

Sub-meter scale lithological heterogeneity and its influence on the CO₂ trapping capacity in CO₂ storage reservoirs

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Submitted in total fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

NOVEMBER 2020

School of Earth Sciences

The University of Melbourne

Australia

Abstract

Lithological heterogeneity at mm- to cm-scale exists in the form of sedimentary structures such as cross bedding and planar bedding in heterogeneous siliciclastic reservoirs. At this scale, sedimentary structures typically consist of two lithologies with significant differences in their porosity, permeability, capillary entry pressure and mineral composition. The lithology with high porosity, high permeability, low capillary entry pressure and a high abundance of quartz and feldspar characterizes the reservoir rock and is conducive to fluid flow. On the other hand, the lithology with low porosity, low permeability, high capillary entry pressure and a high abundance of clay and carbonate minerals characterizes the intraformational baffle and acts as flow barrier. The presence of both lithologies at mm- to cm-scale govern local fluid flow and geochemical reactions. This is especially important in CO₂ storage reservoirs where CO₂ flow and mineralization might be significantly affected. Hence, it is necessary to account for lithological heterogeneity at sub-meter scale in regional scale dynamic simulations. However, intraformational baffles are typically neglected in static reservoir models primarily because small scale intraformational baffles are not commonly resolved by wireline logs. Therefore, their lithological properties are not accounted for in reservoir models. This study addresses the characterization and incorporation of intraformational baffles in reservoir models so that the reservoir scale estimation of carbon mineral trapping capacity can be improved. Firstly, rocks from the CO₂CRC's Otway Research Facility were characterised using a range of sample and data analysis methods. The variability in porosity, permeability, capillary entry pressure, grain size and mineral composition was used to classify five homogeneous rock type classes: coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone. A new workflow was developed where homogeneous rock types and composite rock types consisting of two lithologies characteristic of intraformational baffles were represented. Rock properties for composite rock types were derived so that mm-scale heterogeneity can be upscaled for integration in coarser discretised reservoir models. Lithotype logs of composite rock types were derived and used to build a high resolution 2D static reservoir model of the site. Multiphase fluid flow and reactive transport simulations were run on 120 and 8 realizations, respectively, to develop a detailed understanding of CO₂ flow and geochemical reactions at mm-scale. It was found that the capillary entry pressure characteristic of the reservoir rock significantly governed the range of turning point saturations while the amount of clay and carbonate content of the baffle governed the amount of carbon mineralized. Reactive transport simulations were also run on two 2D reservoir models to quantify the error associated with the estimation of carbon mineral trapping at reservoir scales if intraformational baffles are not accounted for in dynamic simulations. The results show that the neglect of intraformational baffles in reservoir rocks might lead to an underestimation of mineral trapping capacity by nearly 2.5 times.

Declaration

- The thesis comprises my original work towards the completion of PhD except where indicated in the preface;
- Due acknowledgment has been made in the text to all other material used;
- The thesis is fewer than the maximum word limit in length, exclusive of tables, maps, bibliographies and appendices or that the thesis is 63,000 words as approved by the Research Higher Degrees Committee.

Achyut Mishra

Preface

(i) This thesis is submitted as ‘thesis-with-publications’. As such, certain portion of the work towards this thesis was carried out in collaboration with Mr. Lukas Pajank, Dr. Kuncho D. Kurtev, A/Prof. Abhijit Chaudhuri and Prof. Ralf R. Haese. The nature and contribution of collaborators is described as follows:

- Mr. Lukas Pajank: Compilation of lithotype logs of homogeneous rock types (20% of the work done in publication resulting from Chapter 3).
- Dr. Kuncho D. Kurtev: Development of 2D static reservoir models (30% of the work done in publication resulting from Chapter 4).
- A/Prof. Abhijit Chaudhuri: Supervision with the development of averaged geochemical reaction rates (10% of the work done in publication resulting from Chapter 6).
- Prof. Ralf Haese: Supervision and reviewing of the manuscripts published/submitted (10% of the work done in publications resulting from Chapters 3, 4, 5 and 6).

The remaining work was carried out originally by the author.

(ii) No work towards this thesis has been submitted for other qualifications.

(iii) No work towards this thesis was carried out prior to enrolment in the degree.

(iv) No third party editorial assistance was provided in preparation of the thesis.

(v) The contributions of co-authors in multi-authored publications are described as follows:

- Mr. Lukas Pajank: Compilation of lithotype logs of homogeneous rock types.
- Dr. Kuncho D. Kurtev: Development of 2D static reservoir models.
- A/Prof. Abhijit Chaudhuri: Supervision with the development of averaged geochemical reaction rates.
- Prof. Ralf Haese: Supervision and reviewing of the manuscripts published/submitted.

(vi) The publication status of all chapters are as follows:

- Chapter 1: Unpublished material not submitted for publication.
- Chapter 2: Unpublished material not submitted for publication.
- Chapter 3: Published by Geosciences on 24/06.2019. Title: Mishra, A., Pajank, L., Haese, R.R., 2019. High Resolution Characterization of Lithological Heterogeneity of the Paaratte Formation, Otway Basin (Australia), a Coastal to Shallow-Marine Deposit. Geosciences 9 (6), 278.
- Chapter 4: Published by Journal of Marine and Petroleum Geology on 01/04/2020. Title: Mishra, A., Kurtev, K. D., Haese, R. R., 2020. Composite rock types as part of a workflow for the integration of mm-to cm-scale lithological heterogeneity in static reservoir models. Journal of Marine and Petroleum Geology, 114, 104240.

- Chapter 5: Published by the International Journal of Greenhouse Gas Control. Title: Mishra, A. and Haese, R.R., 2020. Quantification of the turning point saturation for cross bedded CO₂ storage reservoirs. International Journal of Greenhouse Gas Control, 103, p.103185.
- Chapter 6: In revision following peer review by the International Journal of Greenhouse Gas Control. Title: Mishra, A., Chaudhuri, A., Haese, R.R. (submitted). Conditions and processes controlling carbon mineral trapping in intraformational baffles. International Journal of Greenhouse Gas Control.
- Chapter 7: Unpublished material not submitted for publication.
- Chapter 8: Unpublished material not submitted for publication.

The four published/submitted papers and the manuscript under preparation for Chapter 7 have been included as the corresponding chapters without any changes to the main text. The only changes made include the following:

- Formatting: layout, line spacing, font type and font size.
- Figure numbers.
- Table numbers.
- Equation numbers.
- Section heading numbers.
- Changes to Figure 4.1: The abbreviation REV (representative elementary volume) in the published paper has been replaced by the abbreviation CRT (composite rock type) in the chapter. Both refer to the same definition.
- Ten geochemical upscaling relationships have been used as input to the dynamic simulations in Chapter 7. Eight of these upscaling relationships are included in Chapter 6 as a part of the paper published. The remaining two upscaling relationships are presented in Appendix F.
- Abbreviations in Chapters 4, 5, 6 and 7: Abbreviations in Chapters 5 and 6 refer to static model realizations using composite rock types and are different from the abbreviations of the same composite rock types in Chapters 4 and 7. The following table provides a correspondence between the two series of abbreviations:

Abbreviation in Chapters 5 and 6	Corresponding abbreviation in Chapters 4 and 7
CSst	H ^{CSst}
FSst	H ^{FSst}
Slt	H ^{Slt}
Mst	H ^{Mst}
CbSst	H ^{CbSst}
I ^{Mst} _{CSst}	P ^{Mst} _{CSst}
I ^{Mst} _{FSst}	P ^{Mst} _{FSst}
I ^{Mst} _{Slt}	P ^{Mst} _{Slt}

I_{CSst}^{Slt}

I_{FSst}^{Slt}

I_{CSst}^{CbSst}

I_{FSst}^{CbSst}

I_{Slt}^{CbSst}

P_{CSst}^{Slt}

P_{FSst}^{Slt}

M_{CSst}^{CbSst}

M_{FSst}^{CbSst}

M_{Slt}^{CbSst}

Both series of abbreviations refer to the same definition of composite rock types.

All the above changes are made to ensure the coherency of the thesis. The main content is the same as in the papers published/under progress.

(vii) The author is grateful to financial support from Melbourne Research Scholarship and project funding from BHP Billiton.

Acknowledgements

I would like to thank my supervisor, Prof. Ralf R. Haese for his constant guidance and motivation. I am extremely grateful to him for giving me the freedom to pursue this research. It has allowed me to grow as an independent researcher and made me confident professionally. Apart from science, I have also learnt a lot from his leadership qualities and managements skills.

I would also like to thank my co-supervisors, Prof. Stephan K. Matthai and Prof. Abhijit Chaudhuri. Prof. Stephan's critical comments have helped me improve the quality of this work. Prof. Abhijit insights helped me in planning the execution of some of the critical studies in this thesis. I am also extremely grateful to Prof. Abhijit's support with logistics during my study away leave.

I am extremely grateful to Mr. James Perry and Prof. Ashokkumar Muthupandian for supporting me with managing the administration work at a point when I had almost given up the hope of starting this PhD due to issues with student visa. The financial support from the University of Melbourne is duly acknowledged.

I would like to thank the team of the GeoCquest project. The project played a major role in providing a general direction to my work. The application of my work to some of the industrial problems has contributed in boosting my confidence. The project gave me the opportunity to collaborate with some of the top scientists in the field and made me a team player. The critical comments from Prof. Sally Benson, Prof. Jerome Neufeld, Prof. Mike Bickle helped in improving the quality of the work. The collaborations with Dr. Maartje Boon and Dr. Kuncho D. Kurtev allowed in developing some of the key results for the thesis as well as for the GeoCquest project. I would also like to thank Prof. Benson and Dr. Boon for hosting me at Stanford University. Prof. Peter Cook's leadership qualities, energy, vision and hard working nature have been a great motivation for me both professionally as well as personally. I would like to thank CO2CRC Limited and BHP Billiton with their support for this project in terms of data and funding.

I would like to thank Mr. Lukas Pajank for his help with compiling the lithotype logs. Many thanks to Dr. Jay Black for his help with the analysis of QEMSCAN data for the mineral specific grain size characterization of the samples. I would also like to thank Dr. Hong Phuc Vu for his help with the GWB software. Thanks to Dr. Ella Maria for her help with TOUGHREACT and Dr. Nick Burke for his motivation.

The support of my friends in Melbourne has been important. Many thanks to Apoorv, Meghalim, Harika, Sushma, Mahesh, Cesar, Piya, Aans, Anthony and Philip for making feel at home and sharing moments of joy and sorrow. Thanks to Mr. Bill Stathopoulos for keeping the environment within the research group light. I am also grateful to my friends from the I2G family for providing me with a platform to explore my interests outside of the PhD. The patience of my friends in India has been

important throughout my PhD journey. Many thanks to them for bearing with me when I had to miss out on some of the important moments in their lives due to other commitments.

I would like to extend my sincere gratitude to my family. My father, Mr. Mahendra Kumar Mishra, has been a constant source of motivation throughout my life. My mother, Mrs. Sushma Mishra, has been a steadfast listener to my problems. Many thanks to my sister, Aagam Mishra, for her support during difficult times.

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Nomenclature

Symbol	Definition	Units
$\bar{\phi}$	Domain averaged porosity	-
ϕ_i	Porosity of the i^{th} cell	-
ϕ	Porosity	-
V_i	Volume of the i^{th} cell	m^3
n	Number of grid cells	-
μ	Fluid viscosity	$\text{kg m}^{-1} \text{sec}^{-1}$
∇P	Pressure gradient	Pa
$\dot{q}$	Volumetric source/sink term	$\text{m}^2 \text{sec}^{-1}$
q	Darcy volumetric flow rate	$\text{m}^3 \text{sec}^{-1}$
A_c	Domain area cross sectional to flow	m^2
k_p	Absolute permeability	m^2
$\bar{k}_p$	Upscaled absolute permeability	m^2
L	Domain length along flow direction	m
N_c	Capillary number	-
$\bar{k}_z$	Effective vertical permeability	m^2
P_c	Capillary pressure	Pa
$\bar{P}_c$	Average capillary pressure	Pa
H	Domain height	m
S_w	Wetting phase saturation	-
$S_{nw,r}$	Residual saturation of the non-wetting phase	-
$S_{w,c}$	Connate saturation of the non-wetting phase	-
$P_c(S_w)$	Capillary pressure as a function of saturation	Pa
N_g	Gravity number	-
$\Delta\rho$	Fluid density difference	kg m^{-3}
g	Gravitational acceleration	m sec^{-2}
$\Delta\bar{\Omega}_p$	Average fluid potential difference in phase p	Pa
$\Delta\Omega_i$	Phase potential difference in cell i	Pa
Ω_i	Phase potential in cell i	Pa
T_i	Transmissivity of phase p	$\text{m}^2 \text{sec}^{-1}$
$\bar{k}_{rp}$	Upscaled relative permeability of phase p	m^2
$\bar{\mu}_p$	Averaged viscosity of phase p	$\text{kg m}^{-1} \text{sec}^{-1}$
$\bar{S}_p$	Averaged saturation of phase p	-
S_i	Saturation of phase p in cell i	-
R	Reaction rate	mol sec^{-1}
$\bar{R}$	Averaged reaction rate for a given mineral	mol sec^{-1}
$\bar{R}_x$	Domain averaged reaction rate of mineral x	mol sec^{-1}
$A_{i,x}$	Specific surface area of mineral x in cell i	$\text{cm}^2 \text{gm}^{-1}$
$r_{i,x}$	reaction rate of mineral x in cell i	mol sec^{-1}
k	reaction rate constant	$\text{mol cm}^{-2} \text{sec}^{-1}$
$\bar{A}$	Effective specific surface area of mineral	$\text{cm}^2 \text{gm}^{-1}$
M_x	Mass accumulation term	kg m^{-3}
F	Mass flux term	$\text{kg m}^{-2} \text{s}^{-1}$
κ	Component term	-
S_β	Saturation of phase β	-
X_β^κ	Mass fraction of component κ present in phase β	-
ρ_R	Grain density	kg m^{-3}

C_R	Specific heat capacity of the rock	$J K^{-1}$
T	Temperature	K
U_β	Specific internal energy in phase β	$J kg^{-1}$
u	Darcy flow velocity	$m sec^{-1}$
u_β	Darcy velocity for phase β	$m sec^{-1}$
c_i	Concentration of the i^{th} secondary specie	$mol L^{-1}$
c_j	concentration of the j^{th} basis species	$mol L^{-1}$
γ	thermodynamic activity coefficient	-
K	Equilibrium constant	-
v	Stoichiometric coefficient	-
D	Ion specific diffusion coefficient	$m^2 sec^{-1}$
S_R	Mineral saturation ratio	-
SI	Mineral saturation index	-
r	Reaction rate	$mol sec^{-1}$
A	Specific reactive surface area per kg H_2O	$cm^2 gm^{-1}$
k_{25}	Rate constant at $25^{\circ}C$	$mol cm^{-2} sec^{-1}$
E_a	Activation energy	$J mol^{-1}$
R_g	Universal gas constant	$J mol^{-1} K^{-1}$
a_H	activity of H^+	$mol L^{-1}$
a_{OH}	activity of OH^-	$mol L^{-1}$
fr_m	Volume fraction of mineral m in the rock	-
fr_u	Volume fraction of the unreactive rock	-
P_e	Capillary entry pressure	Pa
h_{FWL}	Height of CO_2 above free water level	M
h	Variogram lag distance	m
R_v	Variogram range	m
S_v	Sill value of the variogram	-
N_v	Nugget value of the variogram	-
D_v	Correlation length in the variogram model	M
Γ	Semi variance	-
$2\Gamma(h)_{exp}$	Variance in exponential variogram model	-
$2\Gamma(h)_{sph}$	Variance in spherical variogram model	-
$2\Gamma(h)_{gau}$	Variance in gaussian variogram model	-
m	van Genuchten Empirical parameter	-
λ	Brooks Corey empirical parameter	-
S_{nt}	Threshold CO_2 saturation	-
$S_{e,w}$	Effective water saturation	-
S_{e,co_2}	Effective CO_2 saturation	-
$S_{w,irr}$	Irreducible water saturation	-
$S_{CO_2,r}$	Residual CO_2 saturation	-
σ	CO_2 water interfacial tension	$N m^{-1}$
$S_{CO_2,tp}^{max}$	Maximum CO_2 turning point saturation	-
$\hat{S}_{CO_2,tp}^{max}$	Dimensionless maximum CO_2 turning point saturation	-
ϕ_f	Foreset porosity	-
ϕ_l	Lamina porosity	-
k_f	Foreset permeability	mD
k_l	Lamina permeability	mD
Pe_f	Foreset entry pressure	Pa
Pe_l	Lamina entry pressure	Pa

m_f	Foreset van Genuchten empirical exponent	-
m_l	Lamina van Genuchten empirical exponent	-
$k_{r,w}$	Water relative permeability	-
k_{r,CO_2}	CO ₂ relative permeability	-
m_r	Relative permeability-saturation empirical parameter	-
m_c	Capillary pressure-saturation empirical parameter	-
M	Amount of given mineral at time t	mol
$M_{min,t}^C$	Mass of carbon mineralized per unit rock volume	g cm ⁻³
M_M^C	Molar mass of carbon	g mol ⁻¹
$V_{f,t}^j$	Volume fraction of the carbonate mineral at time t	-
V_M^j	Molar volume of the carbonate mineral j	cm ³ mole ⁻¹
n_S^j	Stoichiometry of carbon in one formula unit of mineral j	-
V_T	Total volume of a given model realization	cm ³
$M_{baffle}^{initial}$	Initial amount of a given mineral in the baffle	mol
$M_{reservoir\ rock}^{initial}$	Initial amount of a given mineral in the reservoir rock	mol
$\Delta \bar{M}$	Change in total mineral content over time Δt	mol
Δt	Time step	sec
$\bar{M}^{initial}$	Total initial amount of a mineral in the given realization	mol
f	Binary variable depending on mineral contribution	-
P_o	Capillary strength parameter	Pa
$S_{e,nwt}$	Effective trapped saturation of the non-wetting phase	-
$S_{e,wtp}$	Effective turning point saturation of the wetting phase	-
$S_{w,tp}$	Turning point saturation of the wetting phase	-
$S_{nw,r}$	Residual non-wetting phase saturation	-
$S_{nw,max}$	Maximum saturation of the non-wetting phase	-

List of Abbreviations

Abbreviation	Definition
EqD	Equivalent grain diameter
SA	Segmented area
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
CRT	Composite rock type
QEMSCAN	Quantitative Analysis of Minerals by Scanning Electron Microscopy
MICP	Mercury intrusion capillary pressure
CSst	Coarse sandstone
FSst	Fine sandstone
Slt	Siltstone
Mst	Mudstone
CbSst	Carbonate-cemented sandstone
H ^{CSst}	Homogeneous rock type composed of coarse sandstone
H ^{FSst}	Homogeneous rock type composed of fine sandstone
H ^{Slt}	Homogeneous rock type composed of siltstone
H ^{Mst}	Homogeneous rock type composed of mudstone
H ^{CbSst}	Homogeneous rock type composed of carbonate-cemented sandstone
X ^{FSst} _{CSst}	Cross bedded rock type composed of coarse and fine sandstones
P ^{Mst} _{CSst}	Planar bedded rock type composed of mudstone and coarse sandstone
P ^{Mst} _{FSst}	Planar bedded rock type composed of mudstone and fine sandstone
P ^{Slt} _{CSst}	Planar bedded rock type composed of siltstone and coarse sandstone
P ^{Slt} _{FSst}	Planar bedded rock type composed of siltstone and fine sandstone
P ^{Mst} _{Slt}	Planar bedded rock type composed of mudstone and siltstone
M ^{CbSst} _{CSst}	Massive bedding interface between carbonate-cemented and coarse sandstones
M ^{CbSst} _{FSst}	Massive bedding interface between carbonate-cemented and fine sandstones
M ^{CbSst} _{Slt}	Massive bedding interface between carbonate-cemented sandstone and siltstone
M ^{CbSst} _{Mst}	Massive bedding interface carbonate-cemented sandstone and mudstone
I ^{Mst} _{CSst}	Interface between mudstone and coarse sandstone
I ^{Mst} _{FSst}	Interface between mudstone and fine sandstone
I ^{Slt} _{CSst}	Interface between siltstone and coarse sandstone
I ^{Slt} _{FSst}	Interface between siltstone and fine sandstone
I ^{Mst} _{Slt}	Interface between mudstone and siltstone
I ^{CbSst} _{Mst}	Interface between carbonate-cemented sandstone and coarse sandstone
I ^{CbSst} _{FSst}	Interface between carbonate-cemented sandstone and fine sandstone
I ^{CbSst} _{Slt}	Interface between carbonate-cemented sandstone and siltstone
I ^{CbSst} _{Mst}	Interface between carbonate-cemented sandstone and mudstone
IAR _φ	Interfacial anisotropy ratio in porosity
IAR _k	Interfacial anisotropy ratio in permeability
IAR _{Pe}	Interfacial anisotropy ratio in capillary entry pressure
IAR _m	Interfacial anisotropy ratio in relative permeability empirical parameter

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Chapter 1

Introduction

1.1. Geological carbon storage

Carbon dioxide (CO₂) is one of the gases that contributes to the Earth's greenhouse effect. Over the last 250 years, the atmospheric concentration of CO₂ has gone up from ~280 ppm to ~400 ppm (Earth System Research Laboratory; Houghton, 2009). The rapid increase of atmospheric CO₂ since industrialization is attributed to anthropogenic activity (Joos and Bruno, 1996; Hellevang and Aagaard, 2015; Matthews et al., 2009; Zeebe et al., 2016). Consequently, this has enhanced the greenhouse effect and resulted in a global temperature rise, a phenomena commonly known as the global warming (Houghton, 2009). Global warming is thought to have adverse effects on life and the environment (Cline, 1992; Fowler and Hennessy, 1995; Hoel and Kverndokk, 1996; Houghton, 2009; Martens, 2013; Meehl et al., 2005; Tan and Shibasaki, 2003; Weart, 2008; Yafeng and Shiyin, 2000; Zhang et al., 2015). In order to control global warming, it is important to find solutions to bring down the atmospheric CO₂ concentrations. Several methods have been developed to check the rise of CO₂ from anthropogenic sources (Beaumont et al., 2014; Bhattacharyya et al., 2008; Brown, 1992; Day et al., 2005; Ghommam et al., 2012; Mitra and Zaman, 2014; Ogawa et al., 2006; Rahman et al., 2017). Geological carbon storage is one such way which is considered effective, economical and safe (Bachu, 2002; Flett et al., 2005; Friedmann, 2007; Gunn et al., 2012; Oldenburg and Unger, 2003; D. Zhang and Song, 2014). In this approach, CO₂ is injected in the sub-surface instead of emitting it in the atmosphere (Benson et al., 2012; Benson and Orr, 2008; Metz et al., 2005).

