by which berthierine transforms into chlorite, leaving a gap for future research.

Similarly, Ajdukiewicz and Larese (2012) performed several hydrothermal reactor experiments using natural clay-coated and uncoated sandstone samples. The main objectives were to examine the premise that quartz cementation is prevented by clay coats formation and to explore the underlying mechanisms of this prevention. The investigation revealed a significant presence of micro quartz underneath the chlorite grain coats. They proposed that clay coats effectiveness in

inhibiting quartz cementation is temperature dependent. At over 115°C temperatures, clay coats allow quartz nucleation, and subsequently, these coats enable the nucleation of quartz cement within the microporosity between clay crystals. Nonetheless, the authors deduced that particles of clays within the coatings play a crucial role in preserving porosity by serving as protective barriers against the early fusion and growth of cement. Therefore, the extent of quartz overgrowth at elevated thermal conditions depends on the structure of the clay coat, which varies based on the origin and composition of clay mineral coats. The intrusion of quartz overgrowth into the primary pores occurs solely at discontinuities or breaks in the coat.

In their study, Haile et al. (2015) carried out hydrothermal experiments using pure quartz and feldspar to simulate clay coat formation. They synthesized clay mineral coats by using different conditions of temperature, pH and aqueous supersaturation in a multi-batch reactor equipment. The research revealed that smectite and chlorite grain coatings can form on pure quartz and feldspar surfaces at 100-150°C temperature conditions, provided there was enough supersaturation and time. The synthesized coats resembled the morphology of those found naturally, as noted by Haile et al. (2015)

Murphy (2016) undertook hydrothermal-reactor experiments utilizing samples (sandstones) from the Norwegian North Sea and synthetic brine. The aim was to observe and quantify any alterations in the mineralogy of illite or any clay mineral. Using a combination of petrographic and chemical analyses with computer geochemical modeling, evidence emerged that the crystal structure of illite changes in a relatively short time frame (several weeks) under the applied physical conditions (450 bars and 150° C) and geochemical conditions of the experiments. Specifically, there was a noticeable shift in the clay mineral composition, marked by K-feldspar and illite dissolution and the emergence of muscovite.

Birkle et al. (2019) performed experiments at temperatures between 100 and 150°C and pressures ranging from 300 to 450 bars using natural sandstone cores of the Unayzah Formation, Saudi Arabia. These experiments were designed to examine brine-sediment interactions pertinent to the diagenetic evolution of illite in the Unayzah sandstone reservoir. The findings revealed the onset of illite precipitation on kaolinite grains, which took place under deep burial conditions (150°C and 450 bars). While temperature was the primary influencing factor, the substrate of the grain surface, mobility of potassium on a macro scale, and initial grain mineralogy also played roles in the varied distribution of illite within the Unayzah Formation.

Charlaftis et al. (2021) conducted hydrothermal reactor experiments on naturally occurring sandstone samples, rich in berthierine, from the Oseberg Field in the Cook Formation, Norway. These experiments lasted for three days, using a silica-saturated solution and a range of temperatures from 100 to 250°C. The objective was to synthetically produce quartz cement and delineate the mechanisms underlying reservoir quality evolution. The results demonstrated that Fe-rich chlorite coats could originate from the transformation of precursor berthierine through both dissolution-precipitation and solid-state transformation mechanisms. The study also quantified the influence of temperature and precursor minerals on the precipitation of authigenic chlorite coats.

Recently, Bello et al. (2022) conducted hydrothermal reactor experiments on modern-day unconsolidated sediments from Bute Inlet, British Columbia, Canada. These experiments were conducted at a temperature of 250°C for a duration of 72 hours. The aim was to investigate the potential precipitation of chlorite and microquartz coats on detrital grains (quartz and feldspar) and to determine their effect in preventing the development of quartz and albite cements. The study revealed that in areas with a high concentration of precursor chlorite, the volume of chlorite coatings increased significantly. The coatings synthesized during these experiments bore a

morphological resemblance to those found in ancient sandstone reservoirs. Furthermore, these coatings effectively prevented the precipitation of quartz and albite cements during the experimental process.

Over the past three decades, experimental diagenesis studies have offered valuable insights into the mechanisms of clay mineral formation during burial diagenesis. However, except for the work by Bello et al. (2022), these studies predominantly relied on ancient sandstone reservoir cores or pure detrital grain crystals. This focus constrains our spatial understanding of clay mineral formation, particularly in complex depositional environments such as aeolian and marginal marine settings. Hence, there is a pressing need for more detailed experimental simulations on clay mineral formation using spatially distributed modern sediments, to cover the varied sub-environments from proximal to distal within the sandstone depositional environments. Such efforts would facilitate a comprehensive understanding of clay minerals formation and yield data that could serve as an analog for predicting sandstone reservoir quality.

References

- Aagaard, P., Jahren, J.S., Harstad, A.O., Nilsen, O., and Ramm, M., 2000, Formation of grain-coating chlorite in sandstones. Laboratory synthesized vs . natural occurrences : Clay Minerals, v. 35, p. 261–269, doi:10.1180/000985500546639.
- Ajdukiewicz, J.M., and Lander, R.H., 2010, Sandstone reservoir quality prediction: The state of the art: American Association of Petroleum Geologists Bulletin, v. 94, p. 1083–1091, doi:10.1306/intro060110.
- Ajdukiewicz, J.M., and Larese, R.E., 2012a, How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments: AAPG Bulletin, v. 96, p. 2091–2119, doi:10.1306/02211211075.
- Ajdukiewicz, J.M., and Larese, R.E., 2012b, How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments: AAPG Bulletin, v. 96, p. 2091–2119, doi:10.1306/02211211075.
- Al-Ramadan, K., 2014a, Diagenesis of Holocene beachrocks: a comparative study between the Arabian Gulf and the Gulf of Aqaba, Saudi Arabia: Arabian Journal of Geosciences, v. 7, p. 4933–4942, doi:10.1007/s12517-013-1127-7.
- Al-Ramadan, K., 2014b, Illitization of Smectite in Sandstones: The Permian Unayzah Reservoir, Saudi Arabia: Arabian Journal for Science and Engineering, v. 39, p. 407–412, doi:10.1007/s13369-013-0913-6.
- Al-Ramadan, K.A., Hussain, M., Imam, B., and Saner, S., 2004, Lithologic characteristics and diagenesis of the Devonian Jauf sandstone at Ghawar Field, Eastern Saudi Arabia: Marine and Petroleum Geology, v. 21, p. 1221–1234, doi:10.1016/J.MARPETGEO.2004.09.002.
- Al-Ramadan, K., Morad, S., Norton, A., and Hulver, M., 2013a, Linking Diagenesis and Porosity Preservation Versus Destruction to Sequence Stratigraphy of Gas Condensate Reservoir Sandstones; The Jauf Formation (Lower to Middle Devonian), Eastern Saudi Arabia, *in* Linking Diagenesis to Sequence Stratigraphy, v. 45, p. 297–335, doi:10.1002/9781118485347.ch13.
- Al-Ramadan, K., Morad, S., and Plink-Bjorklund, P., 2013b, Distribution of Diagenetic Alterations in Relationship to Depositional Facies and Sequence Stratigraphy of a Wave- and Tide-Dominated Siliciclastic Shoreline Complex: Upper Cretaceous Chimney Rock Sandstones, Wyoming and Utah, USA: IAS Special Publication, v. 45, p. 271–296, doi:10.1002/9781118485347.ch12.
- Al-Ramadan, K., Morad, S., Proust, J.-N., and Al-Aasm, I., 2005, Distribution of diagenetic alterations within the sequence stratigraphic framework of shoreface siliciclastic deposits: evidence from the Jurassic deposits of NE France: Journal of Sedimentary Research, v. 75, p. 10–38.

- Anjos, S.M.C., De Ros, L.F., and Silva, C.M.A., 1999, Chlorite Authigenesis and Porosity Preservation in the Upper Cretaceous Marine Sandstones of the Santos Basin, Offshore Eastern Brazil, *in* Clay Mineral Cements in Sandstones, p. 289–316, doi:<https://doi.org/10.1002/9781444304336.ch13>.
- Aro, O.E., Jones, S.J., Meadows, N.S., Gluyas, J., and Charlaftis, D., 2023, The importance of facies, grain size and clay content in controlling fluvial reservoir quality—an example from the Triassic Skagerrak Formation, Central North Sea, UK: *Petroleum Geoscience*, v. 29, p. petgeo2022- 043.
- Beaufort, D., Cassagnabere, A., Petit, S., Lanson, B., Berger, G., Lacharpagne, J.C., and Johansen, H., 1998, Kaolinite-to-dickite reaction in sandstone reservoirs: *Clay minerals*, v. 33, p. 297–316.
- Beaufort, D., Rigault, C., Billon, S., Billault, V., Inoue, A., Inoue, S., and Patrier, P., 2015, Chlorite and chloritization processes through mixed-layer mineral series in low-temperature geological systems – a review: *Clay Minerals*, v. 50, p. 497–523, doi:DOI: 10.1180/claymin.2015.050.4.06.
- Bello, A.M. et al., 2024a, Diagenesis and reservoir quality evolution of estuarine sandstones: Insights from the Cenomanian-Turonian Yolde Formation, northern Benue Trough, NE Nigeria: *Marine and Petroleum Geology*, v. 169, p. 107073, doi:<https://doi.org/10.1016/j.marpetgeo.2024.107073>.
- Bello, A.M. et al., 2023a, Linking diagenesis and reservoir quality to depositional facies in marginal to shallow marine sequence: An example from the Campano-Maastrichtian Gombe Sandstone, Northern Benue Trough, NE Nigeria: *Marine and Petroleum Geology*, v. 155, p. 106386, doi:<https://doi.org/10.1016/j.marpetgeo.2023.106386>.
- Bello, A.M., Al-Ramadan, K., Babalola, L.O., Alqubalee, A., and Amao, A.O., 2023b, Impact of grain-coating illite in preventing quartz cementation: Example from permo-carboniferous sandstone, Central Saudi Arabia: *Marine and Petroleum Geology*, v. 149, doi:10.1016/j.marpetgeo.2022.106073.
- Bello, A.M., Butt, M.N., Hussain, A., Amao, A.O., Olariu, C., Koeshidayatullah, A.I., Malik, M.H., Al-Hashem, M., and Al-Ramadan, K., 2023c, Impact of depositional and diagenetic controls on reservoir quality of syn-rift sedimentary systems: An example from Oligocene-Miocene Al Wajh Formation, northwest Saudi Arabia: *Sedimentary Geology*, v. 446, p. 106342, doi:10.1016/j.sedgeo.2023.106342.
- Bello, A.M., Charlaftis, D., Jones, S.J., Gluyas, J., Acikalin, S., Cartigny, M., and Al-Ramadan, K., 2022a, Experimental diagenesis using present-day submarine turbidite sands: *Frontiers in Earth Science*, v. 10, p. 1–20, doi:10.3389/feart.2022.952690.
- Bello, A., Jones, S., Gluyas, J., Açıkalin, S., and Cartigny, M., 2021, Role played by clay content in controlling reservoir quality of submarine fan system, Forties Sandstone Member, Central Graben, North Sea: *Marine and Petroleum Geology*, v. 128, p. 105058, doi:10.1016/j.marpetgeo.2021.105058.

- Bello, A.M., Jones, S.J., Gluyas, J., and Al-Ramadan, K., 2022b, Impact of Grain-Coating Clays on Porosity Preservation in Paleocene Turbidite Channel Sandstones: Nelson Oil Field, UK Central North Sea: *Minerals*, v. 12, doi:10.3390/min12050555.
- Bello, A.M., Jones, S.J., Gluyas, J., and Al-Ramadan, K., 2022c, Impact of Grain-Coating Clays on Porosity Preservation in Paleocene Turbidite Channel Sandstones: Nelson Oil Field, UK Central North Sea: *Minerals*, v. 12, doi:10.3390/min12050555.
- Bello, A.M., Salisu, A.M., Alqubalee, A., Amao, A.O., Al-Hashem, M., Al-Hussaini, A., and Al-Ramadan, K., 2024b, Diagenetic controls on the quality of shallow marine sandstones: An example from the Cambro-Ordovician Saq Formation, central Saudi Arabia: *Journal of African Earth Sciences*, v. 215, p. 105295, doi:https://doi.org/10.1016/j.jafrearsci.2024.105295.
- Birkle, P., Van Dijk, C., Dasgupta, K., Murphy, M.J., Kharaka, Y.K., Thordsen, J.J., and Bischoff, J.L., 2019, Controls on illite cementation in unayzah sandstones, Saudi Arabia: Mineralogy, K-Ar dating, numerical modeling, and hydrothermal experiments: *Journal of Sedimentary Research*, v. 89, p. 89–109, doi:10.2110/jsr.2018.71.
- Bjørlykke, K., 1998, Clay mineral diagenesis in sedimentary basins — a key to the prediction of rock properties. Examples from the North Sea Basin: *Clay Minerals*, v. 33, p. 15–34, doi:DOI: 10.1180/000985598545390.
- Bjørlykke, K., 2014, Relationships between depositional environments, burial history and rock properties. Some principal aspects of diagenetic process in sedimentary basins: *Sedimentary Geology*, v. 301, p. 1–14, doi:https://doi.org/10.1016/j.sedgeo.2013.12.002.
- Bjørlykke, K., Ramm, M., and Saigal, G.C., 1989, Sandstone diagenesis and porosity modification during basin evolution: *Geologische Rundschau*, v. 78, p. 243–268, doi:10.1007/BF01988363.
- Bloch, S., Lander, R.H., and Bonnell, L., 2002, Anomalously High Porosity and Permeability in Deeply Buried Sandstone Reservoirs: Origin and Predictability: *AAPG Bulletin*, v. 86, p. 301–328, doi:10.1306/61EEDABC-173E-11D7-8645000102C1865D.
- Bloch, S., and McGowen, J.H., 1994, Influence of Depositional Environment on Reservoir Quality Prediction (M. D. Wilson, Ed.): *Reservoir Quality Assessment and Prediction in Clastic Rocks*, v. 30, p. 0, doi:10.2110/scn.94.30.0041.
- Chamley, H., 1994, Clay Mineral Diagenesis BT - Quantitative Diagenesis: Recent Developments and Applications to Reservoir Geology, in Parker, A. and Sellwood, B.W. eds., Dordrecht, Springer Netherlands, p. 161–188, doi:10.1007/978-94-011-0189-9_5.
- Charlaftis, D., 2021, Assessing sandstone reservoir quality : identifying the reality Dimitrios Charlaftis
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- Charlaftis, D., Jones, S.J., Dobson, K.J., Crouch, J., and Acikalin, S., 2021, Experimental study of chlorite authigenesis and influence on porosity maintenance in sandstones: *Journal of Sedimentary Research*, v. 91, p. 197–212, doi:10.2110/JSR.2020.122.
- Chen, G., Du, G., Zhang, G., Wang, Q., Lv, C., and Chen, J., 2011, Chlorite cement and its effect on the reservoir quality of sandstones from the Panyu low-uplift, Pearl River Mouth Basin: *Petroleum Science*, v. 8, p. 143–150, doi:10.1007/s12182-011-0127-z.
- Deer FRS, W.A., Howie, R.A., and Zussman, J., 2013, *An Introduction to the Rock-Forming Minerals*, doi:10.1180/DHZ.
- Dowey, P.J., Hodgson, D.M., and Worden, R.H., 2012, Pre-requisites, processes, and prediction of chlorite grain coatings in petroleum reservoirs: A review of subsurface examples: *Marine and Petroleum Geology*, v. 32, p. 63–75, doi:https://doi.org/10.1016/j.marpetgeo.2011.11.007.
- Eberl, D., and Hower, J., 1977, The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay: *Clays and Clay Minerals*, v. 25, p. 215–227.
- Ehrenberg, S.N., 1993, Preservation of Anomalously High Porosity in Deeply Buried Sandstones by Grain-Coating Chlorite: Examples from the Norwegian Continental Shelf1: *AAPG Bulletin*, v. 77, p. 1260–1286, doi:10.1306/BDFF8E5C-1718-11D7-8645000102C1865D.
- El-Ghali, M.A.K., Shelukhina, O., Abbasi, I.A., Moustafa, M.S.H., Hersi, O.S., Siddiqui, N.A., Al-Ramadan, K., Alqubalee, A., Bello, A.M., and Amao, A.O., 2024, Depositional and sequence stratigraphic controls on diagenesis in the Upper Cambrian-Lower Ordovician Barik Formation, central Oman: Implications for prediction of reservoir porosity in a hybrid-energy delta system: *Marine and Petroleum Geology*, v. 160, p. 106611, doi:https://doi.org/10.1016/j.marpetgeo.2023.106611.
- Ferrage, E., Vidal, O., Mosser-Ruck, R., Cathelineau, M., and Cuadros, J., 2011, A reinvestigation of smectite illitization in experimental hydrothermal conditions: Results from X-ray diffraction and transmission electron microscopy: v. 96, p. 207–223, doi:doi:10.2138/am.2011.3587.
- Franks, S.G., and Zwingmann, H., 2010, Origin and timing of late diagenetic illite in the Permian–Carboniferous Unayzah sandstone reservoirs of Saudi Arabia: *AAPG Bulletin*, v. 94, p. 1133–1159, doi:10.1306/04211009142.
- García-Romero, E., Lorenzo, A., García Vicente, A., Morales, J., García-Rivas, J., and Suarez, M., 2021, On the structural formula of smectites: a review and new data on the influence of exchangeable cations: *Journal of Applied Crystallography*, v. 54, doi:10.1107/S1600576720016040.

- Griffiths, J., 2018, Mineralogical and textural variation in modern estuarine sands: implications for sandstone reservoir quality: The University of Liverpool (United Kingdom).
- Haile, B.G., Hellevang, H., Aagaard, P., and Jahren, J., 2015a, Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces: *Marine and Petroleum Geology*, v. 68, p. 664–674, doi:<https://doi.org/10.1016/j.marpetgeo.2015.02.006>.
- Haile, B.G., Hellevang, H., Aagaard, P., and Jahren, J., 2015b, Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces: *Marine and Petroleum Geology*, v. 68, p. 664–674, doi:10.1016/j.marpetgeo.2015.02.006.
- Heald, M.T., and Anderegg, R.C., 1960, Differential cementation in the Tuscarora sandstone [Virginia-West Virginia]: *Journal of Sedimentary Research*, v. 30, p. 568–577, doi:10.1306/74D70AA1-2B21-11D7-8648000102C1865D.
- Heald, M.T., and Larese, R.E., 1974, Influence of coatings on quartz cementation: *Journal of Sedimentary Research*, v. 44, p. 1269–1274, doi:10.1306/212F6C94-2B24-11D7-8648000102C1865D.
- Hillier, S., 1999, Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD): *Clay mineral cements in sandstones*, p. 213–251.
- Houseknecht, D.W., 1987, Assessing the Relative Importance of Compaction Processes and Cementation to Reduction of Porosity in Sandstones1: *AAPG Bulletin*, v. 71, p. 633–642, doi:10.1306/9488787F-1704-11D7-8645000102C1865D.
- Howard, J., 1985, Development of Layer Charge and Kinetics of Experimental Smectite Alteration: *Clays and Clay Minerals - CLAYS CLAY MINER*, v. 33, p. 81–88, doi:10.1346/CCMN.1985.0330201.
- Huang, W.-L., Longo, J.M., and Pevear, D.R., 1993, An Experimentally Derived Kinetic Model for Smectite-to-Illite Conversion and Its Use as a Geothermometer: *Clays and Clay Minerals*, v. 41, p. 162–177, doi:DOI: 10.1346/CCMN.1993.0410205.
- Hussain, M., Amao, A.O., Al-Ramadan, K., Babalola, L.O., and Humphrey, J.D., 2022a, Unconventional reservoir characterization using geochemical signatures: Examples from Paleozoic formations, Saudi Arabia: *Marine and Petroleum Geology*, v. 143, p. 105770, doi:<https://doi.org/10.1016/j.marpetgeo.2022.105770>.
- Hussain, A., Bello, A., Butt, M.N., Malik, M.H., Koeshidayatullah, A., Amao, A., Olariu, C., and Al-Ramadan, K., 2024, Diagenetic variability in Tertiary, syn-rift mixed siliciclastic-carbonate depositional system (Lower Musayr Formation), Red Sea, Saudi Arabia: *Sedimentary Geology*, v. 470, p. 106699, doi:<https://doi.org/10.1016/j.sedgeo.2024.106699>.
- Hussain, A., Butt, M.N., Olariu, C., Malik, M.H., Koeshidayatullah, A., Amao, A., and Al-Ramadan, K., 2022b, Unravelling reservoir quality heterogeneity in mixed siliciclastic-carbonate deposits:

An example from Miocene Red Sea rift, NW Saudi Arabia: *Marine and Petroleum Geology*, v. 145, p. 105850, doi:<https://doi.org/10.1016/j.marpetgeo.2022.105850>.

- Imam, M.B., and Shaw, H.F., 1985, The diagenesis of Neogene clastic sediments from the Bengal Basin, Bangladesh: *Journal of Sedimentary Research*, v. 55, p. 665–671, doi:10.1306/212F87B0-2B24-11D7-8648000102C1865D.
- Inoue, A., KOHYAMA, N., KITAGAWA, R., and WATANABE, T., 1987, Chemical and Morphological Evidence for the Conversion of Smectite to Illite: *Clays and Clay Minerals - CLAYS CLAY MINER*, v. 35, p. 111–120, doi:10.1346/CCMN.1987.0350203.
- Inoue, A., Lanson, B., Fernandes, M., Sakharov, B., Murakami, T., Meunier, A., and Beaufort, D., 2005, Illite-smectite mixed-layer minerals in hydrothermal alteration of volcanic rocks: I. One-dimensional XRD structure analysis and characterisation of component layers.: *Clays and Clay Minerals*, v. 53, p. 423–439, doi:10.1346/CCMN.2005.0530501.
- Khan, M.A., Khan, T., Ali, A., Bello, A.M., and Radwan, A.E., 2023, Role of depositional and diagenetic controls on reservoir quality of complex heterogenous tidal sandstone reservoirs: An example from the Lower Goru formation, Middle Indus Basin, Southwest Pakistan: *Marine and Petroleum Geology*, v. 154, p. 106337, doi:<https://doi.org/10.1016/j.marpetgeo.2023.106337>.
- Klopprogge, J.T., Komarneni, S., and Amonette, J.E., 1999, Synthesis of Smectite Clay Minerals: A Critical Review: *Clays and Clay Minerals*, v. 47, p. 529–554, doi:DOI: 10.1346/CCMN.1999.0470501.
- Lander, R.H., Bloch, S., Mehta, S., and Atkinson, C.D., 1991, Burial diagenesis of Paleosols in the giant Yacheng gas field, People's Republic of China; bearing on illite reaction pathways: *Journal of Sedimentary Research*, v. 61, p. 256–268, doi:10.1306/D42676E5-2B26-11D7-8648000102C1865D.
- Lander, R.H., and Walderhaug, O., 1999, Predicting Porosity through Simulating Sandstone Compaction and Quartz Cementation1: *AAPG Bulletin*, v. 83, p. 433–449, doi:10.1306/00AA9BC4-1730-11D7-8645000102C1865D.
- Lanson, B., Beaufort, D., Berger, G., Bauer, A., Cassagnabère, A., and Meunier, A., 2002, Authigenic kaolin and illitic minerals during burial diagenesis of sandstones: a review: *Clay Minerals*, v. 37, p. 1–22, doi:DOI: 10.1180/0009855023710014.
- Lanson, B., Sakharov, B., Claret, F., and Drits, V., 2009, Diagenetic Smectite-to-Illite Transition in Clay-Rich Sediments: A Reappraisal of X-Ray Diffraction Results Using the Multi-Specimen Method: *American Journal of Science*, v. 309, p. 476–516, doi:10.2475/06.2009.03.
- Lynch, F.L., 1996, Mineral/Water Interaction, Fluid Flow, and Frio Sandstone Diagenesis: Evidence from the Rocks1: *AAPG Bulletin*, v. 80, p. 486–504, doi:10.1306/64ED8822-1724-11D7-8645000102C1865D.

- Mansurbeg, H., Morad, S., Salem, A., Marfil, R., El-ghali, M.A.K., Nystuen, J.P., Caja, M.A., Amorosi, A., Garcia, D., and La Iglesia, A., 2008, Diagenesis and reservoir quality evolution of palaeocene deep-water, marine sandstones, the Shetland-Faroes Basin, British continental shelf: *Marine and Petroleum Geology*, v. 25, p. 514–543, doi:<https://doi.org/10.1016/j.marpetgeo.2007.07.012>.
- Marfil, R., Delgado, A., Rossi, C., Iglesia, A. La, and Ramseier, K., 1999, Origin and diagenetic evolution of kaolin in reservoir sandstones and associated shales of the Jurassic and Cretaceous, Salam Field, Western Desert (Egypt): *Clay mineral cements in sandstones*, p. 317–342.
- McBride, E.F., 1989, Quartz cement in sandstones: a review: *Earth-Science Reviews*, v. 26, p. 69–112, doi:[https://doi.org/10.1016/0012-8252\(89\)90019-6](https://doi.org/10.1016/0012-8252(89)90019-6).
- McKinley, J.M., Worden, R.H., and Ruffell, A.H., 1999, Smectite in sandstones: a review of the controls on occurrence and behaviour during diagenesis: *Clay mineral cements in sandstones*, p. 109–128.
- Milliken, K.L., 2003, Late diagenesis and mass transfer in sandstone shale sequences: v. 7.
- Mills, M.M., Sanchez, A.C., Boisvert, L., Payne, C.B., Ho, T.A., and Wang, Y., 2023, Understanding smectite to illite transformation at elevated (>100 °C) temperature: Effects of liquid/solid ratio, interlayer cation, solution chemistry and reaction time: *Chemical Geology*, v. 615, p. 121214, doi:<https://doi.org/10.1016/j.chemgeo.2022.121214>.
- Morad, S., Al-Ramadan, K., Ketzer, M., and De Ros, L., 2010, The impact of diagenesis on the heterogeneity of sandstone reservoirs: A review of the role of depositional fades and sequence stratigraphy: *AAPG Bulletin*, v. 94, p. 1267–1309, doi:10.1306/04211009178.
- Mosser-Ruck, R., and Cathelineau, M., 2004, Experimental transformation of Na,Ca-smectite under basic conditions at 150 °C: *Applied Clay Science*, v. 26, p. 259–273, doi:<https://doi.org/10.1016/j.clay.2003.12.011>.
- Murphy, M.J., 2016, GEOCHEMICAL MODELING AND HYDROTHERMAL EXPERIMENTS USED TO CONSTRAIN THE CONDITIONS OF ILLITE DIAGENESIS IN SEDIMENTARY BASINS A Thesis Presented to The Faculty of the Department of Geology San José State University In Partial Fulfillment of the Requirement:
- Nadeau, P.H., 2004, *Clay Mineral Cements in Sandstones*, edited by Richard H. Worden and Sadoon Morad. Special Publication Number 34 of the International Association of Sedimentologists, 2003; 489 pages. Blackwell Science Ltd., Oxford. [ISBN: 1-40510-587-9] Price £75.: *Clays and Clay Minerals*, v. 52, p. 139–140.
- Nadeau, P.H., Wilson, J., McHardy, W.J., and Tait, J.M., 1985, The Conversion of Smectite to Illite during Diagenesis: Evidence from some Illitic Clays from Bentonites and Sandstones: *Mineralogical Magazine*, v. 49, p. 393–400, doi:10.1180/minmag.1985.049.352.10.

- Naveed Butt, M., G. Franks, S., Hussain, A., Amao, A.O., Muhammad Bello, A., and Al-Ramadan, K., 2024, Depositional and diagenetic controls on the reservoir quality of Early Miocene syn-rift deep-marine sandstones, NW Saudi Arabia: *Journal of Asian Earth Sciences*, v. 259, p. 105880, doi:<https://doi.org/10.1016/j.jseaes.2023.105880>.
- Needham, S.J., Worden, R.H., and McIlroy, D., 2005, Experimental Production of Clay Rims by Microbiotic Sediment Ingestion and Excretion Processes: *Journal of Sedimentary Research*, v. 75, p. 1028–1037, doi:10.2110/jsr.2005.078.
- Oluwadebi, A.G., Taylor, K.G., and Dowey, P.J., 2018, Diagenetic controls on the reservoir quality of the tight gas Collyhurst sandstone formation, Lower Permian, East Irish Sea Basin, United Kingdom: *Sedimentary geology*, v. 371, p. 55–74.
- Payton, R.L., Chiarella, D., and Kingdon, A., 2022, The influence of grain shape and size on the relationship between porosity and permeability in sandstone: a digital approach: *Scientific Reports*, v. 12, p. 7531, doi:10.1038/s41598-022-11365-8.
- Pittman, E.D., Larese, R.E., and Heald, M.T., 1992, Clay Coats: Occurrence and Relevance to Preservation of Porosity in Sandstones (D. W. Houseknecht & E. D. Pittman, Eds.): *Origin, Diagenesis, and Petrophysics of Clay Minerals in Sandstones*, v. 47, p. 0, doi:10.2110/pec.92.47.0241.
- Primmer, T.J., Cade, C.A., Evans, J., Gluyas, J.G., Hopkins, M.S., Oxtoby, Norman.H., Smalley, P.C., Warren, E.A., and Worden, R.H., 1997, Global Patterns in Sandstone Diagenesis: Their Application to Reservoir Quality Prediction for Petroleum Exploration (J. A. Kupecz, J. Gluyas, & S. Bloch, Eds.): *Reservoir Quality Prediction in Sandstones and Carbonates*, v. 69, p. 0, doi:10.1306/M69613C5.
- Ryu, I.-C., and Niem, A.R., 1999, Sandstone diagenesis, reservoir potential, and sequence stratigraphy of the Eocene Tyee Basin, Oregon: *Journal of Sedimentary Research*, v. 69, p. 384–393, doi:10.2110/jsr.69.384.
- Salisu, A.M., Algheryafi, H., Bello, A.M., Amao, A.O., Al-Otaibi, B., and Al-Ramadan, K., 2024, Depositional and diagenetic controls on the reservoir quality of marginal marine sandstones: An example from the Early Devonian Subbat Member, Jauf Formation, northwest Saudi Arabia: *Marine and Petroleum Geology*, p. 107147, doi:<https://doi.org/10.1016/j.marpetgeo.2024.107147>.
- Salisu, A.M., Alqubalee, A., Bello, A.M., Al-Hussaini, A., Adebayo, A.R., Amao, A.O., and Al-Ramadan, K., 2023, Impact of kaolinite and iron oxide cements on resistivity and quality of low resistivity pay sandstones: *Marine and Petroleum Geology*, v. 158, p. 106568, doi:<https://doi.org/10.1016/j.marpetgeo.2023.106568>.
- Saner, S., Hassan, H., Al-Ramadan, K., and Abdulghani, W.M., 2006, Mineralogical, pore and petrophysical characteristics of the Devonian Jauf Sandstone reservoir, Hawiyah field, eastern

- Saudi Arabia: *Journal of Petroleum Geology*, v. 29, p. 257–272, doi:10.1111/j.1747-5457.2006.00257.x.
- Small, J.S., Hamilton, D.L., and Habesch, S., 1992, Experimental simulation of clay precipitation within reservoir sandstones; 1, Techniques and examples: *Journal of Sedimentary Research*, v. 62, p. 508–519, doi:10.1306/D4267938-2B26-11D7-8648000102C1865D.
- Storvoll, V., Bjørlykke, K., Karlsen, D., and Saigal, G., 2002, Porosity preservation in reservoir sandstones due to grain-coating illite: A study of the Jurassic Garn Formation from the Kristin and Lavrans fields, offshore Mid-Norway: *Marine and Petroleum Geology*, v. 19, p. 767–781, doi:10.1016/S0264-8172(02)00035-1.
- Stricker, S., and Jones, S.J., 2018, Enhanced porosity preservation by pore fluid overpressure and chlorite grain coatings in the Triassic Skagerrak, Central Graben, North Sea, UK (P. J. Armitage, A. R. Butcher, J. M. Churchill, A. E. Csoma, C. Hollis, R. H. Lander, J. E. Omma, & R. H. Worden, Eds.): *Reservoir Quality of Clastic and Carbonate Rocks: Analysis, Modelling and Prediction*, v. 435, p. 0, doi:10.1144/SP435.4.
- Tang, L., Gluyas, J., and Jones, S., 2018, Porosity preservation due to grain coating illite/smectite: Evidence from Buchan Formation (Upper Devonian) of the Ardmore Field, UK North Sea: *Proceedings of the Geologists' Association*, v. 129, p. 202–214, doi:https://doi.org/10.1016/j.pgeola.2018.03.001.
- Taylor, T.R., Giles, M.R., Hathon, L.A., Diggs, T.N., Braunsdorf, N.R., Birbiglia, G. V., Kittridge, M.G., MacAulay, C.I., and Espejo, I.S., 2010, Sandstone diagenesis and reservoir quality prediction: Models, myths, and reality: *American Association of Petroleum Geologists Bulletin*, v. 94, p. 1093–1132, doi:10.1306/04211009123.
- Taylor, T.R., Lander, R.H., and Bonnell, L.M., 2022, Sandstone Petrography, Petrology, and Modeling:, doi:10.2110/sepmcsp.13.
- Ulmer-Scholle, D.S., Scholle, P.A., Schieber, J., and Raine, R.J., 2015, A Color Guide to the Petrography of Sandstones, Siltstones, Shales and Associated Rocks:, doi:10.1306/M1091304.
- Walderhaug, O., 1996, Kinetic Modeling of Quartz Cementation and Porosity Loss in Deeply Buried Sandstone Reservoirs1: *AAPG Bulletin*, v. 80, p. 731–745, doi:10.1306/64ED88A4-1724-11D7-8645000102C1865D.
- Walderhaug, O., and Porten, K.W., 2022, How Do Grain Coats Prevent Formation of Quartz Overgrowths? *Journal of Sedimentary Research*, v. 92, p. 988–1002, doi:10.2110/jsr.2021.049.
- Wilson, M.D., and Pittman, E.D., 1977, Authigenic clays in sandstones; recognition and influence on reservoir properties and paleoenvironmental analysis: *Journal of Sedimentary Research*, v. 47, p. 3–31, doi:10.1306/212F70E5-2B24-11D7-8648000102C1865D.

- Wise, S., Smellie, J., Aghib, F., Jarrard, R., and Krissek, L., 2001, Authigenic smectite clay coats in CRP-3 drillcore, Victoria Land Basin, Antarctica, as a possible indicator of fluid flow: A progress report: *Terra Antarctica*, v. 8.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., Thompson, A., and Chung, P., 2017, Biofilm origin of clay-coated sand grains: *Geology*, v. 45, p. 875–878, doi:10.1130/G39161.1.
- Worden, R.H., Armitage, P.J., Butcher, A.R., Churchill, J.M., Csoma, A.E., Hollis, C., Lander, R.H., and Omma, J.E., 2018a, Petroleum reservoir quality prediction: overview and contrasting approaches from sandstone and carbonate communities (P. J. Armitage, A. R. Butcher, J. M. Churchill, A. E. Csoma, C. Hollis, R. H. Lander, J. E. Omma, & R. H. Worden, Eds.): *Reservoir Quality of Clastic and Carbonate Rocks: Analysis, Modelling and Prediction*, v. 435, p. 0, doi:10.1144/SP435.21.
- Worden, R.H., Armitage, P.J., Butcher, A.R., Churchill, J.M., Csoma, A.E., Hollis, C., Lander, R.H., and Omma, J.E., 2018b, Petroleum reservoir quality prediction: Overview and contrasting approaches from sandstone and carbonate communities: *Geological Society Special Publication*, v. 435, p. 1–31, doi:10.1144/SP435.21.
- Worden, R.H., and Burley, S.D., 2009, Sandstone Diagenesis: The Evolution of Sand to Stone: 1–44 p., doi:10.1002/9781444304459.ch.
- Worden, R.H., Griffiths, J., Wooldridge, L.J., Utley, J.E.P., Lawan, A.Y., Muhammed, D.D., Simon, N., and Armitage, P.J., 2020, Chlorite in sandstones: *Earth-Science Reviews*, v. 204, p. 103105, doi:10.1016/j.earscirev.2020.103105.
- Worden, R., and Morad, S., 2009, Clay Minerals in Sandstones: Controls on Formation, Distribution and Evolution, *in* *Clay Mineral Cements in Sandstones*, v. 34, p. 1–41, doi:10.1002/9781444304336.ch1.
- Worden, R., and Morad, S., 2000, Quartz Cementation in Oil Field Sandstones: A Review of the Key Controversies: *Spec. Publ. Int. Assoc. Sed.*, v. 29, p. 1–20, doi:10.1002/9781444304237.ch1.

CHAPTER 3

EXPERIMENTAL STUDY OF SMECTITE AUTHIGENESIS AND ITS SUBSEQUENT ILLITIZATION: INSIGHTS FROM MODERN ESTUARY SEDIMENTS

3.1. Abstract

Smectite is an important component of siliciclastic reservoirs in many petroliferous basins around the world and has numerous industrial and environmental applications. Beyond its ability to preserve or degrade porosity and permeability in sandstones, smectite also acts as a precursor for other diagenetic cements, such as illite and zeolites. While numerous studies have explored the role of smectite as a precursor for illite and chlorite formation, the controls and mechanisms governing the formation of authigenic smectite coatings from feldspar precursors are rarely investigated. In this study, the authigenic formation of smectite coats and their subsequent illitization were studied using a series of hydrothermal experiments. The starting material was modern quartzo-feldspathic sediments from the sandy intertidal flat of the Anllóns estuary, NW Spain. The experimental solutions were 0.1 M NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (SF1, pH 5.69), natural estuarine water (EW, pH 7.85), and 0.1 M Na_2CO_3 (SF2, pH 11.20). The experiments were conducted at temperatures ranging from 50 °C to 250 °C, over the durations ranging from 168 to 336 hours, with a fixed fluid/sediment ratio of 10:1. The results revealed distinct variations in the synthesized mineral phases, depending on the experimental fluid composition. Detrital K-feldspar dissolution commenced at lower temperatures (< 100 °C), and the subsequent formation of authigenic smectite coats occurred between 150 °C and 250 °C in both SF1 and EW. Geochemical evaluation revealed that SF1 produced more Mg-rich smectite with intermediate compositions, while EW produced mostly Al-rich smectite due to the relatively lower Mg content

in the estuarine water. Smectite formation occurred through dissolution-crystallization and was subsequently illitized via a mixed-layer illite/smectite intermediate phase with increasing temperatures. Illitization began at 200 °C, with required K⁺ supplied by the dissolution of K-feldspar. The processes of smectite formation and its illitization released abundant silica, which precipitated as quartz overgrowths. The resulting authigenic grain coatings were chemically and morphologically similar to those found in natural sandstone reservoirs. As temperature increased (from 150 to 250 °C), the thickness of these coatings grew from 1.9 µm to 49.2 µm, and surface coverage expanded from 24.3% to 96.2%. In contrast to SF1 and EW, SF2 yielded entirely different mineral phases of halite and chabazite (zeolite), attributed to the high alkalinity and Na content of the solution. These findings highlight the potential of hydrothermal experiments to simulate burial diagenesis in marginal marine settings, which can aid in reservoir quality prediction, critical for energy exploration and transition.

3.2. Introduction

Clay minerals in sandstones, with both detrital and diagenetic origins (Worden and Morad, 2009; Dutton et al., 2018; Tang et al., 2018), significantly influence reservoir quality (Worden and Burley, 2003; Saner et al., 2006; Al-Ramadan, 2021; Lander et al., 2022; Taylor et al., 2022). Depending on their type, mode of occurrence, and abundance, clay minerals can either preserve or degrade sandstone reservoir quality (Imam and Shaw, 1985; Pittman et al., 1992; Ehrenberg, 1993; Morad et al., 2010a; Ajdukiewicz and Larese, 2012; Al-Ramadan et al., 2013b; Bello et al., 2021, 2022b; Salisu et al., 2023). For instance, numerous studies have documented the role of clay coatings in inhibiting quartz overgrowths in shallow to deeply buried sandstones, thereby preserving reservoir quality (Heald and Anderegg, 1960; Heald and Larese, 1974; Pittman et al., 1992; Bloch and McGowen, 1994; Bloch et al., 2002; Storvoll et al., 2002; Mansurbeg et al.,

2008; Ajdukiewicz and Lander, 2010; Morad et al., 2010b; Ajdukiewicz and Larese, 2012; Bello et al., 2021, 2024; Walderhaug and Porten, 2022; Khan et al., 2023; El-Ghali et al., 2024). In many deeply buried sandstone reservoirs worldwide, chlorite is commonly identified as the predominant clay coat that prevents the nucleation and growth of quartz (Anjos et al., 1999; Ajdukiewicz and Lander, 2010; Dowey et al., 2012; Beaufort et al., 2015; Stricker and Jones, 2018; Worden et al., 2020; Aro et al., 2023). While illite, smectite, and mixed-layer clay coatings have also been recognized as agents for porosity preservation, they are less frequently noted than chlorite (Al-Ramadan et al., 2004, 2013b, 2013a; Franks and Zwingmann, 2010). Diagenetic clay coatings in sandstones may form either through the heat-induced recrystallization of detrital clay coatings or from in situ development resulting from the authigenic transformation of precursor minerals interacting with pore fluids during burial (Aagaard et al., 2000; Worden and Morad, 2009; Ajdukiewicz and Larese, 2012; Haile et al., 2015). Several laboratory experiments have been conducted to explore the physicochemical controls governing the formation of quartz and clay minerals in sandstones (Boles and Franks, 1979; Pittman et al., 1992; Small et al., 1992; Aagaard et al., 2000; Ajdukiewicz and Larese, 2012; Murphy, 2016; Birkle et al., 2019; Charlaftis et al., 2021, 2022; Bello et al., 2022a). However, few experiments have focused on constraining the mechanisms of authigenic smectite formation (Hajash and Bloom, 1991), despite extensive research on its subsequent illitization during progressive burial (Burst, 1966; Eberl and Hower, 1977; Boles and Franks, 1979; Roberson and Lahann, 1981; Howard and Royd, 1985; Nadeau et al., 1985; Inoue et al., 1987; Whitney and Northrop, 1988; Whitney, 1990; Beaufort et al., 2001; Mosser-Ruck et al., 2001, 2010; Guillaume et al., 2004; Mosser-Ruck and Cathelineau, 2004; McCarty et al., 2009; Ferrage et al., 2011; Mills et al., 2023; Bentabol et al., 2024).

Smectites, chemically more complex than other clay minerals (McKinley et al., 1999), occur in various geological settings (Chamley, 1994; Taylor et al., 2022) and have broad industrial and environmental applications (García-Romero et al., 2021). In sandstones, smectites occur as both detrital and diagenetic materials (Primmer et al., 1997; Ulmer-Scholle et al., 2015). The formation of diagenetic smectite in sandstones occurs early during shallow burial via several authigenic processes, including the replacement of detrital framework grains such as K-feldspar, the transformation of precursor detrital clays, and direct neomorphic precipitation from pore water (McKinley et al., 1999; Ryu and Niem, 1999; Taylor et al., 2022). The structure and composition of smectite minerals are complex, and their authigenic formation is influenced by factors such as pH, pore water chemistry, and the availability of cations (Chamley, 1994; McKinley et al., 1999; Deer et al., 2013; Taylor et al., 2022). Additionally, authigenic smectite coatings are unstable during deeper burial and are transformed into illite or chlorite through mixed-layer phases, depending on the composition of the precursor smectite and the chemistry of the pore fluid (McKinley et al., 1999). Therefore, understanding smectite authigenesis is crucial for evaluating sandstone reservoir quality in different sedimentary settings, including marginal marine environments.

Marginal marine sandstones are key targets for hydrocarbon exploration, carbon capture and storage, and, more recently, hydrogen storage (Lawan et al., 2021; Salisu et al., 2024). The detrital texture and composition of these sandstones vary by depositional sub-environment, creating heterogeneities that significantly affect diagenesis and, consequently, reservoir quality. This variability makes predicting reservoir quality in marginal marine environments a considerable challenge. Recent studies have investigated the factors controlling the occurrence and distribution of detrital clay coatings in modern marginal marine environments (Wooldridge et al., 2017b,

2017a, 2018, 2019; Griffiths et al., 2018, 2019a, 2019b; Virolle et al., 2019b, 2019a, 2020, 2021, 2022; Simon et al., 2021; McGhee et al., 2022; Muhammed et al., 2022). However, the diagenetic alteration of these sediments and the role of detrital precursors in the formation of authigenic clay coatings remain understudied.

Therefore, driven by scientific curiosity and the importance of sandstones in global energy exploration and transition, this study aims to simulate the diagenetic alteration of modern estuary sediments through a series of hydrothermal experiments. Using quartzo-feldspathic sediments from the sandy intertidal flat of the Anllóns Estuary, Galicia (NW, Spain) as starting material, we conducted a series of hydrothermal experiments under varied fluid compositions and temperatures, following the procedures outlined by Charlaftis et al. (2021) and Bello et al. (2022b). Mineralogical and hydrochemical evaluations using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD), and inductively coupled plasma optical emission spectroscopy (ICP-OES) were performed on the sediments and fluid phase, respectively. The objectives of this study are to: 1) Simulate the diagenetic formation of smectite coatings within modern estuary sediments as an analog for ancient smectite coat authigenesis; 2) Investigate the mechanisms of smectite authigenesis and the controls on its subsequent illitization; 3) Assess the role of authigenic grain coatings on the reservoir quality of marginal marine sediments; and 4) Evaluate the impact of fluid chemistry on the diagenetic alteration of modern estuarine sediments.

3.3. Materials and methods

3.3.1. Study area and sampling

This study used samples from the Anllóns Estuary, located in the province of Galicia, on the northwest coast of Spain (Fig. 1). The estuary was chosen due to its mineralogical similarity (quartzo-feldspathic) to many sandstone reservoirs, its accessibility, and the well-documented geology of its hinterland (Dallmeyer et al., 1997; Llana-Fúnez and Marcos, 2001; Arribas et al., 2004; Pérez-Arlucea et al., 2007). Additionally, the occurrence and distribution of detrital clay coats within the Anllóns Estuary are well-established (Dowey et al., 2017).

The Anllóns Estuary is a shallow, deeply incised valley, partially infilled, with a microtidal to mesotidal range (~1.5 m during neap tides and ~3.8 m during spring tides) (Dowey et al., 2017). It covers an area of approximately 4 km² and is fed by the 60 km long Anllóns River, which drains a 516 km² catchment area to the east (Varela et al., 2005). The catchment is predominantly composed of soils developed from granite and schist, which originate from the hinterland geology. The underlying geology of the region is characterized by igneous and metamorphic rocks formed during the Devonian to Late Carboniferous Variscan Orogeny (Dallmeyer et al., 1997; Llana-Fúnez and Marcos, 2001). Anthropogenic impact on the estuary is minimal, with only two managed flood defenses influencing the system (Fig. 1). The estuary is mainly sand-dominated and hosts a variety of sedimentary environments (Fig. 2), including saltmarshes (Fig. 2A), aeolian dunes (Fig. 2B), sandy spit (Fig. 2C), tidal channels and creeks (Figs. 2D-E), as well as sandy and muddy intertidal flats (Figs. 2F-H). Among these, salt marshes and intertidal flats are the predominant sub-environments. The samples used in this study were surface sediments collected from the sandy intertidal flat (Fig. 2G).

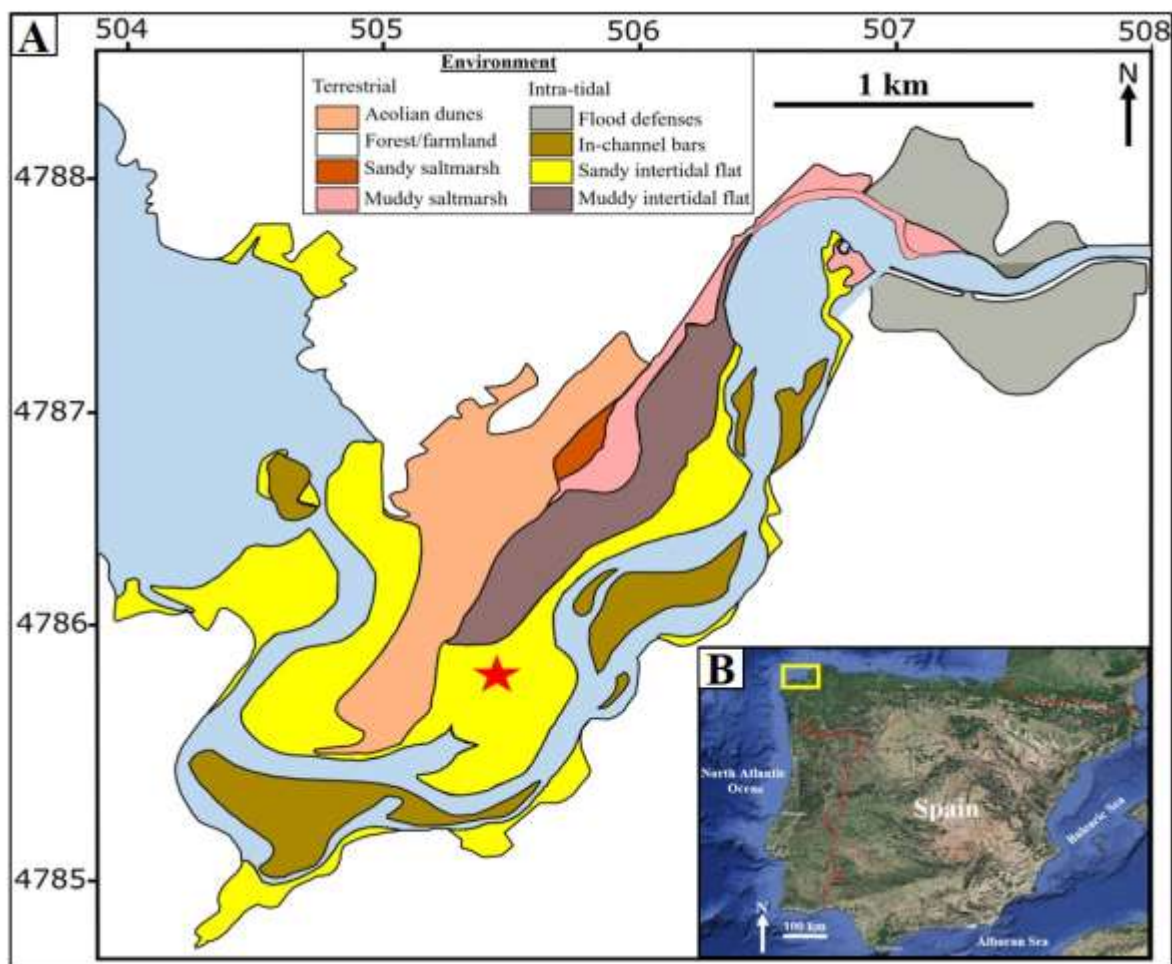


Figure 3.1. A) Simplified geological map of the Anllóns Estuary catchment area, showing the distribution of various sedimentary environments (modified after Dowey et al., 2017). The red star indicates the location of the samples used in this study. B) Regional view of the study area, with the yellow rectangle marking the approximate location of the Estuary.

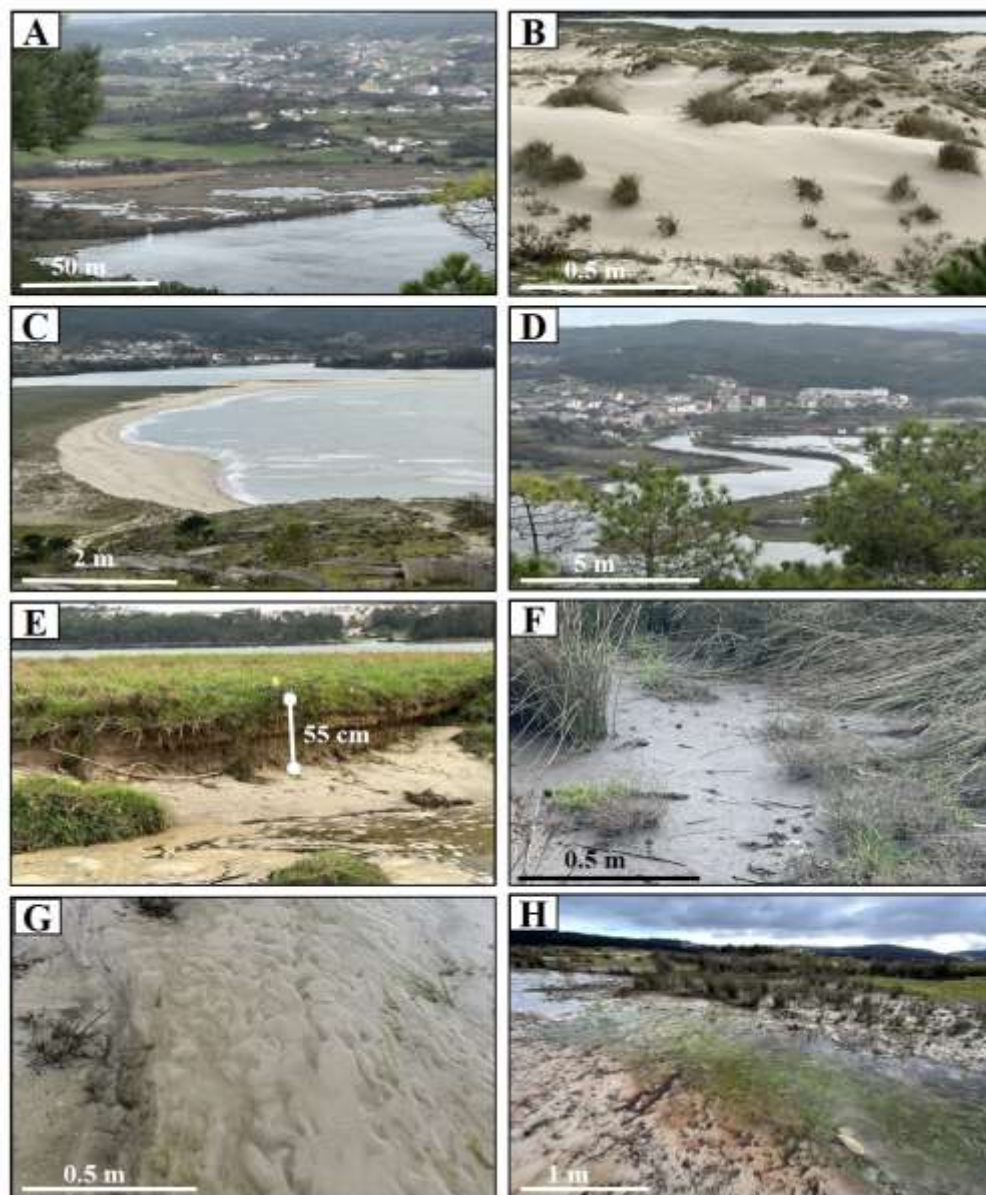


Figure 3.2. Field photographs of the various sedimentary environments within the Anllóns Estuary, taken on November 22, 2023. A) Salt marsh in the northwestern part of the estuary, cut through by tidal creeks and channels that flow into the intertidal flat. B). Aeolian dunes formed on a sandy spit. C) Large sandy spit attached to the frontal part of the estuary. D) Estuary channels and tidal creeks. E) Terrace indicating the boundary between saltmarsh and intertidal flat. F) Vegetated muddy intertidal flat. G) Sandy intertidal flat. H) Partially vegetated muddy intertidal flat. Samples used in this study were taken from the sandy intertidal flat (G).

3.3.2. Hydrothermal reactor experiments

The hydrothermal reactor experiments were conducted using an Ollital OLT-HP-500 multi-position parallel reactor autoclave system, connected to a nitrogen gas cylinder (Fig. 3), at the Experimental Diagenesis Lab, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Saudi Arabia. The autoclave features four stainless steel micro-stirred parallel reactors with independent temperature, pressure, and elapsed time control. The reactor kettles have a capacity of up to 500 mL and can be heated to a maximum temperature of 350 °C and a pressure of 160 bar. Temperature regulation is managed by a Smart PID algorithm control system, providing an accuracy of $\pm 0.1^{\circ}\text{C}$. Before the start of the experiments, the sandy intertidal flat sediments were divided into eight portions of 20 grams each. For each experiment, 20 grams of the sample were placed in a 50 μm stainless steel mesh and transferred to the bottom of the reactor kettles. The kettles were then filled with 200 mL of the respective experimental solutions (Table 1: 0.1 M solutions of NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for experiments 1-6; estuarine water for experiment 7; and 0.1 M Na_2CO_3 for experiment 8), leaving approximately 60% headspace at room temperature and achieving a 10:1 fluid-to-rock ratio. The synthetic fluid used for experiments 1–6 was prepared by combining equimolar concentrations (0.1 M) of NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. This composition was designed to create a simplified system that isolates the major cations (Mg^{2+} , K^+ , Ca^{2+} , and Na^+), which are known to influence authigenic smectite formation under hydrothermal conditions, following the methodology of Haile et al. (2015). Compared to natural seawater, the synthetic fluid differs in ionic composition: it contains approximately 20% of seawater's Na content, ten times higher K and Ca concentrations, and twice the Mg concentration, while its Cl concentration is closer to that of seawater. The reactors were sealed, pressurized with approximately 40 bar of nitrogen gas, and subsequently heated to various

experimental temperatures, ranging from 50 °C to 250 °C (Table 1) at 10°C per minute. Although the initial injected pressure was consistent across all experiments (~40 bar at room temperature), it increased based on the experimental temperature and reaction fluid, eventually stabilizing at the final pressure (Table 1) after 1-4 hours. Samples were held at the target experimental temperatures for durations ranging from 168 to 336 hours under strictly closed conditions, following the procedures outlined by Charlaftis et al. (2021) and Bello et al. (2022a).

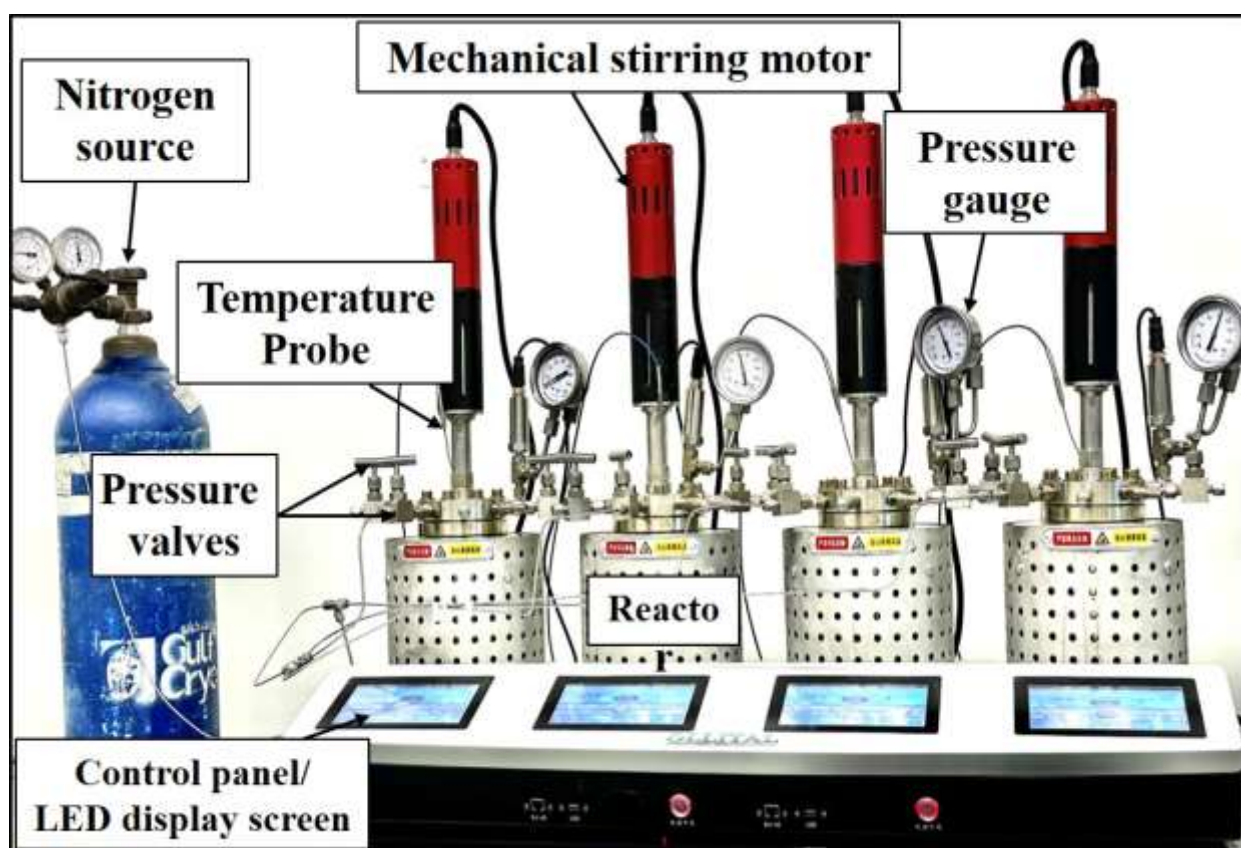


Figure 3.3. Photograph of the experimental setup used in this study. The system comprises four multi-position parallel reactors with kettles, each capable of holding up to 500 mL of solution. The reactors can be heated to a maximum temperature of 350°C and withstand pressures up to 160 bar.

After each experiment, the reactors were switched off and cooled to room temperature. The samples were then retrieved and air-dried. Additionally, post-experiments solutions were recovered, immediately analyzed for pH, and subjected to ICP-OES analysis at room temperature. The synthetic fluid composition used in this study was simplified to include only major cations, with a 10:1 fluid-to-rock ratio to ensure sufficient fluid-rock interaction for stimulating mineral transformations (Murphy, 2016).

Table 3.1. Conditions for the hydrothermal experiments

Experiment	Sample ID	Solution (M)	Temperature (°C)	Duration (hours)	Final Pressure (Bars)
1	SF@50	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	50	336	44.1
2	SF@100	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	100	336	51.8
3	SF@150	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	150	336	63.8
4	SF@200	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	200	336	85.4
5	SF@250_1	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	250	336	125.8
6	SF@250_2	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	250	168	114.2
7	EW@250	Estuarine water	250	336	117.6
8	Na-SF@250	0.1 M Na ₂ CO ₃	250	336	139.9

3.3.3. Analytical Techniques

3.3.3.1. Thin section petrography

Standard petrographic thin sections were prepared to examine the occurrence and distribution of framework grains and detrital grain coating clays in the starting material and the authigenic clay minerals synthesized during the experiments. The thin sections were examined using an Olympus BX53F petrographic microscope.

3.3.3.2. SEM-EDS

Pre- and post-experiment samples were studied using a Zeiss Gemini 550 scanning electron microscope (SEM) in both secondary electron (SE) and backscatter electron (BSE) modes. The SEM was equipped with a backscattered electron detector (BSE) and an Aztec energy-dispersive spectrometer (EDS) system, manufactured by Oxford Instruments, UK. Gently disaggregated loose sediments were bonded to an aluminum stub with carbon tape and then coated with 30.0 nm of gold using a Quorum Q150R sputter coater before SEM analysis. Additionally, polished thin sections were prepared from both reacted and unreacted samples. These thin sections were carbon-coated and analyzed under SEM-BSE and SEM-EDS. The analyses were conducted at a voltage ranging from 10 to 15 kV, with a probe current varying from 1 to 2 nA. The SEM-EDS analyses were performed to investigate the morphology, composition, and mode of occurrence of detrital minerals in the starting material, as well as any authigenic minerals precipitated during the experiments.

The structural formulas of smectite and illite presented in this study were calculated using EDS analyses. Although EDS is inherently semi-quantitative, with uncertainties stemming from detector sensitivity, matrix effects, and limitations in detecting light elements, multiple measures were implemented to enhance data reliability and minimize potential errors. Elemental compositions obtained from EDS were converted into oxides and normalized to a total of 12

cations occupying tetrahedral and octahedral sites, following established protocols for 2:1-layer silicates (Dong et al., 1997). Measurements were performed at an optimized working distance and accelerating voltage (15–20 kV) to ensure accuracy. To account for sample heterogeneity, multiple measurements ($n \geq 10$) were taken on different grains, and averaged compositions were used for structural formula calculations. Octahedral vacancies and interlayer cations were cross-validated against typical smectite and illite compositions reported in the literature (Dong et al., 1997; Huggett et al., 2016) and plotted on ternary diagrams, such as those of Weaver and Pollard (1973) and Velde (1985), to ensure consistency with known compositional fields. While the semi-quantitative nature of EDS introduces inherent uncertainties, particularly in achieving absolute accuracy, the calculated structural formulas provide insights into compositional trends and cation substitutions within smectite, which are critical to understanding its formation and subsequent illitization, sufficient for the objectives of this study.

3.3.3.3. *XRF Analyses.*

The oxide compositions of pre- and post-experiment samples were determined using wavelength-dispersive X-ray fluorescence (WD-XRF) spectroscopy with a Panalytical Zetium spectrometer (Malvern PANalytical). Samples were prepared by fusion with a metaborate flux on the Classic The OX Advanced fusion instrument (Malvern Panalytical). Precisely 1.0 g of the finely ground sample was accurately weighed into a platinum-gold crucible and thoroughly mixed with 10.0 g of anhydrous lithium metaborate flux ($\text{LiBO}_2\text{:Li}_2\text{B}_4\text{O}_7$ in a 49.75:49.75:0.50 ratio). The crucible was then loaded into the automated fusion instrument, which executed the following heating program under an oxidizing atmosphere: an initial hold at 500°C for 2 minutes, followed by a ramp to 1125°C over six 4.5-minute steps, with intermittent rocking at 0-30 rpm and a 0-45° angle to facilitate complete fusion. At the final temperature stage, the molten mixture was swirled vigorously before being poured into a Pi-Au mold and allowed to cool, forming a homogeneous

glass disk. After cooling to room temperature, the anhydrous glass disks were labeled and loaded onto the Zetium spectrometer for quantitative determination of major, minor, and trace oxides. The Zetium features a 4 kW, drift-free, high-resolution Cu anode X-ray tube coupled with a WD-XRF detector equipped with five analyzing crystals: PE002 (Al-Cl), LiF200 (K-Am), PX-1 (O-Mg), Ge11 (enhanced P-Cl sensitivity), and LiF220 (enhanced V-Am resolution). The mineral oxide calibration module was employed to optimize the analytical conditions of the Zetium WD-XRF system for the precise and accurate analysis of geological materials. This module adjusts instrument parameters, such as X-ray tube settings, collimators, detectors, and measurement times, to enhance the detection and quantification of oxides commonly found in geological samples. Detection of unknown elements is supported by the glass sample monitor (Ausmon) check standard for general analyses, which includes major elements (Fe, Mn, Ti, Ca, K, Cl, S, P, Si, Al, Mg, Na, F) and traces of 38 other elements at approximately 2000 ppm levels, making it ideal for rocks, soils, vegetation, and other matrices.

The quantitative analysis utilized synthetic-certified reference materials (CRMs) from the WROXI series, produced under ISO 17034 accreditation. Data accuracy and precision were validated through periodic analyses of the quality control standard. PANalytical SuperQ software was employed for controlled spectral acquisition, matrix deconvolution, and data processing, incorporating integrated quality control protocols.

3.3.3.4. *XRD (Bulk and Clay fraction).*

The bulk and clay fraction (<2 μm) mineralogy of the starting and post-experiment samples was analyzed using X-ray diffraction (XRD) with a Malvern Empyrean PANalytical diffractometer equipped with Ni-filtered Cu $K\alpha$ radiation (PANalytical, Almelo, Netherlands). For bulk mineralogy analysis, samples were air-dried in a fume cupboard at room temperature. The dried

samples were powdered to $<10\ \mu\text{m}$ using a Retsch RM 200 mortar grinder (RETSCH, Haan, Germany). The resulting powders were backloaded into 27 mm sample holders (Malvern PANalytical) and leveled using a glass slide to ensure a uniform surface. Excess material was removed with a pin brush to minimize surface irregularities. The bulk mineralogical analysis was performed under operating conditions of 45 kV and 40 mA. XRD intensities were recorded over a 4.5° – 70° 2θ range with a step size of 0.013° , a counting time of 8.9 seconds per step, and a scan speed of $0.38^{\circ}/\text{s}$. Mineral identification was carried out by comparing the acquired diffractograms with those in the International Centre for Diffraction Data Powder Diffraction File (ICDD PDF, 2024). Quantification of the identified minerals was achieved using the relative intensity ratio (RIR) method as proposed by Chung, (1974). This approach has been validated as reliable for XRD mineral quantification (Hillier, 1999).

To assess the presence of amorphous materials in both the starting material and experimental products, XRD analyses were performed with a low step size (0.013° 2θ) to enhance the signal-to-noise ratio. Each sample was scanned twice to identify any broad diffuse humps associated with amorphous materials within the 15° – 35° 2θ range (Moore and Reynolds, 1998). Additionally, 10 wt.% of NIST standard corundum (Al_2O_3), supplied by Malvern PANalytical, was used as an internal standard. The corundum was thoroughly mixed with the finely ground powders before analysis. Diffraction patterns were examined for elevated baseline intensities, and quantitative estimates of amorphous content were calculated by comparing the relative intensity of the corundum peaks to the sample baseline. Across all analyses, no evidence of amorphous material was detected in the starting material or post-experiment samples.

For the clay fraction ($<2\ \mu\text{m}$), the separation process involved gravity settling combined with ultrasonication and centrifugation. Five grams (5 g) of bulk samples were soaked in deionized

water (DI) overnight to gently disaggregate the loosely cemented post-experiment samples. This step allowed the separation of fine clay particles from coarser sand-sized materials while preserving the clay minerals' integrity. The disaggregated material was dispersed in 100 mL of DI water, subjected to ultrasonication for 20 minutes, and stirred vigorously at 5-minute intervals (Moore and Reynolds, 1998). Coarser particles were removed via gravity settling, and the supernatant containing the clay fraction was concentrated by centrifugation at 5000 rpm for 15 minutes (Wooldridge et al., 2017b). Drops of the clay slurry were pipetted onto SI SUBSTR 32 MM shallow-well sample holders (Malvern PANalytical) to form oriented mounts for clay mineral identification. The mounts were air-dried overnight in a fume hood at room temperature.

The separated clay fractions were analyzed in three states: (1) as air-dried untreated clays, (2) after ethylene glycol (EG) solvation at 70 °C for 20 hours to identify expandable clays, and (3) after heating at 550 °C for 1 hour to distinguish between smectite and illite based on their thermal stability (Moore and Reynolds, 1998). Analyses were conducted over a 4°–40° 2 θ scanning range, with a step size of 0.013° 2 θ and a scan speed of 0.05°/s.

Clay mineral identification was performed using the search-match module in HighScore Plus (v. 4.9), with reference to ICDD PDF-4-2024 and supplementary data from Moore and Reynolds (1998). Peak positions from air-dried clays were used as baselines to track changes after EG solvation and heating treatments, enabling the identification of smectite and illite. For semi-quantitative analysis, HighScore Plus was employed to perform Rietveld refinement using structure files from the Inorganic Crystal Structure Database (ICSD). Structure files were carefully selected to ensure compatibility with oriented clays. Profile-matching techniques were used to verify the fit of the experimental spectra with reference patterns. Preferred orientation effects were corrected using the March-Dollase function integrated into the software. The illite-to-smectite

ratios were calculated based on the refinement of the 001 reflections and verified by comparison with reference patterns. These results were cross-validated using Profex software to ensure consistency. Despite these protocols, the results obtained are considered semi-quantitative due to the limitations of Highscore software in the quantification of oriented clay minerals.

3.3.3.5. ICP-OES

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was employed to analyze the elemental composition (major cations) of the solutions both before and after the hydrothermal experiments. The analyses were performed using a PerkinElmer PlasmaQuant 9000 ICP-OES instrument, which utilizes plasma as an excitation source for detecting optical emissions during analysis. Upon retrieval, the fluids were transferred to vials and diluted with 1% nitric acid (HNO_3) to achieve a final conductivity of less than 2000 $\mu\text{S}/\text{cm}$. This dilution was necessary to ensure the samples fell within the calibration range of the instrument and to prevent clogging of the needle and nebulizer. A certified reference material (CRM; product number 92091) from Supelco Analytical Products (Supelco, Inc., U.S.A.), containing a broad range of elements including Al, As, Ca, Cd, Fe, K, Mg, Na, Sc, and Y, was used as the calibration standard. This CRM was critical for maintaining quality control and ensuring the accuracy, precision, and reliability of the results. Additionally, 0.1 mL of scandium (Sc) was added to each solution as an internal standard to correct for matrix effects and instrumental drift during the analysis. The samples were introduced into the nebulizer via an autosampler, and the emission intensities of each analyte were recorded, with continuous monitoring of the internal standard's performance. The concentrations of individual analytes, including Al, Ca, Fe, K, Mg, and Na were quantified using the calibration curve derived from the CRM. This analytical approach facilitated the quantification of major cations in the solutions both before and after the hydrothermal experiments.

3.3.4. Grain coat coverage and grain-coating thickness.

Grain coating coverage was measured using Petrog (Conwy Valley Systems Ltd, UK), following the procedures outlined by Wooldridge et al. (2017a; 2019). SEM-BSE images from thin sections were imported into Petrog, and the clay coat coverage of 50 sand grains per sample was analyzed. The method involved measuring the total perimeter of each grain and the length covered by the attached clay coating. This was used to calculate the percentage of the grain's perimeter coated by clay in both the starting material and after various hydrothermal treatments. The standard error for each sample analysis was $\pm 2\%$.

Coating thickness was quantified using both two-dimensional (2D) and three-dimensional (3D) approaches. The 2D method involved measuring grain coatings on 50 grains per sample from SEM-BSE images, using Petrog, to assess changes across the different hydrothermal treatments. The 3D method, being more complex, utilized focused ion beam scanning electron microscopy (FIB-SEM) for more detailed analysis.

The FIB-SEM procedure was utilized for high-resolution imaging and analysis of the sample's internal structure at the nanoscale. Sample preparation was conducted using a Zeiss Crossbeam 550 FIB-SEM equipped with a Gallium FIB column. The SmartFIB software (Zeiss) automated sample milling, cross-sectioning, and serial sectioning. A trapezoid-shaped trench, 30 μm wide and 20 μm deep, was milled in three steps: coarse milling at 30 kV/15 nA, intermediate milling at 30 kV/700 pA, and fine polishing at 30 kV/300 pA to ensure a smooth surface.

Tilt correction was applied to improve imaging accuracy, and micrographs were captured to document cross-sectional features. Serial sectioning was then performed with 50 nm slice thicknesses over a 40 μm length, generating multiple layers.

3.4. Results

3.4.1. Composition of the Starting Material

The sandy intertidal flat sediments of the Anllóns Estuary consist of medium-grained, moderately well-sorted sand with an average grain size of 0.27 mm. Results from WD-XRF oxides analyses (Table 2) indicate that SiO₂ (63.76 wt%), CaO (22.17 wt%), Al₂O₃ (5.46 wt%), and K₂O (3.99 wt%) are the dominant elements in the sediment. Minor amounts of Fe₂O₃, MgO, and ClO₂ are also present, while MnO, P₂O₅, SO₃, SrO, and TiO₂ occur in trace quantities (Fig.4; Table 2). Bulk mineralogy analyses (XRD) further reveal that the pre-reacted sediment is dominantly composed of quartz (57.5%), orthoclase (16.7%), and plagioclase (4.6%) (Table 3). Carbonate minerals, mainly calcite (13.1%) and aragonite (6.3%), are also present, along with trace amounts of muscovite (0.3%), biotite (1.0%), and pyrite (0.5%).

Table 3.2. Results of the WDX-XRF analysis of the starting material and post-reacted samples [SM = Starting material]

Identification		Major and minor elements (wt %)								Trace elements (ppm)				
Experiment	Sample ID	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	ClO ₂	MnO	P ₂ O ₅	SO ₃	SrO	TiO ₂
SM	SM@0	63.76	5.46	22.17	1.06	0.31	2.05	3.99	0.16	424.4	818.6	1389.7	1837.6	4561.6
Exp. 1	SF@50	63.03	5.41	21.92	0.97	0.51	2.01	4.20	1.11	407.3	733.3	1484.2	1742.4	2853.8
Exp. 2	SF@100	62.50	5.54	21.85	1.35	0.59	2.02	4.07	1.19	260.3	798.4	1748.3	1756.5	2082.6
Exp. 3	SF@150	64.58	5.24	18.70	0.89	1.70	1.96	4.22	2.00	ND	635.4	1216.7	1419.6	1702.0
Exp. 4	SF@200	64.61	5.91	8.38	4.01	6.86	2.08	4.50	2.72	473.2	966.8	515.2	672.0	3755.7
Exp. 5	SF@250_1	65.37	6.17	2.72	5.31	10.02	1.99	4.67	2.82	451.8	875.5	440.7	286.0	3045.6
Exp. 6	SF@250_2	63.18	5.63	12.05	4.24	5.44	1.89	4.44	2.11	553.4	713.8	1036.7	916.2	3458.6
Exp. 7	EW@250	60.54	6.17	15.69	3.31	3.07	3.07	3.91	1.88	1050.6	918.1	5826.5	1237.7	3830.7
Exp. 8	Na-SF@250	62.87	5.62	21.92	1.13	0.39	3.46	3.68	ND	549.1	861.7	1114.4	1781.4	9387.9

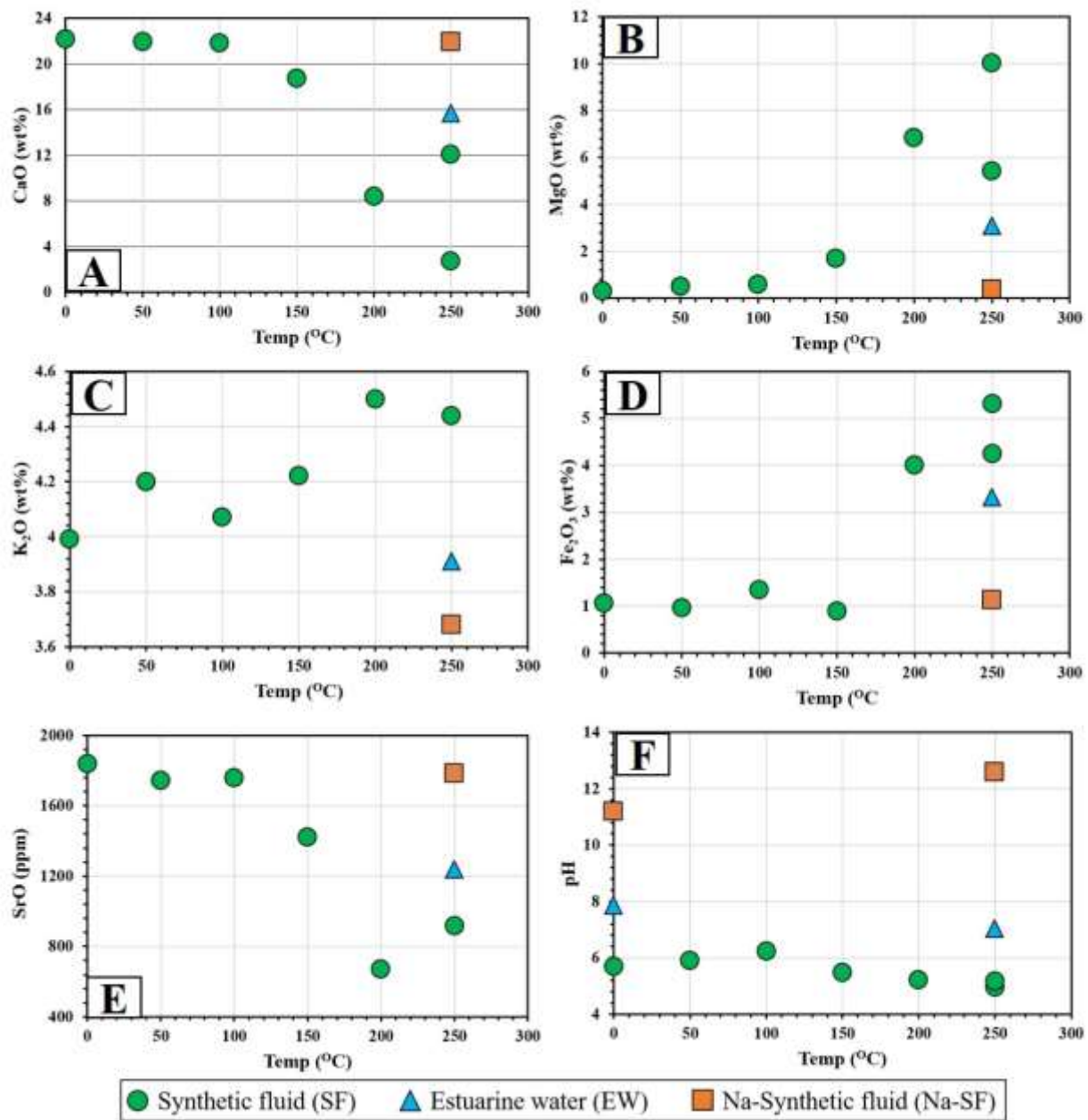


Figure 3.4. Plots of WD-XRF concentrations for CaO, MgO, K₂O, Fe₂O₃, SrO, and pH versus experimental temperatures illustrating their evolution as temperature increases during the hydrothermal experiments. Data points are color-coded according to the brine compositions used in each experiment.

These findings are further supported by thin-section and SEM petrographic analyses, which show that the dominant detrital grains are monocrystalline quartz and K-feldspar (Fig. 5A-C). Carbonate materials are mainly bioclast (Fig. 5C-D). SEM analyses also reveal that the framework quartz and K-feldspar grains are partially coated by detrital grain coats (Fig. 5E-F). These coats are composed of a mix of clay minerals, carbonate fragments, and silt-sized framework grains (Fig. 5G). Even with high-resolution SEM imaging (Fig. 5G), identifying specific clay minerals based on morphology was challenging due to the lack of systematic organization or internal structure. SEM-EDS analyses show that the grain coats are principally composed of Si, O, Al, Ca, Fe, and K (Fig. 5H). XRD analysis of the clay fraction (Table 3, Fig. 6A) confirms that kaolinite and illite are the main detrital clay minerals in the grain coats, along with quartz, calcite, and aragonite (Fig. 6A). The thickness of the detrital grain coats in the starting material ranges from 1.0 to 2.1 μm , with an average of 1.6 μm . The mean grain coat coverage varies between 3.9% and 5.2%, with an average of 4.6% (Table 3).

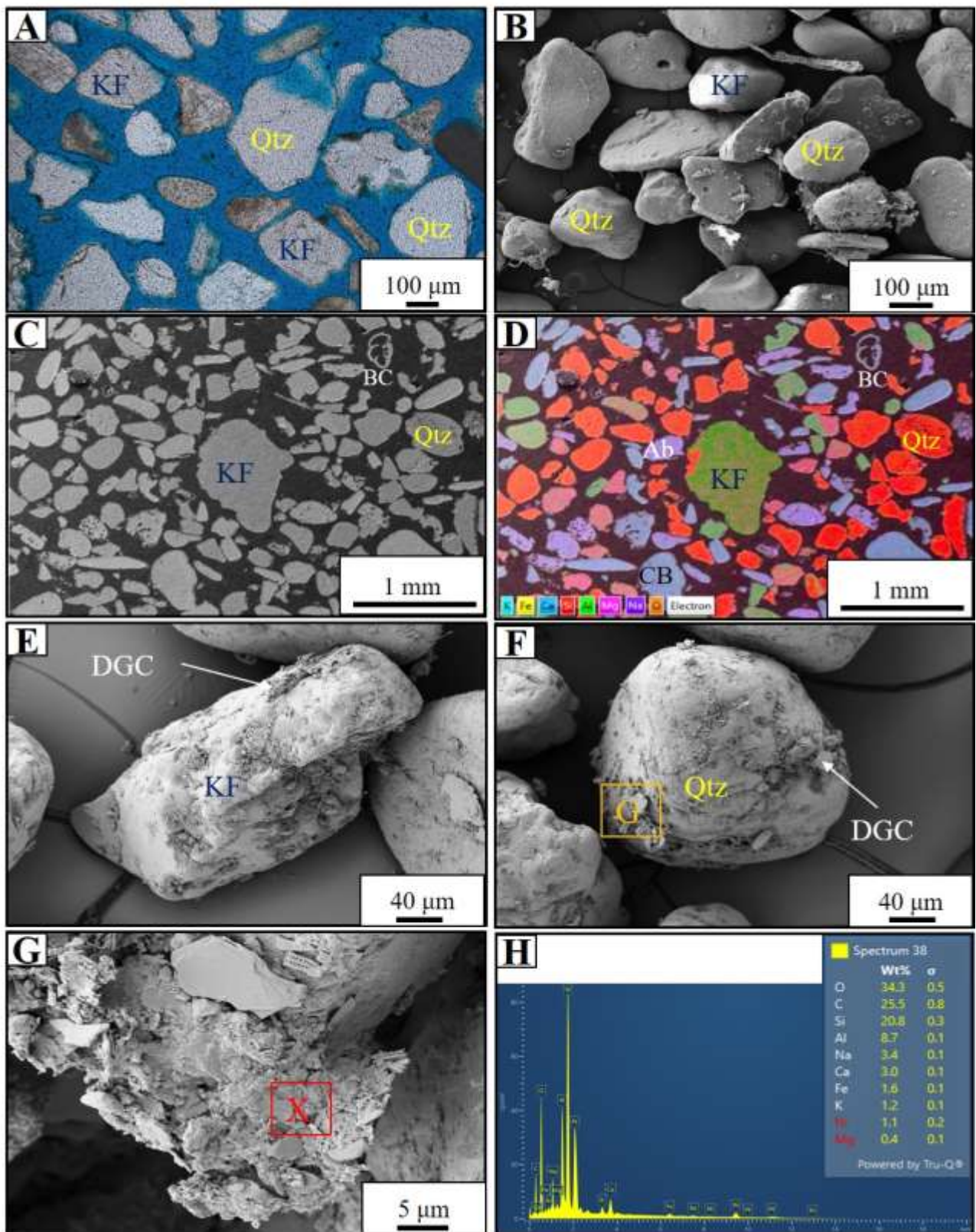


Figure 3.5. Petrographic images displaying the framework grains and detrital grain coat minerals of the starting material. A) Thin-section photomicrograph and (B) SEM image showing detrital quartz (Qtz) and K-feldspar (KF). C) SEM image and (D) EDS map illustrating the distribution of detrital quartz (Qtz), K-feldspar (KF), albite (Ab), carbonates (CB) and bioclast (BC) framework grains. E-F) SEM images showing detrital grain coats (DGC) on K-feldspar (KF) and quartz (Qtz) grains from the sandy intertidal flat. The G label shows the close-up view shown in G G) Close-up view of the detrital grain coat shown in F, revealing that the grain coatings are chiefly composed of detrital clay minerals and carbonate. The red X label indicates the point the EDS shown in H was obtained. H) EDS spectra of the grain coat in G, indicating the presence of kaolinite, illite, and carbonate.

Table 3.3 Bulk and clay fraction composition, percentage clay fraction, thickness, and coverage of clay coat in pre-and post-reacted samples

Sample ID	Bulk mineralogy (%)										Clay fraction wt %	Clay mineralogy (< 2 µm) (%)			Clay coating thickness (µm)			Clay coat coverage (%)		
	Qtz	Orth	Alb	Cal	Arg	Mus	Bio	Pyr	Chb	Hal		Kao	Sme	Ill	Ave	Min	Max	Ave	Min	Max
SM	57.5	16.7	4.6	13.1	6.3	0.3	1.0	0.5	-	-	0.8	82	-	18	1.6	1.0	2.1	4.6	3.9	5.2
Exp. 1	63.7	12.6	3.4	14.5	5.9	0.0	0.0	0.3	-	-	0.6	TR	-	TR	-	-	-	-	-	-
Exp. 2	64.3	13.4	3.4	13.6	5.2	0.0	0.0	0.1	-	-	0.4	TR	-	TR	-	-	-	-	-	-
Exp. 3	70.1	7.1	2.4	16.0	4.2	0.0	0.2	0.0	-	-	4.4	-	87	TR	7.2	1.9	12.5	33.5	24.3	42.6
Exp. 4	74.9	5.5	7.2	9.4	0.0	1.9	1.3	0.0	-	-	5.6	-	70	30	15.6	6.2	25.0	63.6	50.8	76.4
Exp. 5	64.5	7.3	7.3	0.5	0.0	18.7	1.7	0.0	-	-	6.1	-	25	75	29.8	10.4	49.2	80.5	64.9	96.2
Exp. 6	65.3	10.6	8.2	12.1	0.7	1.2	1.8	0.0	-	-	1.8	-	65	35	20.0	9.6	30.4	66.8	57.2	76.4
Exp. 7	63.5	11.0	8.1	12.8	2.0	0.8	1.7	0.1	-	-	5.3	-	43	57	21.4	10.1	32.6	69.5	57.6	81.3
Exp. 8	60.1	12.4	2.1	15.6	0.0	0.0	0.0	0.2	7.4	2.2	-	-	-	-	-	-	-	-	-	-

[SM=starting material; TR=trace; Qtz=quartz; Orth=orthoclase; Alb=albite; Cal=calcite; Arg=aragonite; Mus=muscovite; Bio=biotite; Pyr=pyrite; Chb=chabazite; Hal=halite; Kao=kaolinite; Sme=smectite; Ill=illite; Ave=average; Min=minimum; Max=maximum]

3.4.2. Geochemical and Mineralogical Analysis of Post-reacted Samples

3.4.2.1. Elemental analyses.

The WD-XRF analyses of the post-reacted samples revealed the distribution of major (SiO, Al₂O₃, CaO, Na₂O, K₂O), minor (Fe₂O₃, MgO, ClO₂), and trace (MnO, P₂O₅, SO₃, SrO, TiO₂) oxides (Table 2). The results highlight variations in oxides composition across different hydrothermal experiments (Fig. 4A-E). SiO₂ was consistently the most abundant oxide in all samples (Table 2), followed by CaO and Al₂O₃. Notably, CaO concentrations decreased with rising temperatures in the experiments using synthetic fluids (Exp. 1-6; Fig. 4A). The concentration dropped significantly, from 21.9% in Exp. 1 (50 °C) to 2.7% in Exp. 5 (250 °C). A similar reduction in CaO was observed in the experiment conducted with estuarine water (Exp. 7), while minimal changes were noted in the experiment using Na-rich synthetic fluid (Exp. 8; Table 2). Conversely, MgO (Fig. 4B) and Fe₂O₃ (Fig. 4C) concentrations increased with rising experimental temperatures (Table 2). K₂O levels increased slightly across the experiments (Fig. 4D), whereas Na₂O concentration remained relatively stable, except in Exp. 7 and 8, where it increased from 2.1% in the pre-reacted sample to 3.1% and 3.5%, respectively (Table 2). TiO₂, SrO, and SO₃ were the dominant trace oxides in all samples, followed by P₂O₅ and MnO (Table 2). SrO concentrations decrease with increasing temperature across the hydrothermal experiments (Fig. 4E), chiefly attributed to aragonite's dissolution. As temperature rises, the dissolution of aragonite releases Sr²⁺, leading to a reduction in SrO levels.

