Parameters Controlling Distribution of Diagenetic Alterations within Fluvial and Shallow Marine Sandstone Reservoirs

Evidence from the Libyan Basins

MUFTAH KHALIFA
Dissertation presented at Uppsala University to be publicly examined in Hambergsalen, Villavägen 16, Uppsala, Wednesday, 15 June 2016 at 10:00 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Dr. João Marcelo Medina Ketzer (Pontifícia Universidade Católica do Rio Grande do Sul).

Abstract

This thesis demonstrates that geological setting, depositional facies, open system flux of hot basinal brines and descending of shallow waters have a strong impact on the distribution of the diagenetic alterations within continental and paralic/shallow marine sandstones which in turn control the quality and heterogeneities of the reservoirs.

Geological setting controls the mineralogical and textural maturity of sandstone, whereas depositional facies control the pore water chemistry (marine, brackish or meteoric), sedimentary texture and sand body geometry. Eogenetic alterations in the fluvial deposits are dominated by precipitation of infiltrated clays, kaolinitization of detrital silicates, whereas the shallow marine deposits are dominated by precipitation of early calcite and kaolinite. Conversely mesogenetic alterations are dominated by clay minerals transformation, quartz overgrowths and Ferroan-carbonates, barite and anhydrite. Flux of hot basinal brines is evidenced by precipitation of mesogenetic minerals that lack of internal sources (e.g. barite, anhydrite and ferro carbonate cements), which is evidenced by: (1) restricted occurrence of these minerals in downthrown blocks. (2) The high fluid inclusion homogenization temperatures (Th) of quartz overgrowths (Th > 110-139°C), and carbonate cements (T > 80-140°C), which also have light δ18Ov. prim(-17.6‰ to -6.7‰). Flux of hot basinal brines is further evidenced by occurrence of saddle Fe-dolomite along stylolites. Fluid inclusion microthermometry further revealed a dramatic shift in pore- water chemistry from NaCl dominated brines during precipitation of quartz overgrowths to NaCl-CaCl2 dominated brines during cementation by Fe-dolomite. Presence of mixed brine (NaCl+CaCl2) systems in the fluid inclusions suggests flux of descending waters, which have circulated in the overlying carbonate-evaporite successions. The restricted occurrence of oil-filled inclusion to quartz overgrowths and methane to Fe-carbonate cements suggest migration of oil during precipitation by quartz and migration of methane during precipitation by Fe-carbonate cements. The extensive mesogenetic cements in the down thrown blocks is attributed to flux of basinal brines along deep seated faults, i.e. open system diagenesis.

Integration of fluid inclusion microthermometry, isotopes, Raman spectrometry and thermal tectonic evolution of basins are essential techniques for unraveling the evolution of basinal fluids, cementation conditions and relative timing of hydrocarbons migration.

Keywords: Diagenesis, Structural setting, Depositional facies, Basin thermal history, Thermal/Hot basinal brines, Fluid inclusions, Raman Spectrometry, Stylolites, Hydro-carbon migration

Muftah Khalifa, Department of Earth Sciences, Mineralogy Petrology and Tectonics, Villav. 16, Uppsala University, SE-75236 Uppsala, Sweden.

© Muftah Khalifa 2016

ISSN 1651-6214
urn:nbn:se:uu:diva-284581 (http://urn.kb.se/resolve?urn:nbn:se:uu:diva-284581)
To the spirits of my father, mother, brothers and sisters.

Brothers, sisters and their families,
my wife and children

To whom loves Sciences and wishes
to discover the Nature Secrets
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Reprints were made with permission from the respective publishers.
The papers and manuscript included in this thesis are mainly the result of my efforts in addition to contribution of several co-authors particularly my supervisor Prof. Sadoon Morad. Prof. Morad contributed by his direct supervision to my work through all the published and unpublished manuscript and he took care of the scientific writing corrections and improves of the reading. My individual contributions for each paper are as follows:

**Paper 1**: My contribution was about 65-70% of the total efforts. I collected the core samples, description, samples analyses interpretation and figures, and I contributed in writing of the initial draft of the manuscript.

**Paper 2**: My contribution was about 75-80% of the total efforts. I collected the core samples, description, samples analyses interpretation and figures, and I wrote the initial draft of the manuscript.

**Paper 3**: My contribution was about 85% of the total efforts. I collected the core samples, description, samples analyses interpretation and figures, and I wrote the initial draft of the manuscript.

**Paper 4** (manuscript): My contribution was about 70% of the total efforts, including collecting core samples, description, samples analyses, interpretation, figures, and I wrote the initial draft of the manuscript.
## Contents

1 Introduction .................................................................................................................. 11
  1.1 Aims of the study .................................................................................................. 12
  1.2 Diagenesis ........................................................................................................... 13
  1.3 Methodology ....................................................................................................... 15

2 Impact of diagenetic alterations on siliciclastic reservoirs ...................................... 18
  2.1 Eogenetic alterations in continental and shallow marine sandstones ...................... 18
  2.2 Mesogenetic alterations in continental and paralic/shallow marine sandstones .. 19
    2.2.1 Quartz cementation ....................................................................................... 19
    2.2.2 Cementation by Fe-dolomite/ankerite and siderite ...................................... 20
    2.2.3 Clay mineral transformation ....................................................................... 21
    2.2.4 Feldspar grain albitization and dissolution ................................................ 22
    2.2.5 Barite and anhydrite cements ..................................................................... 23
    2.2.6 Pyrite ......................................................................................................... 23
    2.2.7 Other parameters that enhance precipitation of mesogenetic alterations include: basinal thermal history, heat flow, and flux of hot basinal brines ................................................................. 24

3 Reservoir quality evolution ....................................................................................... 28
  3.1 Reservoir quality and heterogeneity models ...................................................... 28
    3.1.1 Model 1: Summary model of impact of geological setting on distribution of diagenetic alterations: evidences from Cretaceous sandstones, Az-Zahrah Platform-Sirt Basin .................................................. 28
    3.1.2 Model 2: Summary model indicating the impact of a flux of hot basinal brines on the distribution of mesogenetic alterations: evidence from Cretaceous sandstones (Nubian and Bahi formations) Khalifa Field, Al Bayda Platform-Sirt Basin .................................................. 32
    3.1.3 Model 3: Summary model indicates impact of depositional facies on the distribution of diagenetic alterations: .................................................. 36
    3.1.4 Model 4: Summary model indicating shift information water chemistry from quartz-dominated to carbonate dominated, diagenetic conditions, and timing of hydrocarbon migration as evidenced from integration of several petrographical techniques. ...... 40
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-scattered electron imaging</td>
</tr>
<tr>
<td>MPa/km</td>
<td>Mega Pascal/kilometer</td>
</tr>
<tr>
<td>mW</td>
<td>Mega watt</td>
</tr>
<tr>
<td>n.d.</td>
<td>Not detected</td>
</tr>
<tr>
<td>OWC</td>
<td>Oil water contact</td>
</tr>
<tr>
<td>PPL</td>
<td>Plane polarized light</td>
</tr>
<tr>
<td>SD</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>Te</td>
<td>Eutectic temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Th</td>
<td>Homogenization temperature</td>
</tr>
<tr>
<td>Tfm</td>
<td>First melting temperature</td>
</tr>
<tr>
<td>Tm</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>Tmice</td>
<td>Ice melting temperature</td>
</tr>
<tr>
<td>V-CDT</td>
<td>Vienna- Canyon Diablo Troilite</td>
</tr>
<tr>
<td>V-PDB</td>
<td>Vienna-Pee Dee Belemnite</td>
</tr>
<tr>
<td>V-SMOW</td>
<td>Vienna- Standard Mean Ocean Water</td>
</tr>
</tbody>
</table>
The assessment and prediction of the impact of diagenetic alterations on temporal and spatial variations in sandstone reservoir quality are key challenges for hydrocarbon exploration, production and recovery in sedimentary basins.

Diagenetic evolution in siliciclastic deposits is controlled by several interrelated parameters including detrital composition, pore-water chemistry, depositional facies, paleo-climatic conditions, energy of depositions, and burial-thermal history of the basin (Morad et al., 2000). Detrital composition of sandstones is strongly controlled by the tectonic setting of the basin and sediment provenance. Changes in pore-water chemistry, and amounts and types of intrabasinal grains (e.g. mud intraclasts), grain size, sorting and sedimentation rates (i.e. residence time of sediment at near sea floor conditions) are attributed to changes in relative sea level (Morad et al., 2000). Recently some studies demonstrated that the diagenetic evolution of siliciclastic deposits can be better understood and predicted when linked to the sequence stratigraphic framework (Morad et al., 2000; Ketzer, 2003; Al-Ramadan et al., 2005, 2012a and b). Fluxes of external basinal fluids may be also enhance precipitation of mesogenetic cements and as a result there is a strong debate regarding whether deep burial alterations occur in open or closed systems, in which mass transfer may have taken place by: (i) small-scale diffusion in closed mesogenetic systems (Worden and Barclay, 2000), (ii) large-scale cross-formational fluid flow in open systems (Berger et al., 1997), and (iii) fluxes of hot basinal brines through faults in open systems (Burley, 1993; Morad et al., 1994).

The diagenetic regimes are subdivided into (sensu Morad et al., 2000): (i) Eodiagenesis (≤ 70°C; < 2 km), during which the pore-water chemistry is controlled by surface (meteoric and marine) waters. (ii) Mesodiagenesis (>70°C; > 2 km), which is mediated by evolved formation water, flux of hot basinal fluids, elevated temperatures and thermal history of the basin. Several lines of evidence indicate the role of flux of hot basinal fluids through conduit faults in the distribution of mesogenetic alterations, which may be evidenced by cements that lack of internal sources (i.e. barite, anhydrite and Fe-rich carbonates) (Morad et al., 2000).

Understanding the distribution of diagenetic alterations within siliciclastic reservoirs has great importance in the evolution of the reservoir quality and heterogeneities, which are key challenges for hydrocarbon exploration, pro-
duction and drilling of development wells in the reservoirs, as well as planning enhanced oil recovery (EOR) strategies (Kantorowicz et al., 1986; Bloch et al., 1990; Bloch and McGowen, 1994; Csoma and Goldstein, 2012).