In the sub-surface, CO₂ is injected in a layer of reservoir rock which is characterized by high porosity and high permeability. The reservoir rock is typically overlaid by a layer of caprock which is characterized by low porosity and low permeability (Metz et al., 2005). There are four primary mechanisms by which carbon is stored geologically: structural and stratigraphic trapping, solubility trapping, residual trapping and mineral trapping (Metz et al., 2005). As CO₂ is injected into the reservoir rock, it migrates towards shallower depths due to buoyancy until hindered by the caprock. The low permeability of the caprock prevents further CO₂ rise thereby trapping CO₂ (Benson and Cole, 2008). This mechanism is called structural and stratigraphic trapping as CO₂ is geologically stored underneath the stratigraphic unit of the caprock. Stratigraphic trapping has immense potential to store significant amounts of CO₂. However, stratigraphic trapping capacity might be compromised due to the presence of faults within the caprock, providing a leakage pathway. Solubility trapping occurs when the injected CO₂ dissolves in the formation water. The dissolution is gradual (Baz et al., 2014) and is dependent on salinity, pressure and temperature. The reservoir contains free injected CO₂, original formation water and formation water with dissolved CO₂ in it. The CO₂ enriched water is denser than the virgin formation water which sets up convection currents whereby the CO₂ enriched water sinks to greater depths (Flett et al., 2007). Residual or capillary trapping occurs due to the action of capillary forces of the formation

waters (wetting phase) on CO₂ (non-wetting phase). When CO₂ is injected into the reservoir, it displaces a large proportion of formation waters during drainage. Post injection, water flows behind CO₂ due to density contrasts between the less dense CO₂ plume and the denser formation water in a process called imbibition. The capillary forces at the interface of the two fluid phases cause the formation water to trap and immobilise CO₂ as a residual phase in the form of bubbles within the pore throats (Flett et al., 2007; Metz et al., 2005). In mineral trapping, the dissolution of CO₂ leads to the formation of weak carbonic acid. The low pH solution leads to the dissolution of clay minerals like chlorites thereby mobilizing cations such as Ca⁺⁺, Mg⁺⁺ and Fe⁺⁺. Over hundreds to thousands of years, pH increases and the carbonate mineral saturation is reached followed by their precipitation which permanently traps injected CO₂ in the solid phase (Flett et al., 2007; Hellevang, 2015; Metz et al., 2005; Watson et al., 2005; Xu et al., 2005). Comparatively, stratigraphic trapping is the fastest of the four mechanisms and contributes the maximum in terms of trapping while mineral trapping is the slowest but is the most secure mechanism (Figure 1.1) (Metz et al., 2005).

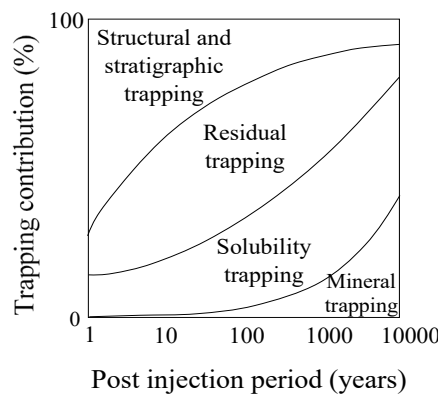


Figure 1.1. Qualitative comparison of the contribution and time scales of the four trapping mechanisms (modified after Metz et al., 2005).

The injection of CO₂ is carried out at depths greater than 800 m. The critical point of CO₂ occurs at a pressure of 7.38 MPa and a temperature of 31.1⁰ C (Andrews, 1869), which roughly corresponds to a depth of 800 m. Hence, CO₂ exists as a supercritical phase at depths greater than 800 m. This allows the storage of about 370 times extra volume of CO₂ within the same pore volume (Price and Smith, 2008).

1.2. Lithological heterogeneity and its significance

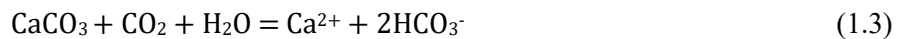
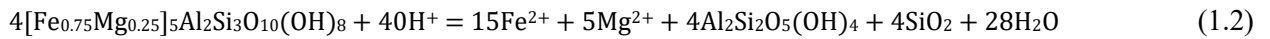
The reservoir rocks into which CO₂ is injected are lithologically heterogeneous (Flett et al., 2005; Flett et al., 2007; Law and Bachu, 1996). Lithological heterogeneity is an integral part of any reservoir though the characterization of heterogeneity depends on the scale and properties of interest. Lithological heterogeneity can be defined in terms of several properties including porosity, permeability, capillary pressures, relative permeability and mineralogy. Heterogeneity can also be characterised and defined at different scales, for example, at kilometre scale in the form of depositional facies environments and structural features such as folds and faults; at cm-scale in the form of sedimentary bedding structures and at micro-meter scale in the form of pore network (Bernabé and Revil, 1995; Cross, 1991; Cross et al., 1993; Haggerty and Gorelick, 1995; Lai et al., 2015; Miall, 2016; Smith et al., 2013).

Heterogeneity at kilometre scales affects regional fluid flow as the clay-rich depositional facies such as pro-delta and structural features such as sealing faults might act as a regional flow barrier. On the other hand, depositional facies such as distributary channels and structural features such as extensional faults might provide preferential pathways for fluid flow. Such faults might lead to the leakage of geologically trapped CO₂ (Christopher et al., 2006; Downey, 1984; Fulljames et al., 1997; Green and Ennis-King, 2010a; Hermanson and Kirste, 2013). Heterogeneity at pore and cm-scales affects local fluid flow and residual CO₂ trapping (Blunt and King, 1991; Fourie et al., 2007; Krevor et al., 2011; Li and Benson, 2015; Meakin and Tartakovsky, 2009; Ni et al., 2019; Pini and Benson, 2017; Saadatpoor et al., 2009a; Saadatpoor et al., 2010a; Saadatpoor et al., 2013). Specifically, the sedimentary structures at cm-scale such as cross bedding, planar bedding, etc. are composed of clay-rich laminae within a reservoir rock (Miall, 2016). These laminae are characterized by low porosity, low permeability, high capillary entry pressure and high clay content and are known as intraformational baffles (Gibson-Poole et al., 2009; Yu et al., 2017). The low permeability and high capillary entry pressure of the baffles impedes the mobility of CO₂. Consequently, CO₂ accumulates within the high porosity reservoir rocks resulting in an enhanced trapping by local capillary forces. The higher the contrast between the capillary entry pressures of the two lithologies, the higher is the amount of CO₂ trapped in the reservoir rock layer (Gershenson et al., 2017; Saadatpoor et al., 2010b; Trevisan et al., 2017).

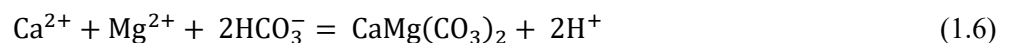
The presence of intraformational baffles also affects carbon mineralization (Hellevang et al., 2005; Hermanson and Kirste, 2013; Higgs et al., 2015; Newell et al., 2008; Watson, 2012; Xu et al., 2005; Xi et al., 2019; Yang et al., 2014). The injected CO₂ dissolves in the formation brine increasing its acidity:



The clay minerals present in the laminae such as chlorites, illite and smectites and the primary carbonate minerals dissolve under acidic conditions and mobilize ions such as Ca⁺⁺, Mg⁺⁺ and Fe⁺⁺:



The dissolution of clay minerals (equation 1.2) consumes protons resulting in an increase of pH. As conditions become less acidic, the released Ca⁺⁺, Mg⁺⁺ and Fe⁺⁺ ions combine with bicarbonate ions (equation 1.1) leading to a precipitation of secondary carbonate minerals such as calcite, siderite, dolomite and ankerite:



The precipitation of secondary carbonate minerals fixes CO₂ in the mineral phase (Hellevang, 2015). On the other hand, the presence of intraformational baffles composed of carbonate-cemented sandstone might

reduce carbon mineralization. Upon reaction with protons, the in-situ carbonate minerals dissolve releasing carbonate ions within the first year of CO₂ injection. The carbonate ions combine with protons to form bicarbonate ions, resulting in an increase of pH within the first few years of injection due to the higher reaction rates of carbonate minerals (equation 1.8).



If the proportion of carbonate minerals is significant, then the pH remains buffered to less acidic values (Newell et al., 2008). The increase in pH reduces the dissolution of clay minerals and hence carbon mineralization. Hence, the presence of intraformational baffles might enhance or reduce carbon mineral trapping (Hermanson and Kirste, 2013; Watson, 2012).

Lithological heterogeneity significantly affects capillary and mineral trapping mechanisms. Neglecting heterogeneity inevitably leads to a greater uncertainty in the estimation of CO₂ velocity, the trapping capacity and the lateral extent of the CO₂ plume (Li and Benson, 2015; Trevisan et al., 2017). Hence, it is important to integrate heterogeneity at different scales in static reservoir models so that the results from dynamic simulations have lesser uncertainty.

1.3. Integration of lithological heterogeneity in static reservoir models

1.3.1. Regional scale lithological heterogeneity

Regional scale lithological heterogeneity in the form of depositional facies is usually implemented in reservoir models using wireline log and seismic data (Bridge and Tye, 2000; Brown, 2011; Doveton and Prenskey, 1992; Hurst et al., 1992). Wireline logs provide one dimensional record of heterogeneity while seismic data incorporates a three dimensional variability in rock properties and can be used to identify the location and extent of depositional facies. Different wireline logs such as gamma ray, neutron porosity, density, etc. incorporate a range of information about the different lithological properties (Rider, 1996). The wireline logs incorporate lithological information at a resolution of few 10s of cm. The wireline logs are imported in reservoir modelling softwares such as Petrel or SKUA and the heterogeneity in rock properties is incorporated in the static models using two broad approaches: the pixel based approach and the object based approach.

1.3.1.1. Pixel based static modelling

The pixel based approach is usually used to populate properties in the inter-well region which typically vary at each point in space, such as porosity and permeability (Aghamoghanov, 2015; Caers et al., 2014; Falivene et al., 2006). Property population is carried out using sequential simulation interpolation methods. Some of the commonly used methods include nearest neighbourhood method, inverse distance weighted method and kriging (Li and Heap, 2008).

The natural neighbourhood method interpolates the value based on the data value in the nearest grid cell by applying weights in proportion to the area of the grid blocks. The inverse weighted approach estimates the value at a grid cell by using a weighted average of the input data. The distance of the grid cell from the input

data is used as weights such that the data points closer to the grid cell have a higher weightage. Kriging is a geostatistical method used for data interpolation given that the data has a certain degree of spatial correlation. The nearest neighbour and the inverse distance weighting methods are deterministic while Kriging quantifies the spatial autocorrelation mean and variance which are used to determine random variables at all locations where the value of the variable is not known. It also accounts for the directional dependence in data due to spatial anisotropy. Kriging requires a variogram models as an input for interpolation (Li and Heap, 2008).

A variogram is a mathematical function describing the degree of spatial variance (2Γ) between data points as a function of distance between the points (Figure 1.2). It denotes the distance (h) up to which the values of a certain rock property can be correlated. The function can be described in terms of 3 parameters: range (R_v), sill (S_v) and nugget (N_v). Range is the maximum distance between the data points up to which they show correlation. Sill the maximum variance between the data point values beyond which data are uncorrelated. It occurs at a maximum correlation length (D_v) between data points. Nugget accounts for large variation in the values of a property that occurs at unresolved spatial scales (Aghamoghanov, 2015). The variogram models are empirically fitted to semi-variance calculated from known data over a range of spatial separation scales. Some common empirical variogram models are exponential ($2\Gamma(h)_{\text{exp}}$), spherical ($2\Gamma(h)_{\text{sph}}$) and gaussian ($2\Gamma(h)_{\text{gau}}$) defined as follows (Chiles and Delfiner, 1999; Cressie, 1993):

$$2\Gamma(h)_{\text{exp}} = N_v + (S_v - N_v) \left(1 - \exp^{-3h/D_v} \right) \quad (1.9)$$

$$2\Gamma(h)_{\text{sph}} = \begin{cases} N_v + (S_v - N_v) \left(\frac{3h}{2D_v} - \frac{h^3}{2D_v^3} \right) & \text{if } h < D_v \\ 1 & \text{if } h > D_v \end{cases} \quad (1.10)$$

$$2\Gamma(h)_{\text{gau}} = N_v + (S_v - N_v) \left(1 - \exp^{-3h^2/D_v^2} \right) \quad (1.11)$$

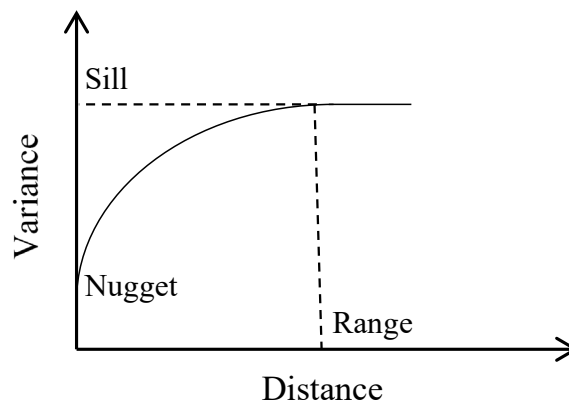


Figure 1.2. A typical variogram model used as an input while interpolating data by Kriging.

The variogram models are direction-dependent as rock properties show different variability in their distribution along different azimuths. Hence, variograms are derived along multiple azimuths to integrate anisotropy in the rock property. Usually, the modelling domain is sub-divided into regions based on depositional environments and different variogram models are used to populate the same rock property in

different regions. This allows constraining the inter-facies variation in the distribution of rock properties and allows for the integration of the impact of depositional environments in static reservoir models. For example, a region with distributary channel facies will be characterized by a larger extent of high porosity-high permeability values compared to a pro-delta facies (Aghamoghlanov, 2015; Caers et al., 2014; Falivene et al., 2006; Li and Heap, 2008).

In the absence of well log data, property population is carried out using a multipoint geostatistical approach based on training images (Caers, 2002, 2003; Caers et al., 2014; Strebelle, 2002). A training image is a conceptual pictorial representation of the anisotropy in data. The training images may be hand sketched or available using outcrop images. Spatial configuration of the constituent facies is determined using the training images. Multipoint geostatistics is then used to derive probability density functions for each facies which can then be used to populate properties in the static reservoir models. The multipoint geostatistical approach is considered as an improvement over many other interpolation methods as it determines data values using more than two input values at each step (Falivene et al., 2006).

1.3.1.2. Object based static modelling

The object based approach involves rock property population in the inter-well region using the shape of geobodies (Falivene et al., 2006; Geel and Donselaar, 2007; Journel et al., 1998). The approach is usually used to populate properties which can be constrained using certain geometrical shapes, such as depositional facies environments. For example, a distributary channel can be implemented in static reservoir models using its sinuosity, cross-sectional shape and lateral extent (Wei et al., 2017).

The dimensions of geobodies can be determined using different methods. Usually, natural analogues are used to constrain the shape and size of the depositional facies environments. Several correlational models have been derived which relate the dimensions that are not directly observable in the well logs and outcrops such as length and width of the facies as a function of dimensions which can directly be constrained from the cores such as the thickness of the facies (Bridge et al., 2000; Bridge and Tye, 2000; Dutton et al., 2000; Gibling, 2006; Ito et al., 2006; Xiaoqing et al., 2013). In certain cases, data from modern analogues using field and satellite studies is used for object based delineation of depositional facies environments (De Rose et al., 2008; Erskine et al., 2016; Reynolds, 1999). In the absence of field data, conceptual figures can also be utilised to determine the shape and extent of geobodies with a certain degree of confidence.

The object based approach has an additional advantage over the pixel based approach as it allows for implementation of geometries that might represent actual shape of the geological bodies as opposed to the geostatistical approach where geometries might not be honoured. However, care must be taken to correctly implement the juxtaposition relations between the geobodies (Falivene et al., 2006).

1.3.2. Sub-meter scale lithological heterogeneity

Intraformational baffles typically exist at mm- to cm-scales which is below the resolution of wireline logs. Hence, intraformational baffles cannot be directly incorporated in reservoir models unlike regional scale heterogeneity. Alternatively, the impact of baffles on flow and geochemical reactions is analysed through local

studies and the results are upscaled for incorporation in coarser discretised static models (Durlofsky, 2003; Durlofsky, 2005; Saadatpoor et al., 2009b). Upscaling is a method to calculate an average value of the rock property of a heterogeneous system using fine scale flow and geochemical behaviour. This leads to the homogenization of a complex system resulting in representative average values. The equivalent homogenised system can then be incorporated in the coarser scale static models without a need for a detailed analysis of the fine scale behaviour (Christie, 1996). Several upscaling approaches have been developed to find a representative average of the rock properties such as porosity, single and two-phase permeabilities, capillary pressure, fluid saturation and geochemical reactions. A few common upscaling approaches are discussed in the following sections.

1.3.2.1. Upscaling porosity

Porosity is defined as the ratio of pore volume to total rock volume. Porosity is homogenised by taking a volume weighted arithmetic average of the porosities characteristic of the constituent lithologies (Durlofsky, 2003). In a static reservoir domain discretised into grid cells, the upscaled porosity is calculated as follows:

$$\bar{\Phi} = \frac{\sum_{i=1}^n V_i \phi_i}{\sum_{i=1}^n V_i} \quad (1.12)$$

where, $\bar{\Phi}$ is the averaged porosity of the domain, ϕ_i is the porosity of the grid cell i , V_i is the volume of the grid cell i (m^3) and n is the number of grid cells.

1.3.2.2. Single phase upscaling

Absolute permeability is the measure of a rock's capacity to transmit fluids through it. A highly permeable rock allows fluid transmission easily due to the connectivity of pore spaces. Absolute permeability is commonly upscaled using the pressure solver approach (Christie, 1996) which involves solving the single phase pressure equation:

$$\dot{q} = \nabla \cdot \left(\frac{1}{\mu} k_p \cdot \nabla P \right) \quad (1.13)$$

where μ is fluid viscosity ($\text{kg m}^{-1} \text{sec}^{-1}$), ∇P is the pressure gradient (Pa), k_p is absolute permeability (m^2) and $\dot{q}$ is the volumetric source/sink term ($\text{m}^2 \text{sec}^{-1}$).

Pressure difference is applied at the opposite boundaries of the heterogeneous domain and the fluid is allowed to flow through. The other boundaries are set at no flow boundary condition (Figure 1.3).

The pressure equation (equation 1.13) is solved for each grid cell of the domain to determine the pressure in each cell which is further used to calculate the flow rates in each grid cell using Darcy's single phase flow equation (Darcy, 1856):

$$q = \left(-\frac{1}{\mu} k_p A_c \cdot \nabla P \right) \quad (1.14)$$

where q is the Darcy volumetric flow rate ($\text{m}^3 \text{sec}^{-1}$) and A_c is the cross-sectional area of the domain (m^2). The flow rates are then summed and used to calculate the effective permeability for the equivalent homogenised domain (Warren and Price, 1961):

$$\bar{k}_p = \frac{\mu L \sum q}{A_c \Delta P} \quad (1.15)$$

where $\bar{k}_p$ is the upscaled absolute permeability (m^2) and L is the length of the domain along the flow direction (m).

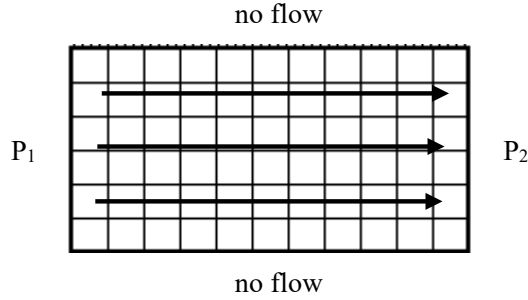


Figure 1.3. Flow simulation set-up to upscale absolute permeability on a discretised domain. P_1 and P_2 are the boundary pressures such that P_2 is lower than P_1 . No flow conditions are set on the remaining boundaries of the domain.

The calculations are repeated along different axes to calculate the direction dependency of the upscaled absolute permeability. The value of effective permeability is strongly dependent on the boundary condition (Christie and Blunt, 2001). The other methods used to upscale single phase permeability include extended local, global and quasi-global approaches (Chen and Durlofsky, 2006; Chen et al., 2003; Christie and Clifford, 1998; Gomez-Hernandez and Journal, 1990). Care must be taken to use these approaches in regions far from the injection well. This is because the flow is radial in the near well region and is significantly affected by the high pressure gradient, in contrary to the linear flow under lower gradient assumptions used in the pressure solver approach (Durlofsky et al., 2000).

1.3.2.3. Two phase upscaling

Relative permeability and capillary pressure are important two phase properties governing fluid flow in a porous media. Relative permeability is a measure of reduction in the flow ability of a fluid due to the presence of other fluids in the system. It results from interfacial tension between the two fluids and the associated contact angle. Capillary pressure is the difference in the pressure of two immiscible fluids across an interface. In a water wet system consisting of brine and CO_2 , the former acts as the wetting phase while the latter acts as the non-wetting phase. Both the properties are dependent on the saturation of the wetting phase. The relationships between relative permeability-fluid saturation and capillary pressure-fluid saturation are shown in figures 1.4a and 1.4b, respectively (Bear, 1972).

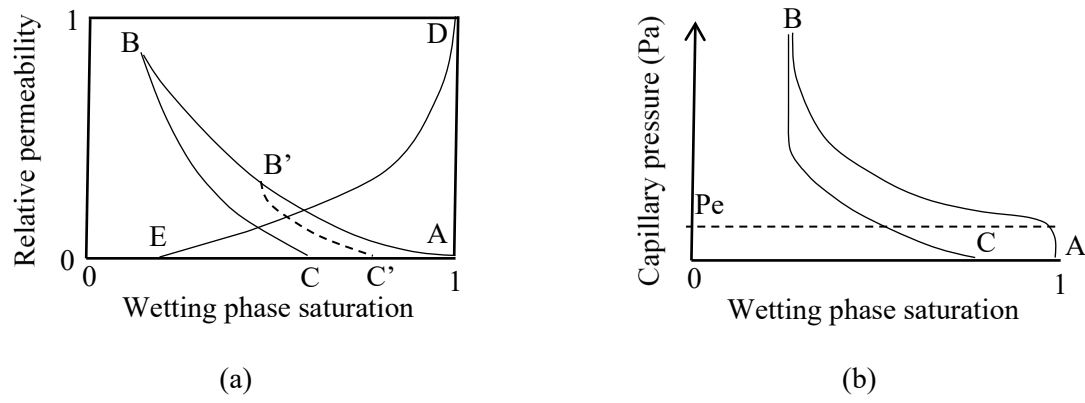


Figure 1.4. (a) Hysteretic relative permeability-saturation relationship; and (b) Hysteretic capillary pressure-saturation relationship. Curve AB=primary drainage curve for the non-wetting phase; curve BC= primary imbibition curve for the non-wetting phase; curve DE=primary drainage curve for the wetting phase; P_e =capillary entry pressure; E=irreducible water saturation; C=maximum residual saturation for the non-wetting phase; B'= relative permeability corresponding to the turning point saturation; C'=residual saturation for the non-wetting phase corresponding to turning point saturation. Hysteresis in wetting phase is not shown.

The saturation of the wetting phase decreases as CO_2 is injected in a system saturated with water. The process is known as drainage. As water saturation decreases, the capillary pressure shows a sharp increase to values of capillary entry pressure. Capillary entry pressure is the minimum pressure required by a fluid phase to break into a rock type and is a function of the minimum pore size characteristic of the rock. As wetting phase saturation decreases further, relative permeability of CO_2 increases while that of water decreases along the primary drainage curves. Drainage can occur until water saturation achieves a minimum value, called irreducible water saturation. At this point, capillary pressure achieves extremely large values while relative permeability of water becomes zero implying that no more water can be flushed out from the system. Also, CO_2 saturation achieves a maximum value at this stage and is called end point CO_2 saturation corresponding to irreducible water content. After this, the saturation of water starts increasing and the process is known as imbibition. The capillary pressure and relative permeability evolve along the primary imbibition curve and the values are different from those achieved during drainage due to hysteresis (Bear, 1972). However, the system might undergo flow reversal from drainage to imbibition at wetting phase saturation between unity and irreducible water saturation. The saturation corresponding to the point at which flow reversal occurs is called turning point saturation (Doughty, 2007). In this case, relative permeability values do not evolve along the primary imbibition curve but rather along a scanning curve. Imbibition stops when saturation of the non-wetting phase achieves a residual value below which CO_2 cannot be flushed out of the system. The residual CO_2 saturation varies between zero and a maximum value corresponding to primary imbibition curve (Bear, 1972; Doughty, 2007).