3.4.2.2. Bulk mineralogy.

X-ray diffraction (XRD) analyses revealed that the bulk mineralogical composition of the post-reacted samples is predominantly quartz, comprising over 60% in all experiments (Table 3). Orthoclase and albite are present in the samples, with orthoclase concentrations showing a general decline as experimental temperature increases, relative to the starting material (Table 3). The

dissolution of orthoclase is influenced by both the duration of the experiments and the composition of the fluid used (Table 3). Specifically, in experiments conducted at 250°C using the same synthetic fluid (SF1), orthoclase decreased to 7.3 wt.% in Exp. 5 (336 hours) but only to 10.6 wt.% in Exp. 6 (168 hours), indicating a clear time-dependent dissolution effect. Furthermore, Orthoclase decreased from 16.7 wt. % to 11 wt. % in Exp. 7 with estuarine water and to 15.7 wt. % in Exp. 8 where Na-synthetic fluid was used. Both experiments were run at 250°C. Calcite and aragonite are the primary carbonate minerals observed, with aragonite concentrations consistently declining as temperature increases. In contrast, calcite concentrations exhibit fluctuations: they increase during Experiments 1 to 3, decrease in Experiments 4 to 7, and then increase again in Experiment 8 (Table 3). Muscovite and biotite are present in minor to trace amounts, while pyrite occurs in trace amounts in some experiments (Table 3). Chabazite (7.4 wt.%) and halite (2.2 wt.%) are exclusively observed in Exp. 8 (Table 3), which was conducted using a Na-rich synthetic fluid that provided favorable conditions for their formation. Although the sediments were collected in a single scoop and evenly divided for each experiment, some degree of random variation still exists.

3.4.2.3. *Mineralogy of clay fraction.*

The XRD analyses of the oriented clay fraction ($< 2 \mu\text{m}$) from the hydrothermal experiments revealed the synthesis of various clay minerals (Fig. 6). The results, presented in Table 3, show that kaolinite and illite were the primary detrital clay minerals in the starting material (Fig. 6A). The transformation of these clay minerals, along with other framework grains, began in Exp. 2, while the formation of smectite started in Exp. 3. Overlaid XRD patterns of the clay fraction in Exp. 4 revealed the presence of smectite and/or mixed-layer illite/smectite as the synthesized clay minerals, with kaolinite completely absent (Fig. 6B). In addition, smectite, mixed-layer illite/smectite, and illite were synthesized in Exp. 5, 6, and 7 (Fig. 6C-D). In the air-dried oriented powder analyses, the primary smectite peak (001) was observed at a d-spacing of 15.00 Å. After

ethylene glycol solvation, this peak shifted to 16.99 Å (Fig. 6C-D), with the (002) reflection observed at 8.50 Å. Upon heating to 550 °C, a broadening of the illite primary peak and the disappearance of the smectite primary peak were observed (Fig. 6C-D).

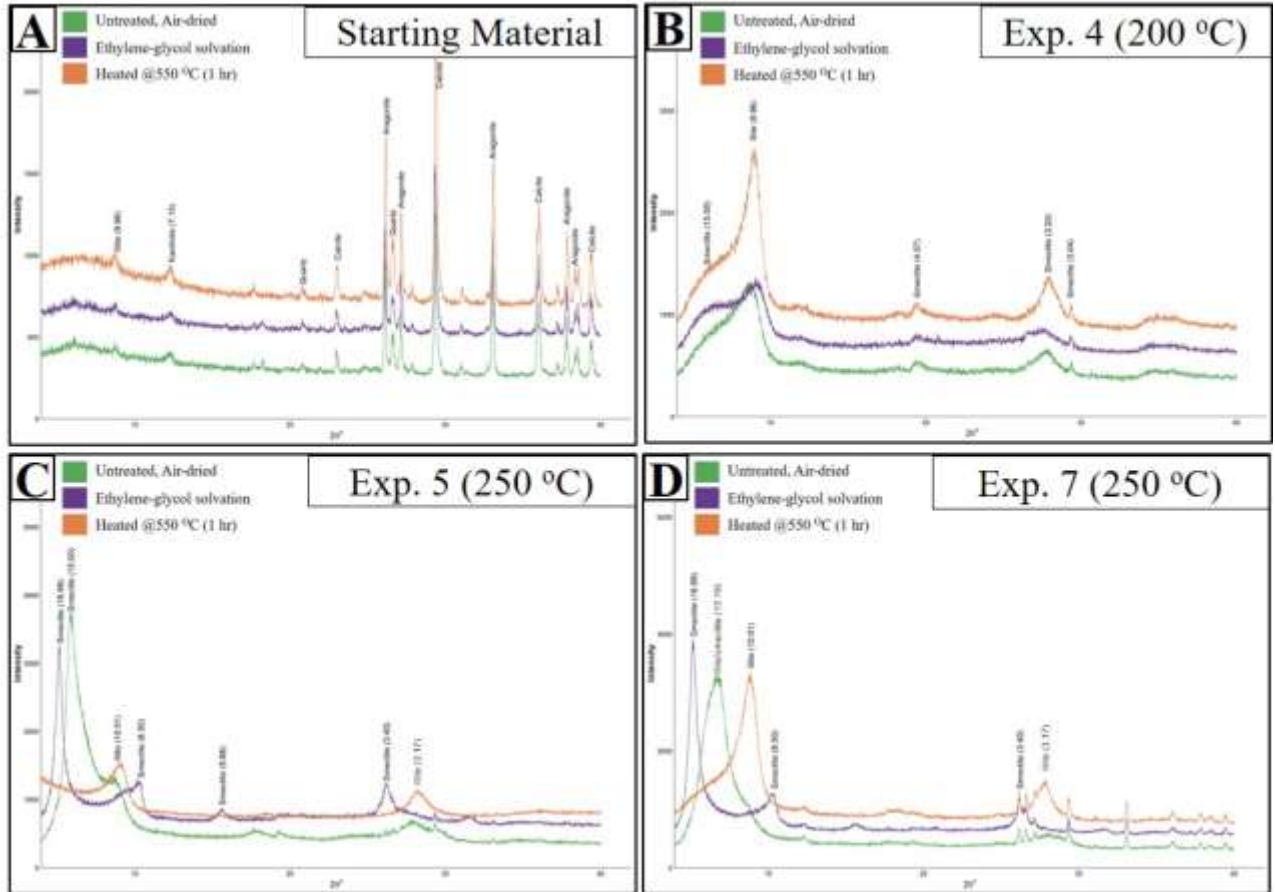


Figure 3.6. XRD patterns of the clay (< 2 μm) minerals present in both the starting material (detrital) and those synthesized in the hydrothermal experiments (authigenic). D-spacing values are provided in parentheses. A) Diffractograms of the starting material revealing the presence of illite and kaolinite as the dominant clay minerals in the studied samples. Both kaolinite and illite are detrital and occur in minor amounts. B) Air-dried, ethylene glycol-solvated, and heated diffractograms from Experiment 4 (200 °C) showing the synthesized clay minerals. The overlaid patterns show the presence of smectite and mixed-layer illite/smectite as the synthesized clay

minerals. Notably, there is a broadening of the illite primary peak in the heated diffractogram. C) Overlaid diffractograms from Experiment 5 (250 °C) indicating the presence of smectite and illite. There is a noticeable positional shift of the smectite primary peak from 15.00 Å in the air-dried XRD pattern to 16.99 Å after ethylene glycol solvation (Moore & Reynolds, 1998). Additionally, the smectite primary peak disappears after heating to 550 °C. D) Post-experiment XRD patterns from Experiment 7 (250 °C, using estuarine water) show smectite, illite/smectite, and illite as the primary synthesized clay minerals. Similar to Experiment 5, there is a positional shift in the smectite primary peak, as well as a broadening of the illite primary peak after heating.

3.4.3. Mineralogical Evaluation of Post-reacted Samples and Synthesized Clay Minerals

3.4.3.1. Experiments 1 and 2.

These experiments were conducted at 50 °C and 100 °C, respectively (Table 1). SEM and SEM-EDS analyses of the low-temperature experiments indicated that the distribution of detrital grains remained largely unchanged compared to the starting material, with no significant alterations observed. Although no new clay minerals formed in either experiment, the dissolution of K-feldspar and detrital grain coats was likely initiated at these temperatures (Table 3), accompanied by the formation of Fe-oxide.

3.4.3.2. Experiments 3 and 4.

The authigenic (experimental) formation of smectite began in Exp. 3, conducted at 150 °C (Fig. 7). SEM analysis reveals the early formation of smectite, coating framework detrital grains, mostly quartz and K-feldspar (Fig. 7A-D). Notably, there was a complete absence of detrital grain-coat aggregate assumed to be dissolved at very low experimental temperatures. The newly formed smectite occurs mainly as grain-coating (Fig. 7B). It varies from an incipient crenulated

morphology (Fig. 7A-B) to honeycomb texture (Fig. 7E) and flakes that are flatly attached to the surface of detrital quartz and strongly curled upward (Fig. 7D). The coating thickness ranges from 1.9 to 12.5 μm (average 7.2 μm), and the coat coverage varies from 24.3% to 42.6% (average 33.5%) (Table 3). Coat coverage is higher on detrital quartz than on K-feldspar. EDS analyses of the smectite show that it is Mg-rich and characterized by Ca and Na as the interlayer cations (Fig. 7F). Additionally, authigenic quartz overgrowths developed simultaneously with poorly formed smectite (Fig. 7C). However, quartz overgrowths are absent where smectite has fully developed and covered the surface of the framework grains (Fig. 7D).

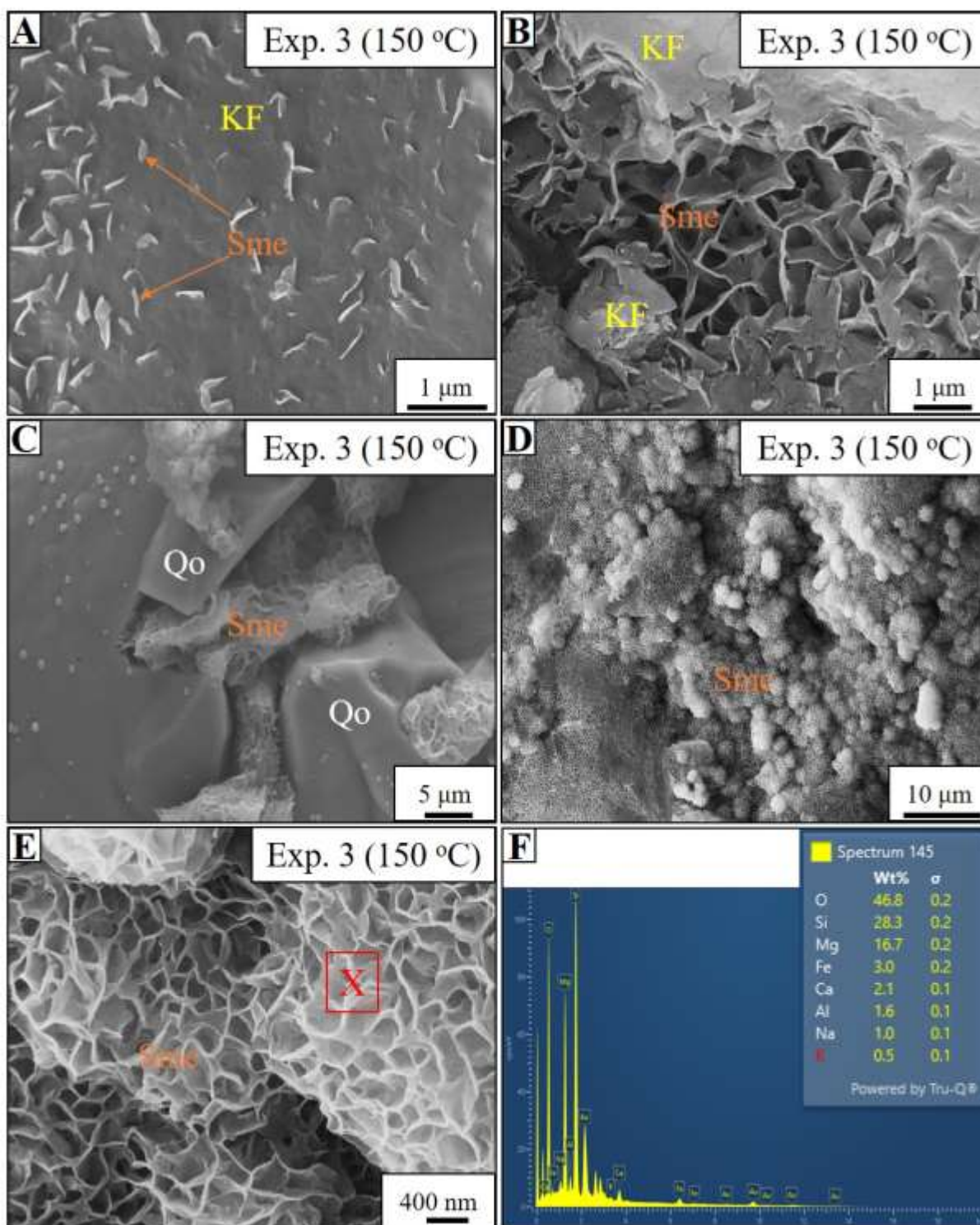


Figure 3.7. SEM-EDS images showing diagenetic features observed in Experiment 3 (150 °C). A) SEM image depicting the early formation of a crenulated smectite coat (Sme) on the surface of a feldspar grain. B) SEM image illustrating the dissolution and alteration of K-feldspar (KF),

accompanied by the development of smectite (Sme). C) SEM image showing authigenic quartz overgrowth (Qo) co-precipitated with poorly developed authigenic smectite (Sme) on a detrital quartz grain. D-E) SEM images displaying smectite coats covering the entire surface of a detrital quartz grain. The smectite flakes are curled upwards and flatly attached to the surface of the quartz grain. The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra of the smectite coat, indicating Mg-rich smectite.

The formation and development of smectite continued in Exp. 4, conducted at 200 °C. SEM analysis shows the formation of widespread grain-replacive smectite that developed adjacent to and on the surface of a pervasively dissolved detrital K-feldspar (Fig. 8A). The percentage of detrital grains coated by authigenic smectite increased significantly compared to Exp. 3 (Fig. 8B). Additionally, the thickness of the grain-coating smectite on detrital quartz increases (Fig. 8C) and ranges from 6.2 to 25.0 μm (average 15.6 μm) (Table 3). Furthermore, the coating coverage became more uniform, ranging from 50.8% to 76.4%, averaging 63.6% in all the analyzed coated grains (Table 3). Moreover, illitization process of the newly formed smectite begins at this experimental temperature. SEM analysis shows the gradual replacement of the authigenic smectite coat by mixed-layer illite/smectite (Fig. 8D-E), which retained the honeycomb texture of smectite, along with spiny terminations of illite (Fig. 8D-E). EDS analyses indicated that the coat mainly consists of Si, O, Al, Mg, Fe, and K (Fig. 8F). Additionally, XRD results of the <2 μm clay fraction reveal the presence of smectite and mixed-layer illite/smectite (Fig. 6B).

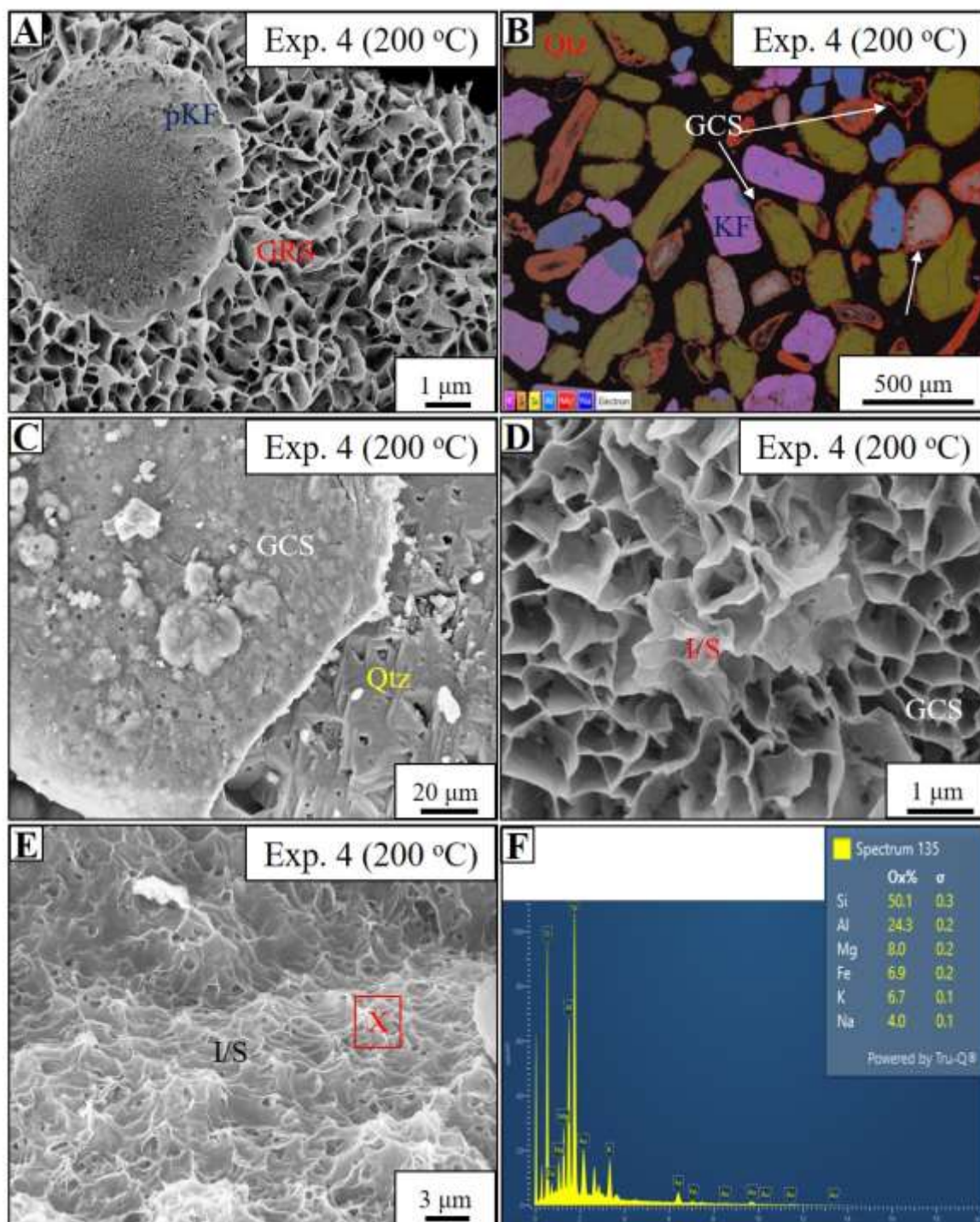


Figure 3.8. Diagenetic characteristics of authigenic clays observed in Experiment 4 (200 °C): A) SEM image showing the formation of grain-replacive smectite (GRS) adjacent to pervasively dissolved K-feldspar (pKF). B) SEM-EDS map and C) SEM image illustrating the development

of grain-coating smectite (GCS) on detrital quartz (Qtz) and K-feldspar (KF). Note the uniform and continuous nature of the coat coverage in B. D) SEM image showing the formation of honeycomb-textured grain-coating smectite (GCS) and mixed-layer illite-smectite (I/S), indicating the initial stages of the illitization process in the authigenic smectite. The clay flakes are strongly curled upward. E) SEM image displaying mixed-layer illite-smectite (I/S) fully coating the surface of a detrital quartz grain. The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra confirming the presence of mixed-layer illite-smectite.

3.4.3.3. *Experiments 5 and 6.*

Both experiments were conducted at 250°C, using the same synthetic fluid solution but with different experimental durations of 336 hours for Exp. 5 and 168 hours for Exp. 6 (Table 1). SEM analysis shows that the illitization of smectite continued in Exp. 5, leading to the partial to complete transformation of smectite into illite (Fig. 9A-C). The newly formed illite mainly resulted from the illitization of smectite and is characterized by aggregated plates of varying sizes with upward spines (Fig. 9A), crenulated curved plates (Fig. 9B), and the honeycomb texture of smectite with spine-like terminations of illite (Fig. 9C). Elemental analyses (EDS) confirmed the presence of illite (Fig. 9D). Illite was predominantly observed as grain-coating (Fig. 9E), with occasional instances of the coats growing outward from adjacent grains and merging to form pore-bridging structures (Fig. 9E). The thickness and coverage of the synthesized clay mineral coatings increased under these experimental conditions. Coat thickness ranged from 10.4 to 49.2 μm (average 29.8 μm), and coverage became uniform across most detrital grains, ranging from 64.9% to 96.2% (average 80.5%) (Table 3). XRD analysis of the clay fraction confirmed the presence of both smectite and illite (Fig. 6C).

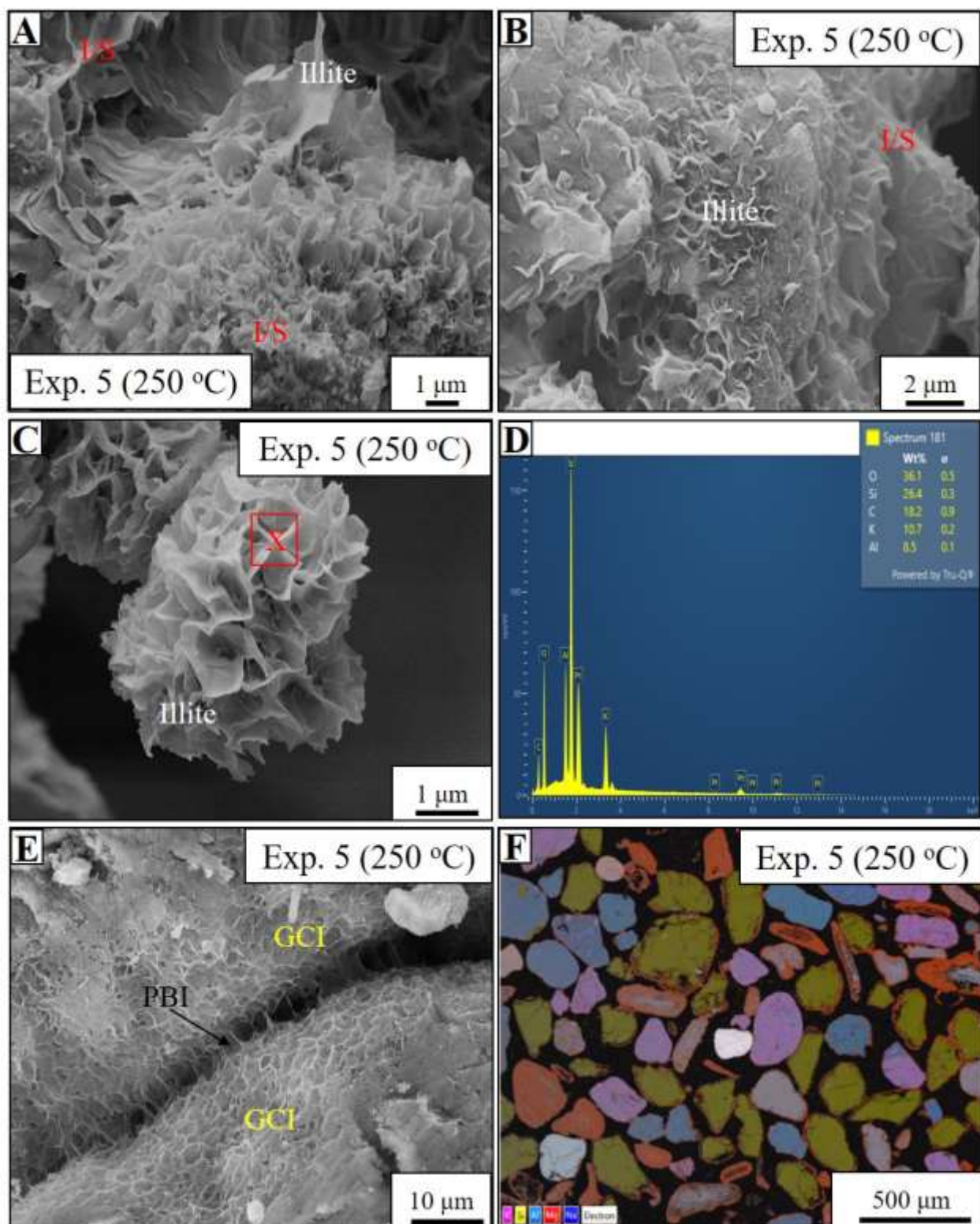


Figure 3.9. Diagenetic illitization of smectite during Experiment 5 (250 °C): A-B) SEM images displaying mixed-layer illite-smectite (I/S) and illite morphologies, from aggregated plates (A) to

crenulated (B), resulting from the complete illitization of smectite. C) The authigenic illite retained the honeycomb morphology characteristic of the illitized smectite. The red X label indicates the point the EDS shown in D was obtained. D) EDS spectra indicating the presence of illite. E) SEM image showing authigenic grain-coating illite (GCI) covering adjacent detrital grains. Note the presence of pore-bridging radial illite (PBI) between the grains. F) EDS map illustrating the degree of clay coat coverage on the detrital grains.

Despite the shorter experimental duration, similar observations were made in Exp. 6. The illitized smectite exhibited only honeycomb morphology and occurred entirely as grain-coating illite. However, coating thickness and coverage were slightly lower than in Exp. 5, with thickness ranging from 9.6 to 30.4 μm (average 20.0 μm) and coverage ranging from 57.6% to 81.3% (average 69.5%) (Table 3). There is increasing coat thickness and coverage with increasing clay fraction (Table 3).

3.4.3.4. Experiment 7.

Although conducted with a different solution than Exp. 5 and 6, results obtained from SEM, EDS, and XRD analyses revealed that similar clay minerals were formed during Exp. 7, which was conducted using estuarine water (Fig. 10). However, the smectite formed is predominantly Al-rich. SEM analyses show the development of grain-replacive smectite adjacent to partially and pervasively dissolved K-feldspar (Fig. 10A-B). The grain-replacive smectite exhibited a honeycomb texture, with upward-curved flakes primarily located at the edges of the dissolved K-feldspar (Fig. 10A). This smectite gradually transformed into mixed-layer illite/smectite (Fig. 10B-D) before being fully illitized (Fig. 10E). EDS analysis confirmed the presence of illite (Fig. 10F). The mixed-layer illite/smectite and illite clays were observed mainly as grain coats (Fig. 10D-E).

The coating thickness ranged from 10.1 to 32.6 μm (average 21.4 μm), and the coat coverage ranged from 57.6% to 81.3% (ave. 69.5%) (Table 3).

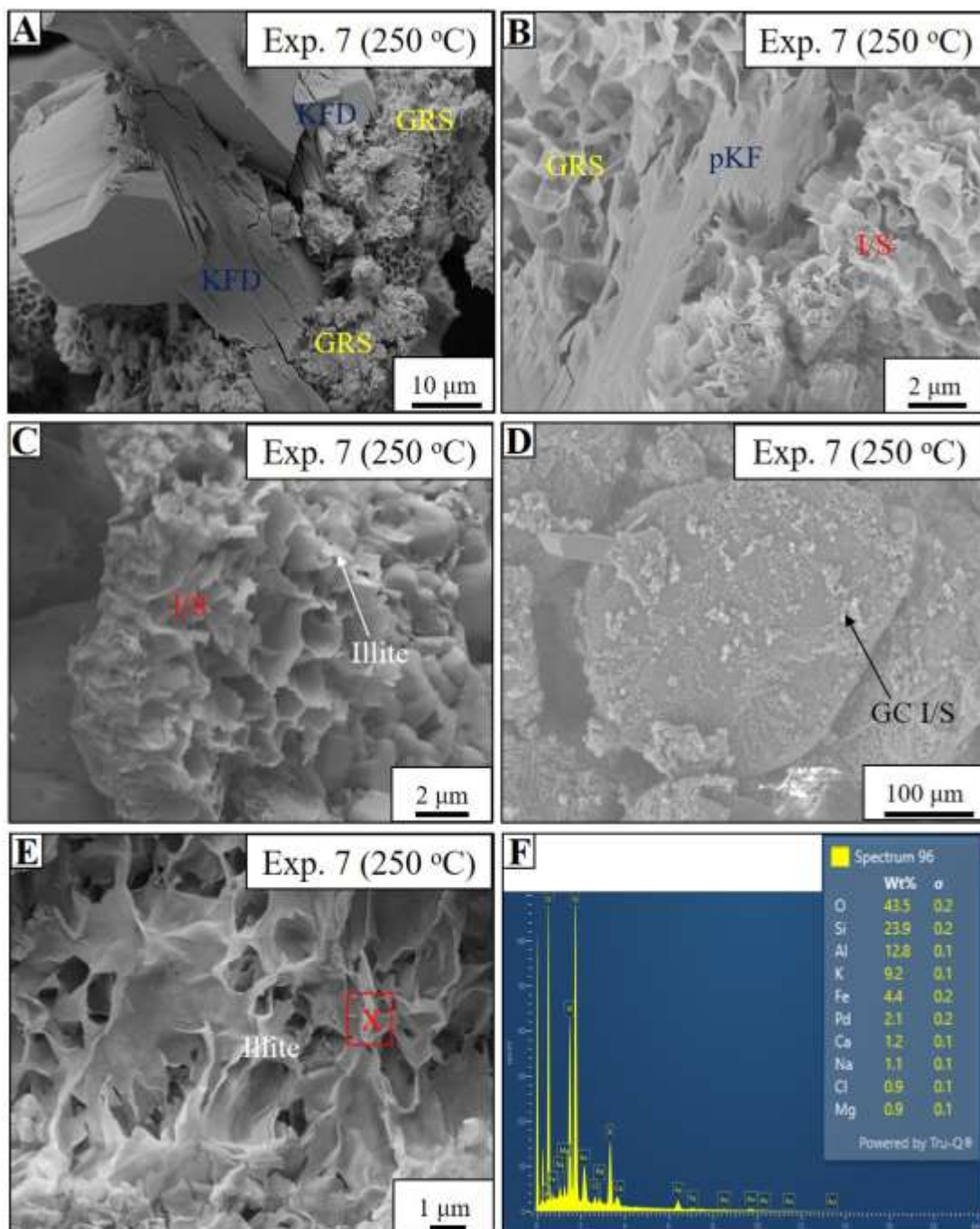


Figure 3.10. Diagenetic features observed in Experiment 7 (250 °C, using estuarine water): A) SEM image showing the partial dissolution of K-feldspar (KFD) and the formation of grain-replacive smectite (GRS). B) SEM image depicting the formation of grain-replacive smectite (GRS) adjacent to pervasively dissolved K-feldspar (pKF). Note the occurrence of mixed-layer illite-smectite (I/S) due to the smectite illitization process. C) Continuous illitization of authigenic smectite led to the development of radial illite adjacent to mixed-layer illite-smectite (I/S). D) Authigenic grain-coating illite-smectite (GC I/S) covering the surface of a detrital quartz grain. E) SEM image showing the complete development of illite transformed from smectite. The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra showing the elemental composition of the identified illite in E.

3.4.3.5. *Experiment 8.*

This experiment was conducted under different chemical conditions from the previous experiments to test the impact of fluid chemistry on the diagenetic alteration of modern estuarine sediments. It utilized a highly alkaline Na_2CO_3 synthetic solution (pH = 11.2) at a temperature of 250 °C for 336 hours (Table 1). Interestingly, none of the clay minerals synthesized in Experiments 1-7 formed under these conditions. Instead, SEM analysis revealed the formation of halite and chabazite (zeolite) minerals (Fig. 11A-E). The early development of halite and acicular chabazite occurred alongside the pervasive dissolution of K-feldspar (Fig. 11A). Halite was characterized by fully developed cubic crystals (Fig. 11B), while chabazite exhibited both stacked acicular crystals (Fig. 11C) and rosette-like morphologies (Fig. 11D–E). While the acicular chabazite occurred on the surface of dissolved K-feldspar, the rosette-like morphology was mostly observed at its edges (Fig. 11E). Elemental (EDS) analyses of the synthesized zeolite showed it was mainly composed of Si, Ca, Na, O, and K (Fig. 11F).

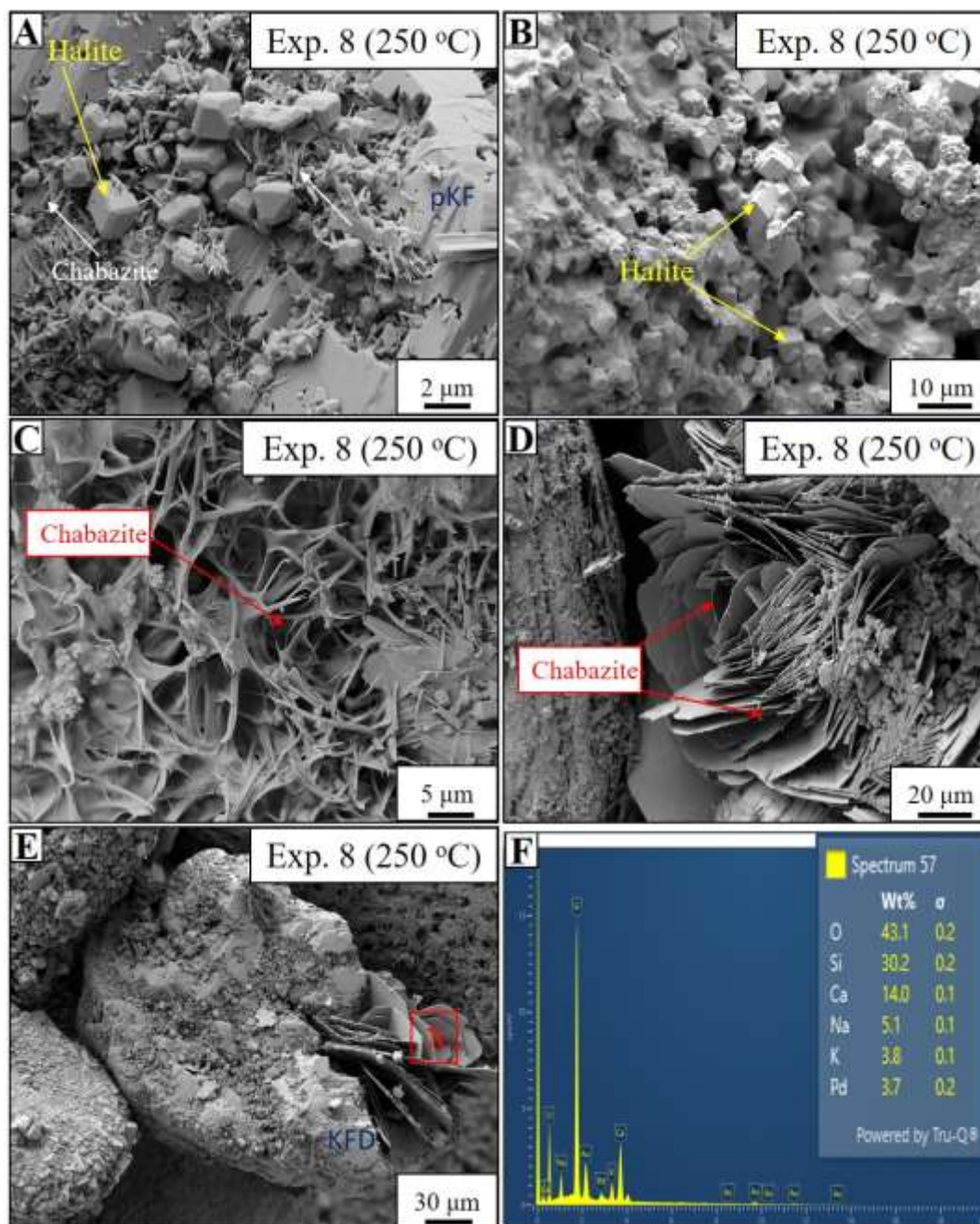


Figure 3.11. Main diagenetic features observed in Experiment 8 (250 °C), using highly alkaline Na_2CO_3 solution (pH = 11.2). A) SEM image showing the pervasive dissolution of K-feldspar (pKF) and the early development of halite and acicular chabazite (zeolite) minerals. B) Formation of fully developed cubic crystals of halite. C-D) SEM images showing the formation of well-developed acicular (C) and rosette-like (D) chabazite (zeolite) mineral. E) SEM image showing

the formation of chabazite at the edge of a dissolving K-feldspar (KFD). The red X label indicates the point the EDS shown in F was obtained. F) EDS spectra showing the elemental composition of identified chabazite in E. Note the absence of smectite and illite, which were observed in previous experiments, highlighting the impact of fluid chemistry on the diagenetic formation of clay minerals.

3.4.4. Fluid Chemistry

Results of the pH and concentrations of major cations (Al, Ca, Fe, Mg, K, Na) in the pre- and post-reacted solutions are presented in Table 4 and Figure 13. The pH values slightly increased in Experiments 1 and 2, but decreased in the subsequent high-temperature experiments (Exp. 3-7), except for Exp. 8, where the pH slightly increased from 11.2 in the pre-reacted solution to 12.6 after the hydrothermal experiment (Fig. 4F). Although aluminum (Al) was not detected in the pre-experiment synthetic fluid, its concentration increased during the experiments conducted with synthetic fluids (Exp. 1-6; Fig. 12A). The concentration rose from 67.2 mg/L in Exp. 1 to 276 mg/L in Exp. 5 (Table 4). A similar trend was observed in Exp. 7, where Al concentration increased significantly from 3.03 mg/L in pre-experiment estuarine water to 495 mg/L in the post-experimental solution (Table 4, Fig. 12A). The concentration of calcium (Ca) also increased significantly with rising experimental temperature (Fig. 12B), likely reflecting the dissolution of carbonate bioclasts from the sediments. In contrast, magnesium (Mg) was consumed during the experiments, as its concentration decreased in all runs except for Exp. 8 (Table 4, Fig. 12C). This is likely due to its incorporation into the newly formed smectites, which commonly take up magnesium during their formation. Iron (Fe) concentrations slightly increased during most experimental runs, except in Exp. 7 (Fig. 12D), likely due to the breakdown of pyrite from the starting material. No clear trend was observed in the concentration of sodium (Na) within the

synthetic fluid and estuarine water experiments (Table 4, Fig. 12E), This is not surprising since Na is not a significant element in the diagenetic products formed from these experiments. However, in the non-marine pore water experiment (Exp. 8), Na was significantly consumed (Table 4), which can be attributed to the formation of halite and chabazite (Table 4), where Na played a prominent role in their mineral structure. The concentration of potassium (K) remained relatively stable in Experiments 1 and 2, it was significantly consumed in Experiments 4, 5, 6, and 7 (Table 4, Fig. 12F), related to the illitization of smectite.

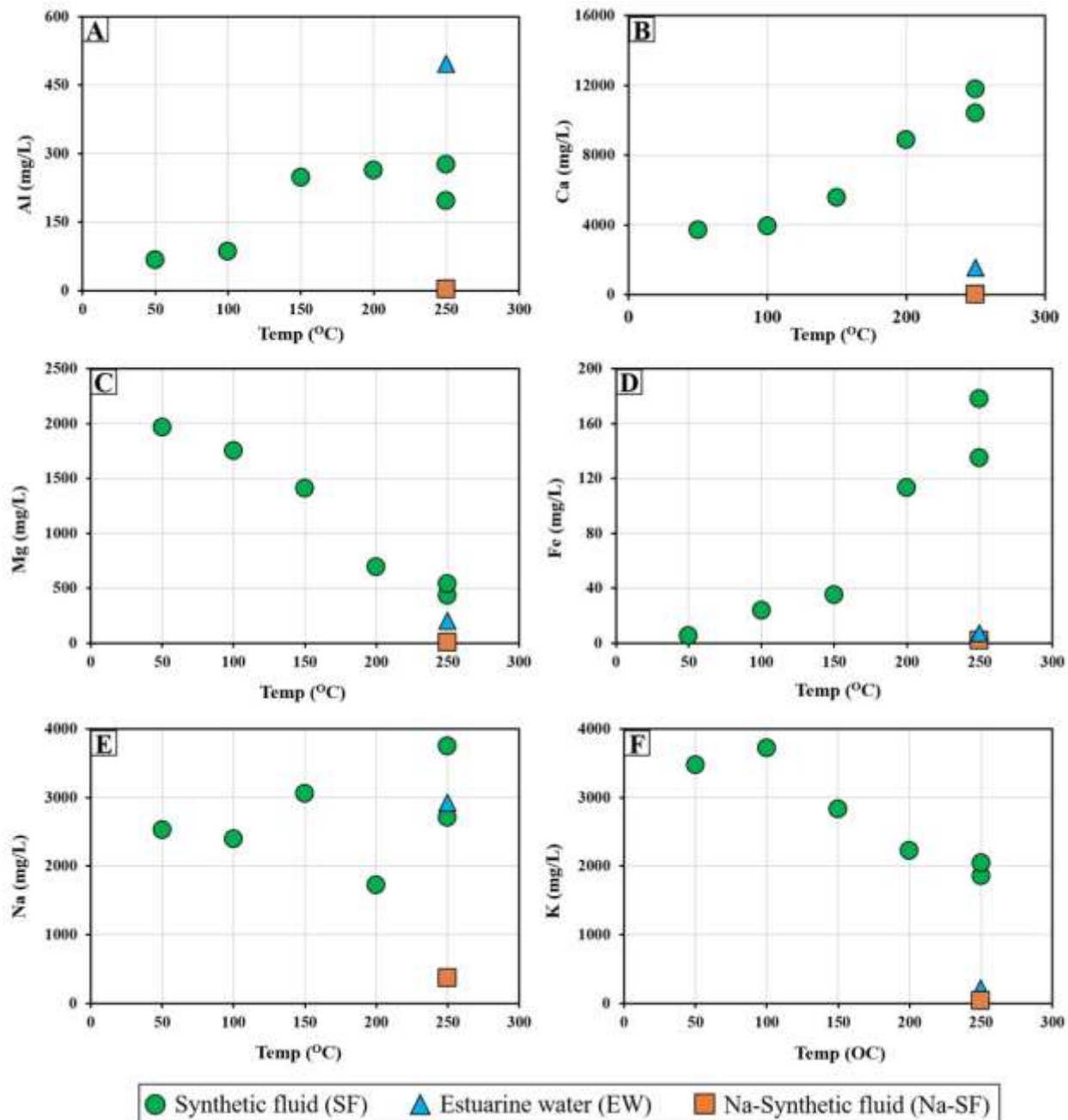


Figure 3.12. Plots of ICP-OES concentrations of Al, Ca, Mg, Fe, Na, and K (in mg/L) versus experimental temperatures in °C, illustrating their evolution with increasing temperature and changes in fluid chemistry. Data points are color-coded according to the brine compositions used in each experiment.

Table 3.4. Results of the ICP-OES analysis showing the concentrations of major cations in solutions before and after the hydrothermal experiments. [Pre-Ex = Pre-Experiment, SF = Synthetic fluid, EW = Estuarine water, Na-SF = Na-rich synthetic fluid, ND = not detected]. Seawater is added for comparison with the composition of the synthetic fluid

Identification		pH	Major cations (mg/L)					
Experiment	Sample ID	pH	Al	Ca	Fe	Mg	Na	K
Pre-Ex. SF	SF@0	5.69	ND	3610	3.9	2160	2100	3930
Pre-Ex. EW	EW@0	7.85	3.03	10.1	3.01	1100	12800	372
Pre-Ex. Na-SF	Na-SF@0	11.2	ND	ND	ND	ND	2285	ND
Exp. 1	SF@50	5.91	67.2	3720	5.43	1963	2525	3480
Exp. 2	SF@100	6.22	86.5	3950	23.5	1750	2400	3720
Exp. 3	SF@150	5.48	248	5570	34.9	1410	3055	2830
Exp. 4	SF@200	5.21	263	8890	113	690	1720	2230
Exp. 5	SF@250_1	4.96	276	11800	178	432	2710	1860
Exp. 6	SF@250_2	5.17	197	10400	135	540	3750	2050
Exp. 7	EW@250	7.02	495	1530	1.92	201	2920	216
Exp. 8	Na-SF@250	12.6	3.41	5.06	6.7	3.06	364	37.1
	Seawater	8.1	2.0	411	2.0	1290	10760	399

3.4.5. 3D Analysis of Synthesized Grain-coat Thickness

The results of SEM and high-resolution FIB-SEM analysis of the synthesized clay mineral coats are displayed in Figure 14. SEM analysis shows that the synthesized grain coatings are continuous and well-developed, coating the majority of the detrital framework grains (Fig. 13A-B). FIB-SEM analysis revealed that the three-dimensional grain coating thickness increases with rising experimental temperature (Fig. 13C-F), consistent with the 2D analysis (Table 3). Additionally, coating thickness is lower in Experiment 6 (Fig. 13C-D) than in Experiment 5 (Fig. 13F), despite being conducted under the same conditions, with Experiment 5 running for twice the duration of Experiment 6.

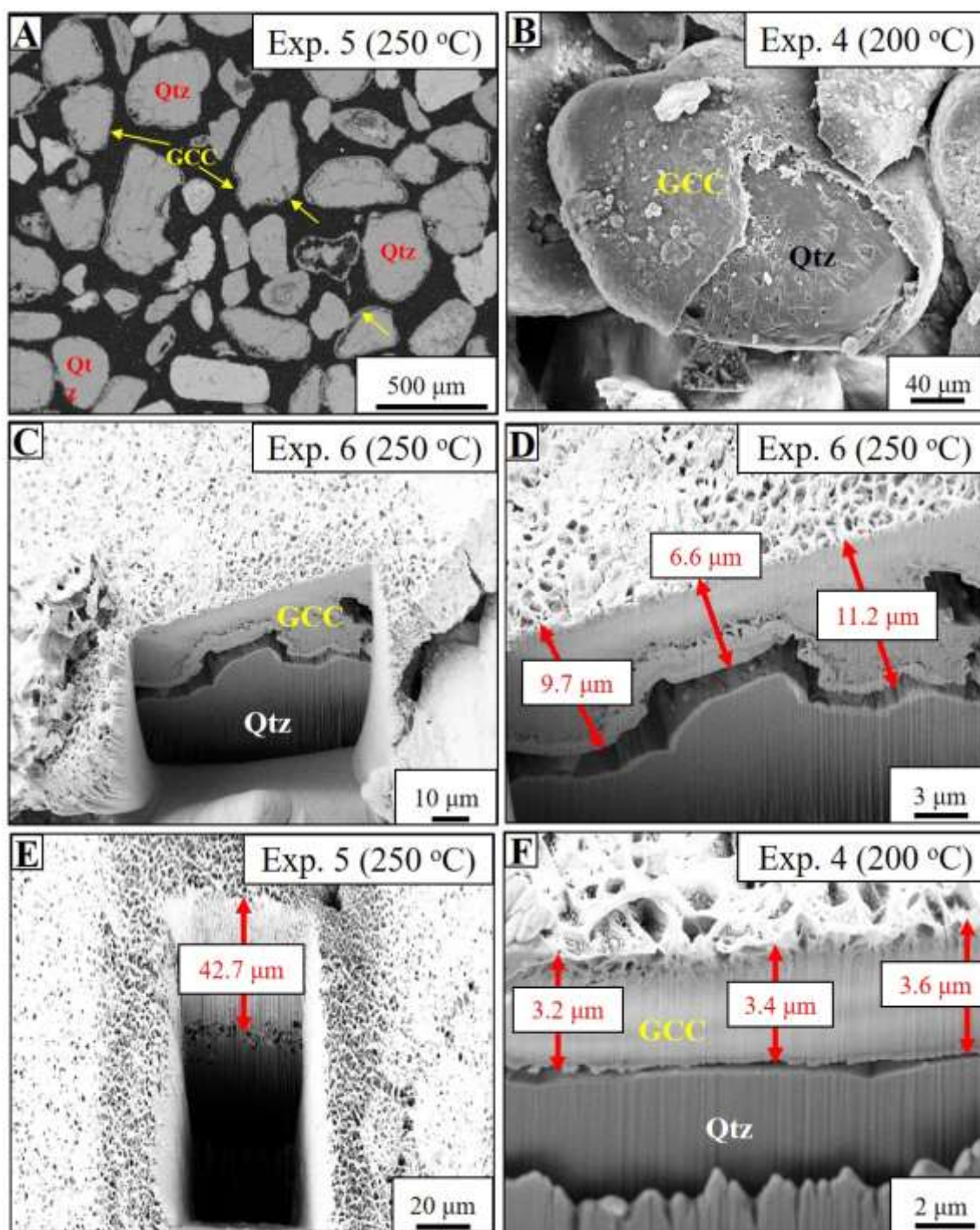


Figure 3.13. Thickness and coverage of the synthesized clay mineral coatings in the hydrothermal experiments. A-B) SEM images showing well-developed and continuous grain-coating clays on detrital grains. Grain-coating clays (GCC) completely cover detrital quartz (Qtz) and inhibit the development of quartz overgrowth. The missing part of the coating in (B) was likely removed

during sample preparation. C-F) FIB-SEM images illustrating the three-dimensional thickness of grain-coating clays across the hydrothermal experiments. The thickness of the grain coatings increases with rising experimental temperatures.

3.4.6. Chemistry of Synthesized Clay Minerals

The structural formulas of the synthesized clay minerals were calculated using their chemistries obtained from EDS analysis. The calculation is further guided by the morphological characteristics of the synthesized clay minerals which aided the elemental analysis of both smectite and illite. The structural formulas of both smectite and illite were calculated based on 12 oxygen atoms. The average composition of the synthesized clay minerals is presented in Table 5. The results revealed that, on average, the amounts of Fe and Mg, in the synthesized smectite decrease with rising experimental temperatures while K increases (Table 5). Conversely, for illite, while the amounts of K increase, Fe and Mg concentrations decrease drastically (Table 5). The Si and total Al contents increased with rising experimental temperature, except in Exp. 6, where a slight drop in Al was observed in smectite (Table 5), likely due to the short experimental duration compared to Exp. 5.

Additionally, the Mg-Al-Fe ternary diagram (Weaver and Pollard, 1973) shows that the synthesized smectites are characterized by varied compositions with respect to the experimental solution and temperature (Fig. 14). The plot indicates that smectite synthesized from synthetic fluid (Exp. 3-6) is predominantly of intermediate composition, tending towards the Mg-rich trioctahedral saponite domain. In contrast, smectite synthesized from estuarine water (Exp. 7) is mainly Al-rich dioctahedral montmorillonite-beidellite, also tending towards an intermediate composition (Fig. 14). Furthermore, a ternary plot of Al-Mg-Fe (Velde, 1985) of the studied clay minerals reveals that the synthesized clays are a combination of dioctahedral (montmorillonite-beidellite), intermediate to trioctahedral (saponite) smectite, and illite (Fig. 15).

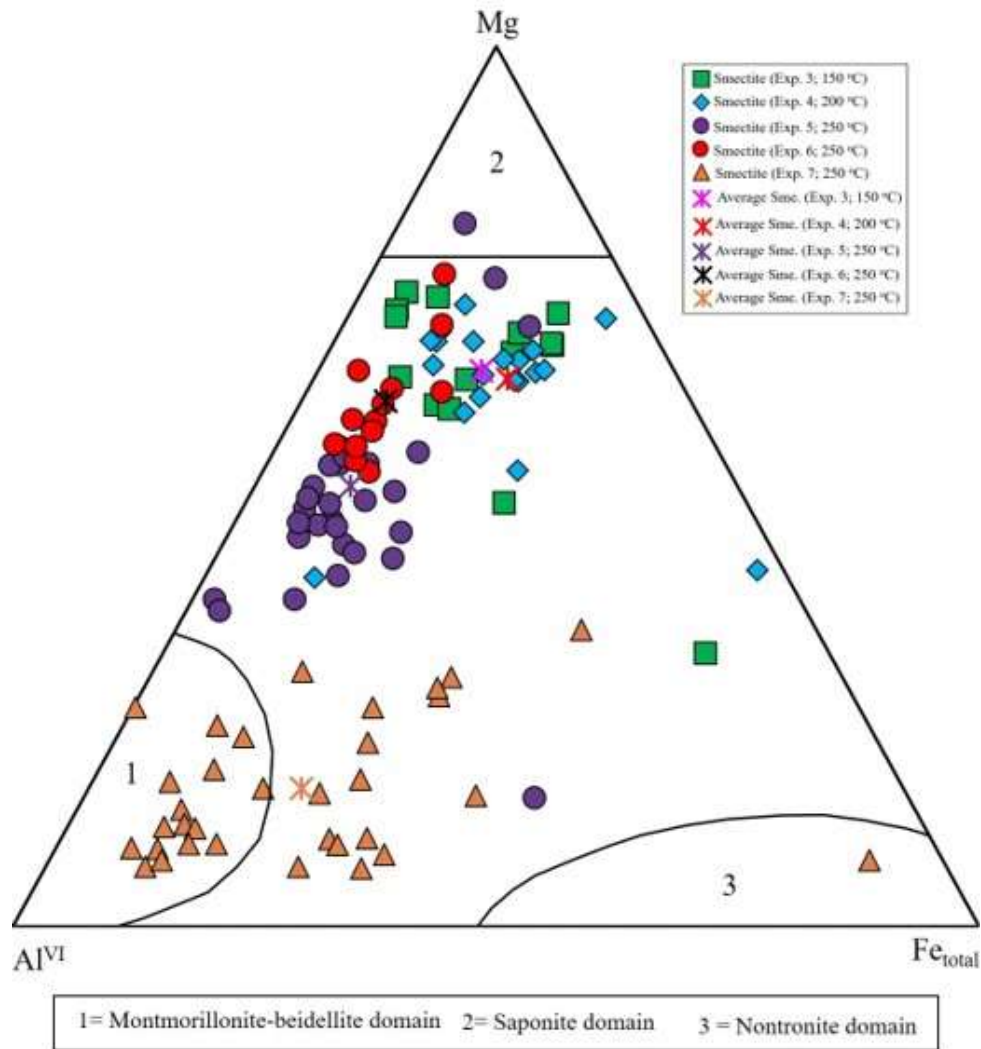


Figure 3.14. Mg-Al-Fe ternary diagram showing the composition and classification of authigenic smectite synthesized during the hydrothermal experiments (adapted from Weaver and Pollard, 1973). The plot reveals that smectite formed from synthetic fluid (Experiments 3–6) predominantly exhibits an intermediate to Mg-rich (saponite) composition, whereas smectite synthesized from estuarine solution (Experiment 8) is mainly Al-rich (montmorillonite-beidellite). As temperature increases, the smectites generally trend from the Mg-rich (trioctahedral) pole toward the Al-rich (dioctahedral) pole

Table 3.5. Mean structural formula of the synthesized smectite and Illite clays, calculated from EDS analyses based on 12 oxygen

		Smectite						Illite		
Element		(Exp. 3; N=15)	(Exp. 4; N=19)	(Exp. 5; N=29)	(Exp. 6; N=11)	(Exp. 7; N=32)	Total (N=106)	(Exp. 5; N=17)	(Exp. 7; N=14)	(Total; N=31)
Structural formula (atoms per formula units; apfu)	Si	3.3	3.6	3.6	3.7	3.7	3.6	2.3	2.3	2.3
	Al ^(IV)	0.2	0.4	0.5	0.3	0.7	0.4	1.2	1.6	1.4
	Al total	0.9	1.0	1.7	1.3	1.9	1.4	2.3	2.5	2.4
	Al ^(VI)	0.7	0.6	1.2	1.0	1.2	0.8	1.1	0.9	1.0
	Fe ²⁺	0.5	0.5	0.2	0.2	0.4	0.5	0.1	0.0	0.1
	Fe ³⁺	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.2	0.1
	Mg	2.2	2.0	1.5	1.9	0.3	1.6	0.3	0.2	0.3
	K	0.0	0.0	0.1	0.2	0.6	0.2	0.6	0.7	0.7
	Na	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
	Ca	0.1	0.1	0.2	0.2	0.5	0.2	0.0	0.0	0.0

atoms

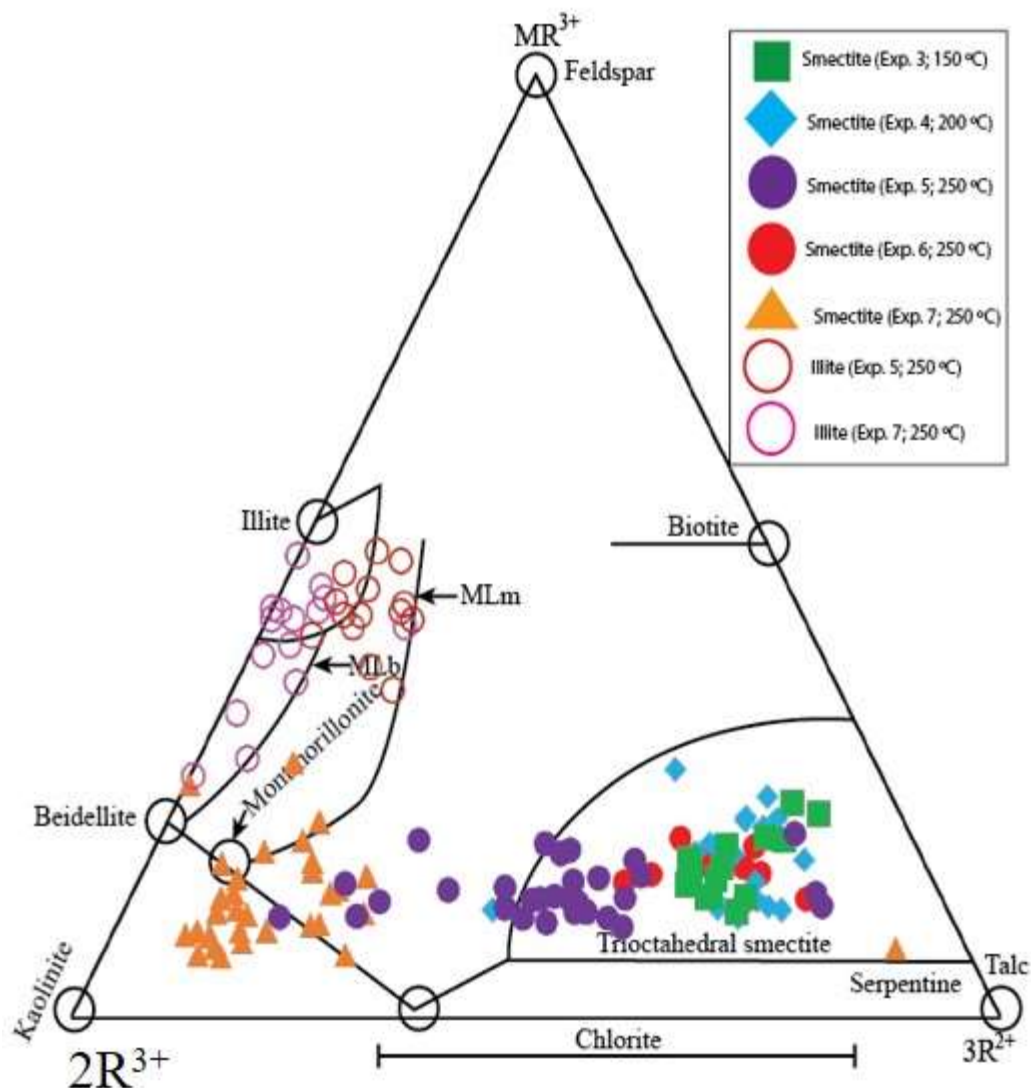


Figure 3.15. MR^{3+} – $2R^{3+}$ – $3R^{2+}$ ternary diagram (adapted from Velde, 1985) showing the transformation of synthesized smectite into mixed-layer illite/smectite and illite clays. [MLm = mixed-layer montmorillonite series; MLb = mixed-layer beidellite series]. MR^{3+} represents trivalent octahedral cations (e.g., Al^{3+} , Fe^{3+}), while $2R^{3+}$ and $3R^{2+}$ denote the sums of normalized octahedral cations. The diagram highlights the balance between Al^{3+} , Mg^{2+} , Fe^{2+} , and Fe^{3+} in octahedral sheets, aiding in clay mineral classification.

3.5. Discussion

3.5.1. Controls and Mechanisms of Authigenic Smectite Formation

Smectite is the primary diagenetic mineral phase synthesized in this study (Table 3; Figs. 8-11). The authigenic formation of smectite requires sources of silica and Al^{3+} , Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+} cations (McKinley et al., 1999). This study demonstrates that the dissolution of unstable detrital minerals, including K-feldspar, carbonate bioclasts, and detrital clay coats (kaolinite and illite), begins at 100 °C (Table 3), and preceded the precipitation of authigenic smectite at 150 °C (Fig. 7). This suggests that the essential silica for precipitation was supplied via the dissolution of K-feldspar and detrital kaolinite, facilitated by the mildly acidic conditions of the synthetic solution used in Experiments 1-6 (pH 5.69). The required Mg was sourced from the experimental solution, as evidenced by the decrease in Mg concentration with increasing temperature in the post-reacted solutions (Table 4; Fig. 12C). Additionally, the amount of authigenic smectite increased with rising experimental temperatures (Table 3; Figs. 8-11), which is further corroborated by the consumption of Mg and Fe (in EW) from the experimental solutions and the release of Al (Table 3; Fig. 12). The composition of authigenic smectite varies based on the silica supply and the chemistry of pore fluids in natural diagenetic systems (Wise et al., 2001; Deer et al., 2013). The Al-Mg-Fe ternary plot (Fig. 14) shows that experiments conducted with Mg-rich synthetic fluid (Exp. 1–6) resulted in the authigenic formation of Mg-rich smectites of intermediate compositions, falling within the montmorillonite-saponite distribution field (Figs. 14-15). The smectites precipitated in Exp. 3–4 were more Mg-dominant, and plot within the saponite domain (Figs. 14-15). As temperature increased in Exp. 5-6, the smectite composition shifted towards an intermediate phase (Fig. 14). This is due to the incorporation of Mg from the reaction fluid, given the insufficient amount of Al at the start of the experiments. However, the increase in temperature accelerates the rate of K-

feldspar dissolution, and the potential increase of Al in the reacting fluid leads to the formation of smectite of intermediate composition (Figs. 14-15). This interpretation is further supported by the quantified increase in Al and decrease in Mg within the structural formula of smectites with increasing temperature (Table 5). Conversely, Exp. 7, conducted with natural estuarine water with low Mg concentration, yielded predominantly homogeneous dioctahedral montmorillonite, with occasional intermediate compositions (Figs. 14-15). The variation in smectite composition was illustrated in Fig. 14, showing the transition from dioctahedral to trioctahedral smectites, similar to the observations of Boles and Franks, (1979). The results of this study align with the findings of Hajash and Bloom, (1991), who also precipitated Mg-rich smectite from the dissolution of feldspathic sand at 200 °C using artificial seawater. Additionally, the required Ca and Na, incorporated as interlayer cations in the precipitated smectites (Fig. 7F), were sourced from the reaction fluid, with Ca also derived from the dissolution of carbonate bioclasts (Table 4). Moreover, the precipitation of quartz overgrowth in Exp. 3 (Fig. 7C) suggests that the dissolution of K-feldspar and detrital kaolinite may have significantly contributed to the silica supply that precipitated as quartz cement.

The synthesized authigenic smectites in this study exhibit morphological and chemical similarities to those observed in natural sandstone reservoirs. For instance, honeycomb-shaped authigenic smectites have been identified as grain coatings in the shallow part of the Lower Cretaceous Tuscaloosa Sandstone, USA (Pittman et al., 1992). Additionally, experiments conducted by Hajash and Bloom (1991) and Haile et al. (2015) produced honeycomb authigenic smectites coating the surfaces of detrital clean feldspar and quartz grains at temperatures ranging from 150 to 200 °C, comparable to the temperature range employed in this study (Table 1). Chemically, the synthesized smectites in this study closely resemble those reported in the Neogene marine sandstones of the

Nantani Formation, Niigata Basin, Japan (Niu et al., 2000). In our study, the silicon (Si) and total aluminum (Al) contents of the neoformed smectites range from 3.3 to 3.7 (average 3.6) and 0.9 to 1.9 (average 1.4) atoms per formula unit (afu), respectively. By comparison, the smectites from the Nantani Formation have Si and total Al contents ranging from 3.5 to 3.9 (average 3.6) and 1.8 to 2.1 (average 1.9) afu. However, a notable distinction lies in the magnesium content. While our synthesized smectites exhibit a Mg content of 0.3–2.2 (average 1.6) afu, the smectites from the Nantani Formation have a significantly lower Mg content of 0.2–0.7 (average 0.3) afu. The relatively high Mg content observed in this study is consistent with findings from Mg-rich smectites in the Neogene Tajo Basin, Iberian Peninsula, Spain (García-Romero et al., 2021). In the Tajo Basin smectites, Mg content ranges from 0.4 to 5.8 (average 2.6) afu, providing further evidence that the chemical composition of synthesized smectites in this study reflects conditions observed in Mg-enriched natural systems. Although authigenic smectite coats in natural systems typically form at lower temperatures (<100 °C), the findings of this study contribute to understanding smectite authigenesis in sandstones. The higher experimental temperatures used here facilitate accelerated reaction kinetics, enabling the replication of diagenetic processes within a shortened timeframe, as opposed to the extended geological timescales over which such transformations naturally occur.

The formation of authigenic smectite occurs through different mechanisms in natural diagenetic systems. Solid-state transformation (SST) and dissolution-crystallization (DC) are the main mechanisms identified for the authigenic formation of smectite during burial (Divis and McKenzie, 1975; Boles and Franks, 1979; Nadeau et al., 1985; Hajash and Bloom, 1991; Lanson et al., 2009). While SST involves the gradual replacement of a precursor, DC involves the dissolution of the precursor material in the pore fluid and the subsequent precipitation of smectite. Our observations

indicate that the formation of authigenic smectite from detrital precursors results from DC. XRD (Table 3; Fig. 6) analysis revealed the complete dissolution of detrital clay coat fragments (kaolinite and illite) before the initial nucleation of smectite coats at 150 °C (Fig. 7A), providing the initial silica required for early smectite precipitation. Additionally, K-feldspar dissolution began above 50 °C and continued throughout the experimental temperatures. This further enriched the reaction fluids with essential silica and cations, enhancing the authigenic formation of smectite coats. This interpretation is supported by the development of smectite coats on clean quartz surfaces, precipitating from the reaction fluid after K-feldspar and detrital coats dissolution (Fig. 8C). This aligns with the findings from Haile et al. (2015), who reported the authigenic formation of smectite coats on clean quartz surfaces with honeycomb morphology, akin to those produced in this study. The thickness and surface coverage of the synthesized smectite increased with rising temperatures, becoming more uniform as K-feldspar concentrations decreased (Table 3, Figs. 9–10). This trend suggests that the dissolution-crystallization mechanism intensified with increasing temperature.

3.5.2. Illitization of Smectite

Authigenic smectites are highly unstable under elevated temperatures and transform into illite through intermediate stages during progressive burial (Pytte and Reynolds, 1989; Lynch, 1996; McKinley et al., 1999; Deer et al., 2013; Ulmer-Scholle et al., 2015; Taylor et al., 2022; Bello et al., 2023; Busch et al., 2024). This study demonstrates that smectite undergoes varying degrees of illitization through a mixed-layer illite/smectite phase, as evidenced by SEM (Figs. 10-11), EDS (Figs. 10D & 11F), and XRD (Table 3; Fig. 6B-D) analysis. The smectite-to-illite transformation initiates at temperatures above 70 °C and becomes widespread with increasing temperature in natural diagenetic systems, reaching near-completion at temperatures above 200 °C (Eberl and

Hower, 1977; Klopogge et al., 1999). Additionally, the transformation of smectite into illite is strongly influenced by the availability of K^+ , which plays a crucial role in the process. However, this transformation is only possible when there is an increase in the layer charge, principally in the tetrahedral layer, due to the loss of silica. The increased layer charge allows K^+ to replace Ca^{2+} and Na^+ in the interlayer spaces of smectite, stabilizing the structure and facilitating the formation of illite. (Boles and Franks, 1979; Huang et al., 1993; Wise et al., 2001; Mosser-Ruck and Cathelineau, 2004; Ferrage et al., 2011). In natural sedimentary systems, the required K^+ is often sourced from migrating fluids or the dissolution of potassium-rich minerals like K-feldspars (Lanson et al., 2002; Franks and Zwingmann, 2010; Bjørlykke, 2014; Khan et al., 2023; Bello et al., 2024). In this study, the required K^+ was likely supplied by both the dissolution of K-feldspar and the experimental fluids. This is supported by the increase in K concentration in the reaction fluid during Exp. 1-2 (Table 4), which corresponds to the period of K-feldspar dissolution and the rapid depletion of K^+ during Exp. 4-7, which coincides with the onset of the illitization process (Table 4; Figs. 8-11).

The illitized smectite displayed honeycomb morphology, characterized by filamentous terminations, indicating that the precursors were replaced by illite (Figs. 10A-C & E). Although the illitization of smectite is widely reported to occur through dissolution-crystallization (DC) (Wilson and Pittman, 1977; Nadeau et al., 1985; Nadeau and Bain, 1986; Whitney and Velde, 1993; Altaner and Ylagan, 1997; Guillaume et al., 2004; Lanson et al., 2009; Ferrage et al., 2011), solid-state transformation (SST) has also been documented (Bell, 1986; Lindgreen and Hansen, 1991). The illite observed in this study mostly maintained the honeycomb morphology of the precursor smectite (Figs. 10C & E), a characteristic commonly attributed to SST (Elliott et al., 1991). However, spiny terminations of illite are observed adjacent to poorly organized

illite/smectite with ragged honeycomb morphology (Figs. 10A & B), suggesting the early dissolution of the honeycomb smectite and its subsequent illitization. Additionally, Putnis, (2009) has shown that it is possible for precursor minerals to retain their morphology under DC transformation. Also, experiments conducted by Ferrage et al., (2011) support the interpretation of the smectite illitization reaction as a dissolution/precipitation process. Thus, the smectite-to-illite transformation in this study is most likely due to DC rather than SST, or a combination of both.

The dissolution of smectite and its subsequent illitization released silica and cations such as Ca, Mg, Na, and Fe as by-products, which could potentially be utilized for other diagenetic reactions under favorable conditions (Boles and Franks, 1979; Worden and Morad, 2009; Bello et al., 2023a, 2023c). This process may have played a role in the formation of quartz overgrowths observed in this study (Fig. 7C). While Al-rich dioctahedral smectite (montmorillonite) is associated with transformation to illite during progressive burial (McKinley et al., 1999; Taylor et al., 2022), Mg-rich trioctahedral smectite (saponite) is generally thought to transform into chlorite (Worden and Morad, 2009). In this study, the synthesized authigenic smectite had a mixed composition of Al-rich and Mg-rich smectites (Fig. 14), both of which transformed into illite at 250 °C (Figs. 10-11). The illitization of Mg-rich smectite, rather than chloritization, can be attributed to the high concentration of K^+ in the reaction fluid, coupled with lower Fe availability under elevated temperatures and the short experimental duration. Further experimentation with longer durations and higher Fe concentrations in the fluid is necessary to explore the potential for chloritization of Mg-rich smectite.

Previous laboratory experimental studies on the conversion of smectite to illite have predominantly utilized bentonites such as MX80 Wyoming bentonite or the SWy-2 reference montmorillonite from the Source Clay Repository of The Clay Minerals Society (Altaner and Ylagan, 1997;

Ferrage et al., 2011; Inoue et al., 2005; Mosser-Ruck et al., 2001; Mosser-Ruck and Cathelineau, 2004). While these studies have provided valuable insights, they primarily rely on highly standardized materials that may not fully capture the complexity of natural sedimentary systems. This study represents the first attempt to constrain the controls on the illitization of smectite using natural, modern sediments that are largely free from weathering, serving as an analog for burial diagenesis.

3.5.3. Impact of Fluid Chemistry on the Diagenetic Alteration of Modern Estuarine Sediments

Fluid-rock interaction plays a crucial role in burial diagenesis (Whitney, 1990), and the composition of the fluid used in experimental diagenesis strongly influences the type and composition of synthesized mineral phases (Mosser-Ruck et al., 2001). Our study utilized three distinct fluids of variable composition and pH (Tables 1 & 4): a 0.1 M solution of CaCl_2 , NaCl , MgCl_2 , and KCl (SF1, pH 5.69), natural estuarine water (EW, pH 7.89), and a highly alkaline 0.1 M Na_2CO_3 solution (SF2, pH 11.20). This resulted in the formation of different mineral phases, as detailed in this study.

Both SF1 and EW facilitated the authigenic formation of smectite coatings, which then progressively transformed into illite with increasing temperature (Figs. 9-11). However, there were slight differences in the chemical composition of the synthesized smectites (Fig. 14). The Mg-rich synthetic fluid (SF1), enriched in Mg, Ca, K, and Na, resulted in smectites that were more Mg-rich and of intermediate composition compared to those formed in natural estuarine water (EW) (Fig. 14). In contrast, the EW, with lower Mg concentrations, predominantly produced Al-rich dioctahedral smectites (Figs. 14-15). This variation is interpreted to be linked to the relatively lower amount of Al and the very high amount of Mg in SF1, forcing the incorporation of Mg into

the smectite structures to maintain charge balance and structural integrity. This finding highlights the importance of Mg in the authigenic formation of smectite under limited Al conditions (Harder et al., 1972). Additionally, a slight decrease in pH was observed in experiments conducted with SF1 and EW (Exp. 1-7) as the experimental temperature increased (Table 4). This decrease is attributed to the release of silica during the dissolution of K-feldspar and detrital kaolinite and the subsequent illitization of smectite. During the illitization process, silica is released into the solution as silicic acid ($\text{Si}(\text{OH})_4$). Silicic acid, being a weak acid, can partially dissociate into hydrogen ions (H^+) and silicate anions (H_3SiO_4^-), thereby increasing the concentration of H^+ ions in the solution and lowering its pH.

In contrast to the authigenic smectites developed using SF1 and EW, the experiment conducted using highly alkaline Na-rich synthetic fluid (SF2) resulted in the formation of completely different mineral phases: halite and chabazite (zeolite) (Fig. 11). This observation highlights the influence of fluid composition on diagenetic pathways. Non-marine pore waters are often NaHCO_3 dominated, and this experiment underscores how sediments exposed to such fluids, compared to those in marine settings, can follow distinctly different diagenetic pathways. Generally, zeolite cements are relatively uncommon in sandstones (Taylor et al., 2022), and chabazite is even rarer compared to other zeolites like analcime and laumontite (Ulmer-Scholle et al., 2015; Mallette et al., 2024). However, where zeolites are reported in petroliferous basins, they tend to have a significant impact on reservoir quality (Iijima, 2001; Sun et al., 2014; Zhu et al., 2020; Lin et al., 2024).

Chabazite typically forms in highly alkaline environments where the pH of pore fluids is above neutral (>7) (Wang et al., 2020; Mallette et al., 2024), and it is mostly associated with volcanoclastic sandstones and hydrothermal systems (Iijima, 2001). Its formation is facilitated by

silica activity and the concentrations of Na, Ca, K, and Al (Montagna et al., 2010; Mallette et al., 2024). This study has shown the formation of chabazite under highly alkaline conditions (pH 11.20, Exp. 8). The authigenic chabazite exhibited an acicular morphology when it formed on the surface of dissolved K-feldspar (Fig. 11A) and developed concurrently with halite (Fig. 11A). However, chabazite formed on the edges of K-feldspar displayed a rosette-like morphology. The silica and K required for chabazite formation are believed to have originated from the dissolution of K-feldspar, similar to what is reported in natural systems (Iijima, 2001; Montagna et al., 2010). The required Na and Ca are sourced from the reaction fluid and the dissolution of carbonate bioclasts, respectively.

The morphology and chemistry of the synthesized chabazite in this study resemble those reported in the Tertiary lacustrine Tuzgolu Basin, Turkey. (Karakaya et al., 2015). Notably, despite using similar starting materials, none of the minerals synthesized in Exp. 1-7 were observed in Exp. 8, and vice versa (Figs. 8-12). This variation is attributed to the differences in fluid chemistry between the experiments, emphasizing the critical role of fluid composition in simulating burial diagenesis in modern sediments.

Experimental studies of smectite formation from feldspar-rich precursors using Mg-rich synthetic solutions, similar in composition to those used in our study by Haile et al., 2015, have yielded honeycomb-like smectite on the surfaces of clean quartz and feldspar grains, resembling the morphologies observed in this work. Additionally, Hajash and Bloom (1991) utilized artificial seawater as the fluid medium to synthesize smectite from feldspar precursors. The Mg-rich synthetic solution in their study contained elevated concentrations of magnesium and other dissolved ions, simulating marine conditions. In contrast, in addition to the Mg-rich synthetic solution, our study utilized natural estuarine water, which has a distinct ionic composition

influenced by the mixing of freshwater and seawater, including variations in salinity and TDS. The use of natural estuarine water to simulate burial diagenesis in modern estuarine sandstone is a novel approach reported for the first time in this study, providing a unique perspective on the diagenetic processes in such environments.

3.5.4. Implications for Reservoir Quality

Sandstone reservoir quality (porosity and permeability) typically decreases with increasing burial depth (Worden and Burley, 2003; Ajdukiewicz and Lander, 2010; Morad et al., 2010a; El-Ghali et al., 2024). After compaction, the predominant factor for porosity and permeability reduction in sandstone reservoirs during deep burial and heating is the emergence of quartz cementation (McBride, 1989; Ehrenberg, 1993; Walderhaug, 1996; Lander and Walderhaug, 1999; Walderhaug and Porten, 2022). Yet, a notable percentage of these deeply buried reservoirs exhibit unexpectedly high levels of porosity and permeability (Bloch and McGowen, 1994; Bello et al., 2023b). The preservation of such unusual porosity and permeability is often attributed to the presence of grain-coating clays, which prevent the formation of porosity-decreasing cement (Ehrenberg, 1993; Anjos et al., 1999; Ajdukiewicz and Larese, 2012; Al-Ramadan et al., 2013b, 2013a; Al-Ramadan, 2014b, 2014a). Authigenic clays such as chlorite, smectite, mixed-layer illite/smectite, and illite significantly influence sandstone reservoir quality depending on their mode of occurrence. For instance, while pore-filling smectite negatively affect reservoir quality by obstructing pore throats (McKinley et al., 1999; Worden and Morad, 2009), grain-coating smectite has been identified as an early diagenetic cement that inhibits the nucleation of quartz cementation in various sandstone reservoirs, thus preserving porosity and permeability (Carrigy and Mellon, 1964; Wilson and Pittman, 1977; Davies et al., 1979; Orhan, 1992; Wise et al., 2001; Ehrmann et al., 2005). During progressive burial, authigenic smectite transforms into mixed-layer illite/smectite and ultimately

illite (McKinley et al., 1999), occurring mostly as grain-coating (Storvoll et al., 2002; Franks and Zwingmann, 2010; Al-Ramadan et al., 2013a; Busch et al., 2024) and pore-bridging (Al-Ramadan et al., 2004; Priestas and Wise, 2007).

This study has shown the authigenic formation of smectite, mixed-layer illite/smectite, and illite grain coats from the reacted sandy intertidal flats in modern estuary sediments (Figs. 8-11). These grain coatings are present on the majority of the detrital framework grains, with thicknesses ranging from 1.9 μm to 42.9 μm , and their coverage spanning 24.3% to 96.2% (Table 3). At experimental temperatures above 150 $^{\circ}\text{C}$, the grain coats became well-developed, and their thickness and coverage increased with rising experimental temperature (Table 3, Figs. 8-11). The effectiveness of clay coatings in retarding the nucleation of quartz overgrowth and preserving reservoir quality in sandstones has been attributed to their thickness and completeness (Lander and Walderhaug, 1999; Anjos et al., 1999; Ajdukiewicz and Larese, 2012; Charlaftis et al., 2021). Consistent with these observations, the thickness and coverage of the synthesized grain coats are sufficient for preserving reservoir quality. Thus, quartz overgrowth was not observed where grain coats were fully developed at temperatures above 200 $^{\circ}\text{C}$.

Furthermore, this study has shown the authigenic formation of quartz overgrowth on detrital quartz grains where clay coatings are poorly developed (Fig. 7C), which, if continuous, may encroach on pores and occlude intergranular porosity, thereby decreasing reservoir quality. Moreover, pore-bridging illite was observed growing within the pore spaces of adjacent grain-coated grains (Fig. 9E), further contributing to the occlusion of intergranular porosity. Therefore, the diagenetic alteration of modern estuarine sediments leads to the formation of authigenic smectite and its subsequent illitization, significantly influencing reservoir quality.

Although recent research has explored the factors influencing the occurrence and distribution of detrital grain coatings in modern marginal marine environments (e.g., Wooldridge et al., 2017a, 2017b, 2018, 2019; Griffiths et al., 2018, 2019a, 2019b; Virolle et al., 2019a, 2019b, 2020, 2021, 2022; Simon et al., 2021; McGhee et al., 2022; Muhammed et al., 2022), this study is, to our knowledge, the first to experimentally simulate the diagenetic alteration of these sediments. It specifically investigates the role of detrital precursors in the formation of authigenic clay coatings in modern estuarine sediments. Moreover, this research provides the first three-dimensional (3D) quantification of coating thickness using focused ion beam-scanning electron microscopy (FIB-SEM). This advanced technique enables detailed characterization of the spatial distribution and variability of clay coatings, which are critical for understanding their three-dimensional characteristics. The results serve as a pilot study for investigating clay coatings in sandstone reservoirs, offering valuable insights for developing predictive models of reservoir quality in the context of energy exploration and transition.

The experimental conditions applied in this study successfully demonstrated the authigenic formation of clay coatings similar to those found in natural systems. Similar approaches could be utilized to better constrain the physicochemical conditions necessary for the diagenetic transformation of detrital clay coats into authigenic coats in various sub-environments within marginal marine sediments, thereby improving the reliability and quality of reservoir prediction models, which are critical for energy exploration and transition.

3.5.5. Limitations of the Study and Future Work

The present study demonstrates that the synthesized grain-coating smectite and its subsequent illitization closely resemble those observed in natural systems, showing similar morphology, texture, and composition. This similarity suggests that detrital framework grains and detrital grain-

coat aggregates in modern sediments could be significant precursors for the formation of smectite coats in various natural systems under suitable conditions. The authigenic formation of smectite in sandstones is driven by the dissolution of unstable detrital minerals such as K-feldspars, detrital grain-coating clays, and the chemistry of pore fluids (Kloprogge et al., 1999; McKinley et al., 1999; Ulmer-Scholle et al., 2015), similar to the conditions simulated in this study. However, the authigenic formation of smectite coats typically occur at shallow burial depths and low temperatures in natural systems (Wise et al., 2001; Priestas and Wise, 2007), eventually transforming into illite and/or chlorite during progressive burial and temperature increase (Perry and Hower, 1970; Taylor et al., 2022).

Although the physicochemical conditions used in this study were designed to closely mimic reservoir conditions and simulate burial diagenesis, there are still differences and limitations. Natural diagenetic conditions cannot be fully replicated through hydrothermal experiments because, in natural systems, the authigenic phases observed in this study develop over prolonged geological timeframes, with complex fluid compositions and/or lower temperature conditions than those used in this study. Here, elevated temperatures are used to accelerate reaction rates, enabling the observation of reactions that would typically occur over millions of years at lower temperatures within experimental timespans of hours. Nevertheless, the experimental approach presented here demonstrates the authigenic development of smectite coatings and their subsequent illitization from modern detrital precursors.

Additional studies are needed to constrain the impact of fluid chemistry on the formation of smectite and its illitization from modern detrital precursors. This will involve using fluid compositions similar to different natural environments, such as typical river or non-marine water,

normal seawater, and brines with variable total dissolved solutes. Future experiments should also explore different fluid-rock ratios, pH levels, and setups that allow for in-situ fluid sampling to analyze the chemical conditions that favor smectite coat formation. Additionally, experiments with longer durations and fluids containing lower K but higher Fe concentrations could help determine whether the synthesized trioctahedral smectite transforms into chlorite. Finally, conducting hydrothermal experiments with sediments from diverse sub-environments in modern estuaries will clarify the role of detrital clay coat distribution in authigenic clay formation, improving predictions of reservoir quality in marginal marine sandstones.

3.6. Conclusions

- A series of hydrothermal experiments simulating burial diagenesis were conducted using quartz-feldspathic modern sediments from the sandy intertidal flat of the Anllóns Estuary, NW Spain, as the starting material. The experiments were performed under varying fluid compositions and temperature stages. The dissolution of K-feldspar and detrital clay coatings began at lower temperatures, preceding the authigenic formation of smectite coatings between 150°C and 250°C. Authigenic smectite formed over an experimental duration of 168–336 hours in both Mg-rich synthetic fluid (pH 5.69) and natural estuarine water (pH 7.85).
- The Mg-rich synthetic fluid produced smectites with a high Mg content and intermediate composition, tending towards trioctahedral saponite, while the estuarine water synthesized Al-rich dioctahedral montmorillonite, due to the lower Mg concentration in natural estuarine water. Both smectites were transformed into illite through a mixed-layer illite/smectite phase as temperature increased ($> 200^{\circ}\text{C}$), with the required K^{+} supplied by the dissolution of K-feldspar and the reacted solutions.

- The authigenic formation of smectite and its subsequent illitization occurred via a dissolution-crystallization mechanism. These processes released abundant silica into the solution, which facilitated the nucleation of quartz overgrowth on detrital quartz grains where authigenic clay coatings were poorly developed.
- The resulting authigenic grain coatings are chemically and morphologically similar to those found in buried sandstones. These coatings cover most of the detrital quartz and feldspar grains. The thickness of the coatings increases from 1.9 μm to 49.2 μm , while surface coverage expands from 24.3% to 96.2% with increasing temperature. These coatings are sufficient to potentially inhibit the nucleation of quartz overgrowth in buried sandstones, thereby preserving reservoir quality.
- The experiments conducted with Na-rich synthetic fluid (pH 11.20) in an attempt to simulate nonmarine pore waters produced entirely different mineral phases, including halite and chabazite (zeolite), attributed to the high alkalinity and Na content of the solution. These observations highlight the significant impact of fluid chemistry on the diagenetic alteration of modern estuarine sediments.

3.7. References

- Aagaard, P., Jahren, J.S., Harstad, A.O., Nilsen, O., and Ramm, M., 2000, Formation of grain-coating chlorite in sandstones. Laboratory synthesized vs. natural occurrences: *Clay Minerals*, v. 35, p. 261–269.
- Ajdukiewicz, J.M., and Lander, R.H., 2010, Sandstone reservoir quality prediction: The state of the art: *American Association of Petroleum Geologists Bulletin*, v. 94, p. 1083–1091.
- Ajdukiewicz, J.M., and Larese, R.E., 2012, How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments: *American Association of Petroleum Geologists Bulletin*, v. 96, p. 2091–2119.
- Al-Ramadan, K., 2014a, Diagenesis of Holocene beachrocks: a comparative study between the Arabian Gulf and the Gulf of Aqaba, Saudi Arabia: *Arabian Journal of Geosciences*, v. 7, p. 4933–4942.
- Al-Ramadan, K., 2014b, Illitization of Smectite in Sandstones: The Permian Unayzah Reservoir, Saudi Arabia: *Arabian Journal for Science and Engineering*, v. 39, p. 407–412.
- Al-Ramadan, K., 2021, The role of diagenesis at unconformities of the Paleozoic siliciclastic succession of central Saudi Arabia: implications for reservoir quality: *Arabian Journal of Geosciences*, v. 14, p.
- Al-Ramadan, K.A., Hussain, M., Imam, B., and Saner, S., 2004, Lithologic characteristics and diagenesis of the Devonian Jauf sandstone at Ghawar Field, Eastern Saudi Arabia: *Marine and Petroleum Geology*, v. 21, p. 1221–1234.
- Al-Ramadan, K., Morad, S., Norton, A., and Hulver, M., 2013a, Linking Diagenesis and Porosity Preservation Versus Destruction to Sequence Stratigraphy of Gas Condensate Reservoir Sandstones; The Jauf Formation (Lower to Middle Devonian), Eastern Saudi Arabia, *in* Linking Diagenesis to Sequence Stratigraphy, v. 45, p. 297–335.
- Al-Ramadan, K., Morad, S., and Plink-Bjorklund, P., 2013b, Distribution of Diagenetic Alterations in Relationship to Depositional Facies and Sequence Stratigraphy of a Wave- and Tide-Dominated Siliciclastic Shoreline Complex: Upper Cretaceous Chimney Rock Sandstones, Wyoming and Utah, USA: *IAS Special Publication*, v. 45, p. 271–296.
- Altaner, S.P., and Ylagan, R.F., 1997, Comparison of Structural Models of Mixed-Layer Illite/Smectite and Reaction Mechanisms of Smectite Illitization: *Clays and Clay Minerals*, v. 45, p. 517–533.
- Anjos, S.M.C., De Ros, L.F., and Silva, C.M.A., 1999, Chlorite Authigenesis and Porosity Preservation in the Upper Cretaceous Marine Sandstones of the Santos Basin, Offshore Eastern Brazil, *in* Clay Mineral Cements in Sandstones, p. 289–316.