1.1 Aims of the study

This study aims to: (i) constrain the impact of structural setting, depositional facies, burial history and flux of hot basinal fluids on distribution of diagenetic alterations in the fluvial and shallow marine sandstone reservoirs from the Sirt and Ghadamis basins, Libya (Fig. 1), (ii) demonstrate that mesogenetic alterations do not occur only in closed systems, but may also be affected by flux of basinal brines through conduit faults in open mesogenetic systems. (iii) The shift in precipitation from quartz to carbonates reflects a dramatic shift in pore-water chemistry. (iv) To predict the relative timing of hydrocarbon migration to quartz overgrowths and Fe-carbonate cements, as evidenced by integration of fluid inclusions, thermal tectonic evolution of the basin and hydrocarbon generation phases.

Two case studies were conducted in the Sirt Basin (Fig. 1), represented by core samples from the Bahi and Nubian sandstones. Three wells were selected from the Bahi and Az-Zahrah oilfields- Az-Zahrah Platform NW part of the basin, and two wells were selected from the Al-Bayda Platform in the southern part of the basin, in which we emphasis the impact of structural setting and flux of hot basinal brines (open system) on distribution of diagenetic alterations in the Cretaceous (fluvial and tidal) sandstone reservoirs is emphasized.

Two topics from one case study were conducted in the Ghadamis Basin, as represented by core samples from the middle Devonian (Aouient Ouenine Formation) sandstones-Al-Wafa Field in the southern part of the basin, in which we studied: 1) the impact of depositional facies (i.e. shoreface sandstones) in the distribution of diagenetic alterations, and 2) integrated petrography, stable isotopes and fluid inclusion microthermometry and Raman Spectrometry, and thermal tectonic evolution of the basin to decipher the precipitation conditions of digenetic cements (i.e. quartz overgrowths and Ferroan carbonates), the shift in pore-water chemistry from quartz to Fe-carbonate cementations and to predict the relative timing of hydrocarbon migration to cementation by quartz overgrowths and diagenetically later Fe-carbonate cements.
1.2 Diagenesis

Prior to evaluation of the impact of structural setting, depositional facies, paleoclimatic conditions, detrital composition and relative changes in the sea-level on distribution of the diagenetic alterations and their impact on sandstone reservoir quality evolution pathways (Morad et al., 2000; Ketzer et al., 2003; Worden and Morad, 2003). It is essential to define diagenesis. Diagenesis is the process by which sediments are lithified to sedimentary rocks, and represents the sum of physical, chemical and biological changes that occur after deposition and continue during burial and uplift (Worden and Morad, 2000).

Digenetic processes are responsible for significant changes in the physical and chemical properties of the sediments, which in turn impacts reservoir quality evolution (Rossi et al., 2002; Al-Ramadan et al., 2005; Abouessa and Morad, 2009). Physical processes are evidenced by mechanical compaction, which includes grain rearrangement, deformation of mud intraclasts and bending of mica flakes, which occur at shallower burial (eodiagenesis; Morad et al., 2000). Chemical compaction includes intergranular quartz grain dissolution, which occurs during burial (mesodiagenesis; Morad et al., 2000), which causes reduction in the sediments bulk volume and quartz cementation, and hence deteriorates primary porosity and permeability. Chemical compactions and stylolites are enhanced by presence of illitic clay coats (Oelkers et al., 2000). The main parameters that control distribution of diagenetic alterations within fluvial and shallow marine sandstones are illustrated in Figure 2.
Figure 2. Flow chart indicating the main parameters that controlling distribution of diagenetic alterations within fluvial and shallow marine sandstones.
Chemical processes include grain dissolution, cementation by quartz overgrowths and carbonate cements, transformation of chemically unstable grains (e.g. feldspar to kaolinite or albite, mica to kaolinite), and transformation of detrital and eogenetic clays (e.g. kaolinite to dickite or illite, smectite to illite or chlorite) (e.g. Morad, et al., 2000). Dissolution processes are enhanced by flushing of sediments by meteoric water or descending of undersaturated waters (Morad et al., 2000; Ketzer et al., 2003; El-ghali et al., 2006). Cementation and compaction processes lead to lithification of the sediments into sedimentary rocks, whereas dissolution processes enhance porosity and permeability of the sediment. (Emery et al., 1990)

Eoegenetic alterations (< 2 km; < 70°C; Morad et al., 2000) are controlled by depositional facies, palaeo-climatic conditions, geological setting sandstone maturity, pore-water chemistry, changes in relative sea level and incorporation of intrabasinal mud intraclasts (De Ros et al., 1994; Taylor et al., 2004; Al-Ramadan et al., 2005; Reed et al., 2005). Eogenetic alterations include precipitation of iron oxides, kaolinitization of feldspar grains, mica and mud intraclasts, feldspar grain dissolution, cementation by chalcedony and grain-coating micro-quartz, as well as infiltrated clay coating, cementation by pre-compactional calcite and dolomite.

Mesogenetic alterations (> 2 km; > 70°C; Morad et al., 2000) are controlled by burial-thermal history, formation-water chemistry and distribution patterns of eogenetic alterations (Burley et al., 1985; Morad et al., 2000). The mesogenetic alterations include albitization and dissolution of feldspar grains, clay transformation (dictitization and illitization of kaolinite, illitization of smectite, chemical compaction, and cementation by quartz overgrowths, Fe-dolomite and ankerite, siderite, anhydrite and barite.

Telodiagensis occurs after the sedimentary sequences, which have undergone eo-and mesogenetic modifications, have been uplifted and subjected to the influence of meteoric waters. The most important telogenetic modifications, which are promoted by flushing of meteoric waters in sandstones, include: (a) dissolution of unstable framework grains (e.g. feldspars, mica, rock fragments, mud intraclasts and heavy minerals (Emery et al., 1990), (b) alteration of eo-and mesogenetic cements, such as dissolution of calcite, dolomite, sulfates, feldspar overgrowths, and oxidation of Fe-carbonates, chlorite and pyrite (Morad et al., 1995), and (c) precipitation of infiltrated clays cover mesogenetic cements (Morad et al., 2000). However, in the case studies included in this thesis there is no clear evidence for telogenetic processes.

1.3 Methodology
The selected core sandstone samples have been described (i.e. grain texture and sedimentary structure) in order to infer the depositional environment.
Thin sections were prepared from selected samples subsequent to vacuum-impregnation with blue epoxy. The modal composition and porosity were obtained by counting 300 points in each thin section (Harwood, 1988).

Representative core chips were coated with gold and examined with a JEOL JSM-T330 scanning electron microscope (SEM). The SEM was performed by the Libyan Petroleum Institute, and the departments of earth sciences and Palaeobiology, Uppsala University, Sweden. The chemical compositions of carbonate cements were obtained using a Field Emission Electron Probe (MP) Microanalyser (FE-EPMA), a JXA-8530F JEOL SUPERPROBE, equipped with four crystal spectrometers (WDS) and backscattered electron detectors (BSE). The operation conditions during the analyses were an accelerating voltage of 20kV, a measured beam current of 8nA and a beam diameter of 1-5 µm. The standards, and count times used were wollastonite (Ca, 10 s), (Mg, 10 s), (Mn, 20 s), hematite (Fe, 20 s), and strontianite (Sr, 20 s). Detectors limits were 48 ppm Mg, 90 ppm Fe, 135 Mn, and 259 ppm Sr.

Selected carbonate cemented samples were analyzed for C- and O-isotopes. The samples were crushed and reacted in vacuum with 100% phosphoric acid; Fe-dolomite/ankerite and siderite at 50°C for 24 h and six days, respectively (e.g. Al-Aasm et al., 1990). The CO₂ gas released was collected and analyzed using a Delta Plus mass spectrometer. Samples containing calcite, dolomite and siderite were subjected to sequential chemical separation treatment (e.g. Al-Aasm et al., 1990). The phosphoric acid fractionation factors used were 1.01060 for dolomite at 50°C, 1.010454 for siderite at 50°C (Rosenbaum and Sheppard, 1986), and 1.01025 for calcite at 25°C (Friedman and O’Neil, 1977). Data are reported in per mil (‰) relative to Vienna Pee Dee Belemnite (V-PDB) standard (Craig, 1957).

The samples were washed with distilled water and then reacted with dilute acetic acid in order to avoid silicate leaching. Correction for isotopes fractionation during the analyses was made by normalization to $^{87}\text{Sr} / ^{86}\text{Sr} = 0.1194$. The mean standard error of mass spectrometry was +/- 0.00003 for standard NBS-987.

The $^{87}\text{Sr} / ^{86}\text{Sr}$ isotope ratio was analysed for a two Fe-dolomite cemented samples, using the method of Schulz et al. (1989). The isotopes were analyzed using the automated Finnigan 261 mass spectrometry equipped with 9 Faraday collectors. Barite (Paper I) was separated from other minerals in the samples by a sequential leaching procedure (Paytan et al., 1993). The selected samples were examined for purity by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive spectrometry (EDS), and only samples that contained > 95% barite were used. S isotope analyses were done by continuous-flow mass spectrometry using a Carlo Erba Na 1500 elemental analyzer connected to a Micromass Isoprime mass spectrometry. Samples of 4-8 mg were introduced in tin boats with ~5 mg vanadium pentoxide mixed in with each sample. A tank of commercial SO₂
was used as a reference gas for δ³⁴S measurements (e.g. Paytan, et al., 2002), and results are reported relative to Vienna Canyon Diablo Troilite (V-CDT) standard.

Fluid inclusions homogenization (T_h), first melting (T_{fm}) and final ice melting (T_{mice}) temperatures were measured both in Fe-dolomite cement and quartz overgrowths. The former is the inclusion’s minimum entrapment temperature (i.e. the minimum temperature of mineral precipitation) (e.g. Goldstein and Reynolds, 1994), whereas the first melting is the temperature at which the first melt drop is seen after complete freezing of inclusions (solid phase). The latter is the temperature at which the last crystal of ice melts in a previously frozen aqueous fluid inclusion and reflects the trapped diagenetic fluid’s salinity (e.g. Goldstein and Reynolds, 1994). Measured T_{mice} can be linked with wt.% NaCl eq. using the relation of Hall et al. (1988) and Bodnar (1993). The microthermometric measurements were performed using a LinkamTHMS600G heating-freezing stage coupled with an Olympus BX60 transmitted-light microscope; the stage thermocouple was calibrated using synthetic pure water and CO₂ inclusions.

The fluid inclusions were analyzed by Raman Microspectroscopy using a HORIBA Jobin-YvonLabRAM HR confocal Raman Microspectrometer. For the measurements we applied 532 nm emission of a frequency-doubled Nd: YAG laser with a grating of 1800 grooves mm⁻¹. The maximum laser power incident on the sample was about 40 mW. The detected phases were identified by their characteristic Raman peaks. A 100× microscope objective was used to focus the laser onto the sample and to collect the Raman signal. Spectra were gathered 2–10× accumulations and 2–150 s acquisition time (all depending on the maximum intensity). Raw data were processed using LabSpec v5.25.15 software designed for Jobin-Yvon Horiba LabRam instruments.