A range of approaches have been developed to upscale two phase properties such as relative permeability and capillary pressure. Some of these approaches are: vertical equilibrium method (Coats et al., 1971; Coats et al., 1967), Hearn's method (Hearn, 1971), Stone's method (Stone, 1991), Kyte and Berry's method (Kyte and Berry, 1975) and transmissibility weighted method (Darman et al., 2001).

The choice of the appropriate two phase upscaling method is significantly affected by the flow regime which can be calculated using capillary and gravity numbers (Zhou et al., 1997). Both the numbers are dimensionless and provide the strength of capillary and gravity forces relative to viscous forces.

Capillary number is given by:

$$N_c = \frac{\text{Capillary force}}{\text{Viscous force}} = \frac{\bar{k}_z \bar{P}_c w L}{q \mu H} \quad (1.16)$$

where N_c is the capillary number, $\bar{k}_z$ is the effective vertical permeability (m^2), q is the Darcy volumetric flow rate ($m^3 \text{ sec}^{-1}$), w is the width of the domain (m), L is the length of the domain (m), H is the height of the domain, and, $\bar{P}_c$ is the average capillary pressure (Pa) which can be obtained as follows:

$$\bar{P}_c = \int_{S_w}^{1-S_{nw,r}} \frac{P_c(S_w)}{1-S_{nw,r}-S_{w,c}} dS \quad (1.17)$$

where S_w is the saturation of the wetting phase, $S_{nw,r}$ is the residual saturation of the non-wetting phase, $S_{w,c}$ is the connate saturation of the wetting phase, $P_c(S_w)$ is the capillary pressure as a function of the wetting phase saturation (Pa).

Gravity number is calculated as:

$$N_g = \frac{\text{Gravity force}}{\text{Viscous force}} = \frac{\bar{k}_z w L \Delta \rho g}{q \mu} \quad (1.18)$$

where N_g is the gravity number, $\Delta \rho$ is the fluid density difference ($kg \text{ m}^{-3}$), g is the gravitational acceleration ($m \text{ sec}^{-2}$).

A high value of capillary number indicates a dominance of capillary forces and low fluid flow rates while a low value of capillary number implies high fluid flow rate conditions. A high value of gravity number indicates dominant gravity forces which might lead to water slumping (Cao and Aziz, 1999). It is difficult to state an absolute value of both the dimensionless numbers as a global indicator of the dominating flow regime. This is because the absolute values vary significantly as a function of heterogeneity and flow rates (Zhou et al., 1997).

Except for the transmissibility weighted approach, all the other upscaling approaches are limited by the nature of flow regime and the geometry of the reservoir. For example, the vertical equilibrium method can be applied only for very small values of flow rate; Hearn's method can be applied only for viscous dominated flow regimes and for non-stratified reservoirs; Stone's method cannot be applied to horizontal reservoirs under capillary dominated flow regime; and Kyte and Berry's method cannot be applied to reservoirs characterised by structural dip. The transmissibility weighted approach can be applied to all flow regimes and is not limited by the structural geology of the reservoir.

In the transmissibility weighted approach (Darman et al., 2001), first the averaged potential difference between the two phases is calculated:

$$\Delta \bar{\Omega}_p = \frac{\sum_{i=1}^n T_i \Omega_i \Delta \Omega_i}{\sum_{i=1}^n T_i \Omega_i} \quad (1.19)$$

where $\Delta \bar{\Omega}_p$ is the averaged potential difference of phase p (Pa), $\Delta \Omega_i$ is the phase potential difference in cell i (Pa), Ω_i is the phase potential in cell i (Pa), T_i is the transmissivity of phase p in cell i ($\text{m}^2 \text{sec}^{-1}$), and n is the total number of cells.

The averaged potential difference is then used to calculate upscaled relative permeability using two-phase Darcy's equation:

$$\bar{k}_{rp} = \frac{\bar{\mu}_p q_p L}{A_c k_p \Delta \bar{\Omega}_p} \quad (1.20)$$

where $\bar{k}_{rp}$ is the upscaled relative permeability of phase p (m^2), $\bar{\mu}_p$ is the average viscosity of phase p ($\text{kg m}^{-1} \text{sec}^{-1}$), q_p is the Darcy volumetric flow rate ($\text{m}^3 \text{sec}^{-1}$), L is the length of the domain along the flow direction (m), A_c is the area of the domain cross sectional to the flow (m^2) and k_p is the absolute permeability (m^2).

The corresponding averaged fluid saturation can be calculated by pore volume weighted averaging of the fluid saturations in each grid block of the domain:

$$\bar{S}_p = \frac{\sum_{i=1}^n V_i S_i}{\sum_{i=1}^n V_i} \quad (1.21)$$

where, $\bar{S}_p$ is the averaged saturation of the phase p, S_i is the saturation of phase p in the grid cell i, V_i is the volume of the grid cell i (m^3) and n is the number of grid cells.

The upscaled capillary pressure can be calculated by inverting all the capillary pressure curves to calculate the distribution of wetting phase at a given value of capillary pressure. The saturations are averaged by volume weighted method. This results in one data point on the upscaled capillary pressure-saturation curve. The process is repeated for different values of capillary pressures to obtain the entire range of capillary pressure-saturation curve (Pickup and Sorbie, 1996; Pickup, 1998).

The two phase upscaling methods allow to integrate the impact of fine scale lithological heterogeneity in coarser scale models and help in the reproduction of fine scale results such as breakthrough time, field pressure fluid flow behaviour and cumulative production. However, the two phase upscaling approaches are computationally challenging compared to single phase upscaling methods and are often not feasible when applied to field cases (Christie, 1996).

1.3.2.4. Averaged geochemical reaction rates

Limited approaches are available in the literature regarding averaging the geochemical impact of lithological heterogeneity at mm- to cm-scale. A common approach is to calculate the dissolution and precipitation rates of the constituent minerals in each grid cell of the heterogeneous domain (Kim et al., 2011). The averaged reaction rate is then calculated using specific surface area weighted average of the rates in each grid cell:

$$\bar{R}_x = \frac{\sum_{i=1}^n A_{i,x} r_{i,x}}{\sum_{i=1}^n A_{i,x}} \quad (1.22)$$

where, $\bar{R}_x$ is the domain averaged reaction rate of mineral x (mol sec⁻¹), $A_{i,x}$ is the specific surface area of mineral x in cell i (cm² gm⁻¹) and $r_{i,x}$ is the reaction rate of mineral x in cell i (mol sec⁻¹).

This approach might not yield convincing results as the domain averaged reaction rate might not be a weighted arithmetic average of the rates in each grid cell. An alternative approach is to calculate the effective specific mineral surface areas and use them to determine the averaged reaction rates of the corresponding minerals (Wen and Li, 2017; Wen and Li, 2018):

$$\bar{R}_x = k\bar{A} \quad (1.23)$$

where, $\bar{R}_x$ is the domain averaged reaction rate of mineral x (mol sec⁻¹), $\bar{A}$ is the effective specific surface area of mineral x (cm² gm⁻¹) and k is the reaction rate constant (mol cm⁻² sec⁻¹).

The effective mineral surface area is a function of the fluid residence time within the domain which is in turn governed by the heterogeneity in permeability. Hence, this approach attempts to quantify the dependence of mineral dissolution and precipitation on the heterogeneity in physical properties such as permeability. However, this approach has been demonstrated for mono-mineral systems and can be quite computationally challenging when used for multi-mineral systems. Also, this approach follows a homogeneous distribution of mineral within the modelling domain. Both these approaches are also limited by the uncertainty around mineral surface area and nucleation rates (Hellevang and Aagaard, 2013; Hellevang et al., 2013). These are important limitations. Firstly, complex mineralogy might significantly affect the nature and extent of geochemical reactions. Secondly, the distribution of different minerals within the domain is important to implement as it governs the evolution of pH and consequently the extent of mineral dissolution and precipitation (Sundal and Hellevang, 2019; Yang et al., 2014).

1.4. Mathematical analysis of fluid flow and geochemical reactions

After the incorporation of heterogeneity in static models, its impact on fluid flow and geochemical reactions is analysed either experimentally or using dynamic simulations. However, the experimental approach is limited to core scale domains for small time durations. The reservoir scale fluid flow might occur over decades while the geochemical reactions might achieve equilibrium in 100s to 1000s of years. For this reason, dynamic simulations are preferred over experiments to study the full reactive transport behaviour of the domain (Steefel et al., 2005). The typical reactive transport simulators, such as TOUGHREACT, solve multiphase fluid flow and chemical reactions (Xu et al., 2011). This section presents the mathematical formulation of the multiphase reactive transport simulations (Xu et al., 2004b).

First, the mass and energy balance equations are defined to describe the fluid and heat flow in multiphase, multicomponent systems. The basic mass balance equation can be written in the following general form:

$$\frac{\partial M_x}{\partial t} = -\nabla F_k + \dot{q}_k \quad (1.24)$$

where, M_x is the mass accumulation (kg m^{-3}), F is the mass flux ($\text{kg m}^{-2} \text{s}^{-1}$), $\dot{q}_\kappa$ is source/sink term, $\kappa = 1, 2, \dots$, NK stands for mass components (water, air, H_2 , solutes, ...), and $\kappa = NK + 1$ is the heat component term.

The mass accumulation term can be represented as:

$$M_{x,\kappa} = \phi \sum (S_\beta \rho_\beta X_\beta^\kappa) \quad (1.25)$$

The total mass of component κ is obtained by summing over the fluid phases β (liquid, gas, NAPL). ϕ is porosity, S_β is the saturation of phase β , ρ_β is the density of phase β , and X_β^κ is the mass fraction of component κ present in phase β .

Similarly, the heat accumulation term in a multiphase system is given by:

$$M_x^{NK+1} = (1 - \phi) \rho_R C_R T + \phi \sum S_\beta \rho_\beta U_\beta \quad (1.26)$$

where ρ_R and C_R are respectively grain density (kg m^{-3}) and specific heat of the rock (J K^{-1}), T is temperature (K), and U_β is specific internal energy in phase β (J kg^{-1}).

Advective mass flux from equation (1.26), F^κ , is summed over individual phase fluxes, F_β , and is given by:

$$F^\kappa = \sum X_\beta^\kappa F_\beta \quad (1.27)$$

where individual phase fluxes can be calculated as:

$$F_\beta = \rho_\beta u_\beta \quad (1.28)$$

Here u_β is the Darcy velocity (m sec^{-1}) in phase β , given as:

$$u_\beta = -k_p \frac{k_{r\beta}}{\mu_\beta} (\nabla P_\beta - \rho_\beta g) \quad (1.29)$$

where $k_{r\beta}$ is the relative permeability for the phase β , μ_β is the viscosity of phase β ($\text{kg m}^{-1} \text{sec}^{-1}$), k_p is the absolute permeability (m^2), g is gravitational acceleration (m sec^{-2}), and,

$$P_\beta = P + P_{c\beta} \quad (1.30)$$

is the fluid pressure in the phase (Pa), which is the sum of the pressure in a reference phase, P , (usually the gas phase) and the capillary pressure, $P_{c\beta}$ (Pa), of the phase β .

Apart from the above mentioned physical laws, chemical reaction laws governing reactions of various species in the solution are also solved. To represent a geochemical system, a subset of aqueous species as is selected as a basis species (or primary species). All other species are called secondary species and can be written in terms of the basis species as:

$$c_i = K_i^{-1} \gamma_i^{-1} \prod (c_j^{\nu_{ij}} \gamma_j^{\nu_{ij}}) \quad (1.31)$$

where c_i is concentration of the i^{th} secondary specie (mol L⁻¹), c_j is concentration of the j^{th} basis species (mol L⁻¹), γ_i and γ_j are thermodynamic activity coefficients, v is the stoichiometric coefficient of the respective species and K_i is the equilibrium constant.

The diffusive transport of ionic species is governed using Fick's law:

$$\frac{\partial c_i}{\partial t} = -D\nabla^2 c_i \quad (1.32)$$

where D is the ion specific diffusion coefficient (m² sec⁻¹).

Calculations for mineral dissolution and precipitation are done by calculating the mineral saturation ratio, S_R :

$$S_{R_m} = K_m^{-1} \Pi (c_j^{v_{mj}} \gamma_j^{v_{mj}}) \quad (1.33)$$

where m is the equilibrium mineral index and K_m is the corresponding equilibrium constant. At equilibrium, we have:

$$SI_m = \log_{10} S_{R_m} = 0 \quad (1.34)$$

where SI_m is called the mineral saturation index.

The kinetics of mineral dissolution and precipitation are derived from Transition State Theory and incorporated by using the following rate expression (Lasaga, 2014):

$$r_n = \pm k_{t_n} A_n |1 - S_{R_n}^\theta|^\eta \quad (1.35)$$

where r_n is reaction rate (mol sec⁻¹), k_{t_n} is the rate constant (mol cm⁻² sec⁻¹), A_n is the specific reactive surface area per kg H₂O (cm² gm⁻¹). The positive values of r_n indicate dissolution while negative values indicate precipitation. The parameters θ and η are determined from experiments. But in lack of experimental values, they are usually taken equal to one. The temperature dependence of the reaction rate constant is expressed by Arrhenius equation (Lasaga, 1984; Steefel and Lasaga, 1994). The dependency of rate constant upon temperature and acidity is given as:

$$k_t = k_{t_{25}}^n \exp \left[\frac{-E_a^n}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{t_{25}}^a \exp \left[\frac{-E_a^a}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_H} + k_{t_{25}}^b \exp \left[\frac{-E_a^b}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{OH}^{n_{OH}} \quad (1.36)$$

where E_a^n , E_a^a and E_a^b are the activation energies (J mol⁻¹) in neutral, acidic and basic mediums, respectively; $k_{t_{25}}^n$, $k_{t_{25}}^a$ and $k_{t_{25}}^b$ are the rate constants (mol cm⁻² sec⁻¹) at 25°C in neutral, acidic and basic mediums, respectively; R_g is the universal gas constant (8.31 J mol⁻¹ K⁻¹); T is absolute temperature (K); a_H and a_{OH} are activities of H⁺ and OH⁻ ions; and n_H and n_{OH} are the respective reaction orders.

The above physical and chemical equations are solved over a spatially and temporally discretised domain. Discretization results in a set of strongly coupled nonlinear algebraic equations with the time-dependent primary thermodynamic variables of all grid blocks as unknowns. The continuum equations are discretized in

space using the integral finite difference method. Surface integrals are approximated as a discrete sum of averages over surface segments (Xu et al., 2004b).

Substituting the volume averaged quantities and surface integral approximations into the mass equation (1.24), a set of first-order ordinary differential equations in time is obtained as follows (Xu et al., 2004b):

$$\frac{\partial M_{x,n}^k}{\partial t} = \frac{1}{V_n} \sum A_{nm} F_{nm}^k + \dot{q}_n^k \quad (1.37)$$

The subscripts (nm) denote suitable averaging at the interface between grid blocks n and m. Time is discretised as a first order finite difference and the solution can be obtained using a range of iteration techniques such as the Newton-Raphson method. Time steps are typically automatically adjusted during a simulation run depending on the convergence rate of the iteration process. Automatic time step adjustment is essential for achieving a solution as the time scales may vary by many orders of magnitude during a simulation run (Xu et al., 2004b).

Porosity changes derived from the mineral volume changes as a result of mineral precipitation and dissolution and are calculated as follows (Xu et al., 2004b):

$$\Phi = 1 - \sum_1^{nm} (fr_m - fr_u) \quad (1.38)$$

where nm is the number of minerals, fr_m is the volume fraction of mineral m in the rock ($V_{\text{mineral}}/V_{\text{total}}$), and fr_u is the volume fraction of the nonreactive rock. Matrix permeability changes are calculated from porosity changes using the empirical relations between porosity, ϕ , and permeability, k_p (m^2), such as the simplified Carman Kozeny equation (Carman, 1937; Carman, 1956; Kozeny, 1927):

$$k_p = k_{p,i} \left[\frac{(1-\phi_i)}{(1-\phi)} \right]^2 \left[\frac{\phi}{\phi_i} \right]^3 \quad (1.39)$$

where $k_{p,i}$ (m^2) and ϕ_i are the initial permeability and porosity, respectively.

1.5. Research gaps and objectives

The thesis is aimed at understanding the impact of mm- to cm-scale lithological heterogeneity in the form of intraformational baffles on reservoir scale carbon capillary and mineral trapping capacities. The following research gaps have been identified:

- i. While regional scale heterogeneity is usually well constrained using wireline and seismic data, there is a lack of sufficient characterization of the reservoir-scale variability in cm-scale lithological heterogeneity. The characterization of sub-meter scale heterogeneity is typically done at core and outcrop scale. Such an approach might provide sufficient data to study the behaviour of local fluid flow and geochemical reactions. However, the approach might not be useful in quantifying the impact of intraformational baffles on carbon trapping capacities at reservoir scales where several local fluid flow and geochemical reactions are coupled.
- ii. There is no method for the direct integration of lithological heterogeneity at mm- to cm-scales in static reservoir models. This is primarily because the intraformational baffles exist below the resolution of

wireline logs. This results in neglect of intraformational baffles in static reservoir models. Consequently, the dynamic simulations might not accurately quantify carbon trapping capacities. Hence, it is important to develop a method to directly integrate the baffles in reservoir models.

- iii. There is a lack of an understanding and quantification of the factors governing CO₂ flow and mineral trapping at mm- to cm-scale. This is especially true for carbon mineral trapping as there are limited studies addressing the impact of baffles on geochemical reactions. Also, the studies often use simplified geochemical systems for qualitatively understanding the processes. However, the field observations suggest the presence of systems with complex mineralogy. It is important to quantify the processes and governing factors for the complete range of rock properties in order to derive accurate averaged rock properties.
- iv. Neglect of intraformational baffles in reservoir scale simulations might lead to an incorrect estimation of carbon mineral trapping capacities. The degree of error might be significant in highly heterogeneous reservoirs. There is a need to account for the error in mineral trapping capacities resulting from neglect of intraformational baffles in reservoir models.

The research gaps translate into the objectives of the thesis. The following four questions are addressed:

- i. How can the regional variability of mm- to cm-scale lithological heterogeneity be derived using the information from discrete local core samples?
- ii. How can the mm- to cm-scale lithological heterogeneity be directly integrated in static reservoir models?
- iii. What are the processes and factors controlling CO₂ flow and geochemical reactions at mm- to cm-scale?
- iv. What is the error in the estimation of reservoir scale carbon mineral trapping capacity if intraformational baffles are neglected?

1.6. Structure of the thesis

The thesis consists of 8 chapters. In the first chapter, the context of the research undertaken is introduced and the objectives are defined. A brief literature review is presented to describe the contemporary research and highlight the gaps. A mathematical description of the common analysis methods of fluid flow and geochemical reactions at mm- to cm-scale is also presented.

Chapter 2 introduces the study area on which the research is based. A description of regional geology in terms of the evolution of tectonic forces and depositional environments is also presented in order to understand the variability in rock properties.

Chapter 3 presents the characterization of intraformational baffles and reservoir rocks from the study area. The chapter addresses the first question of the thesis. Different characterization methods such as core sample analysis, QEMSCAN analysis, Hyperspectral core logging and wireline log analysis are presented. The existing data sets from the same site are also integrated along with the new rock properties derived in the chapter. The cm-scale lithological heterogeneity has been classified into five homogeneous rock type classes. The reservoir scale variability in the abundance and properties of rock types is determined.

Chapter 4 presents a workflow developed for the direct integration of intraformational baffles in reservoir models. The chapter addresses the second question of the thesis. The approach involves modification of homogeneous rock type classes derived in Chapter 3 by systematically combining them as a single lithological unit in the form of composite rock types. The properties of the composite rock types are derived by upscaling the respective properties of the constituent homogeneous rock types. Finally, a lithotype log of the composite rock types is determined and used to develop a high-resolution reservoir model where the intraformational baffles are integrated.

Chapter 5 addresses the impact of heterogeneity in lithological properties at cm-scale on CO₂ flow in cross bedded strata. The chapter explores the third question of the thesis with a focus on multiphase fluid flow and variation in CO₂ saturation during drainage. A range of realizations is developed to cover the heterogeneity in porosity, permeability, capillary entry pressure, relative permeability and capillary pressure. Multiphase flow simulations are run on the realizations and the turning point CO₂ saturation before migration into the baffle is calculated. The results are further used to determine the factors governing pre-imbibition CO₂ saturation distribution at cm-scale.

Chapter 6 addresses the impact of intraformational baffles on carbon mineral trapping. The chapter explores the third question of the thesis with a focus on carbon mineralization. Several realizations are built to cover the range of heterogeneity in mineralogy characteristic of the study area. Reactive transport simulations are run to determine the amount of carbon mineralized in each of the realizations. The results are used to develop an understanding of the impact of variation in mineralogy on the processes controlling carbon mineralization. The results from the fine scale dynamic simulations are averaged to integrate them with the properties of the composite rock types derived in Chapter 4.

Chapter 7 presents reservoir scale multiphase flow and reactive transport simulation results on the high-resolution reservoir model developed in Chapter 4. The chapter addresses the fourth question of the thesis. The model integrates the physical and chemical properties of intraformational baffles derived using upscaling relationships in Chapters 4, 5 and 6. The amount of capillary and mineral trapping capacities of the reservoir are determined. Results are compared with those derived using reactive transport simulations on a reservoir model where intraformational baffles are not accounted for. The comparison helps in quantifying the error associated with reservoir scale capillary and mineral trapping capacities if intraformational baffles are neglected.

Chapter 8 presents conclusions from the thesis and recommendations for future studies.

Chapter 2

Study area and regional geology

2.1. Introduction

The state of Victoria, in Australia generates about 85% of its electricity using brown coal (Gibson-Poole et al., 2006). Brown coal has high moisture content which makes it more emission intensive. In fact, power generation from brown coal combustion is the major contributor of Victorian carbon emissions (Minerals Council of Australia). This makes it important to look for geological carbon storage opportunities in Victoria. CO2CRC Limited is Australia's biggest carbon capture and storage (CCS) research organization that aims to demonstrate safe geological carbon storage at field scale in the Otway Basin, which forms the southern margin of Victoria.

The area of interest for the current study is the CO2CRC's Otway Research Facility site located onshore of the Port Campbell Embayment and lies approximately 300 km southwest of Melbourne in Victoria, Australia (Dance, 2013). The site is a part of the Otway Basin. The stratigraphic unit of interest lies between the depth of 1470-1570 m and is a part of the Paaratte Formation which is a sub-unit of the Otway Basin. The Formation has an average pressure gradient of 9.56 MPa/km and a temperature gradient of 20°C/km. Hence, it offers the favourable P-T conditions for supercritical CO₂ storage (Dance, 2013). Additionally, the project site is also characterised by favourable regional and local scale features for CO₂ trapping such as a low dipping faulted anticlinal structure, low permeability cap rocks and cm-scale lithological heterogeneity (Dance, 2013; Lawrence et al., 2013).

Since, cm-scale heterogeneity significantly affects carbon capillary and mineral trapping mechanisms, it is important to understand the nature of rock properties at the scale. The rock properties are in turn controlled by the facies deposited over time. Hence, it is important to look into the interplay between tectonics and sea level changes that shaped the Otway Basin as a whole. The following section explores the work previously done by other researchers regarding the same.

2.2. Basin location and dimensions

The Otway Basin is a rift-to-passive margin basin that extends from south eastern boundary of the state of South Australia to north western boundary of the state of Tasmania (Moore et al., 2000; Robson et al., 2016). In terms of lateral extent, the basin is about 500 km long with a surface area of about 150,000 km² (Geoscience Australia; Robson et al., 2016). Vertically, the basin is up to 8 km thick. About 80% of the basin lies offshore up to 3000 m depth (Robson et al., 2016; Moore et al., 2000; Stacey et al., 2013). The location of the basin is shown in Figure 2.1.