- Aro, O.E., Jones, S.J., Meadows, N.S., Gluyas, J., and Charlaftis, D., 2023, The importance of facies, grain size and clay content in controlling fluvial reservoir quality—an example from the Triassic Skagerrak Formation, Central North Sea, UK: *Petroleum Geoscience*, v. 29, p. 043.
- Arribas, M.E., Bustillo, A., and Tsige, M., 2004, Lacustrine chalky carbonates: origin, physical properties and diagenesis (Palaeogene of the Madrid Basin, Spain): *Sedimentary Geology*, v. 166, p. 335–351.
- Beaufort, D., Berger, G., Lacharpagne, J.C., and Meunier, A., 2001, An experimental alteration of montmorillonite to a di + trioctahedral smectite assemblage at 100 and 200°C: *Clay Minerals*, v. 36, p. 211–225.
- Beaufort, D., Rigault, C., Billon, S., Billault, V., Inoue, A., Inoue, S., and Patrier, P., 2015, Chlorite and chloritization processes through mixed-layer mineral series in low-temperature geological systems – a review: *Clay Minerals*, v. 50, p. 497–523.
- Bell, T.E., 1986, Microstructure in Mixed-Layer Illite/Smectite and Its Relationship to the Reaction of Smectite to Illite: *Clays and Clay Minerals*, v. 34, p. 146–154.
- Bello, A.M. et al., 2023a, Linking diagenesis and reservoir quality to depositional facies in marginal to shallow marine sequence: An example from the Campano-Maastrichtian Gombe Sandstone, Northern Benue Trough, NE Nigeria: *Marine and Petroleum Geology*, v. 155, p. 106386.
- Bello, A.M., Al-Ramadan, K., Babalola, L.O., Alqubalee, A., and Amao, A.O., 2023b, Impact of grain-coating illite in preventing quartz cementation: Example from permo-carboniferous sandstone, Central Saudi Arabia: *Marine and Petroleum Geology*, v. 149, p. 106073.
- Bello, A.M., Al-Ramadan, K., Koeshidayatullah, A.I., Amao, A.O., Herlambang, A., Al-Ghamdi, F., and Malik, M.H., 2023c, Impact of magmatic intrusion on diagenesis of shallow marine sandstones: An example from Qasim Formation, Northwest Saudi Arabia: *Frontiers in Earth Science*, v. 11, p. 1105547.
- Bello, A.M., Charlaftis, D., Jones, S.J., Gluyas, J., Acikalin, S., Cartigny, M., and Al-Ramadan, K., 2022a, Experimental diagenesis using present-day submarine turbidite sands: *Frontiers in Earth Science*, v. 10, p. 952690.
- Bello, A., Jones, S., Gluyas, J., Açıkalin, S., and Cartigny, M., 2021, Role played by clay content in controlling reservoir quality of submarine fan system, Forties Sandstone Member, Central Graben, North Sea: *Marine and Petroleum Geology*, v. 128, p. 105058.
- Bello, A.M., Jones, S.J., Gluyas, J., and Al-Ramadan, K., 2022b, Impact of Grain-Coating Clays on Porosity Preservation in Paleocene Turbidite Channel Sandstones: Nelson Oil Field, UK Central North Sea: *Minerals*, v. 12, p. 555.
- Bello, A.M., Salisu, A.M., Alqubalee, A., Amao, A.O., Al-Hashem, M., Al-Hussaini, A., and Al-Ramadan, K., 2024, Diagenetic controls on the quality of shallow marine sandstones: An example

- from the Cambro-Ordovician Saq Formation, central Saudi Arabia: *Journal of African Earth Sciences*, v. 215, p. 105295.
- Bentabol, M., Lamarca-Irisarri, D., Van Driessche, A.E.S., Ryan, P.C., and Huertas, F.J., 2024, Illitization of montmorillonite in ammonium solutions under hydrothermal conditions: *Applied Clay Science*, v. 258, p. 107478.
- Birkle, P., Van Dijk, C., Dasgupta, K., Murphy, M.J., Kharaka, Y.K., Thordsen, J.J., and Bischoff, J.L., 2019, Controls on illite cementation in Unayzah sandstones, Saudi Arabia: Mineralogy, K-Ar dating, numerical modeling, and hydrothermal experiments: *Journal of Sedimentary Research*, v. 89, p. 89–109.
- Bjørlykke, K., 2014, Relationships between depositional environments, burial history and rock properties. Some principal aspects of diagenetic process in sedimentary basins: *Sedimentary Geology*, v. 301, p. 1–14.
- Bloch, S., Lander, R.H., and Bonnell, L., 2002, Anomalous High Porosity and Permeability in Deeply Buried Sandstone Reservoirs: Origin and Predictability: *AAPG Bulletin*, v. 86, p. 301–328.
- Bloch, S., and McGowen, J.H., 1994, Influence of Depositional Environment on Reservoir Quality Prediction (M. D. Wilson, Ed.): *Reservoir Quality Assessment and Prediction in Clastic Rocks*, SEPM Short Course, v. 30, p. 41-58.
- Boles, J.R., and Franks, S.G., 1979, Clay diagenesis in Wilcox sandstones of Southwest Texas; implications of smectite diagenesis on sandstone cementation: *Journal of Sedimentary Research*, v. 49, p. 55–70.
- Burst, J.F., 1966, Diagenesis of Gulf Coast Clayey Sediments and Its Possible Relation to Petroleum Migration: *ABSTRACT: AAPG Bulletin*, v. 50, p. 607.
- Busch, B., Böcker, J., and Hilgers, C., 2024, Improved reservoir quality assessment by evaluating illite grain coatings, quartz cementation, and compaction – Case study from the Buntsandstein, Upper Rhine Graben, Germany: *Geoenergy Science and Engineering*, v. 241, p. 213141.
- Carrigy, M.A., and Mellon, G.B., 1964, Authigenic clay mineral cements in Cretaceous and Tertiary sandstones of Alberta: *Journal of Sedimentary Research*, v. 34, p. 461–472.
- Chamley, H., 1994, Clay Mineral Diagenesis BT - Quantitative Diagenesis: Recent Developments and Applications to Reservoir Geology, in Parker, A. and Sellwood, B.W. eds., Dordrecht, Springer Netherlands, p. 161–188.
- Charlaftis, D., Dobson, K.J., Jones, S.J., Lakshtanov, D., Crouch, J., and Cook, J., 2022, Experimental Simulation of Burial Diagenesis and Subsequent 2D-3D Characterization of Sandstone Reservoir Quality: *Frontiers in Earth Science*, v. 10, p. 766145.

- Charlaftis, D., Jones, S.J., Dobson, K.J., Crouch, J., and Acikalin, S., 2021, Experimental study of chlorite authigenesis and influence on porosity maintenance in sandstones: *Journal of Sedimentary Research*, v. 91, p. 197–212.
- Chung, F. H., 1974. Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multicomponent analysis: *Journal of Applied Crystallography*, 7(6), p. 519–525.
- Dallmeyer, R.D., Catalán, J.R.M., Arenas, R., Gil Ibarguchi, J.I., Gutiérrez-Alonso, G., Farias, P., Bastida, F., and Aller, J., 1997, Diachronous Variscan tectonothermal activity in the NW Iberian Massif: Evidence from $^{40}\text{Ar}/^{39}\text{Ar}$ dating of regional fabrics: *Tectonophysics*, v. 277, p. 307–337.
- Davies, D.K., Almon, W.R., Bonis, S.B., and Hunter, B.E., 1979, Deposition and Diagenesis of Tertiary-Holocene Volcaniclastics, Guatemala (P. A. Scholle & P. R. Schluger, Eds.): *Aspects of Diagenesis*, v. 26, p. 281–306.
- Deer, W.A., Howie, R.A., and Zussman, J., 2013, *An Introduction to the Rock-Forming Minerals*, 3rd edition. Mineralogical Society of Great Britain and Ireland, 498 p.
- Divis, A.F., and McKenzie, J.A., 1975, Experimental authigenesis of phyllosilicates from feldspathic sands: *Sedimentology*, v. 22, p. 147–155.
- Dong, H., Peacor, D.R., and Freed, R.L., 1997, Phase relations among smectite, R1 illite-smectite, and illite: *American Mineralogist*, 82(3–4), p. 379–391.
- Dowey, P.J., Hodgson, D.M., and Worden, R.H., 2012, Pre-requisites, processes, and prediction of chlorite grain coatings in petroleum reservoirs: A review of subsurface examples: *Marine and Petroleum Geology*, v. 32, p. 63–75.
- Dowey, P.J., Worden, R.H., Utley, J., and Hodgson, D.M., 2017, Sedimentary controls on modern sand grain coat formation: *Sedimentary Geology*, v. 353, p. 46–63.
- Dutton, S.P.; Hutton, M.E.; Ambrose, W.A.; Childers, A.T.; Loucks, R.G., 2018, Preservation of reservoir quality by chlorite coats in deep Tuscaloosa Sandstones, Central Louisiana, USA: *Gulf Coast Association of Geological Societies*, v. 7, p. 46–58.
- Eberl, D., and Hower, J., 1977, The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay: *Clays and Clay Minerals*, v. 25, p. 215–227.
- Ehrenberg, S.N., 1993, Preservation of Anomalously High Porosity in Deeply Buried Sandstones by Grain-Coating Chlorite: Examples from the Norwegian Continental Shelf: *AAPG Bulletin*, v. 77, p. 1260–1286.
- Ehrmann, W., Setti, M., and Marinoni, L., 2005, Clay minerals in Cenozoic sediments off Cape Roberts (McMurdo Sound, Antarctica) reveal palaeoclimatic history: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 229, p. 187–211.

- El-Ghali, M.A.K., Shelukhina, O., Abbasi, I.A., Moustafa, M.S.H., Hersi, O.S., Siddiqui, N.A., Al-Ramadan, K., Alqubalee, A., Bello, A.M., and Amao, A.O., 2024, Depositional and sequence stratigraphic controls on diagenesis in the Upper Cambrian-Lower Ordovician Barik Formation, central Oman: Implications for prediction of reservoir porosity in a hybrid-energy delta system: *Marine and Petroleum Geology*, v. 160, p. 106611.
- Elliott, W.C., Aronson, J.L., Matisoff, G., and Gautier, D.L., 1991, Kinetics of the Smectite to Illite Transformation in the Denver Basin: Clay Mineral, K-Ar Data, and Mathematical Model Results: *AAPG Bulletin*, v. 75, p. 436–462.
- Ferrage, E., Vidal, O., Mosser-Ruck, R., Cathelineau, M., and Cuadros, J., 2011, A reinvestigation of smectite illitization in experimental hydrothermal conditions: Results from X-ray diffraction and transmission electron microscopy: v. 96, p. 207–223.
- Franks, S.G., and Zwingmann, H., 2010, Origin and timing of late diagenetic illite in the Permian–Carboniferous Unayzah sandstone reservoirs of Saudi Arabia: *AAPG Bulletin*, v. 94, p. 1133–1159.
- García-Romero, E., Lorenzo, A., García Vicente, A., Morales, J., García-Rivas, J., and Suarez, M., 2021, On the structural formula of smectites: a review and new data on the influence of exchangeable cations: *Journal of Applied Crystallography*, v. 54, p. 251–262
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., and Duller, R.A., 2019a, Compositional variation in modern estuarine sands: Predicting major controls on sandstone reservoir quality: *AAPG Bulletin*, v. 103, p. 797–833.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., and Duller, R.A., 2018, Detrital clay coats, clay minerals, and pyrite: A modern shallow-core analogue for ancient and deeply buried estuarine sandstones: *Journal of Sedimentary Research*, v. 88, p. 1205–1237.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., Duller, R.A., and Edge, R.L., 2019b, Estuarine clay mineral distribution: Modern analogue for ancient sandstone reservoir quality prediction: *Sedimentology*, v. 66, p. 2011–2047.
- Guillaume, D., Neaman, A., Cathelineau, M., Mosser-Ruck, R., Peiffert, C., Abdelmoula, M., Dubessy, J., Villiéras, F., and Michau, N., 2004, Experimental study of the transformation of smectite at 80 and 300°C in the presence of Fe oxides: *Clay Minerals*, v. 39, p. 17–34.
- Haile, B.G., Hellevang, H., Aagaard, P., and Jahren, J., 2015, Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces: *Marine and Petroleum Geology*, v. 68, p. 664–674.
- Hajash, A., and Bloom, M.A., 1991, Marine diagenesis of feldspathic sand: A flow-through experimental study at 200°C, 1 kbar: *Chemical Geology*, v. 89, p. 359–377.

- Heald, M.T., and Anderegg, R.C., 1960, Differential cementation in the Tuscarora sandstone [Virginia-West Virginia]: *Journal of Sedimentary Research*, v. 30, p. 568–577.
- Heald, M.T., and Larese, R.E., 1974, Influence of coatings on quartz cementation: *Journal of Sedimentary Research*, v. 44, p. 1269–1274.
- Hillier, S., 1999. Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD): *Clay Mineral Cements in Sandstones*, 213–251.
- Howard, J.J., and Royd, M.D., 1985, Development of Layer Charge and Kinetics of Experimental Smectite Alteration: *Clays and Clay Minerals*, v. 33, p. 81–88.
- Huang, W.-L., Longo, J.M., and Pevear, D.R., 1993, An Experimentally Derived Kinetic Model for Smectite-to-Illite Conversion and Its Use as a Geothermometer: *Clays and Clay Minerals*, v. 41, p. 162–177.
- Huggett, J., Cuadros, J., Gale, A.S., Wray, D., and Adetunji, J., 2016. Low temperature, authigenic illite and carbonates in a mixed dolomite-clastic lagoonal and pedogenic setting, Spanish Central System, Spain: *Applied Clay Science*, 132–133, p. 296–312.
- Iijima, A., 2001, Zeolites in Petroleum and Natural Gas Reservoirs: *Reviews in Mineralogy and Geochemistry*, v. 45, p. 347–402.
- Imam, M.B., and Shaw, H.F., 1985, The diagenesis of Neogene clastic sediments from the Bengal Basin, Bangladesh: *Journal of Sedimentary Research*, v. 55, p. 665–671.
- Inoue, A., Kohyama, N., Kitagawa, R., and Watanabe, T., 1987, Chemical and Morphological Evidence for the Conversion of Smectite to Illite: *Clays and Clay Minerals*, v. 35, p. 111–120.
- Karakaya, M.Ç., Karakaya, N., and Yavuz, F., 2015, Geology and conditions of formation of the zeolite-bearing deposits southeast of ankara (Central Turkey): *Clays and Clay Minerals*, v. 63, p. 85–109.
- Khan, M.A., Khan, T., Ali, A., Bello, A.M., and Radwan, A.E., 2023, Role of depositional and diagenetic controls on reservoir quality of complex heterogenous tidal sandstone reservoirs: An example from the Lower Goru formation, Middle Indus Basin, Southwest Pakistan: *Marine and Petroleum Geology*, v. 154, p. 106337.
- Kloprogge, J.T., Komarneni, S., and Amonette, J.E., 1999, Synthesis of Smectite Clay Minerals: A Critical Review: *Clays and Clay Minerals*, v. 47, p. 529–554.
- Lander, R.H., Bonnell, L.M., Taylor, T.R., and Espejo, I., 2022, Chapter 13 - Reservoir quality and diagenesis of deepwater sandstones, *in* Rotzien, J.R., Yeilding, C.A., Sears, R.A., Hernández-Molina, F.J., and Catuneanu, O.B.T.-D.S.S. eds., Elsevier, p. 471–514.
- Lander, R.H., and Walderhaug, O., 1999, Predicting Porosity through Simulating Sandstone Compaction and Quartz Cementation1: *AAPG Bulletin*, v. 83, p. 433–449.

- Lanson, B., Beaufort, D., Berger, G., Bauer, A., Cassagnabère, A., and Meunier, A., 2002, Authigenic kaolin and illitic minerals during burial diagenesis of sandstones: a review: *Clay Minerals*, v. 37, p. 1–22.
- Lanson, B., Sakharov, B., Claret, F., and Drits, V., 2009, Diagenetic Smectite-to-Illite Transition in Clay-Rich Sediments: A Reappraisal of X-Ray Diffraction Results Using the Multi-Specimen Method: *American Journal of Science*, v. 309, p. 476–516.
- Lawan, A.Y., Worden, R.H., Utley, J.E.P., and Crowley, S.F., 2021, Sedimentological and diagenetic controls on the reservoir quality of marginal marine sandstones buried to moderate depths and temperatures: Brent Province, UK North Sea: *Marine and Petroleum Geology*, v. 128, p. 104993.
- Lindgreen, H., and Hansen, P.L., 1991, Ordering of illite-smectite in Upper Jurassic claystones from the North Sea: *Clay Minerals*, v. 26, p. 105–125.
- Lin, T., Wang, W., Ma, Q., Kang, J., Yang, R., and Liu, X., 2024, Formation mechanism and implication of analcime in the sandstone reservoirs of the Permian Jingjingzigou formation in the Jinan sag, southern Junggar basin, NW China: *Frontiers in Earth Science*, v. 12, p. 1416594.
- Llana-Fúnez, S., and Marcos, A., 2001, The Malpica–Lamego Line: a major crustal-scale shear zone in the Variscan belt of Iberia: *Journal of Structural Geology*, v. 23, p. 1015–1030.
- Lynch, F.L., 1996, Mineral/Water Interaction, Fluid Flow, and Frio Sandstone Diagenesis: Evidence from the Rocks1: *AAPG Bulletin*, v. 80, p. 486–504.
- Mallette, A.J., Espindola, G., Varghese, N., and Rimer, J.D., 2024, Highly efficient synthesis of zeolite chabazite using cooperative hydration-mismatched inorganic structure-directing agents††Electronic supplementary information (ESI) available: The authors have cited additional references within the ESI. See DOI: <https://doi.org/10.1039/D4TA00000A>: *Chemical Science*, v. 15, p. 573–583.
- Mansurbeg, H., Morad, S., Salem, A., Marfil, R., El-ghali, M.A.K., Nystuen, J.P., Caja, M.A., Amorosi, A., Garcia, D., and La Iglesia, A., 2008, Diagenesis and reservoir quality evolution of palaeocene deep-water, marine sandstones, the Shetland-Faroes Basin, British continental shelf: *Marine and Petroleum Geology*, v. 25, p. 514–543.
- McBride, E.F., 1989, Quartz cement in sandstones: a review: *Earth-Science Reviews*, v. 26, p. 69–112.
- McCarty, D.K., Sakharov, B.A., and Drits, V.A., 2009, New insights into smectite illitization: A zoned K-bentonite revisited: *American Mineralogist*, v. 94, p. 1653–1671.
- McGhee, C., Muhammed, D., Simon, N., Acikalin, S., Utley, J.E.P., Griffiths, J., Wooldridge, L., Verhagen, I.T.E., van der Land, C., and Worden, R.H., 2022, Stratigraphy and sedimentary evolution of a modern macro-tidal incised valley: An analogue for reservoir facies and architecture: *Sedimentology*, v. 69, p. 696–723.

- McKinley, J.M., Worden, R.H., and Ruffell, A.H., 1999, Smectite in sandstones: a review of the controls on occurrence and behaviour during diagenesis: Clay mineral cements in sandstones, p. 109–128.
- Mills, M.M., Sanchez, A.C., Boisvert, L., Payne, C.B., Ho, T.A., and Wang, Y., 2023, Understanding smectite to illite transformation at elevated (>100 °C) temperature: Effects of liquid/solid ratio, interlayer cation, solution chemistry and reaction time: *Chemical Geology*, v. 615, p. 121214.
- Montagna, G., Bigi, S., Kónya, P., Szakáll, S., and Vezzalini, G., 2010, Chabazite-Mg: a new natural zeolite of the chabazite series: *American Mineralogist*, v. 95, p. 939–945.
- Moore, D.M. & Reynolds, R.C., 1998, X-Ray Diffraction and the Identification and Analysis of Clay Minerals: *Geological Magazine*, v. 135, p. 819–842.
- Morad, S., Al-Ramadan, K., Ketzer, M., and De Ros, L., 2010a, The impact of diagenesis on the heterogeneity of sandstone reservoirs: A review of the role of depositional fades and sequence stratigraphy: *AAPG Bulletin*, v. 94, p. 1267–1309.
- Morad, S., Al-Ramadan, K., Ketzer, J.M., and De Ros, L.F., 2010b, The impact of diagenesis on the heterogeneity of sandstone reservoirs: A review of the role of depositional fades and sequence stratigraphy: *American Association of Petroleum Geologists Bulletin*, v. 94, p. 1267–1309.
- Mosser-Ruck, R., and Cathelineau, M., 2004, Experimental transformation of Na,Ca-smectite under basic conditions at 150 °C: *Applied Clay Science*, v. 26, p. 259–273.
- Mosser-Ruck, R., Cathelineau, M., Guillaume, D., Charpentier, D., Rousset, D., Barres, O., and Michau, N., 2010, Effects of temperature, pH, and iron/clay and liquid/clay ratios on experimental conversion of dioctahedral smectite to berthierine, chlorite, vermiculite, or saponite: *Clays and Clay Minerals*, v. 58, p. 280–291.
- Mosser-Ruck, R., Pironon, J., Cathelineau, M., and Trouiller, A., 2001, Experimental illitization of smectite in a K-rich solution: *European Journal of Mineralogy*, v. 13, p. 829–840.
- Muhammed, D.D., Simon, N., Utley, J.E.P., Verhagen, I.T.E., Duller, R.A., Griffiths, J., Wooldridge, L.J., and Worden, R.H., 2022, Geochemistry of Sub-Depositional Environments in Estuarine Sediments: Development of an Approach to Predict Palaeo-Environments from Holocene Cores: *Geosciences (Switzerland)*, v. 12, p. 23.
- Murphy, M.J., 2016, Geochemical modeling and hydrothermal experiments used to constrain the conditions of illite diagenesis in sedimentary basins [MSc. Thesis]. San José State University, 69 p.
- Nadeau, P.H., and Bain, D.C., 1986, Composition of Some Smectites and Diagenetic Illitic Clays and Implications for their Origin: *Clays and Clay Minerals*, v. 34, p. 455–464.

- Nadeau, P.H., Wilson, J., McHardy, W.J., and Tait, J.M., 1985, The Conversion of Smectite to Illite during Diagenesis: Evidence from some Illitic Clays from Bentonites and Sandstones: *Mineralogical Magazine*, v. 49, p. 393–400.
- Niu, B., Yoshimura, T. and Hirai, A., 2000. Smectite diagenesis in neogene marine sandstone and mudstone of the Niigata Basin, Japan: *Clays and Clay Minerals*, 48(1), pp.26-42.
- Orhan, H., 1992, Importance of dust storms in the diagenesis of sandstones: a case study, Entrada sandstone in the Ghost Ranch area, New Mexico, USA: *Sedimentary Geology*, v. 77, p. 111–122.
- Pérez-Arlucea, M., Álvarez Iglesias, P., and Rubio, B., 2007, Holocene Evolution of Estuarine and Tidal-flat Sediments in San Simón Bay: *Journal of Coastal Research*, v. 50, p. 163–167.
- Perry, E., and Hower, J., 1970, Burial Diagenesis in Gulf Coast Pelitic Sediments: *Clays and Clay Minerals*, v. 18, p. 165–177.
- Pittman, E.D., Larese, R.E., and Heald, M.T., 1992, Clay Coats: Occurrence and Relevance to Preservation of Porosity in Sandstones (D. W. Houseknecht & E. D. Pittman, Eds.): *Origin, Diagenesis, and Petrophysics of Clay Minerals in Sandstones*, v. 47, p. 241-255.
- Priestas, A.M., and Wise, S.W., 2007, Distribution and origin of authigenic smectite clays in Cape Roberts Project Core 3, Victoria Land Basin, Antarctica: *USGS Open-File Report Short Research Paper*, v. 057, 5p.
- Primmer, T.J., Cade, C.A., Evans, J., Gluyas, J.G., Hopkins, M.S., Oxtoby, Norman.H., Smalley, P.C., Warren, E.A., and Worden, R.H., 1997, Global Patterns in Sandstone Diagenesis: Their Application to Reservoir Quality Prediction for Petroleum Exploration (J. A. Kupecz, J. Gluyas, & S. Bloch, Eds.): *Reservoir Quality Prediction in Sandstones and Carbonates*, AAPG Memoir, v. 69, p. 61-78.
- Putnis, A., 2009, Mineral Replacement Reactions: *Reviews in Mineralogy and Geochemistry*, v. 70, p. 87–124.
- Pytte, A.M., and Reynolds, R.C., 1989, The thermal transformation of smectite to illite, *in* *Thermal history of sedimentary basins: Methods and case histories*, Springer, p. 133–140.
- Roberson, H.E., and Lahann, R.W., 1981, Smectite to Illite Conversion Rates: Effects of Solution Chemistry: *Clays and Clay Minerals*, v. 29, p. 129–135.
- Ryu, I.-C., and Niem, A.R., 1999, Sandstone diagenesis, reservoir potential, and sequence stratigraphy of the Eocene Tyee Basin, Oregon: *Journal of Sedimentary Research*, v. 69, p. 384-393.
- Salisu, A.M., Algheryafi, H., Bello, A.M., Amao, A.O., Al-Otaibi, B., and Al-Ramadan, K., 2024, Depositional and diagenetic controls on the reservoir quality of marginal marine sandstones: An example from the Early Devonian Subbat Member, Jauf Formation, northwest Saudi Arabia: *Marine and Petroleum Geology*, p. 107147.

- Salisu, A.M., Alqubalee, A., Bello, A.M., Al-Hussaini, A., Adebayo, A.R., Amao, A.O., and Al-Ramadan, K., 2023, Impact of kaolinite and iron oxide cements on resistivity and quality of low resistivity pay sandstones: *Marine and Petroleum Geology*, v. 158, p. 106568.
- Saner, S., Hassan, H., Al-Ramadan, K., and Abdulghani, W.M., 2006, Mineralogical, pore and petrophysical characteristics of the Devonian Jauf Sandstone reservoir, Hawiyah field, eastern Saudi Arabia: *Journal of Petroleum Geology*, v. 29, p. 257–272.
- Simon, N., Worden, R.H., Muhammed, D.D., Utley, J.E.P., Verhagen, I.T.E., Griffiths, J., and Wooldridge, L.J., 2021, Sediment textural characteristics of the Ravenglass Estuary; Development of a method to predict palaeo sub-depositional environments from estuary core samples: *Sedimentary Geology*, v. 418, p. 105906.
- Small, J.S., Hamilton, D.L., and Habesch, S., 1992, Experimental simulation of clay precipitation within reservoir sandstones; 1, Techniques and examples: *Journal of Sedimentary Research*, v. 62, p. 508–519.
- Storvoll, V., Bjørlykke, K., Karlsen, D., and Saigal, G., 2002, Porosity preservation in reservoir sandstones due to grain-coating illite: A study of the Jurassic Garn Formation from the Kristin and Lavrans fields, offshore Mid-Norway: *Marine and Petroleum Geology*, v. 19, p. 767–781.
- Stricker, S., and Jones, S.J., 2018, Enhanced porosity preservation by pore fluid overpressure and chlorite grain coatings in the Triassic Skagerrak, Central Graben, North Sea, UK (P. J. Armitage, A. R. Butcher, J. M. Churchill, A. E. Csoma, C. Hollis, R. H. Lander, J. E. Omma, & R. H. Worden, Eds.): *Reservoir Quality of Clastic and Carbonate Rocks: Analysis, Modelling and Prediction*, v. 435, p. 321–341.
- Sun, Y., Liu, X., Zhang, Y., Dong, W., Xu, Y., Shi, G., Lin, Y., and Li, A., 2014, Analcite cementation facies and forming mechanism of high-quality secondary clastic rock reservoirs in western China: *Journal of Palaeogeography*, v. 16, p. 517–526.
- Tang, L., Gluyas, J., and Jones, S., 2018, Porosity preservation due to grain coating illite/smectite: Evidence from Buchan Formation (Upper Devonian) of the Ardmore Field, UK North Sea: *Proceedings of the Geologists' Association*, v. 129, p. 202–214.
- Taylor, T.R., Lander, R.H., and Bonnell, L.M., 2022, *Sandstone Petrography, Petrology, and Modeling*. SEPM Society for Sedimentary Geology, v. 13, 363 p.
- Ulmer-Scholle, D.S., Scholle, P.A., Schieber, J., and Raine, R.J., 2015, *A Color Guide to the Petrography of Sandstones, Siltstones, Shales and Associated Rocks*. Memoir 109: American Association of Petroleum Geologists, Tulsa, Oklahoma. 526 p.
- Varela, M., Prego, R., Pazos, Y., and Moroño, Á., 2005, Influence of upwelling and river runoff interaction on phytoplankton assemblages in a Middle Galician Ria and Comparison with northern

- and southern rias (NW Iberian Peninsula): *Estuarine, Coastal and Shelf Science*, v. 64, p. 721–737.
- Velde, B., 1985, *Clay Minerals: A Physico-chemical explanation of their occurrence: Developemnts in Sedimentology*, p. 32–44.
- Virolle, M., Brigaud, B., Beaufort, D., Patrier, P., Abdelrahman, E., Thomas, H., Portier, E., Samson, Y., Bourillot, R., and Féliès, H., 2022, Authigenic berthierine and incipient chloritization in shallowly buried sandstone reservoirs: Key role of the source-to-sink context: *GSA Bulletin*, v. 134, p. 739–761.
- Virolle, M., Brigaud, B., Bourillot, R., Féliès, H., Portier, E., Duteil, T., Nouet, J., Patrier, P., and Beaufort, D., 2019a, Detrital clay grain coats in estuarine clastic deposits: origin and spatial distribution within a modern sedimentary system, the Gironde Estuary (south-west France): *Sedimentology*, v. 66, p. 859–894.
- Virolle, M., Brigaud, B., Féliès, H., Bourillot, R., Portier, E., Patrier, P., Derriennic, H., and Beaufort, D., 2021, Preservation and distribution of detrital clay coats in a modern estuarine heterolithic point bar in the gironde estuary (Bordeaux, France): *Journal of Sedimentary Research*, v. 91, p. 812–832.
- Virolle, M., Brigaud, B., Luby, S., Portier, E., Féliès, H., Bourillot, R., Patrier, P., and Beaufort, D., 2019b, Influence of sedimentation and detrital clay grain coats on chloritized sandstone reservoir qualities: Insights from comparisons between ancient tidal heterolithic sandstones and a modern estuarine system: *Marine and Petroleum Geology*, v. 107, p. 163–184.
- Virolle, M., Féliès, H., Brigaud, B., Bourillot, R., Portier, E., Patrier, P., Beaufort, D., Jalon-Rojas, I., Derriennic, H., and Miska, S., 2020, Facies associations, detrital clay grain coats and mineralogical characterization of the Gironde estuary tidal bars: A modern analogue for deeply buried estuarine sandstone reservoirs: *Marine and Petroleum Geology*, v. 114, p. 104225.
- Walderhaug, O., 1996, Kinetic Modeling of Quartz Cementation and Porosity Loss in Deeply Buried Sandstone Reservoirs1: *AAPG Bulletin*, v. 80, p. 731–745.
- Walderhaug, O., and Porten, K.W., 2022, How Do Grain Coats Prevent Formation of Quartz Overgrowths? *Journal of Sedimentary Research*, v. 92, p. 988–1002.
- Wang, J., Zhou, L., Liu, J., Li, E., and Xian, B., 2020, Genesis of diagenetic zeolites and their impact on reservoir formation in the Middle Permian Lower-Wuerhe Formation of the Mahu Sag, Junggar Basin, Northwest China: *Energy Exploration & Exploitation*, v. 38, p. 2541–2557.
- Weaver, C.E., Pollard, L.D., 1973, *The Chemistry of Clay Minerals: Developments in Sedimentology*, Elsevier, Amsterdam, v. 15, p. 1–213.
- Whitney, G., 1990, Role of Water in the Smectite-to-Illite Reaction: *Clays and Clay Minerals*, v. 38, p. 343–350.

- Whitney, G., and Northrop, H.R., 1988, Experimental investigation of the smectite to illite reaction; dual reaction mechanisms and oxygen-isotope systematics: *American Mineralogist*, v. 73, p. 77–90.
- Whitney, G., and Velde, B., 1993, Changes in Particle Morphology During Illitization: An Experimental Study: *Clays and Clay Minerals*, v. 41, p. 209–218.
- Wilson, M.D., and Pittman, E.D., 1977, Authigenic clays in sandstones; recognition and influence on reservoir properties and paleoenvironmental analysis: *Journal of Sedimentary Research*, v. 47, p. 3–31.
- Wise, S., Smellie, J., Aghib, F., Jarrard, R., and Krissek, L., 2001, Authigenic smectite clay coats in CRP-3 drillcore, Victoria Land Basin, Antarctica, as a possible indicator of fluid flow: A progress report: *Terra Antarctica*, v. 8, p. 281-298.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., Thompson, A., and Chung, P., 2017a, Biofilm origin of clay-coated sand grains: *Geology*, v. 45, p. 875–878.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., and Utley, J.E.P., 2017b, Clay-coated sand grains in petroleum reservoirs: Understanding their distribution via a modern analogue: *Journal of Sedimentary Research*, v. 87, p. 338–352.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., and Utley, J.E.P., 2019, How to quantify clay-coat grain coverage in modern and ancient sediments: *Journal of Sedimentary Research*, v. 89, p. 135–146.
- Wooldridge, L.J., Worden, R.H., Griffiths, J., Utley, J.E.P., and Thompson, A., 2018, The origin of clay-coated sand grains and sediment heterogeneity in tidal flats: *Sedimentary Geology*, v. 373, p. 191–209.
- Worden, R.H., and Burley, S.D., 2003, Sandstone Diagenesis: The Evolution of Sand to Stone, *in* Sandstone Diagenesis, p. 1–44.
- Worden, R.H., Griffiths, J., Wooldridge, L.J., Utley, J.E.P., Lawan, A.Y., Muhammed, D.D., Simon, N., and Armitage, P.J., 2020, Chlorite in sandstones: *Earth-Science Reviews*, v. 204, p. 103105.
- Worden, R., and Morad, S., 2009, Clay Minerals in Sandstones: Controls on Formation, Distribution and Evolution, *in* Clay Mineral Cements in Sandstones, v. 34, p. 1–41.
- Zhu, S., Cui, H., Jia, Y., Zhu, X., Tong, H., and Ma, L., 2020, Occurrence, composition, and origin of analcime in sedimentary rocks of non-marine petroliferous basins in China: *Marine and Petroleum Geology*, v. 113, p. 104164.

CHAPTER 4

THE ROLE OF FLUID CHEMISTRY ON THE DIAGENETIC TRANSFORMATION OF DETRITAL CLAY MINERALS: EXPERIMENTAL INSIGHTS FROM MODERN ESTUARINE SEDIMENTS

4.1. Abstract

The diagenetic transformation of detrital clay minerals significantly influences sandstone reservoir quality, with fluid chemistry and temperature playing key roles in dictating transformation pathways during burial diagenesis. While these processes are well-documented in basinal settings, the diagenetic alterations of sediments in dynamic environments like estuaries remain underexplored. This study investigates the impact of fluid composition on the transformation of modern estuarine sediments through hydrothermal experiments using sediments from the Gironde Estuary, SW France. A range of natural and synthetic solutions including seawater (SW), 0.1 M KCl (SF1), 0.1 M NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (SF2), estuarine water (EW), and 0.1 M Na_2CO_3 (SF3) were used under temperatures from 50°C to 250°C for 14 days, with a fixed fluid-to-sediment ratio of 10:1. The results revealed distinct mineralogical transformations driven by fluid composition. Dissolution of detrital feldspars and clay materials began at lower temperatures (<100°C). The authigenic formation of smectite and its subsequent illitization in K-rich fluids (SW, SF1) occurred between 150°C and 250°C, replicating potassium-driven illitization processes observed in natural sandstones. Additionally, chlorite formation occurred through the conversion of smectite in SF2 and EW. Geochemical analysis showed that SF2 produced Mg-rich chlorites, while EW yielded Fe-rich chlorites. This aligns with diagenetic trends in coastal environments, where Fe-rich chlorites are typically associated with estuarine systems. The resulting authigenic

illite and chlorite exhibited morphological and chemical characteristics similar to those found in natural sandstones, forming through dissolution-crystallization and solid-state transformation mechanisms. In contrast to illite and chlorite, SF3 produced entirely different mineral phases, including halite and analcime (zeolite), attributed to the high alkalinity and Na-rich composition of the solution. These findings provide valuable insights into the role of fluid chemistry in the diagenetic alteration of modern sediments and their implications for the evolution of sandstone reservoirs, which is critical for energy exploration and transition.

4.2. Introduction

The influence of clay minerals on sandstone reservoir quality has been widely documented (Heald and Larese, 1974; Pittman et al., 1992; Worden and Morad, 2000; Taylor et al., 2010; Wooldridge et al., 2018; Lander et al., 2022; Bello et al., 2023, 2024b; Salisu et al., 2024a). Grain-coating clays, such as chlorite, illite, and mixed-layer clays, have been shown to inhibit authigenic quartz cementation in deeply buried reservoirs, thereby preserving reservoir quality (Ehrenberg, 1993; Bloch et al., 2002; Al-Ramadan et al., 2005; Walderhaug and Porten, 2022). Conversely, pore-filling clays, including smectite, kaolinite, and illite, occupy pore spaces and obstruct fluid flow, significantly reducing reservoir porosity and permeability (McKinley et al., 1999; Franks and Zwingmann, 2010; Khan et al., 2023; Salisu et al., 2023). Numerous studies have investigated the occurrence and distribution of grain-coating clays and their role in preserving reservoir quality (Pittman et al., 1992; Small et al., 1992; Dowey et al., 2012; Haile et al., 2015a). These studies highlight the influence of depositional environments on the distribution of authigenic clay coats. For instance, chlorite commonly occurs in fluvial to marginal marine environments (Dowey et al., 2012), whereas smectite is prevalent in nearshore marine sediments (Almon et al., 1976). Diagenetic clay coatings develop through the recrystallization of detrital precursors or direct

precipitation from pore fluids during burial diagenesis (Worden and Morad, 2009; Ajdukiewicz and Larese, 2012; Bello et al., 2025). These clay coatings significantly influence fluid flow, mineral stability, and reservoir quality across sedimentary systems worldwide, including marginal marine environments (Worden et al., 2018; Wooldridge et al., 2018; Salisu et al., 2024a).

Modern marginal marine sediments, such as those found in estuarine environments, often contain detrital clay coatings that vary in texture and composition based on depositional sub-environments (Wooldridge et al., 2017). These variations create heterogeneities that influence diagenesis and present significant challenges for reservoir quality prediction models (Lawan et al., 2021). Recent works have explored the controls influencing the occurrence and distribution of detrital grain-coating clays in modern marginal marine settings (Griffiths et al., 2018, 2019; Virolle et al., 2019a, 2019b, 2021a, 2021b; Wooldridge et al., 2019; Simon et al., 2021). However, the physicochemical factors controlling the diagenetic transformation of these sediments remain understudied. Understanding these transformation pathways is particularly important as marginal marine reservoirs gain prominence for groundwater and energy exploration (Bello et al., 2024a), carbon capture and storage (CCS), and hydrogen storage (Lawan et al., 2021; Bello et al., 2024a; Salisu et al., 2024a), due to their porosity, permeability, and mineralogical stability. The ability to predict how clay minerals will evolve under burial conditions is essential for evaluating the long-term storage capacity and injectivity of these reservoirs.

Variations in fluid chemistry, temperature, and pressure dictate the transformation pathways of detrital materials during burial diagenesis (Bjørlykke et al., 1989; Worden and Burley, 2009; Bello et al., 2022b). For example, the presence of Al^{3+} , Mg^{2+} , and Fe^{2+} in formation brines is crucial for chlorite formation during fluid-rock interactions (Beaufort et al., 2015; Worden et al., 2020), while K^{+} is essential for the precipitation of authigenic illite (McKinley et al., 1999; Beaufort et al., 2001;

Lanson et al., 2002). Changes in the fluid-rock ratio, fluid chemistry, and pH of formation water can result in the development of different authigenic clay minerals during burial, even when derived from the same detrital mineral precursors (Mosser-Ruck et al., 2010; Charlaftis et al., 2022). Consequently, understanding the mineralogical and geochemical pathways that govern clay diagenesis has become increasingly important, particularly in the context of sustainable practices such as geothermal energy production and carbon capture and storage (CCS) technologies, which are vital for the energy transition.

This study investigates the role of fluid chemistry in the diagenetic alteration of detrital clay minerals, using sediments from the Gironde Estuary, SW France, as an analog for ancient marginal marine sandstones. These fresh sediments, free from extensive weathering or diagenetic alterations, provide a suitable framework for simulating burial diagenesis under controlled conditions and investigating the formation of clay minerals during the sand-to-stone transition. Hydrothermal reactor experiments were conducted to replicate diagenetic conditions, exposing sediments to fluids with varying pH and compositions under controlled temperatures. The specific objectives were to: (1) simulate the diagenetic formation of clay minerals in modern estuary sediments as analogs for deep burial diagenesis; (2) determine the mechanisms of formation for these clay minerals; (3) assess the impact of fluid chemistry on clay mineral transformation pathways; and (4) evaluate the relevance of the hydrothermal experiments to natural sandstone diagenesis.

4.3. Study area and geologic background of the sample

This study utilized sediments from the modern Gironde Estuary, located in the Nouvelle-Aquitaine region of southwestern France (Figure 1A). The estuary is one of Europe's largest estuarine

systems, covering an approximate surface area of 630 km² (Sottolichio et al., 2011; Virolle et al., 2021b). It extends about 160 km inland from its mouth to its upstream tidal limit (Virolle et al., 2019b). The estuary is fed by two principal rivers, the Garonne and Dordogne, which drain waters from the Pyrenees and the Massif Central, respectively, forming an extensive watershed (Coynel et al., 2004). The Gironde Estuary is macrotidal and characterized by semi-diurnal tides, with tidal ranges varying from 1.5 m during neap tides to 5.5 m during spring tides (Castaing, P. & Allen, 1981; Virolle et al., 2021b). Its morphology and hydrodynamics are shaped by a complex interplay of fluvial and tidal processes, resulting in different patterns of sediment transport and deposition (Virolle et al., 2019b). The estuary is typically divided into three main zones based on its morphology and hydrodynamics: the outer estuary funnel, the inner estuary funnel, and the Garonne and Dordogne estuarine channels (Allen, 1991; Billy et al., 2012; Virolle et al., 2019b). A defining feature of the Gironde Estuary is its well-developed Turbidity Maximum Zone (TMZ), a highly dynamic region where suspended sediment concentrations can reach up to 300 g/L during slack water (Castaing, P. & Allen, 1981; Etcheber et al., 2011). The TMZ, which varies seasonally, facilitates hydrodynamic trapping of fine-grained sediments, including clay minerals, fine quartz grains, and organic matter (Virolle et al., 2021b).

The sediment distribution within the estuary reflects its heterolithic nature: sandy tidal bars, point bars, and fine-grained intertidal and subtidal deposits (Virolle et al., 2019b). Specifically, the samples used in this study were collected from estuarine sands and muds within the inner estuary funnel (Figure 1A–C). The estuary's sedimentary framework, with its extensive muddy deposits on estuarine banks and intertidal flats, serves as an analog to many ancient sedimentary systems. Understanding these systems is essential for interpreting sedimentary processes, including the

authigenesis of clay minerals. Additionally, the origin and distribution of detrital clay coats within the Gironde Estuary are well-documented (Virolle et al., 2019c, 2019b, 2020, 2021b).

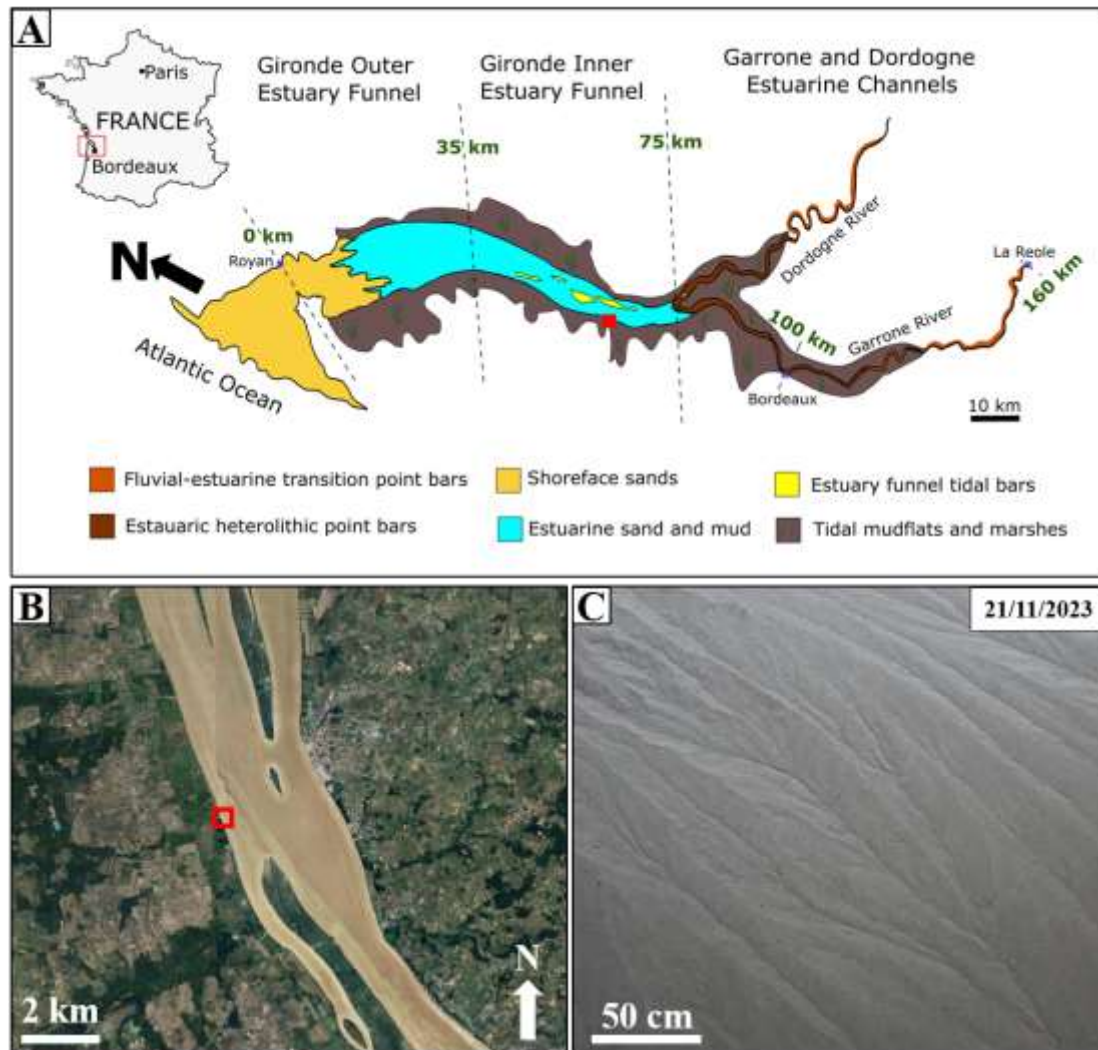


Figure 4.1. (A) Simplified facies map of the Gironde Estuary catchment (modified after (Virolle et al., 2019b)) with the red square indicating the location of the samples analyzed in this study. The inset map provides a country-level view of the study area, with the red rectangle marking the approximate position of the estuary. (B) Google Earth aerial image showing the sample collection area (red square). (C) Field photograph depicting the muddy estuarine sediments utilized in this study.

4.4. Methods

This study integrated several laboratory experiments and analytical techniques, including hydrothermal reactor experiments, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD; bulk and clay fraction), scanning transmission electron microscopy (STEM), inductively coupled plasma optical emission spectroscopy (ICP-OES), and focused ion beam scanning electron microscopy (FIB-SEM). All experiments and analyses were conducted at the laboratories of the Center for Integrative Petroleum Research, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Saudi Arabia. The detailed methodologies for each analysis are outlined below.

4.4.1. Hydrothermal experiments

The hydrothermal reactor experiments were conducted using an Ollital OLT-HP-500 multi-position parallel reactor autoclave system, connected to a nitrogen gas cylinder (Figure 2). This system comprises four stainless steel micro-stirred parallel reactors, each equipped with independent controls for temperature, pressure, and elapsed time. The reactor kettles have a maximum capacity of 500 mL and can be heated to temperatures of up to 350 °C and pressures of 160 bars. Temperature regulation is achieved through a Smart PID algorithm control system, ensuring an accuracy of ± 0.1 °C. The sediment samples were divided into twelve portions before the experiments, each weighing 20 grams. For each experiment, 20 grams of sediment were placed into a 50 μm stainless steel mesh and positioned at the bottom of the reactor kettles. The kettles were then filled with 200 mL of the respective experimental solutions, as outlined in Table 1. The experimental solutions included: Red Sea water for experiments 1–5; a 0.1 M KCl-enriched Red Sea water solution for experiment 6; a single 0.1 M mixed solution containing NaCl, KCl,

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for experiments 7–10; Gironde estuarine water for experiment 11; and a 0.1 M Na_2CO_3 solution for experiment 12. Each salt in the mixed solution for experiments 7–10 was prepared at an individual concentration of 0.1 M, ensuring that all major cations were included at equal molarity.

The reactors were then sealed and pressurized with nitrogen gas to an initial pressure of approximately 40 bar at room temperature. They were subsequently heated to the target experimental temperatures, which ranged from 50 °C to 250 °C (Table 1), at a heating rate of 15 °C per minute. While the initial pressure was consistent across all experiments (~40 bar at room temperature), it increased with temperature and the specific reaction fluid, stabilizing at the final pressure after 1–3 hours (Table 1). The samples were maintained at the designated experimental temperatures for 14 days under strictly closed conditions, following the procedures described by (Charlaftis et al., 2021; Bello et al., 2022b). After each experiment, the reactors were switched off and cooled to room temperature. The sediment samples were then recovered and air-dried. Post-experiment solutions were also retrieved, immediately analyzed for pH, and subjected to ICP-OES analysis at room temperature. The synthetic fluid compositions used in this study were simplified to include only the major cations. The fluid-to-rock ratio of 10:1 ensured sufficient interaction between the fluid and sediment to facilitate mineral transformations.

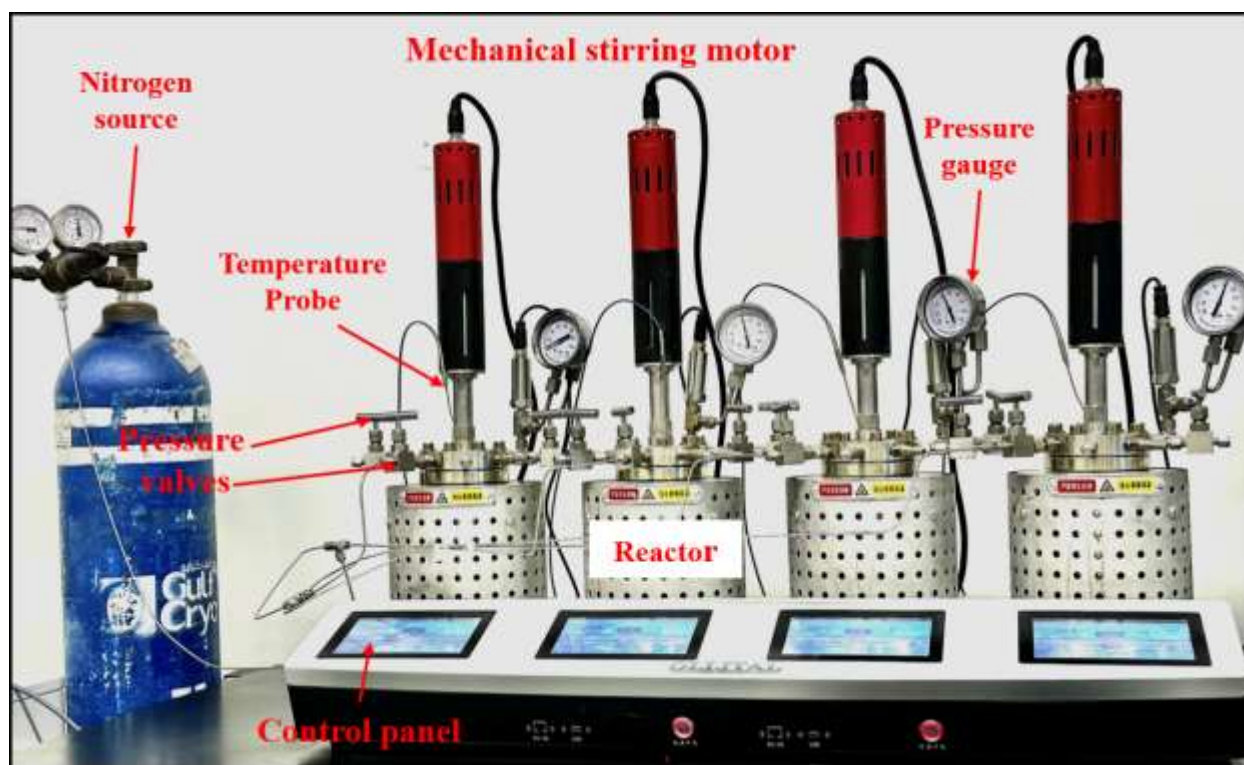


Figure 4.2. Photograph of the experimental setup employed in this study, highlighting the key components of the hydrothermal reactors.

4.4.2. Analytical techniques

4.4.2.1. SEM/SEM-EDS analyses

The pre- and post-experiment samples were analyzed using a Zeiss Gemini 550 scanning electron microscope (SEM). The SEM was equipped with a backscattered electron (BSE) detector and an Aztec energy-dispersive spectrometer (EDS) system, developed by Oxford Instruments, UK. For pre-experiment analysis, loosely disaggregated sediments were bonded to an aluminum stub using carbon adhesive tape while post-experiment consolidated samples were mounted on stubs. Both samples were coated with a 30 nm layer of gold using a Quorum Q150R sputter coater to ensure optimal imaging and analysis (Alqubalee et al., 2023; Salisu et al., 2024b). The SEM analyses were conducted at accelerating voltages ranging between 10 and 15 kV, with probe currents of 1 to 2 nA, respectively. The SEM and SEM-EDS investigations were conducted to examine the

morphology, chemical composition, and textural relationships of detrital minerals in the initial material, as well as the formation and characteristics of any authigenic minerals that developed during the experiments.

Table 4.1. Conditions for the hydrothermal experiments.

Experiment	Sample ID	Solutions	Temperature (°C)	Duration (days)	Final Pressure (Bar)
1	SW@50	Red Sea water	50	14	46.7
2	SW@100	Red Sea water	100	14	52.7
3	SW@150	Red Sea water	150	14	65.1
4	SW@200	Red Sea water	200	14	91.2
5	SW@250	Red Sea water	250	14	116.3
6	SF1@250	0.1 M KCl in Red Sea Water	250	14	117.6
7	SF2@100	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	100	14	56.1
8	SF2@150	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	150	14	67.5
9	SF2@200	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	200	14	79.8
10	SF2@250	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	250	14	108.3
11	EW@250	Estuarine water	250	14	112.5
12	SF3@250	0.1 M Na ₂ CO ₃	250	14	128.7

[SW=seawater; SF= synthetic fluid; EW= estuarine water].

4.4.2.2. *XRF Analysis*

The oxides composition of pre- and post-experiment samples were analyzed using a Panalytical Zetium wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometer. Samples were prepared by fusion with lithium metaborate flux using a Classic The OX Advanced fusion instrument (Malvern Panalytical). For each sample, 1.0 g of finely ground material was mixed with 10.0 g of flux ($\text{LiBO}_2\text{:Li}_2\text{B}_4\text{O}_7$ in a 49.75:49.75:0.50 ratio) in a platinum-gold crucible. The mixture underwent a controlled heating program: an initial hold at 500°C for 2 minutes, a gradual ramp to 1125°C over 27 minutes with intermittent rocking, and final vigorous swirling before being poured into a mold to form homogeneous glass disks. The cooled glass disks were analyzed on the Zetium spectrometer, equipped with a high-resolution Cu anode X-ray tube and specialized analyzing crystals for enhanced sensitivity and resolution across major, minor, and trace elements. The quantitative analysis utilized synthetic-certified reference materials (WROXI series) and was validated with periodic quality control standards. PANalytical SuperQ software was used for spectral acquisition, matrix corrections, and data processing, ensuring accuracy and precision. This methodology, optimized for geological materials, supported the reliable detection of major oxides and trace oxides at ppm levels.

4.4.2.3. *Bulk and clay fraction XRD analysis*

The mineralogical compositions of bulk and clay fractions ($<2\ \mu\text{m}$) in the starting and post-experiment samples were determined via X-ray diffraction (XRD), using the Malvern Empyrean PANalytical diffractometer with Ni-filtered Cu $K\alpha$ radiation. Bulk sediments were air-dried, powdered with a Retsch RM 200 mill, and analyzed under conditions of 45 kV and 40 mA across a $4.5\text{--}70^\circ\ 2\theta$ range with an 8.7-second scan time using the procedures outlined by (Salisu et al., 2023)

Clay fractions ($<2\ \mu\text{m}$) were isolated through gravity settling and centrifugation as described by Salisu et al., (2024). Five grams of bulk sample were dispersed in 100 mL of deionized water, ultrasonicated for 20 minutes with periodic stirring, and settled to remove sand and silt particles. The clay-rich supernatants were concentrated by centrifugation at 5000 rpm for 15 minutes. The separated clay fractions were prepared as oriented aggregates and were analyzed in three states: air-dried, ethylene glycol-solvated, and heated at 550°C (1 hour). Analyses were conducted over a $4-40^{\circ} 2\theta$ range with a $0.05^{\circ}/\text{s}$ step size. Clay minerals were identified using HighScore Plus (v. 4.9), with the ICDD PDF-4-2022 mineralogical library and additional data from (Moore, D.M. & Reynolds, 1998). The baseline peak positions of air-dried clays were compared with those after ethylene glycol (EG) solvation and heating treatments to distinguish the clay minerals. For semi-quantitative analysis, Rietveld refinement was conducted in HighScore Plus using structure files from the Inorganic Crystal Structure Database (ICSD), carefully selected for compatibility with oriented clay samples. Profile-matching techniques ensured alignment between experimental spectra and reference patterns, while the March-Dollase function was applied to correct preferred orientation effects. Profex software was also used for cross-validation to enhance result reliability. Despite following these protocols, the results remain semi-quantitative due to HighScore's inherent limitations in accurately quantifying oriented clay minerals.

4.4.2.4. *STEM analysis*

The morphological and structural characterization of clay minerals was conducted using scanning transmission electron microscopy (STEM) on a Dual Beam Laser FIB-SEM system (Zeiss 550). The integrated STEM detector, positioned beneath the specimen and aligned perpendicularly to the optical axis, collected transmitted electrons that passed through the samples. The separated clay fractions were prepared as aqueous suspensions in deionized water and aspirated onto carbon-coated copper 200-mesh TEM grids (QUANTFOIL, Germany). The grids were dried in a

desiccator before being mounted on a specialized TEM grid holder adapted for the SEM stage. The analyses were conducted under operating conditions of 10 kV accelerating voltage and a probe current of 500 pA. The segmented design of the STEM detector enabled selective enhancement of image contrast by activating or deactivating specific detector segments (aSTEM4 B). Multiple micrographs were acquired under these conditions to ensure thorough characterization of the samples. Additionally, elemental compositions of specific minerals were determined using energy-dispersive X-ray spectroscopy (EDS) at several points of interest.

4.4.2.5. *ICP-OES analysis*

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was employed to determine the elemental composition of major cations in solutions before and after the hydrothermal experiments. Analyses were performed using a PerkinElmer Plasma Quant 9000 ICP-OES instrument, which utilizes plasma as an excitation source to detect optical emissions. Post-experiment fluids were collected, transferred to vials, and diluted to the appropriate ratios prior to analysis. This procedure allowed for the quantification of key cations, including Al, Ca, Fe, Mg, K, and Na, in both pre-and post-experiment solutions.

4.4.2.6. *FIB-SEM analysis*

Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) was employed to examine the internal structure of the samples with high-resolution imaging. The analysis was performed using a Zeiss Crossbeam 550 FIB-SEM equipped with a Gallium FIB column and automated using SmartFIB software. For cross-sectioning, a trapezoidal trench with a 30 μm width and 20 μm depth was milled in three stages. Coarse milling (30 kV, 15 nA) rapidly excavated the trench, followed by intermediate milling (30 kV, 700 pA) to expose the target area. A final fine polishing step (30 kV, 300 pA) created a smooth surface and removed residual debris. Tilt correction was applied to optimize imaging accuracy, and micrographs were captured to document key features. Serial

sectioning was then conducted with a 50 nm slice thickness over a 40 μm length, generating sequential layers for detailed analysis. Both secondary electron (SE) and backscattered electron (BSE) micrographs were automatically recorded for each section, enabling comprehensive characterization of the sample's cross-sectional properties.

4.5. Results

4.5.1. Compositional evaluation of the starting material

The starting material consists of fine to silt-sized grains that are moderately sorted and angular to subangular in shape. WD-XRF oxide analyses (Table 2) indicate that the sediment is dominated by SiO_2 (57.43 wt%), Al_2O_3 (17.43 wt%), CaO (9.87 wt%), Fe_2O_3 (7.38 wt%), K_2O (3.07 wt%), and MgO (2.12 wt%) (Figure 3). Minor amounts of TiO_2 (1.01 wt%) and Na_2O (0.79 wt%) are also present, while ClO_2 , MnO , P_2O_5 , SO_3 , and SrO occur in trace quantities (Table 2). Bulk XRD analysis (Table 3, Figure 4) reveals that the sediment is predominantly composed of quartz (40.7%), plagioclase (14.7%), and orthoclase (5.3%) (Table 3). Additionally, significant amounts of calcite (9.7%) and muscovite (9.3%) are present. Clay minerals, including kaolinite, smectite, and illite, constitute 20.3% of the total bulk mineralogy (Table 3).

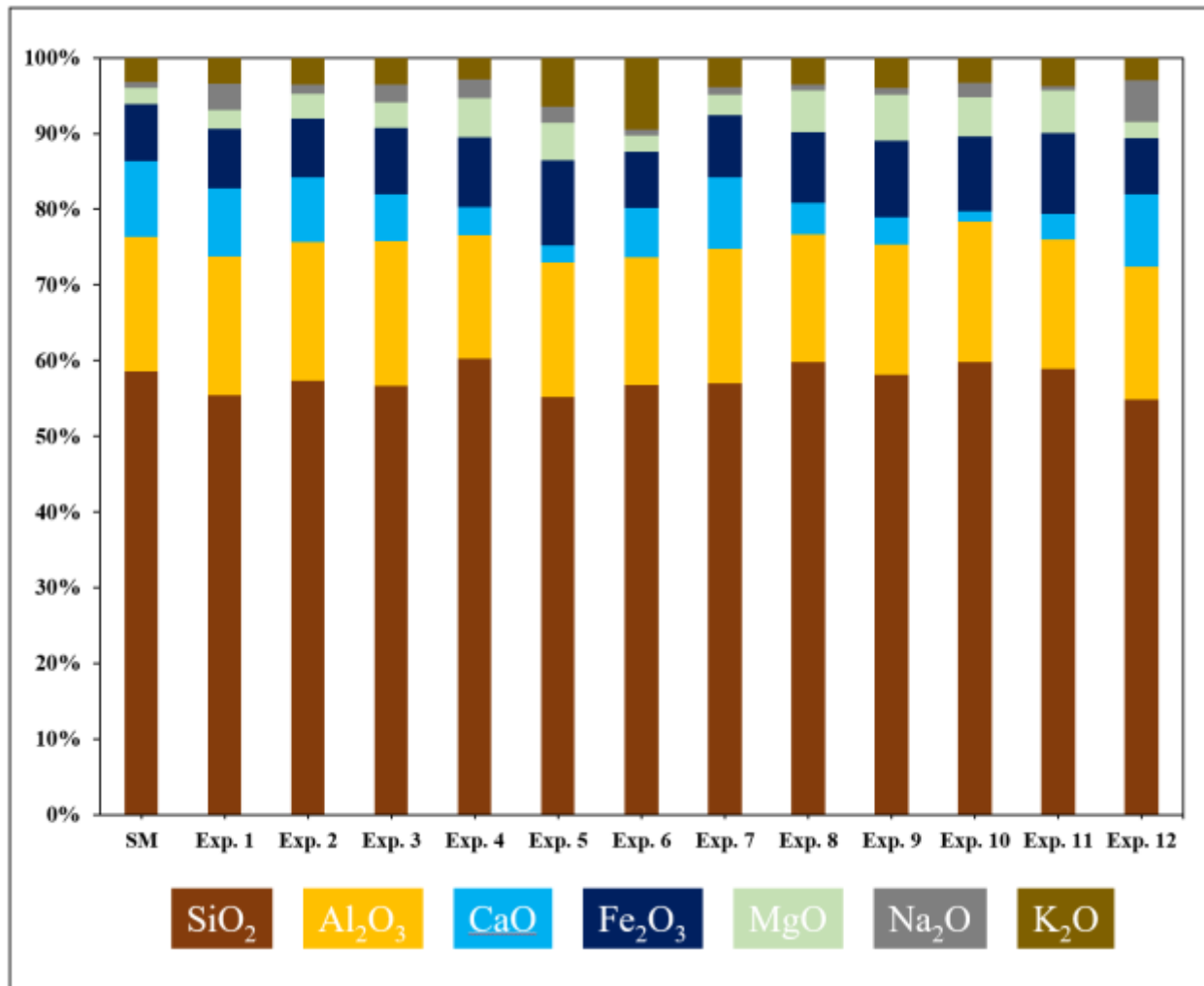


Figure 4.3. A 2D stacked column plot of XRF analysis illustrating the normalized concentration and distribution of major oxides in the sediments before and after the hydrothermal experiments. Note the relative abundance and evolution of CaO, MgO, Fe₂O₃, and K₂O across the different experiments.

Table 4.2. WDX-XRF analysis of the starting material and post-reacted sample. [SM = Starting material; SW=seawater; SF= synthetic fluid; EW= estuarine water].

Experiment	Sample ID	Oxides measured in weight percent (wt %)												
		SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	ClO ₂	MnO	P ₂ O ₅	SO ₃	SrO	TiO ₂
SM	SM@0	57.43	17.43	9.87	7.38	2.12	0.79	3.07	0.09	0.15	0.18	0.14	0.02	1.01
Exp. 1	SW@50	52.86	17.55	8.62	7.48	2.32	3.37	3.24	2.64	0.09	0.18	0.51	0.02	0.94
Exp. 2	SW@100	56.43	18.04	8.43	7.66	3.18	1.21	3.46	0.09	0.13	0.21	0.06	0.02	1.04
Exp. 3	SW@150	54.59	18.36	5.90	8.49	3.23	2.34	3.35	1.62	0.12	0.20	0.54	0.02	0.97
Exp. 4	SW@200	57.30	15.47	3.59	8.68	4.93	2.36	2.73	1.51	0.11	0.16	1.88	0.02	0.90
Exp. 5	SW@250	52.77	16.94	2.22	10.67	4.78	2.01	6.18	2.26	0.10	0.19	0.71	0.02	0.93
Exp. 6	SF1@250	54.59	16.12	6.29	7.19	2.03	0.73	9.14	2.39	0.12	0.18	0.04	0.01	0.98
Exp. 7	SF2@100	55.08	17.15	9.15	7.94	2.64	0.98	3.72	1.66	0.09	0.17	0.11	0.02	0.94
Exp. 8	SF2@150	58.00	16.34	4.04	9.09	5.25	0.78	3.44	1.33	0.08	0.19	0.06	0.01	0.99
Exp. 9	SF2@200	55.85	16.62	3.39	9.79	5.84	0.86	3.79	2.19	0.09	0.19	0.06	0.01	0.96
Exp. 10	SF2@250	58.24	18.08	1.39	9.58	5.06	1.94	3.16	0.77	0.09	0.22	0.16	0.01	1.06
Exp. 11	EW@250	57.06	16.59	3.26	8.23	7.62	0.60	3.59	1.33	0.12	0.19	0.05	0.01	1.35
Exp. 12	SF3@250	53.97	17.26	9.36	7.30	2.14	5.46	2.88	0.09	0.14	0.19	0.04	0.02	0.95

These findings are further supported by SEM and EDS analyses, which demonstrate that the dominant detrital grains are monocrystalline quartz (Figure 5A-B), K-feldspar (Figure 5A), albite, and muscovite (Figure 5B). Carbonate materials are predominantly calcite (Figure 5A). The results also reveal that the framework grains are partially coated with detrital clay and silt-sized materials, which occur as drapes (Figure 5A) and aggregates (Figure 5B). These grain coats are primarily composed of clay minerals, with minor amounts of silt-sized quartz grains and diatoms (Figure 5C-D). However, even under higher-resolution SEM imaging (Figure 5E), it was challenging to identify specific clay minerals based on morphology due to poor crystallization and poorly defined internal structures. EDS analysis confirms that the grain coats are composed of Si, O, Al, K, Fe, Mg, and Ca (Figure 5F). XRD analyses of the clay fraction reveal that the detrital clay mineral assemblage is dominated by kaolinite (51.5%) and illite (41.1%), with minor contributions from smectite (5.3%) and no detectable chlorite (Figure 6A, Table 3). Smectite peaks were identified after ethylene glycol solvation. They disappeared, along with kaolinite, following heating to 550°C for 1 hour (Figure 6A). The d-spacing values of the identified clay minerals are annotated on the overlaid diffraction peaks (Figure 6A).

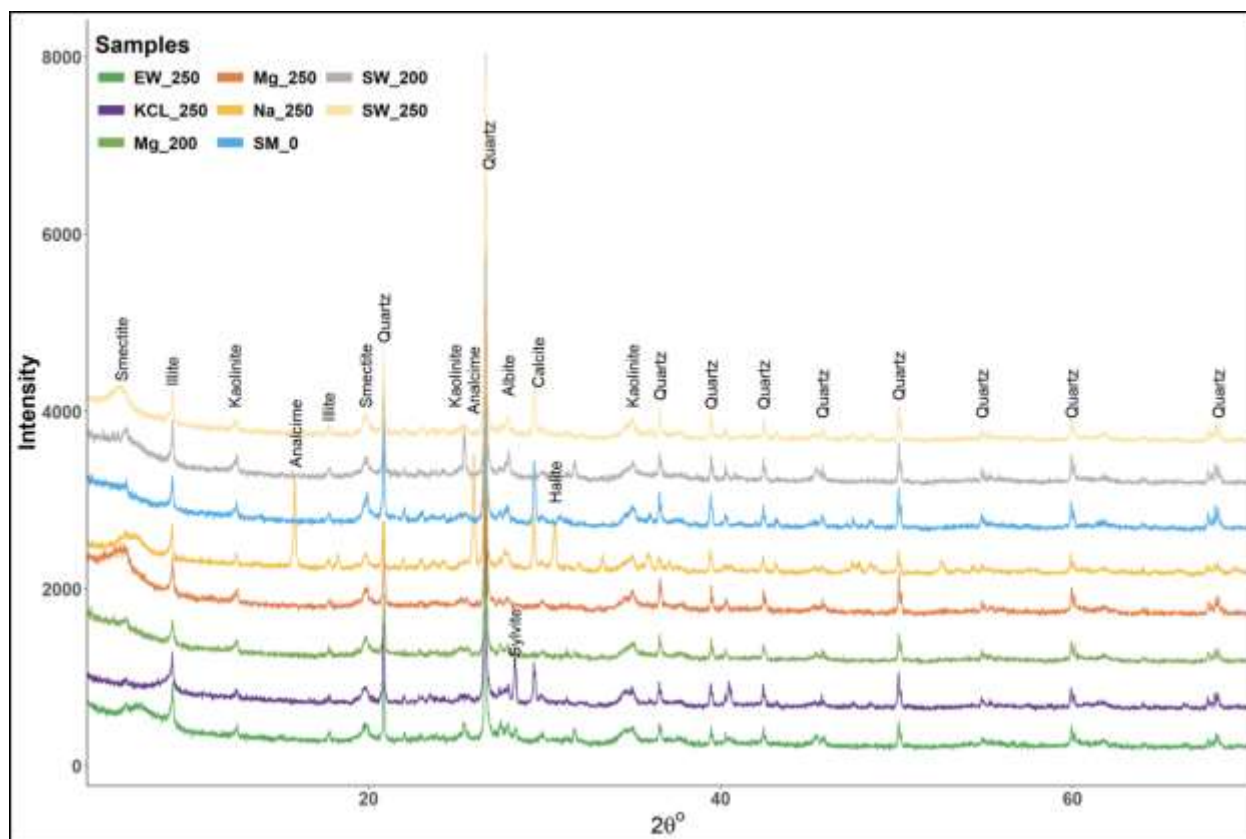


Figure 4.4. A stacked plot of the bulk XRD analysis presenting the diffractograms of the major minerals identified in the starting material (SM) and selected experiments conducted using seawater (SW), estuarine water (EW), Mg-rich synthetic fluids (Mg), K-rich synthetic fluids (KCl), and Na-rich synthetic fluids (Na). Notably, a broad analcime peak is observed in Na_250 (Exp. 12), while it is absent in all other experiments.

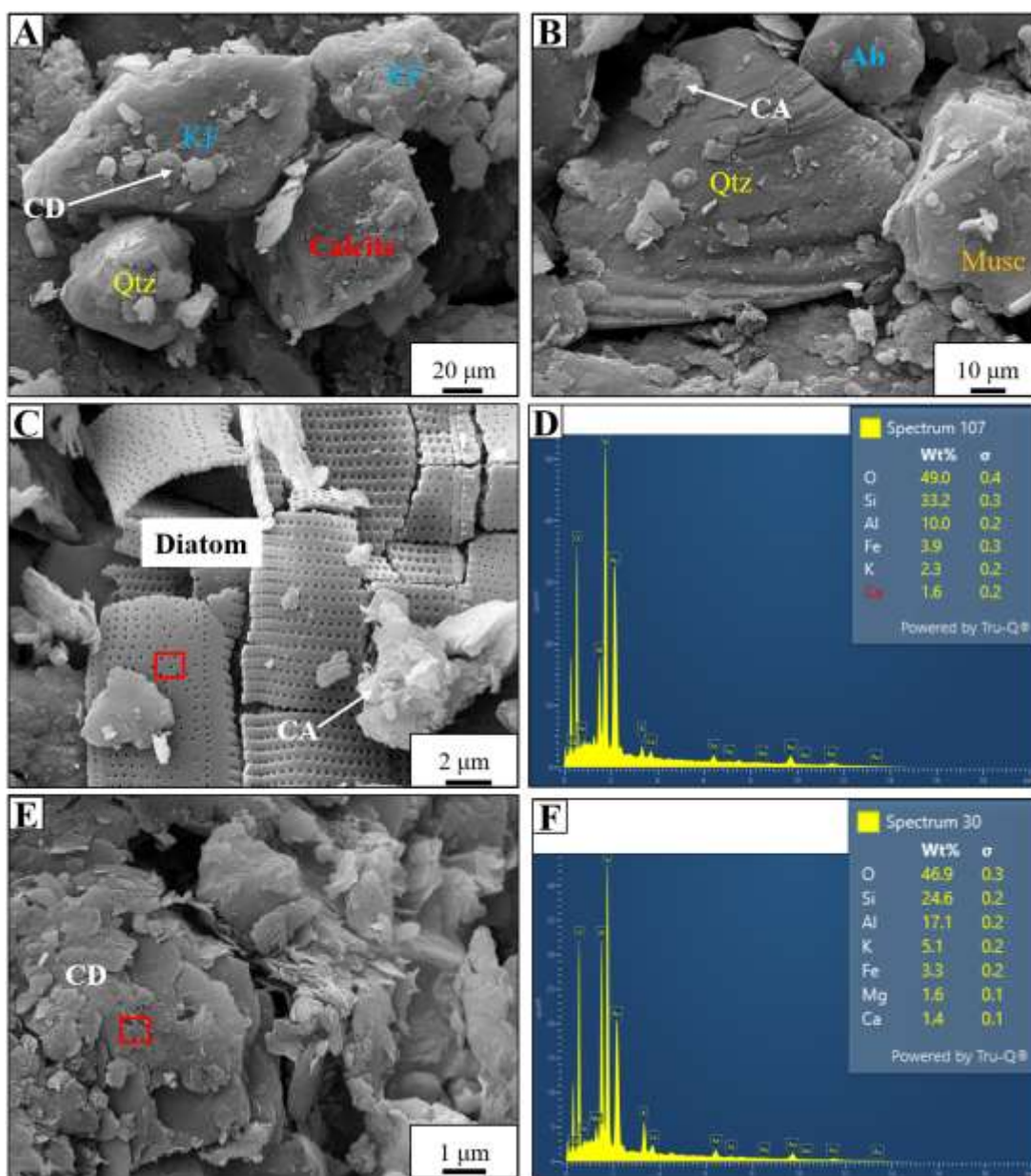


Figure 4.5. SEM and EDS images illustrating detrital framework grains and clay coatings. (A) SEM image showing detrital quartz (Qtz), K-feldspar (KF), and calcite, with clay drapes (CD) coating the K-feldspar. (B) SEM image highlighting detrital albite (Ab), muscovite (Musc), and clay aggregates (CA) coating a quartz grain. (C) SEM image and (D) corresponding EDS spectra depicting a diatom embedded within detrital clay coats, with the red square in (C) marking the point of the EDS analysis shown in (D). (E) High-resolution SEM image of a detrital clay drape

(CD), with the red square indicating the point of the EDS analysis displayed in (F). (F) EDS spectra of the clay drape in (E) revealing the presence of kaolinite, smectite, and illite.

4.5.2. Geochemical and Mineralogical Evaluation of Post-Experiment Samples

A detailed compositional assessment of the reactive fluids and solids retrieved after the hydrothermal experiments was conducted using ICP-OES, WD-XRF, SEM, SEM-EDS, STEM, and XRD analyses. The results demonstrate distinct geochemical and mineralogical changes influenced by the experimental fluids chemistry and increasing temperatures (Figs. 3–13; Tables 2–4). Below, the findings are presented based on the observed changes in experiments conducted with different reactive fluids.

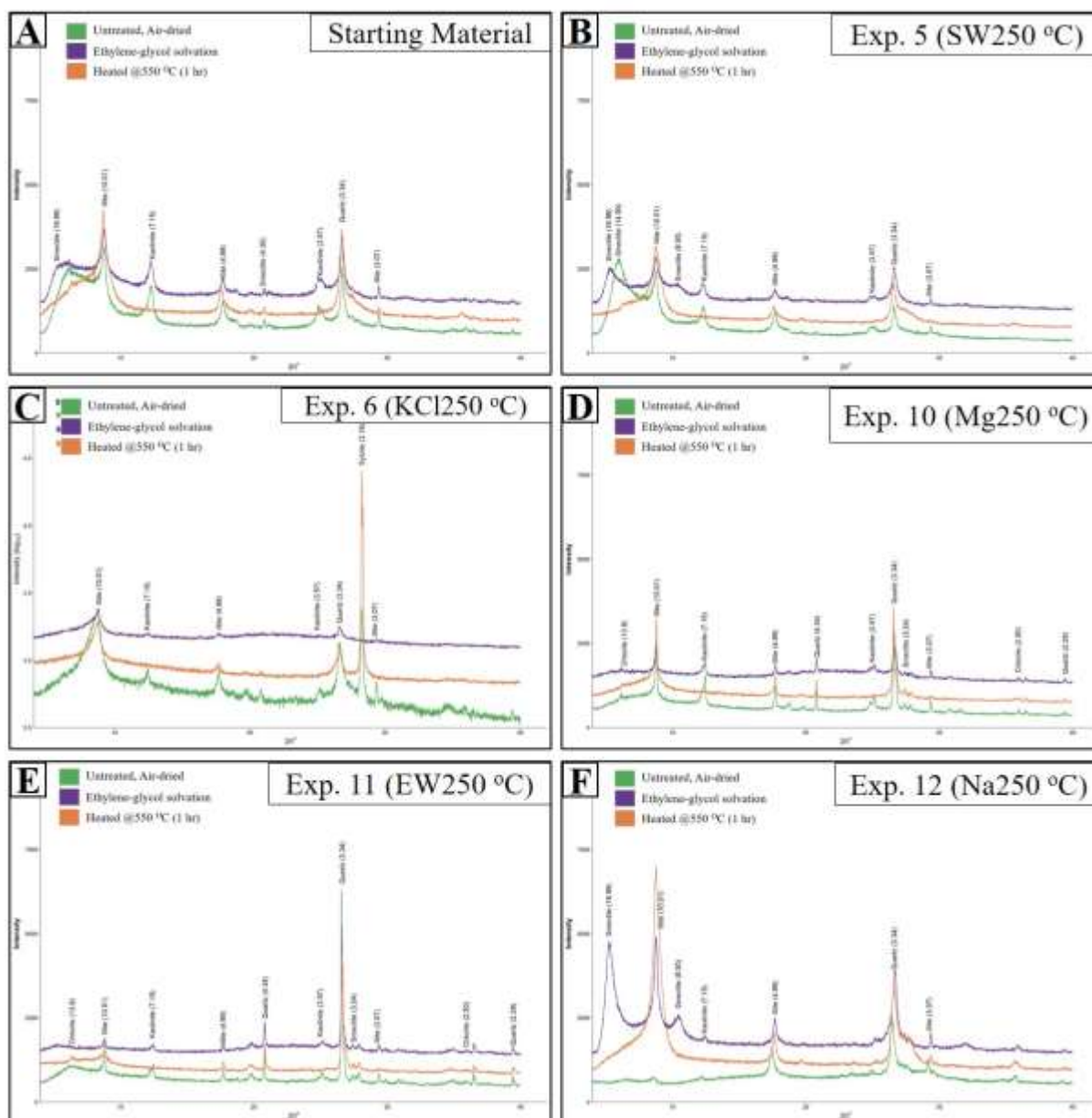


Figure 4.6. XRD patterns of the oriented clay fraction ($< 2 \mu\text{m}$) from the starting material and selected experiments. (A) Overlaid diffractograms of the starting material reveal the presence of smectite, illite, and kaolinite as the primary detrital clays in the sediments. (B) Diffractograms of air-dried, ethylene glycol-solvated, and heated clay fractions from Exp. 5 show the presence of smectite, kaolinite, and illite. Notably, the kaolinite peaks exhibit a decrease in intensity and the primary smectite peak shifts from $14.90 \text{ \AA}$ in the air-dried pattern to $16.99 \text{ \AA}$ following ethylene

glycol solvation. (C) Air-dried, ethylene glycol-solvated, and heated diffractograms from Exp. 6 reveal the presence of illite and kaolinite. Smectite peaks are absent, kaolinite peaks are significantly weakened, and an increase in the intensity of the illite peak is observed, alongside the appearance of sylvite. (D, E) Overlaid diffractograms from Experiments 10 and 11 indicate the authigenic formation of chlorite along with the presence of illite and kaolinite. (F) Diffractograms from Exp. 12 confirm the presence of illite, smectite, and kaolinite.

Table 4.3. Bulk and clay fraction composition in pre-and post-reacted samples. [SM=starting material; Qtz=quartz; Orth=orthoclase; Pla=plagioclase; Cal=calcite; Mus=muscovite; CM=clay minerals; Hal= halite; Syl=sylvite; Ana= analcime; Kao=kaolinite; Sme=smectite; Ill=illite; Chl=chlorite].

Sample ID	Bulk mineralogy (%)										Clay mineralogy (< 2 µm) (%)				
	Qtz	Orth	Pla	Cal	Mus	CM	Hal	Syl	Ana	Total	Kao	Sme	Ill	Chl	Qtz
SM	40.7	5.3	14.7	9.7	9.3	20.3	-	-	-	100.0	52	5	41	-	2
Exp. 1	41.0	8.1	17.3	5.1	7.6	20.9	-	-	-	100.0	50	5	40	-	5
Exp. 2	39.3	7.7	15.2	3.7	6.9	27.2	-	-	-	100.0	48	6	42	-	4
Exp. 3	38.5	7.6	14.9	3.1	6.3	29.6	-	-	-	100.0	41	7	49	-	3
Exp. 4	35.4	4.8	16.5	1.8	5.1	34.7	1.7	-	-	100.0	33	3	58	-	6
Exp. 5	38.9	2.4	15.6	1.2	3.5	38.4	-	-	-	100.0	18	2	76	-	4
Exp. 6	29.4	6.3	14.5	5.8	3.3	37.1	-	3.6	-	100.0	20	TR	80	-	0
Exp. 7	38.2	9.1	18.7	3.0	8.1	22.9	-	-	-	100.0	44	2	48	-	6
Exp. 8	36.9	7.4	14.9	3.9	7.2	29.7	-	-	-	100.0	40	1	52	4	3
Exp. 9	37.6	4.0	15.5	0.5	3.5	38.9	-	-	-	100.0	34	0	55	8	3
Exp. 10	35.2	3.8	9.7	0.3	3.3	46.7	-	-	-	100.0	26	0	52	16	6
Exp. 11	35.1	3.5	14.4	1.9	5.8	36.9	-	-	-	100.0	25	1	48	24	3
Exp. 12	31.2	5.3	12.1	9.1	5.2	13.1	2.4	-	21.7	100.0	16	40	41	-	3

4.5.2.1. Seawater-based experiments (Experiments 1–6)

Experiments 1–5 were performed using natural Red Sea water under increasing temperatures of 50, 100, 150, 200, and 250°C, respectively, with a constant duration of 14 days per experiment, while Exp. 6 was conducted with 0.1 M KCl dissolved in Red Sea water (SF1) at 250°C for 14 days (Table 1). XRF analyses of the sediments from these experiments reveal variations in major and minor oxides with increasing experimental temperature (Table 2, Figure 3). The concentration of SiO₂ fluctuates, increasing from 52.86 wt% in Exp. 1 to 56.43 wt% in Exp. 2, before decreasing to 54.59 wt% in Exp. 6 (Table 2). During Experiments 1–3, the Al₂O₃ content in the reacting solids increases slightly, from 17.55 wt% in Exp. 1 to 18.36 wt% in Exp. 3, but then decreases significantly to 15.47 wt% and 16.94 wt% in Experiments 4 and 5, respectively. Calcium oxide (CaO) consistently decreases with rising experimental temperature, from 8.62 wt% in Exp. 1 to 2.22 wt% in Exp. 5, and increasing to 6.29 wt% in Exp. 6 (Table 2). Similarly, Na₂O shows a slight decrease as temperature increases. In contrast, Fe₂O₃, MgO, and K₂O concentrations generally increase with temperature, except in Exp. 4, where K₂O decreases slightly to 2.73 wt%. Notably, K₂O increases significantly, from 3.07 wt% in the starting material to 9.14 wt% in Exp. 6. Trace oxides such as ClO₂, MnO, P₂O₅, SO₃, and SrO remain relatively stable across all experiments, except for ClO₂, which shows irregular fluctuations (Table 2).

The hydrochemical composition of the Red Sea water and SF1 pre- and post-experiments (Experiments 1–6) is summarized in Table 4 and Figure 10. The pH of the fluids decreases consistently with increasing temperatures, dropping from 8.12 in the initial Red Sea water to 6.34 in Exp. 5. Similarly, in Exp. 6, the pH decreases from 7.78 in the pre-reacted solution to 6.86 post-experiment (Table 4). Total dissolved solids (TDS) increase significantly during the experiments, with TDS rising from 36.71 ppt in the starting solution of Experiments 1–5 to 58.95 ppt and 105.2

ppt in Experiments 4 and 5, respectively. For Exp. 6, TDS increases from 43.95 ppt pre-experiment to 104.5 ppt post-experiment (Table 4). ICP-OES analysis highlights variations in six major cations (Al, Ca, Fe, Mg, K, Na) during the experiments. Aluminum (Al) concentration rises steadily from 57.7 mg/L in the starting solution to 420 mg/L in Exp. 1 and 1080 mg/L in Exp. 5, corresponding to increasing temperatures. Calcium (Ca) shows a marked increase in the fluid phase, from 396 mg/L in the starting solution to 67,000 mg/L in Exp. 5, contrasting with its rapid depletion in the solids (Table 2). Potassium (K) concentrations increase during Experiments 1 and 2 but decline in Exp. 3 before being significantly consumed in Experiments 4–6 (Table 4). Iron (Fe) concentrations increase slightly with temperature, while magnesium (Mg) and sodium (Na) concentrations decrease (Table 4).