The fluid inclusion analyses were performed by the Lithosphere Fluid Research Lab. Institute of Geography and Earth Sciences-Hungary, and by the fluid inclusion Lab. Department of Earth Sciences, University of Pavia-Italy.

Porosity and permeability were measured on core plugs obtained from the core samples. The porosity measurements were performed using a helium porosimeter, whereas permeability measurements were achieved using a helium permeameter by applying a confining pressure of 100 to 400 psi. Prior to measurements, the core plugs were examined carefully for microfractures, cleaned in an oil extractor, and dried in a vacuum oven at 60°C for 24 hours.

The analyses were performed by the Core laboratory, Libyan Petroleum Institute.
2 Impact of diagenetic alterations on siliciclastic reservoirs

2.1 Eogenetic alterations in continental and shallow marine sandstones

The case studies show that the most common eogenetic alterations in the continental (braided fluvial), paralic (tidal and shoreface) sandstones include:

I Mechanical compaction of ductile grains manifested by grain re-arrangement and squeezing of mud intraclasts into pseudomatrix (papers I-IV).

II Grain coating illite formed by mechanical infiltration of suspended mud rich waters in continental deposits (Moraes and De Ros, 1990) (i.e. fluvial and tidally reworked sandstones; papers I and II).

III Kaolinitization/dissolution of framework silicate grains (i.e. feldspars, mica and mud intraclasts) due to flux of meteoric waters into sediments during fall in relative sea level (Ketzer et al., 2003; El-ghali et al., 2006; Mansurbeg et al., 2006) (i.e. fluvial and tidal sandstones; papers I-IV).

IV Cementation by early calcite, which occurs as pervasively cemented few meter thick sandstone beds (i.e. tidally reworked (paleosols) and tidal sandstones- papers I, and carbonate cemented sandstones bed paper-III). Early calcite cement was probably precipitated from meteoric and/or mixed meteoric and marine waters (Simpson and Hutcheon, 1995; Morad et al., 2000).

V Micro-quartz and chalcedony (i.e. fluvial sandstones paper II), which possibly originated from dissolution of amorphous silica sponge spicules and skeletons of radiolaria and diatoms (e.g. Hendry and Trewin, 1995; Williams et al., 1985). Presence of micro-quartz grain coating in the fluvial sandstones (Paper II) inhibited precipitation of extensive syntaxial quartz cement, and hence preserved the reservoir quality (e.g. French et al., 2012).
Iron oxide, Fe needed for precipitation of iron oxides are possibly sourced from alteration of iron rich minerals (i.e. hematite, biotite and clays) (e.g. Boles and Franks, 1979) (e.g. fluvi al sandstones paper I).

Occurrence of framboidal pyrite are attributed to the presence of iron and sulfate forming minerals; Fe was probably sourced from alterations of Fe rich minerals (i.e. hematite, biotite and clays), whereas the SO₄ was probably sourced from alterations of organic matter (e.g. Raiswell, 1982) (e.g. shoreface sandstones paper III).

Distribution of eogenetic alterations are strongly facies related, whereas their abundance are attributed to geological setting, provenances, detrital composition and relative change in sea level (e.g. Morad et al., 2000). Abundance of eogenetic alterations causes lowering of primary porosity and permeability of the sandstones, which in turn controls the distribution of mesogenetic alterations, and hence deteriorates reservoir quality.

2.2 Mesogenetic alterations in continental and paralic/shallow marine sandstones

The distribution of mesogenetic alterations is influenced by the abundance and distribution patterns of eogenetic alterations, formation water chemistry, fluxes of basinal brines and thermal tectonic evolution of the basins (Morad, et al., 2000). The most common mesogenetic alterations in the studied sandstones are:

2.2.1 Quartz cementation

Cementation by quartz overgrowths occur primarily as syntaxial overgrowths around clean surfaces of quartz grains. Si is sourced internally from stylolitization and intergranular pressure dissolution of quartz grains and, to a limited extent, from alteration of feldspars and transformation of clays (Hendry and Trewin, 1995; Gluyes et al., 2000), and/or externally sourced due to flux of basinal brines (Worden and Morad, 2000). Cementation by quartz overgrowths is more extensive in the water zone than in the oil zone because silica is soluble in water but not in oil (Worden and Morad, 2000). Occurrence of poorly coalesced quartz overgrowths in the shoreface sandstones (paper III) are enhanced by early/partial emplacement of hydrocarbons, which inhibited precipitation of syntaxial quartz overgrowths (e.g. Walderhaug, 1996; Bjørkum et al., 1998).
Pressure dissolution and cementation by quartz overgrowths are most extensive at temperatures >100°C and burial depths >3 km (e.g. McBride, 1989, Walderhaug, 1996). Fluid inclusion thermometry indicates that quartz overgrowths precipitated at temperatures of 110°C to 139°C (paper I-IV).

2.2.2 Cementation by Fe-dolomite/ankerite and siderite

Petrographic observations revealed the presence of two generations of carbonate cements, including: (i) early pre-compactional (eogenetic) calcite, which engulfs grains showing point contacts and no evidence of quartz overgrowths, and (ii) post-compational (mesogenetic) Fe-dolomite, ankerite and siderite (i.e. papers I-IV), which is evidenced by their engulfment to mesogenetic quartz overgrowths (e.g. papers I-IV) and their presence along stylolite seams (e.g. paper III&IV).

Mesogenetic Fe-dolomite and ankerite of the Sirt and Ghadamis basins are characterized by a high Fe content (Nesse, 2009), high homogenization temperatures (T_h: 80°C-140°C), and lighter δ^{18}Ov-PDB isotope values (-17.6‰ to -7.6‰; paper I-IV), using dolomite-water fractionation equation of Land (1983), the δ^{18}Ov-SMOW values for pore water range between (-2.1‰ and +3‰). The higher values suggest precipitation from basinal brines, whereas the lower values suggest involvement of meteoric waters, through descend and dilute the basinal brines of the reservoirs (e.g. Egeberg and Aagaard, 1989; Wilkinson, et al., 1995) (e.g. papers III and IV). The lighter δ^{13}C values (-7.6‰ to -2.0‰) suggest that dissolved carbon was derived from thermal decarboxylation of organic matter (Irwin et al., 1977; Spötl and Pimat, 1998) (e.g. papers I-IV).

Mesogenetic calcite is also characterized by lighter δ^{18}Ov-PDB values (-10.0‰ and -8.8‰), and precipitated at temperatures ranging between 125°C to160°C. Using the calcite-water oxygen fractionation equation of Friedman and O’Neil (1977), the δ^{18}Ov-SMOW values for pore water range between 0‰ and +2‰ (Fig. 3A; paper II). Hence, the precipitation of calcite suggests contribution of hot basinal brines. The δ^{13}C values (-6.4‰ to -3.4‰) values (e.g. paper II) suggest that the dissolved carbon was derived from thermal decarboxylation of organic matter (Irwin et al., 1977).

Using the δ^{18}O of siderite (-15.5‰ to -14.7‰; Fig. 3B; e.g. paper I) and assuming δ^{18}Ov-SMOW for pore water (0‰ to +2‰) and applying the oxygen isotope-water fractionation equation of Carothers et al., (1988) suggests precipitation at temperatures of 160-190°C. The high Mg contents (10-18 mole %) and the high precipitation temperatures support a mesogenetic origin for siderite (e.g. paper I and II). Ca, Mg and Fe ions that contribute in the precipitation of ferroan carbonate (e.g. siderite) cements were possibly sourced from brines that circulated in carbonate/evaporite rich formations (Dworkin and Land, 1994; Khalifa and Morad, 2012; Al-Ramadan, et al., 2012).
2.2.3 Clay mineral transformation

Figure 3. Ranges of temperatures and oxygen isotopes (δOᵥ-PDB) values (-10.0‰ to -8.8‰) of the late calcite (orange), assuming a precipitation temperature range between 125°C-160°C and using the fractionation equation of Freidman and O’Neil (1977), precipitated from waters with δOᵥ-SMOW values range between 0‰ to +2‰.

B) Ranges of δOᵥ-PDB values (-15.5‰ to -14.7‰), the oxygen isotope-water fractionation equation of Carothers et al. (1988), and assuming δOᵥ-SMOW values of 0‰ and +2‰ for the formation waters during mesodiagenesis (McBride, 1989) suggests that precipitation occurred at 160°C-190°C, which are typical for hot basinal temperatures.

(a) Dickitization of kaolinite occurs during burial and at high temperature >100°C via dissolution-processes (Ehrenberg, et al., 1993; Morad et al., 1994). Conversion of kaolinite into dickite rather than illite enhanced by low K⁺/H⁺ activity ratio in pore water (Ehrenberg, 1991; Morad, et al., 1994); the low αK⁺/αH⁺ ratio has been suggested to be enhanced by flux of organic acids (Surdam, et al., 1989; Worden and Barclay, 2000) and the low content of K-feldspar grains in the sandstones (Ehrenberg, 1991) (e.g. paper III).

(b) Illitization of smectite (infiltrated clay and mud intraclasts). Illitization processes take place at high temperatures (>90°C) (Glasmann et al., 1989). Illitization of smectite, is promoted by high αK⁺/αH⁺ activity ratio in pore water, is related to an abundance of K-silicate grains (i.e. K-feldspar). The K⁺ ions needed for illitization processes are possibly in part sourced from albitization-dissolution of K-feldspar grains (Morad et al., 2000), and/or externally sourced from flux of basinal brines.
The various textural and occurrence habits of illite suggest variations in formation processes; mat-like, honeycomb-like, lath-like and flaky-like illite suggest formation due to illitization of smectite (i.e. grain coating clays and mud intraclasts) (Moraes and De Ros, 1990, Morad et al., 2000), whereas the fibrous, filamentous and hair-like illite, which grow at the termination of the illite flakes (i.e. honeycomb-and laths-like illite) suggest precipitation from pore-water (Güven et al., 1980; 2001; Worden and Morad, 2003). However, distribution and abundance of illitic clays are controlled by depositional facies and incorporation of intrabasinal mud intraclasts into shoreface sandstones (e.g. papers I & III).