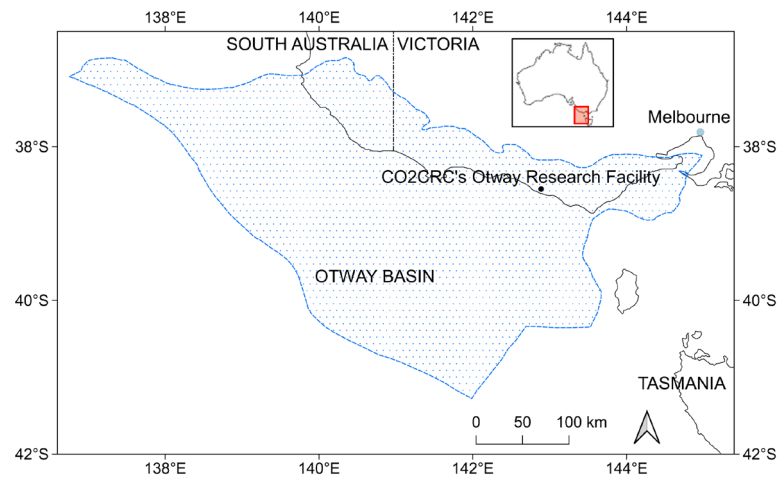


Figure 2.1. Location of the Otway Basin and the CO2CRC's Otway Research Facility (modified after Geoscience Australia).

2.3. Tectonic evolution and structural elements

The evolution of the Otway Basin started in Tithonian-Barremian being coincident with the first of the two rift events associated with the breakup of Australia and Antarctica (Holford et al., 2011; Krassay et al., 2004; Moore et al., 2000; Norvick, 2005; Robson et al., 2016; Willcox and Stagg, 1990). The first rift event led to north-south extension thereby resulting in the formation of a series of east-west to northeast-southwest striking faults (Finlayson et al., 1996; Krassay et al., 2004; Morton et al., 1994; Perincek and Cockshell, 1995). The tectonic extension resulted in the formation of 13 half grabens: Penola, Tantanoola, Mocamboro, Digby, Tahara, Ardonachie, Morenda, Windermere, Koroit, Elingamite, Ross Creek, Gellibrand and Ombersely troughs; and, five structural highs: the Kalangadoo, Lake Condah, Branxholme, Stoneyford and Moorlie. Most of these half grabens are oriented northwest-southeast (Woollands and Wong, 2001).

The first rift event was followed by regional sag owing to thermal subsidence during Aptian to Albian after which the region experienced uplift, compression and inversion during mid-Cretaceous (Geoscience Australia).

The second rift event soon followed during the Turonian-Maastrichtian. This phase was characterized by northeast-southwest extension and resulted in the formation of east-west to northwest-southeast oriented faults. Also during this phase, the western end of the Otway Basin opened up to the sea. Contrary to the formation of several half grabens during Late Jurassic-Early Cretaceous, rifting in the Late Cretaceous basin structure is dominated by a single structural element, the Voluta Trough (Woollands and Wong, 2001).

The separation between Australia and Antarctica gradually initiated at the end of the second rifting event. This resulted in a 67 Ma break-up unconformity. The continental separation triggered passive margin subsidence. Post middle Eocene, the spreading rate suddenly increased which in turn enhanced the subsidence (Cande and Mutter, 1982; Robson et al., 2016). The rapid basin subsidence was quickly followed by another major transgression event which truncated the sediment supply (Woollands and Wong, 2001). The transgression event was accompanied by further thermal subsidence as well as gradual compression (Geoscience Australia).

The Late Cretaceous-Tertiary events after the second rifting lead to the formation of structural elements that can be divided into three groups on the basis of age. The first group comprises of the Otway Ranges, Barongarook High, Barrabool Hills and Bellarine High that formed under northwest-southeast compressional regime during Late Miocene-Pliocene. This group is located in the eastern Otway Basin. The second group comprises of the Merino Uplift and the Dartmoor Ridge and is located in the central Otway Basin. The third group comprises of the early Tertiary structures namely the Colac sub-basin, Torquay sub-basin, Portland Trough, Northern Platform and Bridgewater High (Woollands and Wong, 2001).

2.4. Stratigraphy

The stratigraphy of the Otway Basin ranges from Late Jurassic to Tertiary and consists of five groups (oldest to youngest)- Otway, Sherbrook, Wangerrip, Nirranda and Heytesbury (Table 2.1). Three major unconformities have been identified between the groups- the Otway and the Sherbrook groups being separated by an unconformity between Early and Late Cretaceous; the Sherbrook and the Wangerrip groups being separated by the 67 Ma break-up unconformity between late Cretaceous and Paleocene; and Nirranda and Heytesbury groups being separated by an unconformity between Eocene and Oligocene (Woollands and Wong, 2001).

The groups are further subdivided into formations. The Otway Group was deposited during Early Jurassic-Late Cretaceous and consists of (oldest to youngest) the Casterton, Pretty Hill, Laira and Eumeralla formations (Parker, 1995; Ryan et al., 1995). The Pretty Hill and the Laira formations together form the Crayfish Subgroup (Woollands and Wong, 2001). The Casterton Formation represents the pre-rift or an early syn-rift sequence while the Crayfish Group is the early syn-rift sequence (Morton et al., 1994). These two units were deposited in the accommodation space created within the series of half grabens formed during the first rift event (Finlayson et al., 1996; Krassay et al., 2004; Morton et al., 1994; Perincek and Cockshell, 1995; Robson et al., 2016) while the Eumeralla Formation was deposited in early Aptian during the post rift subsidence that followed the first rift event (Hill and Durrand, 1993; Krassay et al., 2004).

Deposited during Campanian-Maastrichtian, the Sherbrook Group followed the Eumeralla Formation. This period was marked by a decrease in faulting as compared to the Turonian-Santonian (Robson et al., 2016). The Sherbrook Group consists of 7 formations (oldest to youngest)- Waarre, Flaxman, Belfast, Nullawarre, Skull Creek, Paaratte and Timboon (Woollands and Wong, 2001).

Unconformably overlying the Sherbrook Group is the Wangerrip Group which was deposited during the period of slow spreading following the 67 Ma break-up unconformity during late Maastrichtian to middle Eocene. The Wangerrip Group consists of (oldest to youngest)- K/T Shale, Pebble point, Pember Mudstone and Dilwyn formations. These formations were deposited during thermal subsidence that followed the break-up unconformity (Woollands and Wong, 2001).

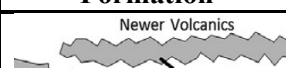
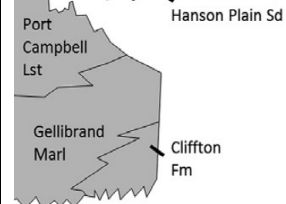
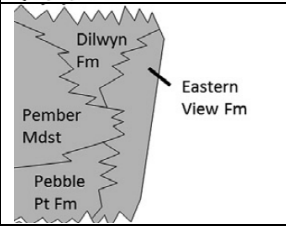
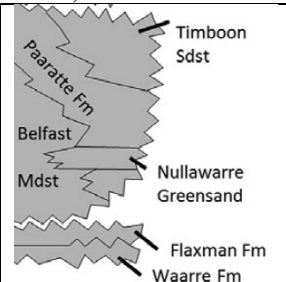
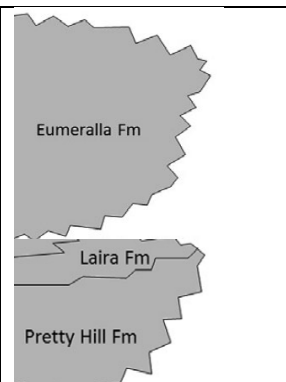
TIME UNITS		TECTONIC HISTORY	SEA LEVEL CYCLE	STRATIGRAPHIC UNITS	
Period	Epoch			Group	Formation
Quaternary	Holocene	Undifferentiated	----	----	
Neogene	Miocene	Subsidence	Sixth	Heytesbury	
Paleogene	Oligocene				
	Eocene	Unconformity			
		Local inversion	Fifth	Nirranda	
	Fourth				
	Paleocene	Thermal subsidence	Third	Wangerrip	
Cretaceous	Late	Unconformity (Continental separation)			
		Second rift event	Second	Sherbrook	
			First		
	Early	Unconformity (Mid Cretaceous uplift event)			
		Regional sag (Thermal subsidence)	Non marine deposition	Otway	
First rift event					
Jurassic	Late				

Table 2.1. Stratigraphy of the Otway Basin along with the tectonic history and sea level changes (modified after Robson et al., 2016; Woollands and Wong, 2001).

The transgression event at the end of middle Eocene lead to the formation of Nirranda and Heytesbury groups. The Nirranda Group was deposited during the tectonic phase of local inversion (Woollands and Wong, 2001). On the other hand, the Heytesbury Group was formed during the tectonic phase of subsidence with

periodic inversion and uplift (Bailey et al., 2014; Holford et al., 2011). The Nirranda Group consists of two formations (oldest to youngest)- the Mepunga and the Narrawaturk while the Heytesbury Group comprises of 3 formations (oldest to youngest)- Clifton, Gellibrand and Port Campbell. Overlying the Heytesbury Group are the undifferentiated Quaternary formations- Hanson (older) and Narracoorte (younger) (Woollands and Wong, 2001).

2.5. Depositional environments and facies

The depositional environment evolution of the Otway Basin is strongly controlled by the changes in tectonics and sea level. Six cycles of sea level changes have been identified in the basin between Late Cretaceous and Quaternary (Table 2.1) (Woollands and Wong, 2001).

The deposition of the Otway group precedes the first cycle of sea level change and is controlled by tectonics. The base of the Otway Group, the Casterton Formation, was deposited in a volcanic setting which evolved to a mixed lacustrine to swamp environment towards its top. The setting controlled the lithology of the Casterton Formation which consists of interbedded carbonaceous shale with basalts and minor sandstone (Morton et al., 1994). The Pretty Hill Formation was deposited in a braided fluvial setting and consists of basal sandstones overlain by carbonaceous shale (Woollands and Wong, 2001). The sedimentary environment consists of proximal alluvial fans and braided streams (Reynolds, 1971). The Laira Formation was deposited in mixed fluvial to shallow lacustrine settings and comprises of an interbedded sequence of mudstone and siltstone. The Eumeralla Formation was also deposited in mixed fluvial to shallow lacustrine environments and comprises of a sequence of interbedded volcanoclastic sandstone, mudstone and coal (Woollands and Wong, 2001).

The effect of sea level change started dominating the lithology with the commencement of the Sherbrook Group. The group witnessed two cycles of sea level changes with the Waarre, Flaxman, Belfast and Nullawarre formations depositing during the first cycle while the Skull Creek, Paaratte and Timboon formations depositing during the second cycle of sea level change (Woollands and Wong, 2001). The depositional environment in the Waarre Formation corresponded to the lowstand system tract conditions and was characterised by marginal marine setting at the base to tidal plain setting towards the top. The lithology of the Waarre Formation consists of siltstone and interbedded calcareous sandstone at the base to coarse grained sandstone at the top (Woollands and Wong, 2001). The Flaxman Formation represents the first transgressive marine horizon (Boyd and Gallagher, 2001; Buffin, 1989) and was deposited under a marginal marine environment corresponding to the transgressive system tract conditions. The lithology consists of mudstone, siltstone and sandstone (Woollands and Wong, 2001). The Belfast Formation overlies the Flaxman Formation and was deposited under a prodeltaic environment corresponding to the transgressive system tract conditions (Woollands and Wong, 2001). Lithologically, the Belfast Formation is comprised of pale grey to black pyritic silty mudstones (Hawkins and Dellenbach, 1971). The Belfast Mudstone passes inshore into regressive non-marine, fluvio-deltaic sequences- Nullawarre Greensand, the Paaratte Formation and the Timboon Sandstone Member (Morton, 1990). The Nullawarre Formation was deposited under mid to outer shelf environment under the highstand system tract conditions and is composed of sandstone. The Skull Creek Formation was deposited under prodeltaic environment corresponding to the transgressive system tract conditions. It is composed of black silty mudstone.

The Skull Creek Formation is overlain by the Paaratte Formation which was deposited under lower delta plain environment under highstand system tract conditions. Lithologically, the Paaratte Formation is comprised of sandstone and shale. The Timboon Formation is the topmost unit of the Sherbrook unit and was deposited under upper deltaic plain environment corresponding to the highstand system tract position of the second cycle of sea level change. It is composed of sandstone and minor micaceous silty mudstone (Woollands and Wong, 2001).

The Wangerrip Group consists of transgressive-regressive units (Morton et al., 1994). The formations of the Wangerrip Group were deposited during the third cycle of sea level change where the Pebble Point Formation corresponds to lowstand system tract, the Pember Mudstone Formation corresponds to transgressive system tract and the Dilwyn Formation corresponds to the highstand system tract positions. The K/T shale is interpreted as a flooding surface associated with the break-up of the Australia-Antartica plates (Woollands and Wong, 2001). The Pebble Point Formation was deposited in low energy marginal marine conditions and is comprised of sandstone and carbonaceous sandy claystone (Morgan, 1985; Morton et al., 1994; White, 1995). The Pember Mudstone Formation was deposited in prodeltaic conditions and is comprised of silty mudstone. The Dilwyn Formation was deposited in shallow marine conditions and is comprised of sandstone and mudstone (Woollands and Wong, 2001).

The Nirranda Group developed in open marine conditions resulting in mixed carbonates and siliciclastic sedimentation (Krassay et al., 2004; O'Brien and Thomas, 2007). The Mepunga Formation was deposited during the fourth cycle of sea level change in a beach barrier to estuarine setting while the Narrawaturk Formation was deposited during the fifth cycle of sea level change in an outer to mid-shelf environment. Both the formations consist of non-marine to outer shelf sand, silt, marl and calcareous mudstone (Woollands and Wong, 2001).

The Heytesbury Formation was deposited during the sixth cycle of sea level change. The Clifton Formation corresponds to lowstand system tract position and was deposited in an inner to mid-shelf setting. The Gellibrand Formation corresponds to transgressive system tract position of the sea level change and was deposited in an outer shelf environment. The Port Campbell Formation corresponds to the highstand system tract position and was deposited in a mid-shelf setting. All the formations are composed of open marine carbonate sequences (Woollands and Wong, 2001).

The Quaternary formations Hanson and Narracoorte are tectonically undifferentiated. The Hanson formation is comprised of recent volcanics while the Narracoorte formation is comprised of limestones (Woollands and Wong, 2001).

Chapter 3

High resolution characterization of lithological heterogeneity of the Paaratte Formation, Otway Basin (Australia), a coastal to shallow-marine deposit

3.1. Introduction

Flow and reactive transport modelling have evolved to be an effective tool to reconstruct and predict the fluid flow and chemical evolution of a system (Steefel et al., 2005). To achieve meaningful results from such modelling studies, it is important to replicate realistic fluid flow paths in simulations. This is usually achieved by constructing static models and then using them as a basis in flow and reactive transport simulations. Various regional structural features are implemented in geostatic models followed by the population of flow and petrophysical properties using wireline and seismic data (Doyen, 2007; Ringrose and Bentley, 2015). Such geostatic models often have dimensions of the order of kilometres. To computationally manage multiphase and coupled reactive transport simulation runs on such large scale, grid blocks with a vertical resolution of meters and a lateral resolution of tens of meters are implemented. While the use of geostatic models is helpful in replicating fluid flow paths based on field data, the limitation posed by large grid dimension persists. To further improve the results, it is important to implement sub-meter scale lithological heterogeneities in geostatic models (Gershenzon et al., 2017; Trevisan et al., 2017). Such high resolution lithological heterogeneity exists in the form of intercalated layers of fine and coarse sediments, cemented intervals and sedimentary structures such as cross, planar and massive bedding (Miall, 2016). Any layers composed of low porosity-low permeability rock types are known as intraformational baffles, which occur within high porosity-high permeability reservoir rock (Ennis-King et al., 2005). Intraformational baffles can significantly affect fluid flow pathways as well as fluid-rock reactions due to their low porosity, low permeability, higher capillary entry pressures and relatively abundant reactive minerals such as clays (Ennis-King et al., 2005; Liang et al., 2018; Ringrose et al., 1993; Yang et al., 2014). The proportion of baffles in the reservoir can significantly alter the results from dynamic simulations (Flett et al., 2007). Hence, it is critical to incorporate the properties of intraformational baffles in reservoir scale models in order to improve simulation results. This is not directly possible as the incorporation of intraformational baffles in reservoir scale models requires sub-metre scale grid sizes and, thereby, increases computational limitations. One possible way to accomplish this task is to study the processes at sub-metre scales and then upscale flow (Mikes et al., 2006) and geochemical (Wen and Li, 2017) responses in larger scale models. This allows lithological heterogeneity at sub-metre scale to be incorporated in reservoir scale models and should significantly improve the prediction of fluid plume migration and associated geochemical reactions.

The first important step towards implementing this approach is to define rock types based on lithological properties which are subsequently used to populate the geostatic models. The present study addresses this by

developing a database of high resolution lithological properties in terms of rock type classes. Rock properties are analyzed on samples from the Paaratte Formation at the CO2CRC's Otway Research Facility site, which is a test and demonstration site for geological CO₂ storage in the state of Victoria, Australia (CO2CRC Limited). The Paaratte Formation is a sedimentary unit consisting of three units, the lowermost of which comprises three parasequences (Boyd and Gallagher, 2001; Dance et al., 2012). Lithological properties have been analysed for the lower two parasequences of the deepest unit (Unit A), which spans over approximately 100 meters in thickness. The two parasequences of interest are composed of four depositional facies: distributary channel, proximal mouthbar, distal mouthbar and delta front (Dance et al., 2012). Each of these facies is known to consist of lithological heterogeneity vertically at sub-meter scale (Geary et al., 2001; Geary and Reid, 1998; Lawrence et al., 2013). Rock properties used in this study to characterize the rock types are: porosity, permeability, capillary entry pressure, mineral composition and grain size distribution.

Porosity, permeability and capillary entry pressure have been measured on discrete cores and wireline logs and the data is published for the two wells in the study area, CRC-2 and CRC-3 (Dance, 2018; Daniel, 2012; Daniel et al., 2012; Lawrence et al., 2013). Continuous semi-quantitative mineral composition was measured on 104-meters of core from CRC-3 using hyperspectral core logging as part of the current study. Quantitative mineral composition and mineral specific grain sizes were also analysed on 30 discrete samples from CRC-3 using QEMSCAN analysis.

The aforementioned properties have been used to define five distinct rock type classes: coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone. The classification of rock type classes is geologically reasonable as it is based on the relationship of lithological properties and depositional environments in the Paaratte parasequences.

The rock type classes need to be spatially mapped in order to support dynamic simulations. For this purpose, a continuous depth log of the five rock type classes is derived for the wells CRC-2 and CRC-3 followed by their cross correlation to deduce the vertical and lateral continuity of rock types between the two wells.

The rock type classes within the two coastal to shallow-marine parasequences provide new insight into sub-seismic lithological heterogeneity and will support dynamic simulations accounting for sub-metre scale heterogeneity in multiphase flow and reactive transport simulations.

3.2. Study area overview and geological setting

3.2.1. Study area overview

The CO2CRC's Otway Research Facility site is located onshore of the Otway Basin. It is approximately 300 km southwest of Melbourne in Victoria, between the coastal towns of Port Campbell to the east, and Warrnambool to the west (Figure 3.1) (Dance, 2013). The choice of the study area was determined by two factors. Firstly, the Paaratte Formation at the site contains abundant lithological heterogeneity (Geary et al., 2001; Geary and Reid, 1998; Lawrence et al., 2013) at sub-metre scale, and second, relevant field data on small scale lithological heterogeneity was made available through CO2CRC Limited.

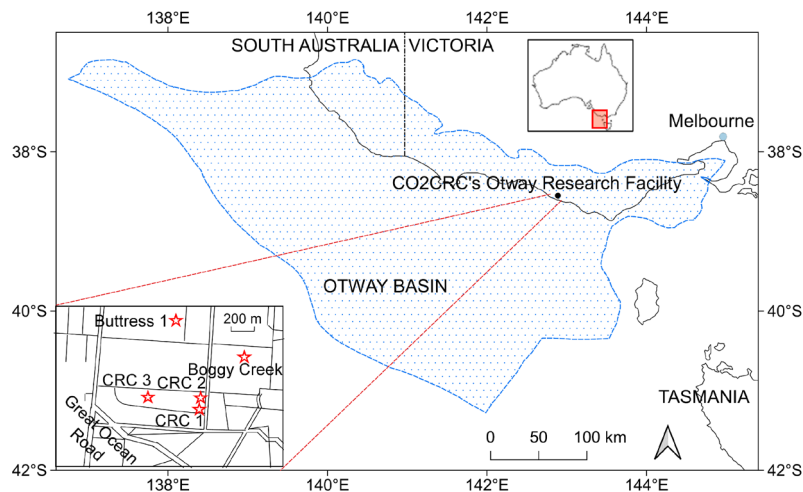


Figure 3.1. Location of the CO2CRC's Otway Research Facility, Otway Basin (modified after Geoscience Australia and CO2CRC Limited).

While several wells exist at or nearby the CO2CRC's Otway Research Facility, the current study focuses on data from the wells CRC-2 (38° 31' 50.06" S, 142° 48' 41.45" E) and CRC-3 (38° 31' 42.3" S, 142° 48' 17.8" E) (Combinable Magnetic Resonance Report; Lawrence et al., 2013), because of the abundance and type of data available. The wireline and core data from both the wells have been characterized very well (Dance, 2018; Daniel, 2012; Daniel et al., 2012; Lawrence et al., 2013). The two wells are located about 630 metres apart.

3.2.2. Basin location and evolution

The Otway Basin, which is a rift-to-passive margin basin that extends from the southeastern boundary of South Australia to the northwestern boundary of Tasmania (Dance, 2013; Moore et al., 2000). The basin is about 500 km long. It covers a surface area of 150,000 km² and is up to 8 km thick. The majority of the basin (~120,000 km²) lies offshore up to 3000 m below sea surface (Dance, 2013; Exxon and Lee, 1987; Miyazaki et al., 1990; Moore et al., 2000; Robertson et al., 1978; Stacey et al., 2013).

An interplay of tectonic forces and sea level change shaped the present-day Otway Basin. The basin evolution began in Tithonian-Barremian stages with the first of the two rift events associated with the breakup of Australia and Antarctica (Dance, 2013; Holford et al., 2011; Krassay et al., 2004; Moore et al., 2000; Norvick, 2005; Willcox and Stagg, 1990). The first rifting event led to thermal subsidence and regional sag during the Aptian to Albian stages (Geoscience Australia), while the second rifting event was followed by passive margin subsidence (Cande and Mutter, 1982; Dance, 2013).

The variation in tectonic forces over time led to a total of six major cycles of sea level change in the Otway Basin between Late Cretaceous and Quaternary. This resulted in the formation of five Groups in the Basin (oldest to youngest): Otway, Sherbrook, Wangerrip, Nirranda and Heytesbury (Woollands and Wong, 2001). The lowermost Otway Group precedes the first cycle of sea level change and the deposition was controlled by tectonic activity. The depositional environments of the Otway Group varied from volcanoclastic at the base to fluvial and shallow lacustrine at the top. The sediments deposited range from interbedded carbonaceous shale and basalts to interbedded volcanoclastic sandstone, mudstone and coal (Morton et al., 1994; Woollands and

Wong, 2001). The effect of sea level change dominated the lithology with the commencement of the Sherbrook Group where the depositional environment varied from marginal marine within a low stand system tract at the base to upper deltaic plain environment within a high stand system tract at the top (Boyd and Gallagher, 2001; Buffin, 1989; Woollands and Wong, 2001). The sediments deposited include shale, black pyritic mudstone, siltstone, interbedded calcareous sandstone and coarse grained sandstone (Hawkins and Dellenbach, 1971; Woollands and Wong, 2001). The Wangerrip Group consists of transgressive-regressive units (Morton et al., 1994) deposited under conditions varying from low energy marginal marine at the base to shallow-marine at the top. The sediments deposited include carbonaceous claystone, mudstone and sandstone (Morgan, 1985; Morton, 1990; White, 1995; Woollands and Wong, 2001). The Nirranda Group developed in open marine conditions resulting in mixed carbonates and siliciclastic sedimentation (Krassay et al., 2004; O'Brien and Thomas, 2007), while the Heytesbury Group deposited during the sixth cycle of sea level change with a depositional environment varying from inner shelf at the base to mid-shelf at the top. The Heytesbury Group is composed of open marine carbonate sequences (Woollands and Wong, 2001).