Bulk mineralogical results from XRD analyses indicate that quartz remains the dominant mineral throughout the experiments (Table 3, Figure 4), though its concentration decreases slightly from 41.0% in Exp. 1 to 38.9% in Exp. 5 and 29.4% in Exp. 6. Orthoclase decreases significantly, from 8.1% in Exp. 1 to 2.4% in Exp. 5, while plagioclase undergoes a moderate decrease (Table 3). Both muscovite and calcite dissolve rapidly with rising temperatures, with calcite reducing from 5.1% in Exp. 1 to 1.2% in Exp. 5. Conversely, clay mineral content increases significantly, from 20.9% in Exp. 1 to 38.4% in Exp. 5 and 37.1% in Exp. 6. Halite is observed in minor amounts (1.7%) in Exp. 4, while sylvite appears at 3.6% in Exp. 6 (Table 3). Oriented XRD analyses of the clay fraction ($<2\ \mu\text{m}$) identify kaolinite, smectite, and illite (Table 3, Figure 6B–C). In Exp. 5, the primary smectite peak (001) is detected at a d-spacing of 14.9 Å in the air-dried analysis, shifting to 16.99 Å after ethylene glycol treatment, with a 002 peak at 8.5 Å. The 001 peak disappears after heating to 550°C for 1 hour (Figure 6B). Smectite is absent in Exp. 6 (Figure 6C). Kaolinite's 001 and 002 peaks at 7.15 Å and 3.57 Å, respectively, are observed in both air-dried and ethylene

glycol-treated samples but disappear after heating in Exp. 5. In Exp. 6, kaolinite peaks appear weaker compared to Exp. 5 (Figure 6C). Illite's 001, 002, and 003 peaks are identified at 10.01 Å, 4.99 Å, and 3.07 Å, respectively, and are present in both untreated and treated analyses (Figure 6B–C). Semi-quantitative analyses of the clay fraction reveal that kaolinite decreases with increasing temperatures, while smectite fluctuates irregularly (Table 3). Kaolinite declines from 50% in Exp. 1 to 18% in Exp. 5 and 20% in Exp. 6. Smectite decreases slightly in the low-temperature experiments, from 5% in Exp. 1 to 4.9% in Exp. 2, before increasing to 7.2% in Exp. 3. It subsequently declines to 3%, 2%, and trace amounts in Experiments 4, 5, and 6, respectively. In contrast, illite increases significantly, from 40% in Exp. 1 to 76% and 80% in Experiments 5 and 6, respectively (Table 3). Minor silt-sized quartz is also observed in the clay fraction, and sylvite peaks appear in Exp. 6 (Figure 6C).

SEM and EDS analyses of low-temperature experiments (Experiments 1 and 2) show minimal changes in detrital grain distribution, with no significant mineralogical transformations, observed (Figure 7A). However, SEM reveals the disaggregation and partial dissolution of aggregated detrital grain coats in Exp. 2 (Figure 7A). During Exp. 3 (150°C), smectite precipitates adjacent to kaolinite platelets, forming incipient crenulated to honeycomb morphologies (Figure 7B). These newly formed smectite coatings develop further in Exp. 4 (200°C), displaying improved internal structures and crystallinity (Figure 7C). Illitization of smectite begins in Exp. 4 and progresses into Exp. 5 (250°C). SEM shows the replacement of smectite by mixed-layer illite/smectite and eventually illite, which retains the honeycomb morphologies of smectite but develops spiny terminations characteristic of illite (Figure 7D–E). EDS confirms that the newly formed illite is dominated by Si, O, Al, and K, with minor Fe (Figure 7F). STEM analyses further identify pseudohexagonal kaolinite, smectite, and illite in Exp. 5 (Figure 8).

In Exp. 6, SEM and EDS analyses reveal similar transformations to those observed in Exp. 5. SEM observations show the dissolution of kaolinite and the formation of sylvite adjacent to mixed-layer illite/smectite (Figure 9A–B). Newly formed illite from smectite displays rugged honeycomb morphologies, while illitized kaolinite exhibits flaky to radial morphologies with hairy spikes (Figure 9C). EDS analysis confirms that illite is dominated by Si, Al, O, K, and minor amounts of Fe and Ca (Figure 9D).

Table 4.4. ICP-OES analysis showing the concentrations of major cations in solutions before and after the hydrothermal experiments.

Identification			Major cations (mg/L)						TDS (ppt)
			pH	Al	Ca	Fe	Mg	Na	
SW	SW@0	8.12	57.7	396	638	1820	18650	798	36.71
Exp. 1	SW@50	7.21	420	7730	770	1740	15680	6460	56.19
Exp. 2	SW@100	6.88	542	14260	1080	1400	14900	7100	56.73
Exp. 3	SW@150	6.42	648	22500	1690	939	12060	6060	58.01
Exp. 4	SW@200	6.41	782	44800	2310	631	5950	2470	58.94
Exp. 5	SW@250	6.34	1080	67000	2350	431	5510	2000	105.2
SF1	SF1@0	7.78	70.1	410	650	1690	16430	17200	43.95
Exp. 6	SF1@250	6.86	477	58000	919	818	9600	9060	104.5
SF2	SF2@0	5.71	ND	8730	ND	15500	12800	7650	45.33
Exp. 7	SF2@100	6.22	47.8	21400	13.7	3690	12500	9280	56.15
Exp. 8	SF2@150	6.45	126	29900	16.6	3520	10610	10300	62.08
Exp. 9	SF2@200	6.28	520	42500	60.1	600	6820	2990	60.69
Exp. 10	SF2@250	6.22	787	48400	132	167	2590	2620	62.29
EW	EW@0	7.26	5.2	12.1	112	381	10600	70.5	13.02
Exp. 11	EW@250	6.91	120	14200	5.1	120	8700	1250	26.39
SF3	SF3@0	11.32	ND	ND	ND	ND	8250	ND	13.79
Exp. 12	SF3@250	8.31	860	2910	1820	38.4	390	1140	7.79

[TDS= total dissolved solids; SW=seawater; SF= synthetic fluid; EW= estuarine water].

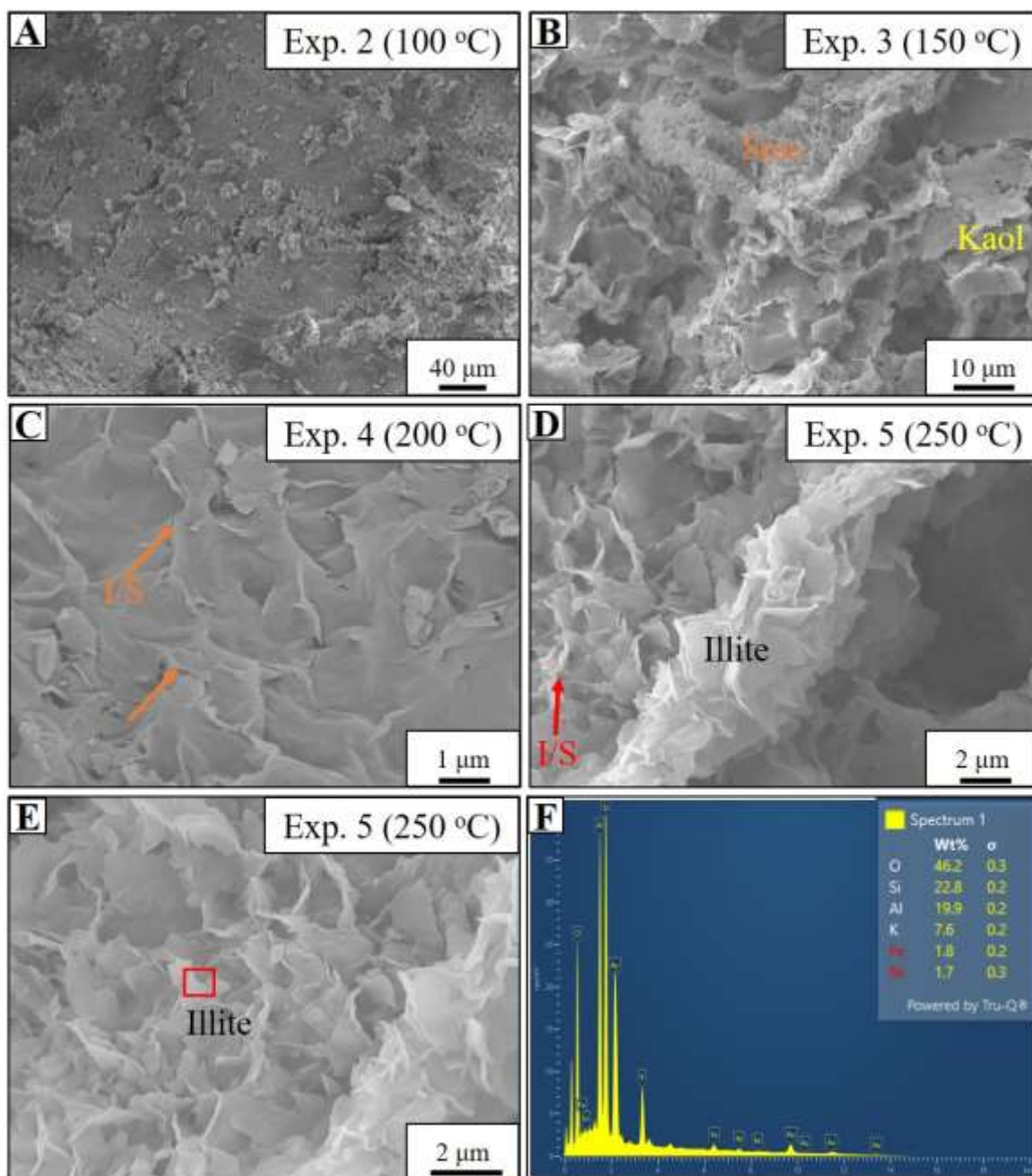


Figure 4.7. SEM and SEM-EDS images illustrating the diagenetic features in seawater-based experiments (1–5). (A) SEM image depicting the onset of clay disaggregation and dissolution in Exp. 2. (B) SEM image showing the authigenic formation of honeycomb smectite (Sme) adjacent to kaolinite (Kaol) in Exp.3. (C) SEM image highlighting the formation of mixed-layer illite/smectite (I/S) with initial crenulated to honeycomb morphologies in Exp. 4. (D) SEM image

showing the formation of illite adjacent to mixed-layer I/S in Exp. 5, where the illite retains the honeycomb morphology of smectite. (E) Fully developed illite with honeycomb morphology and spiny terminations. (F) EDS spectra confirming the presence of illite. The location of the EDS point is shown in E (red square).

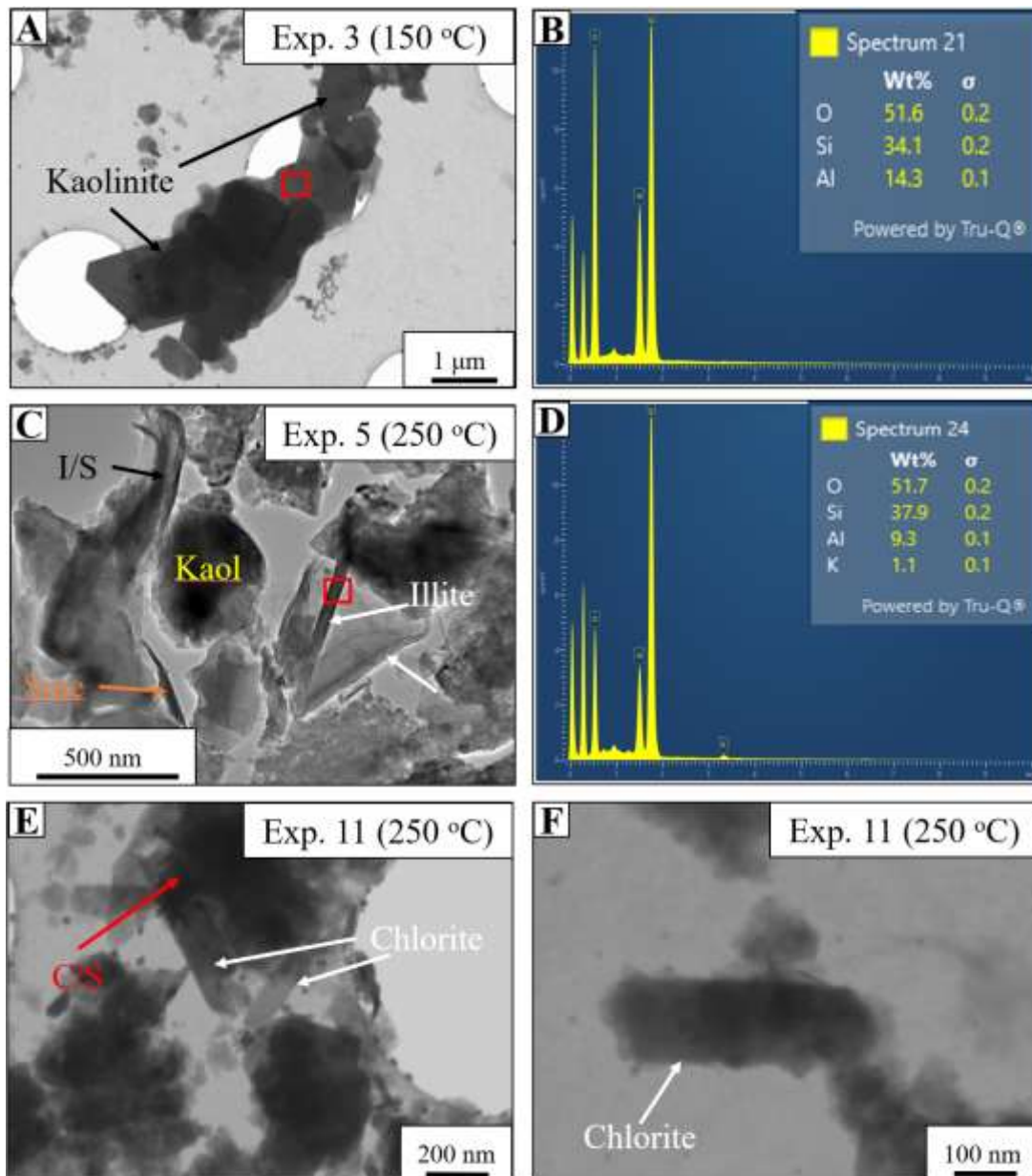


Figure 4.8. Diagenetic features of post-experiment clay minerals from STEM and STEM-EDS analyses. (A) STEM image showing hexagonal kaolinite aggregates during Exp. 3. The red square indicates the location of EDS analysis shown in B. (B) EDS spectra confirming the presence of kaolinite. (C) STEM image illustrating the polycrystalline nature of clays in Exp. 5, where illite developed adjacent to illite/smectite (I/S), smectite, and pseudohexagonal kaolinite. (D) Elemental analysis (EDS) highlighting authigenic illite. The location of the EDS point is shown in C (red square). (E) STEM image showing authigenic chlorite and mixed-layer chlorite/smectite (C/S) in Exp. 11. (F) Close-up view of an elongated chlorite crystal in Exp. 11.

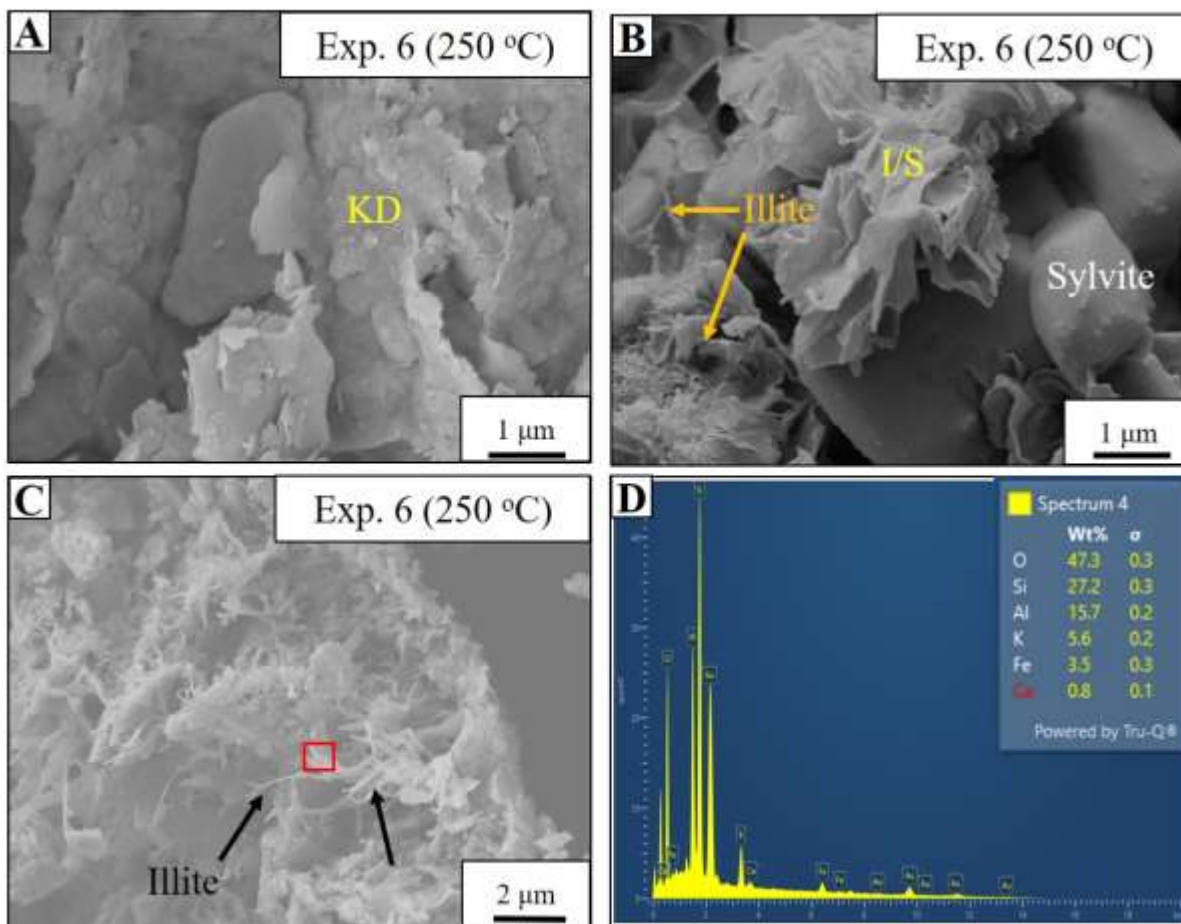


Figure 4.9. Diagenetic features observed in Exp. 6. (A) SEM image showing kaolinite dissolution (KD). (B) SEM image revealing the occurrence of illite with a rugged honeycomb morphology,

alongside mixed-layer illite/smectite (I/S) and newly formed sylvite. (C) Newly formed illite. The illite displayed lath-like to radial flakes morphology. The red square marks the EDS point shown in D. D) EDS spectra of the observed illite.

4.5.2.2. *Mg-rich synthetic fluid-based experiments (Experiments 7–10)*

Experiments 7, 8, 9, and 10 were conducted at temperatures of 100, 150, 200, and 250 °C, respectively, using a 0.1 M NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ synthetic solution (SF2) for 14 days each. Results from these experiments highlight some differences in mineralogical and chemical transformations, compared to seawater-based experiments. XRF analysis revealed that SiO_2 content increased from 55.08 wt% in Exp. 7 to 58.00 wt% in Exp. 8, slightly decreased in Exp. 9, and rose again in Exp. 10 (Table 2, Figure 3). Al_2O_3 concentrations exhibited a minor decrease in Exp. 8, remained relatively stable in Exp. 9, and increased in Exp. 10 (Table 2). CaO concentrations significantly decreased with increasing experimental temperatures, from 9.15 wt% in Exp. 7 to 1.39 wt% in Exp. 10. Notably, both Fe_2O_3 and MgO concentrations increased with rising experimental temperatures, with MgO rising from 2.64 wt% in Exp. 7 to 5.06 wt% in Exp. 10 (Table 2). The concentrations of Na_2O and K_2O remained relatively unchanged across the experiments (Table 2).

XRD analysis of the bulk mineralogy identified quartz and feldspars (orthoclase and plagioclase) as the dominant minerals in all experiments. Quartz concentrations fluctuated slightly, decreasing in Exp. 10 after an increase in Exp. 9 (Table 3). Orthoclase and plagioclase feldspars decreased with increasing temperature (Table 3). Calcite and muscovite were also present but decreased in concentration with rising temperatures from Exp—7 to 10 (Table 3). The total clay mineral content in the bulk mineralogy increased progressively, rising from 22.9% in Exp. 7 to 46.7% in Exp. 10 (Table 3). Kaolinite, illite, and chlorite were detected in oriented clay fraction XRD analyses

(Figure 6D). In Exp. 10, kaolinite exhibited characteristic peaks at 7.15 Å (001) and 3.57 Å (002) in air-dried and ethylene glycol-treated samples, which disappeared upon heating (Figure 6D). Illite peaks were consistent across all untreated and treated analyses (Figure 6D). Smectite was present in minor to trace amounts and decreases with increasing temperature, with only a weak peak observed at 3.24 Å in Exp. 10 (Figure 6D). A distinctive feature of these experiments was the authigenic formation of chlorite, which began in Exp. 8 and increased with temperature. Chlorite exhibited a primary (001) peak at 13.99 Å (Figure 6D), with low-intensity peaks identified in both air-dried and treated samples. Semi-quantitative analysis showed that kaolinite concentration in the clay fraction decreased with increasing temperature, while smectite decreased from 2% in Exp. 7 to trace amounts in Exp. 10. Illite concentration increased in Experiments 8 and 9 before slightly declining in Exp. 10 (Table 3). Chlorite concentrations consistently increased, rising from 4% in Exp. 7 to 16% in Exp. 10 (Table 3).

The pH and TDS of the pre-experiment solution (SF2) were measured at 5.71 and 45.33 ppt, respectively (Table 4). Post-experiment, the pH increased to 6.22 in Exp. 7 and remained stable throughout the experiments, while TDS rose from 56.15 ppt in Exp. 7 to 62.29 ppt in Exp. 10 (Table 4). ICP-OES analysis of the reacting fluid showed that Al and Fe, initially absent in the pre-reacted solution, were detected post-experiment with concentrations increasing with temperature (Table 4). Ca concentration increased substantially, reaching 48,400 mg/L in Exp. 10 from an initial 8,730 mg/L. Conversely, Mg was consumed, decreasing from 15,500 mg/L in the starting solution to 167 mg/L in Exp. 10 (Table 4, Figure 10). Na concentrations decreased during the experiments, while K showed irregular fluctuations, increasing in Experiments 7 and 8 but decreasing in Experiments 9 and 10 (Table 4, Figure 10).

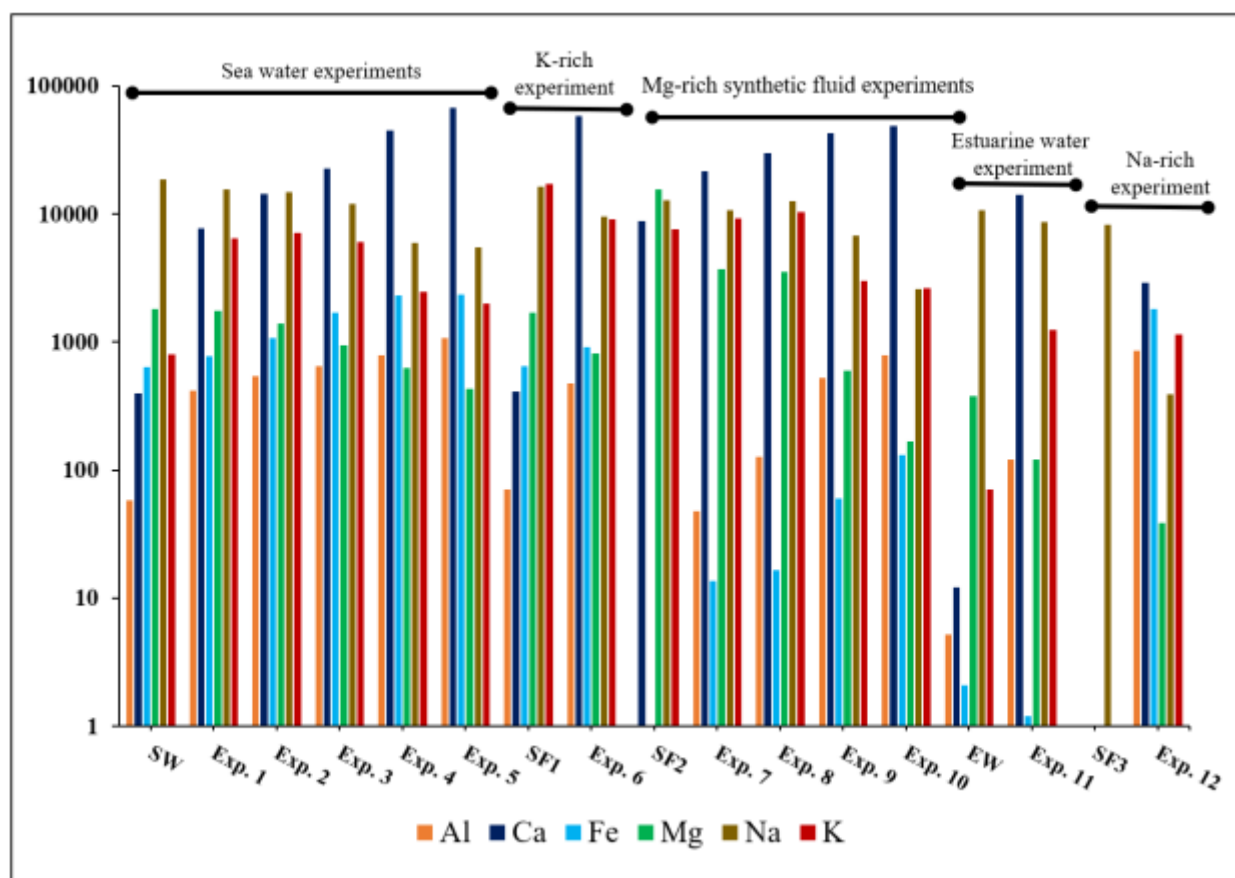


Figure 4.10. Clustered histogram displaying the concentrations of Al, Ca, Fe, Mg, Na, and K in pre-experiment solutions and their subsequent evolution post-experiments.

SEM analysis revealed the onset of detrital aggregate dissolution without new mineral formation in Exp. 7 (Figure 11A). However, evidence of smectite transformation was observed in Exp. 8 (Figure 11B). Mixed-layer chlorite-smectite with a rugged, honeycomb morphology appeared in Exp. 9, adjacent to kaolinite platelets (Figure 11C). Additionally, abundant microcrystalline quartz aggregates developed alongside the transforming mixed-layer chlorite-smectite in Exp. 9 (Figure 11D). Fully developed chlorite with a mixed honeycomb-to-rosette morphology was observed in Exp. 10 (Figure 11E), suggesting partial replacement of smectite while retaining its morphology.

EDS analysis identified Si, O, Al, Mg, and Fe as the major elements in the newly formed chlorite, with minor amounts of Na, K, and Ca (Figure 11F).

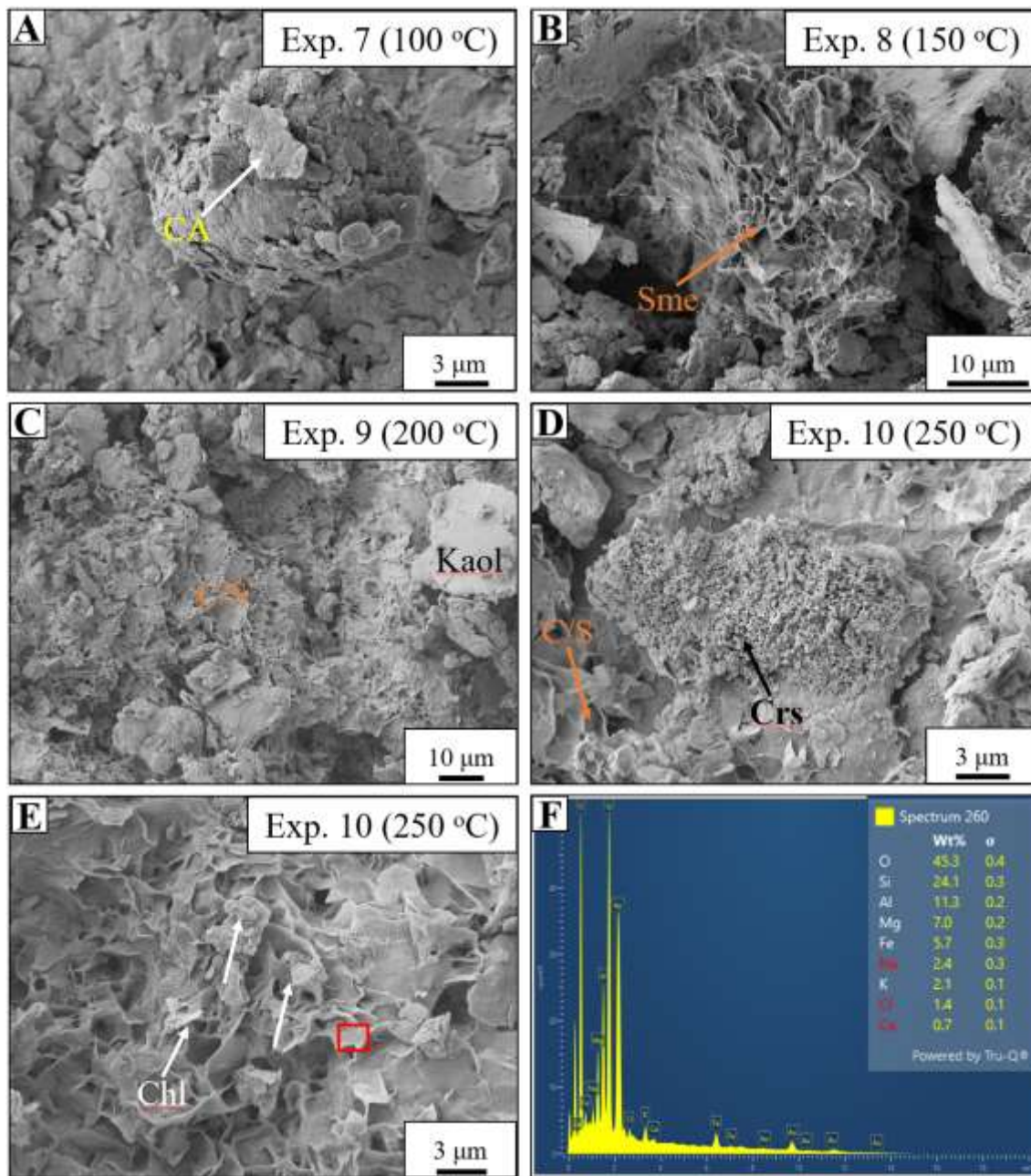


Figure 4.11. Main diagenetic features observed in Experiments 7–10 (conducted using Mg-rich synthetic fluid). (A) SEM image illustrating the onset of detrital clay aggregate dissolution in Exp. 7. (B) SEM image showing the initial transformation of smectite in Exp. 8. (C) SEM image

highlighting the formation of mixed-layer chlorite/smectite (C/S) with rugged honeycomb morphology adjacent to kaolinite (Kaol). (D) SEM image depicting the formation of microcrystalline quartz (Crs) crystal aggregates alongside transforming chlorite/smectite (C/S). (E) SEM image showing the development of chlorite with mixed honeycomb-to-rosette morphology. The red square marks the location of the EDS spectra shown in F. (F) EDS spectra indicating the Mg-rich nature of the newly formed chlorite.

4.5.2.3. *Estuarine water-based experiment (Experiment 11)*

This experiment was conducted at 250°C for 14 days using natural estuarine water collected from the Gironde estuary, SW France. Comprehensive geochemical and mineralogical analyses were performed on both the solids and solutions before and after the hydrothermal reaction. XRF, XRD, and SEM analyses revealed that all authigenic clay minerals formed in Exp. 10 were also present in Exp. 11, albeit with minor compositional differences (Figs. 3, 6, and 12). The oxides identified in the XRF analysis exhibited similar trends to those observed in Exp. 10. The key distinction lies in the amounts of Fe₂O₃ and MgO (Table 2). While MgO decreased slightly in Exp. 11 (8.23 wt%) compared to Exp. 10 (9.58 wt%), Fe₂O₃ increased significantly to 7.62 wt% from 5.06 wt% (Table 2). Additionally, concentrations of other minor and trace elements remained largely unchanged (Table 2, Figure 3). All minerals identified in the bulk and clay fraction XRD analyses of Exp. 10 were also detected in Exp. 11, with some variation in concentration (Table 3, Figs. 4 and 6). Notably, the concentration of authigenic chlorite increased from 16% in Exp. 10 to 24% in Exp. 11, as quantified from the clay fraction XRD analyses (Table 3, Figure 6E).

The pH of the pre-experimental estuarine water was 7.26 but slightly decreased to 6.91 after the hydrothermal experiment (Table 4). In contrast, the TDS increased from 13.02 ppt to 26.39 ppt post-experiment (Table 4). ICP-OES analysis indicated an increase in Al, Ca, and K concentrations

in the post-experimental reacting fluid, while Fe was significantly depleted (Table 4). Mg and Na concentrations decreased after the hydrothermal reaction (Table 4, Figure 10).

SEM and STEM analyses provided evidence of authigenic chlorite formation and mixed-layer clays. Small acicular crystals of Fe-oxides (Figure 12A) was observed adjacent to kaolinite (Figure 12B). Moreover, SEM analysis revealed that chlorite in Exp. 11 formed by replacing smectite through mixed-layer stages (Figure 12C-E). The mixed-layer chlorite/smectite exhibited honeycomb to web-like morphologies and was found adjacent to newly formed small aggregates of microcrystalline quartz (Figure 12C). Fully developed authigenic chlorite exhibited rosette morphologies (Figure 12D-E). Elemental analysis of the authigenic chlorite showed Si, O, Al, and Fe as major constituents, with minor amounts of Mg, K, and Ca. This composition differed slightly from the chlorite observed in Exp. 10, which was richer in Mg than Fe (Figure 11F). Furthermore, STEM analysis revealed elongated chlorite crystals (Figure 8E-F) closely associated with mixed-layer chlorite/smectite (Figure 8E).

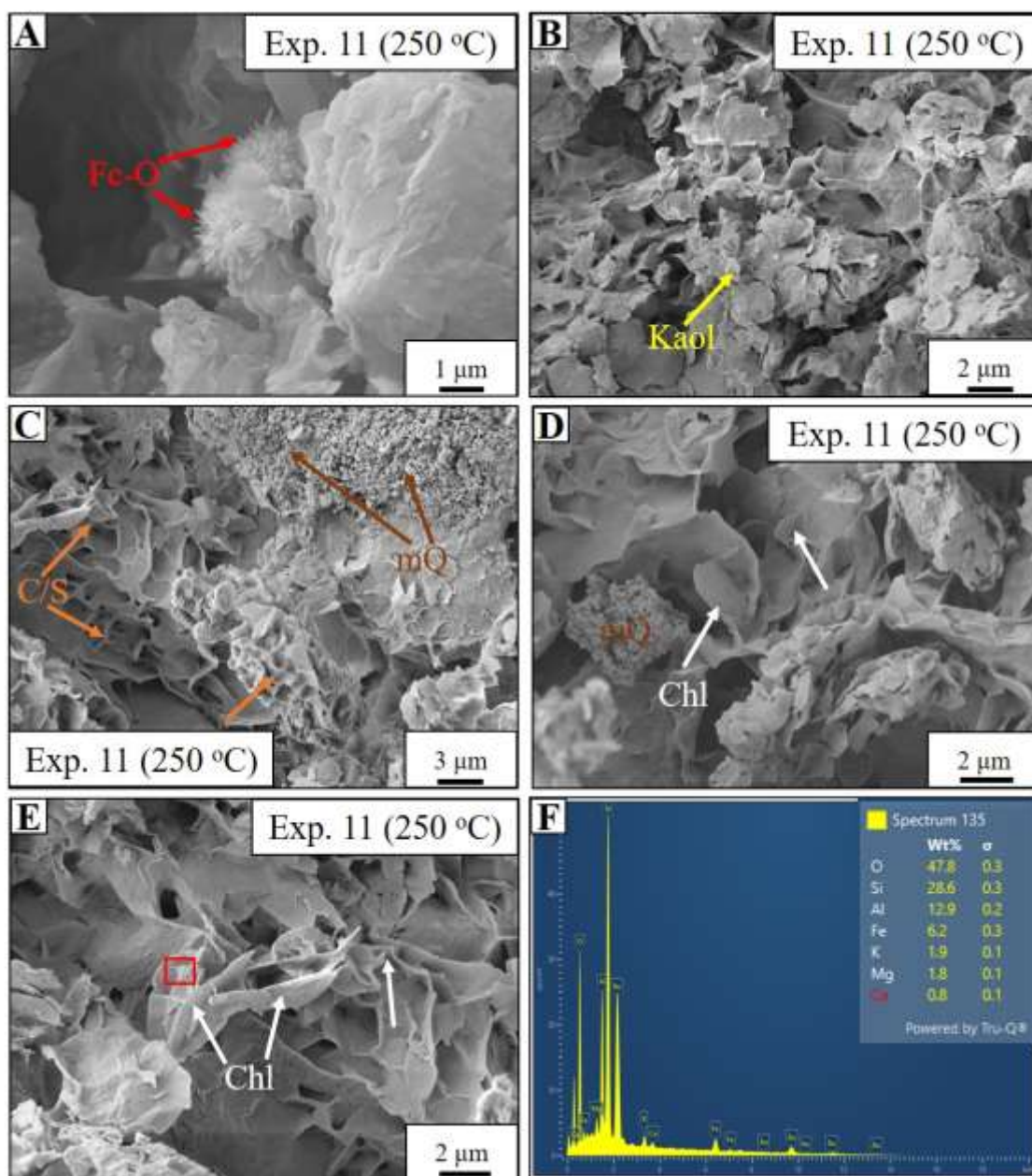


Figure 4.12. Diagenetic features observed in the estuarine water experiment (Exp. 11). (A) SEM showing acicular crystals of neoformed Fe-oxides (Fe-O). (B) SEM image illustrating the initial transformation of kaolinite (Kaol). (C) SEM image depicting the formation of microcrystalline quartz (mQ) near transforming chlorite/smectite (C/S), which exhibits honeycomb to web-like morphologies. (D–E) SEM images showing the formation of chlorite with rosette morphology. (F)

EDS spectra indicating that the chlorite formed in this experiment is Fe-rich. The location of the EDS analysis is marked by the red square in (E).

4.5.2.4. *Na-rich synthetic fluid-based experiment (Experiment 12)*

This experiment utilized a highly alkaline 0.1 M synthetic Na_2CO_3 solution at 250°C for 14 days. Post-reaction XRF analysis of the sediment indicated a substantial increase in Na_2O to 5.46 wt% from 0.79 wt% in the starting material (Table 2). This concentration was significantly higher than in all previous experiments (Table 2, Figure 3). While K_2O concentrations increased in most prior experiments, they decreased to 2.88 wt% in Exp. 12 from 3.07 wt% in the starting material. Concentrations of CaO , MgO , Fe_2O_3 , and other trace oxides remained relatively stable compared to the starting material (Table 2, Figure 3).

The bulk mineralogical analysis of Exp. 12 showed key differences compared to the starting material, including a decrease in total clay minerals and the presence of analcime (zeolite) unique to this experiment (Table 3, Figure 4). The concentration of clay minerals decreased to 13.1% from 20.3% in the starting material, contrasting with prior experiments, where clay mineral concentrations increased with rising temperature (Table 3). A high-intensity broad peak of authigenic analcime was identified (Figure 4), accounting for 21.7% of the total post-experimental bulk mineralogy (Table 3). This mineral was absent in all previous experiments (Figure 4). Additionally, halite was identified, with a measured concentration of 2.4% (Table 3, Figure 4). Clay fraction XRD analysis revealed kaolinite, illite, and smectite as the primary clay minerals (Figure 6F). Kaolinite concentration decreased to 16%, smectite increased to 40%, and illite remained relatively unchanged at 41% compared to the starting material (Table 3).

The pre-experimental solution had a high pH of 11.32 and a TDS of 13.79 ppt. After the experiment, the pH and TDS decreased to 8.31 and 7.79 ppt, respectively (Table 4). Sodium (Na), the dominant cation in the starting solution, was significantly depleted from 8250 mg/L to 390 mg/L after the reaction (Table 4, Figure 10). Furthermore, ICP-OES analysis revealed that Mg and Fe dissolved during the experiment and were detected in the reactive fluid post-experiment (Table 4).

SEM analysis showed no evidence of structurally developed illite or chlorite; however, detrital clay aggregates in the starting material exhibited signs of disaggregation, marking the initial stages of dissolution and/or transformation (Figure 13A-B). Interestingly, SEM analysis confirmed the formation of halite and analcime (zeolite) (Figure 13C-E). Fully developed halite occurred as clear cubic crystals (Figure 13C), while analcime exhibited massive aggregates (Figure 13D) and acicular to botryoidal morphologies (Figure 13E). The massive analcime aggregates formed within dissolving kaolinite (Figure 13D) and transitioned to acicular or botryoidal morphologies when fully developed (Figure 13E). Elemental analysis (EDS) of analcime identified Si, O, Na and Al as its primary constituents (Figure 13F).

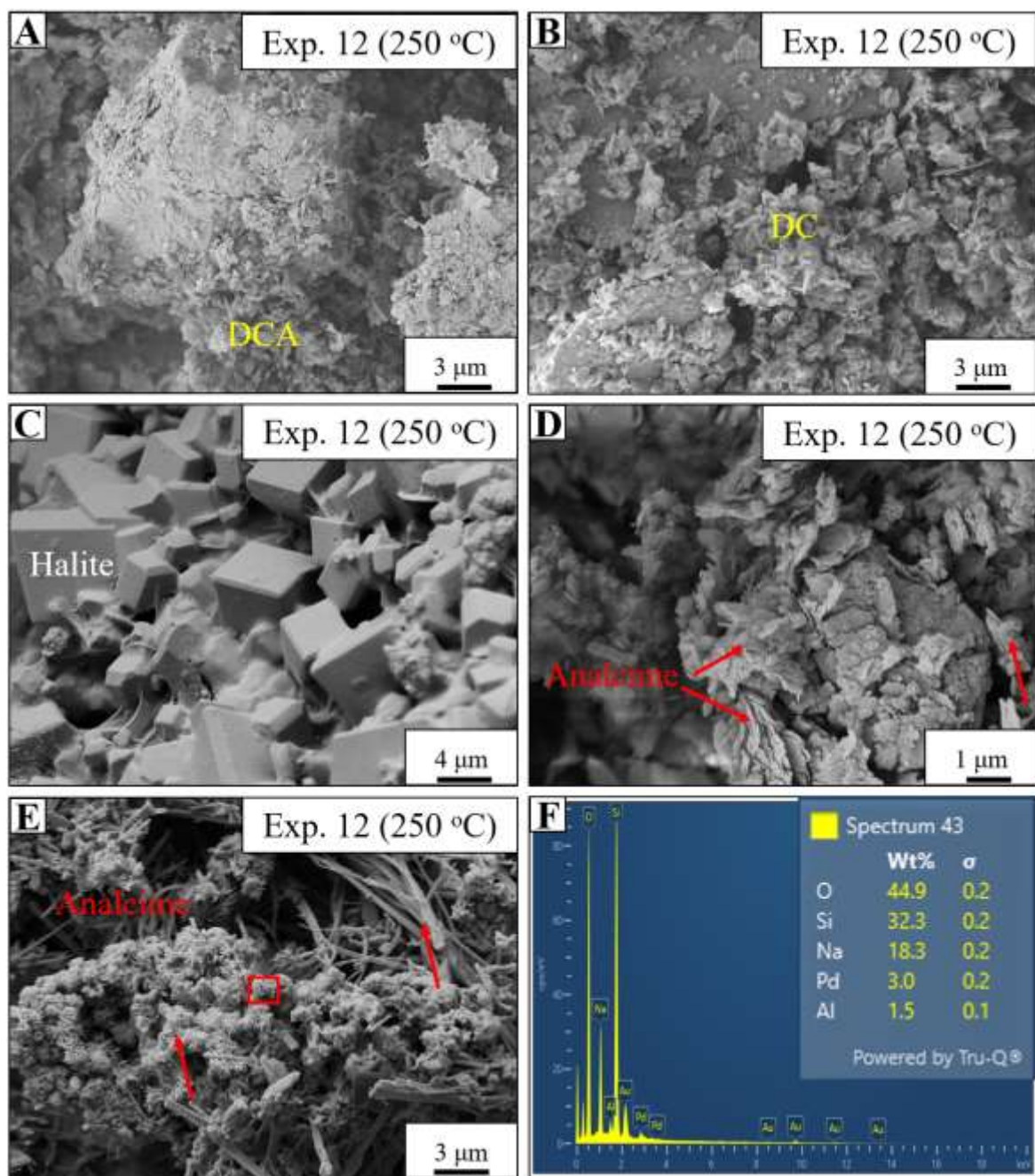


Figure 4.13. Main diagenetic features in Exp. 12 (conducted with Na-rich synthetic fluid). (A) SEM image showing the onset of detrital clay disaggregation (DCA). (B) SEM image showing detrital clay dissolution (DC). (C) SEM image highlighting the formation of cubic halite crystals. (D–E) SEM images depicting the development of massive aggregates (D) and acicular-to-

botryoidal (E) authigenic analcime. (F) EDS spectra of the newly formed analcime, indicating its high Na content. The red square in (E) marks the location of the EDS analysis.

4.5.3. FIB-SEM observations

The morphology, composition, distribution, and spatial relationships between framework grains and authigenic clay minerals were further investigated using FIB-SEM and EDS analyses (Figure 14A–F). The 2D internal structure analysis of the post-reacted samples revealed that authigenic clay minerals occurred both as pore-filling phases (Figs. 14A–C) and as grain coatings (Figure 14E). Highly microporous pore-filling clay minerals were observed cementing detrital grains in Exp. 3 (Figs. 14A–B) but appeared to become less microporous in Exp. 5 (Figure 14C). Additionally, quartz overgrowths were observed surrounding detrital quartz grains where authigenic grain-coating clays were absent (Figure 14C). EDS analysis confirmed that the quartz overgrowth consists of Si and O (Figure 14D). Grain-coating chlorite was identified surrounding detrital K-feldspar grains in Exp. 11 (Figure 14E). Elemental analysis via EDS indicated that chlorite was composed predominantly of O, Si, Al, and Fe, with minor amounts of Mg, K, and Ni (Figure 14F).

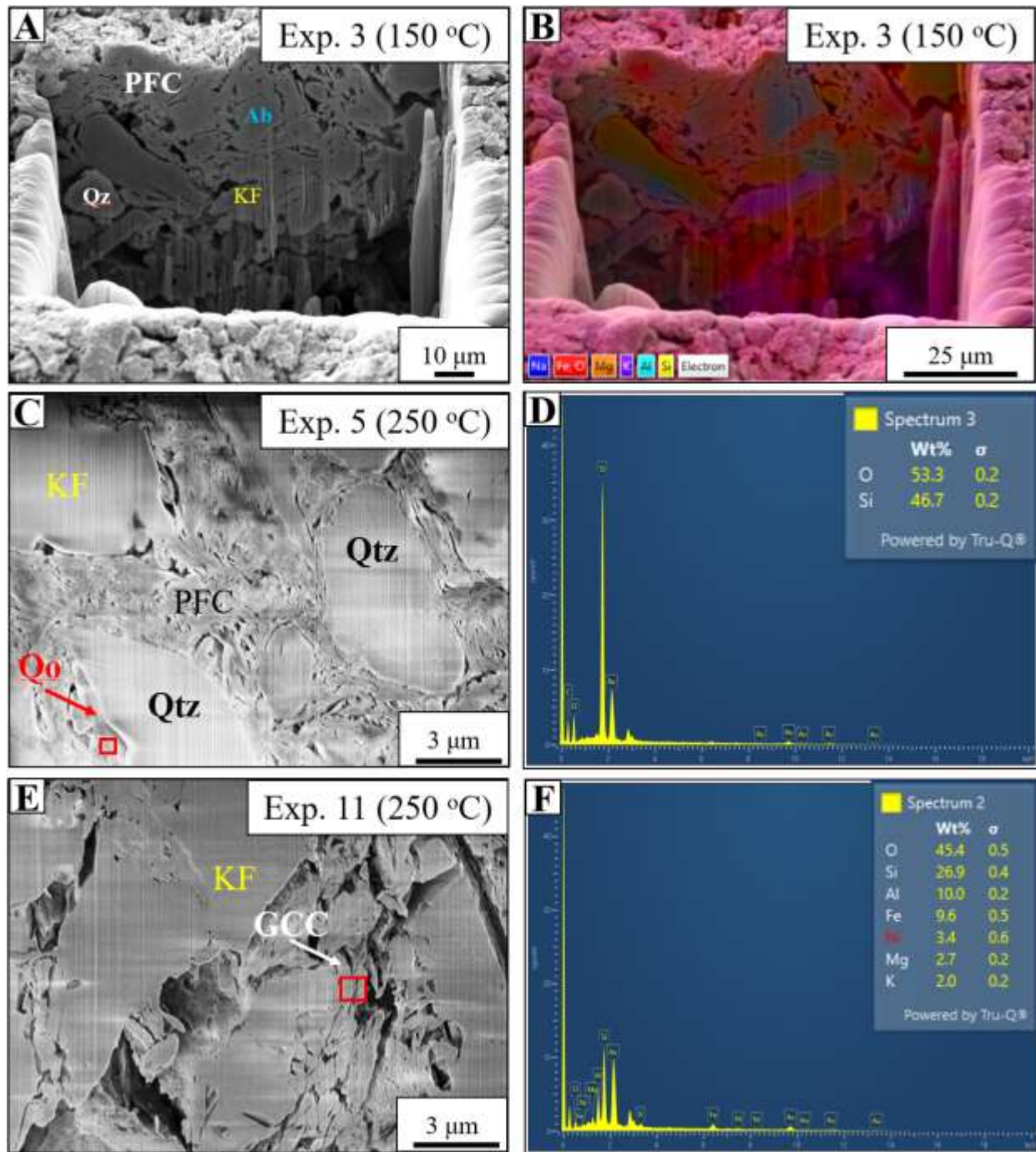


Figure 4.14. FIB-SEM and EDS images illustrating the internal structure of clay minerals and their relationships with detrital framework grains. (A) FIB-SEM image showing microporous pore-filling clay minerals (PFC) cementing detrital quartz (Qz), K-feldspar (KF), and albite (Ab) in Exp. 3. (B) EDS map of (A). (C) SEM image showing less microporous pore-filling clays (PFC)

cementing quartz (Qtz) and K-feldspar (KF) in Exp. 5. Quartz overgrowths (Qo) are observed at the edges of detrital quartz. (D) EDS spectra of the quartz overgrowth, indicating Si and O as the main constituents. The red square in (C) marks the EDS analysis location. (E) FIB-SEM image showing grain-coating chlorite (GCC) on detrital grains in Exp. 11. (F) EDS spectra of the GCC, showing its Fe-rich content. The red square in (E) marks the EDS analysis location.

4.6. Discussion

4.6.1. Controls and mechanisms of authigenic illite formation

Illite is one of the primary clay minerals synthesized in the present study (Figs. 6–9), predominantly from seawater-based experiments (Experiments 1–6). These experiments resulted in smectite's transformation into illite, a common diagenetic pathway observed in many natural sedimentary environments (Berger et al., 1997; Franks and Zwingmann, 2010; Al-Ramadan, 2014; Bello et al., 2022a). The formation of authigenic illite in siliciclastic rocks occurs due to the progressive transformation of precursor minerals such as K-feldspar, kaolinite, or smectite, beginning at low temperatures during burial and continuing under elevated temperatures and pressures (Worden and Morad, 2009; Taylor et al., 2022). This study has demonstrated the illitization of authigenic smectite to varying extents through mixed-layer illite/smectite stages, as evidenced by XRD (Table 3, Figure 6), SEM (Figs. 7 and 9), and STEM (Figure 8A–D) analyses. The authigenic smectite developed from the dissolution of unstable detrital materials, including orthoclase, calcite, and detrital clay aggregates. This process began at lower-temperature experiments (Experiments 1–2), which provided the necessary silica and cations for smectite neoformation (Table 3, Figure 7A). Consequently, well-crystallized authigenic smectite developed at 150°C (Exp. 3, Figure 7B). With increasing temperature during progressive burial in natural sedimentary systems, smectite becomes unstable and transforms into illite through mixed-layer stages (McKinley et al., 1999; Bentabol et al., 2024).

The smectite-to-illite transformation is influenced by temperature, fluid composition, and the availability of K^+ (MOSSER-RUCK et al., 2001; Drief et al., 2002; Mosser-Ruck and Cathelineau, 2004; Ferrage et al., 2011; Mills et al., 2023). In the present study, this transformation began at 150°C through the formation of mixed-layer illite/smectite (Figure 7B–C) and reached a plateau at 250°C (Figs. 7E and 8C). The required K^+ was supplied through multiple sources, including the dissolution of K-feldspar and the K^+ present in the experimental solutions. This conclusion is supported by the observed increase in K concentration in the reaction fluid during Experiments 1–2 (Table 4), which corresponds to the dissolution of detrital orthoclase (Table 3), and the subsequent rapid depletion of K^+ during Experiments 4–6, coinciding with the onset of the illitization process (Table 4; Figs. 7–9). Additionally, the illitization of smectite has been experimentally documented under varied pH conditions, ranging from acidic (Small, 1994; Du et al., 2021) to neutral (Guillaume et al., 2004; Mosser-Ruck et al., 2010; Ferrage et al., 2011) and low alkaline (Johnston and Miller, 1984; Drief et al., 2002) conditions. Experimental studies by (Johnston and Miller, 1984) and (Drief et al., 2002) have shown that near neutral to high alkaline pH (7–11) increases Si and Al mobility, thereby enhancing illite development. The illite formed in the KCl-rich seawater experiment (Exp. 6) is more developed (Figure 9C) and constitutes over 80% of the total clay fraction (Table 3) compared to the illite formed in Exp. 5, which was conducted using seawater under the same temperature (250°C). One plausible explanation for this variation in transformation rate is the higher K^+ availability in Exp. 6 compared to Exp. 5 (Table 4). Experimental studies by (Drief et al., 2002) have shown that the rate of smectite-to-illite transformation strongly depends on the concentration of K^+ in the reacting fluid. Experiments conducted under high K^+ concentrations yield more structurally developed illite from smectite (Huang et al., 1986), consistent with the observations in this study. Furthermore, the honeycomb

and lath-like morphologies of the synthesized smectite and illite closely resemble those observed in natural sandstones (Franks and Zwingmann, 2010; Al-Ramadan, 2014; Ulmer-Scholle et al., 2015).

The mechanisms responsible for the smectite-to-illite transformation have been extensively debated over the past decades and are reviewed by (Altaner and Ylagan, 1997; Ferrage et al., 2011). The two most widely accepted mechanisms are dissolution-crystallization (DC) (Nadeau et al., 1985; Lanson et al., 2009; Ferrage et al., 2011) and solid-state transformation (SST) (Roberson and Lahann, 1981; Bell, 1986). In the seawater experiments (Experiments 4–5), the illitized smectite mostly retained the honeycomb morphology of smectite, characterized by curling illite flakes tangential to detrital grains (Figure 7C). This characteristic is commonly attributed to SST (Ferrage et al., 2011). However, spikes of illite flakes were observed adjacent to poorly organized illite/smectite with a ragged honeycomb morphology (Figs. 7D–E), suggesting the early dissolution of honeycomb smectite and its subsequent illitization. Additionally, studies by (Putnis, 2009) and (Ferrage et al., 2011) have shown that precursor minerals can retain their morphology under DC transformation. Furthermore, the illite developed in KCl-rich seawater (Exp. 6) is characterized by lath-like morphology, indicating the dissolution of smectite and the precipitation of illite. This observation aligns with experimental studies by (Whitney and Northrop, 1988) and (Mills et al., 2023) which reported the formation of lath-like illite from smectite dissolution under similar temperature and fluid-rock ratios. Moreover, DC has been identified as the primary mechanism of smectite-to-illite transformation in natural fluid-dominated hydrothermal systems (Inoue et al., 1987, 2005; Ylagan et al., 2000), based on observations of morphological changes and chemical variations, consistent with the findings of this study. Therefore, the smectite-to-illite transformation observed in this study (Experiments 4–6) is most likely due to DC rather than SST.

4.6.2. Authigenic formation of chlorite

As demonstrated in this study, the authigenic formation of chlorite is a key feature observed in experiments conducted with Mg-rich synthetic fluid (SF2; Experiments 7–10) and natural estuarine water (Experiment 11) (Figs. 11–12). The findings indicate that chlorite formed through the transformation of smectite, proceeding via intermediate mixed-layer chlorite/smectite (C/S) phases, as evidenced by SEM (Figs. 11–12), STEM (Figure 8E–F), and XRD (Figure 6D–E) analyses. In natural sedimentary systems, the chloritization of smectite is predominantly reported to occur through dissolution-crystallization (DC; (Środoń, 1999; Worden and Morad, 2009; Mosser-Ruck et al., 2016), with occasional occurrences of solid-state transformation (SST; (Robinson et al., 2002). Additionally, temperature, fluid composition, and fluid-rock ratios are critical in facilitating the smectite-to-chlorite transformation (Keith and Bargar, 1988; Mosser-Ruck et al., 2016; Worden et al., 2020).

During the DC mechanism, chlorite forms from the chemical components released during the dissolution of smectite, including silica, aluminum, and interlayer cations, while incorporating Fe^{2+} and Mg^{2+} supplied either by detrital minerals (e.g., biotite or volcanic fragments) or pore fluids (Worden et al., 2020). In this study, the chlorite synthesized in Exp. 11 exhibits a well-developed rosette morphology (Figure 12E) that is closely associated with dissolved, honeycomb-like smectite through interstratified C/S phases (Figs. 8E, 12C), characteristic of the DC transformation. In addition, although the chlorite synthesized in Exp. 10 retains the honeycomb morphology of its precursor smectite (Figure 11E) and exhibits interstratified C/S phases (Figure 11C), the C/S is assumed to be newly formed through DC. The required Fe and Mg for the synthesis of chlorite in this study are provided by the experimental solutions, in addition to the

dissolution of newly formed Fe-oxide in Exp.11 (Figure 12A). Thus, our results suggest that chlorite formation predominantly occurs via the DC mechanism.

The chlorites formed in this study exhibit morphology comparable to both experimentally synthesized chlorites and natural authigenic chlorites found in ancient sandstone reservoirs. For instance, honeycomb and rosette morphologies have been reported in experimental studies by [53] and in the Triassic Yanchang Formation of the Ordos Basin, China (Li et al., 2021), as well as in numerous natural sandstone reservoirs (Dowey et al., 2012; Ulmer-Scholle et al., 2015; Taylor et al., 2022). Furthermore, the release of Si and Al into the experimental solution during smectite transformation appears to have contributed significantly to the formation of by-products such as microcrystalline quartz (Figs. 11D, 12C–E) and quartz cement (Figure 14C).

4.6.3. Role of Fluid Chemistry on the Transformation Pathways of Modern Estuarine Sediments

The chemistry of pore fluids during fluid-rock interactions is critical in determining the pathways and extent of diagenetic alteration of detrital clay minerals in modern sediments (Worden and Burley, 2009). Variations in pH, redox potential, salinity, and dissolved ion concentrations influence the mechanisms of mineral transformation and the resulting mineral phases (Velde and Meunier, 2008; Chamley, 2013; Millot, 2013). These variations are particularly significant in dynamic environments such as estuaries, where fluid composition fluctuates due to freshwater-seawater interactions and organic matter degradation (Worden and Burley, 2009). Additionally, the fluid composition used in hydrothermal experiments is crucial in shaping the mineralogy and chemistry of the synthesized minerals (Mosser-Ruck et al., 2010, 2016). This study utilized five distinct fluids of variable composition resulting in the formation of distinct mineral phases.

Both SW and SF1 facilitated the authigenic formation of smectite from detrital clay precursors and its subsequent transformation into illite. The illitization of smectite was more pronounced in Experiments 5 and 6, conducted at 250°C. Nonetheless, slight differences were observed in the smectite illitization rate and the resulting illite's chemistry. The most significant change in the experimental alteration was an increase in potassium (K) in the interlayer sites, accompanied by a decrease in sodium (Na) and calcium (Ca) (Figs. 8D & 9D). The XRD peaks of the authigenic illite were broader in Exp. 6 (Figure 6C) than in Exp. 5 (Figure 6B). Additionally, XRD patterns indicated the presence of smectite alongside illite in Exp. 5 (Figure 6B). In contrast, smectite was undetectable in Exp. 6 (Figure 6C). Sylvite was also formed in Exp. 6 (Table 3, Figure 6C). A plausible explanation for these variations is the higher concentration of K in Exp. 6 compared to Exp. 5, which accelerated the rate of smectite illitization. Kinetic modeling of smectite illitization by (Huang et al., 1986) demonstrated that elevated K concentrations in pore fluids enhance illitization and accelerate the reaction rate. The slight decrease in pH observed in the experiments is attributed to the release of silica and Fe (Table 4) during the dissolution of detrital clay minerals and the transformation of smectite into illite.

Distinctively, the Mg-rich synthetic fluid (SF2) and the estuarine water (EW) resulted in the formation of chlorite from smectite (Figs. 11-12). However, slight differences were observed in the chemistries of the authigenic chlorites. Chlorites formed from SF2, enriched in Mg, Ca, K, and Na, were dominantly Mg-rich (Figure 11 F). In contrast, chlorites formed from the natural Gironde estuarine water, which contains higher Fe and lower Mg concentrations than SF2, were Fe-rich chlorites (Figure 12F). This observation can be attributed to the relative scarcity of Mg in estuarine water, which forces the chlorites to incorporate more Fe into their structures to maintain charge balance and structural integrity. This is supported by the rapid depletion of Mg in SF2

(Experiments 7-10), which was relatively higher than in Exp. 11 (EW), and the consumption of Fe in Exp.11 (Table 4). These findings align with the preferential formation of authigenic chlorite in ancient sedimentary environments. In natural sandstone reservoirs, Mg-rich chlorites are commonly associated with continental sandstones, whereas Fe-rich chlorites are prevalent in marginal marine environments such as deltas and estuaries (Dowey et al., 2012; Worden et al., 2020).

In contrast to the formation of illite and chlorite in Experiments 1-11, Exp.12, conducted using highly alkaline Na-rich synthetic solutions (SF3), resulted in the formation of halite and analcime (zeolite) that were not observed in the previous experiments (Figure 13). Zeolite minerals are generally rare in sandstones (Ulmer-Scholle et al., 2015; Taylor et al., 2022). However, where present, they exert significant control on reservoir quality (Iijima, 2001; Lin et al., 2024). Analcime is one of the most common zeolites and is an important component of many petroliferous reservoirs worldwide (Ulmer-Scholle et al., 2015; Yao et al., 2017; Niegel and Franz, 2023). Although authigenic analcime has been reported to occur from clay mineral precursors (Zhu et al., 2020), its formation in sandstones is commonly associated with the transformation of clinoptilolite from volcanic glass during burial (Iijima, 1975, 2001). The formation of analcime typically occurs under highly alkaline conditions (Malette et al., 2024) and is facilitated by the availability of silica, as well as Na (Lin et al., 2024). In this study, analcime was formed from the dissolution of detrital clay minerals, which provided the required silica whereas Na was supplied from the dissolution of calcite and the experimental fluid, respectively (Table 4). The availability of Na and its concentration in pore fluids is essential for analcime stability and its preferential formation over other zeolites (Chipera and Apps, 2001). In this study, analcime developed concurrently with halite (Figure 13C).

Despite the use of the same starting material in this study, different minerals were synthesized under varying experimental conditions. These variations are directly associated with the differences in fluid chemistry employed in the experiments. These findings underscore the complex interplay between fluid chemistry and diagenetic processes in modern estuarine sediments.

4.6.4. Relevance of hydrothermal experiments to natural sandstone diagenesis

Although the experimental conditions in this study were designed to simulate natural diagenetic processes, they inevitably represent simplified models of natural sandstone diagenesis. One key limitation is the time scale: natural diagenesis occurs over geologic timescale (millions of years), allowing for gradual reactions influenced by fluctuating temperature, pressure, and fluid composition. In contrast, laboratory experiments accelerate these processes by using elevated temperatures to condense reactions into hours or days. Furthermore, the use of uniform starting materials and static fluid compositions restricts the ability to replicate the inherent heterogeneity of natural systems, where pore-fluid chemistry evolves with burial depth, sediment provenance, and organic matter degradation.

Despite these limitations, hydrothermal experiments remain valuable proxies for investigating diagenetic processes in natural sandstone reservoirs, as they enable the controlled simulation of mineralogical and geochemical transformations. The findings of this study demonstrate strong alignment with key processes observed in natural systems. For instance, the illitization of smectite in potassium-rich fluids (e.g., SF1) closely mirrors potassium-driven transformations documented in sandstone reservoirs (Boles and Franks, 1979; Worden and Morad, 2009; Bello et al., 2024b). Similarly, the formation of Mg-rich and Fe-rich chlorites in experiments using SF2 and EW aligns with chlorite development in continental and marginal marine environments, respectively. In

deeply buried sandstone reservoirs, Fe-rich chlorites are commonly associated with marginal marine settings, such as estuaries and deltas, where Fe-rich flocculated materials are present (Ehrenberg, 1993; Dowey et al., 2012; Worden et al., 2020). This observation agrees with the Fe-rich chlorites formed from the natural Gironde estuarine water used in this study.

Another significant finding is the synthesis of analcime from detrital clays under highly alkaline, Na-rich conditions, which broadens the understanding of analcime formation beyond its conventional association with volcanic glass (Iijima, 2001). By employing diverse fluid compositions including natural seawater, estuarine water, and synthetic solutions with varied ionic concentrations and pH levels, this study provides a comprehensive perspective on how fluid chemistry governs diagenetic pathways. These results emphasize the relevance of hydrothermal experiments in mimicking the geochemical processes that drive the diagenetic transformation of detrital clay minerals during burial. Furthermore, they highlight the potential of modern estuarine sediments as analogs for diagenetic processes, underscoring the critical role of dynamic fluid compositions in shaping mineralogical transformations and reservoir quality.

To deepen the understanding of the impact of fluid chemistry on the diagenetic pathways of modern estuarine sediments, future research should focus on longer experimental durations and the incorporation of dynamic fluid flow to reflect the evolving nature of natural sandstone diagenesis. In addition, conducting geochemical modeling using data from experimental studies would enhance the extrapolation of laboratory findings to geological time scales. While these areas of improvement are necessary, the findings of this study provide a solid foundation for understanding diagenetic alteration in modern estuarine sediments and their implications for sandstone reservoir evolution.

4.7. Conclusions

- During the hydrothermal experiments, the Dissolution of detrital feldspars and clay aggregates occurred at temperatures below 100°C, followed by the authigenic formation of smectite at 150°C.
- At higher temperatures (150°C to 250°C), K-rich fluids (SW, SF1) facilitated the illitization of smectite, replicating potassium-driven processes observed in natural reservoirs. This transformation predominantly occurred via dissolution-crystallization, with the required K⁺ supplied by the dissolution of K-feldspar and the experimental solutions.
- The chloritization of smectite occurred in both Mg-rich synthetic fluids (SF2) and natural Gironde Estuary water (EW) at 250°C, producing chlorites with distinct chemistries. SF2 yielded Mg-rich chlorites, while EW produced Fe-rich chlorites, consistent with diagenetic trends in marginal marine environments where Fe-rich chlorites are associated with estuarine and deltaic systems.
- The formation of authigenic chlorites involved a combination of dissolution-crystallization and solid-state transformation. The transformation of smectite into chlorite released abundant silica into the experimental solutions, resulting in the precipitation of microcrystalline quartz and quartz overgrowths.
- Analcime (zeolite) was synthesized under highly alkaline (pH 11.32), Na-rich conditions (SF3), advancing the understanding of zeolite formation beyond its traditional association with volcanic glass precursors.
- The synthesized mineral phases exhibited chemical and morphological similarities to those found in natural sedimentary systems, highlighting the critical role of fluid chemistry in

influencing diagenetic pathways and improving our understanding of detrital clay transformations during burial diagenesis.

4.8. References

- Ajdukiewicz, J.M., and Larese, R.E., 2012, How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments: AAPG Bulletin, v. 96, p. 2091–2119, doi:10.1306/02211211075.
- Allen, G.P., 1991, Sedimentary processes and facies in the Gironde estuary: a recent model for macrotidal estuarine systems: Canadian Society of Petroleum Geologists, v. 16, p. 29–39.
- Almon, W.R., Fullerton, L.B., and Davies, D.K., 1976, Pore space reduction in Cretaceous sandstones through chemical precipitation of clay minerals: Journal of Sedimentary Research, v. 46, p. 89–96, doi:10.1306/212F6EC9-2B24-11D7-8648000102C1865D.
- Alqubalee, A., Salisu, A.M., Bello, A.M., Al-Hussaini, A., and Al-Ramadan, K., 2023, Characteristics, distribution, and origin of ferruginous deposits within the Late Ordovician glaciogenic setting of Arabia: Scientific Reports, v. 13, p. 18430, doi:10.1038/s41598-023-45563-9.
- Al-Ramadan, K., 2014, Illitization of Smectite in Sandstones: The Permian Unayzah Reservoir, Saudi Arabia: Arabian Journal for Science and Engineering, v. 39, p. 407–412, doi:10.1007/s13369-013-0913-6.
- Al-Ramadan, K., Morad, S., Proust, J.-N., and Al-Aasm, I., 2005, Distribution of diagenetic alterations within the sequence stratigraphic framework of shoreface siliciclastic deposits: evidence from the Jurassic deposits of NE France: Journal of Sedimentary Research, v. 75, p. 10–38.
- Altaner, S.P., and Ylagan, R.F., 1997, Comparison of Structural Models of Mixed-Layer Illite/Smectite and Reaction Mechanisms of Smectite Illitization: Clays and Clay Minerals, v. 45, p. 517–533, doi:DOI: 10.1346/CCMN.1997.0450404.
- Beaufort, D., Berger, G., Lacharpagne, J.C., and Meunier, A., 2001, An experimental alteration of montmorillonite to a di + trioctahedral smectite assemblage at 100 and 200°C: Clay Minerals, v. 36, p. 211–225, doi:DOI: 10.1180/000985501750177942.
- Beaufort, D., Rigault, C., Billon, S., Billault, V., Inoue, A., Inoue, S., and Patrier, P., 2015, Chlorite and chloritization processes through mixed-layer mineral series in low-temperature geological systems – a review: Clay Minerals, v. 50, p. 497–523, doi:DOI: 10.1180/claymin.2015.050.4.06.
- Bell, T.E., 1986, Microstructure in Mixed-Layer Illite/Smectite and Its Relationship to the Reaction of Smectite to Illite: Clays and Clay Minerals, v. 34, p. 146–154, doi:DOI: 10.1346/CCMN.1986.0340205.
- Bello, A.M. et al., 2024a, Diagenesis and reservoir quality evolution of estuarine sandstones: Insights from the Cenomanian-Turonian Yolde Formation, northern Benue Trough, NE Nigeria: Marine and Petroleum Geology, v. 169, p. 107073, doi:https://doi.org/10.1016/j.marpetgeo.2024.107073.

- Bello, A.M. et al., 2025, Linking provenance and diagenesis to reservoir quality evolution of sandstones: The Paleocene-Eocene Kerri-Kerri Formation, northeastern Nigeria: *Marine and Petroleum Geology*, v. 172, p. 107227, doi:<https://doi.org/10.1016/j.marpetgeo.2024.107227>.
- Bello, A.M. et al., 2022a, Role of diagenetic alterations on porosity evolution in the cretaceous (Albian-Aptian) Bima Sandstone, a case study from the Northern Benue Trough, NE Nigeria: *Marine and Petroleum Geology*, v. 145, p. 105851, doi:[10.1016/j.marpetgeo.2022.105851](https://doi.org/10.1016/j.marpetgeo.2022.105851).
- Bello, A., Amao, A., Alqubalee, A., Al-Hashem, M., albarri, H., almasrahy, M., Al-Ramadan, K., and Babalola, L., 2024b, Diagenetic Controls on Reservoir Porosity of Aeolian and Fluvial Deposits: A Case Study from Permo-Carboniferous Sandstones of Saudi Arabia: *Arabian Journal for Science and Engineering*, v. 49, doi:[10.1007/s13369-023-08590-2](https://doi.org/10.1007/s13369-023-08590-2).
- Bello, A.M., Butt, M.N., Hussain, A., Amao, A.O., Olariu, C., Koeshidayatullah, A.I., Malik, M.H., Al-Hashem, M., and Al-Ramadan, K., 2023, Impact of depositional and diagenetic controls on reservoir quality of syn-rift sedimentary systems: An example from Oligocene-Miocene Al Wajh Formation, northwest Saudi Arabia: *Sedimentary Geology*, v. 446, p. 106342, doi:<https://doi.org/10.1016/j.sedgeo.2023.106342>.
- Bello, A.M., Charlaftis, D., Jones, S.J., Gluyas, J., Acikalin, S., Cartigny, M., and Al-Ramadan, K., 2022b, Experimental diagenesis using present-day submarine turbidite sands: *Frontiers in Earth Science*, v. 10, p. 1–20, doi:[10.3389/feart.2022.952690](https://doi.org/10.3389/feart.2022.952690).
- Bentabol, M., Lamarca-Irisarri, D., Van Driessche, A.E.S., Ryan, P.C., and Huertas, F.J., 2024, Illitization of montmorillonite in ammonium solutions under hydrothermal conditions: *Applied Clay Science*, v. 258, p. 107478.
- Berger, G., Lacharpagne, J.-C., Velde, B., Beaufort, D., and Lanson, B., 1997, Kinetic constraints on illitization reactions and the effects of organic diagenesis in sandstone/shale sequences: *Applied Geochemistry*, v. 12, p. 23–35.
- Billy, J., Chaumillon, E., Fénies, H., and Poirier, C., 2012, Tidal and fluvial controls on the morphological evolution of a lobate estuarine tidal bar: The Plassac Tidal Bar in the Gironde Estuary (France): *Geomorphology*, v. 169–170, p. 86–97, doi:<https://doi.org/10.1016/j.geomorph.2012.04.015>.
- Bjørlykke, K., Ramm, M., and Saigal, G.C., 1989, Sandstone diagenesis and porosity modification during basin evolution: *Geologische Rundschau*, v. 78, p. 243–268, doi:[10.1007/BF01988363](https://doi.org/10.1007/BF01988363).
- Bloch, S., Lander, R.H., and Bonnell, L., 2002, Anomalously High Porosity and Permeability in Deeply Buried Sandstone Reservoirs: Origin and Predictability: *AAPG Bulletin*, v. 86, p. 301–328, doi:[10.1306/61EEDABC-173E-11D7-8645000102C1865D](https://doi.org/10.1306/61EEDABC-173E-11D7-8645000102C1865D).
- Boles, J.R., and Franks, S.G., 1979, of Southwest Texas : Implications of: v. 49, p. 55–70.

- Castaing, P. & Allen, G.P., 1981, Mechanisms controlling seaward escape of suspended sediment from the Gironde: a macrotidal estuary in France: *Marine Geology*, v. 40, p. 101–118.
- Chamley, H., 2013, *Clay sedimentology*: Springer Science & Business Media.
- Charlaftis, D., Dobson, K.J., Jones, S.J., Lakshtanov, D., Crouch, J., and Cook, J., 2022, Experimental Simulation of Burial Diagenesis and Subsequent 2D-3D Characterization of Sandstone Reservoir Quality: *Frontiers in Earth Science*, v. 10, doi:10.3389/feart.2022.766145.
- Charlaftis, D., Jones, S.J., Dobson, K.J., Crouch, J., and Acikalin, S., 2021, Experimental study of chlorite authigenesis and influence on porosity maintenance in sandstones: *Journal of Sedimentary Research*, v. 91, p. 197–212, doi:10.2110/JSR.2020.122.
- Chipera, S.J., and Apps, J.A., 2001, Geochemical stability of natural zeolites: *Reviews in mineralogy and geochemistry*, v. 45, p. 117–161.
- Coyne, A., Schäfer, J., Hurtrez, J.-E., Dumas, J., Etcheber, H., and Blanc, G., 2004, Sampling frequency and accuracy of SPM flux estimates in two contrasted drainage basins: *Science of The Total Environment*, v. 330, p. 233–247, doi:https://doi.org/10.1016/j.scitotenv.2004.04.003.
- Dowey, P.J., Hodgson, D.M., and Worden, R.H., 2012, Pre-requisites, processes, and prediction of chlorite grain coatings in petroleum reservoirs: A review of subsurface examples: *Marine and Petroleum Geology*, v. 32, p. 63–75, doi:https://doi.org/10.1016/j.marpetgeo.2011.11.007.
- Drief, A., Martinez-Ruiz, F., Nieto, F., and Velilla Sanchez, N., 2002, Transmission Electron Microscopy Evidence for Experimental Illitization of Smectite in K-Enriched Seawater Solution at 50°C and Basic pH: *Clays and Clay Minerals*, v. 50, p. 746–756, doi:10.1346/000986002762090146.
- Du, J., Cai, J., Chao, Q., Song, M., and Wang, X., 2021, Variations and geological significance of solid acidity during smectite illitization: *Applied Clay Science*, v. 204, p. 106035.
- Ehrenberg, S.N., 1993, Preservation of Anomalously High Porosity in Deeply Buried Sandstones by Grain-Coating Chlorite: Examples from the Norwegian Continental Shelf: *AAPG Bulletin*, v. 77, p. 1260–1286, doi:10.1306/BDF8E5C-1718-11D7-8645000102C1865D.
- Etcheber, H. et al., 2011, Monitoring water quality in estuarine environments: Lessons from the MAGEST monitoring program in the Gironde fluvial-estuarine system: *Hydrology and Earth System Sciences - HYDROL EARTH SYST SCI*, v. 15, p. 831–840, doi:10.5194/hess-15-831-2011.
- Ferrage, E., Vidal, O., Mosser-Ruck, R., Cathelineau, M., and Cuadros, J., 2011, A reinvestigation of smectite illitization in experimental hydrothermal conditions: Results from X-ray diffraction and transmission electron microscopy: *Journal of Metamorphic Geology*, v. 29, p. 207–223, doi:10.1111/j.1365-3113.2011.00587.x.

- Franks, S.G., and Zwingmann, H., 2010, Origin and timing of late diagenetic illite in the Permian–Carboniferous Unayzah sandstone reservoirs of Saudi Arabia: AAPG Bulletin, v. 94, p. 1133–1159, doi:10.1306/04211009142.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., and Duller, R.A., 2018, Detrital clay coats, clay minerals, and pyrite: A modern shallow-core analogue for ancient and deeply buried estuarine sandstones: Journal of Sedimentary Research, v. 88, p. 1205–1237, doi:10.2110/jsr.2018.56.
- Griffiths, J., Worden, R.H., Wooldridge, L.J., Utley, J.E.P., Duller, R.A., and Edge, R.L., 2019, Estuarine clay mineral distribution: Modern analogue for ancient sandstone reservoir quality prediction: Sedimentology, v. 66, p. 2011–2047, doi:10.1111/sed.12571.
- Guillaume, D., Neaman, A., Cathelineau, M., Mosser-Ruck, R., Peiffert, C., Abdelmoula, M., Dubessy, J., Villi  ras, F., and Michau, N., 2004, Experimental study of the transformation of smectite at 80 and 300  C in the presence of Fe oxides: Clay Minerals, v. 39, p. 17–34, doi:DOI: 10.1180/000985543910117.
- Haile, B.G., Hellevang, H., Aagaard, P., and Jahren, J., 2015a, Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces: Marine and Petroleum Geology, v. 68, p. 664–674, doi:https://doi.org/10.1016/j.marpetgeo.2015.02.006.
- Haile, B.G., Hellevang, H., Aagaard, P., and Jahren, J., 2015b, Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces: Marine and Petroleum Geology, v. 68, p. 664–674, doi:10.1016/j.marpetgeo.2015.02.006.
- Heald, M.T., and Larese, R.E., 1974, Influence of coatings on quartz cementation: Journal of Sedimentary Research, v. 44, p. 1269–1274, doi:10.1306/212F6C94-2B24-11D7-8648000102C1865D.
- Huang, W.L., Bishop, A.M., and Brown, R.W., 1986, The effect of fluid/rock ratio on feldspar dissolution and illite formation under reservoir conditions: Clay Minerals, v. 21, p. 585–601.
- Iijima, A., 1975, Effect of pore water to clinoptilolite-analcimealbite reaction series: Jour Fac Sci, Univ of Tokyo, Sec II, v. 19, p. 133–147.
- Iijima, A., 2001, Zeolites in Petroleum and Natural Gas Reservoirs: Reviews in Mineralogy and Geochemistry, v. 45, p. 347–402.
- Inoue, A., KOHYAMA, N., KITAGAWA, R., and WATANABE, T., 1987, Chemical and Morphological Evidence for the Conversion of Smectite to Illite: Clays and Clay Minerals - CLAYS CLAY MINER, v. 35, p. 111–120, doi:10.1346/CCMN.1987.0350203.
- Inoue, A., Lanson, B., Fernandes, M., Sakharov, B., Murakami, T., Meunier, A., and Beaufort, D., 2005, Illite-smectite mixed-layer minerals in hydrothermal alteration of volcanic rocks: I. One-dimensional XRD structure analysis and characterisation of component layers.: Clays and Clay Minerals, v. 53, p. 423–439, doi:10.1346/CCMN.2005.0530501.

- Johnston, R.M., and Miller, H.G., 1984, The effect of pH on the stability of smectite: Atomic Energy of Canada Ltd.
- Keith, T.E.C., and Bargar, K.E., 1988, Petrology and hydrothermal mineralogy of US geological survey Newberry: 2. Drill core from Newberry Caldera, Oregon: *Journal of Geophysical Research: Solid Earth*, v. 93, p. 10174–10190.
- Khan, M.A., Khan, T., Ali, A., Bello, A.M., and Radwan, A.E., 2023, Role of depositional and diagenetic controls on reservoir quality of complex heterogeneous tidal sandstone reservoirs: An example from the Lower Goru formation, Middle Indus Basin, Southwest Pakistan: *Marine and Petroleum Geology*, v. 154, p. 106337, doi:<https://doi.org/10.1016/j.marpetgeo.2023.106337>.
- Lander, R.H., Bonnell, L.M., Taylor, T.R., and Espejo, I., 2022, Chapter 13 - Reservoir quality and diagenesis of deepwater sandstones, *in* Rotzien, J.R., Yeilding, C.A., Sears, R.A., Hernández-Molina, F.J., and Catuneanu, O.B.T.-D.S.S. eds., Elsevier, p. 471–514, doi:<https://doi.org/10.1016/B978-0-323-91918-0.00011-6>.
- Lanson, B., Beaufort, D., Berger, G., Bauer, A., Cassagnabère, A., and Meunier, A., 2002, Authigenic kaolin and illitic minerals during burial diagenesis of sandstones: a review: *Clay Minerals*, v. 37, p. 1–22, doi:DOI: 10.1180/0009855023710014.
- Lanson, B., Sakharov, B., Claret, F., and Drits, V., 2009, Diagenetic Smectite-to-Illite Transition in Clay-Rich Sediments: A Reappraisal of X-Ray Diffraction Results Using the Multi-Specimen Method: *American Journal of Science*, v. 309, p. 476–516, doi:10.2475/06.2009.03.
- Lawan, A.Y., Worden, R.H., Utley, J.E.P., and Crowley, S.F., 2021, Sedimentological and diagenetic controls on the reservoir quality of marginal marine sandstones buried to moderate depths and temperatures: Brent Province, UK North Sea: *Marine and Petroleum Geology*, v. 128, p. 104993, doi:10.1016/j.marpetgeo.2021.104993.
- Lin, T., Wang, W., Ma, Q., Kang, J., Yang, R., and Liu, X., 2024, Formation mechanism and implication of analcime in the sandstone reservoirs of the Permian Jingjingzigou formation in the Jinan sag, southern Junggar basin, NW China: *Frontiers in Earth Science*, v. 12, <https://www.frontiersin.org/journals/earth-science/articles/10.3389/feart.2024.1416594>.
- Li, K., Xi, K., Cao, Y., Niu, X., Wu, S., Feng, S., and You, Y., 2021, Chlorite authigenesis and its impact on reservoir quality in tight sandstone reservoirs of the Triassic Yanchang formation, southwestern Ordos basin, China: *Journal of Petroleum Science and Engineering*, v. 205, p. 108843, doi:<https://doi.org/10.1016/j.petrol.2021.108843>.
- Mallette, A.J., Espindola, G., Varghese, N., and Rimer, J.D., 2024, Highly efficient synthesis of zeolite chabazite using cooperative hydration-mismatched inorganic structure-directing agents††Electronic supplementary information (ESI) available: The authors have cited additional references within the ESI. See DOI: <https://doi.org/10.1039/d3sc05625b>.

- McKinley, J.M., Worden, R.H., and Ruffell, A.H., 1999, Smectite in sandstones: a review of the controls on occurrence and behaviour during diagenesis: Clay mineral cements in sandstones, p. 109–128.
- Millot, G., 2013, *Geology of clays: weathering· sedimentology· geochemistry*: Springer Science & Business Media.
- Mills, M.M., Sanchez, A.C., Boisvert, L., Payne, C.B., Ho, T.A., and Wang, Y., 2023, Understanding smectite to illite transformation at elevated (>100 °C) temperature: Effects of liquid/solid ratio, interlayer cation, solution chemistry and reaction time: *Chemical Geology*, v. 615, p. 121214, doi:<https://doi.org/10.1016/j.chemgeo.2022.121214>.
- Moore, D.M. & Reynolds, R.C., 1998, X-Ray Diffraction and the Identification and Analysis of Clay Minerals: *Geological Magazine*, v. 135, p. 819–842, doi:DOI: 10.1017/S0016756898501501.
- Mosser-Ruck, R., and Cathelineau, M., 2004, Experimental transformation of Na,Ca-smectite under basic conditions at 150 °C: *Applied Clay Science*, v. 26, p. 259–273, doi:<https://doi.org/10.1016/j.clay.2003.12.011>.
- Mosser-Ruck, R., Cathelineau, M., Guillaume, D., Charpentier, D., Rousset, D., Barres, O., and Michau, N., 2010, EFFECTS OF TEMPERATURE, pH, AND IRON/CLAY AND LIQUID/CLAY RATIOS ON EXPERIMENTAL CONVERSION OF DIOCTAHEDRAL SMECTITE TO BERTHIERINE, CHLORITE, VERMICULITE, OR SAPONITE: *Clays and Clay Minerals*, v. 58, p. 280–291, doi:10.1346/CCMN.2010.0580212.
- Mosser-Ruck, R., Pignatelli, I., Bourdelle, F., Abdelmoula, M., Barres, O., Guillaume, D., Charpentier, D., Rousset, D., Cathelineau, M., and Michau, N., 2016, Contribution of long-term hydrothermal experiments for understanding the smectite-to-chlorite conversion in geological environments: *Contributions to Mineralogy and Petrology*, v. 171, p. 97, doi:10.1007/s00410-016-1307-z.
- MOSSER-RUCK, R., PIRONON, J., CATHELINEAU, M., and TROUILLER, A., 2001, Experimental illitization of smectite in a K-rich solution: *European Journal of Mineralogy*, v. 13, p. 829–840, doi:10.1127/0935-1221/2001/0013-0829.
- Nadeau, P.H., Wilson, J., McHardy, W.J., and Tait, J.M., 1985, The Conversion of Smectite to Illite during Diagenesis: Evidence from some Illitic Clays from Bentonites and Sandstones: *Mineralogical Magazine*, v. 49, p. 393–400, doi:10.1180/minmag.1985.049.352.10.
- Niegel, S., and Franz, M., 2023, Depositional and diagenetic controls on porosity evolution in sandstone reservoirs of the Stuttgart Formation (North German Basin): *Marine and Petroleum Geology*, v. 151, p. 106157.
- Pittman, E.D., Larese, R.E., and Heald, M.T., 1992, Clay Coats: Occurrence and Relevance to Preservation of Porosity in Sandstones (D. W. Houseknecht & E. D. Pittman, Eds.): *Origin,*

- Diagenesis, and Petrophysics of Clay Minerals in Sandstones, v. 47, p. 0, doi:10.2110/pec.92.47.0241.
- Putnis, A., 2009, Mineral Replacement Reactions: Reviews in Mineralogy and Geochemistry, v. 70, p. 87–124, doi:10.2138/rmg.2009.70.3.
- Roberson, H.E., and Lahann, R.W., 1981, Smectite to Illite Conversion Rates: Effects of Solution Chemistry: Clays and Clay Minerals, v. 29, p. 129–135, doi:10.1346/CCMN.1981.0290207.
- Robinson, D., Schmidt, S.T., and De Zamora, A.S., 2002, Reaction pathways and reaction progress for the smectite-to-chlorite transformation: Evidence from hydrothermally altered metabasites: Journal of metamorphic Geology, v. 20, p. 167–174.
- Salisu, A.M., Algheryafi, H., Bello, A.M., Amao, A.O., Al-Otaibi, B., and Al-Ramadan, K., 2024a, Depositional and diagenetic controls on the reservoir quality of marginal marine sandstones: An example from the Early Devonian Subbat Member, Jauf Formation, northwest Saudi Arabia: Marine and Petroleum Geology, p. 107147, doi:https://doi.org/10.1016/j.marpetgeo.2024.107147.
- Salisu, A.M., Alhindi, H., Hussaini, S.R., Amao, A.O., Al-Awah, H., Al-ramadan, K., and Koeshidayatullah, A., 2024b, 3D Microporosity Characterizations in the Heterogeneous Middle Jurassic Tuwaiq Mountain Formation: Insights into an Unconventional Sweet Spot: ACS Omega, v. 9, p. 36273–36290, doi:10.1021/acsomega.4c02592.
- Salisu, A.M., Alqubalee, A., Bello, A.M., Al-Hussaini, A., Adebayo, A.R., Amao, A.O., and Al-Ramadan, K., 2023, Impact of kaolinite and iron oxide cements on resistivity and quality of low resistivity pay sandstones: Marine and Petroleum Geology, v. 158, p. 106568, doi:https://doi.org/10.1016/j.marpetgeo.2023.106568.
- Simon, N., Worden, R.H., Muhammed, D.D., Utley, J.E.P., Verhagen, I.T.E., Griffiths, J., and Wooldridge, L.J., 2021, Sediment textural characteristics of the Ravenglass Estuary; Development of a method to predict palaeo sub-depositional environments from estuary core samples: Sedimentary Geology, v. 418, p. 105906, doi:https://doi.org/10.1016/j.sedgeo.2021.105906.
- Small, J.S., 1994, Fluid composition, mineralogy and morphological changes associated with the smectite-to-illite reaction: An experimental investigation of the effect of organic acid anions: Clay Minerals, v. 29, p. 539–554.
- Small, J.S., Hamilton, D.L., and Habesch, S., 1992, Experimental simulation of clay precipitation within reservoir sandstones; 1, Techniques and examples: Journal of Sedimentary Research, v. 62, p. 508–519, doi:10.1306/D4267938-2B26-11D7-8648000102C1865D.
- Sottolichio, A., Castaing, P., Etcheber, H., Maneux, E., Schmeltz, M., and Schmidt, S., 2011, Observations of suspended sediment dynamics in a highly turbid macrotidal estuary, derived from continuous monitoring: Journal of Coastal Research, v. 2, p. 1579–1583.