Chlorite occurs in the studied sandstones, as pore-filling aggregates of pseudohexagonal plates or as rosette-like crystals (10-50 µm across), which suggest formation by direct precipitation from hot brines (Gaupp et al., 1993; Aagaard et al., 2000; Worden and Morad, 2003). Pore-filling chlorite occludes sandstone porosity, whereas pore-lining chlorite preserves the sandstones porosity because precipitation of extensive quartz overgrowths is inhibited (Ehernberg, et al., 1993; Morad et al., 2010).

Chlorite occurs as traces in braided fluvial sandstones of the “up thrown block”, and (up to 5 vol. %) in the tidal sandstones of the “down thrown block” (e.g. paper II). The Fe and Mg needed for precipitation of chlorite in the Nubian sandstones are possibly sourced from the dissolution of Fe-oxide pigments attached to the infiltrated clay (Dixon et al., 1989). Conversely, in the tidal sandstones of the “down thrown block”, constituents needed for chlorite may have been derived from hot basinal brines (e.g. Worden and Morad, 2003).

2.2.4 Feldspar grain albitionization and dissolution

Feldspar grain albitionization is a mesogenetic process that takes place at temperatures > 90°C via dissolution-precipitation, which is evidenced by the formation of tiny parallel aligned albite crystals (Morad, 1986). Digenetic albrite occurs also as overgrowths around feldspar grains and as discrete, pore-filling crystals. Grain replacive albite occurs as numerous tiny (< 5-15µm) euhedral crystals (Morad, 1986). Na needed for albitation processes is possibly sourced from formation waters, which are commonly dominated by Na-Cl-H2O compositions (Morad et al., 2000). Feldspar grain dissolution occurred in the tidal sandstones of the basin margin (e.g. paper I) and in the shoreface sandstones (e.g. paper III and IV) due to flushing of meteoric waters during fall in relative sea level (Nedkvitne and Bjørlykke, 1992) or to descent of meteoric/unsaturated waters (Luczaj and Goldstein, 2000; Ceriani et al., 2002) (e.g. paper IV). Diagenetic K-feldspar overgrowths occurred in
the basin margin setting of the Al-Zahrah Field, but is rarely in the sandstones of the basin-ward settings-the Bahi Field (e.g. paper I).

2.2.5 Barite and anhydrite cements

Local abundance of barite cement (up to 20 vol. %) in the sandstones of the “down thrown block” (Bahi Field) was probably sourced from hot basinal brines (Fisher et al., 2003; Küpeli et al., 2007). These brines ascended along deep-seated normal faults, which may have acted as conduits for fluids flow. The barium and sulfate ions are possibly sourced from dissolution of anhydrite beds in Etel and Argup formations in the Zallah Trough (e.g. Paper I) (i.e. Dworkin and Land, 1994). Barium is possibly also sourced from flux of hot basinal brines due to alterations of granitic-basement rocks (e.g. Juliани et al., 2002). Derivation of Ba\(^{2+}\) and SO\(_4^{2-}\) ions from basinal brines is evidenced by: (a) high homogenization temperatures (145-158°C) and high salinities (18-20 wt.% NaCl equivalent) in the fluid inclusions of barite, and (b) higher \(\delta^{34}S_{CDT}\) values of barite (+28.9‰ to +31.2‰) than those typical for Cretaceous sea waters (+15.5‰ to +20‰) (Paytan et al., 2004). The high \(\delta^{34}S\) isotopic values suggest that the inferred basinal fluids were influenced by sulfate reduction (Chow et al., 2000) (e.g. papers I and II).

Anhydrite engulfs quartz overgrowths and fills intergranular and moldic pores after dissolved feldspar grains, and hence precipitated subsequent to feldspar grain dissolution and albitization. The restricted occurrence of anhydrite to the tidal sandstones of the “up thrown” rather than in the “down thrown block” of the Az-Zahrah Field (e.g. paper I) suggests that the anhydrite was possibly sourced from alterations of the overlying evaporite rich formations (e.g. Etel and Argup formations) (e.g. Dworkin and Land, 1994). The occurrence of anhydrite in the “down thrown block” of the Khalifa Field (e.g. paper II), and its engulfment to quartz overgrowths, which simultaneously precipitated with barite suggest precipitation from fluxes of hot basinal brines.

2.2.6 Pyrite

The presence of coarser-crystalline pyrite cement replacing quartz grains and carbonate cements in the Az-Zahrah Field, close to Zallah Trough supports the occurrence of thermo-chemical sulfate reduction in the basin (e.g. Machel, 1987). Conversely, the occurrence of tiny framboids within concentric cortices and their engulfment by quartz overgrowths and illite suggest an eogenetic origin for pyrite (Morad et al., 2000) (e.g. papers III and IV).
2.2.7 Other parameters that enhance precipitation of mesogenetic alterations include: basinal thermal history, heat flow, and flux of hot basinal brines.

The low present day bottom-hole temperatures (av. 102°C) and the calculated lower geothermal gradients (30°C/km) than the homogenization temperatures of the quartz and carbonate cements (av. 131°C), and the calculated geothermal gradient (40°C/km) in the southern part of the Ghadamis Basin, suggest that the basin was buried to a depth of about 4 km prior to uplift to the present level (e.g. paper III and IV), had been subjected to high events of paleo-heat flow, or had been fluxed with hot basinal brines.

The first postulation evidenced by the thermal history of the Ghadamis Basin (Fig. 4.; after Underdown and Redfern, 2007), which indicates that the basin had been subjected to several major tectonic events including subsidence, uplift, erosion, folding and faulting during Caledonian, Hercynian and Austrian phases (Echikh, 1998). For instance, Figure 4-model (B) indicates that the Devonian successions had been buried to depth of < 2 km prior to uplifting to about 1 km during the Hercynian. Then it was gradually reburial to <4 km during Tertiary time prior to uplifting to shallower depth by the Alpine time, which supports the deep burial postulation.

The heat flow postulation evidenced by the heat flow model (Fig. 5) (after Underdown and Redfern, 2007; 2008), which indicates occurrence of multi-phases of high heat flow events during Triassic and Late Cretaceous-Tertiary times with cooling events in between extending from Jurassic to Cretaceous. The high paleo-heat flow events coincide with basinal extension and thinning of the lithosphere, which combined with uplifting period, supports the postulation of high heat flow events.
Figure 4. Burial history curve models of the Ghadamis Basin: A) Shows pre-Hercynian maximum burial, uplift and erosion, and B) Shows Cenozoic maximum burial, uplift and erosion. Note the estimated amount of subsidence and uplift of the Devonian sediments (red shaded curve) (Modified from; Underdown and Redfern, 2007; Underdown et al., 2007, Underdown and Redfern, 2008).
Figure 5. Heat flow history model of the Ghadamis Basin: note the initial event of high heat flow occurred during the Paleozoic as a result of Triassic rifting, subsequent to cooling event during Jurassic-Cretaceous thermal sag phase, and a final event of higher heat flow recorded during Cenozoic/Tertiary times, particularly over the southern and western margins of the basin (after Underdown and Redfern, 2007; 2008).

Flux of hot basinal brines is evidenced by precipitation of mesogenetic cements such as barite and ferroan carbonate cements, which lack internal sources, and hence, are externally sourced from fluxes of hot basinal brines through conduit faults (Fisher et al., 2003; Marfil et al., 2005, Ben-Litzhak et al., 2014). Contribution of basinal fluids in precipitation of these mesogenetic cements is evidenced by: i) The high homogenization temperatures and salinities of quartz overgrowths, Fe-dolomite/ankerite and barite (e.g. papers I-IV), and ii) Occurrence of Fe-dolomite/saddle dolomite along stylolite seams (Fontana et al., 2014) (paper III).

Early partial emplacement of hydrocarbon inhibits further mesogenetic alterations (i.e. precipitation of quartz overgrowths) (Walderhaug, 1994; Bjørkum et al., 1998), evidenced from the low contents of syntaxial and abundance of poorly coalesced quartz overgrowths, which preserve the reservoir quality (e.g. the upper shoreface sandstones) (paper III and IV) (Fig. 6E &F).
Figure 6. A) Optical photomicrograph (XPL) showing stylolite seams (arrow) marked with illitic clay, fine-to medium-grained, middle shoreface sandstones. B) Optical photomicrograph (PPL) showing ferroan dolomite and ankerite crystals (black arrows) along stylolite seams marked with bitumen (red arrow). Fine-grained, well-sorted lower shoreface sandstones. C) Optical photomicrograph (XPL) showing close view of the image (B), indicating occurrence of ferroan dolomite crystals (Dol) along the stylolite seams (arrow). D) Optical photomicrograph (XPL) showing euhedral saddle dolomite (Dol) engulfing quartz overgrowths (Q Og), which suggest mesogenetic origin of the ferroan carbonates. Fine-grained, lower shoreface sandstones. E) SEM image showing partly coalesced quartz overgrowths covering detrital quartz grains (arrows), and high intergranular porosity (P). Medium-to coarse-grained, upper shoreface sandstones. F) Optical photomicrograph (PPL) showing high intergranular porosity (P) and lack of quartz overgrowth, with evidence of chemical compaction at the contacts of the quartz grains (arrows). Medium-to coarse-grained, upper shoreface sandstones.
3 Reservoir quality evolution

Linking the distribution of diagenetic alterations to depositional facies, structural setting and flux of hot basinal brines to the continental and shallow marine sandstone reservoirs based on the case studies provide important clues to the spatial and temporal distribution of diagenetic alterations and their impact on reservoir quality evolution.

3.1 Reservoir quality and heterogeneity models

This thesis shows that the distribution of diagenetic (eo-and mesogenetic) alterations within fluvial, tidal and shoreface sandstones are controlled by several parameters, including: (A) eogenetic alterations, which are controlled by geological setting, mineralogical, textural maturity and depositional facies of the sands. Depositional facies control sediment textures (size and sorting), primary porosity and permeability, surface water chemistry (marine and meteoric), and presence of intrabasinal mud intraclasts (Morad et al., 2000). (B) Mesogenetic alterations are controlled by the distribution of eogenetic alterations, formation water chemistry, flux of hot basinal fluids, thermal-burial history of the basin and the paleo-heat flow events (e.g. Morad et al., 2000; Morad et al., 2010) (Paper I-IV).

3.1.1 Model 1: Summary model of impact of geological setting on distribution of diagenetic alterations: evidences from Cretaceous sandstones, Az-Zahrah Platform-Sirt Basin.