3.2.3. The Paaratte Formation

For the current study, the stratigraphic interval of interest at the CO2CRC's Otway Research Facility site lies between the depth of 1461–1565 m in the CRC-3 well and is a part of the Paaratte Formation belonging to the Sherbrook Group. The formation occurs between depths of 1120–1570m with the depositional environment being lower delta plain belonging to a highstand system tract (Boyd and Gallagher, 2001; Dance et al., 2012). Lithologically, the Paaratte Formation is comprised of sandstone, siltstone and mudstone with carbonated intervals (Geary et al., 2001; Geary and Reid, 1998; Woollands and Wong, 2001). The cemented intervals are believed to have formed from ion rich meteoric fluids, flowing through the high permeability zones in the formation (Bunch, 2019).

Structurally, the Paaratte Formation is a low dipping faulted anticline with dips ranging between 2°–5° towards the north (Dance et al., 2012). The formation comprises three member units, Unit A, Unit B and Unit C. Unit A (lowermost) comprises three fourth order parasequences with Parasequence-1 at the bottom and Parasequence-3 at the top (Dance, 2018). The current study focuses on Parasequence-1 and -2. Wireline data and core samples belonging to the two parasequences from wells CRC-2 and CRC-3 have been published previously (Daniel, 2012; Daniel et al., 2012; Lawrence et al., 2013) and the data interpreted for sedimentary facies (Figure 3.2). The available wireline data used in the current study includes neutron porosity, apparent matrix density and gamma ray logs. The interpreted sedimentary facies have also been used, and comprise delta front, distal mouthbar, proximal mouthbar and distributary channel facies (Boyd and Gallagher, 2001; Dance et al., 2012; Lawrence et al., 2013). The delta front facies forms the bottommost facies in each of the two Parasequences and is overlain by distal mouthbar, proximal mouthbar and distributary channel facies.

The above-mentioned facies characterization and the previously published flow properties form the foundation of the work presented in this paper.

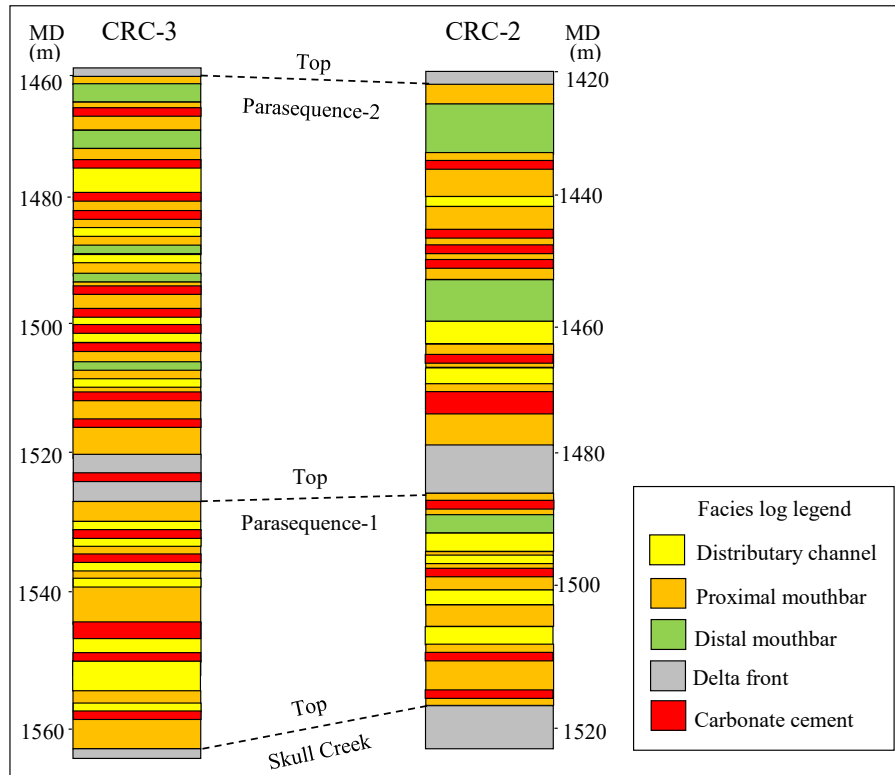


Figure 3.2. Representative facies logs against measured depth (MD) for wells CRC-3 and CRC-2. The four facies are: delta front, distal mouthbar, proximal mouthbar and distributary channel. The facies marked in red correspond to cemented zones (Tess Dance, personal communication; Dance, 2018; Lawrence et al., 2013).

3.3. Methodology

3.3.1. Core sampling and analysis

Cores of 100 metre length from the wells CRC-2 and CRC-3 were inspected visually and lithological variations described. Lithological heterogeneity was found to be abundant at sub-metre scales in the form of sedimentary structures. Broadly, three major types of sedimentary structures were identified: cross-bedding, planar bedding and massive bedding (Figure 3.3). The visual observation of grain sizes in the cores indicated the presence of three broad categories of lithological units: coarse grained, fine grained and cemented. Cross-bedding structures were characteristic of distributary channel facies and were dominated by coarse grained matrix and laminae of fine grained rock types. Core sections characterized by planar bedding were dominated by two different fine grained lithological units and were characteristic of the transition zone between the high energy facies such as distributary channel and proximal mouthbar and the low energy facies such as distal mouthbar and delta front. Massive bedding was typically tightly cemented and was characteristic of carbonate-cemented facies intervals. A visual grain size inspection was carried out in conjunction with the existing porosity and permeability data in order to select 30 representative samples for analysis such that they covered lithological units from all the observed grain sizes. The chosen core samples are described in Appendix A.

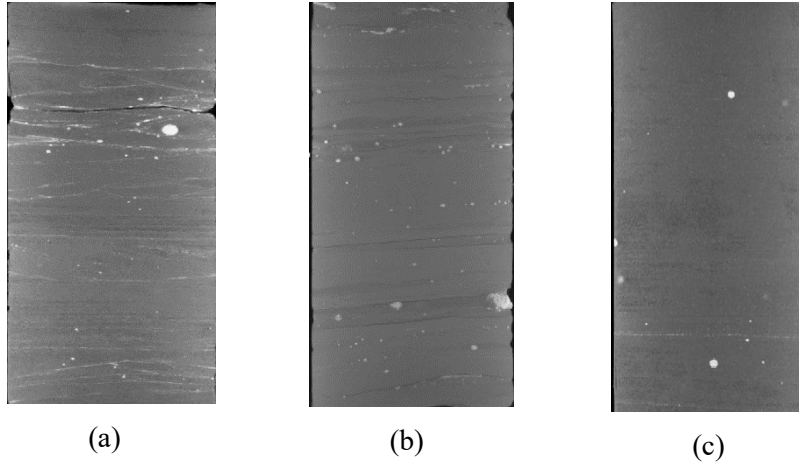


Figure 3.3. X-ray images showing the major sedimentary structures observed in the cores between 1535 and 1538 m from CRC-3 well at the CO2CRC's Otway Research Facility (Knackstedt et al., 2018). (a) Cross-bedding; (b) Planar bedding; (c) Massive bedding. Thin laminae of fine grained rock type (light gray) can be identified between more coarse grained rock type (dark gray) in cross beddings (a). The planar bedding (b) consists of a bimodal distribution of finer grain sizes (dark and light gray). The massive bedding (c) is tightly cemented and structureless. Each image measures 25 cm (vertical) and 10 cm (horizontal).

3.3.1.1. Porosity, permeability and capillary entry pressure analysis

Porosity and permeability data used in this study were published elsewhere (Dance, 2018; Lawrence et al., 2013) and were analysed here in terms of their abundances in different facies. Frequency plots were constructed for the two properties for each of the four facies where number of data values were 30, 105, 9 and 30 for distributary channel, proximal mouthbar, distal mouthbar and delta front facies, respectively, from the entire Paaratte Formation. Out of these, 82 data values belong to the two parasequences of interest (Appendix B, Table B2). The frequency plots provide insights into the distribution of porosity and permeability within each depositional facies which in turn, is genetically related to changes in energy in varying depositional environments and potential diagenetic cementation. Published MICP data has been used to derive the equivalent height of a CO₂ column that the given sample can hold before CO₂ enters the sample (Daniel, 2012; Daniel et al., 2012). Under this condition, the capillary entry pressure (P_e) becomes equal to the buoyancy pressure (P_{bu}), which can be expressed in terms of CO₂ column height (Equation 3.1) (Kaldi et al., 2011).

$$P_e = P_{bu} = 0.433\Delta\rho h_{FWL} \quad (3.1)$$

where $\Delta\rho$ is the density difference between brine and supercritical CO₂, h_{FWL} is the height of CO₂ above free water level (FWL) and 0.433 is the pressure gradient in psi/ft.

The sample specific values of entry pressures have been used to determine the broad range of entry pressures for each rock type class.

3.3.1.2. Quantitative mineral composition analysis

Quantitative Evaluation of Minerals by Scanning Electron Microscopy is referred to as QEMSCAN and is an automated technique that combines SEM and energy dispersive X-ray spectroscopy analysis and produces a high resolution 2D mineral map of a polished rock surface. The technique is used to quantify the mineral composition in terms of the area occupied by the minerals (Ayling et al., 2012; Higgs et al., 2015). The results from QEMSCAN analysis are used to distinguish rock type classes based on their mineral content. The analysis was done on a sample area of 1cm² where each pixel on the mineral map corresponds to a length of 5.93 µm.

The QEMSCAN analysis was done on 30 thin sections prepared on samples from the CRC-3 core (Section 3.3.1, Appendix A). The proportion of major minerals in the four facies is evaluated using the QEMSCAN results corresponding to samples from each facies. As the samples are chosen from all four facies, it is possible to obtain an average value of the volume fraction of different minerals for each facies along with an estimate of their respective deviations.

3.3.1.3. Mineral specific and total grain size analysis

The 2D mineral maps derived by QEMSCAN were further used to determine the spectrum of equivalent grain diameter for each mineral. The grain size analysis was conducted using the Avizo software package (Thermo Scientific™). Backscattered electron images and QEMSCAN mineral maps were imported into Avizo with a resolution of 6 micrometers and converted to their RGB components to help distinguish segmented mineral phases. Specific values of RGB were then used to separately segment the area occupied. A threshold of 0.1% was applied as the minimum segmented area of each mineral. The Separate Objects algorithm in Avizo was used to create artificial grain boundaries for separating the grains which were too close. The artificial grain boundaries were validated using the backscattered electron image. The grain boundaries were manually adjusted where a mismatch was observed from the backscattered electron image. The number of pixels segmented to each mineral were used to calculate their respective area fractions using the Volume Fraction algorithm in Avizo. The size of separated grains was determined using the Label Analysis algorithm in Avizo and the EqDiameter (EqD) measure, which determines the equivalent circular diameter of a grain based on the segmented area (SA) it occupies (Equation 3.2).

$$EqD = \sqrt{\frac{4 \times SA}{\pi}} \quad (3.2)$$

Mineral specific grain size distributions were produced for each sample by binning the area fraction occupied by mineral grains within specific limits of EqD (Equation 3.2). The modal grain sizes for different samples are then used to determine a facies specific grain size distribution.

3.3.1.4. Hyperspectral core logging

Hyperspectral core logging is a method used to derive a continuous log of semi-quantitative mineral composition in cores. The system used here is referred to as Hylogger™. It is a non-invasive, non-destructive method and measures the reflectances in the Visible-Near InfraRed (VNIR), Short-Wave InfraRed (SWIR), and Thermal InfraRed (TIR) wavelengths (Higgs et al., 2015; Schodlok et al., 2016). The reflectances are then

analyzed in The Spectral Geologist™ (TSG) which is a software platform for interpreting the mineral reflectance (Huntington et al., 2010). It is based on the optimization of fitting individual mineral spectra to a measured spectra from a rock sample. Consequently, it is possible to estimate the most dominant minerals at cm scale resolution. These algorithms are built on a library of approximately 500 end member reflectance spectra for commonly occurring minerals (Higgs et al., 2015).

Previous validation work of TIR data suggests a successful correlation with other sample analysis methods like X-ray diffraction (XRD), X-ray fluorescence (XRF) and microprobe data (Cudahy et al., 2009; Haese et al., 2019). The main limitation of hyperspectral logging data is that it only provides counts for the identified minerals and that the technique does not pick up minerals occurring in trace amounts (Higgs et al., 2015).

Hyperspectral core logging was performed on the 104-meter section of the core from the CRC-3 well covering Parasequence-1 and -2 and TIR data were used for further analysis of geologically realistic minerals. The hyperspectral logging resulted in depth continuous measurement of mineral counts at a resolution of 4 cm. The data has then been binned into depth intervals of 20 cm, thus averaging five mineral count values in this interval. The counts are converted into mineral proportions, which were then grouped into three end member mineral classes characteristic of siliciclastic reservoirs (Haese et al., 2019). The mineral classes are: framework minerals (quartz and feldspar), clay minerals (mica, kaolinite, smectite, chlorite) and carbonate minerals (calcite and dolomite). The minerals detected in trace amounts have not been assigned to any end member mineral class. These mineral proportions were accounted for when the rock type classification was developed.

3.3.2. Wireline logging and data analysis

3.3.2.1. Available wireline log data analysis

Neutron porosity, apparent matrix density and gamma ray wireline logs from CRC-2 and CRC-3 (Dance, 2018) were used in this study. The wireline logs express porosity, density and clay abundance and have been used to derive rock type classes at 15 cm resolution (Section 3.3.2.2). Additionally, this study makes use of the Elemental Capture Spectroscopy (ECS) log for CRC-3 (Tess Dance, personal communication). The ECS is a technique developed by Schlumberger which provides relative abundance of common elements such as silicon, iron, calcium, sulphur etc. based on the principles of pulsed neutron spectroscopy (Schlumberger). The data from the ECS log is used to further cross validate mineral abundance derived from other methods presented in this study.

3.3.2.2. Deriving lithotype logs

Three wireline log data sets (apparent matrix density, neutron porosity and gamma ray) were combined to derive lithotype logs using the Kimeleon software (Collins and Doveton, 1986; Kansas Geological Survey).

Kimeleon improves on the differentiation and identification of lithologies by integrating more than one log; thus, avoiding a bias caused by fluid volume that is associated with single porosity readings. Relative dispositions of the three input logs are reliably indicative of the mineralogy and by extension of the rock type, which is reflected in the color gradient pictured by lithotype log (Collins and Doveton, 1986).

The apparent matrix density log is implemented as the red channel, neutron porosity log is implemented as the green channel and gamma ray log is implemented as the blue channel. The three logs are then combined to produce a composite representative colour known as the colourlith. The combination of magnitudes from of apparent matrix density, neutron porosity and gamma ray from wireline data for each depth is unique. The information of individual log curves is transferred and preserved in the colourlith where variation in hue reflects the magnitude of the combined logs.

The lithotype analysis was undertaken for Parasequences-1 and -2 between the depths of 1461 and 1565 m in CRC-3 and between 1422 and 1518 m in CRC-2. Wireline log LAS files were corrected for variations in distances between individual measurements and for duplicate measurements before importing them into Kimeleon. The three false color representations were combined in an in-built model within Kimeleon known as the Rhomaa-NPHI model. The model estimates absolute density by combining apparent density and neutron porosity and integrates this information with gamma ray values to result in the colourlith log. The advantage of using the Rhomaa-NPHI model is that it is known to perform well in discriminating between shale, carbonate-rich rock (dolomite and limestone) and sandstones (Collins and Doveton, 1986). Kimeleon allows limit manipulation for each of the properties, which can enhance or diminish the detail as more extreme magnitudes are being included or excluded. This is reflected in the recognition of more subtle differences between rock properties and thus increased or decreased color variety. Some limit adjustments were required to enhance the difference between siltstone and mudstone and thus the color coding is different from Kimeleon's default.

To confirm the results, the colourlith log derived for CRC-3 was compared to the mineral composition derived by ECS. Even though these outputs are not strictly independent as they are both based on the same dataset, the colourlith and the ECS logs are based on different techniques.

The colourlith log was analyzed for the differences in hues which are then interpreted as specific rock types. CRC-3 served as the primary rock record as it provided the most abundant data (hyperspectral core log, wireline log, sample analysis). Hence, based on the similarity in the colourlith logs of the two wells, the CRC-2 colourlith is assigned rock types equivalent to those in CRC-3. The vertical resolution of the rock record is 10 cm due to the in-built limitations of Kimeleon. The output results in the vertical extent of each rock type class in the two wells in the form of rock type logs. The patterns in the two rock type logs were then used to deduce the lateral extent of rock types between the wells.

3.4. Results

3.4.1. Sample analysis results

3.4.1.1. Porosity, permeability and entry pressure analysis

The frequency distribution plots (Figure 3.4) show a bimodal distribution of porosity and permeability for distal mouthbar and delta front facies and a normal distribution for the distributary channel facies.

A minor bimodal distribution is found for the proximal mouthbar facies. The highest porosity and permeability values are observed for distributary channel while the lowest values are observed for delta front facies. Two classes of dominant porosity and permeability can be defined corresponding to the bimodal distribution: a first class with porosity greater than 0.25 and permeability greater than 100 mD and a second class with porosity and permeability smaller than these values.

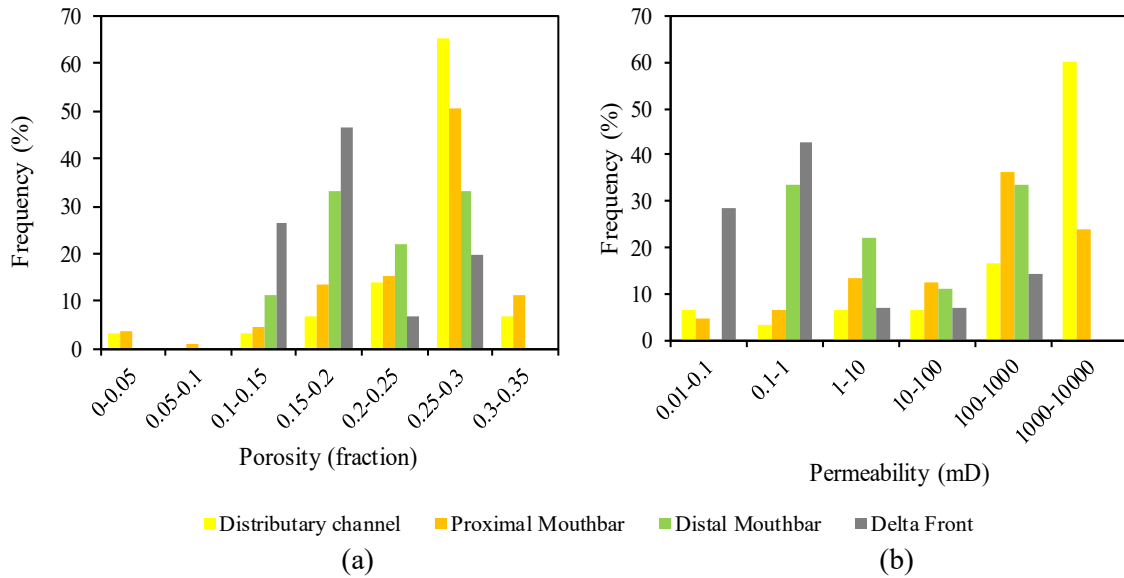


Figure 3.4. Frequency distribution of (a) porosity and (b) permeability values measured for discrete core samples from wells CRC-2 and CRC-3 for each facies.

The previously reported equivalent CO_2 column height data from CRC-2 for samples belonging to the depths 1434.70 m, 1435.31 m, 1439.72 m, 1440.21 m, 1448.58 m, 1485.39 m, 1491.43 m, 1504.45 m, 1507.65 m and 1509.88 m (Daniel, 2012; Daniel et al., 2012) is used to calculate capillary entry pressures for the respective samples (Equation 3.1). The calculated entry pressure varied between 300 Pa and 160,000 Pa (Table 3.1) and is expected to represent the entry pressure for the range of rock types. A conversion factor of 6894.76 was used convert the units from psi to Pa.

Depth (m)	1434.7	1435.3	1439.7	1440.2	1448.6	1485.4	1491.4	1504.5	1507.7	1509.9
h_{FWL} (m)	40.21	5.18	2.77	42.12	45.31	5.21	9.15	0.21	0.18	0.27
P_e (kPa)	142.3	18.5	9.7	149.8	160.1	18.5	32.1	0.7	0.6	0.9

Table 3.1. Capillary entry pressures (P_e) calculated from given CO_2 column height above the free water level (h_{FWL}) for discrete samples.

3.4.1.2. Quantitative mineral and mineral specific grain size analysis

Results obtained from the QEMSCAN analysis include identification of mineral phases making up the respective samples, the areal proportion each mineral occupies on the polished 2D thin section surface and the mineral map of the polished surface. Figure 3.5 shows mineral maps and major mineral phases for the representative samples from distributary channel (sample #93), proximal mouthbar (sample #91) and distal mouthbar (sample #81) facies. The mineral maps provide visual mineralogical and textural information. Clay

content increases from sample #93 to Sample #81 while the grain sizes decrease in the same order. The black area on the mineral maps represents porosity.

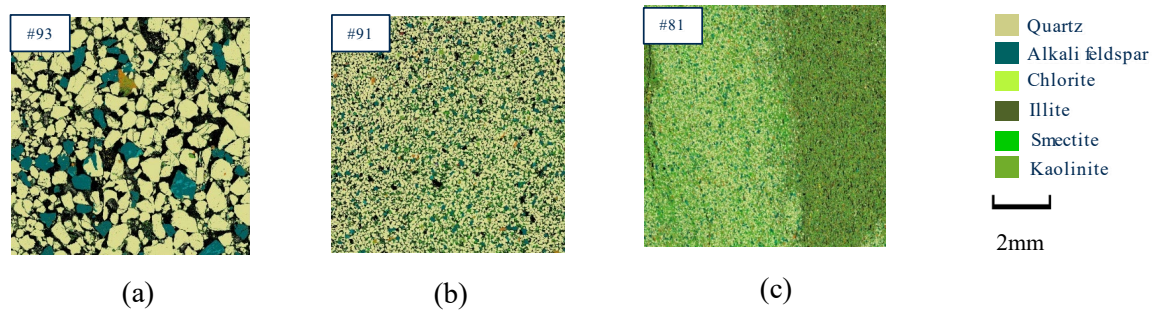


Figure 3.5. Results from QEMSCAN analysis for samples: (a) #93 (distributary channel); (b) #91 (proximal mouthbar); (c) #81 (distal mouthbar).

The minerals detected include framework minerals such as quartz, alkali feldspar and plagioclase; clay minerals such as chlorite, illite, muscovite, kaolinite, pyrophyllite, palygorskite and smectite; and carbonate minerals such as calcite, ankerite, dolomite, siderite and magnesite along with trace minerals such as rutile, pyrite, ilmenite and zircon. The association of mineral classes are in accordance with their definitions given in the TSG software (Haese et al., 2019). Figure 3.6 shows the proportion of major minerals in each facies.