- Środoń, J., 1999, Nature of mixed-layer clays and mechanisms of their formation and alteration: *Annual Review of Earth and Planetary Sciences*, v. 27, p. 19–53.
- Taylor, T.R., Giles, M.R., Hathon, L.A., Diggs, T.N., Braunsdorf, N.R., Birbiglia, G. V., Kittridge, M.G., MacAulay, C.I., and Espejo, I.S., 2010, Sandstone diagenesis and reservoir quality prediction: Models, myths, and reality: *American Association of Petroleum Geologists Bulletin*, v. 94, p. 1093–1132, doi:10.1306/04211009123.
- Taylor, T.R., Lander, R.H., and Bonnell, L.M., 2022, Sandstone Petrography, Petrology, and Modeling:, doi:10.2110/sepmcsp.13.
- Ulmer-Scholle, D.S., Scholle, P.A., Schieber, J., and Raine, R.J., 2015, A Color Guide to the Petrography of Sandstones, Siltstones, Shales and Associated Rocks:, doi:10.1306/M1091304.
- Velde, B.B., and Meunier, A., 2008, The origin of clay minerals in soils and weathered rocks: Springer Science & Business Media.
- Virolle, M., Brigaud, B., Bourillot, R., Féliès, H., Portier, E., Duteil, T., Nouet, J., Patrier, P., and Beaufort, D., 2019a, Detrital clay grain coats in estuarine clastic deposits: origin and spatial distribution within a modern sedimentary system, the Gironde Estuary (south-west France): *Sedimentology*, v. 66, p. 859–894, doi:10.1111/sed.12520.
- Virolle, M., Brigaud, B., Bourillot, R., Féliès, H., Portier, E., Duteil, T., Nouet, J., Patrier, P., and Beaufort, D., 2019b, Detrital clay grain coats in estuarine clastic deposits: origin and spatial distribution within a modern sedimentary system, the Gironde Estuary (south-west France): *Sedimentology*, v. 66, p. 859–894, doi:https://doi.org/10.1111/sed.12520.
- Virolle, M., Brigaud, B., Féliès, H., Bourillot, R., Portier, E., Patrier, P., Derriennic, H., and Beaufort, D., 2021a, Preservation and distribution of detrital clay coats in a modern estuarine heterolithic point bar in the Gironde estuary (Bordeaux, France): *Journal of Sedimentary Research*, v. 91, p. 812–832, doi:10.2110/JSR.2020.146.
- Virolle, M., Brigaud, B., Féliès, H., Bourillot, R., Portier, E., Patrier, P., Derriennic, H., and Beaufort, D., 2021b, Preservation and distribution of detrital clay coats in a modern estuarine heterolithic point bar in the Gironde estuary (Bordeaux, France): *Journal of Sedimentary Research*, v. 91, p. 812–832, doi:10.2110/jsr.2020.146.
- Virolle, M., Brigaud, B., Luby, S., Portier, E., Féliès, H., Bourillot, R., Patrier, P., and Beaufort, D., 2019c, Influence of sedimentation and detrital clay grain coats on chloritized sandstone reservoir qualities: Insights from comparisons between ancient tidal heterolithic sandstones and a modern estuarine system: *Marine and Petroleum Geology*, v. 107, p. 163–184, doi:https://doi.org/10.1016/j.marpetgeo.2019.05.010.
- Virolle, M., Féliès, H., Brigaud, B., Bourillot, R., Portier, E., Patrier, P., Beaufort, D., Jalon-Rojas, I., Derriennic, H., and Miska, S., 2020, Facies associations, detrital clay grain coats and mineralogical

- characterization of the Gironde estuary tidal bars: A modern analogue for deeply buried estuarine sandstone reservoirs: *Marine and Petroleum Geology*, v. 114, p. 104225, doi:<https://doi.org/10.1016/j.marpetgeo.2020.104225>.
- Walderhaug, O., and Porten, K.W., 2022, How Do Grain Coats Prevent Formation of Quartz Overgrowths? *Journal of Sedimentary Research*, v. 92, p. 988–1002, doi:[10.2110/jsr.2021.049](https://doi.org/10.2110/jsr.2021.049).
- Whitney, G., and Northrop, H.R., 1988, Experimental investigation of the smectite to illite reaction; dual reaction mechanisms and oxygen-isotope systematics: *American Mineralogist*, v. 73, p. 77–90.
- Wooldridge, L., Worden, R., Griffiths, J., and Utley, J., 2018, Clay coat diversity in marginal marine sediments: *Sedimentology*, v. 66, doi:[10.1111/sed.12538](https://doi.org/10.1111/sed.12538).
- Wooldridge, L.J., Worden, R.H., Griffiths, J., and Utley, J.E.P., 2017, Clay-coated sand grains in petroleum reservoirs: Understanding their distribution via a modern analogue: *Journal of Sedimentary Research*, v. 87, p. 338–352, doi:[10.2110/jsr.2017.20](https://doi.org/10.2110/jsr.2017.20).
- Wooldridge, L.J., Worden, R.H., Griffiths, J., and Utley, J.E.P., 2019, How to quantify clay-coat grain coverage in modern and ancient sediments: *Journal of Sedimentary Research*, v. 89, p. 135–146, doi:[10.2110/jsr.2019.6](https://doi.org/10.2110/jsr.2019.6).
- Worden, R.H., Armitage, P.J., Butcher, A.R., Churchill, J.M., Csoma, A.E., Hollis, C., Lander, R.H., and Omma, J.E., 2018, Petroleum reservoir quality prediction: Overview and contrasting approaches from sandstone and carbonate communities: *Geological Society Special Publication*, v. 435, p. 1–31, doi:[10.1144/SP435.21](https://doi.org/10.1144/SP435.21).
- Worden, R.H., and Burley, S.D., 2009, Sandstone Diagenesis: The Evolution of Sand to Stone: 1–44 p., doi:[10.1002/9781444304459.ch](https://doi.org/10.1002/9781444304459.ch).
- Worden, R.H., Griffiths, J., Wooldridge, L.J., Utley, J.E.P., Lawan, A.Y., Muhammed, D.D., Simon, N., and Armitage, P.J., 2020, Chlorite in sandstones: *Earth-Science Reviews*, v. 204, p. 103105, doi:[10.1016/j.earscirev.2020.103105](https://doi.org/10.1016/j.earscirev.2020.103105).
- Worden, R., and Morad, S., 2009, Clay Minerals in Sandstones: Controls on Formation, Distribution and Evolution, *in* *Clay Mineral Cements in Sandstones*, v. 34, p. 1–41, doi:[10.1002/9781444304336.ch1](https://doi.org/10.1002/9781444304336.ch1).
- Worden, R., and Morad, S., 2000, Quartz Cementation in Oil Field Sandstones: A Review of the Key Controversies: *Spec. Publ. Int. Assoc. Sed.*, v. 29, p. 1–20, doi:[10.1002/9781444304237.ch1](https://doi.org/10.1002/9781444304237.ch1).
- Yao, G., Li, L., Cai, M., and Liu, Y., 2017, Mechanisms of salinization in a middle Eocene lake in the Tanggu area of the Huanghua Depression: *Marine and Petroleum Geology*, v. 86, p. 155–167.

- Ylagan, R.F., Altaner, S.P., and Pozzuoli, A., 2000, Reaction mechanisms of smectite illitization associated with hydrothermal alteration from Ponza Island, Italy: *Clays and Clay Minerals*, v. 48, p. 610–631.
- Zhu, S., Cui, H., Jia, Y., Zhu, X., Tong, H., and Ma, L., 2020, Occurrence, composition, and origin of analcime in sedimentary rocks of non-marine petroliferous basins in China: *Marine and Petroleum Geology*, v. 113, p. 104164.

CHAPTER 5

DEPOSITIONAL AND DIAGENETIC CONTROLS ON THE RESERVOIR QUALITY OF MARGINAL MARINE SANDSTONES: AN EXAMPLE FROM THE EARLY DEVONIAN SUBBAT MEMBER, JAUF FORMATION, NORTHWEST SAUDI ARABIA

5.1. Abstract

The reservoir quality of marginal marine sandstones can vary significantly across different depositional lithofacies. This variation is primarily due to differences in depositional processes and subsequent diagenetic alterations occurring during various stages of burial. To address this issue, this study focuses on the Early Devonian Subbat sandstones of the Jauf Formation, which serve as an important analogue for subsurface gas reservoirs and have potential for CO₂ sequestration. An integrated approach was employed, including field observations, petrography, geochemical analyses, and petrophysical analyses, to investigate the impact of depositional and diagenetic processes on reservoir quality. The findings indicate that the sandstones range from poorly to well sorted, very fine to medium-grained arkosic and quartz arenites that were deposited in a range of environments including shoreface-to-offshore transition zones, wave-dominated deltas, fluvial and tidal estuarine channels. The sandstones experienced both shallow and deep burial diagenesis, while key diagenetic events affecting reservoir quality include compaction, carbonate cementation, the formation of authigenic clays (kaolinite, illite, and chlorite), quartz overgrowth, and the dissolution of unstable feldspar and mica grains. Authigenic pore-filling cements and grain-coating clays significantly influence reservoir quality. The effect of quartz cementation was minimal where illite and/or chlorite coatings are well-developed. Mechanical

compaction is more pronounced in the shoreface-to-offshore transition compared to the estuarine channels likely due to the higher detrital matrix content (21.7-35%, avg. 26.7%). The well-sorted fluvial to estuarine channel sandstones exhibit the best reservoir quality, with porosity ranging from 15.9% to 25.5% (average 20.4%) and permeability between 433.8 mD and 1261.2 mD (average 720 mD). This high reservoir quality is attributed to the low detrital matrix content (0-1%, average 0.2%) and limited pore-filling cements. In comparison, the moderately sorted, wave-dominated delta sandstones have lower porosity (5.3-11.2%, average 8.2%) and permeability (17.8-80 mD, average 42.8 mD), despite a relatively higher detrital matrix content (0-11.5%, average 2.8%). The poorly sorted shoreface-to-offshore transition sandstones exhibit the lowest reservoir quality, with porosity ranging from 1% to 2% (average 1.5%) and permeability between 0.3 and 1.1 mD (average 0.7 mD). These variations in reservoir quality among different depositional facies are primarily linked to depositional factors (sorting and detrital clay matrix) and shallow to deep burial diagenetic processes (compaction and cementation). A comprehensive understanding of these processes can enhance reservoir quality prediction in the Jauf Formation and similar reservoirs elsewhere.

5.2. Introduction

The efficient exploration and production of hydrocarbons, geothermal energy, and the subsurface storage of CO₂ and hydrogen within siliciclastic reservoirs rely heavily on a comprehensive understanding of reservoir quality (porosity and permeability) (Bjørlykke et al., 1989; Hussain & Al-Ramadan, 2009; Ajdukiewicz & Lander, 2010; Al-Ramadan et al., 2013a, 2014, 2021; Kordi, 2013; Eltom et al., 2015; Worden et al., 2018; Hussain et al., 2020, 2022; Alsuwaidi et al., 2021; Barshep & Worden, 2021; Hassanpouryouzband et al., 2022; Taylor et al., 2022; Bello et al., 2023a, 2023b; Busch et al., 2024; Criniti et al., 2024b). While porosity governs fluid storage

capacity, permeability controls its flow (Qiao et al., 2020; Bello et al., 2022). In marginal marine sandstones, these reservoir properties are shaped by a combination of depositional and diagenetic factors. Depositional controls, such as grain size, sorting, sedimentary structures, and facies distribution, play a crucial role in determining the initial porosity and permeability of the sandstones (Worden et al., 2018; Payton et al., 2022; Khan et al., 2023; Civitelli and Critelli, 2024; Naveed Butt et al., 2024; El-Ghali et al., 2024). Diagenetic processes, including cementation, compaction, and dissolution, further modify these properties during burial (Worden & Burley, 2009; Morad et al., 2010; Critelli et al., 2018; Lawan et al., 2021; Lander et al., 2022; Bello et al., 2023c, 2024; Civitelli et al., 2023, 2024). Variations in detrital framework mineralogy, grain size, and matrix content, which differ by depositional sub-environment, create heterogeneities that significantly influence diagenesis and, consequently, the reservoir quality across different depositional facies (Lawan et al., 2021). This complexity introduces challenges and uncertainties in predicting reservoir quality in marginal marine environments. Recently, a multidisciplinary approach integrating high-resolution stratigraphic analysis, microscale diagenetic investigations, reservoir modeling, and simulations has emerged as a valuable method for studying the complex interplay between depositional and diagenetic controls on the reservoir quality of marginal marine sandstones (Morad et al., 2010; Lawan et al., 2021).

Consequently, a thorough understanding of these processes (depositional and diagenetic) is vital for accurate reservoir quality prediction, essential for successful energy exploration and transition (Bello et al., 2024a, b). Depositional processes constitute the foundational factors influencing sandstone reservoir quality, setting the stage for subsequent diagenetic alterations (Khan et al., 2023). Compaction and the precipitation of pore-filling cements, such as quartz overgrowths, are primary diagenetic mechanisms that typically degrade reservoir quality (Paxton et al., 2002; Critelli

et al., 2018; Walderhaug and Porten, 2022). However, grain-coating cements, such as chlorite and illite, can impede quartz overgrowth and preserve reservoir quality in deeply buried sandstones (Bloch et al., 2002; Ajdukiewicz and Larese, 2012; Wooldridge et al., 2017; Griffiths et al., 2021). Increasing energy demand has prompted the exploration of numerous gas reservoirs around the world (Salem et al., 2005; Olson et al., 2009; Tobin et al., 2010; Lai et al., 2018; Becker et al., 2019; Liu et al., 2021).

One of these reservoirs is the Early Devonian Jauf Formation, a significant siliciclastic gas reservoir in Saudi Arabia (Al-Qahtani & Buhidma, 2001; Koeshidayatullah et al., 2016; Rahmani et al., 2021) and holds potential for effective CO₂ storage (Ye et al., 2023). Despite extensive research on the formation's tectonic setting, paleogeography, sedimentology, and stratigraphy, (Powers et al., 1966; Janjou et al., 1997; Wallace et al., 1997; Rahmani et al., 2002, 2021; Al-Husseini & Matthews, 2006; Al-Ghazi, 2007; Breuer et al., 2015; Algheryafi et al., 2022) the effect of depositional and diagenetic factors on reservoir quality remains understudied (Al-Ramadan et al., 2004, 2013b; Saner et al., 2006). The well-exposed siliciclastic outcrops of the Subbat Member, Jauf Formation provide an ideal opportunity to investigate these influences.

This study integrates field observations of sedimentary facies with comprehensive laboratory analyses, including thin-section petrography, scanning electron microscopy (SEM), elemental composition, bulk and clay fraction mineralogy, porosity, and permeability analysis. The primary objectives are to: 1) Perform a paragenetic analyses of diagenetic events that occurred in the sandstones, 2) examine the depositional processes that influenced the quality of marginal marine sandstone reservoirs, 3) establish the diagenetic processes that shaped reservoir quality, 4) assess the implications of these findings for reservoir quality prediction in the Jauf Formation and analogous reservoirs worldwide.

5.3. Geological background

The study area is part of the Subbat Member of the Devonian Jauf Formation, located in Al Huj, northwestern Saudi Arabia (Fig. 1A). During the Early Devonian, the Arabian Plate was part of an extensive and shallow continental ramp-type margin (Rahmani et al., 2021). Throughout that time, the Arabian Plate formed part of the passive margin of Eastern Gondwana (Fig.1B) and was drifting northwards between southern latitudes of 50° and 40° (Sharland et al., 2001; Stampfli & Borel, 2002). Additionally, the eastern Gondwana margin went through the Asiatic Hunic Terranes rifting (Stampfli et al., 2005). Overall, the Early Devonian climate ranged between cold to cool temperatures during periods of forest growth (Scotese, 2001).

The Arabian Plate underwent several transgressive and regressive periods during the Early Devonian (Konert et al., 2001). These periods are well represented in the Jauf Formation outcrops, which display cycles of siliciclastics alternating with carbonate deposits. Sediments were frequently prograding as thick clastic wedges from the Arabian-Nubian Shield into the north, northeast, and east (Rahmani et al., 2019; Criniti et al., 2023,2024a). However, this sediment supply was not as evident in the northern part of the Arabian Plate, as supported by the development of stromatolite intervals in the Jauf Formation.

The Devonian Jauf Formation was deposited during three 3rd order sequences that can be correlated across the northern and eastern parts of the Arabian Plate (Rahmani et al., 2019). The Jauf Formation is subdivided into five (5) members, defined based on lithological contrast: three members are dominated by siliciclastics, and two members are dominated by carbonate (Fig. 1C). This study focuses on the middle member of the Jauf Formation, the Subbat Member. Previously studied fauna and palynoflora of the Subbat indicated marginal marine settings (Boucot et al., 1989). Previous work on the Subbat Member (Janjou et al., 1997; Rahmani et al., 2002, 2019; Al-

Husseini & Matthews, 2006; Breuer et al. 2015) has addressed the sedimentological and palynological trends within the Formation. This paper adapts the same facies scheme for the Subbat Member from Algheryafi et al., (2022), which was based on an integration between outcrop and shallow cores.

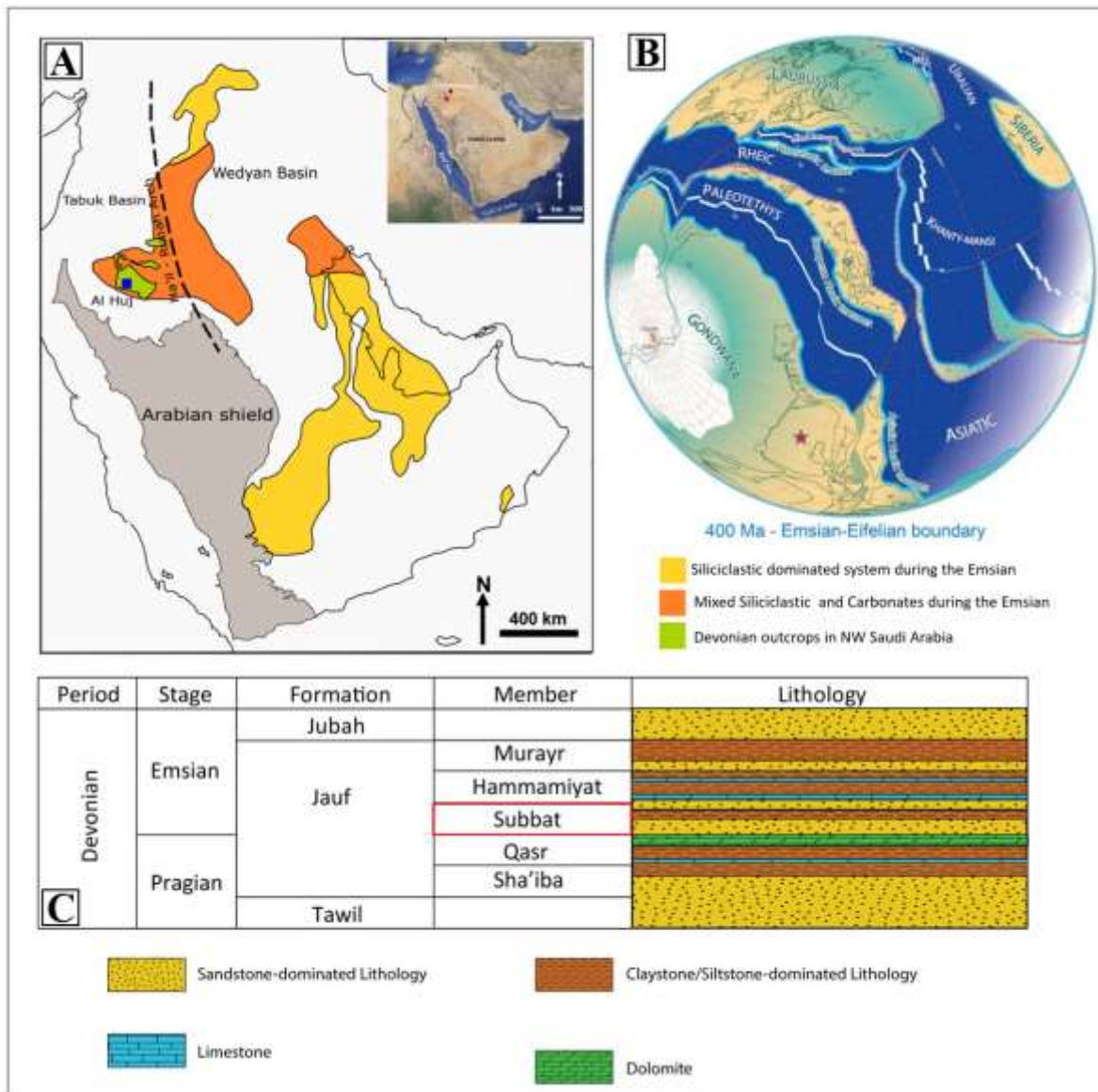


Figure 5.1. (A) Simplified geologic map of Saudi Arabia showing the distribution of the Early Devonian (Emsian) successions and location of the studied section (blue rectangle; redrawn after

Konert et al., 2001; Algheryafi et al., 2022). The inset map is a regional view of the study area showing the approximate location of the study (red star). (B) Paleogeographic reconstruction of the Early Devonian showing the location of the Arabian Plate (red star; Stampfli & Borel, 2010). (C) Stratigraphic Column of the Devonian in Saudi Arabia (after Algheryafi et al., 2022). The red rectangle shows the studied Subbat Member.

5.4. Methodology

This study involves the field investigation and characterization of the Jabal Al Helwat 2 outcrop (28° 47' 18" N, 38° 43' 9" E) of the Subbat Member, Jauf Formation (Fig. 1A). The sedimentary facies within the section were described using lithology, texture, sedimentary structures, and bioturbation. Forty-three (43) representative samples (Fig. 2) covering the described sedimentary facies were collected for subsequent integrated laboratory analyses aimed at investigating the depositional and diagenetic controls on the reservoir quality of the Jauf Formation.

5.4.1. Thin section petrography.

Twenty-two (22) representative samples were selected to prepare standard petrographic thin sections using the procedures described by Reed & Mergner, (1953) and Bello et al., (2021). All thin sections were impregnated with blue epoxy for porosity identification (Salisu et al., 2023) and examined using an Olympus BX53F petrographic microscope. Optical point counting of 300 counts per thin section was performed using Petrog software to quantify detrital framework grain composition, matrix, authigenic minerals, and porosity (primary and secondary). Additionally, Petrog was used to investigate the texture (grain size and sorting) of the samples by measuring the longest axes of 100 detrital (quartz and feldspar) grains.

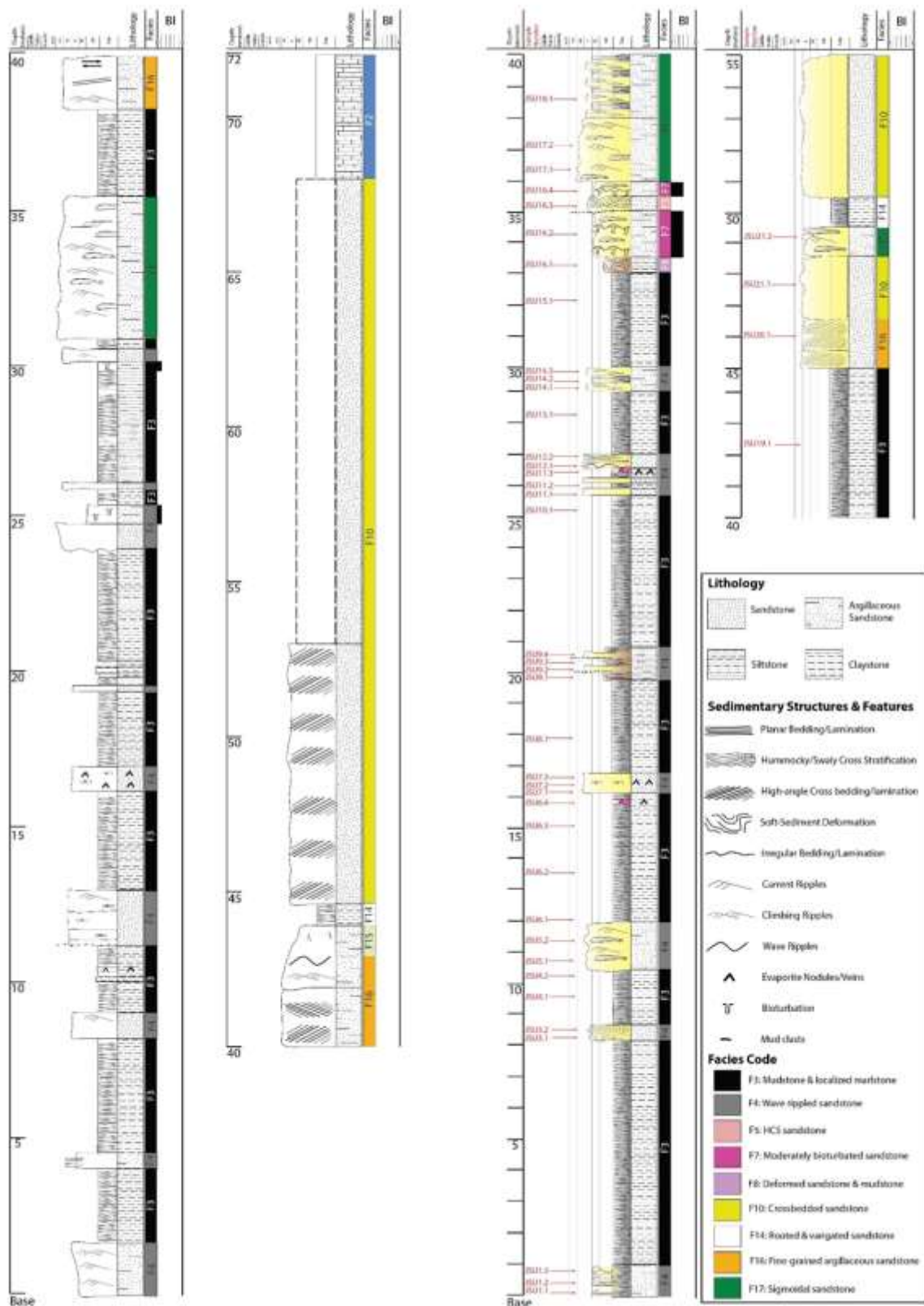


Figure 5.2. Measured outcrop sections of Jabal Al Helwat 2 as described in Algheryafi et al., (2022) and this study. The logged section in this study is around 50 meters away from the previously logged section. Minor variations in the sand distribution of the lower part are caused by the covered sections in each side of the outcrop.

5.4.2. Bulk and clay fraction XRD

Bulk and clay fraction ($< 2 \mu\text{m}$) mineralogy of representative samples were analyzed using X-ray diffraction (XRD) to complement the petrographic data. The analysis was conducted using a Malvern Empyrean PANalytical diffractometer with Ni-filtered Cu K- α radiation. Bulk mineralogy analysis was performed at 45 kV and 40 mA working conditions, with a range of $4.5\text{--}70^\circ 2\theta$ and a scan time of 8.7 seconds. The acquired data was analyzed using the Highscore Plus (v. 4.9) search-match module, fitted with the ICDD PDF-42022 mineralogical library (Amaao et al., 2016).

The clay fraction ($< 2 \mu\text{m}$) was isolated using a combination of gravity settling, ultrasonication, and centrifugation (Moore & Reynolds, 1997). First, 5 g of sample was dispersed in 100 ml of deionized water and ultrasonicated for 20 minutes. Gravity settling then removed sand and silt-sized particles. The remaining supernatant, containing clay-sized particles, was decanted and concentrated by centrifugation at 5000 rpm for 15 minutes to obtain the final clay fraction (Wooldridge et al., 2017).

Samples were prepared as oriented aggregates and analyzed under three conditions: air-dried untreated, after 24-hour ethylene glycol solvation to assess expandable clays (Moore & Reynolds, 1997), and after heating at 550°C for 1 hour. X-ray diffraction analyses were performed using a $4\text{--}40^\circ 2\theta$ scanning range with a $0.05^\circ/\text{s}$ step size. The resulting data were analyzed using the

Highscore Plus (v. 4.9) search-match module, fitted with the ICDD PDF-4-2022 mineralogical library.

5.4.3. XRF Analyses

The elemental compositions of twenty-five (25) representative samples were determined using wavelength-dispersive X-ray fluorescence (WD-XRF) spectroscopy with a PANalytical Zetium spectrometer (Malvern PANalytical). Samples were prepared as 37 mm diameter pressed powder pellets by grinding approximately 10 g of rock powder and mixing it with 10 wt% of an XRF grinding aid (C10: cellulose) before pressing at 2 Nm using a hydraulic press. The Zetium spectrometer features a 4 kW, drift-free, high-resolution Cu anode X-ray tube coupled with a WD-XRF detector equipped with five analyzing crystals: PE002 (Al-Cl), LiF200 (K-Am), PX-1 (O-Mg), Ge11 (enhanced P-Cl sensitivity), and LiF220 (enhanced V-Am resolution). This configuration enables quantitative analysis of major, minor, and trace elements across the periodic table. The quantitative analysis utilized synthetic certified reference materials (CRMs) from the WROXI series, produced under ISO 17034 accreditation. Periodically analyzed quality control standards validated data accuracy and precision. The obtained results were analyzed using PANalytical's SuperQ software, which controlled spectral acquisition, matrix deconvolution, and data processing with integrated quality control protocols.

5.4.4. SEM-EDS analyses

Representative rock chips were stub-mounted and studied using a Zeiss Gemini 550 scanning electron microscope (SEM). The SEM was equipped with a backscattered electron detector (BSE) and an Aztec energy-dispersive spectrometer (EDS) system, manufactured by Oxford Instruments, UK. The samples were coated with 30 nm of platinum using a Quorum Q150R sputter coater prior

to SEM analysis. The analysis was conducted under voltage and probe currents of 15 kV and 2 nA, respectively. The SEM-EDS analyses were performed to investigate the morphology, mode of occurrence, and composition of detrital framework grains, matrix, and cements, as well as their textural relationships.

5.4.5. Porosity and permeability measurements

Various methods were used to determine the porosity and permeability of the studied samples. First, petrographic point count porosity was measured for twenty-two (22) representative thin sections. In addition, ten selected core plugs (1.5-inch diameter) were extracted from the studied samples to conduct porosity measurements using a helium gas expansion porosimeter (AP-128-003-0; Vinci Technologies, France). The porosimeter measured bulk porosity up to 60% (Alqubalee et al., 2022).

Permeability ($n = 22$) was initially measured using TinyPerm©, a portable handheld air permeameter manufactured by New England Research, USA, following the procedures outlined by Hussain et al., (2022). The TinyPerm is equipped with NER-supplied Android™, which automatically stores permeability measurements through wireless transmission from the permeameter (Bello et al., 2023a) These permeability results were further validated by additional permeability measurements ($n=10$) on the 1.5-inch core plugs using a gas permeameter GP-101AE (manufactured by Porous Materials, Inc., USA). Klinkenberg correction was applied to the obtained gas permeability results to determine liquid permeability (Klinkenberg, 1941).

5.5. Results

5.5.1. Facies scheme

This study examined a well-exposed outcrop section (Jeb Al Helwat 2) of the Subbat Member, Jauf Formation (Figs. 2 & 3A). Nine lithofacies were delineated based on lithology, sedimentary structures, and bioturbation: stratified to structureless mudstone (F3), wave-rippled sandstone (F4), hummocky cross-stratified sandstone (F5), moderately bioturbated sandstone (F7), deformed sandstone and mudstone (F8), rooted and variegated sandstone (F14), cross-bedded sandstone (F10), fine argillaceous sandstone (F16), and sigmoidal sandstone (F17) (Fig. 3). The present work adapted the facies scheme (including facies codes, titles, and facie associations) of Algheryafi et al., (2022) for the Subbat Member, which was a detailed sedimentological and sequence stratigraphic study based on outcrops and shallow cores data. The facies description and interpretation are summarized in Table 1.

Table 5.5. Summary of the sedimentary facies descriptions and the assigned facies associations (modified after Algheryafi et al., 2022).

Facies Code & Name	Facies description	Facies Association
F3: Mudstone and localized marlstone (Fig. 3B)	• Stratified to structureless	Wave-dominated delta
F4: Sandstone with wave ripples (Fig. 3C)	• Upper very fine to upper-medium sandstone • Wave and current ripples • Flame structures • Loading features	
F5: HCS sandstone	• Argillaceous very fine sandstone • Hummocky and swaley cross-stratification • Wave and combined-flow ripples	
F7: Moderately bioturbated sandstone (Fig. 3D)	• Very fine silty sandstone • Disrupted horizontal lamination	Lower shoreface-to-offshore transition
F8: Mudstone and siltstone (Fig. 3E)	• Irregular laminations • Soft sediment deformation	
F10: Sandstone with cross-bedding (Fig. 3F)	• Fine to coarse sandstone • Trough cross-bedding, otherwise massive	Fluvial Channels
F14: Rooted and variegated mudstone (Fig. 3H)	• Green to red, rootlets, slickensides • Gypsum beds and veins • Otherwise structureless	
F16: Fine Argillaceous Sandstone (Fig. 3I)	• Argillaceous planar to high angle cross lamination • current and climbing ripples • single and double-mud drapes	Estuarine channels and associated tidal bars
F17: Sigmoidal Sandstone (Fig. 3J)	• Argillaceous medium to coarse sandstone • Flaser lamination, lateral accretion • Double-mud drapes, • Current ripples, sigmoidal	

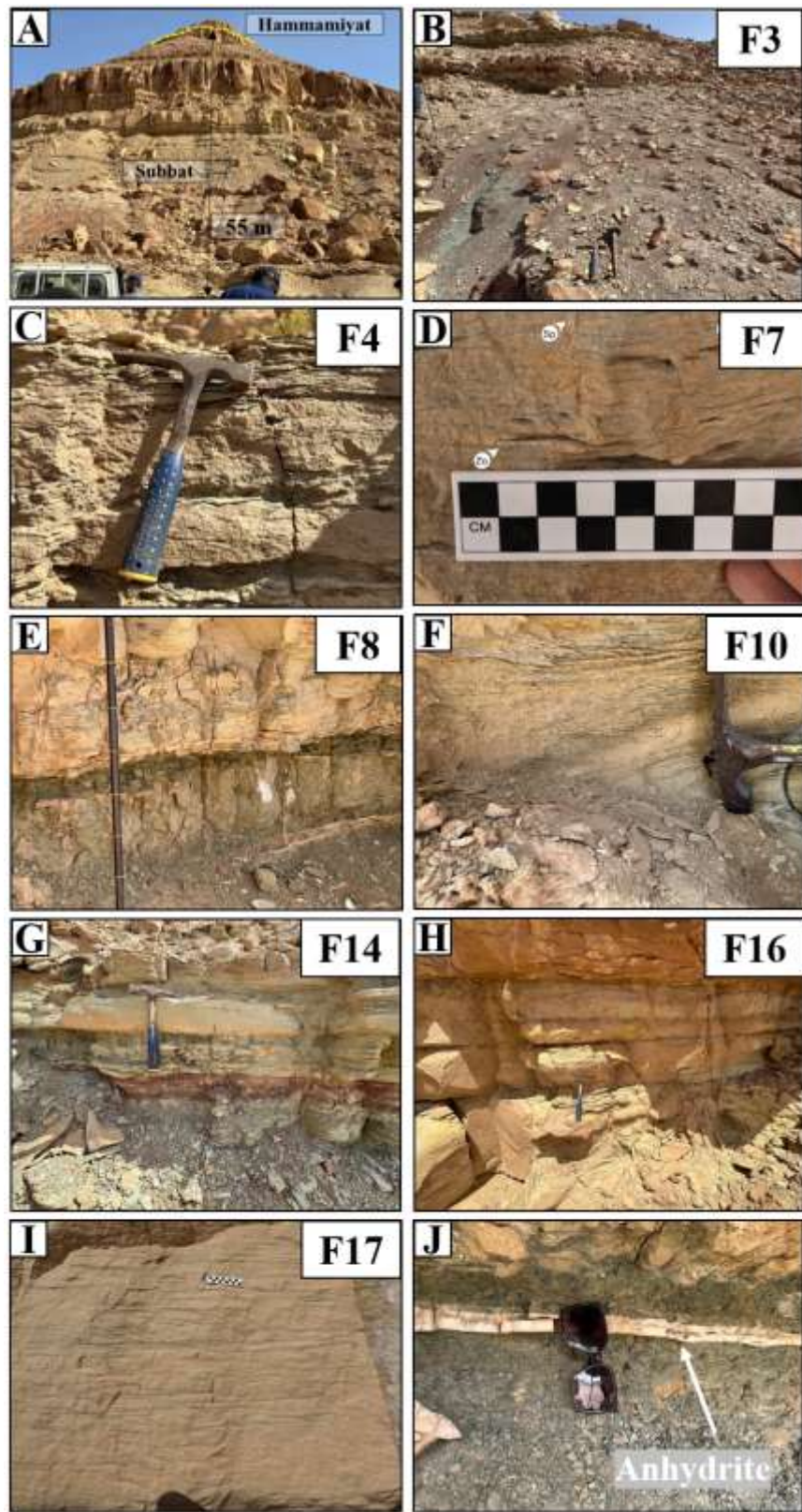


Figure 5.3. Outcrop photographs showing the studied section and the established lithofacies in the Subbat sandstones, Jauf Formation. (A) Studied Jebal Helwat 2 section of the Subbat Member overlaid by the carbonate Hammaiyat Member (B) Stratified to structureless mudstone (F3). (C) Wave-rippled sandstone (F4). (D) Moderately bioturbated sandstone (F7). Note the presence of Zoophycus (Zo) dominated trace fossil assemblage. Additionally, Spirophyton (Sp) traces were identified for the first time in these outcrops. (E) Deformed sandstone and mudstone (F8). (F) Cross-bedded sandstone (F10). (G) Rooted and variegated sandstone (F14). (H) Fine argillaceous sandstone (F16). (I) Sigmoidal sandstone (F17). (J) Continuous thin layers of anhydrite within mudstone and localized marlstone facies.

5.5.2. Facies association and interpretation

The identified lithofacies were grouped into four facies associations: wave-dominated delta (FA2), shoreface-to-offshore transition (FA3), fluvial channels (FA4), and estuarine channels (FA7). The vertical extent and sequence of facies associations are shown in Fig. 2 and compared with those from Algheryafi et al., (2022).

5.5.2.1. Wave-dominated delta (FA2)

Description: The wave-dominated delta facies association (FA2) predominates the lower part of the Subbat Member at the studied area, comprising lithofacies F3, F4, and less commonly, F5. These facies are characterized by sedimentary packages that range from 2-8 m in thickness. The base of the section exhibits an alternating sequence of stratified to structureless mudstone (F3) and wave-rippled sandstone (F4), with a thin interval of hummocky cross-stratified sandstone (F5) capping the unit (Fig. 2). Similar observations were reported in shallow cores by Algheryafi et al., (2022).

Interpretation: The prevalence and alternating occurrence of wave-rippled sandstones and stratified mudstones, along with the less common hummocky cross-stratified sandstone, suggest a distal expression of a wave-dominated delta (Algheryafi et al., 2022). While the wave-rippled sandstones indicate deposition in marginal marine settings, such as deltas (Nichols, 2013), the mudstones likely form in open marine environments. The presence of hummocky cross-stratified sandstone suggests a waning influence of fluvial input, marking a transition from a river-fed delta towards a more open wave-dominated shoreface setting.

5.5.2.2. *Shoreface-to-offshore transition (FA3)*

Description: This facies association comprises lithofacies F7 and F8, with thicknesses ranging from 0.5 to 2 meters. The FA3 is distinguished by moderately bioturbated sandstone (F7), dominated by *Zoophycus* (Zo) trace fossil assemblages, and *Spirophyton* (Sp) traces, identified for the first time in these outcrops (Fig. 3D). Fine to very fine irregular laminated mudstones and siltstones are the dominant facies, typically sandwiching the bioturbated sandstones.

Interpretation: The presence of wave-related sedimentary structures in both laminated mudstones and siltstones, along with the overall trace fossil assemblage, indicates deposition in shoreface-to-offshore transition environments. The combined sedimentary structures suggest elevated wave and storm-influence activity (Leckie and Walker, 1982). Additionally, the moderate bioturbation characterized by *Zoophycus* and *Spirophyton* *ichnofossils* is typically associated with low-energy environments, such as the distal lower shoreface and offshore transition (Olivero, 1996; MacEachern et al., 2007; Knaust and Bromley, 2012).

5.5.2.3. *Fluvial Channel (FA4)*

Description: This facies association occurs in the middle to upper part of the studied section, predominantly comprising F10 with occasional F14. Sedimentary packages range from 1 to 5 meters thick, characterized by very fine to fine-grained trough cross-bedded to massive sandstones (F10) that thickens upward. Rooted to variegated mudstones (F14) are less common and bounded by cross-bedded sandstones when present.

Interpretation: The presence of planar to trough cross-bedded massive sandstones indicates deposition under strong current conditions, typical of subaqueous dunes in migrating fluvial channels (Miall, 1985). The underlying rooted and variegated mudstones, sandwiched between cross-bedded sandstones, suggest a slough within a scroll bar, part of a large-scale fluvial system (Galli, 2014; Srisunthon & Choowong, 2019).

5.5.2.4. *Estuarine channels (FA7)*

Description: The Estuarine channels (FA7) facies association occupies the uppermost part of the studied section, marking the boundary between the Subbat member and the upper carbonate Hammamiyat member of the Jauf Formation (Algheryafi et al., 2022). This association is predominantly composed of F16 and F17 lithofacies. Notably, F17 consists of sigmoidal sandstone characterized by flaser lamination, wavy (tidal) lamination, current ripples, and single and double mud drapes, with thicknesses ranging from 1 m to 4 m. Additionally, a thickening upward package of fine argillaceous sandstone (F16), approximately 2 m thick, underlies the sigmoidal sandstone.

Interpretation: The observed sedimentary structures suggest deposition within an estuarine environment. The presence of single and double mud drapes (Ashour et al., 2014), along with flaser laminations and current ripples, indicates dominant tidal processes (Dalrymple, 2010; Ashour et al., 2014). The stacked, sigmoidal, fining-upward sandstones are interpreted as fluvial-

tidal to tidal channels Overall, these facies assemblages represent estuarine channels and their associated tidal bars.

5.5.3. Petrography

5.5.3.1. Texture

The grain size distribution of the studied samples reveals a predominance of very fine to medium grain sizes, with variations ranging from very fine ($n = 7$) to fine ($n = 2$), medium ($n = 12$), and less commonly, coarse ($n = 1$) grained sand (Fig. 4). Sorting characteristics show a mix of poorly sorted (5 samples), moderately well sorted (10 samples), and well sorted (7 samples) (Table 2).

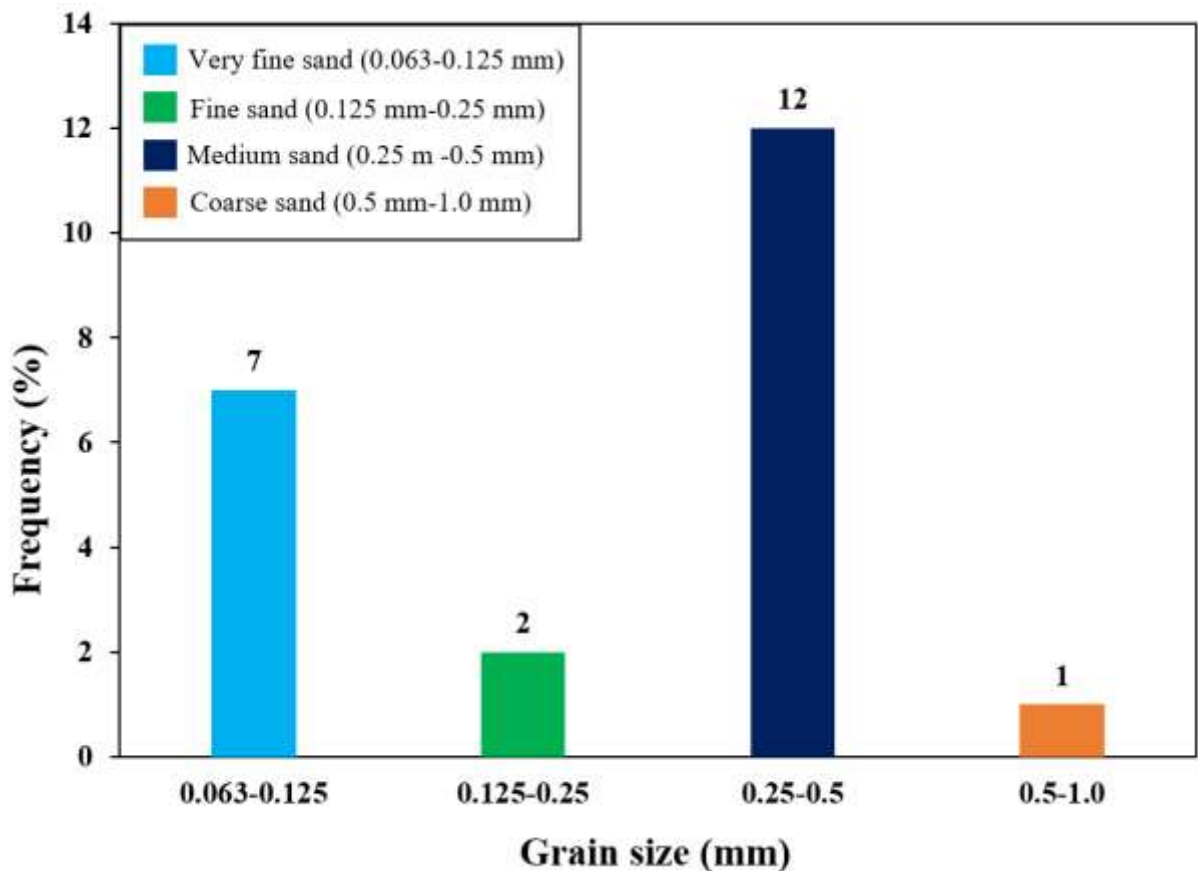


Figure 5.4. Histogram showing the grain size distribution of the studied samples

Table 5.2: Petrographic point counts and permeability data for the Jauf Formation

Sample ID and Facies Association		Detrital Grains (%)									Matrix (%)	Cements (%)										Porosity (%)		Permeability (mD) and Texture			
Sample ID	FA	MQ	PQ	OT	MC	PL	BT	MU	RF	HM	DM	PFK	GRK	PFI	GC1	IK	GCC	TPC	Qo	PFG	PFF	PFFeO	IP	GDP	PM	MGS	SO
JSU3.1	FA 2	66.7	0.3	0.3	0.0	0.0	0.0	1.0	0.0	0.5	0.5	10.0	1.0	5.0	0.0	2.0	0.0	0.0	0.0	1.0	0.0	0.0	11.2	0.5	67.2	0.4	1.4
JSU3.2	FA 2	62.0	0.0	0.3	0.0	0.0	0.0	0.7	0.0	0.0	3.0	1.5	7.0	2.0	0.0	1.5	0.0	7.5	1.0	3.0	0.0	0.5	7.5	2.5	46.9	0.5	1.7
JSU3.2C	FA 2	71.9	0.5	0.5	0.2	0.5	0.0	2.0	1.5	0.0	0.0	1.0	5.0	1.0	0.0	0.5	0.0	5.0	0.0	0.0	0.0	0.1	9.3	1.0	17.8	0.3	1.3
JSU4.2	FA 2	62.3	0.3	0.1	0.3	0.0	1.5	0.5	0.0	0.0	3.0	3.5	2.0	8.7	0.0	0.3	0.0	4.5	2.5	0.0	0.0	0.0	9.0	1.5	45.9	0.3	1.5
JSU5.1	FA 2	37.8	0.0	0.0	0.1	0.0	1.5	0.0	0.0	0.0	7.0	1.0	1.3	2.0	0.0	0.0	0.0	10.0	0.5	25.5	0.0	0.0	11.0	2.3	17.8	0.4	1.2
JSU5.2	FA 2	66.3	0.0	1.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	1.3	0.0	1.0	0.0	0.0	0.0	2.0	0.0	15.1	0.0	0.0	7.0	4.3	68.6	0.4	1.3
JSU7.1	FA 2	65.0	0.0	1.0	0.0	0.0	0.0	1.0	0.5	0.0	2.5	2.0	1.5	3.0	0.0	0.0	0.0	11.0	0.0	1.0	0.0	0.5	10.0	1.0	41.4	0.9	1.3
JSU7.3	FA 2	70.7	0.0	0.3	0.0	0.1	0.0	0.0	1.0	1.0	0.5	2.5	1.0	1.0	0.0	0.0	0.0	5.0	0.0	9.1	0.0	0.0	5.3	2.5	80.0	0.3	1.4
JSU12.1	FA 2	55.0	0.6	0.1	0.7	0.3	0.0	0.0	0.0	0.0	2.0	1.0	1.5	3.0	0.0	0.0	0.0	20.3	4.0	1.5	0.0	0.0	8.0	2.0	31.0	0.3	1.6
JSU12.2	FA 2	70.3	0.0	1.5	0.5	0.6	0.5	0.0	1.5	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	10.0	1.0	0.0	0.1	0.0	10.7	1.3	23.5	0.3	1.4
JSU16.1	FA 3	14.3	0.0	4.1	2.5	1.0	2.5	5.0	0.0	0.0	35.0	7.5	1.2	12.5	0.1	9.0	1.0	1.0	0.8	0.0	0.0	1.0	2.0	0.0	1.1	0.1	1.6
JSU16.2	FA 3	17.8	0.0	12.0	5.0	2.1	2.5	1.0	0.0	0.0	24.1	8.0	2.0	9.5	0.0	7.0	0.0	2.0	2.0	0.0	0.0	3.0	1.5	0.0	0.6	0.1	1.6
JSU16.3	FA 2	24.5	0.0	13.9	6.1	1.9	0.0	1.5	0.0	0.0	11.5	5.0	1.5	7.5	5.0	2.5	2.6	4.0	4.0	0.0	0.0	1.5	5.5	1.5	31.2	0.1	1.4
JSU16.4	FA 3	24.3	0.0	10.1	4.3	2.0	1.7	0.5	0.0	0.0	21.7	7.0	3.0	9.7	0.0	3.5	0.0	1.0	7.2	0.0	0.0	3.0	1.0	0.0	0.3	0.1	1.6
JSU17.1	FA 7	27.3	0.0	9.3	3.0	1.3	0.7	0.0	0.5	0.0	0.0	11.0	1.3	5.0	11.0	2.0	2.0	2.9	0.0	0.0	0.0	0.0	20.7	2.0	869.3	0.1	1.1
JSU17.2	FA 7	25.2	0.0	13.0	5.0	2.2	0.3	0.0	0.7	0.5	0.0	7.0	1.0	3.9	7.0	3.0	1.3	2.5	0.4	0.0	0.0	0.5	22.5	4.0	790.3	0.1	1.1
JSU17.4C	FA 7	28.3	0.7	12.5	8.3	3.0	0.2	1.0	1.0	0.0	0.0	6.0	0.1	2.5	4.5	2.0	1.5	2.0	0.0	3.0	1.0	0.0	18.4	4.0	498.7	0.1	1.1
JSU18	FA 7	29.7	0.0	15.2	7.0	3.9	0.0	1.0	1.5	0.3	0.0	5.0	2.1	3.5	4.0	2.0	3.0	2.5	0.0	0.0	0.5	0.0	16.5	2.3	433.8	0.2	1.1
JSU20	FA 7	33.0	0.3	11.2	6.9	1.0	0.5	1.7	2.5	0.0	0.5	3.0	1.0	2.0	4.0	1.0	2.0	0.0	1.0	0.0	0.2	1.2	25.5	1.5	1261.2	0.1	1.1
JSU21.1	FA 4	35.6	0.6	10.3	4.0	1.0	1.7	0.5	1.3	0.6	1.0	1.0	2.0	2.3	5.0	1.0	3.9	2.7	0.5	1.0	0.0	0.0	23.0	1.0	561.3	0.1	1.1
JSU21.2	FA 7	29.8	1.2	11.2	3.9		2.5	1.0	0.5	0.0	0.0	4.0	2.0	6.0	5.0	3.0	4.0	2.3	1.0	1.0	0.8	1.0	15.9	3.9	631.3	0.1	1.1
	Min	14.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.3	0.1	1.1
	Max	71.9	1.2	15.2	8.3	3.9	2.5	5.0	2.5	1.0	35.0	11.0	10.0	12.5	11.0	9.0	4.0	20.3	7.2	25.5	1.0	3.0	25.5	4.3	1261.2	0.9	1.7
	Average	42.4	0.2	6.1	2.8	1.0	0.8	0.9	0.6	0.1	5.4	3.8	2.2	4.4	2.2	1.9	1.0	4.7	1.2	2.9	0.1	0.6	11.5	1.9	262.8	0.3	1.3

[MQ = monocrystalline quartz; PQ = polycrystalline quartz; OT = orthoclase; MC = microcline; PL = plagioclase; BT = biotite; MU= muscovite; RF = rock fragments; HM = heavy minerals; DM = detrital matrix; PFK = pore-filling kaolinite; GRK = grain-replacive kaolinite; PFI = pore-filling illite; GCI = grain-coating illite; IK = Illite-kaolinite; GCC = grain-coating chlorite; TPC = total pore-filling carbonates (calcite, dolomite, ankerite and siderite); Qo = quartz overgrowths; PFF = pre-filling feldspar; PFFeO = pore-filling Fe-oxide; PFG = pore-filling gypsum; IP = Intergranular porosity; GDP = grain-dissolution porosity (including feldspar and calcite dissolution porosity); PM = permeability (mD); MGS = mean grain size (mm); SO = sorting (Trask coefficient)]

Detrital Composition

The detrital components primarily consist of monocrystalline quartz (Fig. 5A), which ranges from 14.3% to 71.9%, with an average of 42.4%. Polycrystalline quartz (Fig. 5B) is rare (0-1.2%, avg. 0.2%). Additionally, K-feldspar grains (Fig. 5C), comprising orthoclase (0-15.2%, avg. 6.1%) and microcline (0-8.3%, avg. 2.8%), are more abundant than plagioclase (0-3.9%, avg. 1%) (Fig. 5D). Rock fragments (0-2.5%, avg. 0.6%) are primarily sedimentary in origin, consisting of very fine-grained sandstones with mudclasts (Fig. 5E). Furthermore, Muscovite (0-5%, avg. 0.9%) is slightly more abundant than biotite (0-2.5%, avg. 0.8%) (Fig. 5F), while heavy minerals occur in trace amounts (Table 2). Based on Folk's classification (1980), the studied sandstones are classified as arkoses and quartz arenites (Fig. 6).

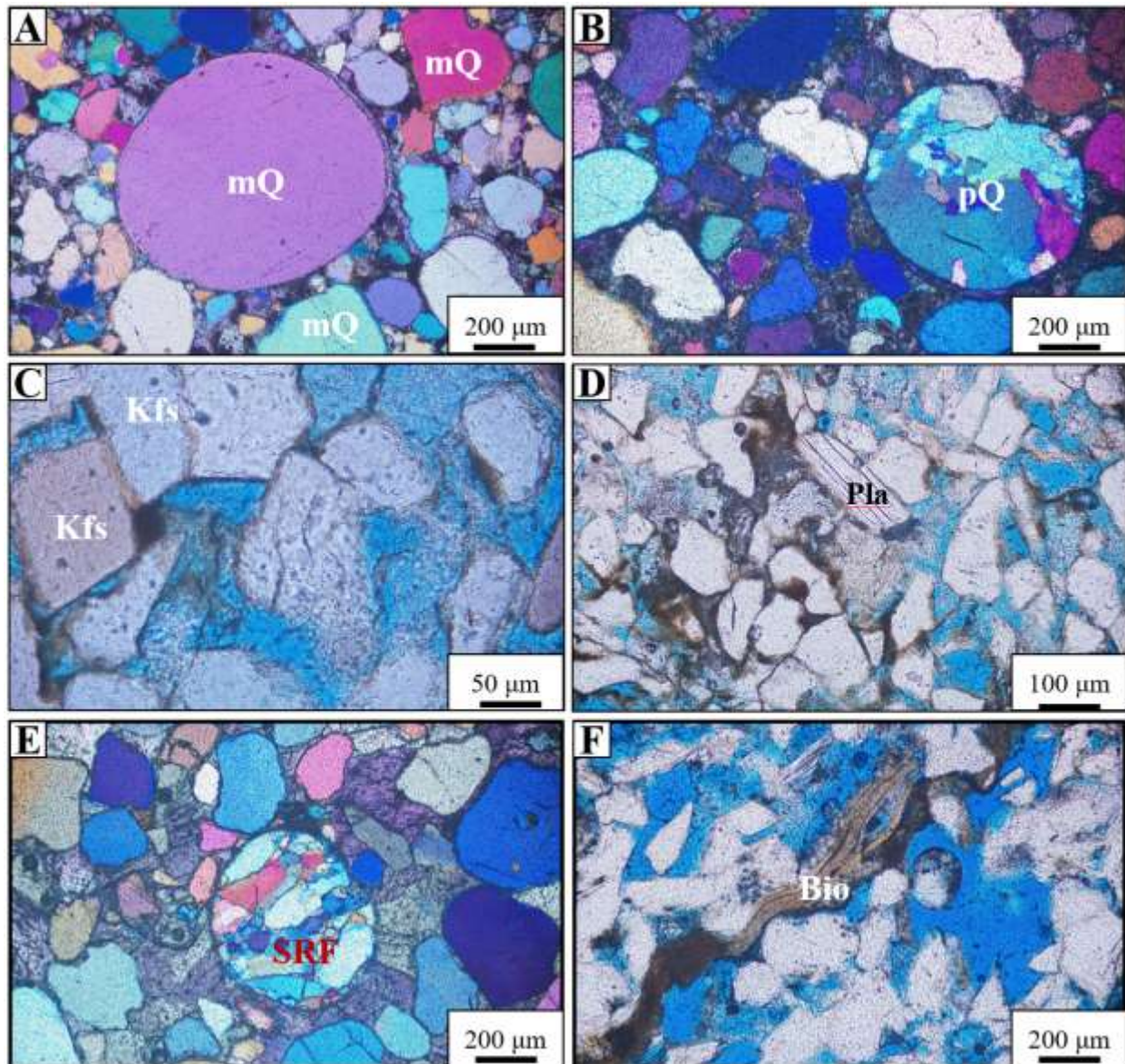


Figure 5.5. Photomicrographs of the main type of framework grains within the studied samples (A) Cross-polarized light (XPL) thin-section image showing detrital, monocrystalline quartz (mQ). (B) XPL image showing detrital polycrystalline quartz (pQ). (C) Pane-polarized (PPL) thin-section image showing detrital k-feldspar grains (Kfs). (D) PPL photomicrograph showing plagioclase (Pla). (E) XPL image showing sandstone rock fragment (SRF). (F) PPL image showing detrital biotite (Bio).

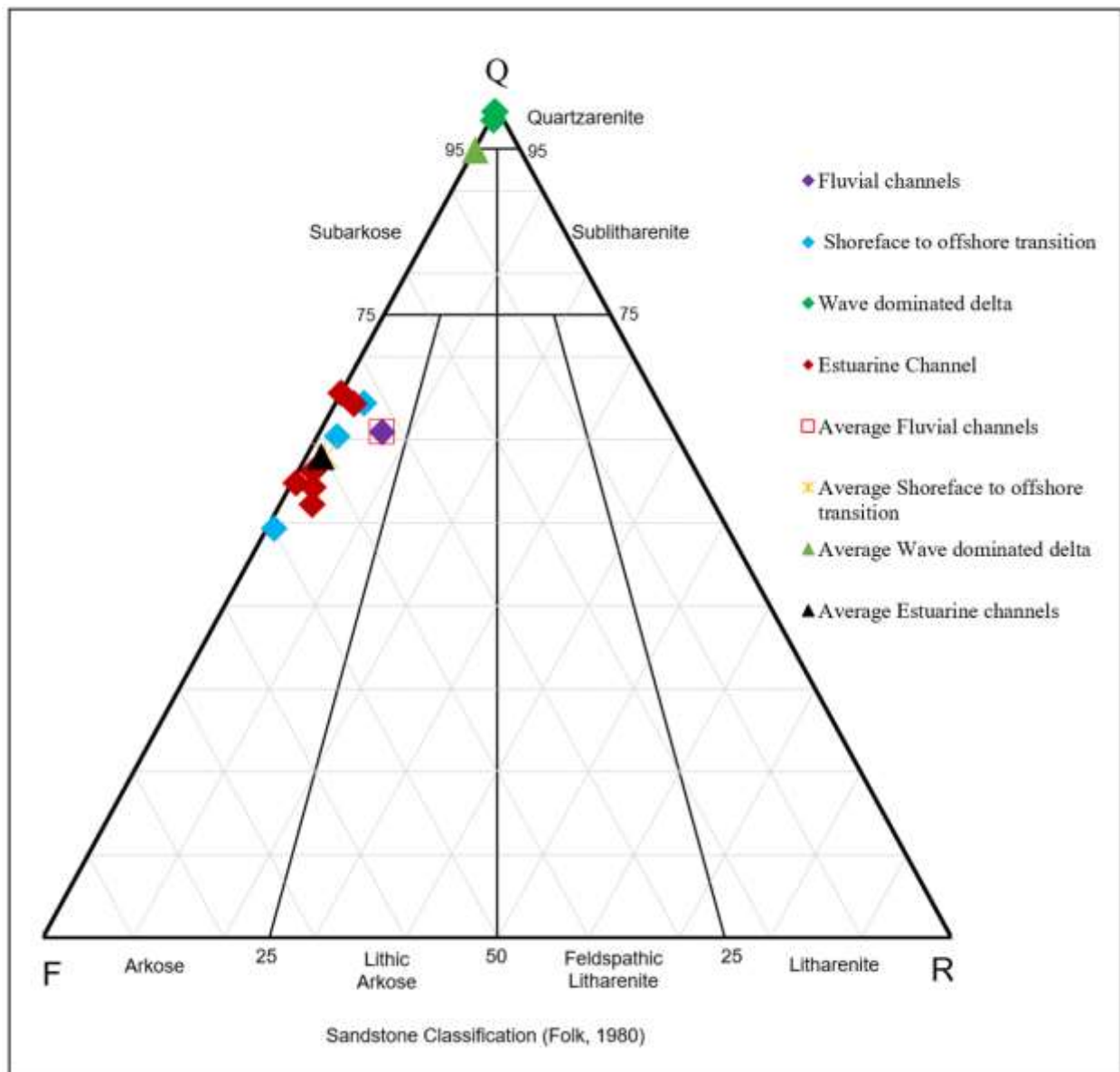


Figure 5.6. Sandstone classification for the studied Subbat Member, Jauf Formation, according to Folk's classification (1980).

5.5.3.2. *Geochemical Analysis*

XRF analysis revealed the distribution of major (Si, Al, Ca, Mg, K) and minor (Na, Mn, Fe, S, Ti, P, Cl, Ba) (Fig. 7A) elemental composition, their oxides (Fig. 7B), and trace (Sr, Y, Rb, Nb, Cr, Cu, Zr, Zn) (Fig. 7C) elements within the Subbat Member. The results show variations in elemental and oxide compositions across different facies associations (Fig. 7). Silicon (Si) is the most abundant element in most samples, while Calcium (Ca) concentrations vary with depositional environments, being more abundant in wave-dominated delta facies. Conversely, Potassium (K) demonstrated higher concentrations in fluvial and estuarine channels compared to the wave-dominated delta facies (Fig. 7A). Strontium (Sr) is the most prevalent trace element, present in all studied samples (Fig. 7C).

Bulk mineralogical composition, determined through X-ray diffraction (XRD), revealed quartz as the dominant mineral, ranging from 4.4% to 84.7% with an average of 40.7% (Table 3, Fig. 8). Orthoclase followed as the second most abundant framework mineral, succeeded by microcline, muscovite, albite, and biotite. Fe-dolomite, ankerite, and calcite are the primary carbonates, with rare occurrences of siderite (Table 3). Illite, kaolinite, and less commonly, chlorite are the main clay minerals, while anhydrite, hematite, and goethite occur in trace amounts, except in two samples where anhydrite exceeds 10% (Table 3).

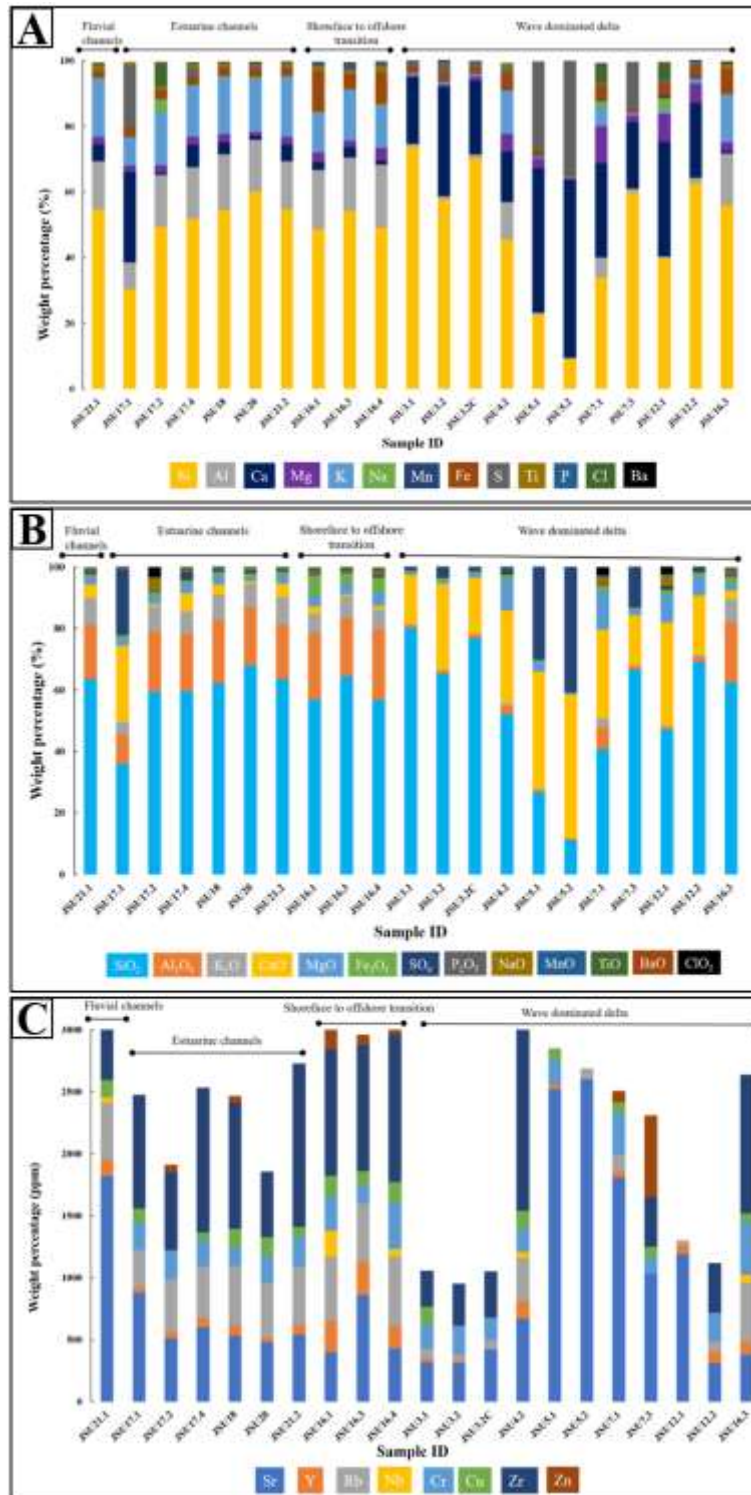


Figure 5.7. Mean elemental (A), oxides (B), and trace elements (C) plot with depositional environments derived from WD-XRF. Note the relative abundance of Ca and K within the different depositional facies in relation to the distribution of carbonates and clay cements.

Table 5.3. Results of the whole-rock XRD analysis for the Jauf Formation

Sample ID	Facies Association	Bulk mineralogy (wt. %)																
		Qtz	Orth	Mic	Ab	Mus	Bio	Dol	Cal	Ank	Anh	Sid	Kao	Ill	Chl	Hem	Goe	Total
JSU1.2	FA 2	29.3	36.8	5.6	2.8	1.4	1.1	1.7	0.2	0.0	1.7	0.0	10.6	4.9	3.6	0.1	0.2	100.0
JSU3.1	FA 2	84.7	0.5	0.2	0.8	0.2	0.0	0.3	10.3	0.0	0.9	0.0	1.0	0.9	0.0	0.0	0.2	100.0
JSU3.2	FA 2	73.3	0.8	1.5	1.7	0.4	0.0	0.5	17.6	0.0	2.5	0.0	1.1	0.3	0.0	0.0	0.3	100.0
JSU3.2C	FA 2	81.0	0.3	0.5	0.4	0.1	0.1	2.7	11.5	0.1	1.1	0.0	0.8	1.2	0.0	0.0	0.2	100.0
JSU4.1	FA 2	9.2	4.2	2.9	0.7	25.0	1.6	17.7	0.0	1.4	0.7	0.0	5.4	30.9	0.2	0.0	0.1	100.0
JSU5.1	FA 2	47.8	0.8	0.4	1.2	0.4	0.0	13.5	0.1	0.3	33.3	0.1	0.7	1.4	0.0	0.0	0.0	100.0
JSU6.1	FA 2	10.5	4.1	4.9	0.5	15.9	1.3	16.7	0.2	5.3	3.4	0.0	4.0	33.1	0.0	0.0	0.1	100.0
JSU7.3	FA 2	73.5	0.4	0.2	0.0	0.0	0.0	3.8	0.0	3.3	16.9	0.0	0.8	1.1	0.0	0.0	0.0	100.0
JSU7.1	FA 2	44.5	1.7	2.7	1.0	1.7	0.4	27.2	0.0	9.3	0.1	0.0	2.0	9.3	0.0	0.0	0.1	100.0
JSU9.3	FA 2	4.4	8.7	0.7	0.0	1.1	0.8	36.3	0.3	21.9	0.5	0.0	2.1	22.6	0.1	0.3	0.2	100.0
JSU12.1	FA 2	58.8	0.0	0.0	0.6	0.0	0.0	23.2	0.3	14.8	0.8	0.0	0.8	0.5	0.0	0.2	0.0	100.0
JSU12.2	FA 2	71.6	0.0	1.2	0.5	0.1	0.0	15.5	0.0	7.1	1.7	0.0	0.9	1.3	0.0	0.0	0.1	100.0
JSU14.2	FA 2	27.4	12.1	10.0	2.8	2.7	0.9	13.9	0.1	1.4	0.9	0.0	6.4	20.3	0.9	0.0	0.2	100.0
JSU15	FA 2	21.9	16.7	4.9	2.1	16.0	1.1	0.0	0.3	0.0	0.8	0.0	13.0	23.2	0.0	0.0	0.0	100.0
JSU16.1	FA 3	11.3	5.5	5.8	1.8	26.3	2.5	0.0	0.0	0.0	0.0	0.2	11.4	34.0	0.5	0.2	0.5	100.0
JSU16.2	FA 3	31.9	29.4	8.3	3.8	1.7	0.6	0.0	0.2	0.0	0.0	0.2	12.0	9.6	2.1	0.1	0.3	100.0
JSU16.3	FA 2	29.8	27.6	9.0	3.0	2.4	1.3	0.1	0.0	0.0	0.2	0.0	9.6	13.9	2.7	0.1	0.2	100.0
JSU17.4C	FA 7	35.4	26.3	9.9	3.5	1.2	0.0	4.4	0.5	0.0	2.2	0.1	10.1	4.5	1.7	0.0	0.2	100.0
JSU20	FA 7	43.6	21.8	11.8	2.1	1.0	0.3	0.0	0.3	0.0	0.6	0.2	11.3	5.0	1.7	0.0	0.3	100.0
JSU21.1	FA 4	37.8	28.8	10.8	3.9	0.9	0.0	4.4	0.1	0.0	0.4	0.2	6.5	4.6	1.5	0.1	0	100.0
JSU21.2	FA 7	27.0	37.3	9.4	2.9	1.1	0.2	6.6	0.2	0.0	0.2	0.2	8.9	4.5	1.4	0.1	0.0	100.0
	Min	4.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.3	0.0	0.0	0.0	100.0
	Max	84.7	37.3	11.8	3.9	26.3	2.5	36.3	17.6	21.9	33.3	0.2	13	34	3.6	0.3	0.5	100.0
	Average	40.7	12.6	4.8	1.7	4.7	0.6	9.0	2.0	3.1	3.3	0.1	5.7	10.8	0.8	0.1	0.2	100.0

[Qtz=quartz; Orth=orthoclase; Mic=microcline; Ab=albite; Mus=muscovite; Bio=biotite; Dol=dolomite; Cal=calcite; Ank=ankerite;

Anh=anhydrite; Sid=siderite; Kao=kaolinite; Ill=illite; Chl=chlorite; Hem=hematite; Goe=Goethite].

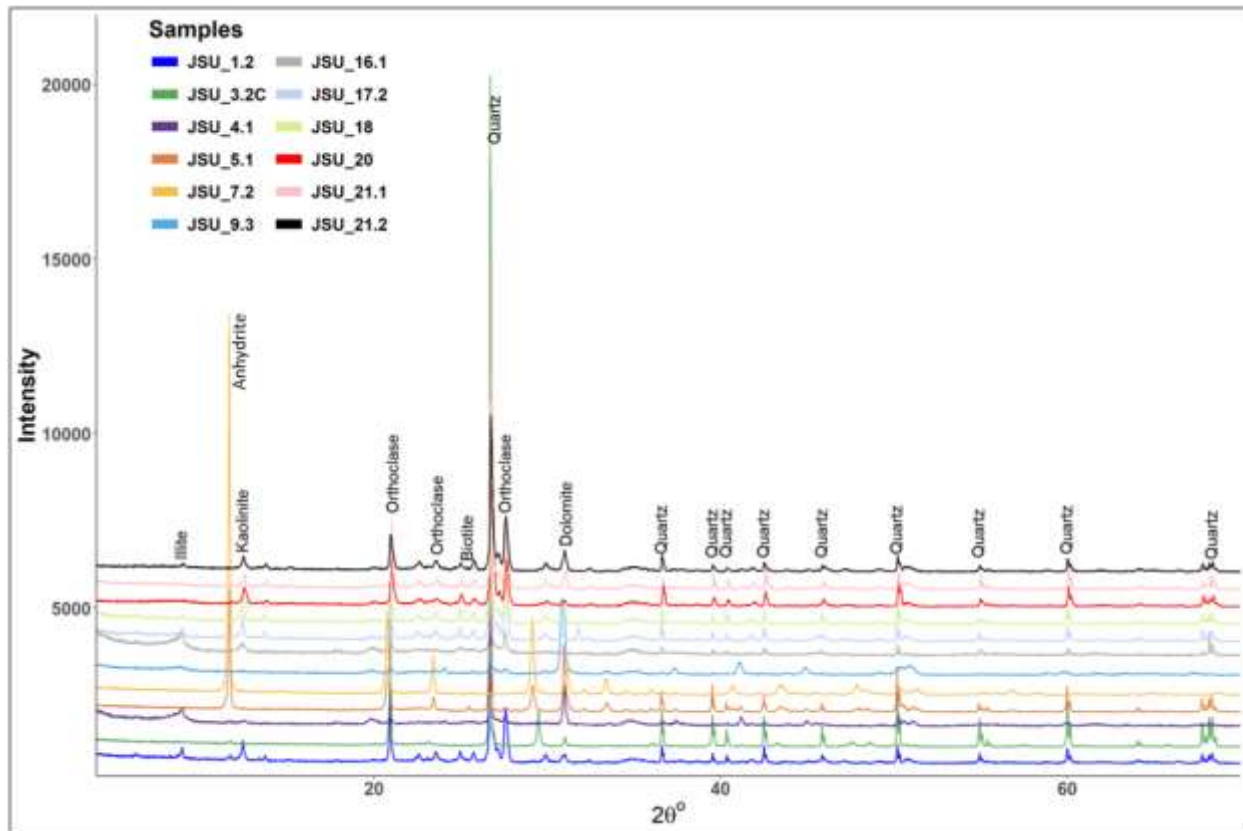


Figure 5.8. Bulk XRD pattern of framework minerals from representative samples of the studied sandstones.

5.5.3.3. *Compaction*

The assessment of mechanical and chemical compaction within the Jauf Formation sandstones and siltstones was conducted through the analysis of grain contact types (Fig. 9). Long and point contacts are the predominant grain contacts (Fig. 9A), while concavo-convex (Fig. 9B) and sutured (Fig. 9C) contacts are less common. Additionally, mica grains exhibit a flat and slightly deformed morphology (Fig. 9D). The degree and impact of mechanical compaction on porosity loss were evaluated using the methods described by Lundegard (1992) and Houseknecht (1987). A comparison of compaction-corrected porosity (COPL) and cementation-corrected

porosity (CEPL) reveals that porosity loss is attributed to both compaction and cementation, with compaction being the dominant factor in 11 out of 17 samples (Fig. 10).

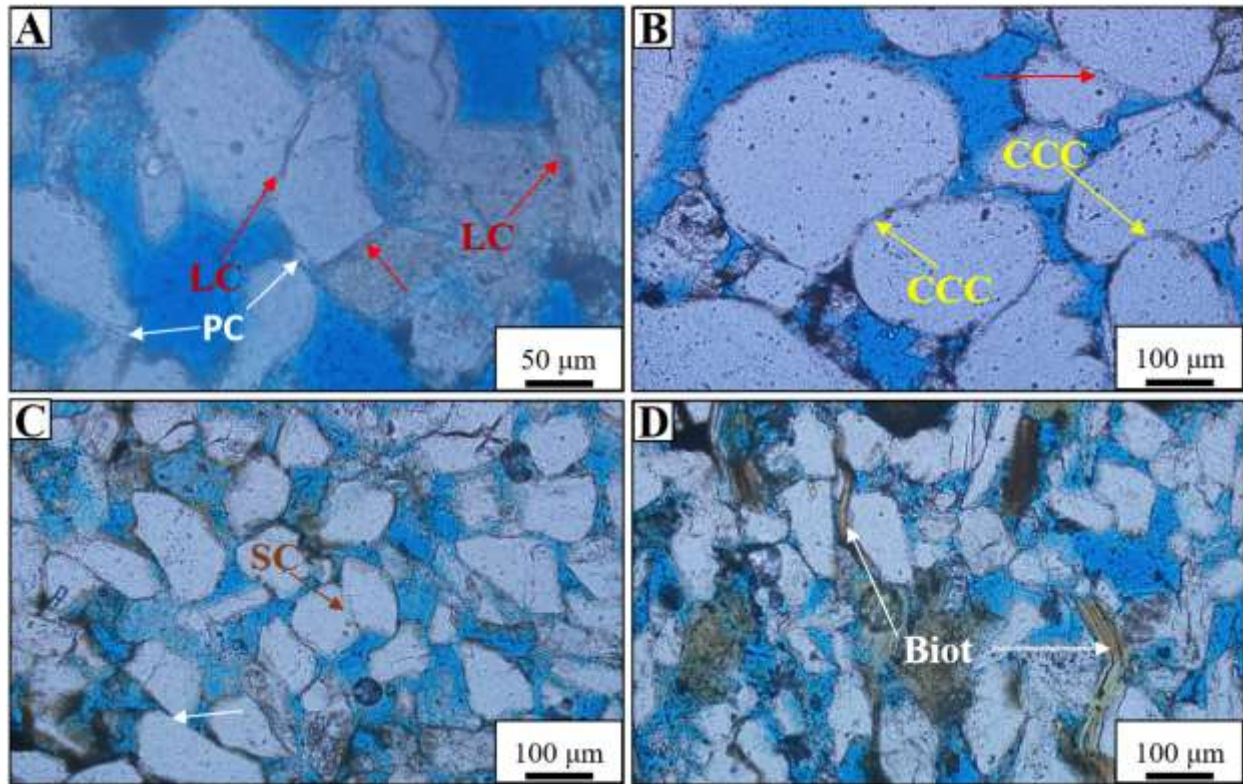


Figure 5.9. Variation in grain contact showing the degree in mechanical and chemical compaction. (A) Thin-section photomicrograph showing point contact and long grain contact (B) Thin-section image showing concavo-convex contact with the red arrow showing long-grain contact. (C) PPL image showing poorly developed sutured contact, noting the onset of pressure dissolution. (D) Thin-section image showing slightly deformed biotite grains suggesting a low impact of mechanical compaction.

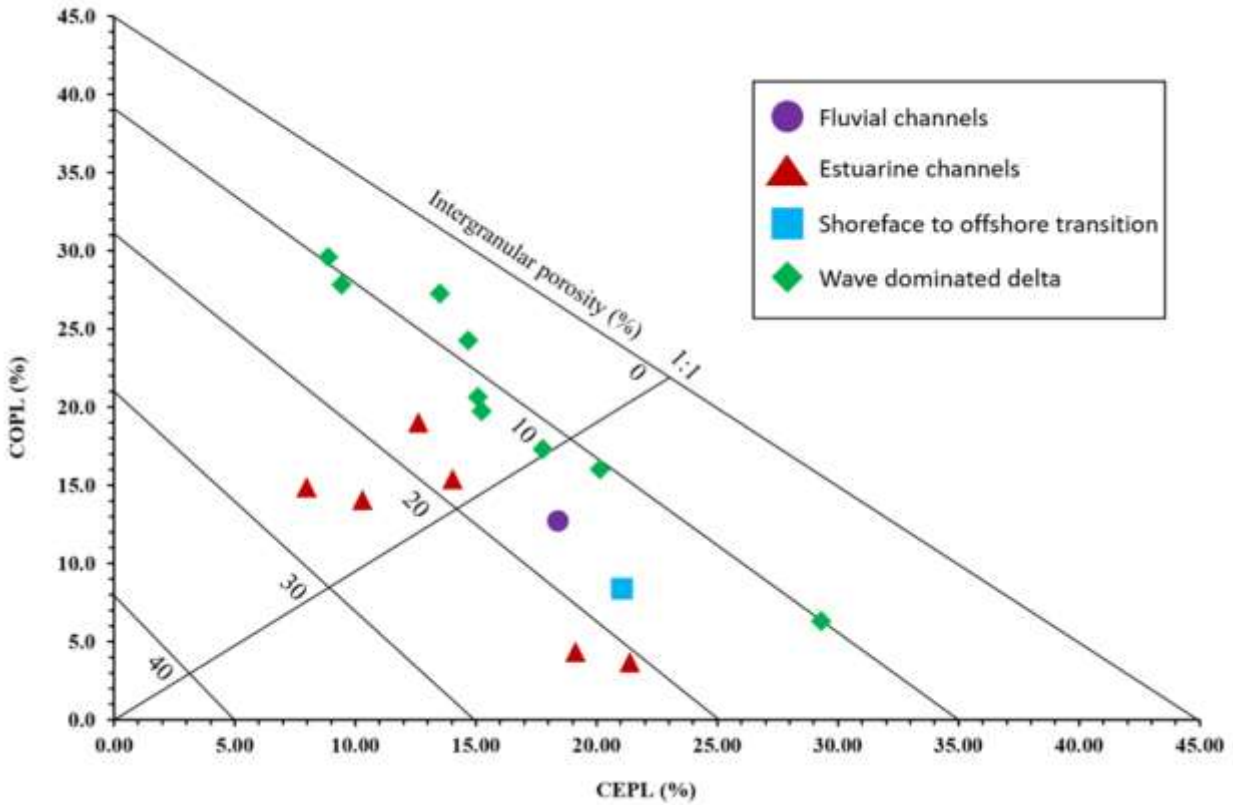


Figure 5.10. Cross-plot porosity reduction due to compaction (COPL) versus porosity loss due to cementation (CEPL) showing that porosity is dominantly reduced by mechanical compaction than cementation.

5.5.3.4. Authigenic composition

The analyzed samples exhibit a diverse range of authigenic minerals, including illite, kaolinite, Fe-dolomite, calcite, ankerite, chlorite, quartz overgrowth, and, to a lesser extent, anhydrite, k-feldspar overgrowth, siderite, and Fe-oxide cements (Table 2).

5.5.3.5. Clay mineral cements

The integration of petrography, clay fraction XRD, SEM, and SEM-EDS analyses (Figs. 11-14) revealed the presence of kaolinite, illite-kaolinite, illite, and chlorite clay minerals in the studied

samples. These minerals exhibit varying amounts, modes of occurrence, and distribution across the depositional facies.

Kaolinite: Present in most of the studied samples (Table 2), Kaolinite ranges from 0 to 11% (avg. 3.8%). Thin section and SEM analysis (Fig. 11) show that kaolinite primarily occurs as pore-filling (Fig. 11A-D) and grain-replacive (Figs. 11E-H). Pore-filling kaolinite displays blocky, vermicular to booklet morphology (Fig. 11A-C). Authigenic kaolinite partially (Fig. 11E) to pervasively (Fig. 11F) dissolved k-feldspar and muscovite (Fig. 11H). Intercrystalline microporosity is observed in both pore-filling and grain-replacive kaolinite (Fig. 11A & H). The presence of kaolinite is further confirmed by its characteristic peaks in the clay fraction XRD analysis (Fig. 12).

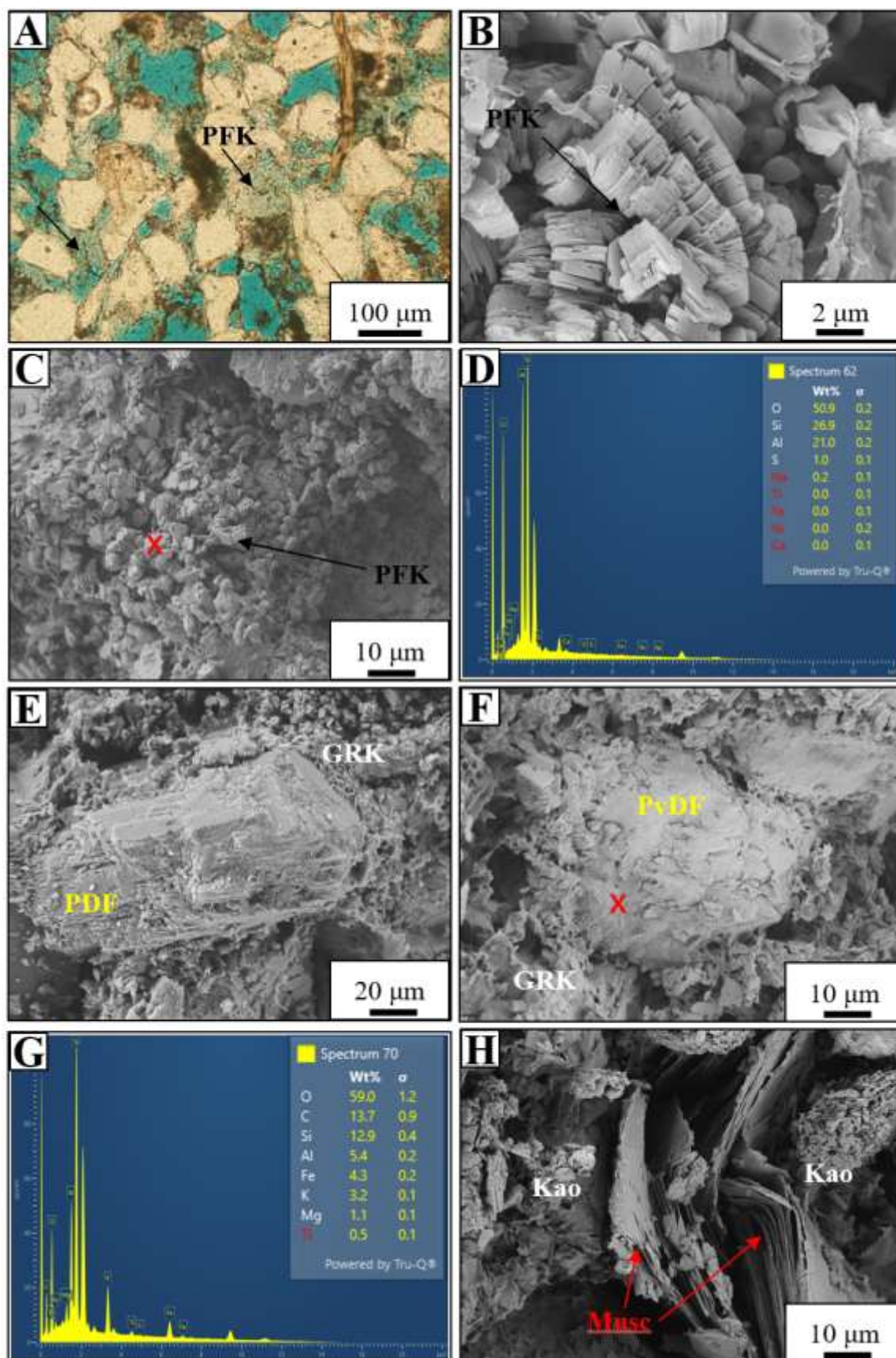


Figure 5.11. Thin-section photomicrographs and SEM-EDS images showing the occurrence and distribution of authigenic kaolinite in the Subbat sandstones. (A) Thin section photomicrograph pore-filling kaolinite. (B) SEM image showing the stacked booklet to vermicular nature of the pore-filling kaolinite. (C) Dense, stacked booklet pore-filling kaolinite. Note the intense micropores within kaolinite (D) EDS spectra for the measured composition of kaolinite in C (red X). (E) SEM image showing grain replacive kaolinite (GRK) adjacent to partially dissolved detrital k-feldspar (PDF). (F) SEM image showing pore-filling, grain replacive kaolinite (GRK) adjacent to pervasively dissolved K-feldspar (PvDF). (G) EDS spectra showing the measured composition of k-feldspar in F (red X). (H) Sem image showing partially dissolved detrital muscovite (Musc) and grain relcive kaolinite (GRK).