A summary model has been developed to demonstrate the relationship between distribution of diagenetic alterations, depositional facies and geological setting of the Az-Zahrah and Bahi fields NW Sirt Basin Libya (Fig. 7). The studied Bahi sandstones occur in both the Az-Zahrah and the Bahi fields, which are separated by Zallah Trough margin. The Az-Zahrah field area located on Az-Zahrah high “uplifted basin margin”, and is thus at a high structural setting compared to the Bahi Field, which is located “basin-ward”. The sandstones framework composition are vary from arkose to subarkose sandstones at the basin-margin to quartz arenites, and to less extent subarkose at the basin-ward. The tidal sandstones from the Az-Zahrah high were fluxed with meteoric waters, as evidenced by extensive dissolution resulting
in abundance of moldic porosity rather than kaolinitization of the feldspar grains. Kaolin dominates the tidal sandstones of the Bahi Field rather than the other depositional facies, while carbonate cements dominate the paleosols of the Bahi Field. The abundance of moldic porosity enhanced the reservoir quality of the tidal sandstones of the Az-Zahrah high compared to the sandstones from the Bahi Field. The latter sandstones were subjected to a flux of hot basinal brines evidenced by precipitation of barite, anhydrite, Fe-carbonates (Fe-dolomite, ankerite and siderite) and an abundance of quartz overgrowths in the tidal and fluvial sandstones. The basinal brines are probably flux-through-conduit normal faults (see Fig. 7; paper I). As a result the sandstones of the Az-Zahrah high “basin margin” have better reservoir quality compared to sandstones of the Bahi Field, which are located in “basin-ward” setting.

Figure 7. Reservoir quality evolution model showing that structural setting and primary sand composition of the Bahi Formation-Sirt Basin control distribution of the diagenetic alterations. Note that flux of undersaturated/meteoric waters resulted in extensive dissolution of feldspar grains, and thus enhanced the reservoir quality of the basin margin (uplifted area), conversely flux of basinal hydrothermal fluids resulted in precipitation of sulphates, Fe-carbonate and extensive silica cements, which deteriorate the sandstones reservoir quality of the basin-ward.
Figure 8. Cross plots of core plug porosity-permeability measurements display: A) Positive correlation ($r = +0.88$) between horizontal and vertical permeability. B) Weak positive correlation ($r = +0.18$) between porosity and horizontal permeability, which may be attributed to cementation by quartz overgrowths and chemical compactions, which occlusion the pore-throats.
Better reservoir quality (porosity: av.18%; permeability: av. 400 mD) occurred in the tidal sandstones of the Az-Zahrah Field/basin-margin than in the fluvial and tidal sandstones of the Bahi Field/Basin-ward (porosity av. 13% and 12%, and permeability av. 45mD and 1mD) respectively. Strong positive correlation (r = +0.88; Fig. 8A) between vertical and horizontal permeability of the studied sandstones can be attributed to rare occurrences of mud-or mica-rich laminae, whereas the weak positive correlation (r = +0.18; Fig. 8B) between porosity and horizontal permeability can be attributed to an influences of low permeability due to compaction and extensive cementation by quartz overgrowths, which occlusion pore-throats.

Mechanical and chemical compactions caused stronger loss of intergranular porosity than cementation (41% and 32 %, respectively in the Sirt Basin; Fig. 9). Grain-coating illite, illitic laminae and mica in the studied sandstones enhanced pressure dissolution and chemical compaction. Thus, the structural setting and the depositional facies have strongly impacted the distribution of diagenetic alterations within the tidal and fluvial sandstones, which, in turn, impacted the evolution of the reservoir quality and heterogeneity (e.g. paper I).

Figure 9. Plot of cement volume verses total intergranular volume (Houseknecht, 1987; modified by Ehrenberg, 1989) of the Bahi Sandstone-Cretaceous- Sirt Basin showing that the intergranular porosity has been destroyed to greater extent by mechanical and chemical compactions then by cementation.
3.1.2 Model 2: Summary model indicating the impact of a flux of hot basinal brines on the distribution of mesogenetic alterations: evidence from Cretaceous sandstones (Nubian and Bahi formations) Khalifa Field, Al Bayda Platform-Sirt Basin.

There is strong controversy in the literature regarding whether deep burial/mesogenetic alterations in sandstones occur in open or closed systems (e.g. Bjørkum and Gjelsvik, 1988; Worden and Barclay, 2000). Some authors have suggested that deep burial alteration occurs in open systems (e.g. Hurts and Irwin, 1982; Land et al., 1997), in which mass transfer takes place by large scale cross-formational flows of solutions (e.g. Gassman, 1992, Berger et al., 1997), which may be derived from adjacent mudstone successions (e.g. Events, 1989, Milliken et al., 1994; Land, et al., 1997; Thyne, 2001). Others suggest the role of fluxes of hot basinal brines through faults (e.g. Sullivan et al., 1990; Burley et al., 1993; De Ros et al., 2000). Still, other authors have suggested that deep-burial alterations in sandstones took place mainly by small-scale diffusion in closed systems (e.g. Bjørkum and Gjelsvik, 1988; Worden et al., 1998).

The extensive mesogenetic cementation by quartz overgrowths, barite and anhydrite, Fe-dolomite/ankerite and siderite in the down thrown rather than up thrown block (Figs. 10 A-F and 11) suggest fluxes of hot basinal brines through conduit faults in open systems (e.g. Fisher et al., 2003; Küpeli, et al., 2007) (Fig. 12). This interpretation is supported by: (i) relatively high homogenization temperatures (110-125°C) of primary fluid inclusions within quartz overgrowths and the high salinity (17 wt% NaCl eq.), (ii) high Mg contents of mesogenetic siderite (Morad, 1998) and the high precipitation temperatures (155-200°C) (Khalifa and Morad, 2012), and (iii) the calculated high geothermal gradient at the time of quartz precipitation (about 48°C/km), which is close to the geothermal gradient of the syn-rift in the eastern part of the Sirt Basin (50°C/km; Ceriani et al., 2002). Hence precipitation and distribution of mesogenetic barite, quartz overgrowths and Fe-dolomite/ankerite, calcite and Mg-rich siderite suggest contribution of open mesogenetic systems, which was enhanced by fluxes of hot basinal brines along conduit faults. Ba\(^{2+}\) and SO\(_4\)^{2-} ions were probably sourced from alterations of anhydrite beds/formations in the deeper portions of the Zallah Trough margin or from alterations of the above carbonate-evaporite rich sequences (e.g. paper II). However, Ba\(^{2+}\) ions may also be sourced from alteration of granitic basement rocks (Juliani et al., 2002).

This study demonstrates that mesodiagenesis of sandstones does not always occur in closed systems, but may instead involve mass flux by hot basinal brines in open systems that were probably fault controlled.
Figure 10. A) Optical photomicrograph (XPL) showing a late calcite (Ca) cement engulfs quartz overgrowth (Q Og; yellow arrows) and barite (Ba), and (Q) for quartz grain. Medium-grained, tidal sandstones of downthrown block. (B) Optical photomicrograph (XPL) showing a quartz overgrowth (Q Og; white arrows) engulfed by late anhydrite (Any; yellow arrow). Note that anhydrite also engulfs barite (Ba; red arrow). Medium grained tidal sandstones of downthrown block. (C) BSE image showing euhedral crystal of Fe-dolomite (Dol) overgrown by ankerite (Ank), partially occupied the intergranular porosity (P) and engulfing quartz overgrowths (arrows). Note chemical zoning, which attributed to the gradual increase of Fe and Mg contents in the formation waters during precipitation. Fine-to medium-grained, middle shoreface sandstones. (D) BSE image showing siderite (Sd) replacing mud intraclast (MI), and engulfing Fe-dolomite and ankerite (Ank), and (Q) for quartz grain. Coarse grained, braided fluvial sandstones of upthrown block.
Figure 11. Paragenetic sequences suggest the relative timing relationship between the diagenetic alterations, encountered in the tidal and fluvial sandstones-Al Bayda Platform, Sirt Basin. The assumed broad boundary between eo- and mesodiagenesis is approximately around ±70°C (according to Morad et al., 2000). Note the variations in distribution of the eo- and mesodiagenetic cements within the different depositional facies and structural settings: yellow and blue rectangles represent the fluvial and tidal sandstones of the upthrown block, whereas red rectangles represent the tidal sandstones of the downthrown block. The size of the rectangles is proportionately proportional to the abundance of the cements.
Figure 12. North-South cross-section displaying the location of the studied wells in the Khalifa Field-Al Bayda Platform: F24I-59W well is located close to a major normal fault with throw of 150 m, whereas F22-59W well is located on the up-thrown block (1.6 km apart). Depths and throws are obtained from seismic and borehole logs (unpublished internal geophysical and geological reports from the Waha Oil Company).
3.1.3 Model 3: Summary model indicates impact of depositional facies on the distribution of diagenetic alterations:

This study will hopefully throw some light on the importance of depositional facies (i.e. shoreface sandstones) for the distribution of diagenetic alterations within F3 sandstones (middle Devonian) of the Aouinet Ouenine Formation. Depositional setting of paralic sediments are strongly influenced by the primary deposition processes and conditions: (a) changes in pore water chemistry from marine to meteoric owing to fall in relative sea level, (b) variations in sediment textures (grain size and sorting), (c) sand maturity, (d) primary depositional porosity and permeability, and (e) the incorporation of intrabasinal grains (i.e. mud intraclasts) (Morad et al., 2000). These parameters control the distribution of eogenetic alterations, which were enhanced by an abundance of ductile grains (e.g. feldspars, mica and mud intraclasts) and flux of meteoric waters through permeable sand bodies (Morad et al., 2000). The mesogenetic alteration is controlled by the formation water chemistry, the burial thermal history of the basin and the distribution patterns of the eogenetic alterations. The eogenetic alteration includes: (i) mechanical compaction, which developed earlier after precipitation of sediments manifested by grain rearrangement and deformation of mud intraclasts, (ii) dissolution and kaolinitization of feldspar and mud intraclasts, and (iii) precipitation of pyrite. However, the limited occurrences of eogenetic alterations are attributed to depositional sand maturity.

The mesogenetic alterations include dissolution and albitization of feldspar grains, dickitization of kaolinite, illitization of smectite, intergranular quartz grain dissolution and stylolites, precipitation of syntaxial and poorly coalesced quartz overgrowths, and Fe-dolomite and ankerite cements (Fig. 13).