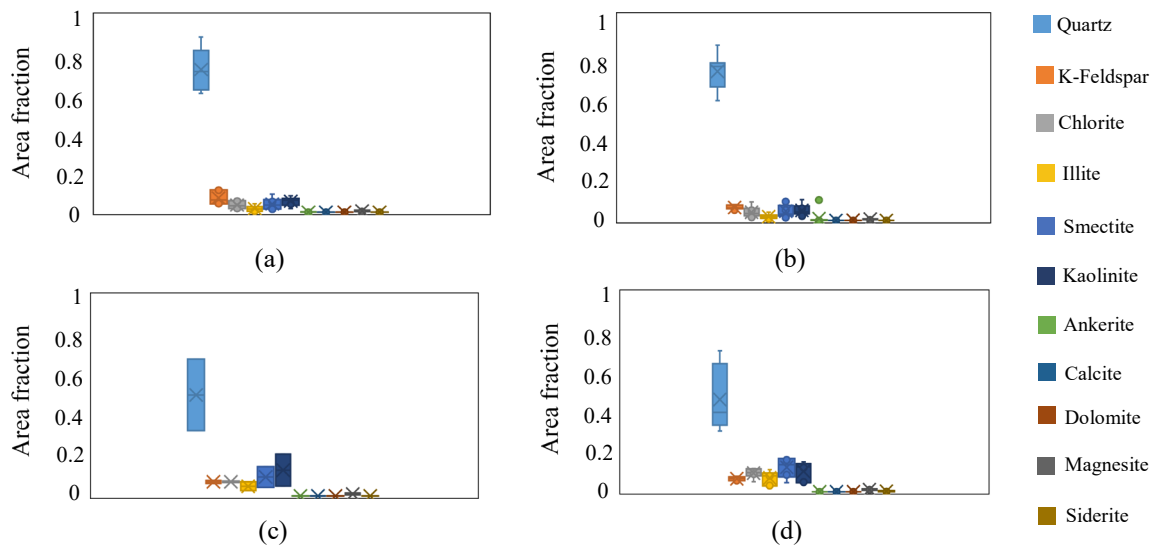


Figure 3.6. Proportion of major minerals in: (a) Distributary channel; (b) Proximal mouthbar; (c) Distal mouthbar; (d) Delta front. Box-and-whisker plots show mean (cross within the box), median (bar within the box), 25th and 75th quartile (lower and upper boundary of the box) and lower and upper limit of the data range (ends of the whisker).

The QEMSCAN results for samples chosen from distributary channel and proximal mouthbar facies are dominated by framework minerals like quartz and feldspar while the samples chosen from distal mouthbar and delta front facies show a higher proportion of clay minerals like kaolinite, illite, chlorite and smectite. The proportion of quartz ranges between 60–90% in distributary channel samples and decreases to 30–70% in distal mouthbar and delta front samples. The proportion of clay minerals such as chlorite, illite, smectite and kaolinite is higher in distal mouthbar and delta front facies where it varies between 10–20% as compared to distributary

channel and proximal mouthbar facies where their maximum amount is less than 10%. From the results, the bulk clay mineral proportion for distributary channel and proximal mouthbar varies between ~10% to ~30% and for distal mouthbar and delta front varies between 25%–60%. A detailed description of the mineral maps of all the 30 samples along with quantitative mineralogy is given in Appendix C.

The equivalent grain diameter of minerals varies between 0.01mm to ~0.6 mm. Figure 3.7 shows the modal grain size distribution characteristic of each facies. The modal grain size is as high as 0.6 mm for distributary channel facies. The modal grain size decreases subsequently in proximal mouthbar, distal mouthbar and delta front facies. The latter two facies are characterized by modal grain size smaller than 0.1 mm. The data was further used to plot area fraction covered against equivalent grain diameter for each mineral. The results for all the samples are presented in Appendix D.

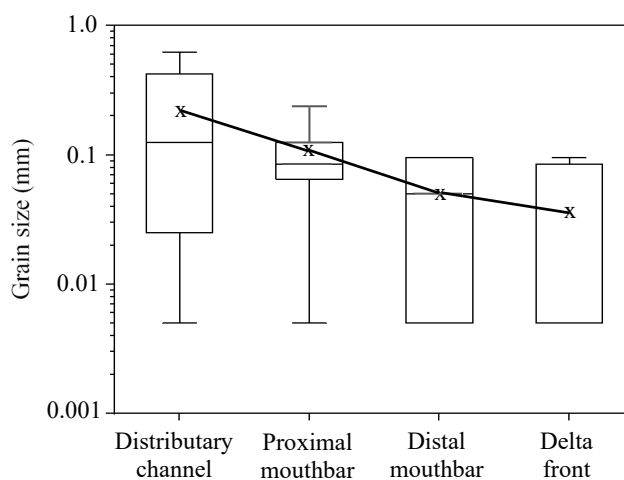


Figure 3.7. Modal grain size distribution characteristic of the four facies. Box-and-whisker plot shows mean (cross within the box), median (bar within the box), 25th and 75th quartile (lower and upper boundary of the box) and lower and upper limit of the data range (ends of the whisker).

3.4.2. Hyperspectral reflectance analysis

Figure 3.8(a) shows the results obtained from the hyperspectral (TIR) core analysis for CRC-3. The minerals detected include framework minerals like quartz and alkali feldspar; clay minerals such as mica, kaolinite, smectite and chlorite; and carbonate minerals such as dolomite and calcite along with some minerals present in trace amounts like illite, siderite, magnesite, ankerite, rutile and ilmenite. Quartz is the most dominant mineral detected in the core. Among the clay minerals, kaolinite and smectite are the most dominant. Their proportion varies through depth. Six different carbonate-cemented layers have been observed between the depths of 1480 and 1482 m (Cb-1), 1508 m (Cb-2), 1514 and 1515 m (Cb-3), 1532 and 1533 m (Cb-4), 1547 and 1549 m (Cb-5) and 1556 and 1558 m (Cb-6). Clay minerals are dominant between depths of 1461 and 1475 m (Cl-1) and between 1520 and 1530 meters (Cl-2), while framework minerals dominate between depths of 1475 and 1480 m (F-1). Intercalations of clay minerals with the framework minerals occur between the depths 1483 and 1507 m (I-1), 1535 and 1545 m (I-2) and between 1548 and 1557 m (I-3). These intercalated zones depict the depths of intraformational baffles.

Figure 3.8(b) shows the proportion of the three end member mineral classes for each of the four facies as obtained from normalizing the respective contents of the major minerals. The proportion of the clay minerals is less than 30% in distributary channel while it is as high as 40% in delta front deposits. The proximal and distal mouthbars have intermediate clay content. The proportion of carbonates is less than 10% in delta front but reaches up to 60% in distributary channel sediments.

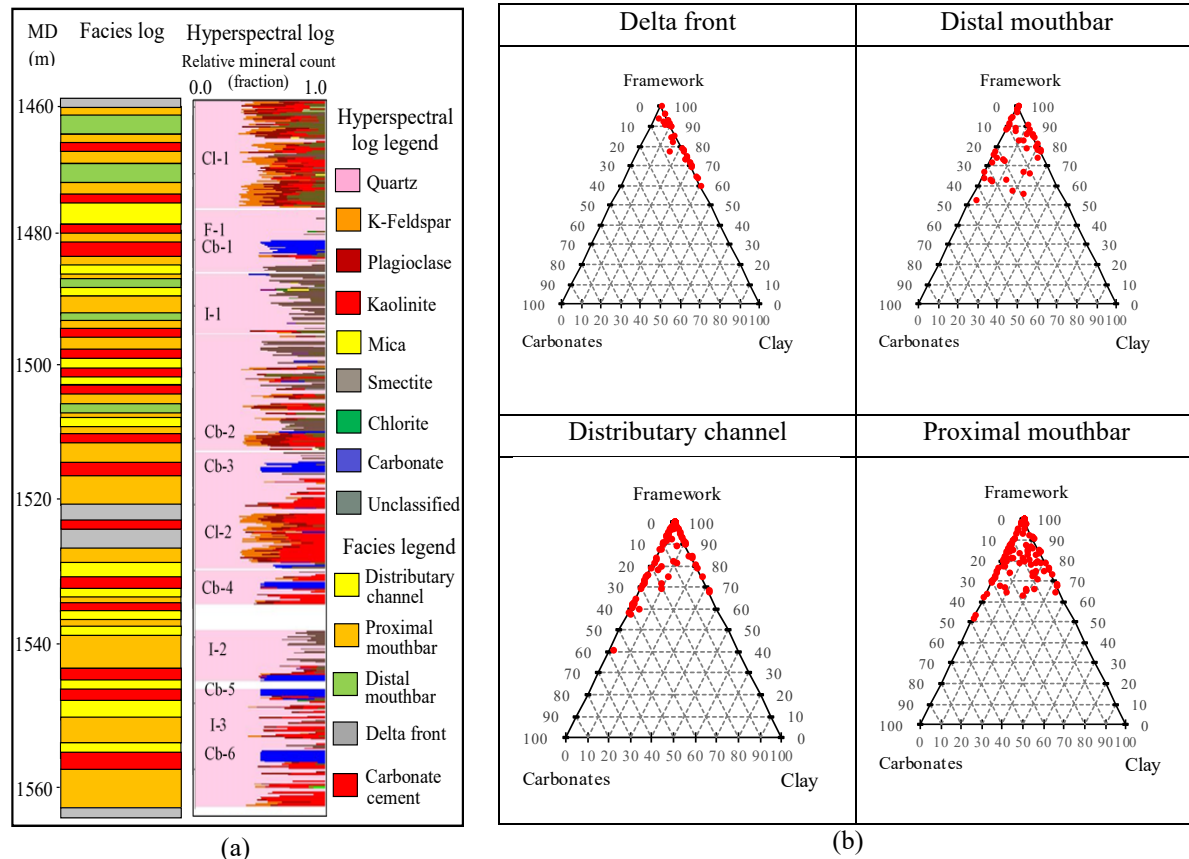


Figure 3.8. (a) Relative mineral count log as obtained by hyperspectral logging compared with the facies log for the CRC-3 core. The hyperspectral log shows various layers rich in framework (F), clay (Cl) and carbonate (Cb) minerals. The layers rich in clay intercalated within the framework minerals (I) are also shown; (b) Ternary plots showing the relative abundance of the three end member mineral classes in each of the four facies.

3.4.3. Colourlith and ECS logs and their correlation

Colourlith logs are compared with the ECS log (Combinable Magnetic Resonance Report) (Figures 3.9 and 3.10) showing that high proportions of quartz and feldspar correspond with red channel values in excess of 200, while sequences with higher clay content agree with blue channel values greater than 200. The presence of carbonates closely corresponds with green channel values more than 200. The three major shades also indicate the presence of three broad rock types. Furthermore, the red hue transitions into purple and greenish blue shades with colour shade values less than 200 for the three colour channels before merging with the blue hue, which is representative of clay rich intervals. This indicates the presence of two additional rock types between the framework and clay rich end members.

Hence, the analysis of colourlith logs leads to five rock type classes observed in the two parasequences: rock type 1 (red), rock type 2 (purple), rock type 3 (greenish blue), rock type 4 (blue) and rock type 5 (green).

Parasequence-2 (Figure 3.9) in CRC-3 ranges between 1461.6 and 1525 m depth. Overall, there are three distinctive sections, two clay dominated sections at the top and the bottom with a sand dominated section in the middle. The top clay section starts at 1461.6 m but extends to the overlying delta front facies and terminates at 1474.6 m. There are occasional interbedded sands and thin carbonated layers. The sand dominated section between 1474.6 and 1499.2 m is interrupted twice by clays at 1482 and 1492.4 m, which are 0.4 and 1.8 m thick respectively. Parasequence-2 in CRC-2 ranges from 1420 to 1486 m depth. It starts with a 15 m thick clay dominated layer with occasional sand extending to the overlying delta front facies. A 2 m thick carbonate-rich layer is identified at 1438 m. A 15 m thick sand bed ranges between 1440 and 1455 m depth. Towards the bottom of the interval, the lithology is clay dominated with minor intervals of sand. Additional carbonate-rich layers are identified at 1447 m, 1454 m, 1465m and 1472 m. Parasequence-2 terminates at the base of delta front facies, which is clay dominated.

Parasequence-1 (Figure 3.10) in CRC-3 ranges between 1525 and 1565.2 m depth. The changes between lithologies are progressive. The profile starts at the top with a clay dominated sequence (1525-1535.4 m) that overlies a delta front facies with numerous sand interbeds; two carbonate layers occur at 1528.8 and 1531.6 m. The interbedded sand layer transitions into mudstone with depth, which transitions towards the base into the underlying Skull Creek Formation. Two carbonate-rich layers have been identified at 1546.4 and 1556.4 m, which are 2.8 and 2.0 m thick respectively. Parasequence-1 in CRC-2 ranges from 1486 to 1518 m depth. It starts with a clay layer and transitions into a 2.7 m thick layer of sand. The remaining part of Parasequence-1 consists of interbedded clay and sand layers. Similar to CRC-3, the abundance of clay increases with depth and into the Skull Creek. There are two carbonate-rich layers at 1512.0 and 1517.3, which are 1.4 and 0.8 m thick respectively.

The sequence of rock types reflected in the two colourlith logs is similar for both parasequences and is traceable between the wells. As the distance between the well is only 630 m, the similarity in the rock type pattern is reasonable and lends confidence in the cross-well correlation of mud rich facies such as delta front and distal mouthbar (Figures 3.9 and 3.10). The rock types constituting sand rich facies such as distributary channel cannot be confidently correlated as channels are known to be discontinuous between the two wells (Dance, 2018).

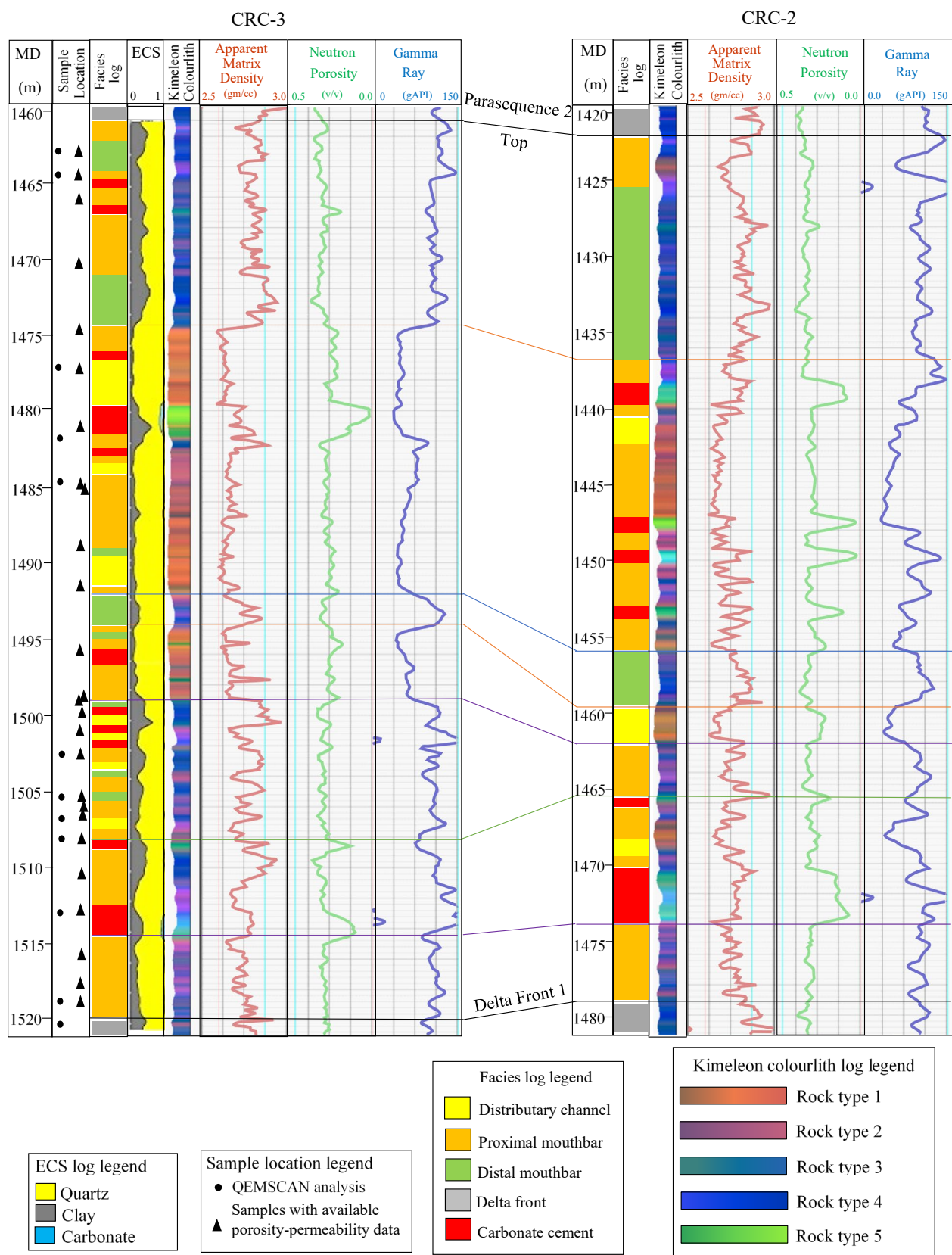


Figure 3.9. Colourslith logs for Parasequence-2 of well CRC-2 and CRC-3. The ECS log (Combinable Magnetic Resonance Report) is matched against the colourslith log and the hues in the two wells are cross correlated.

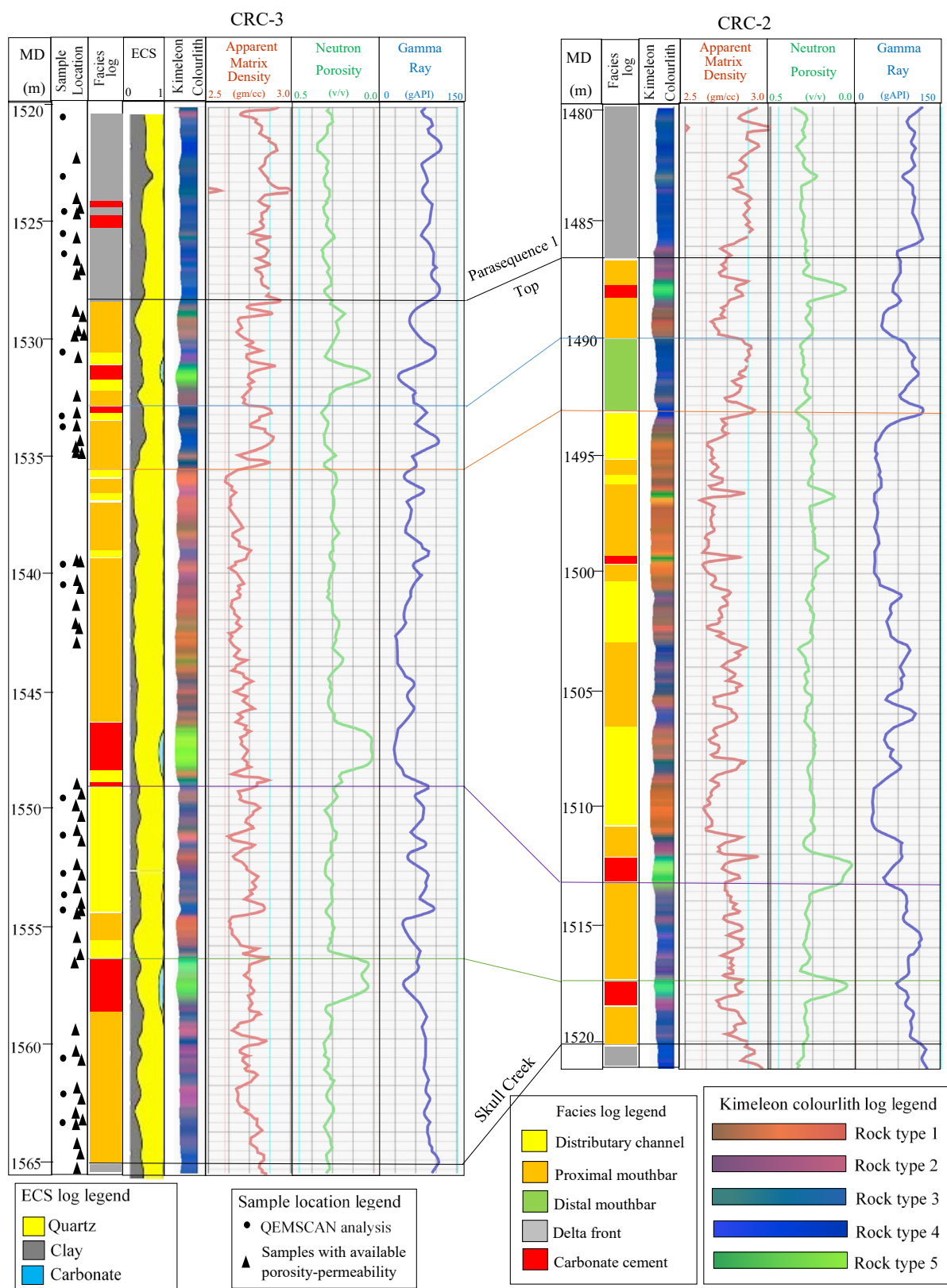


Figure 3.10. Colourslith logs for Parasequence-1 of wells CRC-2 and CRC-3. The ECS log (Combinable Magnetic Resonance Report) is matched against the colourslith log and the hues in the two wells are cross correlated.

3.5. Discussion

3.5.1. Rock types and properties

Hyperspectral core logging, the combined wireline logs and discrete sample analysis show that there is significant lithological heterogeneity within Parasequence-1 and Parasequence-2 of the Paaratte Formation at the CO2CRC's Otway Research Facility. The porosity and permeability analysis shows a bimodal distribution within the distal mouthbar and the delta front facies (Figure 3.4), which suggests that the depositional environment was characterized by phases of low and high energy. The bimodal distribution of porosity and permeability for distributary channel and proximal mouthbar are skewed towards higher porosity and permeability values indicating their primary deposition under higher energy conditions where medium to coarse sand is deposited. Grain size analysis confirms a coarse grained quartz and feldspar rich lithology with a modal grain size of 0.21 mm and 0.13 mm for distributary channel and proximal mouthbar, respectively (Figures 3.5, 3.6 and 3.7). The larger grain size for the samples belonging to distributary channel facies is expected as proximal mouthbars are located further downstream of the distributary channel facies and consequently experiences lower depositional energy conditions. Low porosity and permeability is more common in distal mouthbar and delta front facies (Figure 3.4) indicating sediment deposition under lower energy conditions. Clay size particles are expected to be dominant under such low energy conditions. This is confirmed by grain size analysis as the samples belonging to distal mouthbar and delta front facies show a higher proportion of clay minerals with modal grain size less than 0.05 mm (Figures 3.5, 3.6 and 3.7). The clay content increases while grain size decreases from distributary channel to proximal mouthbar and further to distal mouthbar and delta front facies. It is clear that the variations in physical properties and the mineral composition result from changes in the energy of the depositional environment.

The porosity and permeability results are coupled with the results from grain size analysis, semi-quantitative and quantitative mineral compositions to define rock type classes.

The bimodal distribution of porosity and permeability (Figure 3.4) suggests to subdivide the entire porosity spectrum into two categories or rock type classes: a. rocks with a porosity and permeability greater than 0.25 and 100 mD, respectively, and b. rocks with a porosity and permeability values less than 0.25 and 100 mD, respectively. However, the range in permeability for the two rock types is large and would lead to a large uncertainty in flow simulations. We have therefore further classified the data. The former class is subdivided into two subcategories: a. with permeability values less than 10 mD, and b. with permeability values between 10–100 mD. Similarly, the latter permeability class is subdivided into two subcategories: a. with permeability values between 100–1000 mD, and b. with permeability values greater than 1000 mD.