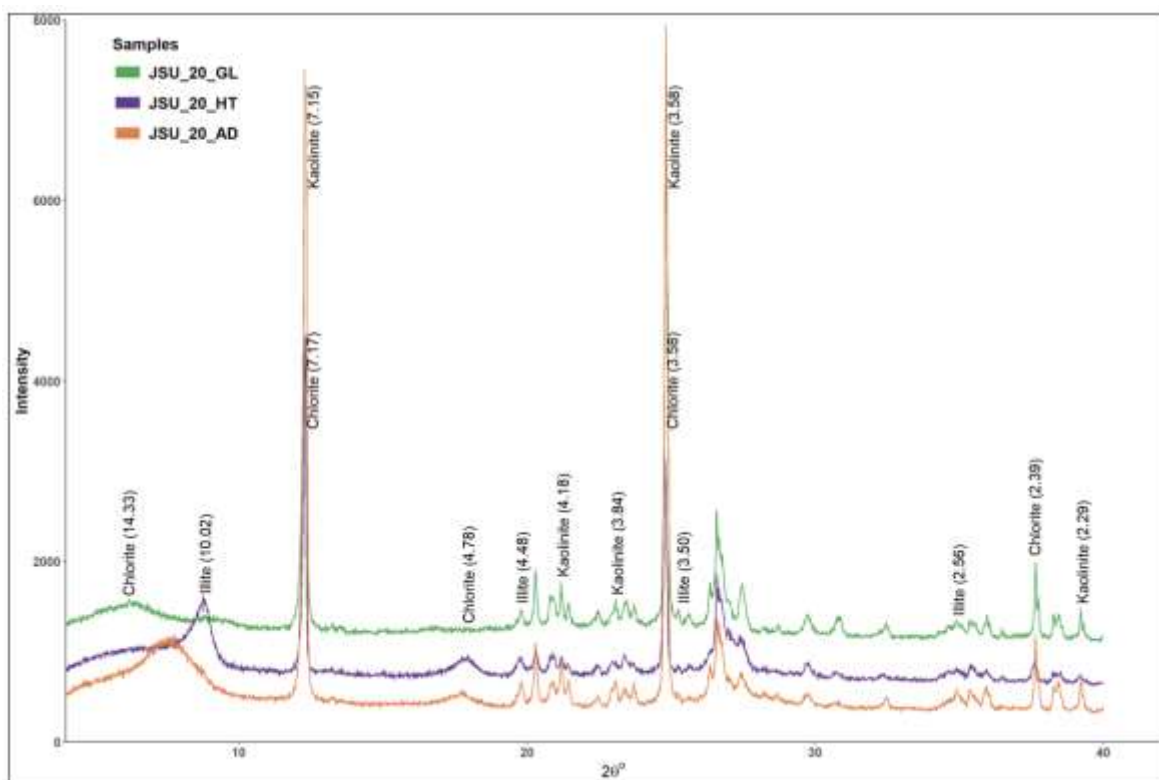


Figure 5.12. XRD patterns of the clay fraction (< 2 μm) showing the dominant clay minerals in the Jauf Formation sandstones.

Illite: Illite is the predominant clay cement in the studied samples and occurs in various forms, including grain coating (Fig. 13A-B), pore-filling (Fig. 13C-D), and less frequently, mixed illite-kaolinite (Fig. 13G-H). Grain-coating illite, (0-11%, avg. 2.2), appears yellowish to dark brown under thin sections, often stained by hematite (Fig. 13A). SEM analysis reveals its radial, honeycomb to platy fibrous and lath-like morphology (Fig. 13), with a uniform coating thickness of 5 to 21 μm . The grain-coating illite is mostly observed in the fluvial and estuarine facies and rarely in other sedimentary facies (Table 2). Pore-filling illite (1-12.5%, avg. 4.4%) reduces pore volumes by occluding intergranular porosity (Fig. 13E). It commonly occurs adjacent to pore-filling kaolinite and, in some cases, encases kaolinite (Figure 13G-H). The clay fraction XRD profile confirms the presence of illite, with prominent peaks identified (Fig. 12)

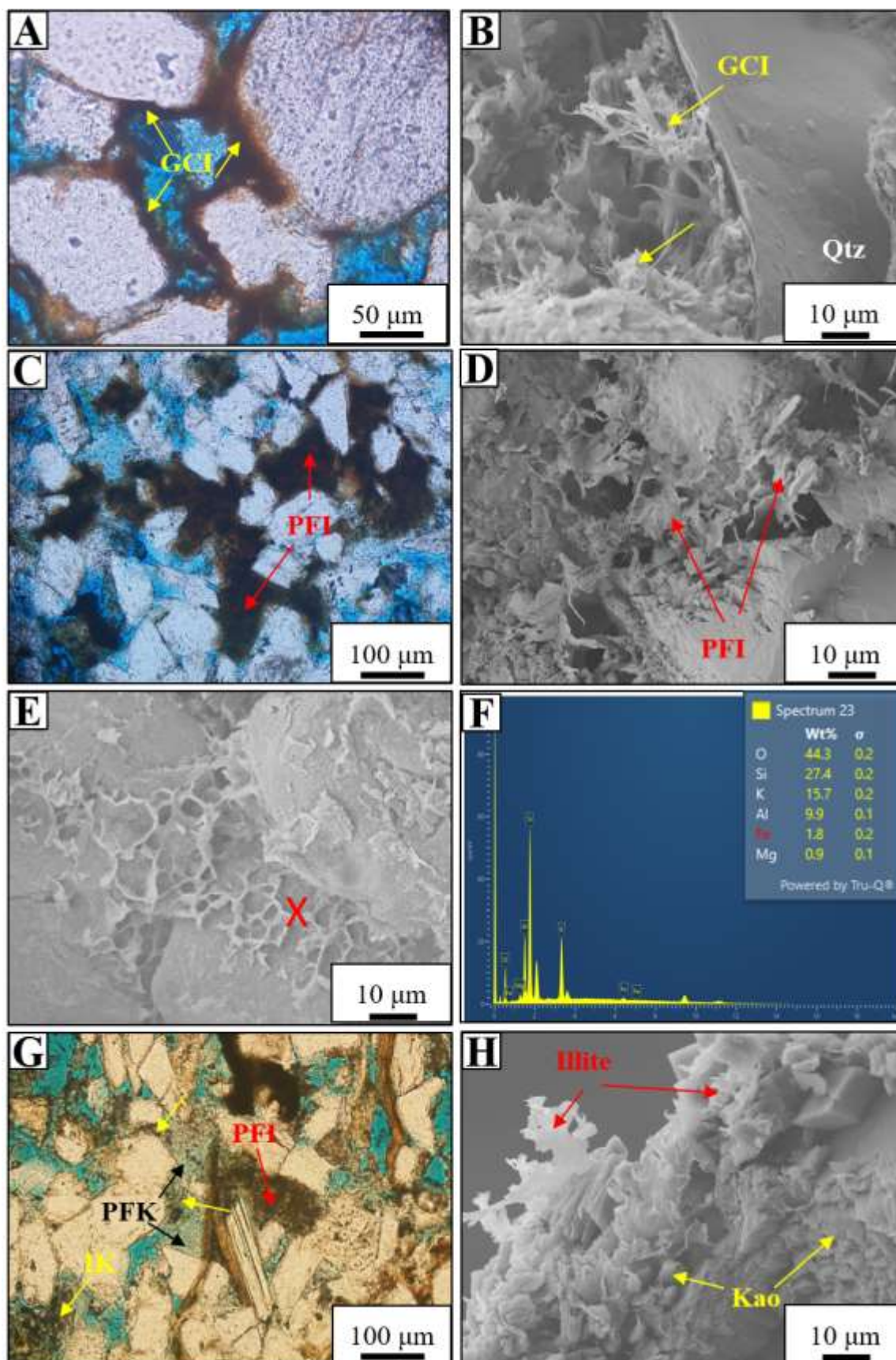


Figure 5.13. Petrographic images displaying the type and mode of occurrence of authigenic illite in the Jauf Formation. Thin section (A), and SEM (B) images showing radial grain-coating illite (CGI) on detrital quartz (Qtz) grains. Thin-section (C) and SEM (D) images showing fibrous to lath-like pore-filling illite (PFI). (E) Honeycomb grain-coating illite on detrital grains. The honeycomb morphology is preserved from the precursor illitized smectite. (F) EDS spectra for the measured composition of illite in E (red X). Thin-section (G) and SEM (H) images showing the occurrence of illite mixed with kaolinite indicating illitization of kaolinite.

Chlorite: Predominantly found in fluvial and estuarine samples (Table 2), chlorite (0-4%, avg. 1%), primarily occurs as a grain-coating cement (Fig. 14A-B). Thin section (Fig. 14A) and SEM (Fig. 14B) analysis reveals that quartz overgrowth occurs where chlorite does not develop (Fig. 14B-C). The grain-coating chlorite exhibits rosette to cabbage head morphology (Fig. 14D-E) and its presence is also confirmed by peaks in the clay fraction profile (Fig. 12).

5.5.3.6. *Quartz cements*

Syntaxial quartz overgrowth cement occurs on the outline of framework quartz grains (Fig. 14A), and is characterized by euhedral crystal morphology (Fig. 14C). The quartz cement content ranges from 0 to 7.2% (avg. 1.2%), and is absent in areas where detrital quartz grains are coated by chlorite (Fig. 14A). Thin section observation further demonstrates that quartz overgrowth terminates at the grain contact (Fig. 14A).

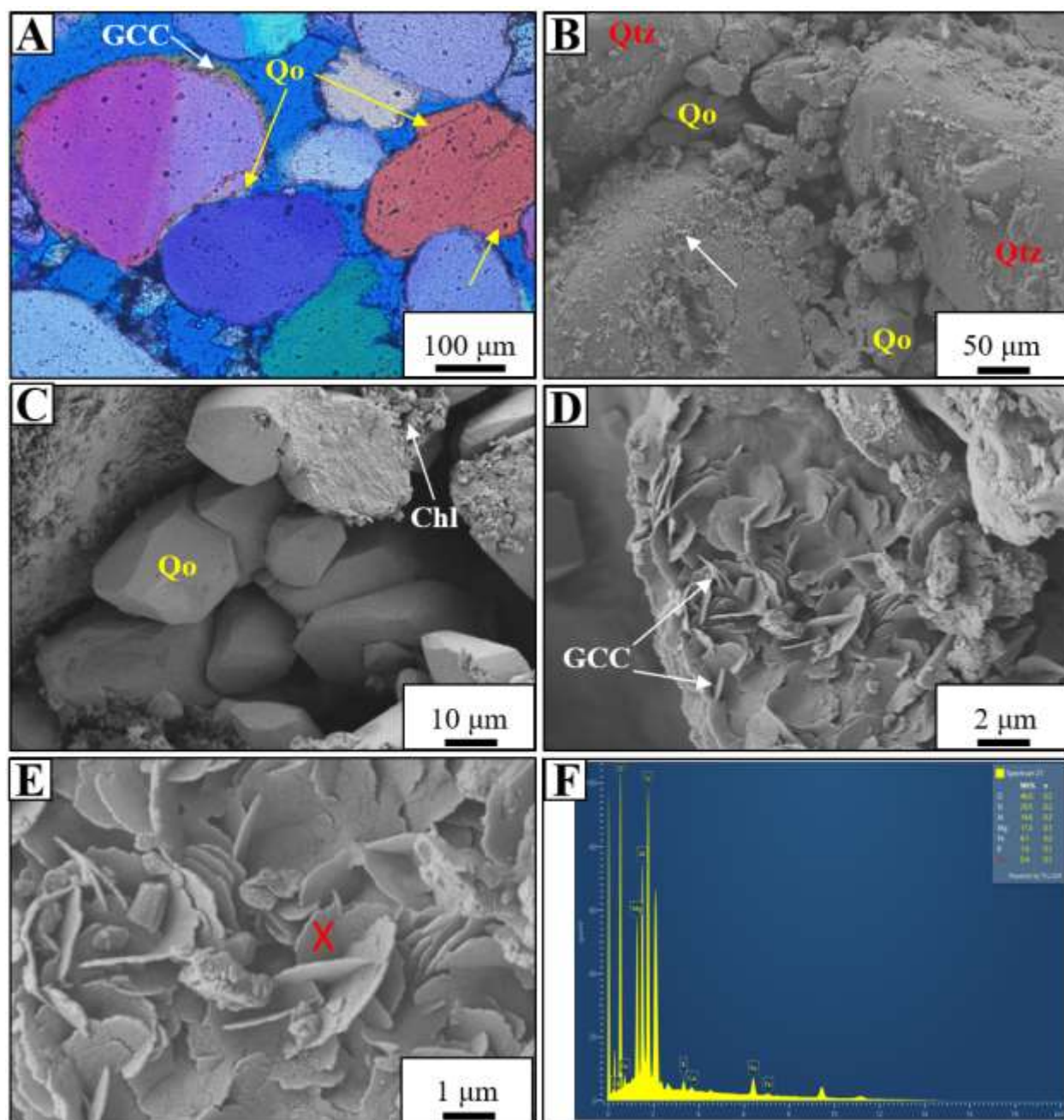


Figure 5.14. Thin-section and SEM-EDS showing authigenic chlorite and quartz cement. Thin-section (A) and SEM (C-D) images showing quartz overgrowth (Qo) growing where grain-coating chlorite (GCC) is absent. (D-E) Sem images showing the rosette morphology of grain-coating chlorite. (F) EDS spectra showing the composition of the measured chlorite in E (red X).

5.5.3.7. *Carbonate cements*

The most common carbonate cements within the studied samples are calcite and Fe-dolomite/ankerite with a rare occurrence of siderite (Fig. 15).

Fe-dolomite/ankerite: Fe-dolomite is the dominant carbonate cement, ranging in volume from 0-15.2% (avg. 2.3%). Thin section (Fig. 15A & B) and SEM (Fig. 15C) analysis reveals that Fe-dolomite occurs as pore-filling, poikilitopic nodules, where detrital framework grains appear to float and rarely come into contact with each other (Figs. 15A & C). Quartz overgrowth is absent where quartz grains are completely embedded in Fe-dolomite cement (Fig. 15A & C). However, partially dissolved poikilitopic Fe-dolomite appears to encase k-feldspar cement (Fig. 15B). Fe-dolomite cements engulf patchy to uniform calcite (Fig. 15A & E) and are engulfed by Fe-oxide (Fig. 15B) and ankerite (Fig. 15F). EDS analyses confirm the presence of Fe within the Fe-dolomite cements (Fig. 15D).

Calcite: Calcite cement occurs in trace amounts, except in three samples where it exceeds 10% (Table 2). It appears patchy to uniform (Fig. 15A & E) and is mostly engulfed by Fe-dolomite (Fig. 15A). SEM analysis shows calcite as subhedral to euhedral pore-filling crystals, which are largely replaced by pore-filling Fe-dolomite (Fig. 15E).

Ankerite: Ankerite occurs as a "rusty" Fe-oxide-stained pore-filling cement (Fig. 15F), forming a rhombohedral overgrowth on authigenic Fe-dolomite (Fig. 15G). It is absent in most samples, ranging from 0-9.3% (avg. 1.6) where present, and encases Fe-dolomite (Fig. 15F). EDS analysis reveals a high Fe content and the presence of Mn, which may have substituted Mg (Fig. 15H).

Siderite: Siderite occurs in trace amounts, primarily surrounding ankerite, which replaces pore-filling Fe-dolomite (Fig. 15F).

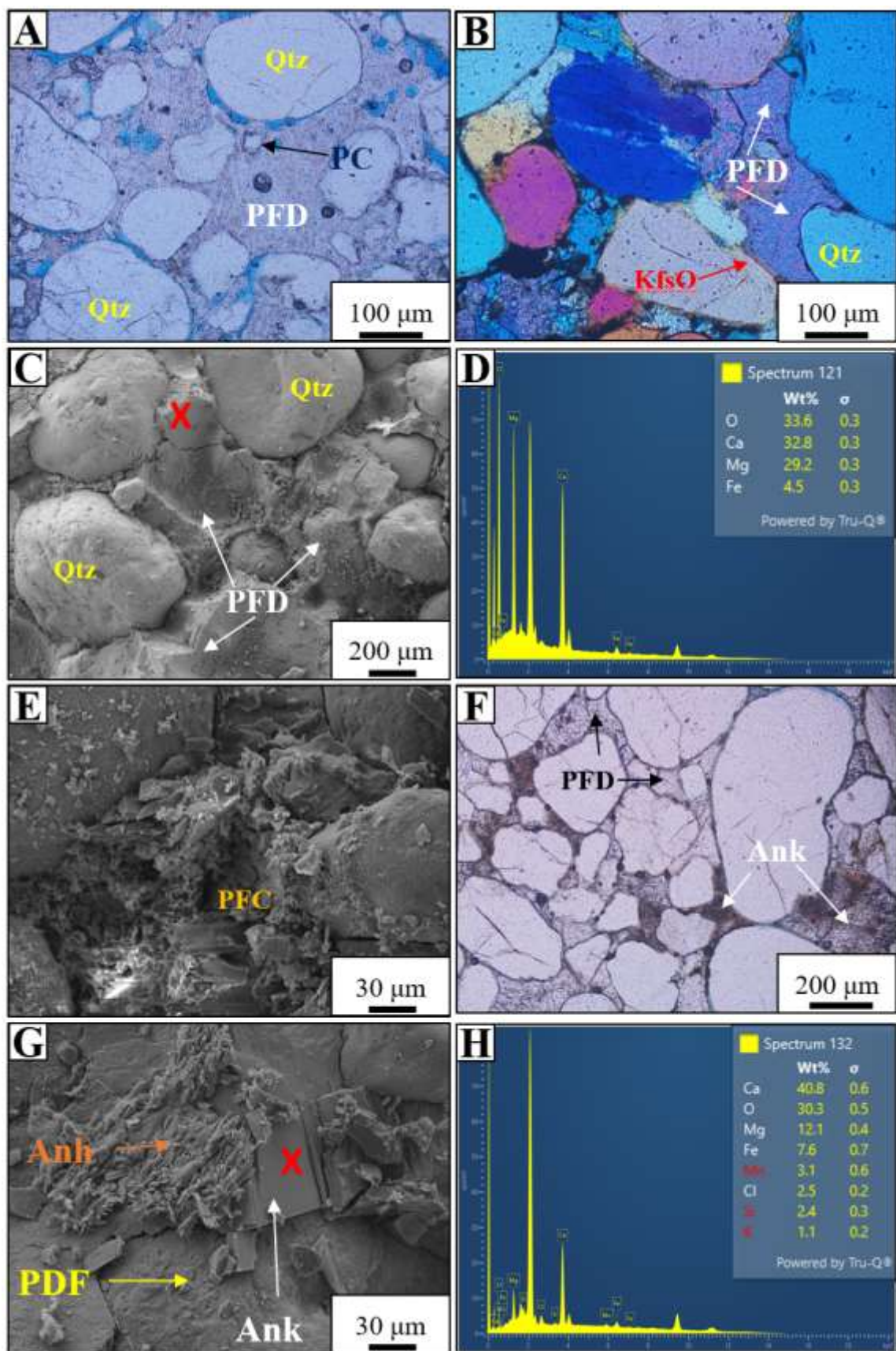


Figure 5.15. Petrographic images displaying authigenic carbonate cements. (A) Thin-in section photomicrograph showing nodular poikilitopic pore-filling Fe-dolomite. Note the floating detrital grains (PDF) that engulf and replace patchy remnants of pore-filling calcite (PC). (B) XPL image pore-filling Fe-dolomite (PDF) encasing k-feldspar overgrowth. (C) SEM image showing the blocky nature of pore-filling Fe-dolomite (PDF). (D) EDS spectra showing the composition of the Fe-dolomite. Note the Mg/Fe ration. (E) SEM image showing the remnants of subhedral to euhedral crystals of pore-filling calcite in PFD. (F) thin-section image showing pore-filling ankerite (Ank) replacing Fe-dolomite pore-filling (PDF). (G) SEM image showing euhedral ankerite (Ank) over (PFD). The ankerite is encased by anhydrite (Anh). (H) EDS spectra showing the measured composition of ankerite. Note the presence of Mn and the Mg/Fe ratio as compared to D.

5.5.3.8. *Minor authigenic cements*

Anhydrite, Fe-oxides (goethite and hematite), and K-feldspar overgrowth constitute minor authigenic cement phases within the studied samples. Authigenic anhydrite is present in trace amounts, except in two samples where it exceeds 10% (Table 2). It appears as an aggregate of nodular and elongated, poikilitopic, pore-filling cement in thin section (Fig. 16A) and SEM (Fig. 16B-C). Anhydrite predominantly forms euhedral crystals on authigenic Fe-dolomite (Fig. 16B) and ankerite (Fig. 15G). Fe-oxide cements, comprising goethite and hematite, range from trace amounts in most samples to 3% in a few samples (avg. 0.6%). These cements exhibit a dark brown to black color and primarily occur as Fe-dolomite-replacive (Fig. 16E) and pore-filling cements (Fig. 16F). K-feldspar overgrowth is a rare cement phase, constituting less than 1% of the rock volume (avg. 0.1%). It displays a rhombic, euhedral morphology, often encased by Fe-dolomite (Fig. 15A) and illite-kaolinite cements (Fig. 16G)

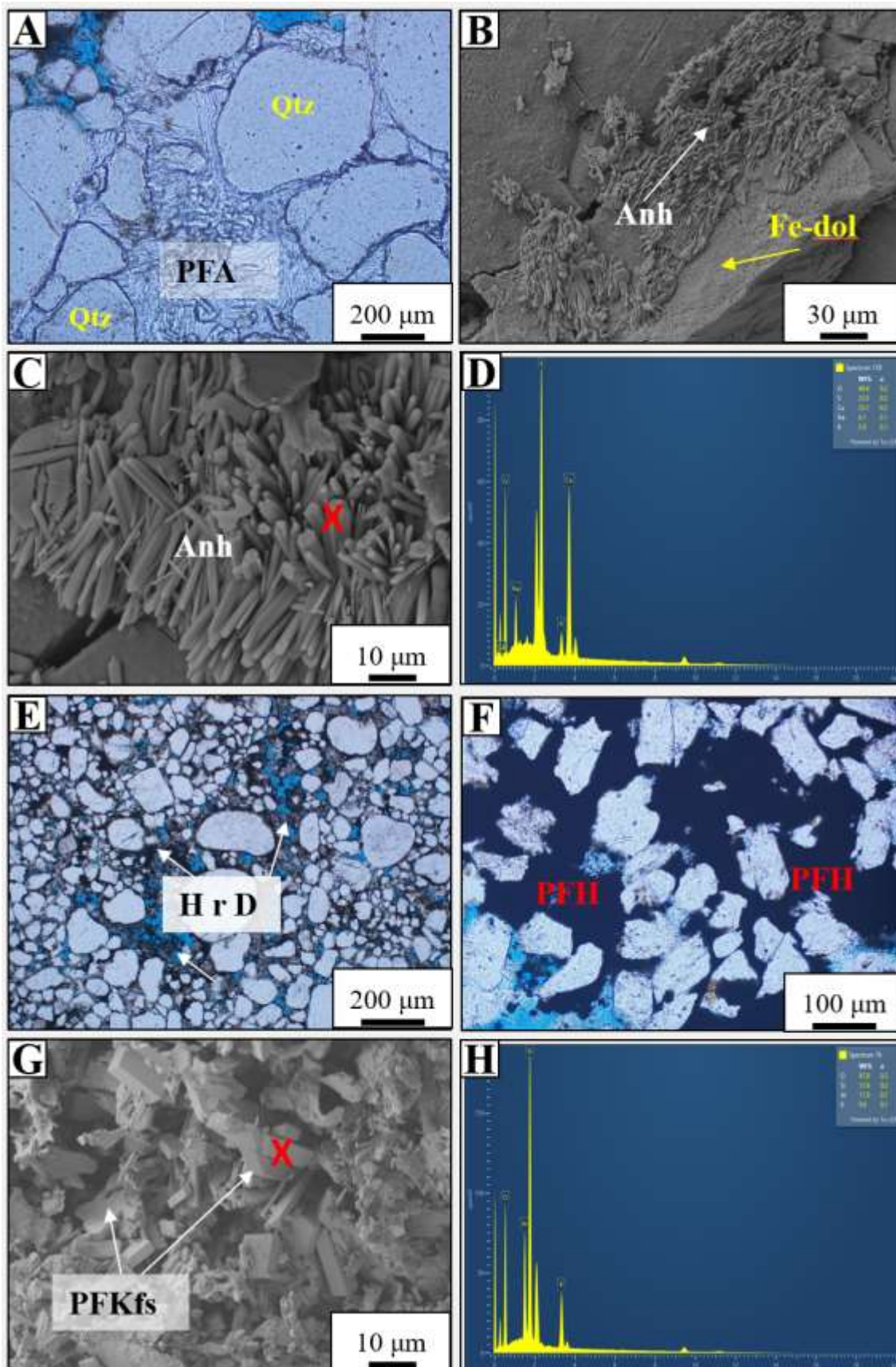


Figure 5.16. Thin-section and SEM-EDS images showing minor authigenic cements within the studied sandstones. (A) Thin-section image showing nodular, poikilitopic, pore-filling anhydrite (PFA). (B-C) SEM images showing the occurrence of euhedral needle to prismatic crystals of anhydrite (Anh) occurring above Fe-dolomite (Fe-dol). (D) EDS spectra showing the measured composition of anhydrite in C (red X). (E) thin-section image showing pore-filling hematite replacing dissolved Fe-dolomite. (F) Thin-section photomicrograph showing pore-filling hematite filling secondary porosity created by Fe-dolomite dissolution. (G) SEM image showing pore-filling k-feldspar overgrowth (PFKfs) encased by kaolinite and illite. (H) EDS spectra showing the measured composition of k-feldspar overgrowth in G (red X).

5.5.4. Grain dissolution and secondary porosity

Petrographic examination of the studied samples revealed the development of secondary porosity within the sandstones through the dissolution of detrital feldspar grains (Fig. 17A-C) and, less commonly, calcite and Fe-dolomite cements (Fig. 17D). Moldic porosity resulting from the complete dissolution of feldspar grains was also identified (Fig. 17C). While dissolution processes enhance overall optical porosity, authigenic minerals, such as kaolinite and ankerite, often replace the dissolved material, limiting the net porosity gain. Dissolution porosity ranges from 0.5 to 4.3% (avg. 1.9%) and is present in most analyzed samples (Table 2).

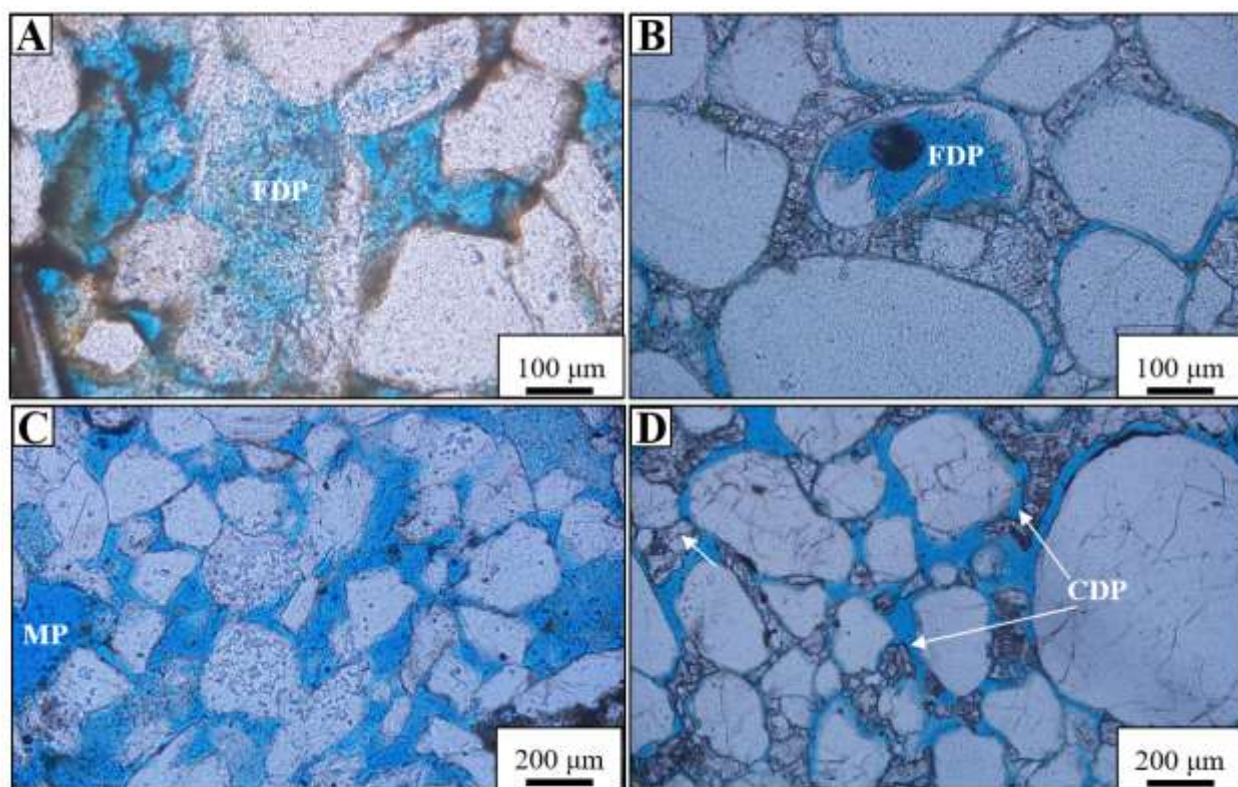


Figure 5.17. Thin-section photomicrographs showing secondary porosity created by the dissolution of detrital feldspar grains and carbonate cements. (A-B) PPL image partial to pervasive dissolution of k-feldspar creating feldspar dissolution porosity (FDP). (C) Moldic porosity (MP) created by the complete dissolution of k-feldspar grain. (D) Carbonate dissolution porosity (CDP). Note the remnants of the carbonate cements from the dissolved poikilitopic crystal.

5.5.5. Petrophysical analysis

Petrographic analysis identified two porosity types within the Subbat sandstones: primary intergranular porosity and secondary intragranular porosity associated with feldspar and Fe-dolomite dissolution (Fig. 17). Primary intergranular porosity ranges from 1.0 to 25.5% (avg. 11.5%), while dissolution porosity varies from 0 to 4.3% (avg. 1.9%). Optical porosity values exhibit variation across depositional facies. The highly cemented shoreface-to-offshore transition

facies display the lowest porosity values (1-2%, avg. 1.5%), whereas wave-dominated delta facies exhibit moderate porosity values (5.3-11.2%, avg. 8.6%). Distinctively, the clay-coated fluvial and estuarine channels facies possess the highest porosity values (15.9-25.5%, avg. 20.4%). Although optical porosity is partially lower than measured helium porosity due to the influence of microporosity, both measurements exhibit a positive trend, with a correlation coefficient (R^2) of 0.9 (Fig. 18A).

Permeability values range from 0.3 to 1261.2 mD (avg. 262.8 mD) and increase with increasing porosity (Fig. 18B). Similar to porosity distribution, fluvial and estuarine facies display the highest permeability values (avg. 720 mD), while shoreface-to-offshore and wave-dominated delta facies) exhibit the lowest (avg. 0.7mD) and intermediate permeability (avg. 42.8mD values, respectively. A positive correlation between spot permeability and measured air permeability is observed ($R^2 = 0.9$) (Fig. 18C).

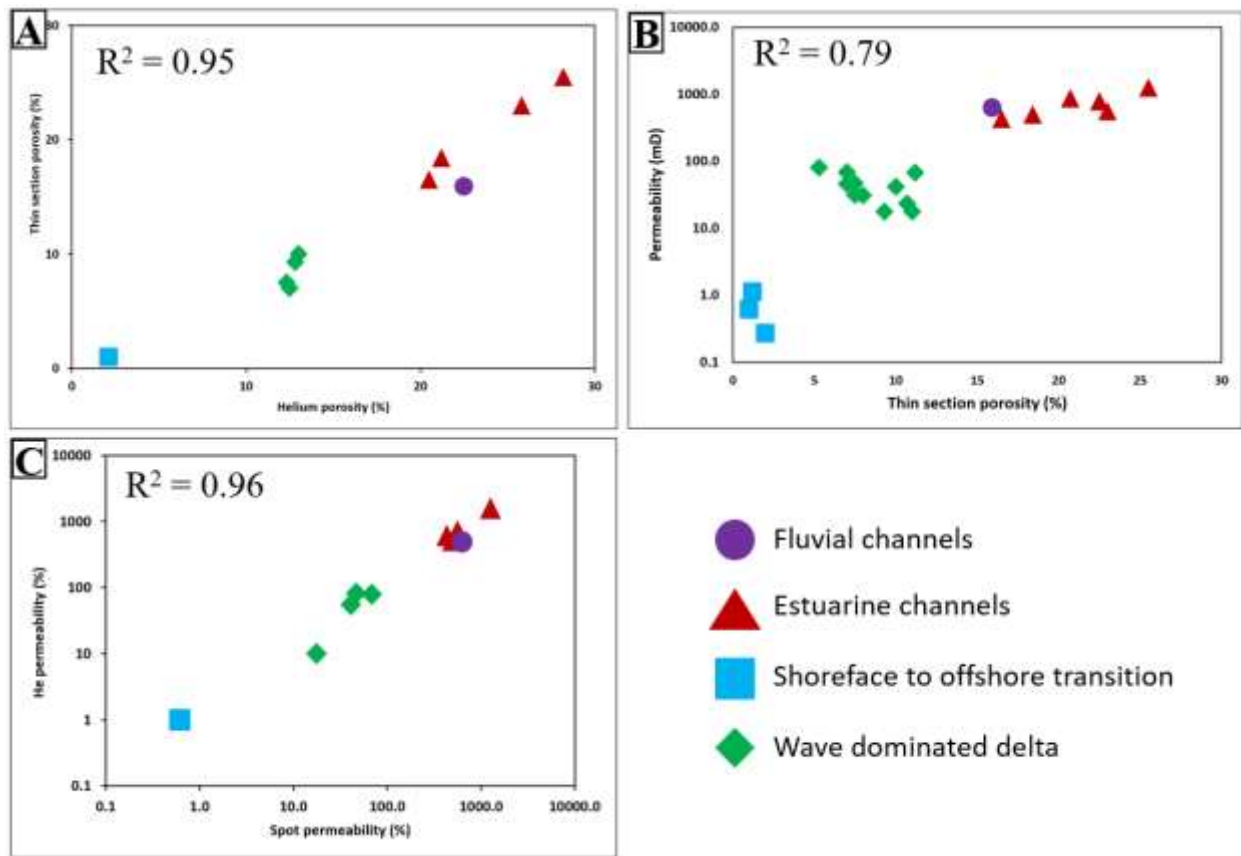


Figure 5.18. (A) Cross plot of thin-section porosity with Helium porosity of selected samples showing excellent correlation. (B) Cross-plot of Thin-section porosity and permeability, permeability increases with increasing porosity. (C) cross-plot of He permeability with spot permeability showing good correlation.

5.6. Discussion

5.6.1. Paragenetic Analyses

Petrographic observations documented in this study, provided insights into the spatial and textural characteristics of the framework grains and authigenic components in the studied sandstones of the Subbat Member, Jauf Formation. These observations, along with the sequential relationships among the various components, aided the establishment of a diagenetic sequence of events that influenced the reservoir quality of the Jauf sandstones (Fig. 19). While the overall diagenetic sequence aligns with previous subsurface studies of the Jauf Formation (Saner et al., 2006; Al Ramadan et al., 2013b), local differences were observed. The identified diagenetic minerals and their petrographic relationships indicate that the sandstones experienced both shallow burial (eodiagenesis: < 2 km and < 70°C) and deep burial (mesodiagenesis: >2 km and > 70°C) diagenetic alterations (Morad et al., 2010).

Paragenetic event	Early Diagenesis (Eodiagenesis < 70 °C)	Burial diagenesis (Mesodiagenesis > 70 °C)	Effects on porosity	
			+ve	-ve
Clay infiltration				
Calcite				
Grain/carbonate dissolution				
Kaolinite				
K-feldspar cement				
Fe-dolomite/ankerite				
Siderite				
Fe-oxides				
Mechanical compaction				
Illite				
Chlorite				
Pressure dissolution				
Quartz overgrowth				
Anhydrite				

Figure 5.19. Simplified Paragenetic analyses showing the sequence of diagenetic events in the Jauf Formation and their impacts on porosity

5.6.2. Early diagenesis

The nodular, poikilotopic calcite cement associated with loose and floating detrital grains—lacking syntaxial overgrowth—are interpreted as an early diagenetic phase that precipitates before significant mechanical compaction. This interpretation aligns with previous studies of the subsurface Jauf Formation by Saner et al. (2006). The calcite cement likely precipitated from marine or mixed marine-meteoric waters (Rahman and Worden, 2016; Taylor et al., 2022). However, within the sandstones, the calcite cement has largely dissolved and been replaced by Fe-dolomite/ankerite cement (Fig. 15A). Petrographic evidence suggests that Fe-dolomite/ankerite formed during shallow burial diagenesis. The nodular, poikilotopic pore-filling Fe-

dolomite/ankerite are thought to have replaced calcite during eodiagenesis, prior to significant mechanical compaction. This is evidenced by the presence of patchy remnants of calcite within the pore-filling Fe-dolomite and the observation of floating detrital grains without quartz overgrowths (Fig. 15A-C). The occurrence of ankerite within and above pore-filling Fe-dolomite (Fig. 15G) suggests that it formed contemporaneously with Fe-dolomite.

Authigenic kaolinite (grain-replacive and pore-filling) is interpreted to have developed during shallow burial due to the influx of meteoric water, which dissolved chemically unstable feldspar and mica grains (Fig. 11E-H). The encasement of syntaxial K-feldspar cements by nodular poikilotopic Fe-dolomite (Fig. 15A) suggests that K-feldspar precipitated during early burial diagenesis and predate the formation of Fe-dolomite. Fe-oxides, which occur as pore-filling and replace poikilotopic Fe-dolomite (Fig. 16E), are interpreted to have formed during early burial diagenesis, postdating Fe-dolomite.

Mechanical compaction is interpreted to have been initiated during shallow burial and continued into deep burial diagenesis.

5.6.3. Burial diagenesis

Petrographic evidence indicates that mesodiagenetic processes in the Jauf sandstones include the authigenic formation of illite, chlorite, quartz cements, and anhydrite. Observations from SEM-EDS and thin-section analyses reveal various forms and occurrences of illite (Fig. 13). The preserved honeycomb structure of illite (Fig. 13E) is interpreted as having developed from the illitization of infiltrated smectite during mesodiagenesis (McCarty et al., 2009; Worden & Morad, 2009; Bello et al., 2021). Although precursor smectite has not been observed, it is inferred to have been completely illitized, consistent with previous studies by Al-Ramadan et al. (2013b). Furthermore, illitization of kaolinite is suggested where illite has been identified replacing

kaolinite (Fig. 13G-H). The dissolution of kaolinite and its subsequent illitization have been widely reported in sandstone reservoirs (Lanson et al., 2002; Mantovani et al., 2010; Taylor et al., 2010; Bello et al., 2024), with the necessary K^+ likely sourced from the dissolution of K-feldspar and/or mica grains (Franks & Zwingmann, 2010; Birkle, 2019). The development of illite occurred contemporaneously with the authigenic formation of chlorite and preceded quartz overgrowth.

Quartz cementation, characterized by syntaxial overgrowth, is a product of deep burial conditions (depth > 2 km, temperature > 70°C) (McBride, 1989; Critelli and Nilsen, 1996; Lander et al., 2008 and many others). Petrographic observations show that quartz overgrowths develop on quartz grains where illite and chlorite coatings are absent (Figs. 13A & 14A), indicating that quartz overgrowths postdate clay coatings and form during deep burial. Pressure dissolution, evidenced by concavo-convex and sutured grain contacts, may have contributed to the silica needed for quartz cementation (Taylor et al., 2010). Silica may also have been derived from feldspar and mica dissolution (Milliken and Laubach, 2000). Following quartz overgrowth, the authigenic precipitation of anhydrite occurs, encasing quartz cements and thus postdating the quartz overgrowths

5.6.4. Depositional controls on reservoir quality

Depositional processes exert a significant influence on sandstone reservoir quality by controlling the distribution of facies, grain size, and matrix content (Bloch and McGowen, 1994; Lima and De Ros, 2002; Bello et al., 2021). This study reveals that very fine to fine-grained sandstones with minimal detrital matrix (avg. 0.2%) exhibit the highest reservoir quality (Fig. 20A-D). Conversely, very fine-grained sandstones with high detrital matrix (avg. 19.1%) demonstrate the poorest reservoir properties. Additionally, medium to coarse-grained sandstones with intermediate detrital matrix show moderate reservoir quality (Fig. 20A-D). Interestingly, the impact of grain size on

reservoir quality depends on matrix content and subsequent authigenic cements. Traditionally, very fine to fine-grained sandstones are associated with low reservoir quality. However, a positive correlation exists between detrital matrix content with both porosity (Fig. 20C) and permeability (Fig. 20D), suggesting that pore-filling detrital matrix influences reservoir quality in the Jauf Formation.

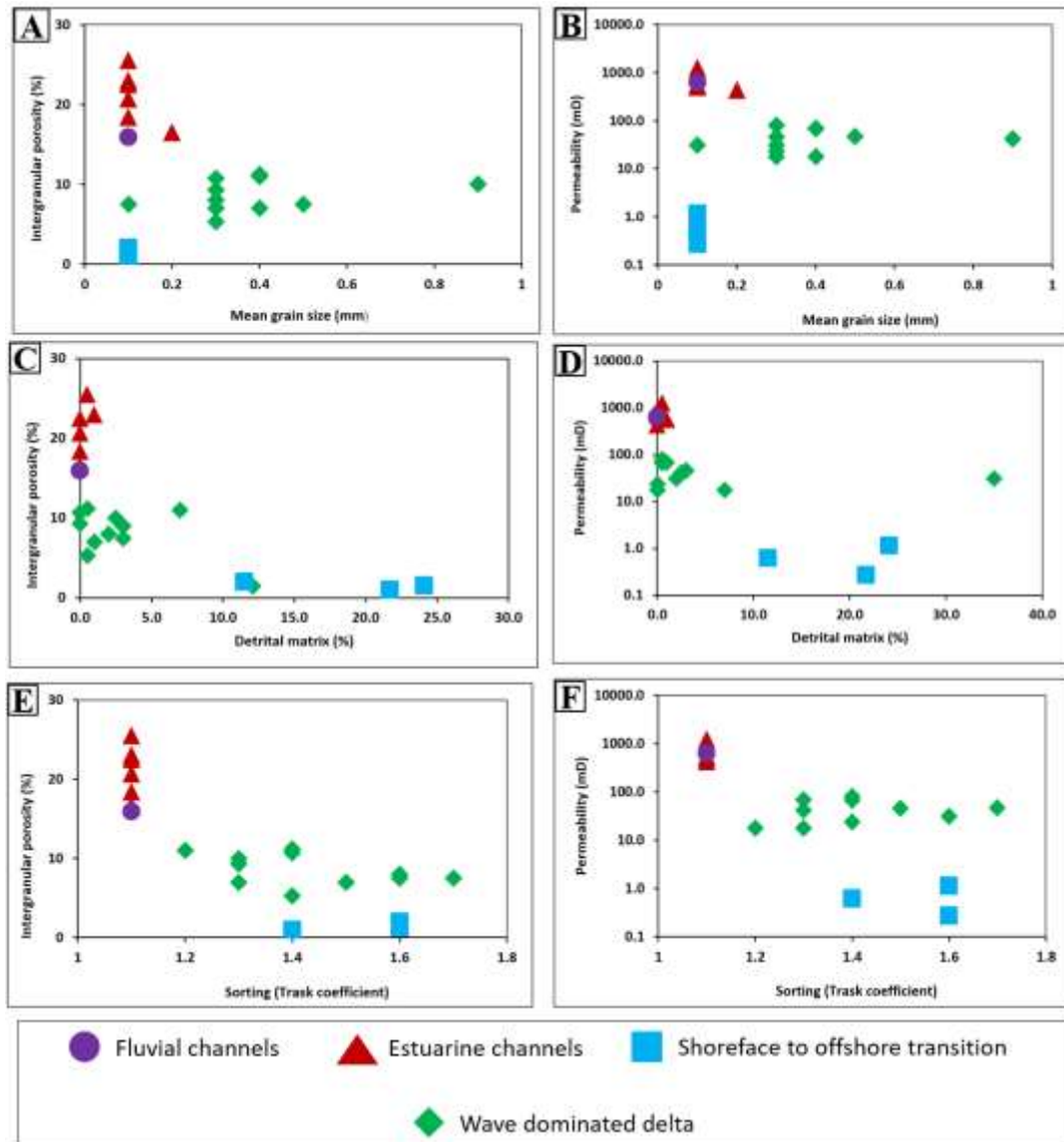


Figure 5.20. Cross-plots of depositional processes with porosity and permeability showing their impact on reservoir quality. Plot of mean grain size with porosity (A) and permeability (B) showing an irregular relationship. Reservoir quality increases with increasing grain size except in fluvial and estuarine facies where porosity and permeability increase are independent of grain size. Cross plots of detrital matrix with porosity (C) and permeability (D) show that porosity and permeability increase with decreasing detrital matrix content in the sandstones. (E-F) Plot of sorting versus porosity (E) and permeability (F) show that sorting reservoir quality increases with better sorting.

Sandstones with low detrital matrix consistently exhibit higher porosity and permeability, regardless of grain size, compared to sandstones with high detrital matrix. The high amount of detrital matrix within the shoreface to offshore transition facies is attributed to sediments reworking by wave action and bioturbation (Morad et al., 2010). Consequently, fluvial to estuarine facies, characterized by lower matrix content, exhibit the highest reservoir quality compared to wave-dominated delta and shoreface-to-offshore transition facies. The higher matrix content within the shoreface-to-offshore transition facies likely reduces porosity and permeability by promoting mechanical compaction, obstructing intergranular porosity, and increasing flow tortuosity (Bello et al., 2023a).

Sandstone reservoir quality is significantly influenced by grain sorting (Bloch and McGowen, 1994). Cross-plots of sorting with porosity (Fig. 20E), and permeability (Fig. 20F) demonstrate that moderately to well-sorted sandstones exhibit the best reservoir properties compared to poorly sorted counterparts. Overall, well-sorted fluvial and estuarine facies, with minimal detrital matrix, possess the highest reservoir quality in the Jauf Formation. In contrast, wave-dominated delta sandstones exhibit relatively lower reservoir quality due to poor sorting and slightly higher clay matrix (Fig. 20). The shoreface-to-offshore transition sandstones have the lowest reservoir quality, primarily attributed to finer grain size, poor sorting, and elevated matrix content. Figure 21 illustrates the negative correlation between detrital matrix content and reservoir quality, emphasizing the detrimental impact of the matrix on porosity and permeability.

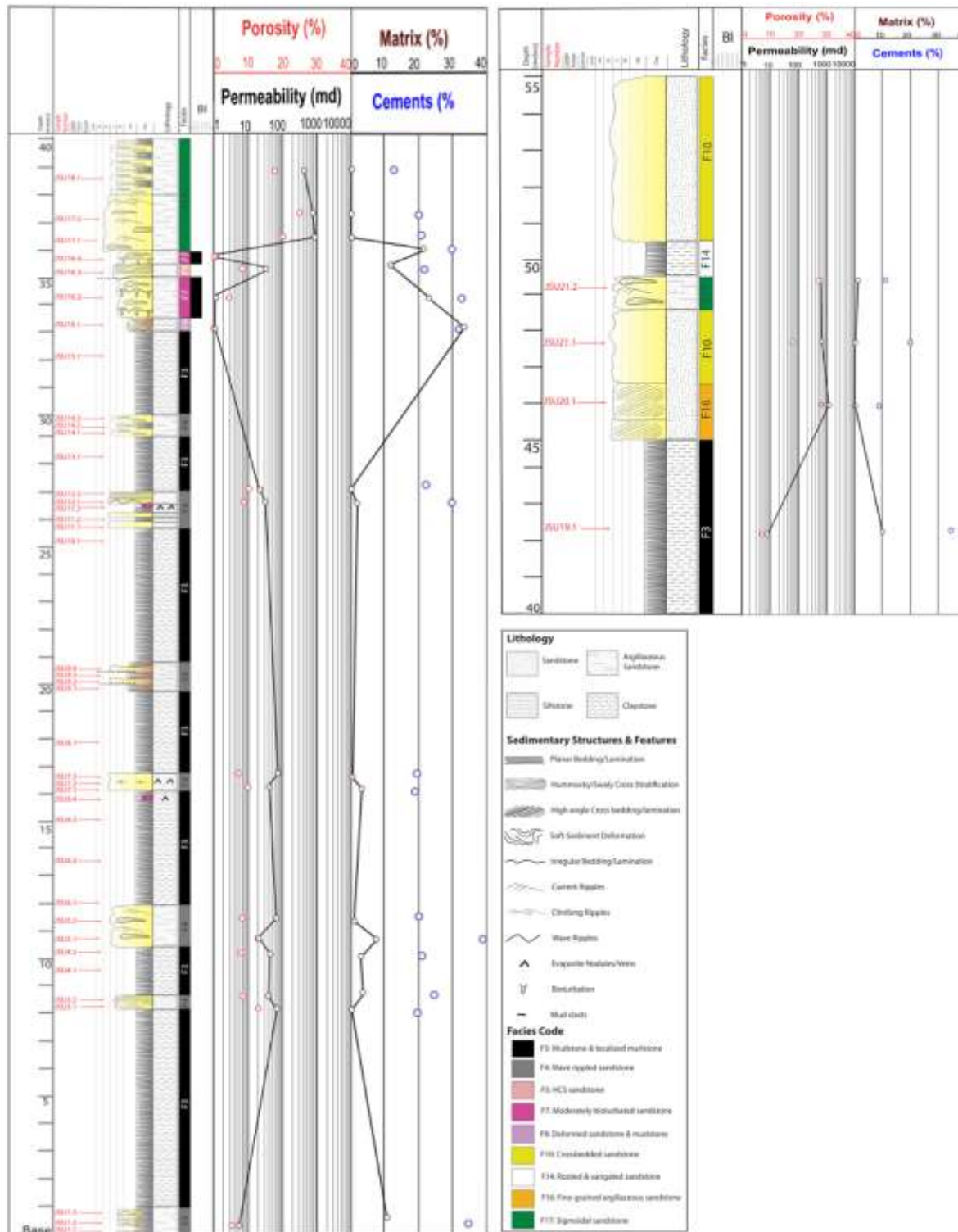


Figure 5.21. Interpreted stratigraphic chart of the studied section showing the relationship between porosity and permeability, detrital matrix, and pore-filling authigenic cements

5.6.5. Diagenetic controls on reservoir quality

Diagenetic processes play a crucial role in influencing the reservoir quality of sandstones (Al-Ramadan et al., 2005; Carraciolo et al., 2014; Ulmer-Scholle et al., 2015; Bello et al., 2024). In the Jauf sandstones, reservoir quality is significantly affected by mechanical and chemical compaction, various forms and degrees of cementation, and, to a lesser extent, dissolution. Petrographic analysis reveals that these sandstones have undergone both shallow burial (eodiagenesis) and deep burial (mesodiagenesis) diagenesis, as evidenced by the presence of point, long, concavo-convex, and occasionally sutured grain contacts. Additionally, ductile framework mica grains (muscovite and biotite) are observed compacting around rigid detrital grains (Fig. 9D). Initial mechanical compaction leads to the formation of point and long grain contacts (Fig. 9A), while pressure dissolution is indicated by concavo-convex and, less commonly, sutured contacts (Fig. 9B-C).

A plot comparing porosity loss due to compaction (COPL) with porosity loss due to cementation (CEPL) demonstrates that porosity is more significantly reduced by compaction than by cementation (Fig. 10). The average porosity loss due to compaction is higher in the shoreface-to-offshore transition (21.5%) and wave-dominated delta (20.98%) facies compared to the tidal estuarine channels (12%). Therefore, compaction was more pronounced in sandstones with higher detrital matrix content. Overall, the impact of compaction on the porosity of the Jauf sandstones is less pronounced compared to other sandstones that have undergone deep burial. This is primarily attributed to the low proportion of ductile grains (avg. 2%) and the early precipitation of poikilotopic carbonate cements which prevent significant porosity reduction due to compaction. Dissolution of feldspar and carbonate grains created secondary porosity, although its contribution

to overall reservoir quality is limited due to its relatively small volume (0.5-4.3%, average 1.9%; Table 2).

The evolution of reservoir quality in Jauf sandstones has been significantly impacted by cementation, in addition to compaction (Figs. 22 & 23). Pore-filling carbonate cements, including calcite, Fe-dolomite, ankerite, and siderite, have substantially reduced porosity (Fig. 22A) and permeability (Fig. 22B) in the studied sandstones. The wave-dominated delta facies, which have experienced extensive carbonate cementation up to 20.3% (avg. 6.9%), exhibit lower porosity (avg. 8.2%; Fig. 22A) and permeability (avg. 42 mD; Fig. 22B) compared to the less carbonate-cemented tidal estuarine channel sandstones (average carbonate cement: 2.1%, average porosity: 20.4%; average permeability: 720 mD). In contrast, shoreface-to-offshore transition sandstones, despite having low carbonate cementation (avg. 2.3%), exhibit very low porosity (avg. 1.5%) and permeability (avg. 0.7 mD). This is attributed to the higher amount of pore-filling detrital matrix (up to 35%) and the increased impact of mechanical compaction on these sandstones. Similarly, pore-filling authigenic clay cements (kaolinite and illite), have shown a relatively lower impact on reservoir quality (Fig. 22C-D). Shoreface-to-offshore transition sandstones, with the highest pore-filling clay cement content (avg. 22.1%), have the lowest reservoir quality compared to the wave-dominated delta and estuarine channel sandstones, which have lesser amounts of pore-filling clay cements averaging 9.8% and 12.2%, respectively. Additionally, authigenic clay cements appear highly microporous under thin-section and SEM observations. This microporosity within authigenic clay minerals increases surface area and elevates capillary pressure in sandstone reservoirs (Jiang et al., 2011), leading to the trapping of irreducible water saturation (Darling & Sneider et al., 1993) and potentially underestimating electrical resistivity (Salisu et al., 2023).

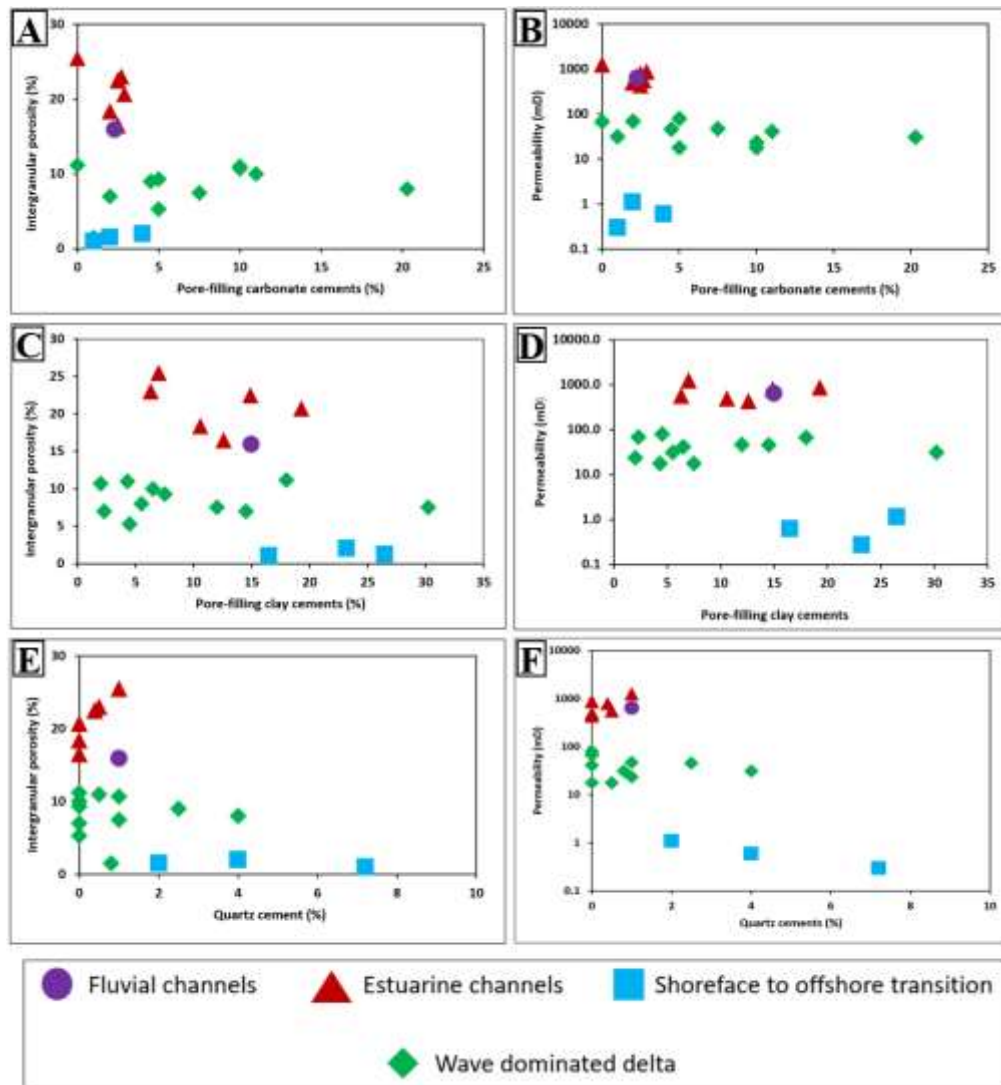


Figure 5.22. Impacts of authigenic cements on reservoir properties of the Jauf sandstones. Cross-plot of pore-filling carbonate cements with porosity (A) and permeability bimodal relationship depositional facies. Reservoir properties increase with decreasing pore-filling carbonate cements except in the shoreface-to-offshore transition where reservoir properties are independent of pore-filling carbonate cements. Plots of pore-filling clay cements versus porosity (C) and permeability (D) showing general increase in porosity and permeability with decreasing pore-filling clay cements. Cross-plots of quartz cements with porosity (E) and permeability (F) showing inverse relationships. Porosity and permeability increase with decreasing quartz cements.

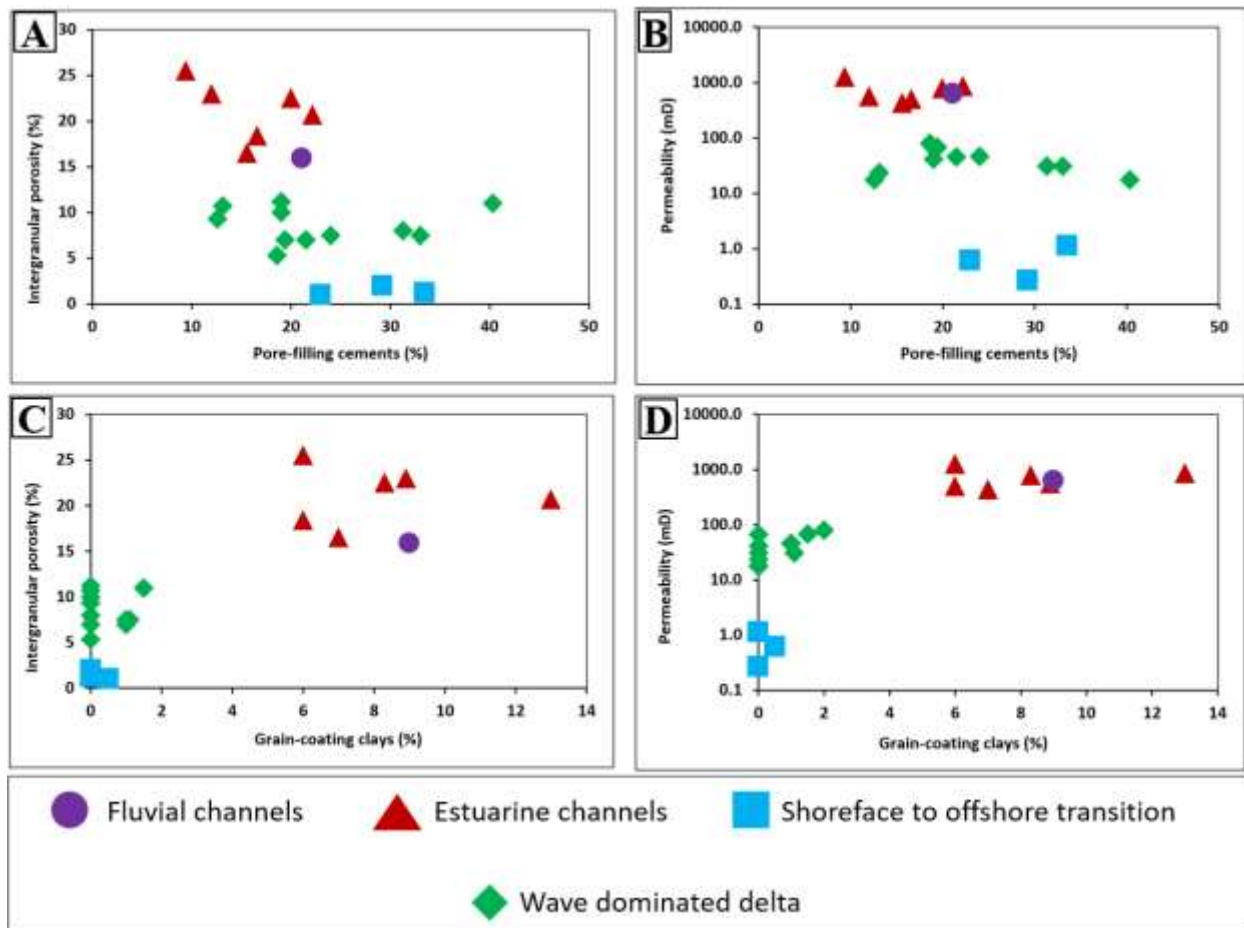


Figure 5.23. Controls of authigenic cements on reservoir quality. Cross-plots of total pore-filling cements with porosity (A) and permeability (B). Overall, reservoir properties increase with decreasing pore-filling cements. Cross plots of grain-coating clays with porosity (C) and permeability (D) show a positive correlation. Porosity and permeability increase with increasing grain-coating clays.

Authigenic quartz cementation is a primary factor contributing to porosity reduction in deeply buried sandstones (McBride, 1989; Walderhaug, 1996; Worden & Morad, 2000; Taylor et al., 2022). However, grain-coating clays, such as illite and chlorite, can inhibit quartz cementation, thereby preserving porosity and permeability (Ehrenberg et al., 1993; Bloch et al., 2002; Ajdukiewicks & Larese, 2012; Al-Ramadan et al., 2013b; Bello et al., 2021; Walderhaug & Porten,

2022). In the studied Jauf sandstones, quartz cementation is less prevalent in the fluvial-estuarine channel facies, where illite and chlorite grain coatings are well developed, resulting in high reservoir quality (Figs. 22E-F & 23C-D). In contrast, the wave-dominated delta and shoreface facies display less extensive clay coatings and higher quartz cementation (up to 4% and 7.5%, respectively), leading to poorer reservoir quality. Fe-oxides, anhydrite, and k-feldspar cements generally occur in trace amounts and have a minimal impact on reservoir quality.

Overall, the diagenetic analysis of the Jauf sandstones indicates that the tidal estuarine channel facies, characterized by low levels of cementation and compaction and the highest concentration of grain-coating clays, exhibit the best reservoir quality (Fig. 23A-D). The wave-dominated delta facies, which are comparatively more compacted and cemented and possess fewer grain-coating clays, display moderate reservoir quality. In contrast, the shoreface-to-offshore transition facies, marked by high compaction, pervasive cementation, and minimal grain-coating clays, have the poorest reservoir quality (Fig. 23A-D).

5.7. Conclusion

- The Jauf Formation sandstones examined in this study are primarily composed of very fine to medium-grained, poorly to well-sorted quartz arenites and arkoses, deposited across a range of environments, including shoreface-to-offshore transitions, wave-dominated deltas, fluvial channels, and tidal estuaries.
- Depositional factors such as grain size, sorting, and detrital matrix content play a critical role in determining reservoir quality. Fluvial and estuarine channels, which contain very fine to medium-grained, well-sorted sandstones with minimal detrital matrix (avg. 0.2%), exhibit the highest reservoir quality. In contrast, the fine to medium-grained, moderately sorted sandstones of wave-dominated delta facies, with slightly higher matrix content (avg. 2.9%), demonstrate moderate reservoir quality. Shoreface-to-offshore transition sandstones, which are very fine-grained and poorly sorted, possess the highest detrital matrix (avg. 19.1%) and exhibit the poorest reservoir quality.
- Reservoir quality evolution in the Jauf sandstones is largely governed by shallow burial (eodiagenesis) and deep burial diagenesis (mesodiagenesis). The degree of pore-filling clay (kaolinite and illite) and quartz cementation varies significantly across different depositional facies.
- The shoreface-to-offshore transition facies, characterized by well-developed pore-filling clay and quartz cements, exhibit the lowest reservoir quality. This is due to the limited presence of grain-coating illite and chlorite, which otherwise inhibit quartz cementation. In contrast, the fluvial to tidal estuarine sandstones possess the most developed grain-coating clays, resulting in higher reservoir quality.

- Intergranular porosity loss in the Jauf sandstones is primarily due to mechanical compaction, particularly in shoreface-to-offshore transition facies, where high detrital matrix content enhanced compaction.
- Cementation by pore-filling Fe-dolomite/ankerite cements is pervasive in the wave-dominated delta facies, significantly reducing reservoir quality. These carbonate cements act as barriers to fluid flow in contrast to the less-cemented fluvial and estuarine channel sandstones, which maintain higher reservoir potential.

5.8. References

- Ajdukiewicz, J. M., & Lander, R. H. (2010). Sandstone reservoir quality prediction: The state of the art. *American Association of Petroleum Geologists Bulletin*, 94(8), 1083–1091. <https://doi.org/10.1306/intro060110>
- Ajdukiewicz, J. M., & Larese, R. E. (2012). How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments. *AAPG Bulletin*, 96(11), 2091–2119. <https://doi.org/10.1306/02211211075>
- Al-Ghazi, A. (2007). New evidence for the Early Devonian age of the Jauf Formation in northern Saudi Arabia. *Revue de Micropaléontologie*, 50(1), 59–72. <https://doi.org/https://doi.org/10.1016/j.revmic.2007.01.005>
- Algheryafi, H., Viseras, C., Polo, C., & Al-Ramadan, K. (2022). Facies architecture and paleogeography evolution of regressive wave-dominated shorelines transitioning into tide-dominated estuaries: Early Devonian Subbat Member, Jauf Formation, Saudi Arabia. *Journal of Sedimentary Research*, 92(10), 955–987. <https://doi.org/10.2110/jsr.2021.112>
- Al-Husseini, M., & Matthews, R. K. (2006). Devonian Jauf Formation, Saudi Arabia: Orbital Second-order Depositional Sequence 28. *GeoArabia*, 11(2), 53–70. <https://doi.org/10.2113/geoarabia110253>
- Al-Qahtani, M., & Buhidma, I. (2001). Improved Near-Well Reservoir Characterisation of a Complex Gas Condensate Reservoir in Saudi Arabia by Integrating Core, Log, Seismic and Extended Well Test Data. <https://doi.org/10.2118/68140-MS>
- Alqubalee, A., Muharrag, J., Salisu, A. M., & Eltom, H. (2022). The negative impact of Ophiomorpha on reservoir quality of channelized deposits in mixed carbonate siliciclastic setting: The case study of the Dam Formation, Saudi Arabia. *Marine and Petroleum Geology*, 140, 105666. <https://doi.org/10.1016/J.MARPETGEO.2022.105666>
- Al-Ramadan, K. (2014). Diagenesis of Holocene beachrocks: a comparative study between the Arabian Gulf and the Gulf of Aqaba, Saudi Arabia. *Arabian Journal of Geosciences*, 7(11), 4933–4942. <https://doi.org/10.1007/s12517-013-1127-7>
- Al-Ramadan, K. (2021). The role of diagenesis at unconformities of the Paleozoic siliciclastic succession of central Saudi Arabia: implications for reservoir quality. *Arabian Journal of Geosciences*, 14(6), 484. <https://doi.org/10.1007/s12517-021-06845-6>
- Al-Ramadan, K. A., Hussain, M., Imam, B., & Saner, S. (2004). Lithologic characteristics and diagenesis of the Devonian Jauf sandstone at Ghawar Field, Eastern Saudi Arabia. *Marine and Petroleum Geology*, 21(10), 1221–1234. <https://doi.org/10.1016/J.MARPETGEO.2004.09.002>
- Al-Ramadan, K., Morad, S., & Plink-Bjorklund, P. (2013a). Distribution of Diagenetic Alterations in Relationship to Depositional Facies and Sequence Stratigraphy of a Wave- and Tide-Dominated Siliciclastic Shoreline Complex: Upper Cretaceous Chimney Rock Sandstones, Wyoming and Utah, USA. *IAS Special Publication*, 45, 271–296. <https://doi.org/10.1002/9781118485347.ch12>

- Al-Ramadan, K., Morad, S., Norton, A., & Hulver, M. (2013b). Linking Diagenesis and Porosity Preservation Versus Destruction to Sequence Stratigraphy of Gas Condensate Reservoir Sandstones; The Jauf Formation (Lower to Middle Devonian), Eastern Saudi Arabia. In *Linking Diagenesis to Sequence Stratigraphy* (Vol. 45, pp. 297–335). <https://doi.org/10.1002/9781118485347.ch13>
- Al-Ramadan, K., Morad, S., Proust, J.-N., & Al-Aasm, I. (2005). Distribution of diagenetic alterations within the sequence stratigraphic framework of shoreface siliciclastic deposits: evidence from the Jurassic deposits of NE France. *Journal of Sedimentary Research*, 75, 10–38.
- Alsuwaidi, M., Mohamed, A. A. I., Mansurbeg, H., Morad, S., Alsuwaidi, A., Al-Shalabi, E. W., Gomes, J., Al-Ramadan, K., Mohammed, I. Q., & Farouk, S. (2021). Depositional and diagenetic controls on reservoir quality of microporous basinal lime mudstones (Aptian), United Arab Emirates. *Sedimentary Geology*, 420. <https://doi.org/10.1016/j.sedgeo.2021.105925>
- Amao, A., Al-Ramadan, K., & Koeshidayatullah, A. (2016). Automated mineralogical methodology to study carbonate grain microstructure: an example from oncoids. *Environmental Earth Sciences*, 75. <https://doi.org/10.1007/s12665-016-5492-x>
- Ashour, A., Düringer, P., Schuster, M., Pelletier, J., & Rubino, J. (2014). Small-scale sedimentary structures and their implications in recognizing large-scale ancient tidal bedforms. Example from Dur At Talah outcrop, Late Eocene, Sirt Basin, Libya. *Journal of African Earth Sciences*, 100, 346–364. <https://doi.org/10.1016/j.jafrearsci.2014.07.008>
- Barshep, D., & Worden, R. (2021). Reservoir Quality of Upper Jurassic Corallian Sandstones, Weald Basin, UK. *Geosciences*, 11, 446. <https://doi.org/10.3390/geosciences11110446>
- Becker, I., Busch, B., Koehrer, B., Adelmann, D., & Hilgers, C. (2019). Reservoir Quality Evolution of Upper Carboniferous (Westphalian) Tight Gas Sandstones, Lower Saxony Basin, NW Germany. *Journal of Petroleum Geology*, 42(4), 371–392. <https://doi.org/https://doi.org/10.1111/jpg.12742>
- Bello, A. M., Al-Ramadan, K., Babalola, L. O., Alqubalee, A., & Amao, A. O. (2023c). Impact of grain-coating illite in preventing quartz cementation: Example from permo-carboniferous sandstone, Central Saudi Arabia. *Marine and Petroleum Geology*, 149. <https://doi.org/10.1016/j.marpetgeo.2022.106073>
- Bello, A. M., Butt, M. N., Hussain, A., Amao, A. O., Olariu, C., Koeshidayatullah, A. I., Malik, M. H., Al-Hashem, M., & Al-Ramadan, K. (2023a). Impact of depositional and diagenetic controls on reservoir quality of syn-rift sedimentary systems: An example from Oligocene-Miocene Al Wajh Formation, northwest Saudi Arabia. *Sedimentary Geology*, 446, 106342. <https://doi.org/10.1016/j.sedgeo.2023.106342>
- Bello, A. M., Salisu, A. M., Alqubalee, A., Amao, A. O., Al-Hashem, M., Al-Hussaini, A., & Al-Ramadan, K. (2024a). Diagenetic controls on the quality of shallow marine sandstones: An example from the Cambro-Ordovician Saq Formation, central Saudi Arabia. *Journal of African Earth Sciences*, 215, 105295. <https://doi.org/https://doi.org/10.1016/j.jafrearsci.2024.105295>

- Bello, A. M., Usman, M. B., Abubakar, U., Al-Ramadan, K., Babalola, L. O., Amao, A. O., Sarki Yandoka, B. M., Kachalla, A., Kwami, I. A., Ismail, M. A., Umar, U. S., & Kimayim, A. (2022). Role of diagenetic alterations on porosity evolution in the cretaceous (Albian-Aptian) Bima Sandstone, a case study from the Northern Benue Trough, NE Nigeria. *Marine and Petroleum Geology*, 145. <https://doi.org/10.1016/j.marpetgeo.2022.105851>
- Bello, A. M., Usman, M. B., Amao, A. O., Al-Ramadan, K., Al-Hashem, M., Kachalla, A., Abubakar, U., Salisu, A. M., Mukkafa, S., Kwami, I. A., Aro, O. E., Butt, M. N., Maigari, A. S., Yusuf, A., Chiroma, L. U., & Akinsanpe, O. T. (2024b). Diagenesis and reservoir quality evolution of estuarine sandstones: Insights from the Cenomanian-Turonian Yolde Formation, northern Benue Trough, NE Nigeria. *Marine and Petroleum Geology*, 169, 107073. <https://doi.org/https://doi.org/10.1016/j.marpetgeo.2024.107073>
- Bello, A. M., Usman, M. B., Ismail, M. A., Mukkafa, S., Abubakar, U., Kwami, I. A., Al-Ramadan, K., Amao, A. O., Al-Hashem, M., Salisu, A. M., Kachalla, A., Abubakar, M. B., Maigari, A. S., & Chiroma, L. U. (2023b). Linking diagenesis and reservoir quality to depositional facies in marginal to shallow marine sequence: An example from the Campano-Maastrichtian Gombe Sandstone, Northern Benue Trough, NE Nigeria. *Marine and Petroleum Geology*, 155(May), 106386. <https://doi.org/10.1016/j.marpetgeo.2023.106386>
- Bello, A., Jones, S., Gluyas, J., Açıklın, S., & Cartigny, M. (2021). Role played by clay content in controlling reservoir quality of submarine fan system, Forties Sandstone Member, Central Graben, North Sea. *Marine and Petroleum Geology*, 128, 105058. <https://doi.org/10.1016/j.marpetgeo.2021.105058>
- Birkle, P., Van Dijk, C., Dasgupta, K., Murphy, M. J., Kharaka, Y. K., Thordsen, J. J., & Bischoff, J. L. (2019). Controls on illite cementation in unayzah sandstones, Saudi Arabia: Mineralogy, K-Ar dating, numerical modeling, and hydrothermal experiments. *Journal of Sedimentary Research*, 89(2), 89–109. <https://doi.org/10.2110/jsr.2018.71>
- Bjørlykke, K., Ramm, M., & Saigal, G. C. (1989). Sandstone diagenesis and porosity modification during basin evolution. *Geologische Rundschau*, 78(1), 243–268. <https://doi.org/10.1007/BF01988363>
- Bloch, S., & McGowen, J. H. (1994). Influence of Depositional Environment on Reservoir Quality Prediction. In M. D. Wilson (Ed.), *Reservoir Quality Assessment and Prediction in Clastic Rocks* (Vol. 30, p. 0). SEPM Society for Sedimentary Geology. <https://doi.org/10.2110/scn.94.30.0041>
- Bloch, S., Lander, R. H., & Bonnell, L. (2002). Anomalous High Porosity and Permeability in Deeply Buried Sandstone Reservoirs: Origin and Predictability. *AAPG Bulletin*, 86(2), 301–328. <https://doi.org/10.1306/61EEDABC-173E-11D7-8645000102C1865D>
- Boucot, A.J., McClure, H.A., Alvarez, F., Ross, J.R.P., Taylor, D.W., Struve, W., Savage, N.N., & Turner, S. (1989). New Devonian fossils from Saudi Arabia and their biogeographical affinities: *Senckenbergiana Lethaea*, v. 69, p. 535–597.
- Breuer, P., Miller, M. A., Leszczyński, S., & Steemans, P. (2015). Climate-controlled palynofacies and miospore stratigraphy of the Jauf Formation, Lower Devonian, northern Saudi Arabia.

- Review of Palaeobotany and Palynology, 212, 187–213.
<https://doi.org/https://doi.org/10.1016/j.revpalbo.2014.09.005>
- Busch, B., Böcker, J., & Hilgers, C. (2024). Improved reservoir quality assessment by evaluating illite grain coatings, quartz cementation, and compaction – Case study from the Buntsandstein, Upper Rhine Graben, Germany. *Geoenery Science and Engineering*, 241, 213141. <https://doi.org/https://doi.org/10.1016/j.geoen.2024.213141>
- Caracciolo L., Arribas J., Ingersoll R.V., & Critelli S. (2014). The diagenetic destruction of porosity in plutoniclastic petrofacies: The Miocene Diligencia and Eocene Maniobra formations, Orocopia Mountains, southern California, USA, in R.A. Scott, H.R. Smyth, A.C. Morton & N. Richardson (eds.), *Sediment Provenance Studies in Hydrocarbon Exploration and Production. Geological Society, London, Special Publication*, 386, p. 49-62, doi: 10.1144/SP386.9.
- Civitelli, M., & Critelli, S. (2024). The interplay of detrital modes and depositional facies on diagenesis and petrophysics of deep-marine Miocene sandstones (Cilento Group), southern Apennines, Italy. *Marine and Petroleum Geology* 167, 1-16 (106943), doi: 10.1016/j.marpetgeo.2024.106943.
- Civitelli, M., Critelli, S., Ingersoll, R.V. (2024). Interpreting post-depositional alterations in deep-marine sandstones: Butano Sandstone, central California, USA. Submitted to *Marine and Petroleum Geology* 163, 1-11 (106733), doi: 10.1016/j.marpetgeo.2024.106733.
- Civitelli, M., Ravidà, D.C.G., Borrelli, M., Criniti, S., & Falsetta, E. (2023). Diagenesis and petrophysics of Miocene sandstones within southern Apennines foreland, Italy. *Marine and Petroleum Geology* 155, 106411, <https://doi.org/10.1016/j.marpetgeo.2023.106411>.
- Criniti, S., Durante, M. G., Macario, A., Cesarano, M., Matano, F., Di Nocera, S., Civitelli, M., Falsetta, E., Borrelli, M., Zimmaro, P., & Critelli S. (2024b). A geological, petrophysical and ground motion model of the Pavoncelli bis hydraulic tunnel (Southern Apennines, Italy): Implications for reservoir analyses. *Marine and Petroleum Geology* 165 (106867), 1-17, doi: 10.1016/j.marpetgeo.2024.106867.
- Criniti, S., Martín-Martín, M., Hlila, R., Maaté, A., & Maaté, S. (2024a). Detrital signatures of the Ghomaride Culm Cycle (Rif Cordillera, N Morocco): new constraints for the northern Gondwana plate tectonics. *Marine and Petroleum Geology* 165, 106861, <https://doi.org/10.1016/j.marpetgeo.2024.106861>.
- Criniti, S., Martín-Martín, M., Martín-Algarra, A. (2023). New constraints for the western Paleotethys paleogeography-paleotectonics derived from detrital signatures: Malaguide Carboniferous Culm Cycle (Betic Cordillera, S Spain). *Sedimentary Geology* 468, 106534. <https://doi.org/10.1016/j.sedgeo.2023.106534>.
- Critelli, S., & Nilsen, T.H. (1996). Petrology and diagenesis of the Eocene Butano Sandstone, LaHonda Basin, California. *The Journal of Geology*, v. 104, p. 295-315, doi: 10.1086/629826.
- Critelli, S., Perri, F., Arribas, J., & Herrero, M.J. (2018). Sandstone detrital modes and diagenetic evolution of Mesozoic continental redbeds from western-central circum-Mediterranean orogenic belts, in Ingersoll, R.V., Lawton, T.F., Graham, S., eds., *Tectonics, Sedimentary*

Basins and Provenance: A Celebration of William R. Dickinson's Career: *Geological Society of America Special Paper 540*, p. 119-132 doi: 10.1130/2018.2540(06).

Dalrymple, R. (2010). Tidal depositional systems. In *Facies Models 4* (pp. 201–231).

Darling, H.L., & Sneider, R.M. (1993). Productive Low Resistivity Well Logs of the Offshore Gulf of Mexico: Causes and Analysis, Productive Low Resistivity Well Logs of the Offshore Gulf of Mexico. New Orleans Geological Society and the Houston Geological Society, pp. 23–36.

Ehrenberg, S. N. (1993). Preservation of Anomalously High Porosity in Deeply Buried Sandstones by Grain-Coating Chlorite: Examples from the Norwegian Continental Shelf¹. AAPG Bulletin, 77(7), 1260–1286. <https://doi.org/10.1306/BDF8E5C-1718-11D7-8645000102C1865D>

El-Ghali, M. A. K., Shelukhina, O., Abbasi, I. A., Moustafa, M. S. H., Hersi, O. S., Siddiqui, N. A., Al-Ramadan, K., Alqubalee, A., Bello, A. M., & Amao, A. O. (2024). Depositional and sequence stratigraphic controls on diagenesis in the Upper Cambrian-Lower Ordovician Barik Formation, central Oman: Implications for prediction of reservoir porosity in a hybrid-energy delta system. *Marine and Petroleum Geology*, 160, 106611. <https://doi.org/https://doi.org/10.1016/j.marpetgeo.2023.106611>

Eltom, H., Abdullatif, O., Makkawi, M., Al-Ramadan, K., & Abdulraziq, A. (2015). Porosity evolution within high-resolution sequence stratigraphy and diagenesis framework: outcrop analog of the upper Jurassic Arab-D reservoir, Central Saudi Arabia. *Arabian Journal of Geosciences*, 8(3), 1669–1690. <https://doi.org/10.1007/s12517-013-1251-4>

Folk, R.L. (1980). *Petrology of Sedimentary Rocks*. Hemphill Publishing Company, Austin, Texas (182 pp.).

Franks, S. G., & Zwingmann, H. (2010). Origin and timing of late diagenetic illite in the Permian–Carboniferous Unayzah sandstone reservoirs of Saudi Arabia. AAPG Bulletin, 94(8), 1133–1159. <https://doi.org/10.1306/04211009142>

Galli, K. (2014). Fluvial architecture element analysis of the Brushy Basin Member, Morrison Formation, western Colorado, USA. *Volumina Jurassica*, 12(2), 69–106.