The present case study indicates that the variations in distribution of diagenetic alterations are facies related (Fig. 14). For instance, the upper shoreface sandstones are characterized by their relatively coarser grain size and high primary porosity and permeability, kaolin and a low content of quartz overgrowths. The middle shoreface sandstones are characterized by an abundance of quartz overgrowths and occurrence of kaolin, chemical compaction and stylolites, whereas the lower shoreface sandstones are characterized by a finer grain size, occurrence of illitic clays, pseudomatrix, stylolites, abundance of quartz overgrowths and occurrence of Fe-dolomite and ankerite, in addition to, evidences of stylolitization and chemical compaction.
Figure 13. Paragenetic sequence showing the relative timing of the diagenetic alterations in the shoreface sandstones of the Aouinet Ouenine Formation-middle Devonian based on the petrographic observation.

<table>
<thead>
<tr>
<th>Diagenetic minerals</th>
<th>Eodiagenesis</th>
<th>Mesodiagenesis</th>
<th>Shoreface sandstones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;2 kbar, &lt;70°C</td>
<td>&gt; 2 km; &gt; 70°C</td>
<td>Upper</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical Compaction</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain kaolinitization</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feldspar grain dissolution</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Albition of feldspar</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite Dickitization</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical compaction</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz overgrowths</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-dolomite/ankerite</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the upper shoreface, the occurrence of kaolinite is enhanced by fluxes of meteoric waters due to a fall in relative sea level, whereas the low contents of quartz (poorly coalesced) overgrowths can be attributed to early/partial emplacement of oil, which inhibited precipitation of syntaxial quartz overgrowths (Walderhaug, 1984; Bjørkum et al., 1998), as evidenced by presence of oil in fluid inclusion. Conversely, the extensive cementation by syntaxial quartz overgrowths in the middle shoreface sandstones were enhanced by water saturation, which permits continuity of precipitation of mesogenetic cements (i.e. quartz overgrowths). Presence of stylolite seams (i.e. illitic clays) enhanced intergranular quartz grain dissolution, and hence, precipitation of abundance quartz overgrowths (Figs. 13 and 14).

The poor reservoir quality in the lower shoreface may be attributed to their finer grain sizes, presence of stylolites, illitic clay laminae and pseudomatrix, which enhanced chemical compaction, and hence precipitation of extensive quartz overgrowths. Conversely, the excellent reservoir quality in the upper shoreface sandstones are attributed to their coarser grain size, the high primary porosity and permeability, a lack of ductile grains and mud intraclasts, in addition to early/partial emplacement of oil, which preserved the reservoir quality via inhibiting formation of syntaxial quartz overgrowths (Figs. 13 and 14).
Figure 14. A conceptual model summarizing the distribution of diagenetic alterations within the shoreface sandstone depositional facies of the Aouinet Ouenine Formation. The model indicates that facies control the distribution of diagenetic cements, grain size and reservoir quality evolution. Note that the formation saturated fluids were also contributed in distribution of diagenetic cements.

The presence of bitumen and saddle dolomite crystals along stylolites suggest formation by fluxed basinal fluids (e.g. Baron and Parnell, 2007; Fontana, et al., 2014) during tectonic compression of the basin (e.g. Marfil et al., 2005), which probably occurred in Cretaceous-Tertiary combined with migration of hydrocarbons (e.g. Echikh, 1998; Dardour, et al., 2004; Underdown et al., 2007).

A strong positive correlation ($r = +0.9$; Fig.15A) between the horizontal and vertical permeabilities is attributed to a rarity of illitic laminae and mica within the sandstone core plug samples, in which their presences acted as barrier for vertical fluids flow. Conversely, the very weak positive correlation ($r = +0.2$; Fig.15B) between horizontal permeability and porosity of the shoreface sandstones is attributed to the poor connectivity of the primary intergranular pores owing to precipitation of quartz overgrowths and chemical compaction, which resulted in occlusion of pore throats (Al-Ramadan et al., 2012b).
Mechanical and chemical compaction processes were more efficient (55%) factors in reservoir quality destruction than cementation (27.6%; Fig. 16). The lower shoreface sandstones suffered more effective mechanical and chemical compactions than the upper and middle shoreface owing to their fine grain size and presence of illitic laminae and stylolites, which enhanced intergranular quartz grain dissolution and compaction.

Figure 15. Cross-plots: A) Porosity versus horizontal permeability displaying weak positive correlation ($r = 0 + 0.2$). B) Horizontal permeability versus vertical permeability of shoreface depositional facies displaying strong positive correlation ($r = +0.9$).

Figure 16. Plot of intergranular volume (intergranular porosity + cement) versus cement volume of the middle Devonian sandstones in the southern Ghadamis Basin: showing that the original intergranular porosity has been reduced mainly by compactions (after Houseknecht, 1987; modified by Ehrenberg 1989).
This study demonstrates the importance of depositional facies on the distribution of diagenetic alterations, particularly clay minerals and quartz overgrowths, on reservoir quality distribution of quartzose shoreface sandstones.

3.1.4 Model 4: Summary model indicating shift information

water chemistry from quartz-dominated to carbonate dominated, diagenetic conditions, and timing of hydrocarbon migration as evidenced from integration of several petrographical techniques.

This paper uses petrography, stable isotopes, fluid inclusion microthermometry and Raman Spectrometry, as well as thermal tectonic evolution of the basin, to decipher the diagenetic conditions of cementation by quartz overgrowths and paragenetically later Fe-dolomite cements in the middle Devonian shoreface sandstones of the Ghadamis Basin, NW Libya. The high homogenization temperatures ($T_h = 119-140^\circ C$) and high salinities (15.5 to 18.5 wt% NaCl eq.), combined with low $\delta^{18}O_{V-PDB}$ values (-17.6 to -13.2‰) and occurrence of saddle crystal shape of Fe-dolomite suggest deep-burial origin (e.g. Davies and Smith 2006; Sirat et al., 2015). Fluid inclusion microthermometry revealed that there was a shift in fluid chemistry from NaCl-dominated waters during cementation by quartz, to NaCl-CaCl$_2$ dominated brines during cementation by Fe-dolomite (e.g. Steele-MacInnis et al., 2011). Fluid inclusions temperature versus salinity plot of quartz and Fe-carbonates (Fig. 17), indicates two stages of carbonate cementation: i) initial stage following precipitation of quartz overgrowths (130-139°C), but precipitated at higher salinities (16.5 to 18.5 wt% NaCl eq.), which is typical for basinal brines compared to the final stage, which precipitated at lower temperatures (119-130°C) and salinities (15.5 to 17 wt% NaCl eq.), and pointing towards the present day reservoir conditions (94-114°C; av. 102°C) and salinities (av. 14.3 wt.% NaCl eq.). The source of the latter fluids was probably descending waters, which have circulated in the overlying carbonate and evaporite successions (i.e. “Mrar Formation” and “Dembaba Formation” Carboniferous) (e.g. Bein and Dutton, 1993; Luczaj and Goldstein, 2000).
Figure 17. Cross plot of fluid inclusion homogenization temperatures ($T_h$) versus salinities. Note the overall trend in decreasing temperature and salinity recorded in Fe-dolomite fluid inclusions assemblages and pointing to present-day conditions in the reservoir.

Using the $\delta^{18}O_{PDB}$ values of Fe-dolomite (-17.6‰ to -13.2‰), homogenization temperatures of (119-140°C), and the fractionation equation of Land (1983), the $\delta^{18}O_{SMOW}$ of the brines is inferred to have ranged from (-2.1‰ to +3‰; Fig. 18), which are higher than the Devonian seawaters $\delta^{18}O_{SMOW} = -1$; Joachimski, et al., 2004; Van Geldern et al., 2006), are attributed to the high precipitation temperatures and to pore-water-mineral reactions (Morad and Eshesse, 1990; Morad et al., 1990; Allan and Wiggins, 1993). The uppermost values are typical for brines in sedimentary basins (Egeberg and Aagaard, 1989; Wilkinson et al., 1995), whereas the lowermost values may suggest the involvement of meteoric waters. The latter option may corroborate the hypothesis of descending cool waters (Ceriani et al., 2002).
Figure 18. Range of fluid inclusion precipitation temperature (119-140°C) and oxygen isotope composition $\delta^{18}O_{\text{V-PDB}}$ values (-17.6‰ and -13.2‰) of the waters that precipitated the Fe-dolomite/ankerite, and using the fractionation equation of Land (1983), indicated $\delta^{18}O_{\text{V-SMOW}}$ values range between (-2.1‰ and +3‰). The negative values suggest precipitation from evolved meteoric waters, whereas the positive values are typical for basinal fluids (e.g. Wilkinson et al., 1995).

The presence of oil filled inclusions in quartz overgrowths (Fig. 19A) suggest that oil migration took place during precipitation of quartz overgrowths, and prior to cementation by Fe-dolomite and ankerite. Conversely, the presence of methane in the fluid inclusions of Fe-dolomite/ankerite cements (Figs. 19B; 20) and its absence in the quartz overgrowths suggest that dolomite precipitated during, whereas quartz overgrowths precipitated prior to gas migration (Fig. 21). The possible pathways of hydrocarbon migration and fluxes of hot basinal fluids versus descending of Ca and Mg rich colder waters are illustrated in Figure 22.

The presence of bitumen and saddle dolomite along the stylolites suggest that the stylolites acted as conduits for fluxes of basinal fluids and oil migration (Fontana et al., 2004; Baron and Parenell, 2007). The stylolite-fissures could be opened due to lateral tectonic compression and folding of the basin during Cretaceous-Tertiary times (Echikh, 1998; Underdown, et al., 2007).
The thermal maturation of the lower Silurian source rock and hydrocarbon migration occurred in two phases: pre-Hercynian (Carboniferous) and post-Hercynian (Late Jurassic-Cenozoic) (Underdown et al., 2007). Dardour et al. (2004) reported that the later stage of maturation and migration of hydrocarbon took place during Late Cretaceous to Early Tertiary times, which coincide with timing of uplifting and lateral tectonic compression of the basin (Echikh, 1998).

Hence, this study demonstrates that the use of petrography, stable isotopes, microthermometry and Raman spectrometry of fluid inclusions in quartz overgrowths and paragenetically later carbonate cements, and thermal tectonic evolution of the basin help constraining the conditions of diagenesis, shift in brines composition and relative timing of hydrocarbon migration to precipitation of mesogenetic cements within sedimentary basins.

Figure 19. A) Optical photomicrograph (XPL) showing blue-fluorescing fluid inclusions (arrows) suggest filling by oil. Medium-to coarse-grained, upper shoreface sandstones. B) Fluid inclusion within Fe-carbonate crystal (arrows) in extensively carbonates cemented sandstones bed.