Rock types were further constrained in terms of their mineral composition using the semi-quantitative and quantitative mineral analysis. The results from hyperspectral analysis were used to characterize the rock types in terms of bulk carbonate content as the Hylogger output helps in identifying carbonate-cemented zones (Figure 3.8). A threshold of 5% carbonate mineral fraction was chosen as a distinguishing criteria between the

carbonate and non-carbonate samples for the purpose of rock type characterization. This criteria is later confirmed by the results obtained from QEMSCAN analysis.

The combined criteria of porosity and permeability and the semi-quantitative mineral composition as described above was applied to the five preliminary rock type classes from the colourlith analysis. The resultant rock type classes and their respective properties are described as: coarse sandstone (porosity > 0.25; permeability > 1000 mD; carbonate mineral proportion < 5%), fine sandstone (porosity > 0.25; permeability between 100–1000 mD; carbonate mineral proportion < 5%), siltstone (porosity < 0.25; permeability between 10–100 mD; carbonate mineral proportion < 5%), mudstone (porosity < 0.25; permeability < 10 mD; carbonate mineral proportion < 5%), carbonate-cemented sandstone (porosity < 0.25; permeability < 1000 mD; carbonate mineral proportion > 5%). 80 out of the total 82 samples fall into one of the five categories (Table B2, Appendix B). The remaining 2 data points remain unclassified.

The five preliminary rock type classes are further constrained in terms of bulk clay content based on QEMSCAN results. Quantitative mineralogy data from the 30 samples (Appendix C) was first assigned to one of the five preliminary rock type classes based on the knowledge of available porosity and permeability data (Table B1, Appendix B). Hence, 5 samples fell under rock type 1, 13 under rock type 2, 4 under rock type 3, 7 under rock type 4 and 1 under rock type 5 (Table B1, Appendix B). The mean proportion of each mineral was calculated based on the QEMSCAN analysis for each rock type class along with their standard deviations (Table 3.2).

As can be seen from Table 3.2, the standard deviations of different mineral fractions for each rock type class are typically small. The mineral composition data from QEMSCAN analysis is added to rock type classes in terms of the range of bulk clay mineral content obtained for all samples belonging to each rock type class. Clay mineral content for coarse sandstone rock type class varies between 5–20%; for fine sandstone rock type class varies between 10–30%; for siltstone rock type class varies between 25–60%; for mudstone rock type class varies between 40–60% and for carbonate-cemented sandstone rock type class is less than 10%. Hence, each rock type class has a distinct range of clay mineral content, which adds another unique and significant criteria to the rock type classification.

Rock type classes were further constrained in terms of the modal grain size class for each rock type. Given the variability in the modal grain size distribution, the most recurring modal grain size among samples of the same rock type has been chosen to differentiate one rock type class from the other. The coarse sandstone rock type class has the largest grain size with the most recurring modal grain size class being 0.40–0.45mm. The fine sandstone class has the second highest grain size values with the most recurring modal grain size class being 0.08–0.09mm. Siltstone and mudstone both have the most recurring modal grain size classes smaller than 0.01mm. Though modal grain size classes of siltstone and mudstone are both <0.01 mm, the siltstones have a bimodal distribution while mudstones strictly have only one dominant grain size class (Appendix D). The carbonate-cemented sandstone has the modal grain size class of 0.07–0.08mm.

Minerals	Rock Type 1		Rock Type 2		Rock Type 3		Rock Type 4		Rock Type 5	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Quartz	0.783	8.13%	0.7201	6.24%	0.5275	13.50%	0.3508	5.29%	0.6917	0.00%
Alkali Feldspar	0.076	3.40%	0.0654	1.01%	0.0591	0.57%	0.0691	1.53%	0.0512	0.00%
Kaolinite	0.0415	1.52%	0.0466	1.67%	0.1237	7.04%	0.1539	3.19%	0.0331	0.00%
Smectites	0.0334	2.51%	0.045	2.36%	0.1014	3.74%	0.1368	2.83%	0.0145	0.00%
Chlorite	0.0233	0.89%	0.0515	2.64%	0.0599	0.19%	0.09	1.51%	0.0144	0.00%
Illite	0.0086	0.57%	0.0214	0.65%	0.0437	1.98%	0.0824	1.37%	0.0099	0.00%
Magnesite	0.006	0.32%	0.0056	0.27%	0.0098	0.33%	0.018	0.99%	0.0172	0.00%
Siderite	0.0001	0.01%	0.0011	0.23%	0.001	0.06%	0.0039	0.51%	0.0001	0.00%
Ankerite	0.0019	0.23%	0.0013	0.46%	0	0.00%	0	0.00%	0.0992	0.00%
Calcite	0	0.00%	0	0.01%	0	0.00%	0	0.00%	0.0008	0.00%
Dolomite	0.0004	0.04%	0.0003	0.09%	0	0.00%	0	0.00%	0.0206	0.00%
Plagioclase	0.0121	0.45%	0.0195	0.64%	0.0262	0.60%	0.0254	0.60%	0.0186	0.00%
Muscovite	0.009	0.69%	0.0127	0.50%	0.0321	2.21%	0.0517	1.69%	0.0108	0.00%
Pyrite	0.0026	0.16%	0.0014	0.10%	0.0094	1.33%	0.0138	1.55%	0.0001	0.00%
Pyrophyllite	0.0007	0.04%	0.0004	0.03%	0.0016	0.08%	0.0009	0.03%	0.0004	0.00%
Ilmenite	0.0006	0.06%	0.0025	0.10%	0.0014	0.09%	0.0006	0.01%	0.0061	0.00%
Rutile	0.0006	0.04%	0.0029	0.11%	0.0028	0.06%	0.0023	0.03%	0.0071	0.00%
Zircon	0.0002	0.01%	0.0023	0.36%	0.0006	0.03%	0.0004	0.01%	0.0042	0.00%

Table 3.2. Mean mineral composition and standard deviations the five rock type classes based on QEMSCAN data. The mean is based on the data from 5 samples for rock type 1, 13 samples for rock type 2, 4 samples for rock type 3, 7 samples for rock type 4 and 1 sample for rock type 5.

Rock type classes and their representative properties are presented in Table 3.3. Characteristic capillary entry pressure ranges are added for each rock type class (Table 3.1). The given rock type names reflect relative differences in modal grain size, but do not strictly comply with the Wentworth classification for detrital sediments (1922).

The five rock type classes (Table 3.3) were assigned to the 82 classifiable core samples and their sampling depth was assigned to the respective depth in the hyperspectral and colourlith logs of CRC-3 (Table B2, Appendix B). This resulted in a 1-D distribution of rock types at discrete depths. The correlation between the rock types at discrete depths and the respective color shade in the colourlith log (Figures 3.9 and 3.10) validated the preliminary rock types as determined from the colourlith logs (Section 3.4.3). It now becomes clear that rock type 1 identified on the colourlith log is coarse sandstone, rock type 2 is fine sandstone, rock type 3 is siltstone, rock type 4 is mudstone and rock type 5 is carbonate-cemented sandstone. Based on the colourlith logs, the vertical variation of the five rock type classes and their respective properties is obtained at a resolution of 10 cm.

Rock Type	Porosity Range (fraction)	Permeability Range (mD)	Bulk Carbonate Content (%)	Mean Bulk Clay Content (%)	Most Recurring Modal Grain Size Range (mm)	Capillary Entry Pressure (Pa)
Coarse sandstone	>0.25 (#21)	>1000 (#21)	<5 (#21)	5–20 (#5)	0.40–0.45 (#5)	100–1000
Fine sandstone	>0.25 (#23)	100–1000 (#23)	<5 (#23)	10–30 (#13)	0.08–0.09 (#13)	100–1000
Siltstone	<0.25 (#5)	10–100 (#5)	<5 (#5)	25–60 (#4)	<0.01 (#4)	1000–10000
Mudstone	<0.25 (#21)	<10 (#21)	<5 (#21)	40–60 (#7)	<0.01 (#7)	1000–10000
Carbonate-cemented sandstone	<0.25 (#10)	<10 (#10)	>5 (#10)	<10 (#1)	0.07–0.08 (#1)	10000–160000

Table 3.3. The five rock type classes along with the defining criteria of flow properties, mineral compositions and grain size distribution. # gives the number of samples used for analysis of the respective property. Carbonate mineral % has been derived from hyperspectral analysis while clay mineral % and modal grain size class have been derived from QEMSCAN analysis.

3.5.2. Correlation of hyperspectral, ECS and colourlith logs

Hyperspectral, ECS and colourlith logs for the CRC-3 well were compared to each other to investigate the robustness of the different approaches and report any inconsistencies in the output obtained from the respective techniques. The hyperspectral log in Figure 3.8a shows clay dominated intervals between the depths of 1461 and 1475 m and between 1520 and 1530 m which is reflected in the colourlith output where the same intervals are dominated by mudstone. The ECS log in the same intervals shows a higher proportion of clay. The hyperspectral log shows a framework dominated interval between 1475 and 1480 m. This observation is again reflected in colourlith and the ECS log which show higher proportions of coarse sandstone and quartz, respectively, in the same interval. The hyperspectral log shows six intervals strongly enriched in carbonate, namely between the depths of 1480 and 1482 m, 1508 and 1509 m, 1514 and 1515 m, 1532 and 1533 m, 1547 and 1549 m and 1556 and 1558 m. These intervals are dominated by carbonate-cemented sandstone in the colourlith log and show a small proportion of carbonates in the ECS log. The correlation is also tested for the framework and clay intercalated intervals on the hyperspectral log between the depths of 1483 and 1498 m, 1535 and 1545 m and 1548 and 1555 m. The respective intervals show hues of red, purple and blue on the colourlith log indicating the intercalation of coarse sandstone, fine sandstone and mudstone. These intervals are expected to be lithologically heterogeneous and consist of intraformational baffles. This information is difficult to deduce from the ECS log. Additionally, the colourlith identifies thin carbonate-rich sequences that do not seem to be pictured in the ECS log.

Overall, the distribution of lithology on the three logs agrees very well. Our approach to use three independent data sets for the characterization of a heterogeneous sedimentary reservoir is successful.

3.5.3. Rock type abundance and variability

The colourlith logs (Figures 3.9 and 3.10) are compared to the facies logs (Figure 3.2) for CRC-2 and CRC-3 to obtain the abundance of different rock types within the four sedimentary facies (Figure 3.11). The rock type abundances are found to be similar for the two wells. The abundance of the rock types in different facies shows a relationship with the characteristic energy of the depositional environments. Coarse sandstone and fine sandstone constitute more than 50% of distributary channel and proximal mouthbar. The

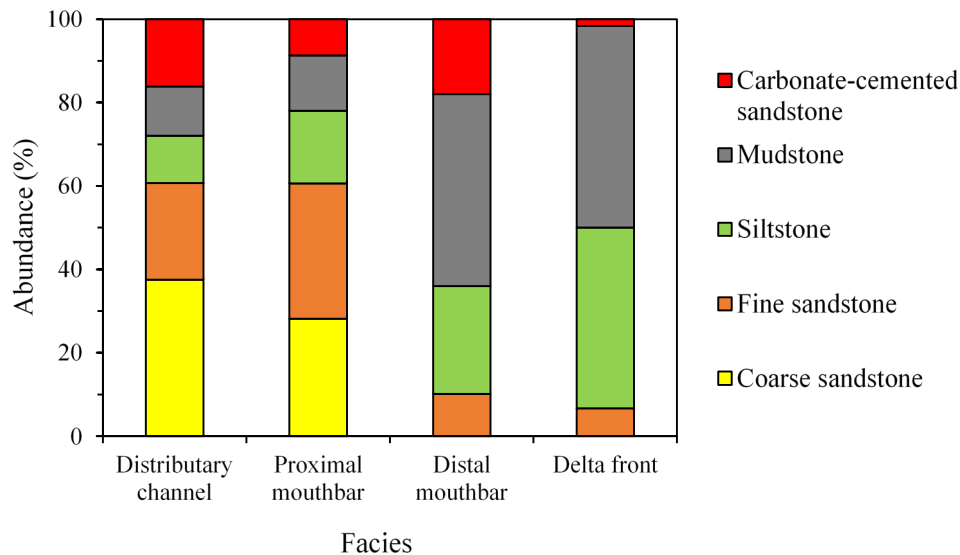


Figure 3.11. Abundance of the five rock type classes in the four depositional facies.

abundance of coarse sandstone decreases from distributary channel to proximal mouthbar and reduces to a nil in distal mouthbar and delta front facies. The proportion of siltstone and mudstone increases subsequently in the facies deposited under low energy conditions. Volumetrically, siltstone and mudstone together account for more than 70% of distal mouthbar and more than 90% of delta front facies. The results presented in Figure 3.11 appear to contradict results shown in Figure 3.7 given a higher proportion of fine grained sediment is shown for the distributary channel facies as compared to the proximal mouthbar facies. This is only locally true and results from the subjective sampling for QEMSCAN analysis where a disproportionally large number of samples comprise of intraformational baffles.

Cross-well correlation gives the lateral variability of the rock types (Figures 3.9 and 3.10). The high energy facies terminate between the two wells (Dance, 2018) and, hence, limit the lateral extent of the constituent rock types. The vertical variability of rock types is given in terms of the range of their bed thickness in the two wells (Figure 3.12). The bed thickness for a given rock type is seen to vary for different facies. The facies deposited under higher energy conditions like distributary channel and proximal mouth bar show greater thickness of rock types characterized by larger grain sizes such as coarse sandstone and fine sandstone. Coarse sandstone makes the bulk of the high energy facies and its bedding thickness ranges between 20 cm to 3.5 m in distributary channel and between 20 cm to 2.8 m in proximal mouthbar (Figure 3.12 (a) and (b)). The thickness of siltstone and mudstone is higher in low energy facies and varies between 20 cm to 1.5 m in distal mouthbar and between 20 cm and 1 m in delta front (Figures 3.12 (c) and (d)).

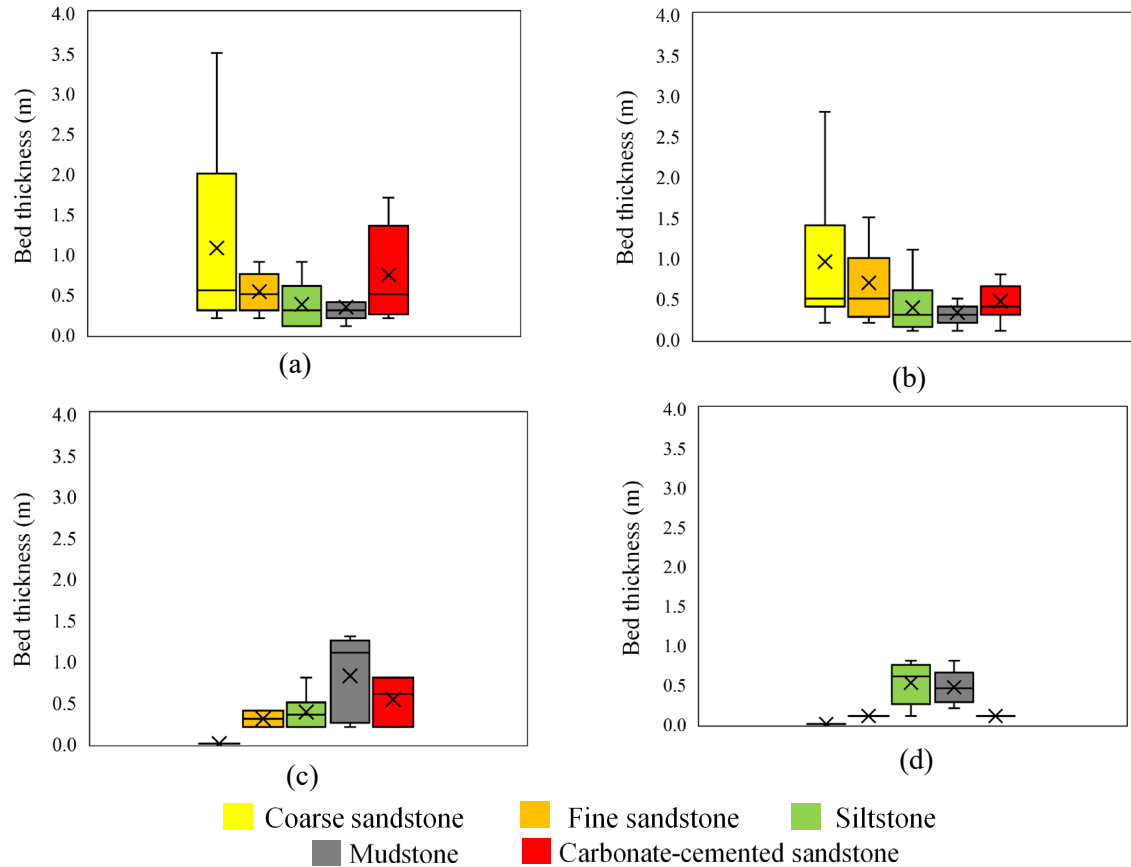


Figure 3.12. Range of bed thickness of the five rock types in (a) Distributary channel; (b) Proximal mouthbar; (c) Distal mouthbar; (d) Delta front. Box-and-whisker plots show mean (cross within the box), median (bar within the box), 25th and 75th quartile (lower and upper boundary of the box) and lower and upper limit of the data range (ends of the whisker).

3.5.4. Implications of high resolution rock typing

The vertical distribution of rock types, their cross-well correlation and abundance in different facies has important implications. The cross-well correlation of rock properties adds significant details to the already existing facies correlation between the wells (Figure 3.2). As already discussed, the cm to metre scale heterogeneity plays an important role in fluid flow and geochemical reactions (Ennis-King et al., 2005; Gershenzon et al., 2017; Liang et al., 2018; Ringrose and Bentley, 2015; Trevisan et al., 2017; Yang et al., 2014). In coarse gridded geostatistical models, the geometry of geobodies is usually determined by using data from analogue sites in order to better constrain the geological model (Collins and Doveton, 1986). However, such an approach may not always be accurate. In the absence of analogue data, lithological properties are usually populated using variograms based on wireline logs. Such an approach may be impractical in reservoir models populated with large number of rock properties as variograms are required as an input for each property (Ringrose and Bentley, 2015). The independent population of different properties might also result in some grid cells with an unrealistic combination of various flow and petrophysical properties. Also, this approach is not suitable for populating mineral data into the geostatistical model. The high resolution rock typing presented

in this study overcomes these challenges by using abundant data from two closely spaced wells. By coupling different flow, petrophysical and mineralogical properties in one rock type class, the number of variograms reduces to just one for each rock type class. The quantitative estimates of lateral and vertical variability of rock types and their abundance in different facies is useful in building better informed variograms as well as a more confident determination of the geometry of the geobodies. The variograms can then be used to populate coarse and fine sandstones in reservoir and siltstone and mudstone in seals based on the abundance of each rock type in each facies. Ultimately this improves the accuracy of reservoir models. The rock type classes and their correlation is useful in constructing high resolution and more confident accurate geostatic models which will consequently contribute towards improving dynamic simulation results and perhaps our understanding of the results.

3.6. Conclusions

The lowermost two parasequences of the Paaratte Formation Unit A, composed of coastal to shallow-marine sediments were used to derive a rock type classification scheme accounting for porosity and permeability, mineral composition and grain size distribution. All properties presented in this work are statistically distinct for each rock type class. The fact that the properties are derived from real samples while honoring concepts of depositional environments makes the presented rock type characterization practical and geologically consistent. The scheme can be further improved by including properties like relative permeability-saturation curves, capillary pressure-saturation curves and reactive mineral surface areas for each rock type. A major advantage of the rock typing presented here is that it meaningfully integrates the available flow, petrophysical and mineralogical properties. The rock type correlation between wells presents a high resolution extent of lithological heterogeneity vertically as well as laterally for the CO2CRC's Otway Research Facility. The results uniquely provide a fine scale structural framework for running detailed simulations addressing CO₂ flow and reactions. The work presented in this study shall contribute to the existing geostatistical models of the CO2CRC's Otway Research Facility and may support geostatic modelling at other sites composed of coastal to shallow-marine sediments and subsequent flow and reactive transport simulations.

Chapter 4

Composite rock types as part of a workflow for the integration of mm- to cm-scale lithological heterogeneity in static reservoir models

4.1. Introduction

Sedimentary reservoirs are common hosts for hydrocarbon (Buller et al., 2005; Gabrielsen, 2010; Neglia, 1979) and groundwater resources (MacDonald et al., 2012; Thangarajan, 2007; Toth, 2009) as well as targets for geological carbon storage (Baklid et al., 1996; Bradshaw et al., 2000; Korbøl and Kaddour, 1995; Metz et al., 2005; Pires et al., 2011; Pruess et al., 2003; Van der Meer, 1996). Their importance has driven the technologies associated with their characterization and static modelling with the aim to improve the results from dynamic simulations (Cipolla et al., 2011; Gao, 2011; Haldorsen and Damsleth, 1993).

Sedimentary reservoirs are inherently heterogeneous in their lithology (Doughty et al., 2001; Flett et al., 2005; Law and Bachu, 1996; Lindeberg, 1997). Lithological heterogeneity might exist in the form of variable depositional facies at regional scale and sedimentary structures like cross bedding, planar bedding and massive bedding, at macroscales (Cross, 1991; Cross et al., 1993; Garland et al., 1999; Miall, 2016; Pranter et al., 2007; Pranter et al., 2005). Heterogeneity at these different scales has varying impacts on the results from dynamic simulations (Arya et al., 1988; Corbett et al., 1992; Hewett, 1986; White and Horne, 1987). While some of the implemented depositional facies might act as regional seals for fluid flow (Christopher et al., 2006; Downey, 1984; Fulljames et al., 1997), heterogeneity in sedimentary structures might create unexpected fluid flow pathways and thereby govern local tortuosity and effective permeability (Gershenson et al., 2017; Green and Ennis-King, 2010a; Saadatpoor et al., 2009a; Trevisan et al., 2017). The latter exists at mm- to cm-scales and is especially important for studies addressing geological carbon storage. Certain sedimentary structures are comprised of laminae characterized by lower porosity and permeability and higher capillary entry pressures. Due to this, laminae act as flow barriers also referred to as baffles and enhance carbon storage by local capillary forces (Frykman et al., 2009; Gibson-Poole et al., 2009; Green and Ennis-King, 2010a; Yu et al., 2017). Clay minerals such as chlorites, smectites and illite react with CO₂-enriched water which may lead to the precipitation of carbonates and enhances carbon mineral trapping (Hermanson and Kirste, 2013; Higgs et al., 2015; Watson, 2012; Watson et al., 2005).

The importance of mm- to cm-scale heterogeneity warrants the need for its integration in reservoir models. However, heterogeneity at such fine scales is often neglected in regional scale geological models. There are two technical reasons for this. Firstly, the conventional approaches of reservoir modelling populate the voxels with rock properties using wireline logs. Sedimentary heterogeneity, however, exists at scales below the resolution of wireline logs and is lost in the process of averaging the properties at log resolution (Doveton and Prenskey, 1992; Ruhovets et al., 1992). This is especially true for mm- to cm-scale lithological interfaces which

have significant differences in rock properties and hence are important for flow and fluid-rock reactions. Several deconvolution algorithms have been developed to extract finer scale information from the logs (Sheng et al., 1987) but these are associated with considerable uncertainty compared to sedimentary structures observed in core inspection. Secondly, reservoir modelling softwares are not built to handle mm- to cm-scale grid size resolution. Usually, the software algorithms for property population fail at such high resolutions. These limitations result in the neglect of mm- to cm-scale heterogeneity in reservoir models which ultimately might lead to an incorrect quantification of fluid flow, reactive transport and CO₂ trapping especially for highly heterogeneous reservoirs.