Griffiths, J., Worden, R. H., Utley, J. E. P., Brostrøm, C., Martinius, A. W., Lawan, A. Y., & Al-Hajri, A. I. (2021). Origin and distribution of grain-coating and pore-filling chlorite in deltaic sandstones for reservoir quality assessment. *Marine and Petroleum Geology*, 134(September). <https://doi.org/10.1016/j.marpetgeo.2021.105326>

Hassanpouryouzband, A., Adie, K., Cowen, T., Thaysen, E. M., Heinemann, N., Butler, I. B., Wilkinson, M., & Edlmann, K. (2022). Geological Hydrogen Storage: Geochemical Reactivity of Hydrogen with Sandstone Reservoirs. *ACS Energy Letters*, 7(7), 2203–2210. <https://doi.org/10.1021/acsenergylett.2c01024>

Houseknecht, D. W. (1987). Assessing the Relative Importance of Compaction Processes and Cementation to Reduction of Porosity in Sandstones¹. AAPG Bulletin, 71(6), 633–642. <https://doi.org/10.1306/9488787F-1704-11D7-8645000102C1865D>

Hussain, A., Butt, M. N., Olariu, C., Malik, M. H., Koeshidayatullah, A., Amao, A., & Al-Ramadan, K. (2022). Unravelling reservoir quality heterogeneity in mixed siliciclastic-

- carbonate deposits: An example from Miocene Red Sea rift, NW Saudi Arabia. *Marine and Petroleum Geology*, 145, 105850. <https://doi.org/https://doi.org/10.1016/j.marpetgeo.2022.105850>
- Hussain, M., & Al-Ramadan, K. (2009). Microfacies analysis of Wadi Waqb member (Miocene) in Wadi Aynunah, northwest of Saudi Arabia. *Carbonates and Evaporites*, 24(2), 139–149. <https://doi.org/10.1007/BF03182089>
- Hussain, M., Al-Shaibani, A., Al-Ramadan, K., & Wood, W. W. (2020). Geochemistry and isotopic analysis of brines in the coastal sabkhas, Eastern region, Kingdom of Saudi Arabia. *Journal of Arid Environments*, 178, 104142. <https://doi.org/https://doi.org/10.1016/j.jaridenv.2020.104142>
- Hussain, M., Amao, A. O., Al-Ramadan, K., Babalola, L. O., & Humphrey, J. D. (2022). Unconventional reservoir characterization using geochemical signatures: Examples from Paleozoic formations, Saudi Arabia. *Marine and Petroleum Geology*, 143, 105770. <https://doi.org/https://doi.org/10.1016/j.marpetgeo.2022.105770>
- Janjou, D., Halawani, M.A., Al-Muallem, M.S., Robelin, C., Brosse, J.M., Courbouleix, S., Dagain, J., Genna, A., Razin, P., Roobol, J.M., Shorbaji, H., & Wyns R. (1997). Explanatory notes to the geologic map of the Al Qalibah Quadrangle, Kingdom of Saudi Arabia: Ministry of Petroleum and Mineral Resources, Geoscience Map GM-135, scale 1:250,000, sheet 28C, 44 p.
- Jiang, L., Sun, J., Liu, X., & Wang, H. (2011). Study of different factors affecting the electrical properties of natural gas reservoir rocks based on digital cores. *Journal of Geophysics and Engineering*, 8, 366. <https://doi.org/10.1088/1742-2132/8/2/021>
- Khan, M. A., Khan, T., Ali, A., Bello, A. M., & Radwan, A. E. (2023). Role of depositional and diagenetic controls on reservoir quality of complex heterogenous tidal sandstone reservoirs: An example from the Lower Goru formation, Middle Indus Basin, Southwest Pakistan. *Marine and Petroleum Geology*, 154, 106337. <https://doi.org/https://doi.org/10.1016/j.marpetgeo.2023.106337>
- Klinkenberg, L. J. (1941). The permeability of porous media to liquids and gases. *Drilling and Production Practice* 1941, 200–213.
- Knaust, D., & Bromley, R. G. (2012). Trace Fossils as Indicators of Sedimentary Environments, *Developments in Sedimentology* 64.
- Koeshidayatullah, A., Al-Ramadan, K., & Hughes, G. W. (2016). Facies mosaic and diagenetic patterns of the early Devonian (Late Pragian–Early Emsian) microbialite-dominated carbonate sequences, Qasr Member, Jauf Formation, Saudi Arabia. *Geological Journal*, 51(5), 704–721. <https://doi.org/10.1002/gj.2678>
- Konert, G., Afifi, A. M., Al-Hajri, S. A., & Droste, H. J. (2001). Paleozoic stratigraphy and hydrocarbon habitat of the Arabian plate. *GeoArabia*, 6(3), 407–442. <https://doi.org/10.2113/geoarabia0603407>

- Kordi, M. (2013). Characterization and prediction of reservoir quality in chlorite-coated sandstones: evidence from the Late Cretaceous Lower Tuscaloosa Formation at Cranfield Field, Mississippi, U. S. A.
- Lai, J., Wang, G., Wang, S., Cao, J., Li, M., Pang, X., Zhou, Z., Fan, X., Dai, Q., Yang, L., He, Z., & Qin, Z. (2018). Review of diagenetic facies in tight sandstones: Diagenesis, diagenetic minerals, and prediction via well logs. *Earth Sci Rev* 185, 234–258. <https://doi.org/https://doi.org/10.1016/j.earscirev.2018.06.009>
- Lander, R. H., Bonnell, L. M., Taylor, T. R., & Espejo, I. (2022). Chapter 13 - Reservoir quality and diagenesis of deepwater sandstones (J. R. Rotzien, C. A. Yeilding, R. A. Sears, F. J. Hernández-Molina, & O. B. T.-D. S. S. Catuneanu, Eds.; pp. 471–514). Elsevier. <https://doi.org/https://doi.org/10.1016/B978-0-323-91918-0.00011-6>
- Lander, R. H., Larese, R. E., & Bonnell, L. M. (2008). Toward more accurate quartz cement models: The importance of euhedral versus noneuhedral growth rates. *AAPG Bulletin*, 92(11), 1537–1563. <https://doi.org/10.1306/07160808037>
- Lanson, B., Beaufort, D., Berger, G., Bauer, A., Cassagnabère, A., & Meunier, A. (2002). Authigenic kaolin and illitic minerals during burial diagenesis of sandstones: a review. *Clay Minerals*, 37(1), 1–22. <https://doi.org/DOI: 10.1180/0009855023710014>
- Lawan, A. Y., Worden, R. H., Utley, J. E. P., & Crowley, S. F. (2021). Sedimentological and diagenetic controls on the reservoir quality of marginal marine sandstones buried to moderate depths and temperatures: Brent Province, UK North Sea. *Marine and Petroleum Geology*, 128(October 2020), 104993. <https://doi.org/10.1016/j.marpetgeo.2021.104993>
- Leckie, D. A., & Walker, R. G. (1982). Storm-and Tide-Dominated Shorelines in Cretaceous Moosebar-Lower Gates Interval—Outcrop Equivalents of Deep Basin Gas Trap in Western Canada. *AAPG Bulletin*, 66(2), 138–157. <https://doi.org/10.1306/03B59A53-16D1-11D7-8645000102C1865D>
- Lima, R. D., & De Ros, L. F. (2002). The role of depositional setting and diagenesis on the reservoir quality of Devonian sandstones from the Solimões Basin, Brazilian Amazonia. *Marine and Petroleum Geology*, 19(9), 1047–1071. [https://doi.org/https://doi.org/10.1016/S0264-8172\(03\)00002-3](https://doi.org/https://doi.org/10.1016/S0264-8172(03)00002-3)
- Liu, Y., Zhang, X., Shi, J., Guo, W., Kang, L., Yu, R., Sun, Y., Wang, Z., & Pan, M. (2021). A reservoir quality evaluation approach for tight sandstone reservoirs based on the gray correlation algorithm: A case study of the Chang 6 layer in the W area of the as oilfield, Ordos Basin. *Energy Exploration & Exploitation*, 39(4), 1027–1056. <https://doi.org/10.1177/0144598721998510>
- Lundegard, P. D. (1992). Sandstone porosity loss; a “big picture” view of the importance of compaction. *Journal of Sedimentary Research*, 62(2), 250–260. <https://doi.org/10.1306/D42678D4-2B26-11D7-8648000102C1865D>
- MacEachern, J. A., Bann, K. L., Pemberton, S. G., & Gingras, M. K. (2007). The Ichnofacies Paradigm: High-Resolution Paleoenvironmental Interpretation of the Rock Record. In J. A. MacEachern, K. L. Bann, M. K. Gingras, & S. G. Pemberton (Eds.), *Applied Ichnology* (Vol. 52, p. 0). SEPM Society for Sedimentary Geology. <https://doi.org/10.2110/pec.07.52.0027>

- Mantovani, M., Escudero, A., & Becerro, A. I. (2010). Effect of pressure on kaolinite illitization. *Applied Clay Science*, 50(3), 342–347. <https://doi.org/https://doi.org/10.1016/j.clay.2010.08.024>
- McBride, E. F. (1989). Quartz cement in sandstones: a review. *Earth-Science Reviews*, 26(1), 69–112. [https://doi.org/https://doi.org/10.1016/0012-8252\(89\)90019-6](https://doi.org/https://doi.org/10.1016/0012-8252(89)90019-6)
- McCarty, D. K., Sakharov, B. A., & Drits, V. A. (2009). New insights into smectite illitization: A zoned K-bentonite revisited. *American Mineralogist*, 94(11–12), 1653–1671. <https://doi.org/10.2138/am.2009.3260>
- Miall, A. D. (1985). Architectural-element analysis: A new method of facies analysis applied to fluvial deposits. *Earth-Science Reviews*, 22(4), 261–308. [https://doi.org/https://doi.org/10.1016/0012-8252\(85\)90001-7](https://doi.org/https://doi.org/10.1016/0012-8252(85)90001-7)
- Milliken, K., & Laubach, S. (2000). Brittle Deformation in Sandstone Diagenesis as Revealed by Scanned Cathodoluminescence Imaging with Application to Characterization of Fractured Reservoirs (pp. 225–243). https://doi.org/10.1007/978-3-662-04086-7_9
- Moore, D. M., & Reynolds, R. C., Jr. (1997). X-Ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd ed. xviii + 378 pp. Oxford, New York: Oxford University Press. ISBN 0 19 508713 5. *Geological Magazine*, 135(6), 819–842. <https://doi.org/DOI:10.1017/S0016756898501501>
- Morad, S., Al-Ramadan, K., Ketzer, J. M., & De Ros, L. F. (2010). The impact of diagenesis on the heterogeneity of sandstone reservoirs: A review of the role of depositional fades and sequence stratigraphy. *American Association of Petroleum Geologists Bulletin*, 94(8), 1267–1309. <https://doi.org/10.1306/04211009178>
- Naveed Butt, M., G. Franks, S., Hussain, A., Amao, A. O., Muhammad Bello, A., & Al-Ramadan, K. (2024). Depositional and diagenetic controls on the reservoir quality of Early Miocene syn-rift deep-marine sandstones, NW Saudi Arabia. *Journal of Asian Earth Sciences*, 259, 105880. <https://doi.org/https://doi.org/10.1016/j.jseaes.2023.105880>
- Nichols, G.J., (2013). *Sedimentology and Stratigraphy*: Wiley, 432 p.
- Olivero, D. (1996). Zoophycos distribution and sequence stratigraphy. Examples from the Jurassic and Cretaceous deposits of southeastern France. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 123(1), 273–287. [https://doi.org/https://doi.org/10.1016/0031-0182\(95\)00120-4](https://doi.org/https://doi.org/10.1016/0031-0182(95)00120-4)
- Olson, J. E., Laubach, S. E., & Lander, R. H. (2009). Natural fracture characterization in tight gas sandstones: Integrating mechanics and diagenesis. *AAPG Bulletin*, 93(11), 1535–1549. <https://doi.org/10.1306/08110909100>
- Paxton, S., Szabo, J. O., Ajdukiewicz, J., & Klimentidis, R. (2002). Construction of an intergranular volume compaction curve for evaluating and predicting compaction and porosity loss in rigid-grain sandstone reservoirs. *AAPG Bulletin*, 86, 2047–2067. <https://doi.org/10.1306/61EEDDFA-173E-11D7-8645000102C1865D>

- Payton, R. L., Chiarella, D., & Kingdon, A. (2022). The influence of grain shape and size on the relationship between porosity and permeability in sandstone: a digital approach. *Scientific Reports*, 12(1), 7531. <https://doi.org/10.1038/s41598-022-11365-8>
- Powers, R. W., Ramirez, L. F., Redmond, C. D., & Elberg, E. L. J. (1966). *Geology of the Arabian Peninsula Sedimentary Geology of Saudi Arabia*. U.S. Geological Survey Professional Paper, 560-D, 154.
- Qiao, J., Zeng, J., Jiang, S., Ma, Y., Feng, S., Xie, H., Wang, Y., & Hu, H. (2020). Role of pore structure in the percolation and storage capacities of deeply buried sandstone reservoirs: A case study of the Junggar Basin, China. *Marine and Petroleum Geology*, 113, 104129. <https://doi.org/10.1016/j.marpetgeo.2019.104129>
- Rahman, M. J. J., & Worden, R. H. (2016). Diagenesis and its impact on the reservoir quality of Miocene sandstones (Surma Group) from the Bengal Basin, Bangladesh. *Marine and Petroleum Geology*, 77, 898–915. <https://doi.org/10.1016/j.marpetgeo.2016.07.027>
- Rahmani, R. A., Steel, R. J., & Al-Duaiji, A. A. (2019). High Resolution Sequence Stratigraphy and Sedimentology of the Prolific Devonian Jauf Formation Gas Reservoir: Transgressive Tidal Estuarine and Regressive Wave-Dominated Shoreface Deposits, Kingdom of Saudi Arabia. In H. R. AlAnzi, R. A. Rahmani, R. J. Steel, & O. M. Soliman (Eds.), *Siliciclastic Reservoirs of the Arabian Plate* (Vol. 116, p. 0). The American Association of Petroleum Geologists. <https://doi.org/10.1306/13642175M1183806>
- Rahmani, R., Steel, R., & Al-Duaiji, A. (2002). High-resolution sequence stratigraphy of the Devonian Jauf gas reservoir: a shoreface and estuarine embayment succession, greater Ghawar area, eastern Saudi Arabia. *GeoArabia*, Abstract.
- Rahmani, R., Steel, R., & Al-Duaiji, A. (2021). Ch 1 High Resolution Sequence Stratigraphy and Sedimentology of the Prolific Devonian Jauf Formation Gas Reservoir: Transgressive Tidal Estuarine and Regressive Wave- Dominated Shoreface Deposits, Kingdom of Saudi Arabia. *AAPG Memoir*, 116.
- Reed, F. S., & Mergner, J. L. (1953). Preparation of rock thin sections*. *American Mineralogist*, 38(11–12), 1184–1203.
- Salem, A. M., Ketzer, J. M., Morad, S., Rizk, R. R., & Al-Aasm, I. S. (2005). Diagenesis and Reservoir-Quality Evolution of Incised-Valley Sandstones: Evidence from the Abu Madi Gas Reservoirs (Upper Miocene), the Nile Delta Basin, Egypt. *Journal of Sedimentary Research*, 75(4), 572–584. <https://doi.org/10.2110/jsr.2005.047>
- Salisu, A. M., Alqubalee, A., Bello, A. M., Al-Hussaini, A., Adebayo, A. R., Amao, A. O., & Al-Ramadan, K. (2023). Impact of kaolinite and iron oxide cements on resistivity and quality of low resistivity pay sandstones. *Marine and Petroleum Geology*, 158, 106568. <https://doi.org/10.1016/j.marpetgeo.2023.106568>
- Saner, S., Hassan, H., Al-Ramadan, K., & Abdulghani, W. M. (2006). Mineralogical, pore and petrophysical characteristics of the Devonian Jauf Sandstone reservoir, Hawiyah field, eastern Saudi Arabia. *Journal of Petroleum Geology*, 29, 257–272. <https://doi.org/10.1111/j.1747-5457.2006.00257.x>

- Scotese, C. (2001). Atlas of Earth History (Vol. 1).
- Sharland, P., Archer, R., Casey, D., Davies, R., Hall, S. H., Heward, A., Horbury, A., & Simmons, M. (2001). Arabian Plate Sequence Stratigraphy. *GeoArabia*. In *GeoArabia Special Publication* (Vol. 2).
- Srisunthon, P., & Choowong, M. (2019). Quaternary meandering evolution and architecture of a point bar in the Mun River on the sandstone-dominated Khorat Plateau from northeastern Thailand. *Quaternary International*, 525, 25–35. <https://doi.org/https://doi.org/10.1016/j.quaint.2019.09.005>
- Stampfli, G. M., & Borel, G. D. (2002). A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrons. *Earth and Planetary Science Letters*, 196(1), 17–33. [https://doi.org/https://doi.org/10.1016/S0012-821X\(01\)00588-X](https://doi.org/https://doi.org/10.1016/S0012-821X(01)00588-X)
- Stampfli, G., Raumer, J., & Borel, G. (2005). Paleozoic evolution of pre-Variscan terranes: From Gondwana to the Variscan collision. *Geol. Soc. Am.*, 364. <https://doi.org/10.1130/0-8137-2364-7.263>
- Taylor, T. R., Giles, M. R., Hathon, L. A., Diggs, T. N., Braunsdorf, N. R., Birbiglia, G. V., Kittridge, M. G., MacAulay, C. I., & Espejo, I. S. (2010). Sandstone diagenesis and reservoir quality prediction: Models, myths, and reality. *American Association of Petroleum Geologists Bulletin*, 94(8), 1093–1132. <https://doi.org/10.1306/04211009123>
- Taylor, T. R., Lander, R. H., & Bonnell, L. M. (2022). Sandstone Petrography, Petrology, and Modeling. *SEPM Society for Sedimentary Geology*. <https://doi.org/10.2110/sepmcsp.13>
- Tobin, R. C., McClain, T., Lieber, R. B., Ozkan, A., Banfield, L. A., Marchand, A. M. E., & McRae, L. E. (2010). Reservoir quality modeling of tight-gas sands in Wamsutter field: Integration of diagenesis, petroleum systems, and production data. *AAPG Bulletin*, 94(8), 1229–1266. <https://doi.org/10.1306/04211009140>
- Ulmer-Scholle, D. S., Scholle, P. A., Schieber, J., & Raine, R. J. (2015). A Color Guide to the Petrography of Sandstones, Siltstones, Shales and Associated Rocks. *American Association of Petroleum Geologists*. <https://doi.org/10.1306/M1091304>
- Walderhaug, O. (1996). Kinetic Modeling of Quartz Cementation and Porosity Loss in Deeply Buried Sandstone Reservoirs1. *AAPG Bulletin*, 80(5), 731–745. <https://doi.org/10.1306/64ED88A4-1724-11D7-8645000102C1865D>
- Walderhaug, O., & Porten, K. W. (2022). How Do Grain Coats Prevent Formation of Quartz Overgrowths? *Journal of Sedimentary Research*, 92(10), 988–1002. <https://doi.org/10.2110/jsr.2021.049>
- Wallace, C.A., Dini, S.M., & Al-Farasani, A.A. (1997). Explanatory notes to the geological map of the Al Jawf Quadrangle, Kingdom of Saudi Arabia. *Geoscience Map GM-128C*, scale 1:250,000, sheet 29D. Deputy Ministry for Mineral Resources, Ministry of Petroleum and Mineral Resources, Kingdom of Saudi Arabia. 31 p

- Wooldridge, L. J., Worden, R. H., Griffiths, J., & Utley, J. E. P. (2017). Clay-coated sand grains in petroleum reservoirs: Understanding their distribution via a modern analogue. *Journal of Sedimentary Research*, 87(4), 338–352. <https://doi.org/10.2110/jsr.2017.20>
- Worden, R. H., & Burley, S. D. (2009). Sandstone Diagenesis: The Evolution of Sand to Stone. In *Sandstone Diagenesis* (Issue March). <https://doi.org/10.1002/9781444304459.ch>
- Worden, R. H., Armitage, P. J., Butcher, A. R., Churchill, J. M., Csoma, A. E., Hollis, C., Lander, R. H., & Omma, J. E. (2018). Petroleum reservoir quality prediction: overview and contrasting approaches from sandstone and carbonate communities. Geological Society, London, Special Publications, 435(1), 1–31. <https://doi.org/10.1144/SP435.21>
- Worden, R. H., Armitage, P. J., Butcher, A. R., Churchill, J. M., Csoma, A. E., Hollis, C., Lander, R. H., & Omma, J. E. (2018). Petroleum reservoir quality prediction: overview and contrasting approaches from sandstone and carbonate communities. In P. J. Armitage, A. R. Butcher, J. M. Churchill, A. E. Csoma, C. Hollis, R. H. Lander, J. E. Omma, & R. H. Worden (Eds.), *Reservoir Quality of Clastic and Carbonate Rocks: Analysis, Modelling and Prediction* (Vol. 435, p. 0). Geological Society of London. <https://doi.org/10.1144/SP435.21>
- Worden, R., & Morad, S. (2000). Quartz Cementation in Oil Field Sandstones: A Review of the Key Controversies. *Spec. Publ. Int. Assoc. Sed.*, 29, 1–20. <https://doi.org/10.1002/9781444304237.ch1>
- Worden, R., & Morad, S. (2009). Clay Minerals in Sandstones: Controls on Formation, Distribution and Evolution. In *Clay Mineral Cements in Sandstones* (Vol. 34, pp. 1–41). <https://doi.org/10.1002/9781444304336.ch1>
- Ye, J., Afifi, A., Rowaihy, F., Baby, G., De Santiago, A., Tasianas, A., Hamieh, A., Khodayeva, A., Al-Juaied, M., Meckel, T. A., & Hoteit, H. (2023). Evaluation of geological CO₂ storage potential in Saudi Arabian sedimentary basins. *Earth-Science Reviews*, 244, 104539. <https://doi.org/https://doi.org/10.1016/j.earscirev.2023.104539>

CHAPTER 6

EXPERIMENTAL STUDY OF CHLORITE AUTHIGENESIS: INSIGHTS FROM K-FELDSPAR PRECURSOR

6.1. Abstract

Chlorite, a critical diagenetic clay mineral, significantly influences porosity and permeability in deeply buried sandstone reservoirs. Authigenic chlorite developed from various clay and non-clay mineral precursors. Although chlorite formation from clay precursors is well-studied, its direct formation from non-clay precursors, such as K-feldspar, remains underexplored. Here, we present the first systematic hydrothermal-reactor experiments demonstrating chlorite authigenesis from K-feldspar in an arkosic sandstone (Subbat Member, Jauf Formation, NW Saudi Arabia). Closed-system autoclave experiments were conducted at 80–250 °C and ~10–16 MPa for 2–4 weeks, with a fluid-to-rock ratio of 10:1, using natural Red Sea water and synthetic Mg-rich brine. Integrated petrographic, mineralogical and geochemical analyses reveal a multistage reaction pathway for chlorite authigenesis: (1) dissolution of detrital K-feldspar, kaolinite, and hematite cements from 80 °C releases Al, Si, K, and Fe into the reacting fluid; (2) nucleation of smectite occurs at ~150 °C, forming honeycomb and grain-coating textures; (3) smectite transforms into well-crystallized chlorite between 200–250 °C via a dissolution–precipitation mechanism, with fluid chemistry dictating Fe vs. Mg enrichment; and (4) silica released from feldspar and kaolinite dissolution precipitates as quartz overgrowths on detrital quartz. Continuous chlorite grain coatings inhibit quartz cementation, preserving intergranular porosity, whereas pore-filling chlorite reduces microporosity from 0.6% to 0.5%, underscoring the importance of chlorite texture and distribution for reservoir quality. These findings provide detailed insights into the K-feldspar-to-chlorite

conversion through a smectite intermediary phase, with significant implications for predicting reservoir quality in K-feldspar-rich sandstone formations worldwide.

6.2. Introduction

Clay minerals, particularly chlorite, play a pivotal role in determining the reservoir quality of deeply buried sandstones by influencing porosity and permeability (Heald and Larese, 1974; Pittman et al., 1992; Bjørlykke, 1998; Lander and Walderhaug, 1999; Worden and Burley, 2009; Worden and Morad, 2009; Ajdukiewicz and Larese, 2012; Oluwadebi et al., 2018; Worden et al., 2018; Al-Ramadan, 2021; Barshep and Worden, 2022; Bello et al., 2022a; Salisu et al., 2024a). Their formation and distribution are governed by a complex interplay of factors, including temperature, fluid chemistry, time, and the nature of detrital precursors (Bjørlykke et al., 1989; Bjørlykke, 1998; Worden and Burley, 2009; Worden and Morad, 2009). Among these precursors, potassium feldspar (K-feldspar) is abundant in sedimentary environments and undergoes various diagenetic transformations (Huang et al., 1986; Daneshvar and Worden, 2018; Yuan et al., 2019). While the alteration of K-feldspar to illite and smectite has been extensively studied (Lahann, 1980; Nadeau and Bain, 1986; Klopogge et al., 1999; McKinley et al., 1999; Niu et al., 2000; Haile et al., 2015; Daneshvar and Worden, 2018), its transformation into chlorite under hydrothermal conditions remains underexplored.

Chlorite, a hydrous aluminosilicate clay mineral rich in iron and magnesium, is one of the most widespread clay minerals in siliciclastic sedimentary basins, forming across a wide range of temperatures (Worden and Morad, 2009; Deer et al., 2013; Beaufort et al., 2015; Worden et al., 2020). It is a critical component in the diagenesis of sandstone reservoirs due to its impact on porosity and permeability (Ehrenberg, 1993; Aagaard et al., 2000a; Worden et al., 2020). Chlorite occurs in sandstones in either detrital or authigenic forms (Worden et al., 2020), with authigenic

chlorite, especially when present as grain coatings, playing a significant role in preserving reservoir quality (Chen et al., 2011; Worden et al., 2018; Li et al., 2021). Grain-coating chlorite inhibits quartz cementation, a process that typically reduces porosity in deeply buried sandstones subjected to high temperatures and pressures (Ehrenberg, 1993; Anjos et al., 1999; Aagaard et al., 2000b; Bloch et al., 2002; Ajdukiewicz and Lander, 2010; Kordi, 2013; Dutton et al., 2018; Stricker and Jones, 2018; Worden et al., 2020; Charlaftis et al., 2021; Aro et al., 2023). This preservation mechanism is essential for maintaining economically viable porosity and permeability in hydrocarbon reservoirs, as evidenced by numerous studies. (Ehrenberg, 1993; Anjos et al., 1999; Durand et al., 2000; Bloch et al., 2002; Dowey et al., 2012; Griffiths et al., 2021; Bello et al., 2022b)

The formation of authigenic chlorite is controlled by a complex interplay of factors, including temperature, pressure, fluid chemistry, and the availability of precursor minerals such as berthierine, odinite, smectite, and kaolinite (Worden et al., 2020). Numerous studies have explored chlorite formation from these precursors under various diagenetic conditions (Ryan and Reynolds Jr, 1996; McKinley et al., 1999; Aagaard et al., 2000b; Beaufort et al., 2015; Haile et al., 2015; Bourdelle et al., 2021; Charlaftis et al., 2021). However, the transformation of K-feldspar, a common detrital mineral in arkosic sandstones, into chlorite remains largely understudied. Experimental studies simulating burial diagenesis have primarily focused on smectite illitization and chloritization from pre-existing clay minerals (Eberl and Hower, 1977; Boles and Franks, 1979; Lahann, 1980; Roberson and Lahann, 1981; Johnston and Miller, 1984; Pytte and Reynolds, 1989; Whitney, 1990; Huang et al., 1993; Small, 1994; Meunier et al., 2000; Beaufort et al., 2001; Robinson et al., 2002; Mosser-Ruck and Cathelineau, 2004; Lanson et al., 2009; McCarty et al., 2009; Al-Ramadan, 2014; Mosser-Ruck et al., 2016; Salisu et al., 2025b), with limited attention

devoted to non-clay precursors like feldspars (Huang et al., 1986; Haile et al., 2015; Yuan et al., 2019). Given that feldspar dissolution releases key elements such as aluminum (Al), potassium (K), and silicon (Si), all crucial for the crystallization of new clay phases, understanding K-feldspar's reactivity in natural diagenetic fluids is vital for reconstructing the genesis of authigenic clay minerals. The mode of occurrence of the resultant chlorite (e.g., grain-coating versus pore-filling) is equally significant due to its direct implications for reservoir quality.

The present study aims to experimentally investigate chlorite formation from K-feldspar and kaolinite under simulated burial conditions, using an arkosic sandstone from the Early Devonian Subbat Sandstone Member of the Jauf Formation (NW Saudi Arabia) as the starting material, which is rich in K-feldspar and kaolinite. Through controlled hydrothermal experiments, combined with integrated petrographic, mineralogical, and geochemical analyses, this study seeks to: (1) elucidate the role of detrital K-feldspar in chlorite authigenesis; (2) investigate the mechanisms of K-feldspar conversion to chlorite; (3) assess the presence of smectite as an intermediate phase; (4) evaluate the impact of chlorite formation on quartz cement inhibition and reservoir quality; and (5) explore the influence of fluid composition on clay transformation pathways.

6.3. Geological Background of the Sample

This study uses an outcrop sample from the Early Devonian Subbat Sandstone Member of the Jauf Formation, located near Al Huj in northwestern Saudi Arabia. During the Early Devonian, the Arabian Plate experienced multiple transgressive and regressive periods (Konert et al., 2001), which are well-represented in the Jauf Formation outcrops. These outcrops exhibit cyclic alternations of siliciclastic and carbonate deposits. Sediments prograded as thick clastic wedges from the Arabian-Nubian Shield toward the north, northeast, and east (Rahmani et al., 2002, 2019). However, sediment supply was less pronounced in the northern Arabian Plate, as indicated by

stromatolite intervals within the Jauf Formation (Algheryafi et al., 2022). The Devonian Jauf Formation was deposited during three third-order sequences, correlatable across the northern and eastern Arabian Plate (Rahmani et al., 2019). Lithologically, the formation is subdivided into five members: three siliciclastic-dominated units and two carbonate-dominated units. This study focuses on a fine-grained, argillaceous, estuarine-channel sandstone from the Subbat Member of the Jauf Formation. The sample was selected due to its arkosic composition, characterized by abundant detrital K-feldspar with kaolinite and hematite cements. The sedimentology and diagenetic evolution of the Subbat Sandstone Member have been previously documented by Algheryafi et al. (2022) and Salisu et al. (2024).

6.4. Methodology

6.4.1. Hydrothermal reactor experiments

The hydrothermal reactor experiments were conducted using a LABE fixed-head reactor autoclave system (LABE Instruments Co., Shanghai, China), connected to a nitrogen gas cylinder (Fig. 6.1). The autoclave is equipped with stainless steel micro-stirred reactors featuring controls for temperature, pressure, and elapsed time. The reactor vessels have a capacity of up to 500 mL and can withstand heating to a maximum temperature of 500°C and pressures up to 40 MPa. Temperature regulation is achieved through a Smart PID algorithm control system, ensuring an accuracy of $\pm 0.1^\circ\text{C}$. Before the start of the experiments, a freshly collected sample of Subbat sandstone was divided into eight portions of 20 grams each. For each experiment, 20 grams of the sample were enclosed in a 50- μm stainless steel mesh and transferred to the bottom of the reactor vessels. The vessels were then filled with 200 mL of the respective experimental solutions (Table 1: Red Sea water for experiments 1–6; and 0.1 M solutions of NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for experiment 7), leaving approximately 60% headspace at room temperature to

achieve a 10:1 fluid-to-rock ratio. The reactors were sealed and pressurized with approximately 6 MPa of nitrogen gas were subsequently heated at a rate of 10 °C per minute to target temperatures ranging from 50 °C to 250 °C (Table 1). Although the initial injected pressure remained consistent across all experiments (~6 MPa at room temperature), it increased depending on the experimental temperature and reaction fluid, stabilizing at the final pressure after 1–2 hours. The experiments were maintained at the designated temperatures for periods ranging from 14 to 30 days under closed-system conditions, following the protocols established by Bello et al., (2025) and Salisu et al., (2025a, 2025b). Upon completion of each experiment, the reactors were switched off and allowed to cool to room temperature. The samples were then retrieved and air-dried. Additionally, post-experiment solutions were recovered and immediately analyzed for pH and subjected to total reflection X-ray fluorescence (TXRF) analysis, both conducted at room temperature.

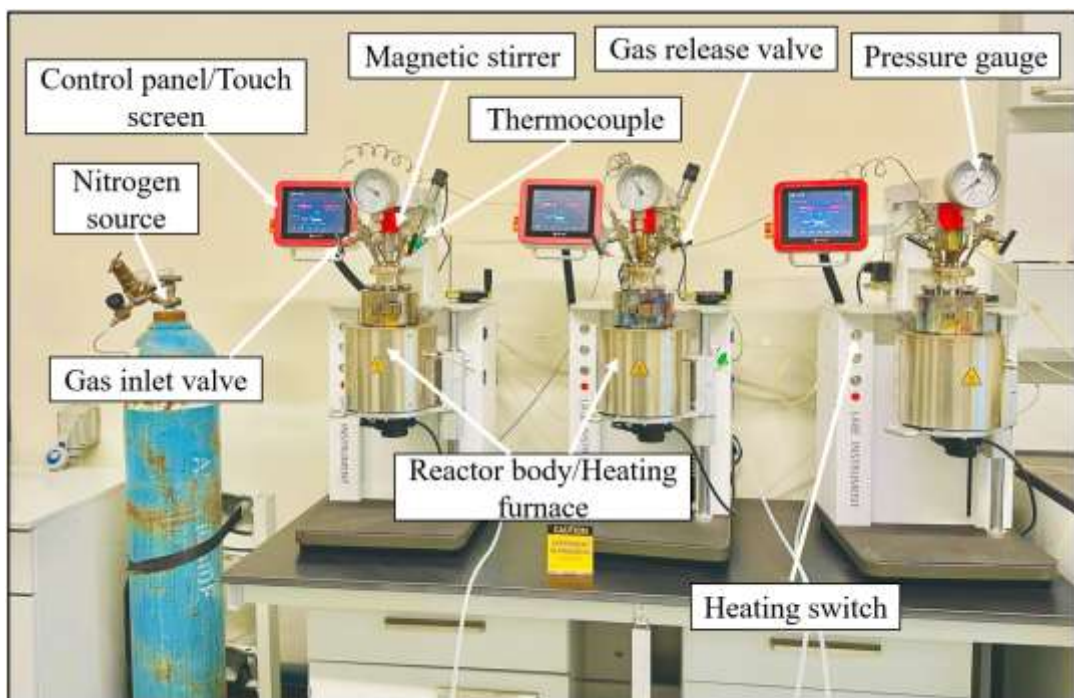


Figure 6.1. Photograph of the experimental setup employed in this study, highlighting the key components of the hydrothermal reactors.

Table 6. Conditions for the hydrothermal experiments

Experiment	Sample ID	Solution (M)	Temperature (°C)	Duration (weeks)	Final Pressure (MPa)
1	SW@80	Red Sea water	80	2	8.3
2	SW@100	Red Sea water	100	2	9.1
3	SW@150	Red Sea water	150	2	10.2
4	SW@200	Red Sea water	200	2	12.5
5	SW@250_1	Red Sea water	250	2	14.1
6	SW@250_2	Red Sea water	250	4	16.3
7	SF@250	0.1M NaCl, KCl, CaCl ₂ .2H ₂ O, MgCl ₂ .6H ₂ O	250	2	13.9

6.4.2. Analytical Techniques

6.4.2.1. TXRF Analysis

A benchtop S4 T-Star 800 total-reflection X-ray fluorescence (TXRF) spectrometer was used for multi-elemental analysis of the fluids recovered from the hydrothermal experiments. The instrument features a triple-excitation configuration, with a primary Mo-target microfocus tube at 17.5 keV, a secondary W-target microfocus tube at 35 keV, and an 8.4 keV multilayer-monochromator tertiary source, each operating under identical conditions (50 $\mu\text{m} \times 50 \mu\text{m}$ hotspot, up to 50 kV/50 W, air-cooled). The detector is a thermoelectrically cooled silicon drift detector (100 mm² active area; ≤ 149 eV resolution at Mn K α /100 kcps; >100 kcps maximum count rate; <10 % dead time at 40 kcps). Signals are processed through a 90 kcps spectroscopic amplifier and a 4096-channel ADC. The sample carousel holds up to 90 specimens in ten trays of nine positions each. Sample carriers were siliconized quartz discs (30 mm diameter, 3.0 ± 0.1 mm thickness). Before analysis, discs were cleaned sequentially with acetone and a non-ionic detergent (RBS), then treated with 10 μL of a silicon-isopropanol solution to render the surface hydrophobic, ensuring optimal retention of the droplet during drying. Element-specific internal standardization was applied for each excitation mode. Analytical-grade Ga, Sc, and Pd stock solutions (200 mg/L) served as internal standards: Ga for Mo-excitation lines, Sc for W-L lines, and Pd for W-Bremsstrahlung lines. Samples were prepared by mixing 50 μL of the recovered fluid with 50 μL of the appropriate internal standard solution to yield a final internal standard concentration of 50 mg/L. Data reduction and peak deconvolution were performed using SPECTRA 7.0 software.

Method validation employed certified reference materials LGC6019 (River Thames water) and VHG-QWPTM-15 (WP Trace Metals), each analyzed in quadruplicate. For routine analyses, sample-standard mixtures were vortexed, and 10 μL aliquots were pipetted onto quartz discs and

dried at 70 °C for 10–15 minutes. All samples were run in duplicate, with a 1000-second acquisition time per sample to balance detection limits and throughput. This protocol enabled the simultaneous determination of over 30 elements, including major cations (Ca, Mg, P, S, Cl, K), transition metals (Mn, Fe, Ni, Cu, Zn), and trace elements (As, Br, Rb, Sr, Pb).

Thin section petrography.

Petrographic thin sections were prepared using conventional methods to evaluate the distribution of framework grains, detrital clay coatings, and authigenic minerals in both untreated and post-reacted samples. Observations were conducted using an Olympus BX53F polarized-light microscope to characterize mineralogical textures and spatial relationships.

6.4.2.2. Scanning Electron Microscopy–Energy Dispersive Spectroscopy (SEM-EDS)

Pre and post-experiment samples were analyzed using a Zeiss Gemini 550 scanning electron microscope operated in secondary electron (SE) and backscattered electron (BSE) modes. Before analysis, samples were sputter-coated with a 30 nm palladium-gold layer (Quorum QR150R) to ensure conductivity, then analyzed at 10–15 kV accelerating voltage and 1–2 nA probe current. Elemental composition of detrital and authigenic phases was determined via an Oxford Instruments Aztec EDS system, facilitating morphological and mineral-chemistry correlations.

6.4.2.3. Wavelength-Dispersive X-Ray Fluorescence (WD-XRF)

Bulk oxide chemistry was quantified using a PANalytical Zetium WD-XRF spectrometer. Exactly 1.00 g of finely ground sample was fused with 10.00 g of anhydrous lithium metaborate flux ($\text{LiBO}_2\text{:Li}_2\text{B}_4\text{O}_7 = 49.75\text{:}49.75\text{:}0.50$) in platinum-gold crucibles using a Classie OX Advanced fusion system. Fusion protocols included heating to 500°C (2 min) followed by incremental ramping to 1125°C (4.5 min/step) under continuous agitation. The resulting glass disks were cast, cooled, and analyzed using a 4 kW Cu anode X-ray tube and five analyzing crystals (PE002,

LiF200, PX-1, Ge11, LiF220) to optimize detection of major and trace oxides. Analytical accuracy was validated using ISO 17034-accredited WROXI reference materials, with data processed via PANalytical SuperQ software, using the detailed procedures outlined by Salisu et al. (2025).

6.4.2.4. *XRD X-Ray Diffraction (XRD) Analysis (Bulk and Clay fraction)*

The mineralogy of bulk samples and the clay fraction (<2 µm) from both starting and post-experiment samples was analyzed using X-ray diffraction (XRD) on a Malvern Empyrean PANalytical diffractometer equipped with Ni-filtered Cu K α radiation (PANalytical, Almelo, Netherlands). For bulk mineralogy, samples were air-dried in a fume hood at room temperature and ground to <10 µm using a Retsch RM 200 mortar grinder (RETSCH, Haan, Germany). The powders were backloaded into 27 mm sample holders (Malvern Panalytical), leveled with a glass slide, and excess material was removed with a pin brush to ensure a smooth surface. Bulk XRD analysis was conducted at 45 kV and 40 mA, scanning from 4.5° to 70° 2 θ with a step size of 0.013°, a counting time of 8.9 seconds per step, and a scan speed of 0.38°/s. Minerals were identified by comparing diffractograms with the International Centre for Diffraction Data Powder Diffraction File (ICDD PDF-2024).

The clay fraction (<2 µm) was isolated through a combination of gravity settling, ultrasonication, and centrifugation. Five grams of pre- and post-experiment sandstone bulk samples were soaked in deionized water overnight and gently disaggregated and ground using a mortar and pestle, while preserving clay mineral integrity. The disaggregated sample was dispersed in 100 mL of deionized water, ultrasonicated for 20 minutes with vigorous stirring every 5 minutes, and coarser particles were removed by gravity settling. The supernatant containing the clay fraction was concentrated by centrifugation at 5000 rpm for 15 minutes (Wooldridge et al., 2017). Drops of the clay slurry

were pipetted onto SI SUBSTR 32 MM shallow-well sample holders (Malvern Panalytical) to create oriented mounts, which were air-dried overnight in a fume hood at room temperature.

Clay fractions were analyzed in three states: (1) air-dried untreated, (2) solvated with ethylene glycol at 70°C for 20 hours to identify expandable clays, and (3) heated at 550°C for 1 hour to differentiate kaolinite from chlorite based on thermal stability (Moore & Reynolds, 1998). XRD scans covered a 4°–40° 2 θ range with a step size of 0.013° and a scan speed of 0.05°/s. Clay minerals were identified using the search-match module in HighScore Plus (v. 4.9), referencing ICDD PDF-4-2024 and supplementary data from Moore and Reynolds, (1998).

6.4.2.5. *Microcomputed Tomographic analyses (XCT)*

A 5 mm-diameter cylindrical core was prepared from the starting material and scanned by microcomputed tomography both before and after Experiment 6 (seawater, 250 °C, 1 month) to monitor porosity evolution. X-ray μ CT data were acquired on a Thermo Fisher Heliscan MK1 system at 95 kV tube voltage, 50 μ A target current, and 2.1 s exposure time. A 360° circular scan trajectory with 3,600 projections yielded a 3.3 μ m isotropic voxel size for high-resolution imaging. From the resulting cylindrical tomograms, cuboidal subvolumes were extracted, and a size cutoff was applied to isolate and visualize interconnected pore structures. The data were processed in Avizo (Thermo Fisher) using an AI-based trainable segmentation workflow that included shear correction, removal of bad slices, alignment correction, cropping, FFT filtering, non-local means denoising, and intensity normalization. Porosity values were then calculated from the segmented volumes. All scanning and image-processing procedures followed the protocols of Salisu et al. (2024b) and Alhindi et al. (2025), ensuring consistency and reproducibility.

6.5. Results

6.5.1. Composition of the Starting Material

The Subbat Sandstone was selected for this study because of its uniform arkosic composition, high K-feldspar content, appreciable kaolinite abundance, and trace hematite cement, key ingredients for authigenic chlorite formation. This fine-grained, moderately well-sorted sandstone has a mean grain size of 0.13 mm. Petrographic point-count analysis of the unreacted sandstone reveals that it consists predominantly of detrital, monocrystalline quartz (34.0 %; Fig. 6.2A), K-feldspar (19.6 %), mica (2.2 %), and plagioclase (1.0 %). Authigenic hematite occurs as a pore-filling cement (0.3 %; Fig. 6.2B). Kaolinite averages 5.2 % and is chiefly found as a pore-filling clay (Fig. 6.2A, C, D), often closely associated with partially to pervasively dissolved K-feldspar where it appears as grain-replacive cement (Fig. 6.2C). Illite is present both as a grain-coating phase (4.7 %) and as a pore-filling cement (2.3 %). Overall, the sandstone is dominantly arkosic and exhibits an average intergranular porosity of 25 %. SEM observations of the starting material show authigenic kaolinite with a characteristic booklet morphology and grain-replacive textures (Fig. 6.2C, D). Euhedral, rhombic K-feldspar overgrowths occur on detrital K-feldspar grains adjacent to pore-filling kaolinite (Fig. 6.2E). EDS analyses confirm that these overgrowths are rich in O, Si, Al, and K (Fig. 6.2F). Results from WD-XRF oxides analyses (Table 2; Fig. 6.3) indicate that SiO₂ (80.83 wt%), Al₂O₃ (10.94 wt%), and K₂O (5.69 wt%) are the dominant elements in the starting material. Minor amounts of Fe₂O₃, MgO, and ClO₂ are also present, while Rb₂O, P₂O₅, SO₃, SrO, and TiO₂ occur in trace quantities (Table 2). Bulk mineralogy analyses (XRD) further reveal that the pre-reacted sediment is dominantly composed of quartz, orthoclase, and kaolinite (Fig. 6.4).

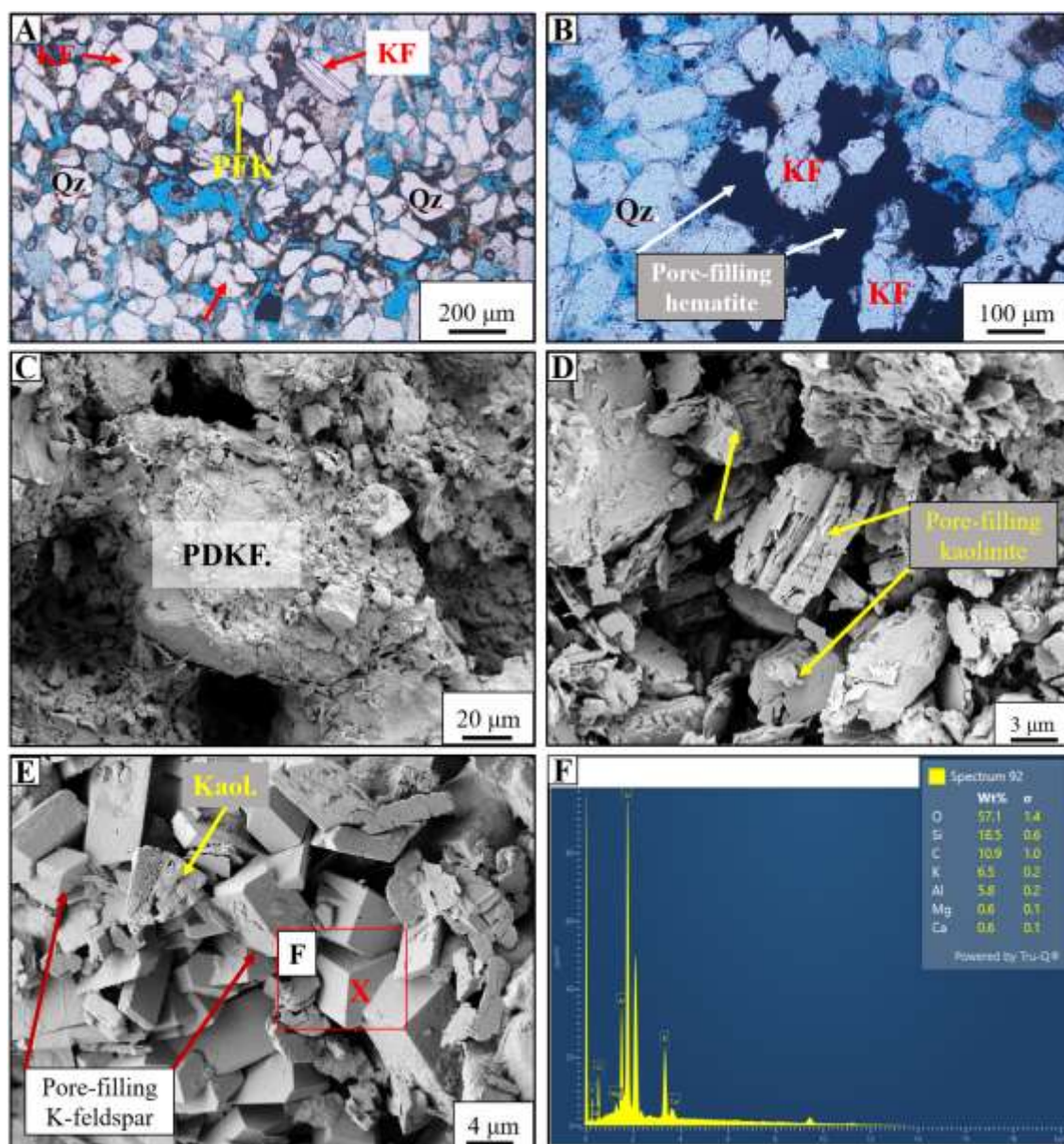


Figure 6.2. Petrographic images showing the framework grains and cements of the pre-experimental Subbat sandstone sample. A-B) Thin-section photomicrographs showing the quartz (Qz) and K-feldspar (KF) dominated nature of the sandstone and the occurrence of pore-filling kaolinite (PFK) and pore-filling hematite cements within the pores. C) SEM image of a partially dissolved K-feldspar (PDKF). D) SEM image displaying a booklet pore-filling kaolinite. E) SEM image showing the occurrence of well-developed pore-filling K-feldspar overgrowth enclosed by kaolinite (Kaol.). The red X label indicates the point at which the EDS shown in F was obtained. F) EDS spectra of the K-feldspar overgrowth in E.

6.5.2. Geochemical Analysis of pre-and post-reacted sample

The WD-XRF analyses of the post-reacted samples reveal the distributions of major oxides (SiO_2 , Al_2O_3 , K_2O , Fe_2O_3 , MgO), minor oxides (CaO , Na_2O , ClO_2), and trace oxides (Rb_2O , P_2O_5 , SO_3 , SrO , TiO_2) (Table 2). These results highlight compositional variations across different hydrothermal experiments (Fig. 6.3A–D). SiO_2 is consistently the most abundant oxide in all samples (Table 2), followed by Al_2O_3 and K_2O . Notably, the concentrations of SiO_2 and CaO decrease with increasing experimental temperature (Fig. 6.3A–B), whereas Fe_2O_3 (Fig. 6.3C) and MgO (Fig. 6.3D) increase as temperature rises. Although Al_2O_3 and K_2O fluctuate slightly, their overall concentrations remain stable throughout the experiments (Table 2). Among the trace oxides, TiO_2 , Rb_2O , and SO_3 are the most abundant, followed by P_2O_5 and SrO (Table 2).

Table 7. Results of the WDX-XRF analysis of the starting material and post-reacted samples [SM = Starting material]

Identification		Major and minor elements (wt %)								Trace elements (ppm)				
Experiment	Sample ID	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	ClO ₂	Rb ₂ O	P ₂ O ₅	SO ₃	SrO	TiO ₂
SM	SM@0	80.83	10.94	1.39	0.89	0.43	0.29	5.65	0.10	190	340	500	180	2080
Exp. 1	SW@80	79.85	10.57	1.13	1.02	0.53	0.65	5.51	0.47	200	320	3360	180	2410
Exp. 2	SW@100	79.49	10.71	1.02	1.01	0.58	0.97	5.49	0.73	170	340	1610	170	2370
Exp. 3	SW@150	77.90	10.49	0.65	1.02	0.57	0.63	5.58	0.42	200	200	10940	280	2650
Exp. 4	SW@200	77.32	10.52	0.44	1.89	0.76	0.67	5.12	0.45	160	290	10770	350	2150
Exp. 5	SW@250_1	77.21	10.70	0.16	2.92	1.21	0.84	5.10	0.46	180	310	860	300	2210
Exp. 6	SW@250_2	77.28	10.88	0.12	3.85	1.45	0.71	4.44	0.44	210	310	1080	200	2260
Exp. 7	SF@250	77.66	10.93	0.16	2.59	1.28	0.26	5.29	0.48	230	300	2040	180	2350

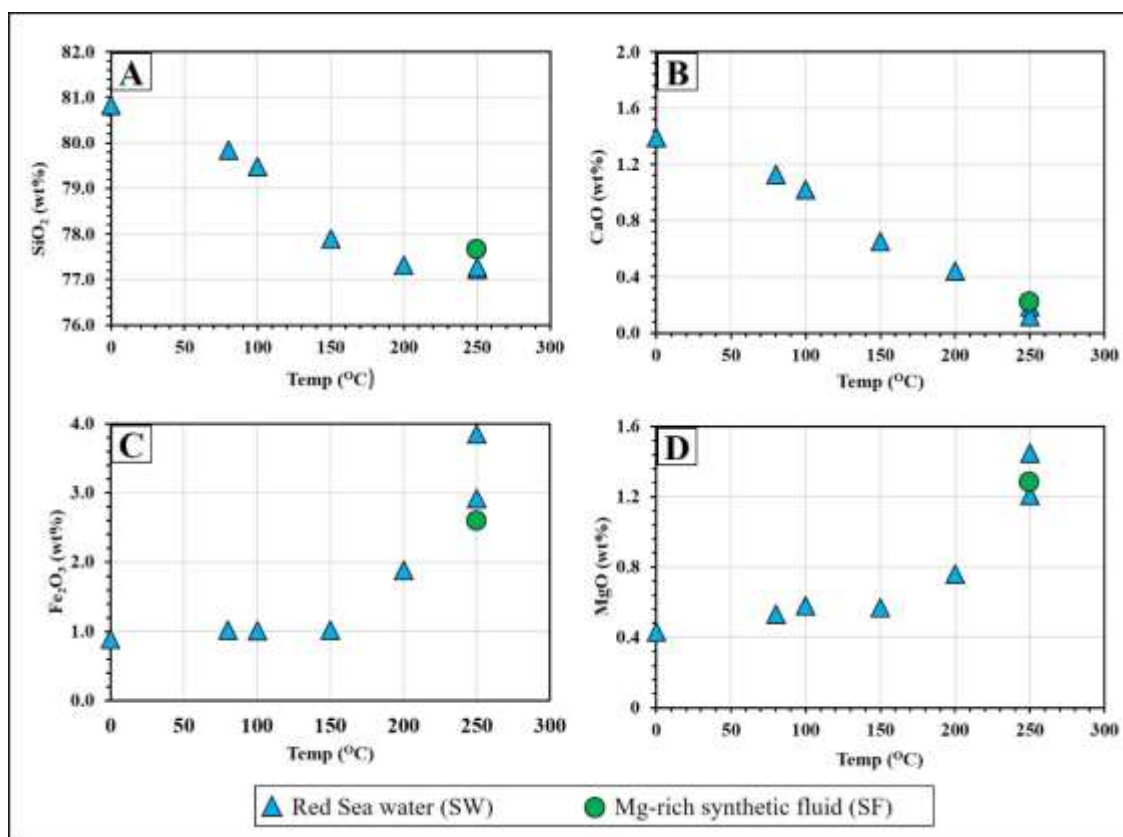


Figure 6.3. Plots of WD-XRF concentrations for SiO₂, CaO, Fe₂O₃, and MgO versus experimental temperatures illustrating their evolution as temperature increases during the hydrothermal experiments. Data points are color-coded according to the brine compositions used in each experiment.

XRD analyses of both the bulk samples (Fig. 6.4) and the clay fraction (<2 μm; Fig. 6.5) identify several clay minerals. In the bulk analyses, quartz, orthoclase, and kaolinite dominate in all experiments (Fig. 6.4). Examination of the oriented clay fraction reveals authigenic smectite and chlorite formation in Experiments 5–7 (Figs. 6.5B–D). The starting material (air-dried and treated) contains predominantly kaolinite and illite (Fig. 6.5A). Initial transformations of these clay

minerals and detrital K-feldspar occur in Experiments 1–2, with smectite first appearing in Experiment 3. Authigenic smectite and chlorite become evident by Experiments 5–7 (Figs. 6.5B–D). In the air-dried oriented powder, the primary smectite (001) peak appears at a d-spacing of 15.00 Å (Fig. 6.5B) and disappears upon heating to 550 °C for 1 hour. Although kaolinite peaks collapse and vanish upon heating in the starting material (Fig. 6.5A), they persist after heating in Experiments 5–7, indicating chlorite development during the hydrothermal experiments (Figs. 5B–D).

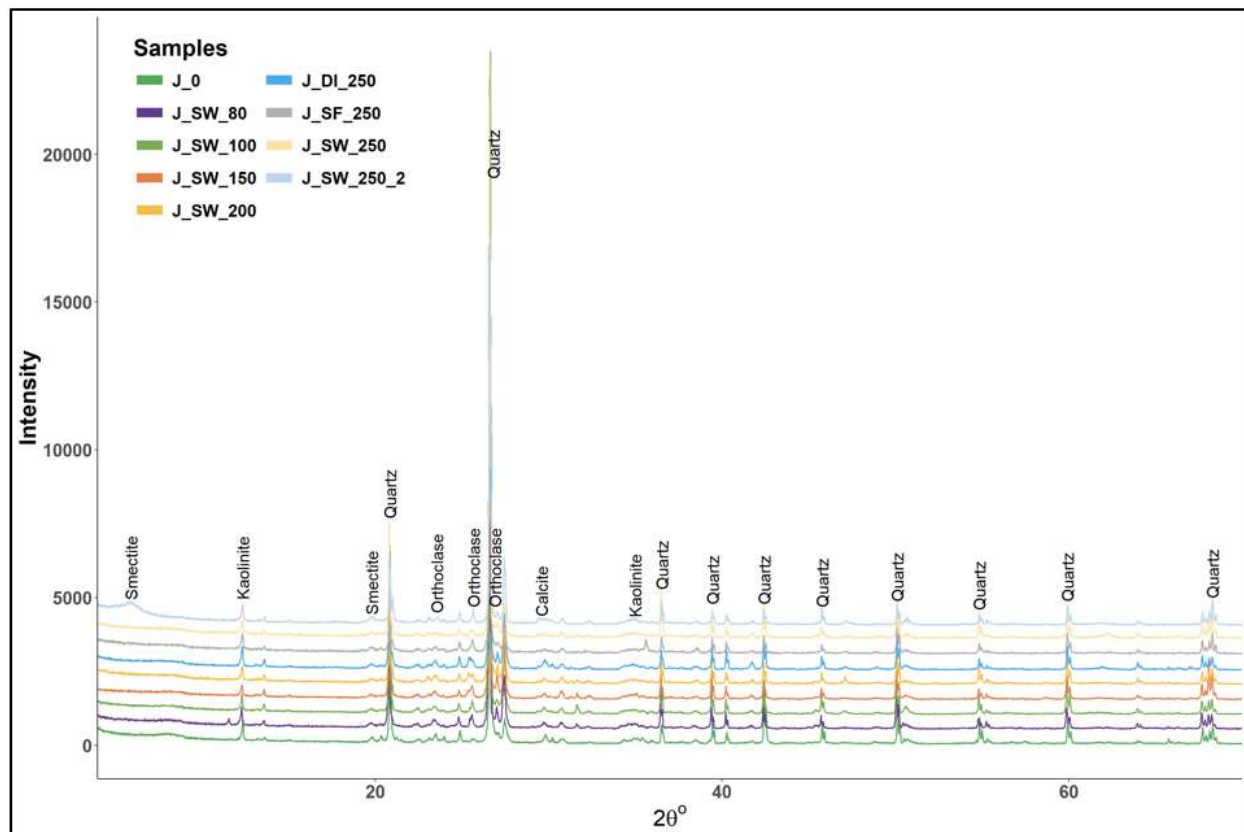


Figure 6.4. A stacked plot of the bulk XRD analysis presenting the diffractograms of the major minerals identified in the starting material (J_0) and experiments conducted using seawater (SW) and Mg-rich synthetic fluid (SF).

(Fig. 6.6). However, initial dissolution of kaolinite (Fig. 6.6A) and K-feldspar (Figs. 6.6B–E) was evident at these temperatures. In Experiment 1, kaolinite crystals exhibited numerous shallow depressions, indicating the onset of dissolution (Fig. 6.6A). Concurrently, detrital K-feldspar began to disintegrate early in Experiment 1 (Fig. 6.6B), progressing to partial and pervasive dissolution in Experiment 2 (Fig. 6.6C–D). Additionally, crystals of the K-feldspar overgrowth began dissolving during Experiment 2 (Fig. 6.6E). SEM analysis of the Experiment 2 sample also reveals the development of quartz overgrowth on detrital quartz grains (Fig. 6.6F).

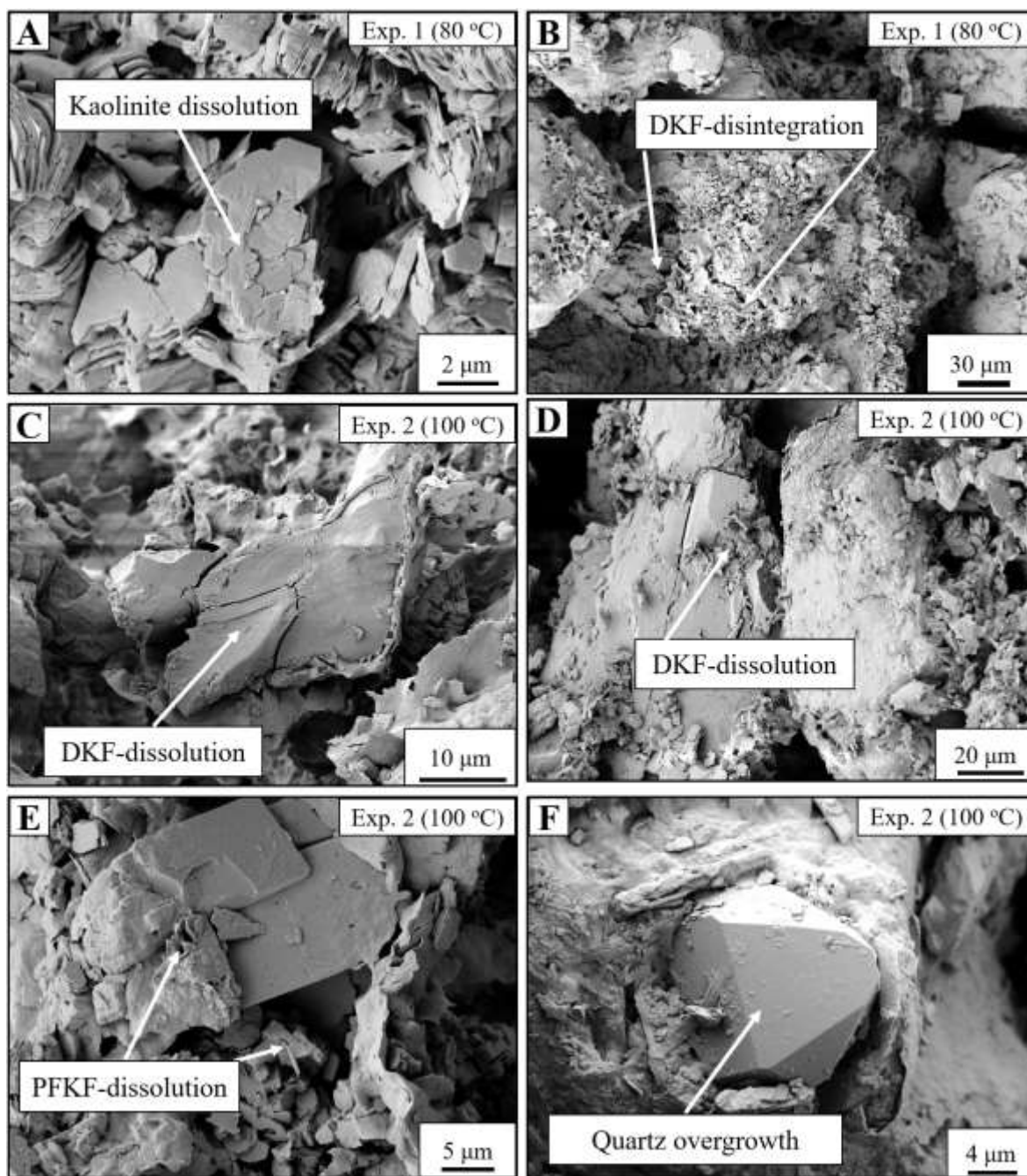


Figure 6.6. SEM images showing the early diagenetic features observed in Exp.1-2. A) Initial kaolinite dissolution in Exp. 1. B) early disintegration of detrital K-feldspar (DKF). C-D) Feldspar-dissolution pits and cracks indicating the dissolution of detrital K-feldspar (DKF). E) Initial dissolution of pore-filling K-feldspar (PFKF). F) Authigenic formation of quartz overgrowth in Exp. 2.

6.5.3.2. *Experiments 3 and 4.*

At 150 °C (Exp. 3), pervasive dissolution of kaolinite (Fig. 6.7A) and K-feldspar (Fig. 6.7B) continued. Notably, authigenic smectite began to form at this temperature (Figs. 6.7C–F). SEM analysis reveals pore-filling smectite platelets engulfing partially dissolved kaolinite (Fig. 6.7C) and the initial nucleation of thin, patchy, grain-coating smectite rims on detrital K-feldspar surfaces (Fig. 6.7D). Although smectite adjacent to K-feldspar was in the early stages of development, the platelets enveloping kaolinite were fully formed (Figs. 6.7E–F).

The formation and development of smectite adjacent to pervasively dissolved K-feldspar were continued in Experiment 4 (Fig. 6.8), conducted at 200 °C. SEM analysis revealed the growth of widespread grain-replacive, honeycomb-textured smectite that formed adjacent to and on the surfaces of pervasively dissolved detrital K-feldspar and overgrowth crystals (Fig. 6.8A, B). This authigenic smectite engulfs the disintegrating K-feldspar overgrowth (Fig. 6.8A, B). Additionally, grain-coating smectite on detrital grain surfaces became both extensive and continuous (Fig. 6.8C), with a significant increase in the percentage of detrital grains coated by authigenic smectite compared to Experiment 3.

Furthermore, at this temperature, chloritization of the newly formed smectite begins (Fig. 6.8D). SEM micrographs show authigenic smectite platelets gradually replaced by well-developed, rosette-like clusters of authigenic chlorites (Fig. 6.8D). Fully developed grain-coating chlorite platelets formed on the entire surfaces of detrital grains, adjacent to partially dissolved authigenic smectite (Fig. 6.8E). EDS analyses indicate that these authigenic chlorites are richer in Fe than Mg (Fig. 6.8F). This observation aligns with WD-XRF elemental analysis results, which showed an increase in Fe content from 0.89 wt% in the starting material to 1.89 wt% in Experiment 4 (Table 2).

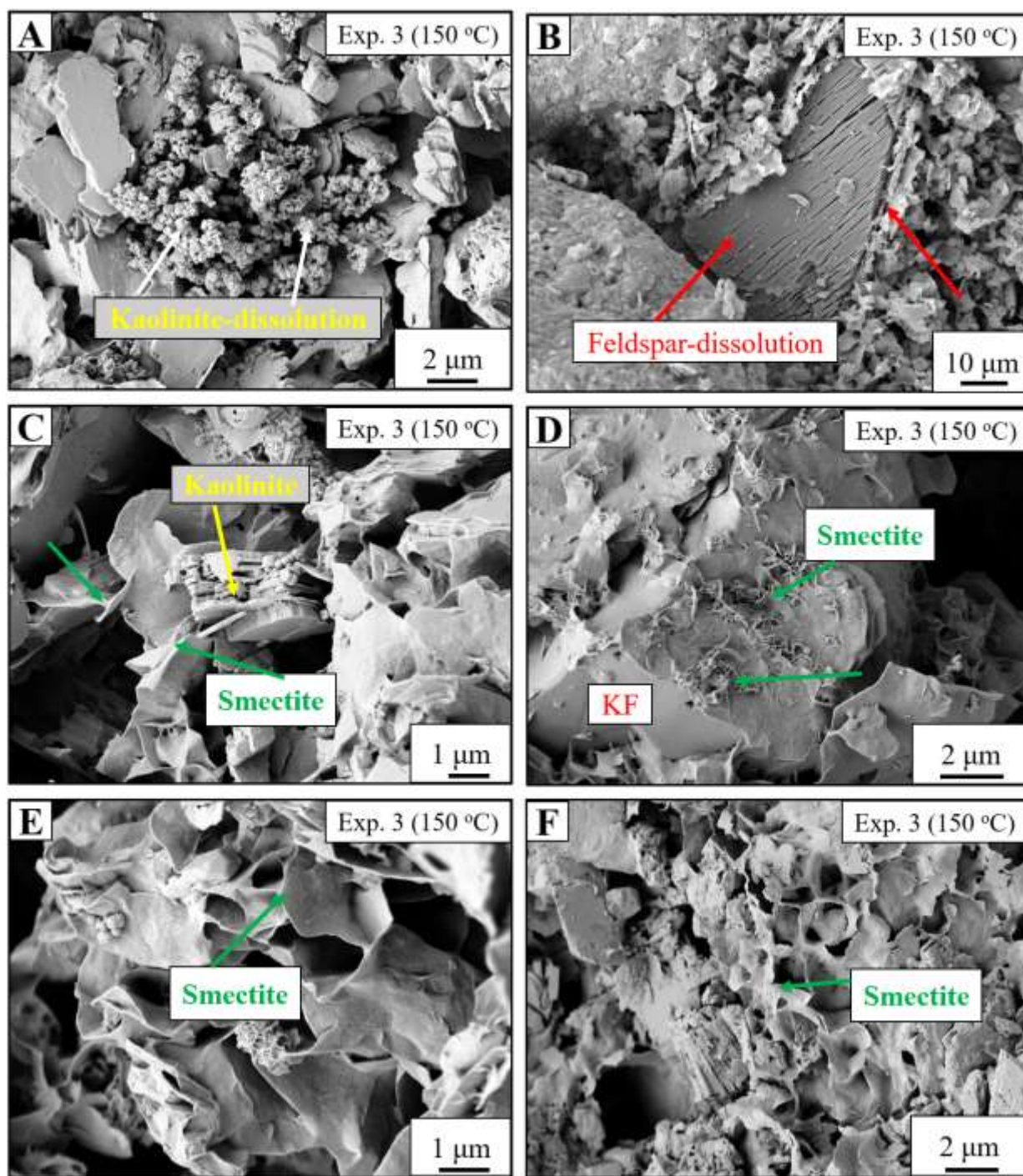


Figure 6.7. SEM images displaying the diagenetic features observed in Exp. 3, conducted at 150 °C. Pervasive dissolution of kaolinite (A) and K-feldspar (B). Authigenic precipitation of smectite encasing kaolinite. D) Incipient precipitation of smectite coats on detrital K-feldspar (KF). (E-F) Authigenic smectite platelets engulfing detrital pore-filling kaolinite.

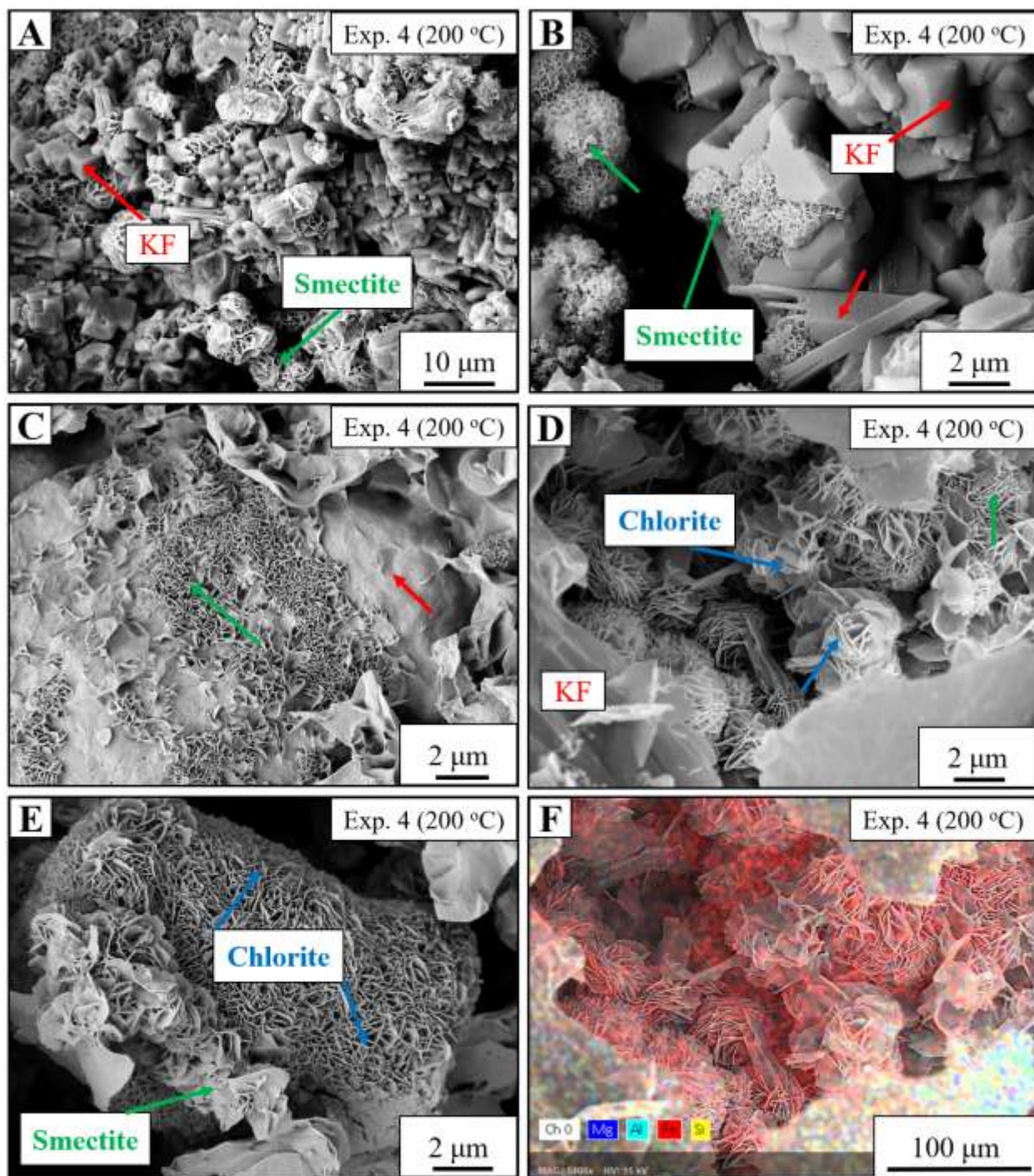


Figure 6.8. Main diagenetic characteristic of the authigenic clays observed in Experiment 4 (200 °C): A-B) SEM images showing the formation of grain-replacive honeycomb smectite adjacent to pervasively dissolved pore-filling K-feldspar (KF) overgrowth. C) SEM image illustrating the development of grain-coating smectite on detrital K-feldspar grain (red arrow). D) High-resolution

SEM image showing the authigenic formation of rosette to cabbage-head chlorite adjacent to smectite (green arrow). (E) SEM image displaying the occurrence of rosette chlorite entirely coating a detrital feldspar grain, and occurring adjacent to partially dissolved smectite. F) EDS map indicating the dominance of Fe over Mg in the newly formed chlorite.

6.5.3.3. *Experiments 5 and 6.*

Both experiments were carried out at 250 °C using natural Red Sea water, with durations of 14 days for Experiment 5 and one month for Experiment 6 (Table 1). SEM analysis of Experiment 5 reveals the incipient development of authigenic smectite forming on K-feldspar dissolution pits (Fig. 6.9A). As smectite grows, honeycomb-like aggregates encase partially dissolved K-feldspar (Fig. 6.9A–C). Chloritization of smectite continued in this experiment, leading to the partial to complete transformation of smectite into chlorite (Fig. 6.9A–C). The newly formed chlorite appears as aggregated plates of varying sizes (Fig. 6.9C). Authigenic quartz overgrowth also co-precipitates with smectite (Fig. 6.9D), and fully developed grain-coating chlorite platelets curl upward on detrital grains (Fig. 6.9E). EDS mapping shows that smectite is Mg-rich, whereas the synthesized chlorite is predominantly Fe-rich (Fig. 6.9F).

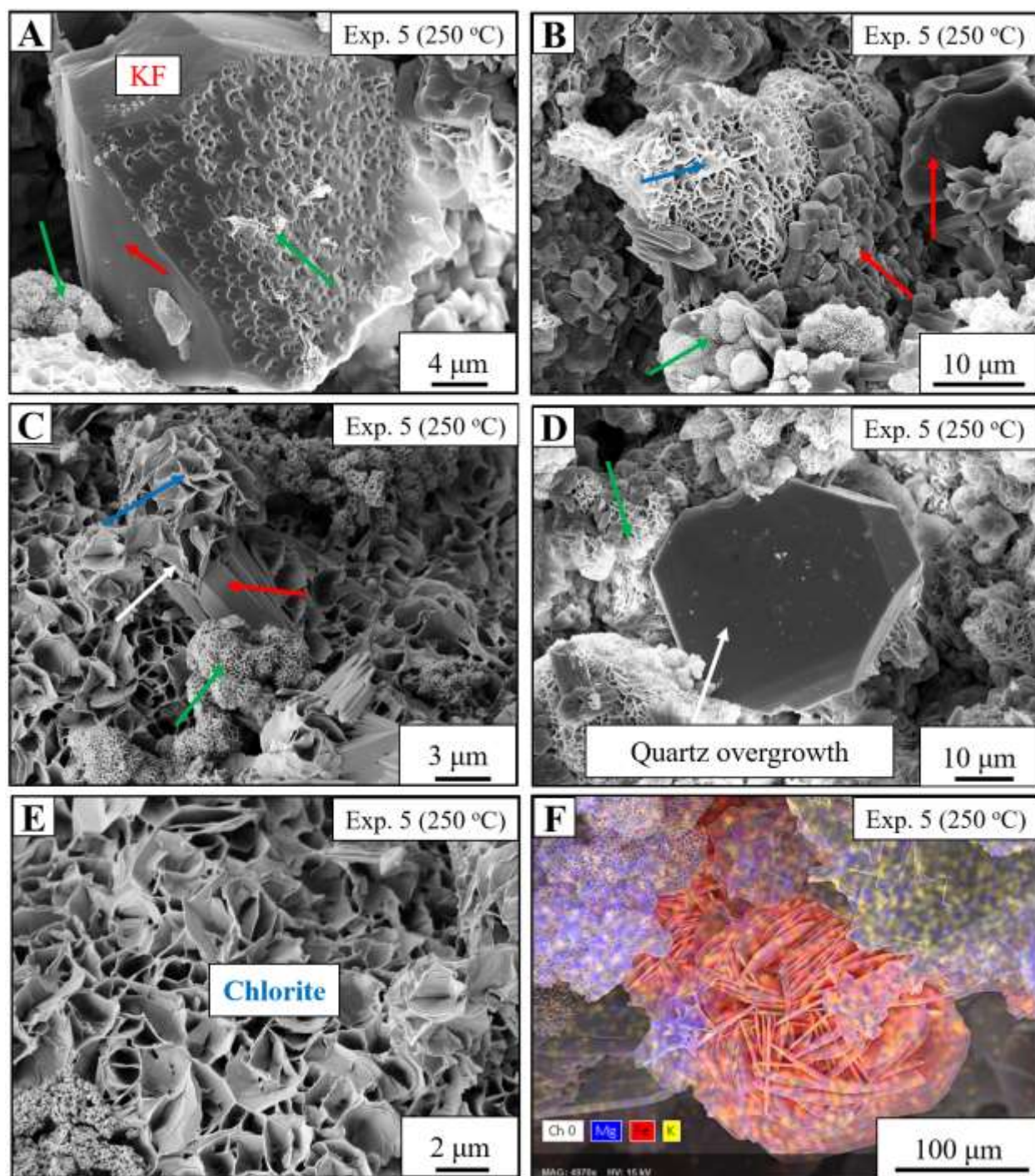


Figure 6.9. Diagenetic features observed in Experiment 5 (seawater, 2 weeks @ 250 °C): A) SEM image showing the incipient development of authigenic smectite (green arrow) on the surface of feldspar (KF) dissolution pits. B-C) SEM images showing the continuous development of

authigenic clays with chlorite (blue arrow) forming adjacent to honeycomb authigenic smectite (blue arrow), which encases partially dissolved K-feldspar (red arrow). D) SEM image showing authigenic quartz overgrowth co-precipitating with authigenic smectite. E) SEM image illustrating the formation of a continuous rosette chlorite coat on detrital K-feldspar. F) EDS map of authigenic smectite and chlorite. The map illustrates that authigenic smectite is Mg-rich, while the synthesized chlorite is Fe-rich.

With the longer duration of Experiment 6, similar features persist but with more advanced chloritization (Fig. 6.10). Chloritized smectite exhibits well-defined platelets (Fig. 6.10A–B) and rosette- to cabbage head-shaped morphologies (Fig. 6.10C–F). These platelets occur adjacent to K-feldspar (Fig. 6.10A) and honeycomb smectite (Fig. 6.10C). Rosette- and cabbage head-like chlorite coexist with honeycomb smectite beside pervasively dissolved K-feldspar (Fig. 6.10C–D). Thus, the primary difference between Experiments 5 and 6 is the completeness and refinement of chlorite morphology in Experiment 6 compared to Experiment 5.

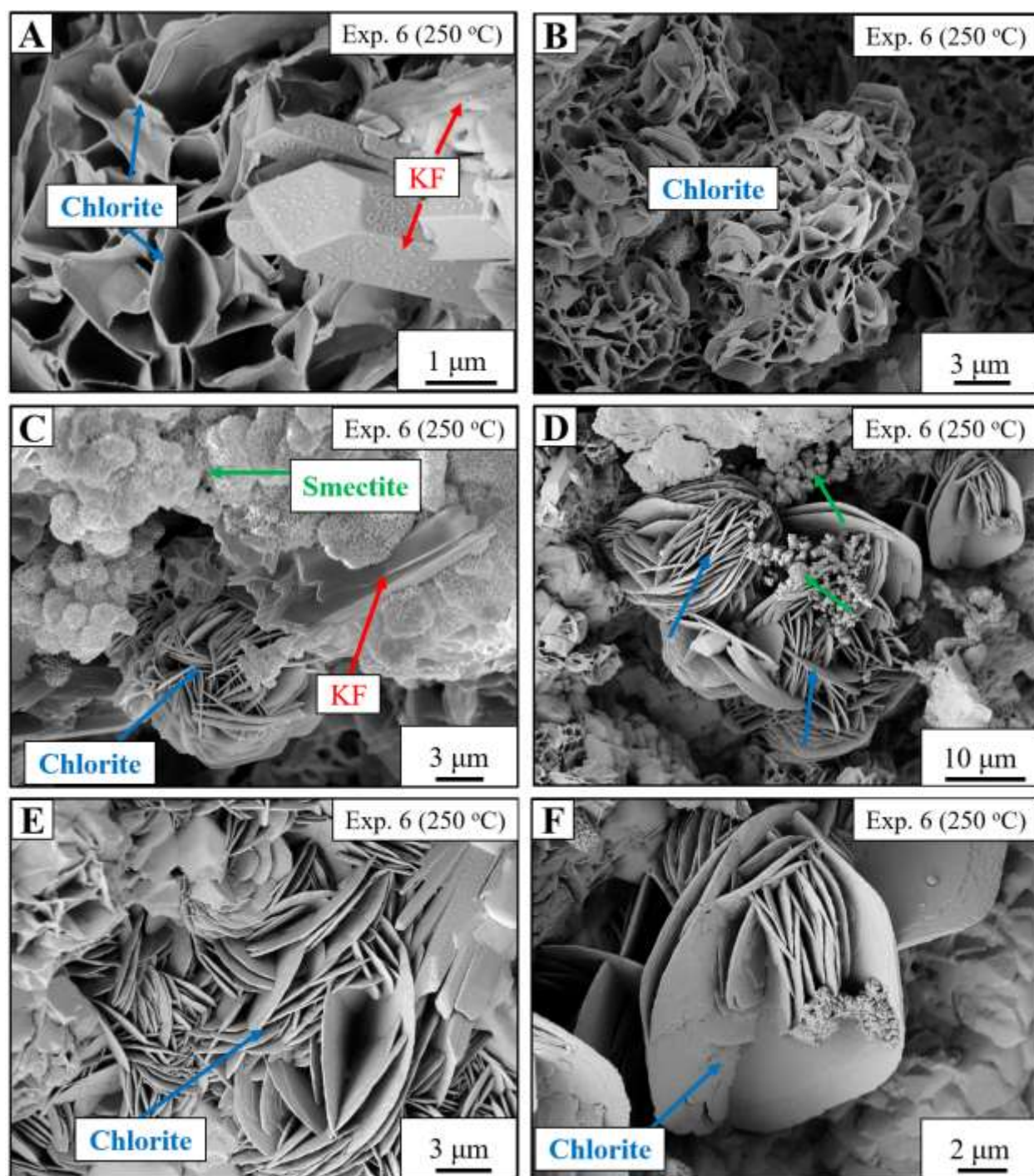


Figure 6.10. SEM images showing the main diagenetic characteristics observed in Experiment 6 (seawater, 1 month @ 250 °C): A-B) Rosette-like aggregates of chlorite developing adjacent to detrital K-feldspar (KF). C-D) Rosette to cabbage head like chlorite (blue arrow) co-existing with

authigenic honeycomb smectite (green arrow) adjacent to pervasively dissolved K-feldspar (red arrow).
E-F) Fully developed authigenic chlorite crystal.

6.5.3.4. *Experiment 7.*

Although Experiment 7 was conducted with a synthetic Mg-rich solution instead of natural Red Sea water, SEM, EDS (Fig. 6.11), and XRD (Figs. 6.4, 6.5) analyses reveal a similar sequence of diagenetic changes. SEM images show pervasive dissolution of K-feldspar and the initial growth of authigenic smectite crystals (Figs. 6.11A–B). This grain-replacive smectite displays a characteristic honeycomb texture (Fig. 6.11A) and progressively transforms into chlorite platelets via mixed-layer intermediates (Figs. 6.11C–E). The authigenic chlorite plates curl upward, forming continuous coatings on detrital grain surfaces adjacent to the partially dissolved smectite (Figs. 6.11D–E). EDS results of these chlorite coatings show they are relatively Mg-rich (Fig. 6.11F) compared to the predominantly Fe-rich chlorites produced in the seawater experiments (Fig. 6.9F).

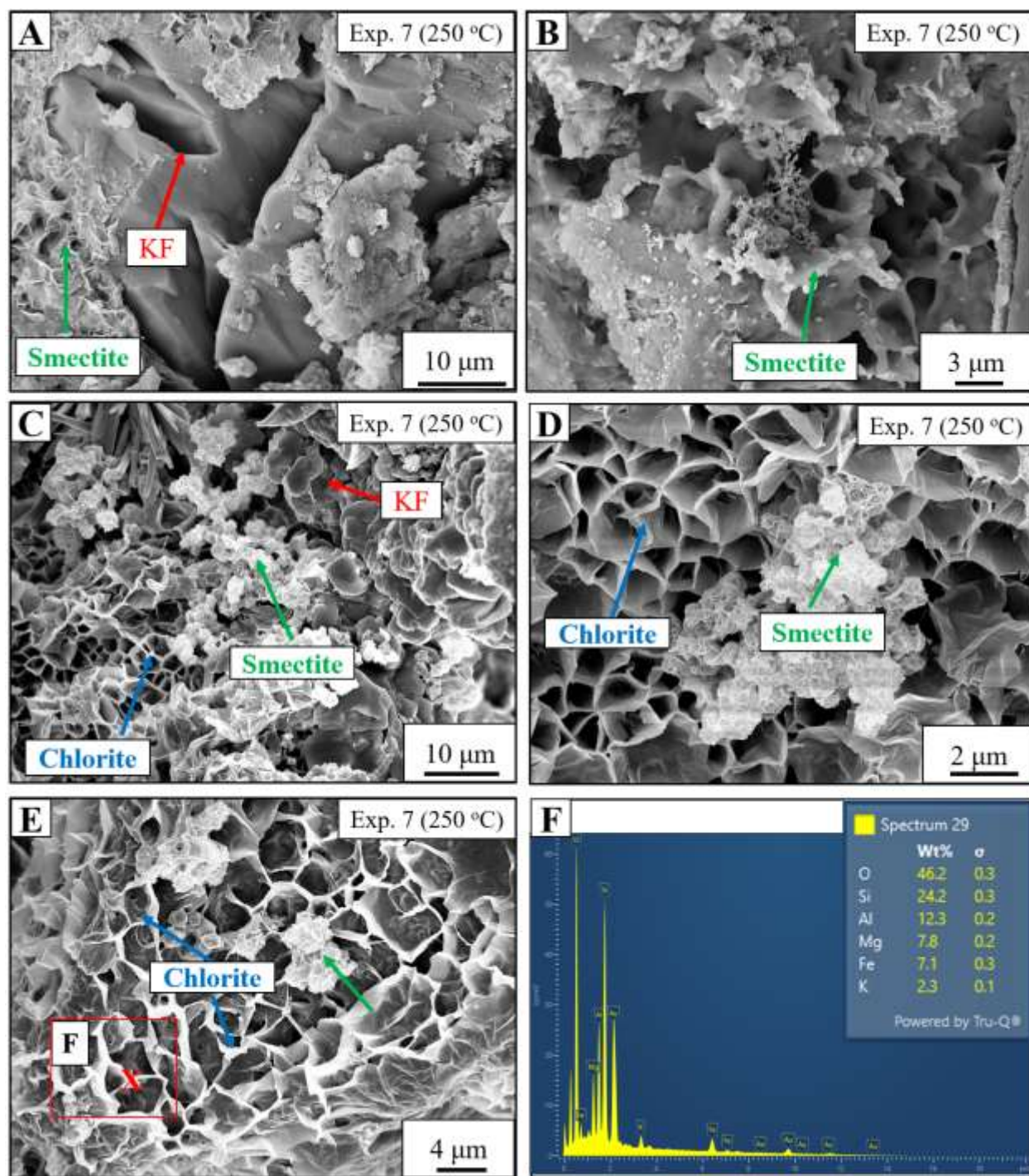


Figure 6.11. Main diagenetic features observed in Experiment 7 (synthetic fluid, 2 weeks @ 250 °C): A-B) SEM images indicating the pervasive dissolution of K-feldspar and the incipient development of authigenic smectite crystals. C-E) SEM images showing the formation of chlorite

adjacent to honeycomb smectite. The red X label indicates the point at which the EDS shown in F was obtained. F) EDS spectra of the chlorite shown in E. Note the Mg richness of the chlorite.

6.5.4. Mineralogical and porosity evolution

The diagenetic evolution of framework minerals, clay cement phases, and porosity was examined using QEMSCAN (Fig. 6.12) and X-ray microcomputed tomography (XCT; Fig. 6.13). QEMSCAN maps show that K-feldspar and quartz are the dominant detrital grains in the starting material (Fig. 6.12A), with kaolinite and illite acting as the primary clay cements. Intergranular pores are abundant, yielding a total porosity of 24.2%. Throughout all experiments (Figs. 6.12B–D), quartz and K-feldspar remained the principal detrital minerals, while authigenic smectite and chlorite appeared alongside kaolinite and illite. Chlorite and illite occurred both as grain-coating rims and pore-filling cements (Fig. 6.12C–D), whereas kaolinite predominantly occurs as pore-filling. Pervasive K-feldspar dissolution occurred adjacent to authigenic chlorite and smectite (Fig. 6.12D). As temperature increased, the abundance of pore-filling clays and dissolved K-feldspar increased, leading to a progressive decrease in intergranular porosity (Figs. 6.12B–D).

Micropore development within dissolved K-feldspar and clay-mineral matrices was assessed via XCT (Fig. 6.13). Both pre- and post-experimental scans reveal isolated pore networks (Figs. 6.13A–D), likely enhanced by dissolution of K-feldspar and kaolinite. Despite analyzing the same sample before and after treatment, microporosity in the segmented volume decreased subtly from 0.6% to 0.5% (Figs. 6.13B–F).