Figure 20. Raman spectra indicating the presence of a peak at 2917 cm\(^{-1}\) suggesting the presence of methane in fluid inclusions liquid/gas in Fe-dolomite cement.
<table>
<thead>
<tr>
<th>Diagenesis</th>
<th>Eodiagenesis &lt; 2 km; &lt;70°C</th>
<th>Mesodiagenesis &gt; 2 km; &gt;70 - 150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical compaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feldspar kaolinitization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite dickitization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical compaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz overgrowths</td>
<td></td>
<td>130-139°C</td>
</tr>
<tr>
<td>Oil migration</td>
<td></td>
<td>119-140°C</td>
</tr>
<tr>
<td>Fe-dolomite/ankerite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane migration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil emplacement</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 20. Paragenetic sequences of diagenetic minerals in the F3 sandstones middle Devonian as evidenced from petrographical observations and fluid inclusions analyses of both quartz overgrowths and ferroan carbonate cements.
Figure 21. Schematic model for the F3 sandstone reservoir suggesting the possible pathways hydrocarbon (oil and gas) migration, flux of basinal brines and descending of meteoric waters, which coincided with basin tectonics (i.e. compression and uplift) (Echikh, 1998).
4 Summary of the papers

4.1 Paper I. Impact of Structural Setting on Diagenesis of Fluvial and Tidal Sandstones: The Bahi Formation, Upper Cretaceous, NW Sirt Basin, North Central Libya

This petrographic, mineral chemical, fluid inclusion, and stable isotopic study shows that the distribution of diagenetic modifications and their influence on reservoir quality and heterogeneity in tidal and fluvial sandstones of the Upper Cretaceous Bahi sandstones in the rift Sirt Basin, NW Libya varies systematically along a series of closely-spaced, dominantly normal faults between the basin margin and more basin ward-located areas.

Shallow eogenetic modifications resulting from the percolation of meteoric waters; include infiltration of grain coating clays, kaolinitization of detrital silicates, and cementation by dolomite and K-feldspar overgrowths. Meso-genetic alterations (> 70°C; > 2 km) include feldspar albitization, illitization of infiltrated clay and kaolinite, conversion of kaolinite to dickite, and cementation by quartz overgrowths ($T_h$ 112°C to 134°C), Barite ($T_h$ 145°C to 158°C) and Fe-carbonates. The restriction of barite and Fe-carbonate cements to the basin-ward-located sandstones suggests formation by hydrothermal fluids along the faults. Extensive feldspar dissolution and formation of moldic pores in the sandstones from the basin margin were probably caused by deep percolation of meteoric waters. Results from this study regarding the structural control on the special distribution of diagenetic alterations have implications for constraining the flux of pore fluids and, by extension, reservoir quality in analogous picratonic rift basins.
4.2 Paper II. Open versus closed mesogenetic systems in Cretaceous fluvial and tidal sandstones, Sirt Basin, Libya

This study constrains factors controlling the distribution of diagenetic alteration and their impact on reservoir quality of the Cretaceous sandstones from the Al-Bayda Platform located in the southern Sirt Basin (Libya). These factors include the presence of early cements as well as the influx of hot basinal brines. The studied samples come from two blocks in the Khalifa Field, which are dislocated by a major normal fault. The deep-burial (mesogenetic) alteration includes the partial to pervasive replacement of early (eogenetic) dolomite and calcite cements by ferroan-dolomite, ankerite and siderite, precipitation of grain-coating chlorite, and cementation by quartz overgrowths, barite and anhydrite, particularly in the downthrown block. The association of quartz overgrowths with barite suggests that deep burial was influenced by the influx of hot basinal brines through faults. Conversely, deep-burial alteration in braided fluvial deposits of the Nubian sandstones of the upthrown block include: illitization of eogenetic smectite, quartz cementation and formation of chlorite.

This study shows that deep burial of the studied sandstones did not occur in a closed system, but was affected by the influx of hot basinal brines through faults, which formed during basin rifting. This interpretation is supported by the relatively high homogenization temperatures (100–110°C; corrected to 110–125°C) of primary fluid inclusions within quartz overgrowths, which exceed the maximum burial temperatures experienced by the Cretaceous succession, and by the high salinity of these inclusions.

4.3 Paper III. Impact of depositional facies on the distribution of diagenetic alterations in the Devonian shoreface sandstone reservoirs, southern Ghadamis Basin, Libya

The middle Devonian, shoreface quartzarenites (present-day burial depths 2833-2786 m) are important oil and gas reservoirs in the Ghadamis Basin, western Libya. This integrated petrographic and geochemical study aims to unravel the impact of depositional facies on distribution of diagenetic alterations and, consequently, related reservoir quality and heterogeneity of the sandstones. Eogenetic alterations include formation of kaolinite, pseudomatrix and minor pyrite. The mesogenetic alterations include cementation by quartz overgrowths, Fe-dolomite/ankerite, and illite, transformation of kaolinite to dickite, illitization of smectite, intergranular quartz dissolution and
stylolitization, and albitization of feldspar. The coarser-grained upper shoreface sandstones combined with less extensive chemical compaction and smaller amounts of quartz overgrowths account for their better primary reservoir quality compared to the finer-grained, middle-lower shoreface sandstones. The formation of kaolin in the upper and middle shoreface sandstones is attributed to a greater flux of meteoric water. The more abundant quartz overgrowths in the middle and lower shoreface are attributed to a greater extent of stylolitization, which was promoted by more abundant illitic clays. This study demonstrate that linking the distribution of diagenetic alterations to depositional facies of shoreface sandstones leads to a better understanding of the impact of these alterations on the spatial and temporal variation in quality and heterogeneity of the reservoirs.

4.4 Paper IV: Quartz and Fe-dolomite cements as records of a dramatic shift in formation-water chemistry: Devonian shoreface sandstones, the Ghadamis Basin, Libya

This paper deals with the diagenetic conditions encountered during cementation by the closely associated quartz overgrowths and later paragenetically Fe-dolomite/ankerite in Devonian shoreface sandstones, the Ghadamis Basin, NW Libya. The high homogenization temperatures (T_h = 119-140°C), low δ^{18}O values (-17.6 to -13.2‰) and occurrence of saddle crystal shape of the Fe-dolomite suggest a high temperature and deep-burial origin. Fluid inclusion microthermometry reveal that there was a shift in fluid chemistry from NaCl brines during quartz cementation to NaCl-CaCl_2 brines during cementation by Fe-dolomite. The latter fluids probably circulated through overlying carbonate and evaporite successions before descending deep into the basin. The presence of oil-filled inclusion in quartz overgrowths suggests that cementation occurred during oil migration, whereas the presence of methane in inclusions in the Fe-dolomite cement suggests precipitation during gas migration. The similarity in T_h ranges for Fe-dolomite and quartz overgrowths despite the shift in formation-water chemistry suggests precipitation under similar geothermal conditions.
5 Conclusions

Constraining the distribution of diagenetic alterations to depositional facies, geological settings and fluxes of hot basinal fluids allow a better understanding of the spatial and temporal distribution of reservoir quality and heterogeneity of fluvial, paralic and shallow marine sandstones of the Sirt and Ghadamis basins, Libya. Integration of petrographical observations, stable isotopes, fluid inclusions, Raman Spectrometry, and thermal tectonic evolution of the studied basins revealed the conditions of diagenesis, the shift in porewater chemistry, and the relative timing of hydrocarbon migration. Hence, linking diagenetic alterations to these parameters revealed that:

- Formation of grain coating and mechanically infiltrated clays as well as kaolinitization of feldspars are attributed to flow of meteoric water in fluvial deposits or its percolation in shallow marine sediments during fall in relative sea level.
- The presence of grain-coating illite, micro-quartz and chlorite, and the early emplacement of hydrocarbons have contributed in preserving the reservoir quality via inhibiting precipitation of syntaxial quartz overgrowths.
- The extensive dissolution of feldspar grains, which resulted in considerable improvement of reservoir quality in the sandstones of the Az-Zahrah Field, is attributed to the descending of meteoric waters along basin-margin faults.
- Quartz overgrowths and carbonates are the most abundant diagenetic minerals in the paralic and shallow marine sandstones compared to kaolinite and illite, which dominate in the braided fluvial sandstones.
- Precipitation of syntaxial quartz overgrowths are enhanced by a lack of clay coatings (e.g. illite and chlorite) and micro-quartz in the braided fluvial sandstones, and by water saturation, stylolites and chemical compaction in the shoreface sandstones.
- Fluxes of hot basinal fluids along deep conduit faults (open system) provided mass needed for cementation by barite, anhydrite, Fe-carbonates and, to some extent, by quartz overgrowths.
- In the Sirt Basin, the fluxes of hot basinal brines are evidenced by the high homogenization temperatures of quartz overgrowths, Fe-carbonate cements, calcite, barite and the low oxygen isotopes, in
addition to occurrence of well-developed pseudohexagonal plates of pore-filling chlorite, which is enhanced by presence of set of normal deep seated faults.

- The extensive mesogenetic alterations (i.e. Fe-carbonates, barite, anhydrite and quartz overgrowths) in the basin margin/down thrown blocks compared to basin-ward/up thrown blocks of the Cretaceous sandstones-Sirt Basin, may be attributed to fluxes of hot basinal brines through conduit faults.

- The high fluid inclusion homogenization temperatures of the quartz overgrowths and the Fe-carbonate, and the low $\delta^{18}$O$_{V-PDB}$ values, as well as an occurrence of saddle crystal shape of Fe-dolomite/ankerite in the shoreface sandstones suggest precipitation during mesogenetic origin.

- Flux of hot basinal brines into the shoreface sandstones-Ghadamis Basin are evidenced by the presence of saddle dolomite crystals in the vicinity of stylolites, the high homogenization temperatures of quartz overgrowths and carbonate cements, as well as the positive $\delta^{18}$O$_{V-SMOW}$ values.

- Mesogenetic alterations do not always occur in a closed system, but may instead involve mass flux with hot basinal brines along deep-seated faults in an open system.

- Fluid inclusions microthermometry reveal that there was a shift in pore-water chemistry from NaCl-dominated during cementation by quartz overgrowths to NaCl-CaCl$_2$-dominated brines during cementation by Fe-carbonate.

- The NaCl-CaCl$_2$ mixed brines are suggested to owe their origin to descending waters, which have circulated in the overlying thick Carboniferous-Cretaceous carbonate and evaporite successions during period of uplift.