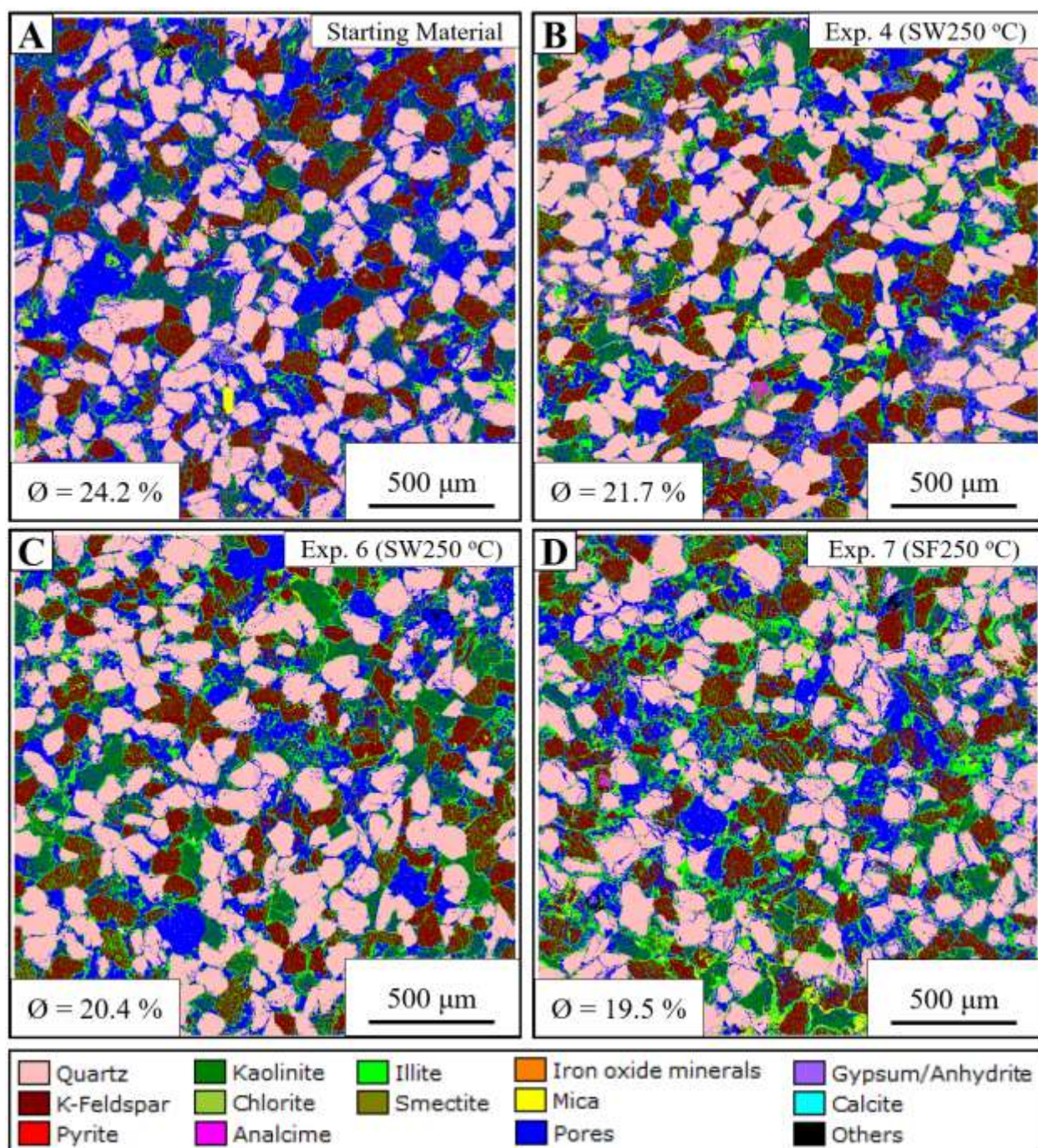


Figure 6.12. QEMSCAN mineralogical maps displaying the occurrence and distribution of detrital grains and clay mineral cements in the starting material (A) and selected experiments (B-D). Note the increasing amount of clay minerals replacing K-feldspar grains across the experiments

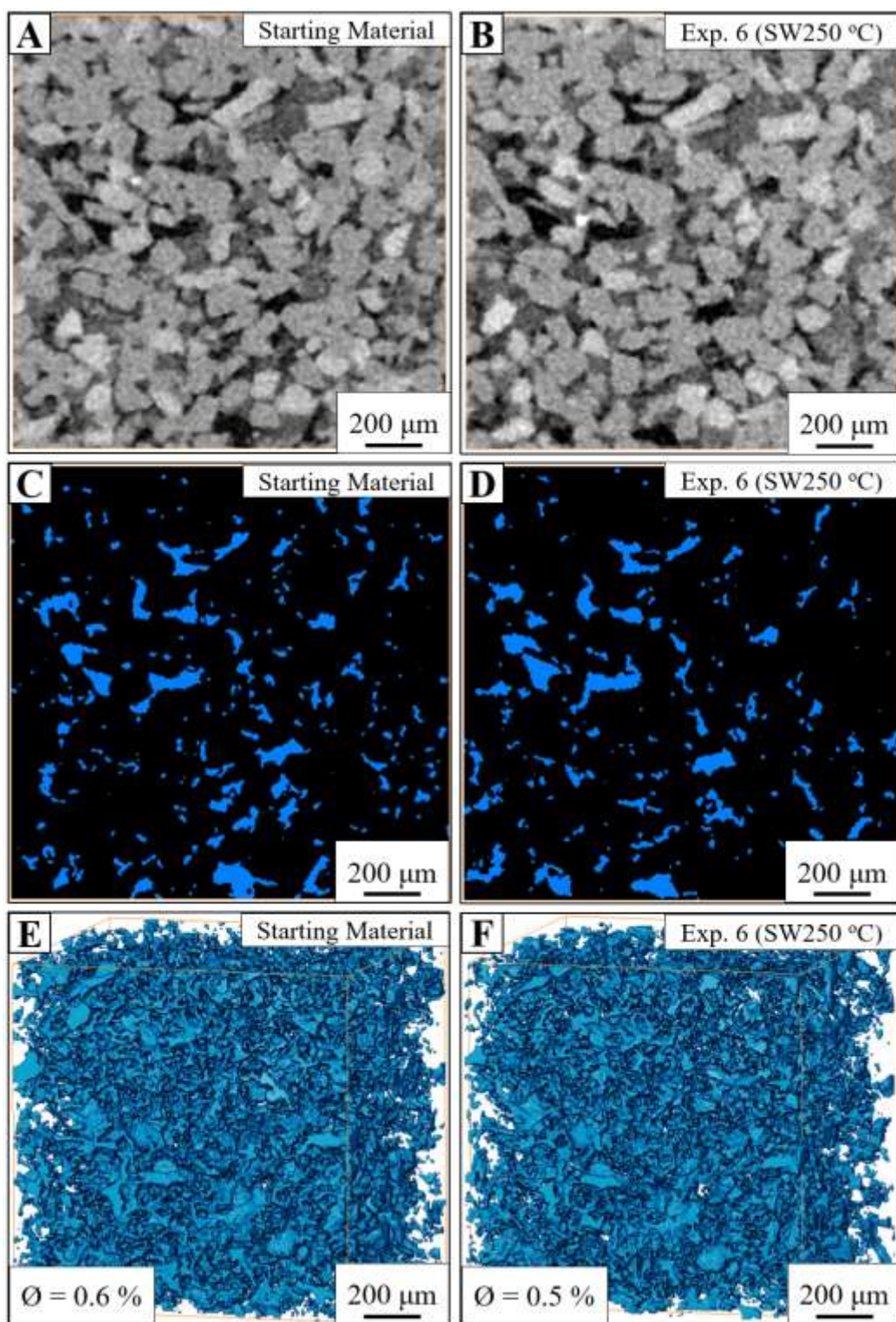


Figure 6.13. Micro-CT images and pore network of the sample before and after experiment 6 (seawater, 1 month @ 250 °C). A) 2D grayscale tomographic image from a 2 cm cylindrical core

before experiment (A) and after experiment 6 (B), scanned at 3.3 μm resolution. (C-D) 2D segmented slice of (A-B). (E-F) 3D voxelized rendering of the total resolved porosity. The total resolved microporosity value is 0.6 mD in the starting material and 0.5 mD in Experiment 6.

6.5.5. Chemistry of reaction fluids

Results of the pH measurements and total X-ray fluorescence (TXRF) concentrations of the major cations (Al, Fe, Mg, Ca, K, and Na) in the pre- and post-experimental solutions are presented in Table 3 and Figure 6.14. Al increased slightly from 1.7 mg/L in the initial Red Sea water to 2.1 mg/L and 2.5 mg/L in Experiments 1 and 2, respectively, before declining to 1.8 mg/L, 1.2 mg/L, and 0.4 mg/L in Experiments 3, 4, and 5, respectively, and becoming undetectable in Experiment 6 (Table 3). Al was initially undetected in the starting synthetic fluid, but rose to 1.3 mg/L during Experiment 7 (Table 3). Fe increases significantly from 2.1 mg/L in the Red Sea water to 241 mg/L in Experiment 3, corresponding to hematite dissolution, and then falls to 41 mg/L in Experiment 6, likely being consumed by the newly formed chlorite (Table 3; Fig. 6.14A). Mg concentrations decreased in all experiments except Experiment 1 (Table 3; Fig. 6.14B), consistent with its incorporation into authigenic smectite. Ca also increased significantly with temperature (Table 3; Fig. 6.14C), probably reflecting dissolution of carbonate cements in the sandstone. Na showed no clear trend (Table 4), as expected given its minor role in the diagenetic products from these experiments. K rose in Experiments 1 and 2, due to dissolution of K-feldspar and kaolinite (Fig. 6.6), then declined in the subsequent experiments (Table 3). Finally, pH decreased steadily with increasing experimental temperature (Table 4; Fig. 6.14D), while the TDS value increases across the hydrothermal experiments (Table 3).

Table 3: TXRF analysis showing the concentrations of major cations in solutions before and after the hydrothermal experiments

Identification		pH	Major cations (mg/L)						TDS (ppt)
			Al	Ca	Fe	Mg	Na	K	
SW	SW@0	8.1	1.7	420	2.1	1420	11070	341	37.40
Exp. 1	SW@80	6.9	2.1	690	6.8	1650	13400	520	57.56
Exp. 2	SW@100	6.8	2.5	870	41	1410	14100	630	57.96
Exp. 3	SW@150	6.5	1.8	940	241	1051	10830	361	56.47
Exp. 4	SW@200	5.9	1.2	1517	150	971	8910	137	56.85
Exp. 5	SW@250_1	4.4	0.4	2171	121	615	10500	92	59.28
Exp. 6	SW@250_2	4.2	ND	3790	41	521	11410	62	62.63
SF	SF@0	5.8	ND	4200	ND	3210	2490	4100	38.12
Exp. 7	SF@250	3.8	1.3	5120	2.1	420	2710	735	52.65

[TDS= total dissolved solids; SW=Red Sea water; SF= synthetic fluid; ND= not detected]

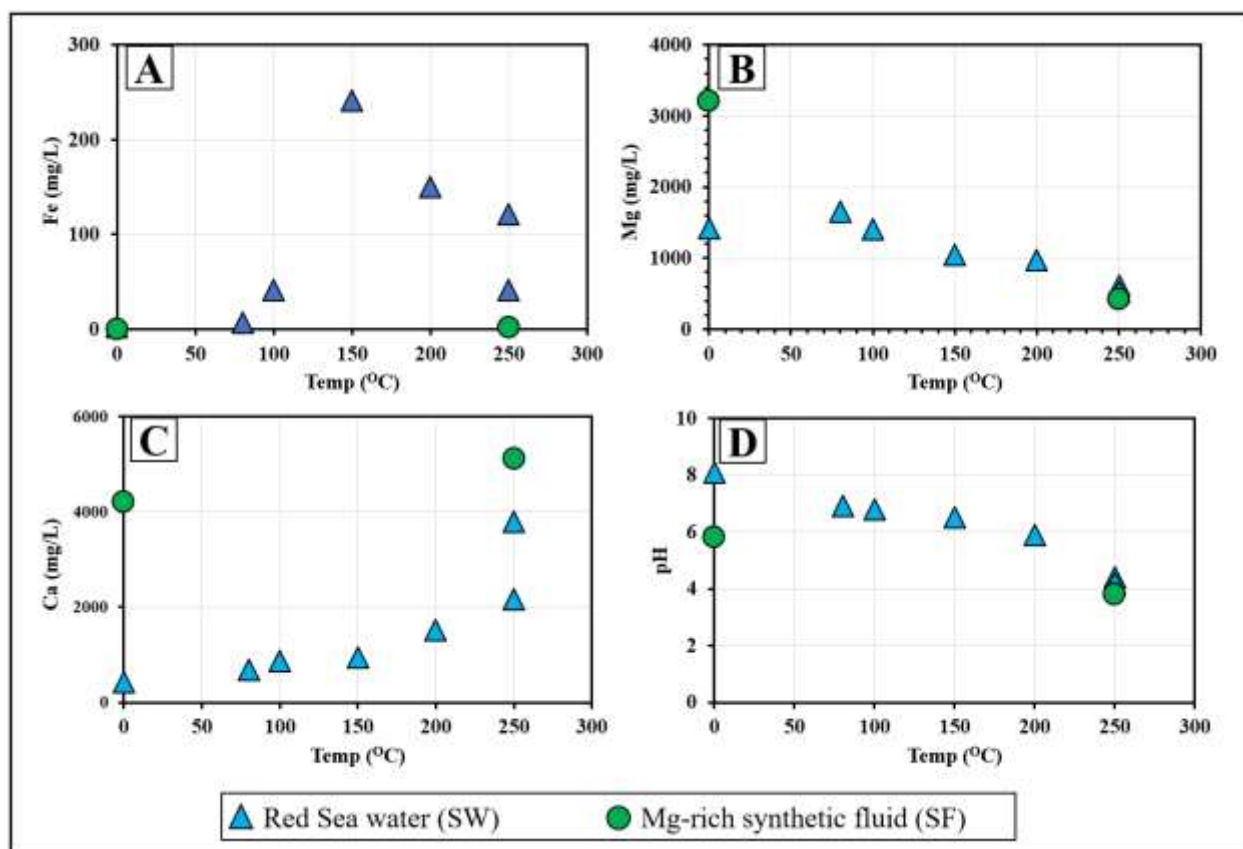


Figure 6.14. Plots of TXRF concentrations of Fe, Mg, Ca (mg/L), and pH versus the experimental temperatures in °C, illustrating their evolution with increasing temperature and changes in fluid chemistry. Data points are color-coded according to the brine compositions used in each experiment.

6.6. Discussion

This study represents the first attempts for a systematic hydrothermal demonstration of chlorite authigenesis from K-feldspar under simulated burial conditions. By integrating petrographic, geochemical, and mineralogical analyses, we show how temperature-driven dissolution of detrital precursors (K-feldspar and kaolinite), fluid–rock interactions, and cation availability govern chlorite nucleation and growth.

6.6.1. Controls and mechanisms of chlorite authigenesis

The formation of authigenic chlorite in this study is mainly governed by the dissolution of detrital K-feldspar and kaolinite, which releases Al, Si, and K into the evolving diagenetic fluid and thus establishes the chemical environment necessary for clay-mineral nucleation (Hellmann et al., 2021). SEM observations reveal the development of feldspar dissolution pits forming at temperatures as low as 80 °C (Fig. 6.6), and intensifying between 150 to 250 °C (Figs. 6.7-6.11), consistent with previous diagenetic studies in Proterozoic sandstones where feldspar breakdown precedes chloritization (Morad and Aldahan, 1987). Kaolinite, initially present as a pore-filling cement (Fig. 6.2), also dissolves from 80 °C upward (Fig. 6.6-6.10), contributing additional Al and Si to the evolving experimental brine (Li et al., 2021). Meanwhile, the required Fe and Mg for the chloritization process were derived from the dissolution of detrital hematite and the experimental solutions, as evidenced by the WD-XRF (Table 2; Fig. 6.3) and TXRF (Table 3; Fig. 6.14). The critical temperature window for chlorite nucleation in our closed-system hydrothermal experiments lies between 200 °C and 250 °C, which corresponds to the upper diagenetic temperature range reported for natural chloritization in deeply buried sandstone reservoirs (Morad and Aldahan, 1987). Nucleation occurs along grain margins where precursor clays or feldspar

surfaces remain, implying a heterogeneous nucleation mechanism. The elevated temperature (200–250 °C), pressure (~10–16 MPa), and a fluid-to-rock ratio of 10:1 used in this study may likely further accelerate reaction kinetics, in agreement with models that predict faster clay transformations under increased physicochemical driving forces (Huang et al., 1986; Bjorkum and Gjelsvik, 1988; Robinson et al., 2002).

Our experimental evidence indicates that chlorite formation proceeds via a multistage pathway rather than by direct transformation of K-feldspar or kaolinite. Initial precursor dissolution is followed by the nucleation and growth of intermediate phases, notably smectite (Figs. 6.3–6.14). The onset of chlorite crystallization appears between 200–250 °C, coinciding with the peak of feldspar dissolution (Figs. 6.7–6.11) and elevated concentrations of Fe and Mg in the experimental solutions (Table 3; Fig. 6.14). This suggests that chlorite formation is strongly temperature-dependent and is facilitated by favorable chemical conditions created by the breakdown of precursor minerals and interacting brine through a dissolution-precipitation mechanism (DC) (Worden et al., 2020). Importantly, the transformation from dominantly a non-clay precursor (K-feldspar) to chlorite differentiates this study from earlier works that focused on clay–clay transformations (Guillaume et al., 2004; Mosser-Ruck et al., 2010; Beaufort et al., 2015; Charlaftis et al., 2021; Virolle et al., 2022). This pathway has significant implications for arkosic sandstones, where K-feldspar abundance has traditionally been mainly linked to illitization and smectite formation (Huang et al., 1986; Ylagan et al., 2000; Mosser-Ruck et al., 2016; Xiao et al., 2018; Yuan et al., 2019; Hellmann et al., 2021).

6.6.2. Smectite as an Intermediate Phase in Chlorite Authigenesis

The experiments demonstrate that smectite serves as a crucial kinetic intermediary in the progressive transformation of K-feldspar into authigenic chlorite, mirroring observations in natural sandstone reservoirs (Worden and Morad, 2009; Dowey et al., 2012; Beaufort et al., 2015; Worden et al., 2020; Virolle et al., 2022). Authigenic smectite first appears at 150 °C (Fig. 6.7), forming thin grain coatings and honeycomb-like pore-filling textures (Figs. 6.7C–E). SEM analysis reveals smectite platelets nucleating on partially dissolved K-feldspar surfaces (Fig. 6.7D), creating a substrate for subsequent chloritization. As temperature increases, smectite coatings become continuous, enveloping detrital grains by 200 °C and providing the structural framework for chlorite nucleation (Fig. 6.8). Oriented XRD patterns of the <2 µm clay fraction (Figs. 6.4B–D) further confirm the presence of smectite at intermediate temperatures and chlorite at higher temperatures. The transformation of smectite to chlorite proceeds via a dissolution–precipitation mechanism, consistent with both natural observations in deeply buried sandstone reservoirs and previous experimental studies (Robinson et al., 2002; Beaufort et al., 2015; Haile et al., 2015; Mosser-Ruck et al., 2016; Liu et al., 2020; Worden et al., 2020; Griffiths et al., 2021; Li et al., 2021). SEM images from Experiments 4–7 show chlorite typically nucleating on or adjacent to smectite, indicating a sequential replacement process. In these images, smectite platelets encase partially dissolved kaolinite and K-feldspar surfaces (Figs. 6.8–6.11) before progressively recrystallizing into curled plates, rosettes, and cabbage-head-shaped chlorite crystals at 200–250 °C (Figs. 6.8–6.11).

The chemical composition of these authigenic mineral phases also supports the DC transformation mechanism (Fig. 6.9F): smectite is relatively Mg-rich (Fig. 6.9F), whereas the evolved chlorite is Fe-rich (Fig. 6.9F), demonstrating preferential cation incorporation during chloritization

(Charlaftis et al., 2021). Although long-term hydrothermal experiments (up to nine years at 300 °C) have documented smectite-to-chlorite conversion starting from smectite precursors (Mosser-Ruck et al., 2016), this study is, to our knowledge, the first to reproduce the entire sequence from a non-clay precursor. By directly linking K-feldspar dissolution to smectite authigenesis and subsequent chlorite development, our results have important implications for refining clay-diagenesis models in siliciclastic sedimentary basins.

6.6.3. Influence of fluid composition on chlorite formation

Fluid chemistry exerts a first-order control on both the rate and mineralogy of chlorite authigenesis (Mosser-Ruck et al., 2010, 2016; Worden et al., 2020; Hong et al., 2022; Salisu et al., 2025a). In this study, we employed two distinct fluids: natural Red Sea water (Table 1; Fig. 9) and a synthetic solution containing equimolar concentrations (0.1 M each) of CaCl_2 , NaCl , MgCl_2 , and KCl . Both fluids facilitated the conversion of K-feldspar and kaolinite into chlorite via smectite intermediary phases, although the resulting chlorites differed subtly in chemistry. Experiments using natural Red Sea water (Experiments 1–6), which has a naturally lower Mg concentration, produced predominantly Fe-rich chlorites (Figs. 6.6-6.10). In contrast, the Mg-enriched synthetic brine (Experiment 7) yielded chlorite with higher Mg content (Fig. 6.11F). When abundant, Fe liberated from hematite dissolution preferentially incorporates into the chlorite lattice in natural brines, whereas Mg-dominant fluids favor Mg-chlorite crystallization (Pereira et al., 2022). The absence of Fe in the synthetic fluid forces more Mg into the chlorite structure to maintain charge balance and structural integrity. These observations underscore the direct incorporation of cations from the fluid into authigenic chlorite and highlight fluid composition as a critical control on chlorite chemistry and morphology.

Measured pH values decrease continuously with increasing experimental temperature (Table 3; Fig. 6.14D), promoting enhanced dissolution of both feldspar and kaolinite under more acidic conditions (Stoessell and Moore, 1983). This continuous dissolution of Fe from the hematite, and the increase in experimental temperature, enhanced the depletion of Si and the enrichment of Fe in the synthesized clay minerals, which likely contributes to the lower pH observed in post-experiment solutions (Table 3; Fig. 6.14D), in agreement with the findings of Mosser-Ruck et al. (2010).

Collectively, our results demonstrate that sufficient Fe and/or Mg availability is essential for chlorite crystallization, and that the specific types and concentrations of cations in diagenetic fluids critically determine the resulting clay assemblages. In subsurface reservoirs, variations in salinity and cation sources, whether basinal brines or meteoric waters, will likewise influence clay mineralogy and chlorite characteristics (Dowey et al., 2012; Worden et al., 2020). Therefore, integrating detailed fluid-chemistry parameters into diagenetic models is as important as accounting for pressure and temperature controls.

6.6.4. Implications for reservoir quality in arkosic sandstones

The authigenic formation of chlorite from K-feldspar and smectite has significant implications for reservoir quality. Chlorite occurs primarily as grain coatings and, to a lesser extent, as pore-filling cements (Dowey et al., 2012). When present as continuous grain coatings, chlorite effectively inhibits quartz overgrowth, thereby preserving intergranular porosity even under elevated burial temperatures (Bloch et al., 2002; Dowey et al., 2012; Worden et al., 2020). In these experiments, chlorite coats have been observed to have formed continuous rims around detrital grains, impeding quartz overgrowth and often retaining adjacent open pores despite surrounding clay cementation

(Figs. 6.8E, 6.11E & 6.12D). This aligns with documented case studies of porosity preservation where authigenic chlorite coats exceed 0.5 μm thickness (Ehrenberg, 1993; Ajdukiewicz and Larese, 2012; Charlaftis et al., 2022). However, chlorite also precipitates as pore-filling cement, which contributes to porosity reduction and corresponding permeability loss (Chen et al., 2011; Worden et al., 2020). SEM (Fig. 6.10B) and QEMSCAN (Fig. 6.12C) analyses in this study confirm the formation of pore-filling chlorite. Additionally, QEMSCAN (Fig. 6.12) and Micro-CT (Fig. 6.13) analysis reveal a subtle but measurable decrease in total porosity post-experiment, reflecting the cumulative impact of clay mineral growth. This porosity loss highlights that, while chlorite grain coatings can be porosity-preserving, pore-filling chlorite cements can occlude fine pore throats and decrease effective permeability. Consequently, the net effect of authigenic chlorite on reservoir quality is highly dependent on its spatial distribution and textural form (coating vs. filling textures). Given that our experiments replicate K-feldspar-rich arkosic sandstones, these findings have direct implications for hydrocarbon exploration and production in similar lithologies worldwide. They also emphasize that feldspar-derived chlorite, once considered secondary to clay-derived chlorite, can be a dominant factor in porosity and permeability evolution and should be incorporated into basin-scale reservoir quality models.

6.6.5. Limitations and Recommendations for Future Research

While this study provides valuable experimental insights into chlorite authigenesis from K-feldspar precursors, some limitations must be acknowledged. First, the closed-system hydrothermal experiments do not fully replicate open-system diagenetic conditions typical of subsurface environments, where fluid flow, changing geochemistry, and kinetic factors can significantly alter reaction pathways. Second, the experimental durations (2-4 weeks), though extended, are orders of

magnitude shorter than geological timescales; slower diagenetic reactions or metastable intermediates may therefore be underrepresented.

Future studies should explore flow-through diagenetic experiments to simulate advective fluid transport and evolving chemistries. Varying redox buffers or introducing organic acids would better approximate formation water complexity. Extending runs to months or even years, possibly at lower supersaturations, would help reveal slower transformation pathways. Finally, integrating reactive transport modeling with experimental data will facilitate basin-scale predictions of feldspar-clay reaction fronts, advancing our capacity to forecast reservoir quality in feldspar-rich sandstones.

6.7. Conclusions

- This study presents the first experimental attempt to demonstrate chlorite authigenesis directly from K-feldspar under reservoir-relevant conditions. Burial diagenesis was simulated using closed-system hydrothermal reactors (80–250 °C; ~10–16 MPa; fluid: rock ratio = 10:1), with the Early Devonian arkosic Subbat Sandstone Member of the Jauf Formation (NW Saudi Arabia) serving as the starting material. Integrated petrographic, mineralogical, and geochemical analyses reveal the authigenic formation of smectite and its subsequent transformation into chlorite.
- Progressive dissolution of detrital K-feldspar, kaolinite, and hematite cements commencing at 80 °C released Al, Si, K, Fe, and Mg into solution. This facilitated the nucleation of authigenic smectite at approximately 150 °C, which subsequently transformed into well-crystallized chlorite between 200–250 °C via a dissolution–precipitation mechanism. The resulting authigenic smectite and chlorite closely resemble those found in naturally buried sandstones in both chemical composition and morphology.
- The composition of the reaction fluids exerted a primary control on chlorite chemistry: experiments with natural Red Sea water yielded Fe-rich chlorites, whereas synthetic Mg-rich brines produced Mg-enriched chlorites. This highlights the direct incorporation of cations from diagenetic fluids into the forming chlorite.
- Dissolution of K-feldspar and kaolinite, together with the smectite-to-chlorite transformation, released substantial silica into solution. This silica precipitated as quartz overgrowths on detrital quartz grains, thereby reducing the intergranular porosity of the sandstones.

- Authigenic chlorite formed continuous grain coatings that inhibited quartz overgrowth and preserved intergranular porosity. In contrast, pore-filling chlorite cements reduced microporosity from 0.6 % to 0.5 %, underscoring that chlorite's spatial distribution and texture critically govern its net effect on reservoir porosity and permeability.

6.8. References

- Aagaard, P., Jahren, J., Harstad, A.O., Nilsen, O., and Ramm, M., 2000a, Formation of grain-coating chlorite in sandstones. Laboratory synthesized vs. natural occurrences: *Clay Minerals - CLAY MINER*, v. 35, p. 261, doi:10.1180/000985500546639.
- Aagaard, P., Jahren, J.S., Harstad, A.O., Nilsen, O., and Ramm, M., 2000b, Formation of grain-coating chlorite in sandstones. Laboratory synthesized vs. natural occurrences : *Clay Minerals*, v. 35, p. 261–269, doi:10.1180/000985500546639.
- Ajdukiewicz, J.M., and Lander, R.H., 2010, Sandstone reservoir quality prediction: The state of the art: *American Association of Petroleum Geologists Bulletin*, v. 94, p. 1083–1091, doi:10.1306/intro060110.
- Ajdukiewicz, J.M., and Larese, R.E., 2012, How clay grain coats inhibit quartz cement and preserve porosity in deeply buried sandstones: Observations and experiments: *AAPG Bulletin*, v. 96, p. 2091–2119, doi:10.1306/02211211075.
- Algheryafi, H., Viseras, C., Polo, C., and Al-Ramadan, K., 2022, Facies architecture and paleogeography evolution of regressive wave-dominated shorelines transitioning into tide-dominated estuaries: Early Devonian Subbat Member, Jauf Formation, Saudi Arabia: *Journal of Sedimentary Research*, v. 92, p. 955–987, doi:10.2110/jsr.2021.112.
- Alhindi, H.S., Salisu, A.M., Hussaini, S.R., Al-Ramadan, K., and Koeshidayatullah, A.I., 2025, Novel insights to unconventional carbonate mudstone reservoir with quantitative nanoporosity characterization and modeling of Tuwaiq Mountain Formation: *Geoenergy Science and Engineering*, v. 244, p. 213394, doi:https://doi.org/10.1016/j.geoen.2024.213394.
- Al-Ramadan, K., 2014, Illitization of Smectite in Sandstones: The Permian Unayzah Reservoir, Saudi Arabia: *Arabian Journal for Science and Engineering*, v. 39, p. 407–412, doi:10.1007/s13369-013-0913-6.
- Al-Ramadan, K., 2021, The role of diagenesis at unconformities of the Paleozoic siliciclastic succession of central Saudi Arabia: implications for reservoir quality: *Arabian Journal of Geosciences*, v. 14, p. 484, doi:10.1007/s12517-021-06845-6.
- Anjos, S.M.C., De Ros, L.F., and Silva, C.M.A., 1999, Chlorite Authigenesis and Porosity Preservation in the Upper Cretaceous Marine Sandstones of the Santos Basin, Offshore Eastern Brazil, *in* *Clay Mineral Cements in Sandstones*, p. 289–316, doi:https://doi.org/10.1002/9781444304336.ch13.
- Aro, O.E., Jones, S.J., Meadows, N.S., Gluyas, J., and Charlaftis, D., 2023, The importance of facies, grain size and clay content in controlling fluvial reservoir quality—an example from the Triassic Skagerrak Formation, Central North Sea, UK: *Petroleum Geoscience*, v. 29, p. petgeo2022- 043.

- Barshep, D.V., and Worden, R.H., 2022, Reservoir quality and sedimentology in shallow marine sandstones: Interplay between sand accumulation and carbonate and clay minerals: *Marine and Petroleum Geology*, v. 135, p. 105398, doi:10.1016/j.marpetgeo.2021.105398.
- Beaufort, D., Berger, G., Lachapagne, J.C., and Meunier, A., 2001, An experimental alteration of montmorillonite to a di + trioctahedral smectite assemblage at 100 and 200°C: *Clay Minerals*, v. 36, p. 211–225, doi:DOI: 10.1180/000985501750177942.
- Beaufort, D., Rigault, C., Billon, S., Billault, V., Inoue, A., Inoue, S., and Patrier, P., 2015, Chlorite and chloritization processes through mixed-layer mineral series in low-temperature geological systems – a review: *Clay Minerals*, v. 50, p. 497–523, doi:DOI: 10.1180/claymin.2015.050.4.06.
- Bello, A.M., Jones, S.J., Gluyas, J., and Al-Ramadan, K., 2022a, Impact of Grain-Coating Clays on Porosity Preservation in Paleocene Turbidite Channel Sandstones: Nelson Oil Field, UK Central North Sea: *Minerals*, v. 12, doi:10.3390/min12050555.
- Bello, A.M., Jones, S.J., Gluyas, J., and Al-Ramadan, K., 2022b, Impact of Grain-Coating Clays on Porosity Preservation in Paleocene Turbidite Channel Sandstones: Nelson Oil Field, UK Central North Sea: *Minerals*, v. 12, doi:10.3390/min12050555.
- Bello, A.M., Salisu, A.M., and Amao, Abduljamiu Olalekan, Umar, Mustapha, Al Ramadan, K., 2025, EXPERIMENTAL DEVELOPMENT OF CHLORITE : INSIGHTS FROM A KAOLINITE PRECURSOR: *Journal of Sedimentary Research*, v. 95, p. 1–24, doi:10.2110/jsr.2024.099.
- Bjorkum, P.A., and Gjelsvik, N., 1988, An isochemical model for formation of authigenic kaolinite, K-feldspar and illite in sediments: *Journal of Sedimentary Research*, v. 58, p. 506–511, doi:10.1306/212F8DD2-2B24-11D7-8648000102C1865D.
- Bjørlykke, K., 1998, Clay mineral diagenesis in sedimentary basins — a key to the prediction of rock properties. Examples from the North Sea Basin: *Clay Minerals*, v. 33, p. 15–34, doi:DOI: 10.1180/000985598545390.
- Bjørlykke, K., Ramm, M., and Saigal, G.C., 1989, Sandstone diagenesis and porosity modification during basin evolution: *Geologische Rundschau*, v. 78, p. 243–268, doi:10.1007/BF01988363.
- Bloch, S., Lander, R.H., and Bonnell, L., 2002, Anomalously High Porosity and Permeability in Deeply Buried Sandstone Reservoirs: Origin and Predictability: *AAPG Bulletin*, v. 86, p. 301–328, doi:10.1306/61EEDABC-173E-11D7-8645000102C1865D.
- Boles, J.R., and Franks, S.G., 1979, Clay diagenesis in Wilcox sandstones of Southwest Texas; implications of smectite diagenesis on sandstone cementation: *Journal of Sedimentary Research*, v. 49, p. 55–70, doi:10.1306/212F76BC-2B24-11D7-8648000102C1865D.

- Bourdelle, F., Dubois, M., Lloret, E., Durand, C., Addad, A., Bounoua, S., Ventalon, S., and Recourt, P., 2021, Kaolinite-to-chlorite conversion from Si, Al-rich fluid-origin veins/Fe-rich Carboniferous shale interaction: *Minerals*, v. 11, p. 804.
- Charlaftis, D., Dobson, K.J., Jones, S.J., Lakshtanov, D., Crouch, J., and Cook, J., 2022, Experimental Simulation of Burial Diagenesis and Subsequent 2D-3D Characterization of Sandstone Reservoir Quality: *Frontiers in Earth Science*, v. 10, doi:10.3389/feart.2022.766145.
- Charlaftis, D., Jones, S.J., Dobson, K.J., Crouch, J., and Acikalin, S., 2021, Experimental study of chlorite authigenesis and influence on porosity maintenance in sandstones: *Journal of Sedimentary Research*, v. 91, p. 197–212, doi:10.2110/JSR.2020.122.
- Chen, G., Du, G., Zhang, G., Wang, Q., Lv, C., and Chen, J., 2011, Chlorite cement and its effect on the reservoir quality of sandstones from the Panyu low-uplift, Pearl River Mouth Basin: *Petroleum Science*, v. 8, p. 143–150, doi:10.1007/s12182-011-0127-z.
- Daneshvar, E., and Worden, R., 2018, Feldspar alteration and Fe minerals: Origin, distribution and implications for sandstone reservoir quality in estuarine sediments, *in Geological Society Special Publication*, v. 435, p. 123–139, doi:10.1144/SP435.17.
- Deer FRS, W.A., Howie, R.A., and Zussman, J., 2013, *An Introduction to the Rock-Forming Minerals*, doi:10.1180/DHZ.
- Dowey, P.J., Hodgson, D.M., and Worden, R.H., 2012, Pre-requisites, processes, and prediction of chlorite grain coatings in petroleum reservoirs: A review of subsurface examples: *Marine and Petroleum Geology*, v. 32, p. 63–75, doi:https://doi.org/10.1016/j.marpetgeo.2011.11.007.
- Durand, C., Cerepi, A., and Brosse, E., 2000, Effect of Pore-Lining Chlorite on Petrophysical Properties of Low-Resistivity Sandstone Reservoir:, doi:10.2118/63070-MS.
- Dutton, S.P.; Hutton, M.E.; Ambrose, W.A.; Childers, A.T.; Loucks, R.G., 2018, Preservation of reservoir quality by chlorite coats in deep Tuscaloosa Sandstones, Central Louisiana, USA: *Gulf Coast Association of Geological Societies*, v. 7, p. 46– 58., http://www.gcags.org/exploreanddiscover/2018/00329_dutton_et_al.pdf.
- Eberl, D., and Hower, J., 1977, The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay: *Clays and Clay Minerals*, v. 25, p. 215–227.
- Ehrenberg, S.N., 1993, Preservation of Anomalously High Porosity in Deeply Buried Sandstones by Grain-Coating Chlorite: Examples from the Norwegian Continental Shelf1: *AAPG Bulletin*, v. 77, p. 1260–1286, doi:10.1306/BDF8E5C-1718-11D7-8645000102C1865D.
- Griffiths, J., Worden, R.H., Utley, J.E.P., Brostrøm, C., Martinius, A.W., Lawan, A.Y., and Al-Hajri, A.I., 2021, Origin and distribution of grain-coating and pore-filling chlorite in deltaic sandstones

for reservoir quality assessment: *Marine and Petroleum Geology*, v. 134, doi:10.1016/j.marpetgeo.2021.105326.

Guillaume, D., Neaman, A., Cathelineau, M., Mosser-Ruck, R., Peiffert, C., Abdelmoula, M., Dubessy, J., Villiéras, F., and Michau, N., 2004, Experimental study of the transformation of smectite at 80 and 300°C in the presence of Fe oxides: *Clay Minerals*, v. 39, p. 17–34, doi:DOI: 10.1180/000985543910117.

Haile, B.G., Hellevang, H., Aagaard, P., and Jahren, J., 2015, Experimental nucleation and growth of smectite and chlorite coatings on clean feldspar and quartz grain surfaces: *Marine and Petroleum Geology*, v. 68, p. 664–674, doi:10.1016/j.marpetgeo.2015.02.006.

Heald, M.T., and Larese, R.E., 1974, Influence of coatings on quartz cementation: *Journal of Sedimentary Research*, v. 44, p. 1269–1274, doi:10.1306/212F6C94-2B24-11D7-8648000102C1865D.

Hellmann, R. et al., 2021, The hydrothermal alkaline alteration of potassium feldspar: A nanometer-scale investigation of the orthoclase interface: *Chemical Geology*, v. 569, p. 120133, doi:https://doi.org/10.1016/j.chemgeo.2021.120133.

Hong, D., Cao, J., Guo, X., Bian, B., and Liu, H., 2022, Diagenetic fluid controls chemical compositions of authigenic chlorite in clastic reservoirs: *Marine and Petroleum Geology*, v. 137, p. 105520, doi:https://doi.org/10.1016/j.marpetgeo.2021.105520.

Huang, W.L., Bishop, A.M., and Brown, R.W., 1986, The effect of fluid/rock ratio on feldspar dissolution and illite formation under reservoir conditions: *Clay Minerals*, v. 21, p. 585–601.

Huang, W.-L., Longo, J.M., and Pevear, D.R., 1993, An Experimentally Derived Kinetic Model for Smectite-to-Illite Conversion and Its Use as a Geothermometer: *Clays and Clay Minerals*, v. 41, p. 162–177, doi:DOI: 10.1346/CCMN.1993.0410205.

Johnston, R.M., and Miller, H.G., 1984, The effect of pH on the stability of smectite: Atomic Energy of Canada Ltd.

Kloprogge, J.T., Komarneni, S., and Amonette, J.E., 1999, Synthesis of Smectite Clay Minerals: A Critical Review: *Clays and Clay Minerals*, v. 47, p. 529–554, doi:DOI: 10.1346/CCMN.1999.0470501.

Konert, G., Afifi, A.M., Al-Hajri, S.A., and Droste, H.J., 2001, Paleozoic stratigraphy and hydrocarbon habitat of the Arabian plate: *GeoArabia*, v. 6, p. 407–442, doi:10.2113/geoarabia0603407.

Kordi, M., 2013, Characterization and prediction of reservoir quality in chlorite-coated sandstones : evidence from the Late Cretaceous Lower Tuscaloosa Formation at Cranfield Field , Mississippi , U . S . A . :

- Lahann, R.W., 1980, Smectite diagenesis and sandstone cement: the effect of reaction temperature.: *Journal of Sedimentary Petrology*, v. 50, p. 755–760, doi:10.1306/212f7ad6-2b24-11d7-8648000102c1865d.
- Lander, R.H., and Walderhaug, O., 1999, Predicting Porosity through Simulating Sandstone Compaction and Quartz Cementation1: *AAPG Bulletin*, v. 83, p. 433–449, doi:10.1306/00AA9BC4-1730-11D7-8645000102C1865D.
- Lanson, B., Sakharov, B., Claret, F., and Drits, V., 2009, Diagenetic Smectite-to-Illite Transition in Clay-Rich Sediments: A Reappraisal of X-Ray Diffraction Results Using the Multi-Specimen Method: *American Journal of Science*, v. 309, p. 476–516, doi:10.2475/06.2009.03.
- Liu, P., Kai, W., Zhu, C., Tang, Y., Zhao, W., Cai, Y., Cai, J., and Ji, J., 2020, Hydrothermal synthesis of chlorite from saponite: Mechanisms of smectite-chlorite conversion and influence of Mg²⁺ and Al³⁺ supplies: *Applied Clay Science*, v. 184, p. 105357, doi:https://doi.org/10.1016/j.clay.2019.105357.
- Li, K., Xi, K., Cao, Y., Niu, X., Wu, S., Feng, S., and You, Y., 2021, Chlorite authigenesis and its impact on reservoir quality in tight sandstone reservoirs of the Triassic Yanchang formation, southwestern Ordos basin, China: *Journal of Petroleum Science and Engineering*, v. 205, p. 108843, doi:https://doi.org/10.1016/j.petrol.2021.108843.
- McCarty, D.K., Sakharov, B.A., and Drits, V.A., 2009, New insights into smectite illitization: A zoned K-bentonite revisited: *American Mineralogist*, v. 94, p. 1653–1671, doi:10.2138/am.2009.3260.
- McKinley, J.M., Worden, R.H., and Ruffell, A.H., 1999, Smectite in sandstones: a review of the controls on occurrence and behaviour during diagenesis: *Clay mineral cements in sandstones*, p. 109–128.
- Meunier, A., Lanson, B., and Beaufort, D., 2000, Vermiculitization of smectite interfaces and illite layer growth as a possible dual model for illite-smectite illitization in diagenetic environments: a synthesis: *Clay Minerals*, v. 35, p. 573–586, doi:DOI: 10.1180/000985500546891.
- Moore, D.M. & Reynolds, R.C., 1998, X-Ray Diffraction and the Identification and Analysis of Clay Minerals: *Geological Magazine*, v. 135, p. 819–842, doi:DOI: 10.1017/S0016756898501501.
- Morad, S., and Aldahan, A.A., 1987, Diagenetic chloritization of feldspars in sandstones: *Sedimentary Geology*, v. 51, p. 155–164, doi:https://doi.org/10.1016/0037-0738(87)90046-7.
- Mosser-Ruck, R., and Cathelineau, M., 2004, Experimental transformation of Na,Ca-smectite under basic conditions at 150 °C: *Applied Clay Science*, v. 26, p. 259–273, doi:https://doi.org/10.1016/j.clay.2003.12.011.
- Mosser-Ruck, R., Cathelineau, M., Guillaume, D., Charpentier, D., Rousset, D., Barres, O., and Michau, N., 2010, EFFECTS OF TEMPERATURE, pH, AND IRON/CLAY AND

LIQUID/CLAY RATIOS ON EXPERIMENTAL CONVERSION OF DIOCTAHEDRAL SMECTITE TO BERTHIERINE, CHLORITE, VERMICULITE, OR SAPONITE: *Clays and Clay Minerals*, v. 58, p. 280–291, doi:10.1346/CCMN.2010.0580212.

Mosser-Ruck, R., Pignatelli, I., Bourdelle, F., Abdelmoula, M., Barres, O., Guillaume, D., Charpentier, D., Rousset, D., Cathelineau, M., and Michau, N., 2016, Contribution of long-term hydrothermal experiments for understanding the smectite-to-chlorite conversion in geological environments: *Contributions to Mineralogy and Petrology*, v. 171, p. 97, doi:10.1007/s00410-016-1307-z.

Nadeau, P.H., and Bain, D.C., 1986, Composition of Some Smectites and Diagenetic Illitic Clays and Implications for their Origin: *Clays and Clay Minerals*, v. 34, p. 455–464, doi:DOI: 10.1346/CCMN.1986.0340412.

Niu, B., Yoshimura, T., and Hirai, A., 2000, Smectite Diagenesis in Neogene Marine Sandstone and Mudstone of the Niigata Basin, Japan: *Clays and Clay Minerals*, v. 48, p. 26–42, doi:10.1346/CCMN.2000.0480104.

Oluwadebi, A.G., Taylor, K.G., and Dowey, P.J., 2018, Diagenetic controls on the reservoir quality of the tight gas Collyhurst sandstone formation, Lower Permian, East Irish Sea Basin, United Kingdom: *Sedimentary geology*, v. 371, p. 55–74.

Pereira, M.L., Matias, D., Viveiros, F., Moreno, L., Silva, C., Zanon, V., and Uchôa, J., 2022, The contribution of hydrothermal mineral alteration analysis and gas geothermometry for understanding high-temperature geothermal fields – The case of Ribeira Grande geothermal field, Azores: *Geothermics*, v. 105, p. 102519, doi:<https://doi.org/10.1016/j.geothermics.2022.102519>.

Pittman, E.D., Larese, R.E., and Heald, M.T., 1992, Clay Coats: Occurrence and Relevance to Preservation of Porosity in Sandstones (D. W. Houseknecht & E. D. Pittman, Eds.): *Origin, Diagenesis, and Petrophysics of Clay Minerals in Sandstones*, v. 47, p. 0, doi:10.2110/pec.92.47.0241.

Pytte, A.M., and Reynolds, R.C., 1989, The thermal transformation of smectite to illite, *in* *Thermal history of sedimentary basins: Methods and case histories*, Springer, p. 133–140.

Rahmani, R.A., Steel, R.J., and Al-Duaiji, A.A., 2019, High Resolution Sequence Stratigraphy and Sedimentology of the Prolific Devonian Jauf Formation Gas Reservoir: Transgressive Tidal Estuarine and Regressive Wave-Dominated Shoreface Deposits, Kingdom of Saudi Arabia (H. R. AlAnzi, R. A. Rahmani, R. J. Steel, & O. M. Soliman, Eds.): *Siliciclastic Reservoirs of the Arabian Plate*, v. 116, p. 0, doi:10.1306/13642175M1183806.

Rahmani, R., Steel, R., and Al-Duaiji, A., 2002, High-resolution sequence stratigraphy of the Devonian Jauf gas reservoir: a shoreface and estuarine embayment succession, greater Ghawar area, eastern Saudi Arabia: *GeoArabia*, Abstract,.

- Roberson, H.E., and Lahann, R.W., 1981, Smectite to Illite Conversion Rates: Effects of Solution Chemistry: *Clays and Clay Minerals*, v. 29, p. 129–135, doi:10.1346/CCMN.1981.0290207.
- Robinson, D., Schmidt, S.T., and De Zamora, A.S., 2002, Reaction pathways and reaction progress for the smectite-to-chlorite transformation: Evidence from hydrothermally altered metabasites: *Journal of metamorphic Geology*, v. 20, p. 167–174.
- Ryan, P.C., and Reynolds Jr, R.C., 1996, The origin and diagenesis of grain-coating serpentine-chlorite in Tuscaloosa Formation sandstone, US Gulf Coast: *American Mineralogist*, v. 81, p. 213–225.
- Salisu, A.M., Algheryafi, H., Bello, A.M., Amao, A.O., Al-Otaibi, B., and Al-Ramadan, K., 2024a, Depositional and diagenetic controls on the reservoir quality of marginal marine sandstones: An example from the Early Devonian Subbat Member, Jauf Formation, northwest Saudi Arabia: *Marine and Petroleum Geology*, p. 107147, doi:https://doi.org/10.1016/j.marpetgeo.2024.107147.
- Salisu, A.M., Alhindi, H., Hussaini, S.R., Amao, A.O., Al-Awah, H., Al-ramadan, K., and Koeshidayatullah, A., 2024b, 3D Microporosity Characterizations in the Heterogeneous Middle Jurassic Tuwaiq Mountain Formation: Insights into an Unconventional Sweet Spot: *ACS Omega*, v. 9, p. 36273–36290, doi:10.1021/acsomega.4c02592.
- Salisu, A.M., Bello, A.M., Amao, A.O., and Al-Ramadan, K., 2025a, The Role of Fluid Chemistry in the Diagenetic Transformation of Detrital Clay Minerals: Experimental Insights from Modern Estuarine Sediments: *Minerals*, v. 15, doi:10.3390/min15030317.
- Salisu, A.M., Bello, A.M., Amao, A.O., Lander, R.H., and Al-Ramadan, K., 2025b, EXPERIMENTAL STUDY OF SMECTITE AUTHIGENESIS AND ITS SUBSEQUENT ILLITIZATION: INSIGHTS FROM MODERN ESTUARY SEDIMENTS: *Journal of Sedimentary Research*, doi:10.2110/jsr.2024.135.
- Small, J.S., 1994, Fluid composition, mineralogy and morphological changes associated with the smectite-to-illite reaction: An experimental investigation of the effect of organic acid anions: *Clay Minerals*, v. 29, p. 539–554.
- Stoessell, R.K., and Moore, C.H., 1983, Chemical Constraints and Origins of Four Groups of Gulf Coast Reservoir Fluids1: *AAPG Bulletin*, v. 67, p. 896–906, doi:10.1306/03B5B6C8-16D1-11D7-8645000102C1865D.
- Stricker, S., and Jones, S.J., 2018, Enhanced porosity preservation by pore fluid overpressure and chlorite grain coatings in the Triassic Skagerrak, Central Graben, North Sea, UK (P. J. Armitage, A. R. Butcher, J. M. Churchill, A. E. Csoma, C. Hollis, R. H. Lander, J. E. Omma, & R. H. Worden, Eds.): *Reservoir Quality of Clastic and Carbonate Rocks: Analysis, Modelling and Prediction*, v. 435, p. 0, doi:10.1144/SP435.4.
- Virolle, M., Brigaud, B., Beaufort, D., Patrier, P., Abdelrahman, E., Thomas, H., Portier, E., Samson, Y., Bourillot, R., and Fénies, H., 2022, Authigenic berthierine and incipient chloritization in

- shallowly buried sandstone reservoirs: Key role of the source-to-sink context: *GSA Bulletin*, v. 134, p. 739–761, doi:10.1130/B35865.1.
- Whitney, G., 1990, Role of Water in the Smectite-to-Illite Reaction: *Clays and Clay Minerals*, v. 38, p. 343–350, doi:DOI: 10.1346/CCMN.1990.0380402.
- Worden, R.H., Armitage, P.J., Butcher, A.R., Churchill, J.M., Csoma, A.E., Hollis, C., Lander, R.H., and Omma, J.E., 2018, Petroleum reservoir quality prediction: Overview and contrasting approaches from sandstone and carbonate communities: *Geological Society Special Publication*, v. 435, p. 1–31, doi:10.1144/SP435.21.
- Worden, R.H., and Burley, S.D., 2009, Sandstone Diagenesis: The Evolution of Sand to Stone: 1–44 p., doi:10.1002/9781444304459.ch.
- Worden, R.H., Griffiths, J., Wooldridge, L.J., Utley, J.E.P., Lawan, A.Y., Muhammed, D.D., Simon, N., and Armitage, P.J., 2020, Chlorite in sandstones: *Earth-Science Reviews*, v. 204, p. 103105, doi:10.1016/j.earscirev.2020.103105.
- Worden, R., and Morad, S., 2009, Clay Minerals in Sandstones: Controls on Formation, Distribution and Evolution, *in Clay Mineral Cements in Sandstones*, v. 34, p. 1–41, doi:10.1002/9781444304336.ch1.
- Xiao, M., Yuan, X., Cheng, D., Wu, S., Cao, Z., Tang, Y., and Xie, Z., 2018, Feldspar Dissolution and Its Influence on Reservoirs: A Case Study of the Lower Triassic Baikouquan Formation in the Northwest Margin of the Junggar Basin, China: *Geofluids*, v. 2018, p. 6536419, doi:https://doi.org/10.1155/2018/6536419.
- Ylagan, R.F., Altaner, S.P., and Pozzuoli, A., 2000, Reaction mechanisms of smectite illitization associated with hydrothermal alteration from Ponza Island, Italy: *Clays and Clay Minerals*, v. 48, p. 610–631.
- Yuan, G., Cao, Y., Schulz, H.-M., Hao, F., Gluyas, J., Liu, K., Yang, T., Wang, Y., Xi, K., and Li, F., 2019, A review of feldspar alteration and its geological significance in sedimentary basins: From shallow aquifers to deep hydrocarbon reservoirs: *Earth-Science Reviews*, v. 191, p. 114–140, doi:https://doi.org/10.1016/j.earscirev.2019.02.004.

CHAPTER 7

CONCLUSIONS AND RECCOMENDATIOIS

7.1. Conclusions

An effort is made in this work to constrain the key factors controlling the authigenic formation of clay minerals in sandstones, with particular focus on the diagenetic transformation of framework grains and detrital clay minerals in marginal marine environments. In the initial phase, the factors influencing the early diagenetic transformation of modern marginal marine sediments were investigated using samples from the Anllóns Estuary (Spain) and the Gironde Estuary (France). Clay minerals such as smectite, illite, and chlorite, as well as zeolites (analcime and chabazite) and halite, were synthesized under varying physicochemical conditions, using different natural and synthetic fluids across a range of temperatures and reaction times. These experiments were designed to understand how variations in fluid chemistry, temperature, time, and detrital precursors influence the diagenetic evolution of marginal marine sandstones, ultimately impacting their reservoir quality. More specifically, the findings shed light on the mechanisms and controls governing smectite formation and its subsequent illitization and chloritization. In the second phase of the work, the depositional and diagenetic controls on the reservoir quality of a Devonian marginal marine sandstone were assessed. Later, an arkosic sample rich in K-feldspar and kaolinite was used to experimentally synthesize the formation of well-developed chlorites, integrating insights gained from experiments on modern sediments as analogs to ancient sandstone reservoirs in marginal marine environments.

The key findings of this study can be summarized as follows:

- 1.** Through a series of hydrothermal reactor experiments simulating burial diagenesis, it was demonstrated that temperature, time, fluid chemistry, and detrital precursors (notably K-feldspar and kaolinite) collectively dictate the sequence and mechanisms of clay mineral authigenesis. At temperatures below 100 °C, detrital K-feldspar and clay aggregates begin to dissolve, while at 150 °C, smectite nucleates via dissolution–precipitation processes in both Mg-rich synthetic fluids and natural seawater/estuarine waters.
- 2.** Increasing the temperature to between 150 °C and 250 °C facilitated the illitization of smectite, a transformation driven by potassium released from feldspar dissolution and supported by the experimental fluids. This process predominantly occurred through a dissolution–crystallization mechanism, replicating potassium-driven diagenetic pathways observed in natural reservoirs.
- 3.** Chloritization of smectite was also observed at 150–250 °C in both Mg-rich synthetic fluids and natural seawater/estuarine waters, producing chlorites with distinct chemistries. Mg-rich fluids generated Mg-rich chlorites, whereas natural fluids favored the formation of Fe-rich chlorites, mirroring diagenetic trends typically associated with deltaic and estuarine systems.
- 4.** The experiments highlighted the significant role of fluid composition in controlling the transformation pathways of clay minerals formation from detrital precursors. In stark contrast to smectite, illite, and Mg- and Fe-rich chlorite formation, highly alkaline, Na-rich fluids (pH $\approx$ 11.2) bypassed clay mineral formation entirely, instead precipitating

- halite and zeolites (analcime and chabazite). This underlines the high sensitivity of diagenetic pathways to pore-water chemistry.
5. A critical outcome of these transformations was the development of authigenic grain coatings, which have a profound influence on reservoir quality. As temperature and reaction time increased, coating thickness grew from approximately 1.9 μm to 49.2 μm , and surface coverage expanded from around 24 % to 96 %. Early-stage thin smectite rims evolved into more rigid, well-ordered illite and chlorite coats, which may inhibit quartz overgrowth and mechanical compaction, thereby preserving porosity and permeability. The synthesized coatings were chemically and morphologically comparable to those observed in buried sandstone reservoirs.
 6. Time proved to be a critical factor for the full development of clay minerals during burial diagenesis, emphasizing the importance of long-term diagenetic processes.
 7. Investigations of a Devonian marginal marine sandstone further confirmed that depositional and diagenetic factors exert first-order controls on reservoir quality. Well-sorted, fine- to medium-grained fluvial–estuarine sandstones with minimal detrital matrix (<0.5 %) exhibited the most extensive grain-coating clays and the highest porosity and permeability. In contrast, poorly sorted shoreface–offshore transition facies (with an average matrix content of ~19 %) contained abundant pore-filling clays and quartz cement, resulting in the poorest reservoir quality.
 8. Specifically, shoreface-to-offshore transition facies, characterized by well-developed pore-filling clay and quartz cements, displayed the lowest reservoir quality due to the limited presence of protective grain-coating illite and chlorite. Conversely, fluvial to

tidal estuarine sandstones, with the most extensive grain-coating clays, exhibited superior reservoir properties.

9. The synthesized mineral phases displayed chemical and morphological similarities to those found in natural sedimentary systems, reaffirming the critical role of fluid chemistry in directing diagenetic pathways and enhancing our understanding of detrital clay transformations during burial.
10. Collectively, these findings, derived from controlled laboratory experiments and validated by natural diagenetic analogs, significantly advance the understanding of the controls on the authigenic formation of clay minerals in marginal marine settings. They emphasize the necessity of incorporating temperature–time histories, fluid chemistry, and detrital mineralogy into predictive models of sandstone reservoir quality.

7.2. Recommendations

Due to certain limitations encountered in this study, additional investigations are necessary to further advance understanding in this field. The following improvements are proposed for future research:

1. To deepen the understanding of the impact of physicochemical factors on the diagenetic transformation of detrital minerals in marginal marine settings, future studies should focus on longer experimental durations and the incorporation of dynamic fluid flow systems. This would better reflect the evolving nature of diagenetic processes in natural sandstone reservoirs.
2. Further research is needed to constrain the influence of fluid chemistry on the formation of authigenic clay minerals from modern detrital precursors. This would involve using fluid

compositions that replicate a variety of natural environments, including river or non-marine waters, normal seawater, and brines with variable total dissolved solids. Future experiments should also examine the effects of different fluid–rock ratios, pH levels, and utilize experimental setups that allow for in-situ fluid sampling, to better characterize the chemical conditions that favor smectite coat formation and its subsequent illitization and/or chloritization.

3. Conducting geochemical modeling based on data from experimental studies is recommended to enhance the extrapolation of laboratory findings to geological timescales.
4. Additionally, hydrothermal experiments using sediments from a range of sedimentary sub-environments should be conducted. This would clarify the role of detrital clay coat distribution in the development of authigenic clays and improve predictions of reservoir quality in sandstone formations.

While these areas of improvement are necessary, the findings of this study provide a solid foundation for understanding diagenetic alteration in modern estuarine sediments and their implications for the evolution of sandstone reservoir quality.

APENDIX

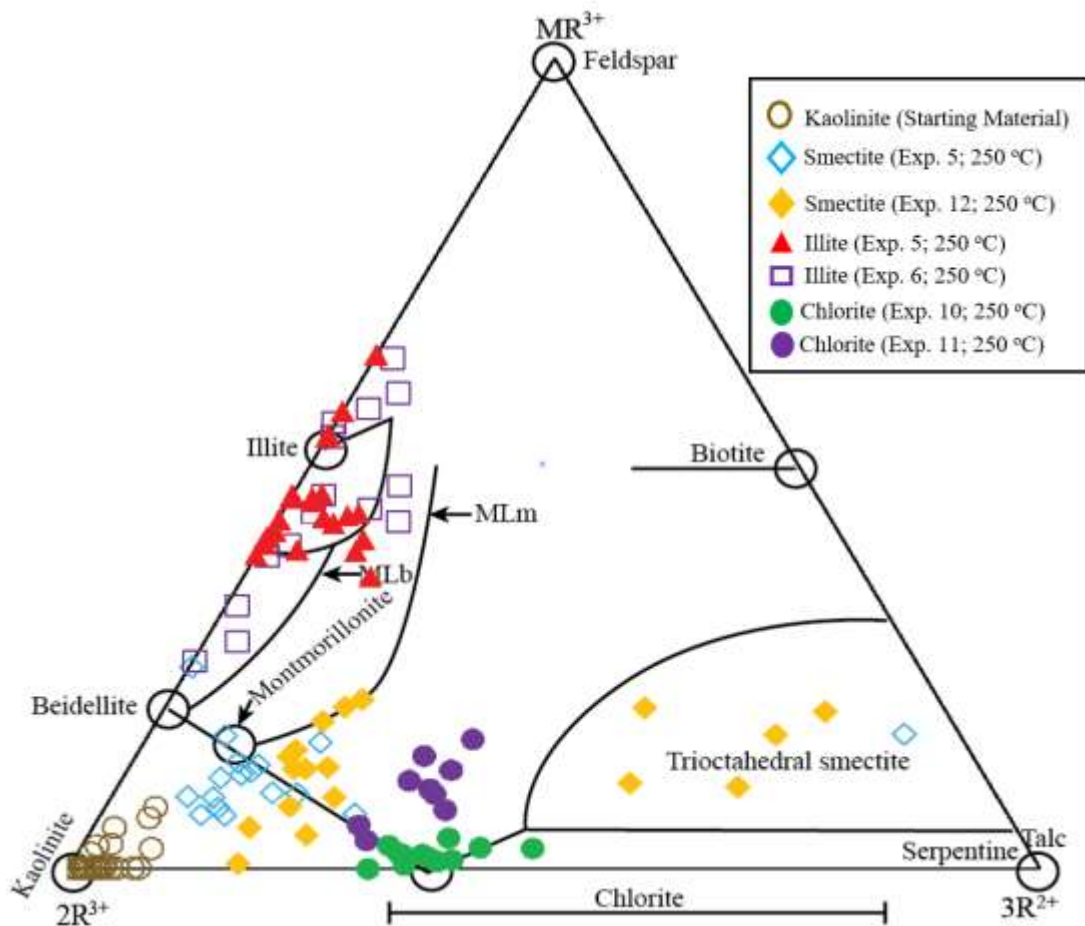


Figure 1: Ternary MR^{3+} - $2R^{3+}$ - $3R^{2+}$ diagram (after Velde, 1985) showing the compositions of the analyzed clay minerals in chapter 4. The plot shows the transformation of detrital starting clays (Kaolinite) into smectite, illite, and chlorite through various mixed-layer phases. [MLm= mixed-layer montmorillonite series; MLb = mixed-layer beidellite series].

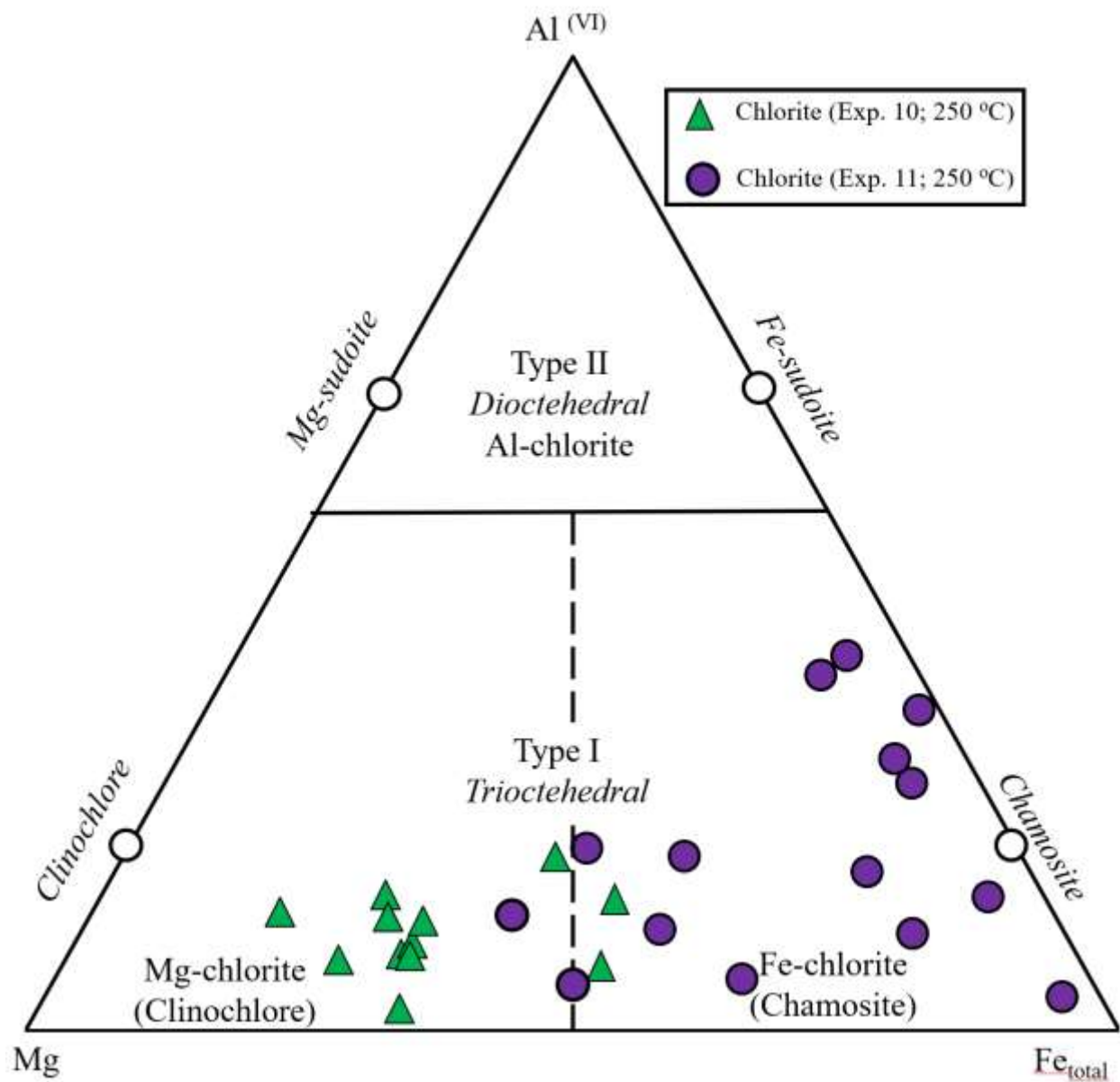


Figure 2: Al-Mg-Fe ternary plot showing the composition of synthesized chlorites in chapter 4 660 (after Zane & Weiss, 1998). The plot indicates that the chlorites synthesized from Mg-rich 661 synthetic fluid (Exp. 10) are Mg-rich (clinochlore) in composition, while those from the estuarine 662 water experiment (Exp. 11) are dominantly Fe-rich (chamosite).

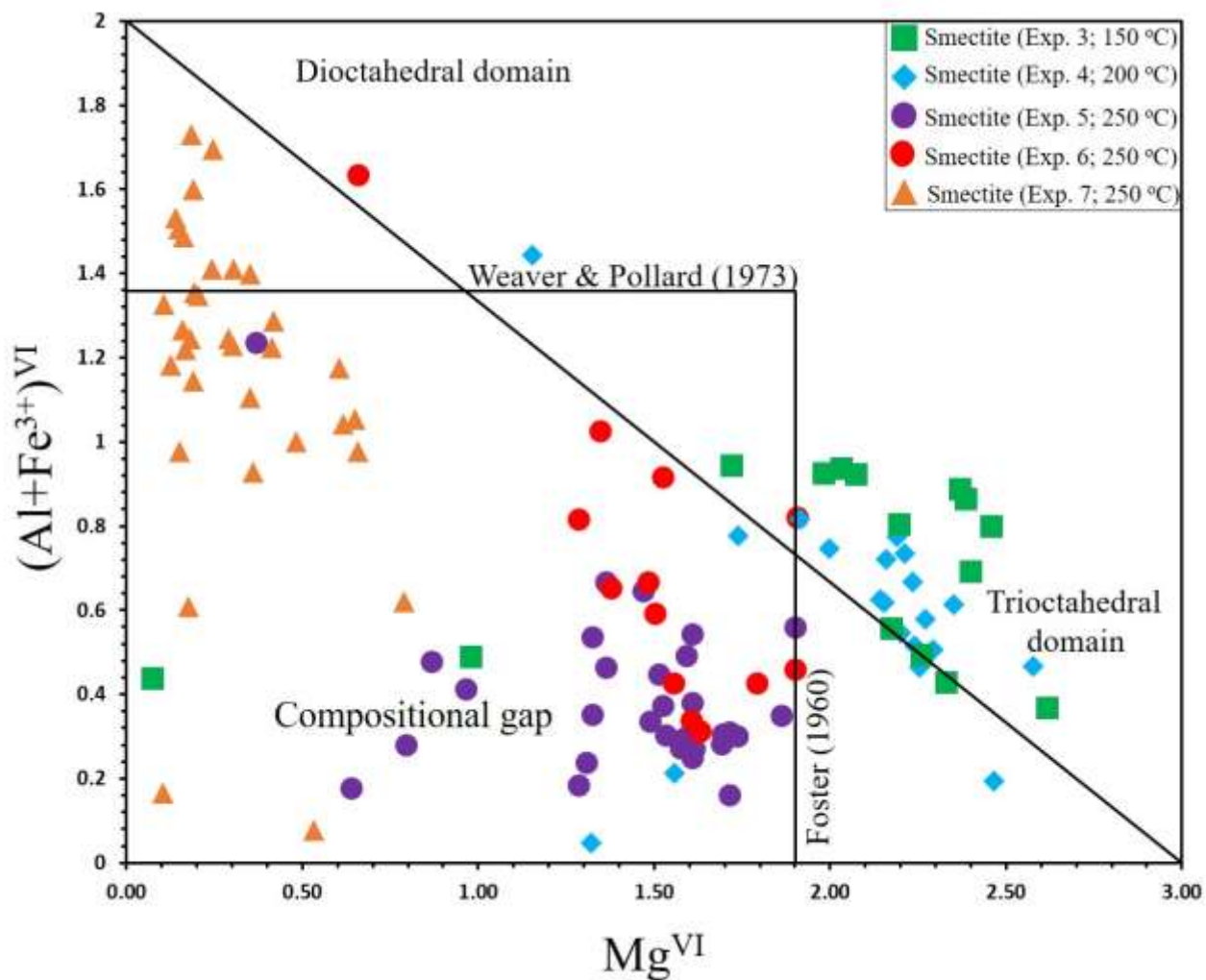


Figure 3. Plot of $(Al + Fe^{3+})^{VI}$ with Mg showing the compositional variations of the synthesized smectite in chapter 3 (adapted from Foster, 1960, and Weaver and Pollard, 1973).

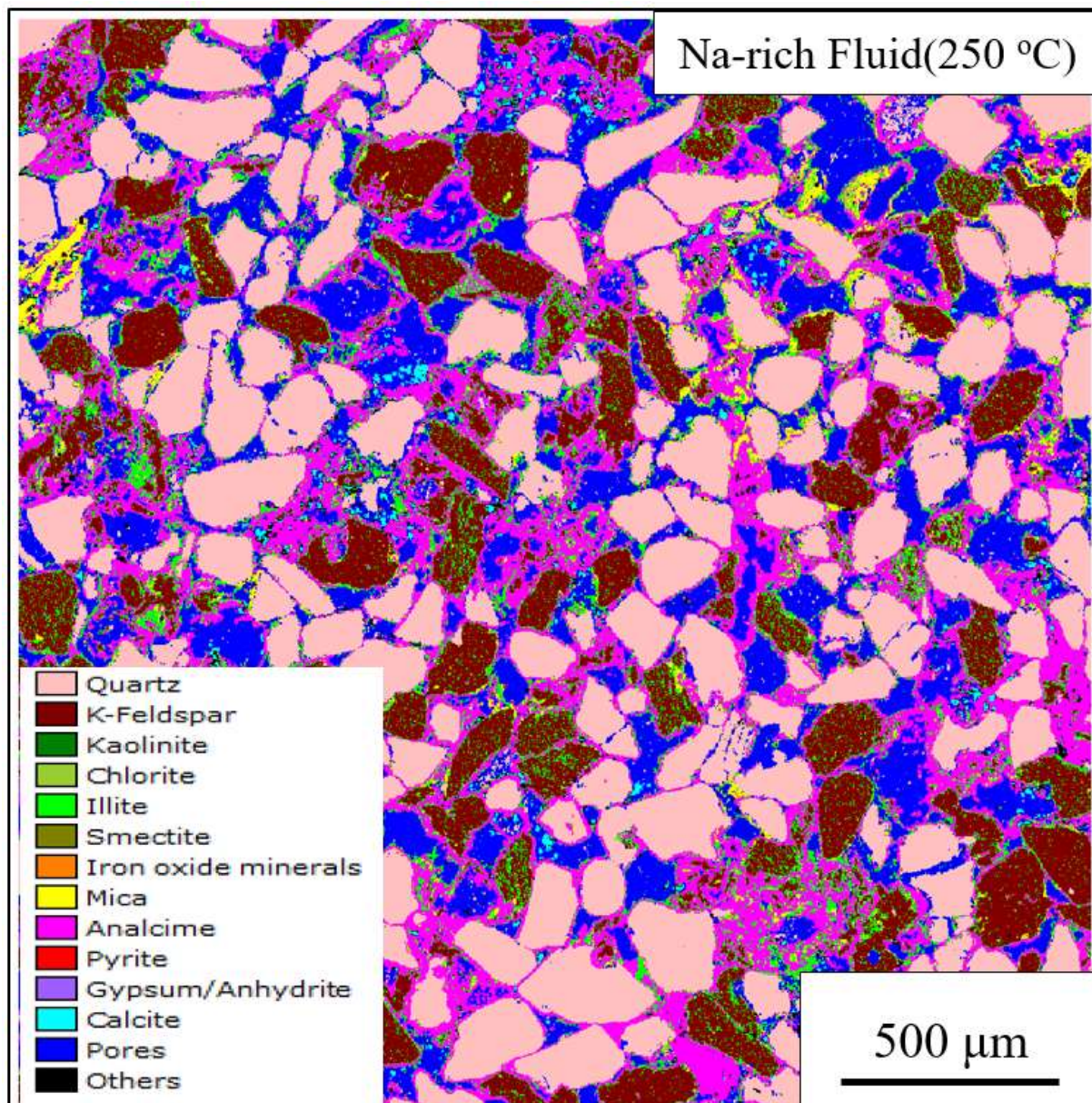


Figure 4. QEMSCAN mineralogical maps displaying the occurrence and distribution of authigenic zeolites (Analcime) synthesized using Na-rich alkaline fluid from arkosic sandstone of Subbat member, Jauf formation, reported in chapter 6.

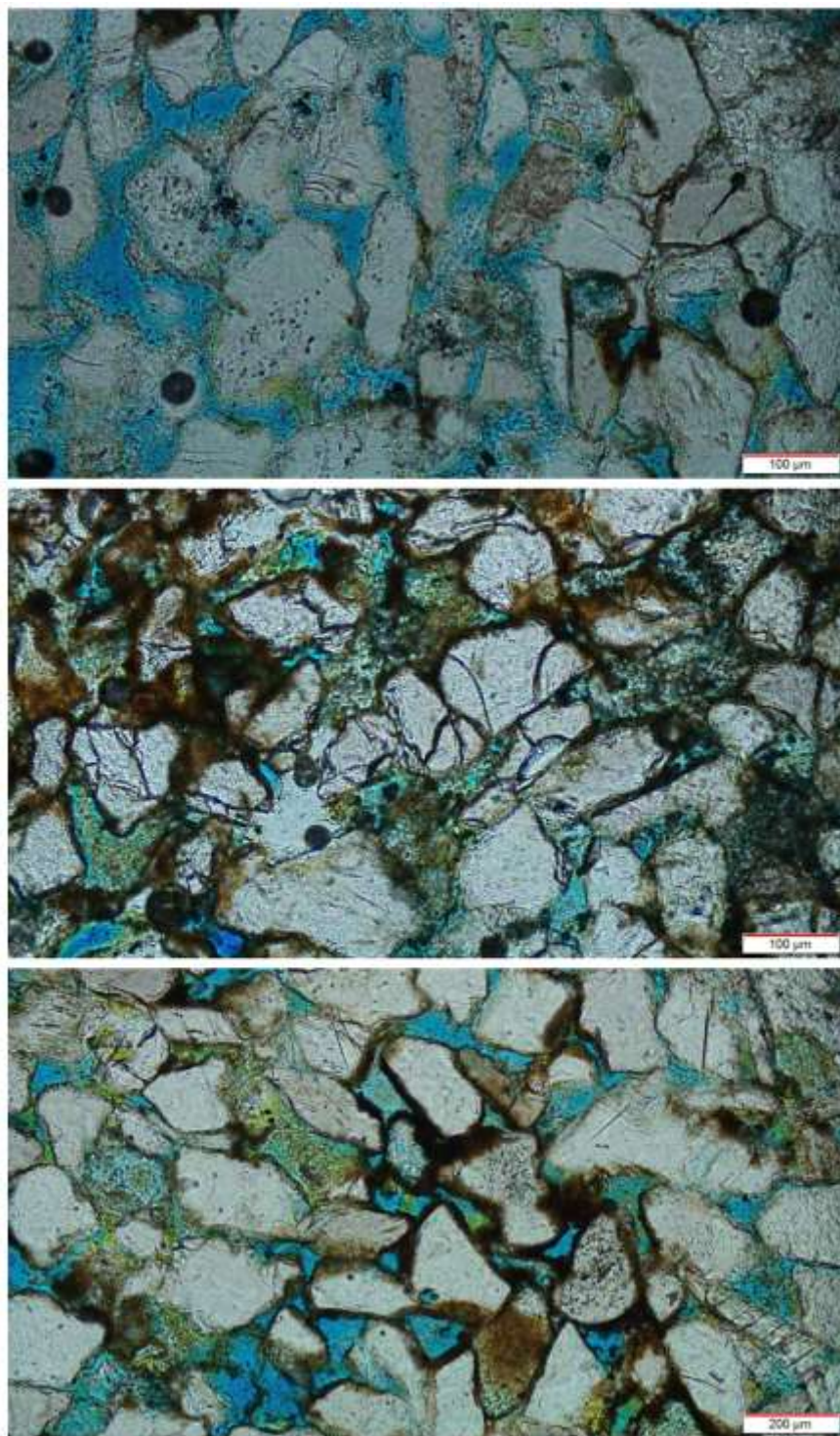


Figure 5. Thin-section micrographs of post-reacted samples showing the development of authigenic chlorite adjacent to pervasively dissolved K-feldspar, as explained in chapter 6.

LIST OF PUBLICATIONS

1. **Salisu, A.M.**, Bello, A.M., Amao, A.O., and Al-Ramadan, K., 2025, The Role of Fluid Chemistry on the Diagenetic Transformation of Detrital Clay Minerals: Experimental Insights from Modern Estuarine Sediments: *Minerals*, v. 15, [doi:10.3390/min15030317](https://doi.org/10.3390/min15030317).
2. **Salisu, A.M.**, Bello, A.M., Amao, A.O., Lander, R.H., and Al-Ramadan, K., 2025, Experimental Study of Smectite Authigenesis and its Subsequent Illitization: Insights from Modern Estuary Sediments: *Journal of Sedimentary Research*. [doi:10.2110/jsr.2024.135](https://doi.org/10.2110/jsr.2024.135).
3. **Salisu, A.M.**, Algheryafi, H., Bello, A.M., Amao, A.O., Al-Otaibi, B., and Al-Ramadan, K., 2024, Depositional and diagenetic controls on the reservoir quality of marginal marine sandstones: An example from the Early Devonian Subbat Member, Jauf Formation, northwest Saudi Arabia: *Marine and Petroleum Geology*, p. 107147, [doi:https://doi.org/10.1016/j.marpetgeo.2024.107147](https://doi.org/10.1016/j.marpetgeo.2024.107147).
4. **Salisu, A.M.**, Alhindi, H., Hussaini, S.R., Amao, A.O., Al-Awah, H., Al-ramadan, K., and Koeshidayatullah, A., 2024, 3D Microporosity Characterizations in the Heterogeneous Middle Jurassic Tuwaiq Mountain Formation: Insights into an Unconventional Sweet Spot: *ACS Omega*, v. 9, p. 36273–36290, [doi:10.1021/acsomega.4c02592](https://doi.org/10.1021/acsomega.4c02592).
5. **Salisu, A.M.**, Alqubalee, A., Bello, A.M., Al-Hussaini, A., Adebayo, A.R., Amao, A.O., and Al-Ramadan, K., 2023, Impact of kaolinite and iron oxide cements on resistivity and quality of low resistivity pay sandstones: *Marine and Petroleum Geology*, v. 158, p. 106568, [doi:https://doi.org/10.1016/j.marpetgeo.2023.106568](https://doi.org/10.1016/j.marpetgeo.2023.106568).
6. Bello, A. M., **Salisu, A. M.**, Alqubalee, A., Amao, A. O., Al-Hashem, M., Al-Hussaini, A., & Al-Ramadan, K. (2024). Diagenetic controls on the quality of shallow marine sandstones: An example from the Cambro-Ordovician Saq Formation, central Saudi

- Arabia. Journal of African Earth Sciences, 215, 105295.
<https://doi.org/https://doi.org/10.1016/j.jafrearsci.2024.105295>
7. Bello, A.M., **Salisu, A.M.**, Amao, A.O., Umar, M., and Al-Ramadan, K., 2025, Experimental Nucleation of Chlorite: Insights from Kaolinite Precursor: Journal of Sedimentary Research, v. 95, p. 1–24, [doi:10.2110/jsr.2024.099](https://doi.org/10.2110/jsr.2024.099).
 8. Alhindi, H.S., **Salisu, A.M.**, Hussaini, S.R., Al-Ramadan, K., and Koeshidayatullah, A.I., 2025, Novel insights to unconventional carbonate mudstone reservoir with quantitative nanoporosity characterization and modeling of Tuwaiq Mountain Formation: Geoenergy Science and Engineering, v. 244, p. 213394, [doi:https://doi.org/10.1016/j.geoen.2024.213394](https://doi.org/10.1016/j.geoen.2024.213394).
 9. Alqubalee, A., **Salisu, A.M.**, Bello, A.M., Al-Hussaini, A., and Al-Ramadan, K., 2023, Characteristics, distribution, and origin of ferruginous deposits within the Late Ordovician glaciogenic setting of Arabia: Scientific Reports, v. 13, p. 18430, [doi:10.1038/s41598-023-45563-9](https://doi.org/10.1038/s41598-023-45563-9).
 10. Alqubalee, A., Muharrag, J., **Salisu, A.M.**, and Eltom, H., 2022, The negative impact of Ophiomorpha on reservoir quality of channelized deposits in mixed carbonate siliciclastic setting: The case study of the Dam Formation, Saudi Arabia: Marine and Petroleum Geology, v. 140, p. 105666, [doi:10.1016/J.MARPETGEO.2022.105666](https://doi.org/10.1016/J.MARPETGEO.2022.105666).
 11. Gaduwang, A.K., Muñoz-López, D., Salisu, A.M., Tawabini, B., Al-Ramadan, K., and Koeshidayatullah, A., 2025, Microfacies control on geomechanical properties of unconventional carbonate reservoirs: insights from a middle jurassic outcrop analogue in Saudi Arabia: Journal of Petroleum Exploration and Production Technology, v. 15, p. 38, [doi:10.1007/s13202-025-01930-y](https://doi.org/10.1007/s13202-025-01930-y).

12. Bello, A.M., Usman, M.B., Amao, A.O., **Salisu, A.M.**, Al-Ramadan, K., Abubakar, U., Mukkafa, S., Kwami, I.A., Chiroma, L.U., Al-Hashem, M., et al., 2025, Linking Provenance and Diagenesis to Reservoir Quality Evolution of Sandstones: The Paleocene-Eocene Kerri-Kerri Formation, Northeastern Nigeria. *Mar Pet Geol* 172, 107227, doi: <https://doi.org/10.1016/j.marpetgeo.2024.107227>.
13. Bello, A.M., Usman, M.B., Amao, A.O., Al-Ramadan, K., Al-Hashem, M., Kachalla, A., Abubakar, U., **Salisu, A.M.**, et al., 2024, Diagenesis and reservoir quality evolution of estuarine sandstones: Insights from the Cenomanian-Turonian Yolde Formation, northern Benue Trough, NE Nigeria: *Marine and Petroleum Geology*, v. 169, p. 107073, doi: <https://doi.org/10.1016/j.marpetgeo.2024.107073>.
14. Bello, A.M., Usman, M.B., Ismail, M.A., Mukkafa, S., Abubakar, U., Kwami, Al-Ramadan, K., Amao, A.O., Al-Hashem, M., **Salisu, A.M.**, et al. 2023, Linking diagenesis and reservoir quality to depositional facies in marginal to shallow marine sequence: An example from the Campano-Maastrichtian Gombe Sandstone, Northern Benue Trough, NE Nigeria: *Marine and Petroleum Geology*, v. 155, p. 106386, doi: [10.1016/j.marpetgeo.2023.106386](https://doi.org/10.1016/j.marpetgeo.2023.106386).
15. **Salisu, A.M.**, Bello, A.M., Amao, A.O., and Al-Ramadan, K., 2025, Experimental Study of Smectite Authigenesis and its Subsequent Illitization: Insights from Modern Estuary Sediments: (Manuscript prepared).

VITAE

Name : Anas Muhammad Salisu |
Nationality : Nigerian |
Date of Birth : 1/1/1994 |
Email : anassalisumuhammad18@gmail.com |
Address : 12, Yerima quarters, Kaura Namoda, Zamfara State, Nigeria |

Academic Background

PH.D. IN GEOLOGY *Sep 2021 - May 2025*
King Fahd University of Petroleum and Minerals, **Dhahran, Saudi Arabia**

M.SC. IN PETROLEUM GEOSCIENCE *Sep 2018 - Sep 2019*
Imperial College London, **London, UK**

B.SC. IN GEOLOGY *Aug 2012 - Nov 2016*
Ahmadu Bello University, **Zaria, Nigeria**

Work Experience

Research/Teaching Assistant **Dhahran, Saudi Arabia.**
King Fahd University of Petroleum and Minerals **September 2021 - Present**

- Providing technical and instructional support to faculty members in designing experiments and implementing data analysis techniques.
- Assisting graduate students in conceptualizing and developing experimental designs for their research in experimental diagenesis.
- Guiding and mentoring research students, ensuring alignment with research objectives and expected outcomes.
- Taught Structural Geology to undergraduate students, preparing lecture materials and delivering engaging lab sessions.
- Prepared lecture notes, quizzes, and assignments, and evaluated student performance.

- Organized and led Petroleum Geology laboratory sessions for undergraduate students, facilitating hands-on learning experiences.
- Designed and developed a systematic framework for clay mineral separation and XRD analysis, critical for experimental diagenesis and reservoir quality evaluation.
- Conducted a series of experimental diagenesis studies to simulate the diagenetic transformation of sandstones and assess its implications for reservoir quality.
- Experimentally synthesized zeolites and clay minerals essential for sustainable energy exploration and production.
- Assisted in organizing and conducting multiple student field trips across various geological formations within the Kingdom.

Assistant Lecturer

Ahmadu Bello University

Zaria, Nigeria.

December 2019 -August 2021

- Taught undergraduate courses including Geochemistry, Sedimentology, and Petroleum Geology.
- Conducted assessments of student performance through exams, presentations, and assignments.
- Participated in Geologic field mapping of the basement complex of Northern Nigeria.
- Attended departmental, faculty meetings and membership of several committees.
- Conducted research in Basin Analyses and Structural Geology.

Graduate Intern

Tullow Oil Plc

London, UK.

June 2019 - September 2019

- Worked collaboratively in a diverse team of Engineers, Geologists, and Geophysicists to deliver a detailed exploration plan for an offshore hydrocarbon field.
- Conducted 1D and 2D basin modeling of the Tchatamba Field, offshore Gabon.
- Gained experience in the use of Petrel, PetroMod, and IP software.
- Developed a 3D structural model of an offshore hydrocarbon field.

Graduate Assistant

Federal University Gusau

Gusau, Nigeria.

Jan 2018 – July 2018

- Prepared laboratory materials and conducted lab sessions in sedimentology.
- Taught Introduction to Physical Geology to undergraduate students.
- Assessed student performance through exams, presentations, and assignments.
- Participated in geologic fieldworks, excursions and orientations.

Geologist

Center for Energy Research and Training (CERT)

Zaria, Nigeria.

Jan 2017 - Dec 2017

- Gained experience in the use of AAS, XRF, and XRD for the geochemical analysis of geological samples.
- Conducted studies on geological formations to evaluate their suitability as potential sites for nuclear waste repositories.
- Participated in several geological field trips within Nigeria.

Research Interest

- Experimental simulation of burial diagenesis and its application for energy exploration and sustainability.
- Rear Earth Elements (REE) and critical minerals exploration in sedimentary rocks.
- Evolution of sandstone reservoir quality during underground CO₂ and hydrogen storage.
- Reservoir quality assessment of siliciclastic acquirers for clean water exploration.

Workshop/Conferences

- ✓ International Petroleum Technology Conference (IPTC), Dhahran, Saudia Arabia, 2024
- ✓ International Meeting for Applied Geoscience and Energy (IMAGE), Houston, U.S.A, 2023.
- ✓ MEOS/GEO, Manama, Bahrain 2023.
- ✓ 5th Edition: AAPG GTW Siliciclastic Reservoirs of the Middle East Al Khobar, Dec 2023.

- ✓ 2nd Edition of the AAPG/SPWLA Low Resistivity Reservoirs: Path to Explore, Discover and Develop, Al Khobar, May 2023.
- ✓ 2nd Edition of the AAPG Integrated Emerging Exploration Concepts, Al Khobar, Nov 2022.
- ✓ PETEX, London, UK 2019.
- ✓ Nigerian Association of Petroleum Explorationists, International conference and exhibition, Lagos, Nigeria, 2018.
- ✓ Nigerian Mining and Geoscience Society, International conference and exhibition, Abuja, Nigeria 2018

Skills

- | | |
|--|---|
| • Ability to work in a multinational diverse environment | • Effective oral and written communication |
| • Experienced in the use and operation of XRD, XRF, SEM, SEM-EDX and Petrographic microscopes. | • Good computer proficiency (MS Office packages) |
| • Clay fraction separation, analyses and identification | • Proactive, self-motivated, and target oriented. |
| • Sandstone Reservoir quality assessment | • Problem-solving and critical-thinking |
| • Experimental diagenesis | • Petrel, Petromod, and Interactive petrophysics (IP) |

Awards

- CPG-KFUPM Team captain and winner of the global AAPG Imperial Barrel Award (IBA), Houston, Aug 2023.
- CPG-KFUPM Team captain and winner of the Middle East AAPG Imperial Barrel Award (IBA), Manama, Feb 2023.
- Graduate scholarship, KFUPM, 2021-2025
- Overall best international students (Past students' prize), M.Sc. Petroleum Geoscience, Imperial College London. 2019

- Petroleum Technology Development Fund (PTDF, Nigeria) MSc Overseas Scholarship Scheme, 2018-2019
- Best Graduating Student, Department of Geology, A.B.U, Zaria, 2016
- Dean's list, Faculty of Physical Sciences, A.B.U Zaria, Nigeria, 2016

Volunteering/Extracurricular activities

- Team Consultant, AAPG-CPG-KFUPM Student chapter, 2025 Session
- Secretary, AAPG-CPG-KFUP Student chapter, 2023 Session
- Secretary, ARMA-KFUPM Student Chapter, 2022 session
- Scribe, 5th Edition: AAPG GTW Siliciclastic Reservoirs of the Middle East Al Khobar, Dec 2023.
- Scribe, 2nd Edition of the AAPG/SPWLA Low Resistivity Reservoirs: Path to Explore, Discover and Develop, Al Khobar, May 2023.
- Scribe, 2nd Edition of the AAPG Integrated Emerging Exploration Concepts, Al Khobar, Nov 2022.
- Secretary, AAPG student chapter, Imperial college London, 2018-2019 session
- President, AAPG Student Chapter, Ahmadu Bello University, Zaria, Nigeria. 2015-2016 session
- Secretary, Student representative council (SRC), A.B.U Zaria, Nigeria 2014-2015 session