- Fluid inclusion compositions indicate that oil migrated during precipitation of quartz overgrowths, whereas gas migrated during cementation by Fe-dolomite and ankerite.

- The presence of bitumen and saddle dolomite crystals along stylolites suggests that the stylolites have acted as conduits for fluxes of basinal brines and migration of hydrocarbons, which enhanced by tectonic compression and uplift of the basin during Cretaceous-Tertiary times.

- Mechanical and chemical compaction were more efficient in destroying reservoir quality than cementation.

- The very weak positive correlation between porosity and permeability is attributed to the poor connectivity of the primary intergranular pores owing to precipitation of quartz overgrowths and compaction processes, which occlude the pore throats.
The strong positive correlation between horizontal and vertical permeability is owed to an absence of clay laminae, which may act as barriers for vertical fluids flow.

Occurrence of Fe-carbonate cemented sandstone bed overlying the shoreface sandstone reservoir may have acted as diagenetic cap rock, whereas the extensive cementation by diagenetic carbonate in the tidally reworked sandstones (paleosols) between the tidal and fluvial sandstone reservoirs in the Cretaceous sandstones of the Az-Zahrah Platform may have caused reservoir compartmentalization.

In summary, this study reveals that the distribution of diagenetic alterations in siliciclastic deposits is controlled by a complex array of inter-related parameters. The linking of diagenesis to depositional facies (i.e. braided fluvial, tidal and shoreface sandstones), structural setting and thermal tectonic evolution (i.e. burial history and heat flow), as well as fluxes of basinal brines and descending of meteoric/shallow waters have important implications for a better understanding and prediction of reservoir quality and heterogeneities prior to exploration as well as development drilling, and also help in planning of enhanced oil recovery programs.

The integration of microthermometry and Raman Spectrometry on fluid inclusions in quartz overgrowths and carbonates helps to constrain fluid evolution, proximate timing of the major mesogenetic cements and migration of hydrocarbons.

Since these parameters are crucial for an understanding of the evolution of reservoir quality and heterogeneities, it is suggested that the approach used in this study should be applied to depositional settings of basins on a worldwide scale.
I den här avhandlingen visas att geologi, avsättningssmiljö och genomströmning av heta lösningar från underliggande bassänger är av stor betydelse för fördelningen av diagenetiska förändringar i kontinentala- och grunda marin sandstenar. I sin tur kontrollerar detta kvaliten och heterogeniteten hos reservoirta. Exemplet är hämtade från de libyska bassängerna.

Geologin kontrollerar mineralogisk och texturell mognad hos sandsten, medan avsättningssmiljön (fluvial och grundhav) kontrollerar porvattenkemin (marin eller meteorisk), sedimentär textur (sortering och kornstorlek), samt sandstenskropparnas geometri. De fluviala avsättningarna består av infilttrationsleror runt kornen, kaolinitisering av detritiska silikater, fältspatöverväxningar och utfällning av järnoxider. Grundhavsavsättningarna karakteriseras av avsättning av tidig kalcit, kaolinit, deformation av mud ”intraklaster” samt pyrit. Fluxer av heta lösningar har sedan avsatt cement av mesogenetiska mineral som barit, anhydrit och karbonater. Denna tolkning stöds av att cement bara återfinns i gränsen bassäng/”downthrown” block (uppsatser I och II), samt av högre fluid inclusion homogeniserings-temperaturer (Th) och lättare δ¹⁸Ov-PDB värden. Även begravningshistoriken och värmeflödet har påverkat cementets temperatur. Flux av hett vattensett ”underifrån” indikeras också av närvaro av Fe-dolomit associerat med styloliter och av förekomst av sadelformade dolomitkristaller, vilka typiskt avsätts i hydrotermala miljöer.

Analys av fluida inklusioner visar på en dramatisk förändring i porvattenkemi, från NaCl dominerade lösningar när kvartsöverväxningarna avsattes, till NaCl-CaCl₂ dominerade när Fe-karbonatcementet tillväxte. Förekomst av mer komplexa NaCl-CaCl₂ lösningar i mellandevonska sandstenar tyder på bidrag av vatten ”ovanifrån”, vilket troligtvis cirkulerade i de överlagrade mäktiga karbonat-evaporit lagerföljerna under perioder av ”uplift”. Den begränsade förekomsten av oljefylltuna inklusioner jämfört med kvartsöverväxningar, och av metan-fylltuna inklusioner jämfört med Fe-dolomit och ankerit, antyder migration av olja när kvarts-överväxningarna bildade, medan metanmigrationen skedde när Fe-karbonatera fäldes ut. Bildning/migrering av kolväten samt utfällning av kvartsöverväxningar skedde troligen under Krita-Tertiär och hänger ihop med ”uplift” av bassängen.

Sandstenarnas primära porositet och permeabilitet har minskat, på grund av de sekundära eo- och mesogenetiska mineralutfällningarna och de mekaniska och kemiska kompakteringsprocesserna. Dock har mantlar av illit och...
klorit runt detritiska korn, mikro-kvarts och dåligt litifierade kvartsöverväxningar, samt partiell tidig mobilisering av olja, bidragit till att bevara reservoirens kvalitet genom att förhindra syntaxiella kvartsöverväxningar. Även den omfattande upplösningen av duktila silikatkorn (fältspater) har bidragit till att förbättra kvaliteten.

En integrering av mikrotermometri på fluida inklusioner, stabila isotoper, och Raman spektroskopi är ett viktigt redskap för att kunna belysa utvecklingen av fluiderna i bassänger, speciellt begravningsmiljön och avsättningsmiljön för kvartsöverväxningarna och Fe-karbonaterna. En sådan förståelse är av största vikt för att kunna fastställa när migrationen och ackumulationen av kolväten ägde rum.

Den här studien visar att fördelningen av diagenetiska förändringar är starkt styrd av de geologiska strukturerne, avsättningsenheterna med deras mättade lösningar, likväl som fluxer av sekundära heta, basala lösningar underifrån, och grundare meteoriskt vatten ovanifrån.
7 Acknowledgments

Deep thanks go to Dr. Abu-Rema Abu-Algasim (the Ex-General Manager of the Libyan Petroleum Institute) for planning the PhD part-time study program. I would like to thank Mr. Ibrahim Al-Bagar (Ex-General Manager of the Libyan Petroleum Institute) and Dr. Bashar Rais (Ex-Manager of the engineering department) for their encouragement and financial support of the part-time PhD study. My great thanks to Dr. Mansour Emtir (The Chairman of Management Committee of the Libyan Petroleum Institute) and Dr. Salem Al Khader (The Management Committee Member for Technical Affairs) for the their encouragement and financial support, and to the staff of Engineering and Exploration Departments for their assessment in the laboratories works.

I would like to thank my supervisor Professor Sadoon Morad. Professor Morad is thanked for his patience, endless revisions of my manuscripts and for helping me through my study program. I am greeting him for his unlimited support and encouragement in all issues related to my study, and his arrangement of my visits to Uppsala University and the Petroleum Institute of Abu Dhabi. Many thanks go to Prof. Ali Sbeta (the internal LPI supervision) for his valuable scientific advices and his assistance in writing the evaluation reports.

I would like to thank Professor Hemin Koyi for his supervision of the last year of my study, and his permission for submit this thesis. My thanks also go to Professor Peter Lazor, the head of Mineralogy, Petrology and Tectonics Program. Professor Örjan Amcoffis also thanked for his help in correction and translation of the summary, and for his valuable advices as co-supervisor, and to Professor Hans Annersten and Professor Valentin Troll for their willingness to help me to finish my thesis work.

Special thanks go to Prof. Veijo Pohjola, Prof. Hemin Koyi, Prof. Peter Lazer and Prof. Sadoon Morad for providing scholarship for the last 6 months and to Mrs. Eva Borgert for her help in solving important administration issues.

I would like to thank my co-author Dr. Marta Gasparrini for her contribution in fluid inclusions and assistance in publishing of paper II.

I further thank Professor Ihsan Al-Aasm for isotopes analyses, Dr. Milos Bartol, and Dr. Micheal Streng for their help in SEM analyses, Professor Malgorzata Moczyladowake-Vidal for her help in science issues, Dr. Jarek Majka, Iwona Klonwska for their help in microprobe analyses, and to Milad
Be Rahuma, Dr. Ashour Aboessa, Dr. Osama Helal, Dr. Mohamed El-gali, Dr. Howri Mansurbeg, Dr. Khalid Al-Ramadan, Dr. Faramarz Nilfousous, Eng. Darina Buhcheva, Eng. Milad Al-Muradi and Dr. Hongling Deng and Dr. Hossein Shomali and Dr. Frances Deegan for their scientific and technical supports. Special thanks go to Dr. Börje Dahrén, Dr. Lukas Fuchs and Eng. Mohamed Bazzi, Eng. Lie Liu and Eng. Miao Lanyun for their help in several technical issues.

Great thanks to my colleagues Tobias Mattsson and Sylvia Berg for their technical support, My great thanks also go to Mr. Taheer Mazloomian and Mr. Leif Nyberg for their help in administration issues, and to the Librarian staff in the Department of Earth Sciences, and to Mr. Martin Östling and Mr. Lars Johansson from the Sweden Geological Survey (SGU) library for their help in providing the unavailable references.

My gratitude to the journals editors: numerous comments and suggestions by two anonymous Marine and Petroleum Geology reviewers and by Associate Editor Marc S. Hendrix have helped us improving the manuscript considerably. Several valuable comments and suggestions by the three reviewers of GeoArabia have helped to improve the manuscript significantly. Editor-in-Charge, Abdulkader M. Afifi, is thanked for managing the review process and Kathy Breining is thanked for proofreading the manuscript. GeoArabia Assistant Editor, Heather Paul-Pattison, are thanked for designing the paper for press. Dr. Jasper Knight the editor in chief of Sedimentary geology and the reviewer Prof. Luiz De Ros are thanked for their valuable comments, corrections and the fast acceptance of the third manuscript.

I conclude my acknowledgement with great gratitude to my family particularly for my wife Aisha, daughter Mabroka and son Ahmid for their patience and support, daughter Mofida for her patience to be alone, great thanks to my other children, brothers and sisters and their families for their encouragement and support all through my study period.
References


58


Morad, S., Al-Aasm, I.S., Longstaffe, F.I., Marfil, R. and De Ros, L.F., 1995. Diagenesis of a mixed siliciclastic/evaporitic sequences of the Middle Muschelkalk (Middle Triassic), the Central Coastal Range, NE Spain. Sedimentology 42, 749-768.


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)