The present study aims to overcome these challenges. The objective of this paper is to present and demonstrate a method for systematically defining a modified rock typing scheme and deriving their lithotype logs so that the regional geological models can be downscaled to account for mm-scale lithological heterogeneity.

For this purpose, a new workflow is presented where information from the wireline logs is coupled to the high resolution data from core samples. The homogeneous rock types identified at mm-scale are combined as composite units, henceforth referred to as composite rock types. A lithotype log of the composite rock types is derived and is used to downscale the depositional facies model to the scale of rock types. The geological model comprised of rock types sits nested within the coarser depositional facies model and complements the conventional reservoir modelling approach. The workflow is applied to the data available from the CO₂CRC's Otway Research Facility site where sedimentary heterogeneity is known to exist at scale of 5 mm (Dance, 2018; Mishra et al., 2019). Such dimensions were found to be beyond the handling limits of SKUA GOCADTM, an industry standard reservoir modelling software. The workflow is utilised to derive lithotype logs discretised at 5 cm resolution while accounting for the sedimentary heterogeneity at 5 mm scale. The lithotype logs are further used to build a reservoir model with a vertical resolution of 5 cm, thereby downscaling the regional scale geological model comprised of depositional facies.

4.2. Methodology

4.2.1. Description of the workflow

4.2.1.1. Determining the number of composite rock types required to cover the range of heterogeneity

The first step of the workflow is to discretise the lithotype log image obtained from the combination of three wireline logs: apparent matrix density, neutron porosity and gamma ray, which were sampled at a resolution of 15 cm. The three logs are implemented as red (R), green (G) and blue (B) channels, respectively, and combined in the Kimeleon software (Collins and Doveton, 1986) resulting in a RGB-based colorlith log. Each color channel value varies between 0 to 255 in a scheme where the data stored by each pixel is 8 bits. The colorlith is further characterised using the homogeneous rock types where each rock type corresponds to a range of colors (Mishra et al., 2019). The lithotype log is then discretised at the level of individual pixels using a code written in Python (see Appendix E). Hence, we obtain the maximum resolution of the lithotype log image.

However, the pixel thickness may not always correspond to the minimum bed thickness of the constituent homogeneous rock types. This is determined in the next step of the workflow, where the minimum bed thickness is the least common multiple of the net height of the colorlith. The minimum bed thickness also corresponds to the highest resolution of reservoir discretization. At this scale, the reservoir will constitute the homogeneous rock types.

The characterization of the colorlith log at the scale of minimum bed thickness has the advantage of directly incorporating mm- to cm-scale heterogeneity in the reservoir model. However, such high reservoir resolutions might not be handled by geomodelling platforms. This limitation is overcome in the next step of the workflow where the resolution of the original lithotype log is coarsened to a scale which can be handled by the reservoir modelling softwares. The algorithm allows to determine the coarsened discretization scales in a step-wise manner where the next scale of coarsening is the greatest common divisor of the bed thicknesses at the current discretization scale. The calculation is repeated until the target scale of discretization is achieved.

The successive coarsening of the lithotype log image leads to an increase in the bed thickness where the new bed intervals now consist of two or more homogeneous rock types and their respective color shades. The algorithm determines, at each step of coarsening, the number of such coarse scale bed units with a distinct yet repeatable combination of the respective color shades. The repeatability of the color shades in the colorlith log helps in classifying these beds as rock types which form the fundamental units of the depositional facies. The algorithm terminates at a step where the coarse scale beds are no longer repeatable. This condition is a limit for the algorithm and is implemented by restricting the proportion of each homogeneous rock type in the coarse scale bed units to be equal. The coarse scale beds with unequal proportions of constituent rock types might be useful for local scale studies but might not always qualify as rock types and hence, will be of limited use for reservoir modelling.

4.2.1.2. Composite rock type characterization

The next step in the workflow is the quantification of the composition and the properties of the determined composite rock types at the coarser discretization scale. This is achieved by using the data from the core samples in conjunction with the color shade codes constituting the coarse scale composites. The latter is indicative of the corresponding homogeneous rock types which compose each composite lithological unit. Correspondence is developed between the rock types comprising the composites and the lithological composition characteristic of the cores. This helps to constrain the types of sedimentary structures and their lithological properties which are further utilised to characterise each coarse scale rock type.

The determination of the composition and sedimentary structures is followed by the quantification of the rock properties for each composite rock type. For this purpose, lithological properties of the constituent homogeneous rock types are averaged or upscaled while accounting for the intrinsic sedimentary structures. Porosity is volumetrically averaged such that the fine and the coarse scale models consist of the same pore volume (Durlofsky, 2003). Permeability, on the other hand, is averaged using the flow upscaling methods in the vertical and the horizontal direction (Durlofsky, 2003; Durlofsky, 2005). The averaged vertical

permeability worked out to be the layer thickness weighted harmonic mean of the permeabilities of the two homogeneous rock types combined as a composite unit. The averaged horizontal permeability is worked out to be the layer thickness weighted arithmetic mean of the two homogeneous rock types. The upscaling of permeability is significantly governed by the geometry of the sedimentary structures characteristic of the composite rock types. Like porosity, mineral composition is also volumetrically averaged such that the total amount of minerals in each composite rock type was the same at both the scales.

4.2.1.3. Statistical significance analysis

The final step in the work flow is the determine the statistical significance of the properties of the composite rock types determined at the coarser scale of discretization by using data from core samples. The respective color shades are averaged at the scale of discretization for each composite unit (see Appendix E), and the averaged colorlith shades cross-plotted against an upscaled rock property measured on the core. This is achieved by using proportions of three mineral groups serving as end members: framework (mostly quartz and feldspar), clay and carbonate minerals (Haese et al., 2019). Cross plots with the data from colorliths are assessed for their statistical significance. The results from the workflow are useful if the three regression relations are significant at the 95% confidence level or more.

At the end of this step, we obtain a modified lithotype log which is discretised at a resolution that can be handled by the modelling software while also being integrating the mm- to cm-scale heterogeneity below the resolution of wireline logs and beyond the operating limits of the softwares. The composite rock types making up the lithotype log are tested for their statistical significance. The workflow can be applied to two or more lithotype logs which can then together be used to build a reservoir model. The entire workflow is presented in Figure 4.1.

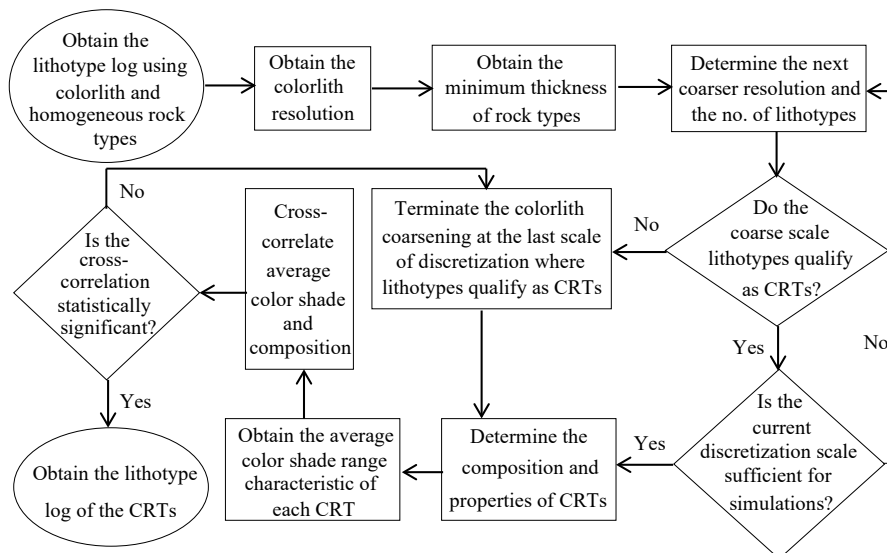


Figure 4.1. Overview of the workflow for determining the number, composition and depth log of the composite rock types (CRTs) at increasingly coarser reservoir discretization scales.

4.2.2. Case study: CO2CRC's Otway Research Facility

4.2.2.1. Study area overview

The application of the presented workflow is demonstrated for the CO2CRC's Otway Research Facility site. The site is located approximately 300 km southwest of Melbourne in Victoria (Figure 4.2) (Dance, 2013).

The current study focuses on data from the wells CRC-2 (38°31'50.06" S, 142°48'41.45" E) and CRC-3 (38°31'42.3" S, 142°48'17.8" E), because of the abundance and type of data available. The two wells are located about 630 meters apart. The wireline and core data from both the wells have been characterized between the depths 1461-1565 m at the location of CRC-3 and 1420-1520 m at the location of CRC-2 (Mishra et al., 2019).

4.2.2.2. Geological setting

The stratigraphic unit of interest in the subsurface is a part of the Paaratte Formation within the Sherbrook Group of the Otway Basin (Figure 4.2). The basin is set in a rift-to-passive margin environment and occupies a surface area of 150,000 km² with a maximum thickness of 8 km (Dance, 2013; Exon and Lee, 1987; Miyazaki et al., 1990; Moore et al., 2000; Robertson et al., 1978; Stacey et al., 2013).

The Basin came into existence in Tithonian-Barremian when Australia and Antarctica rifted apart for the first time (Dance, 2013; Holford et al., 2011; Krassay et al., 2004; Moore et al., 2000; Norvick, 2005; Willcox and Stagg, 1990). The rifting events led to thermal subsidence followed by passive margin

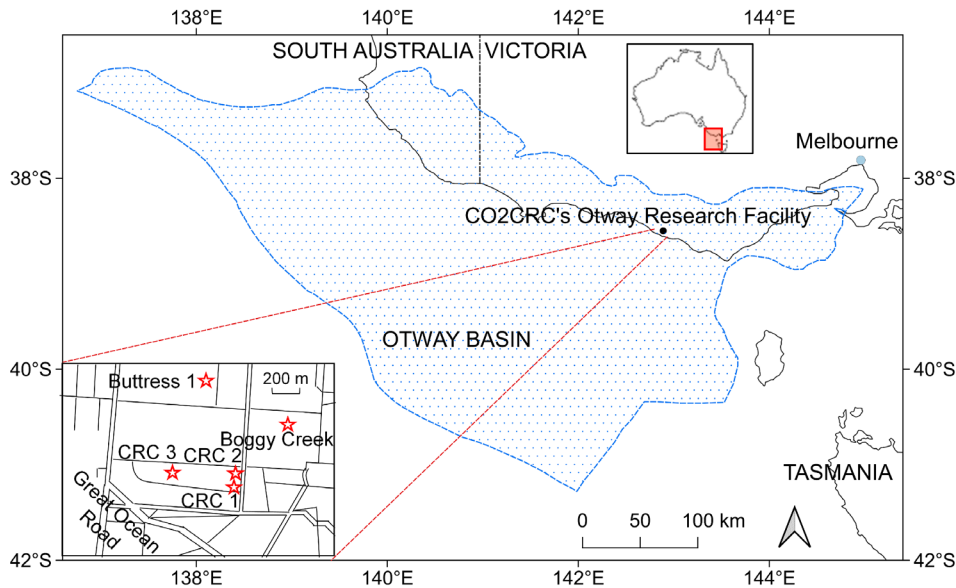


Figure 4.2. Location of the CO2CRC's Otway Research Facility showing the wells CRC-1, CRC-2, CRC-3, Buttress-1 and Boggy Creek. Major roads are shown as parallel solid lines while the footpaths are shown in solid lines. The present study is based on the data from CRC-2 and CRC-3 wells.

subsidence (Cande and Mutter, 1982; Dance, 2013). Further evolution of the Basin was controlled by six major cycles of sea level change between Late Cretaceous and Quaternary and led to the formation of five Groups (oldest to youngest): Otway, Sherbrook, Wangerrip, Nirranda and Heytesbury. The development of the Otway

Group was predominantly controlled by tectonic activity and the depositional environments varied from volcanoclastic at the base to fluvial and shallow lacustrine at the top. The sediments comprising the Group ranged from interbedded carbonaceous shale and basalts to interbedded volcanoclastic sandstone, mudstone and coal (Morton et al., 1994; Woollands and Wong, 2001). The depositional environments of the Sherbrook Group varied from marginal marine within a low stand system tract at the base to upper deltaic plain within a high stand system tract at the top (Boyd and Gallagher, 2001; Buffin, 1989; Woollands and Wong, 2001). The sedimentology comprised shale, black pyritic mudstone, siltstone, interbedded calcareous sandstone and coarse grained sandstone (Hawkins and Dellenbach, 1971; Woollands and Wong, 2001). The Wangerrip Group consists of transgressive-regressive units (Morton et al., 1994) deposited under low energy marginal marine environment at the base to shallow-marine environment at the top. The sedimentology of the Group comprised carbonaceous claystone, mudstone and sandstone (Morgan, 1985; Morton, 1990; White, 1995; Woollands and Wong, 2001). The Nirranda Group developed in open marine conditions consists of mixed carbonates and siliciclastic sediments (Krassay et al., 2004; O'Brien and Thomas, 2007), while the Heytesbury Group deposited under inner shelf conditions at the base to mid-shelf conditions at the top. The Group is characterised by open marine carbonate sequences (Woollands and Wong, 2001).

For the current study, the stratigraphic interval of interest is a part of the Paaratte Formation belonging to the Sherbrook Group. The formation occurs between depths of 1120–1570m where the deposition took place under a lower delta plain environment belonging to a highstand system tract (Boyd and Gallagher, 2001; Dance, 2012). Structurally, the Paaratte Formation is a low dipping faulted anticline with dips ranging between 2°–5° towards the north (Dance, 2012). The formation comprises three member units, Unit A, Unit B and Unit C. Unit A (lowermost) comprises three fourth order parasequences with Parasequence-1 at the bottom and Parasequence-3 at the top (Dance, 2018). The current study utilizes data from Parasequence-1 and -2. Both the parasequences are composed of four facies: delta front, distal mouth bar, proximal mouth bar and distributary channel (Boyd and Gallagher, 2001; Dance, 2018). Lithologically, the parasequences are comprised of sandstone, siltstone and mudstone with carbonate-cemented intervals (Geary et al., 2001; Geary and Reid, 1998; Woollands and Wong, 2001). The data depicts the presence of mm- to cm-scale lithological heterogeneity (Mishra et al., 2019).

4.2.2.3. Available data

Porosity and permeability measured on core samples is available for both the wells while quantitative mineral composition and grain size data is available for 30 core samples from CRC-3 (Mishra et al., 2019) (Table 4.1). The length of each sample was 4 inches and the diameter was 2 inches.

The heterogeneous core samples show three broad classes of sedimentary structures: cross bedding, planar bedding and massive bedding (Figure 4.3). The cross and planar bedded cores are composed of two distinct lithologies as evident from their bimodal grain size distribution. The interfaces between the two massive bedded lithologies can also be identified in the axial core images (Figure 4.3).

The data for the homogeneous samples has been grouped into five rock type classes: coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone. The homogeneous rock types differ from each other in terms of porosity, permeability and mineral composition (Mishra et al., 2019) (Table 4.2).

In addition to the core data, colorlith logs for both the study wells and the regional seismic data are also available. The colorlith logs have been derived using wireline log data in a previous study and interpreted in terms of homogeneous rock types (Mishra et al., 2019) (Figure 4.4). Seismic data is important to integrate regional anisotropy into the reservoir model.

Sample depth (m)	Depositional Facies	Sedimentary structures	Porosity (fraction)	Permeability (mD)	Mineral Composition (fraction)		
					Framework	Clay	Carbonates
1477.20	Distributary channel	Massive bedding	26.9	7410	0.9149	0.0777	0.0074
1533.78	Distributary channel	Massive bedding	21.2	1.07	0.6133	0.3676	0.0191
1549.75	Distributary channel	Massive bedding	28.4	1110	0.8192	0.1644	0.0164
1551.25	Distributary channel	Massive bedding	26.5	615	0.8693	0.1266	0.0041
1552.82	Distributary channel	Massive bedding	29.6	1930	0.9407	0.0566	0.0027
1553.48	Distributary channel	Cross bedding	21.2	130	0.7479	0.2375	0.0146
1554.07	Distributary channel	Cross bedding	16.4	27.5	0.7485	0.2436	0.0079
1464.80	Proximal mouth bar	Massive bedding	28.5	141	0.7781	0.2128	0.0091
1481.55	Proximal mouth bar	Planar bedding	13.1	0.55	0.3903	0.5522	0.0575
1484.45	Proximal mouth bar	Massive bedding	29.7	1010	0.8299	0.168	0.0021
1502.90	Proximal mouth bar	Massive bedding	24.0	357	0.9328	0.0649	0.0023
1506.92	Proximal mouth bar	Massive bedding	29.3	262	0.8808	0.1147	0.0045
1508.80	Proximal mouth bar	Massive bedding	26.6	353	0.7339	0.2594	0.0067
1513.60	Proximal mouth bar	Massive bedding	23.4	198	0.7902	0.0719	0.1379
1518.45	Proximal mouth bar	Massive bedding	27.1	109	0.8753	0.1159	0.0088
1531.50	Proximal mouth bar	Massive bedding	29.0	357	0.7569	0.2391	0.004
1533.86	Proximal mouth bar	Massive bedding	12.6	33.4	0.3771	0.6083	0.0146
1539.50	Proximal mouth bar	Planar bedding	26.8	407	0.8521	0.1183	0.0296
1540.30	Proximal mouth bar	Massive bedding	28.3	4160	0.9192	0.0672	0.0136
1560.95	Proximal mouth bar	Massive bedding	28.0	249	0.8779	0.116	0.0061
1562.60	Proximal mouth bar	Massive bedding	22.7	17	0.7001	0.2938	0.0061
1563.60	Proximal mouth bar	Massive bedding	29.1	535	0.8435	0.152	0.0045
1462.85	Distal mouth bar	Massive bedding	28.8	324	0.8093	0.185	0.0057
1505.00	Distal mouth bar	Planar bedding	14.1	0.9	0.4839	0.5	0.0161
1520.50	Delta front	Massive bedding	28.4	182	0.7224	0.2583	0.0193
1523.90	Delta front	Planar bedding	17.2	0.08	0.5021	0.4841	0.0138
1524.65	Delta front	Planar bedding	21.5	0.64	0.5721	0.4146	0.0133
1524.65	Delta front	Massive bedding	21.5	NA	0.4706	0.5065	0.0229
1525.64	Delta front	Planar bedding	16.3	0.47	0.4934	0.4963	0.0103
1526.05	Delta front	Massive bedding	27.6	268	0.8203	0.1765	0.0032

Table 4.1. Rock properties of the available 30 core samples (Mishra et al., 2019).

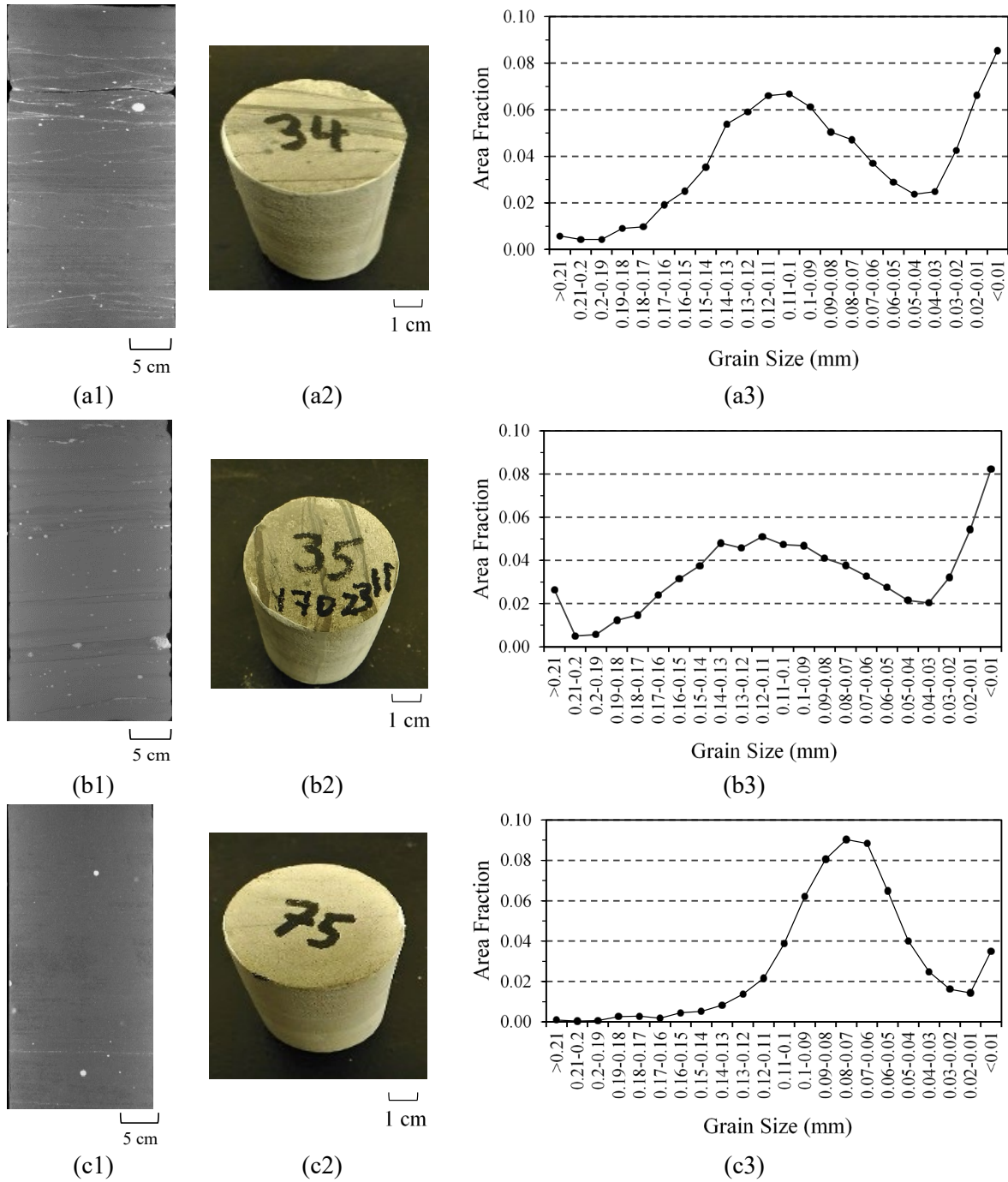


Figure 4.3. Axial x-ray images of the core showing: (a1) cross bedding; (b1) planar bedding; (c1) massive bedding. Cross sectional images of the core plugs showing: (a2) cross bedding (sample depth 1554.07 m); (b2) planar bedding (sample depth 1553.48 m); (c2) massive bedding (sample depth 1513.60 m). Respective grain size distribution for: (a3) cross bedding; (b3) planar bedding; and (c3) massive bedding. The lateral core images show the presence of thin laminae of fine grained rock type (dark gray) between more coarse grained lithologies (light gray) for cross and planar beddings. Lithological interfaces between two massive bedding lithologies can also be identified in the axial core images (Mishra et al., 2019).

Rock Type	Abbreviation	Porosity			Permeability (mD)			Mineral Composition		
		Mean	SD	Range	Mean	SD	Range	Framework	Clay	Carbonates
Coarse sandstone	H ^{CSst}	0.29	0.02	0.25-0.35	3148.5	2266.4	1000-7000	0.88	0.11	0.01
Fine sandstone	H ^{FSst}	0.28	0.01	0.25-0.35	406.5	200.1	100-1000	0.79	0.20	0.01
Siltstone	H ^{Slt}	0.19	0.04	<0.25	44.6	43.2	10-100	0.68	0.31	0.01
Mudstone	H ^{Mst}	0.18	0.03	<0.25	8.3	2.0	<10	0.45	0.53	0.02
Carbonate-cemented sandstone	H ^{CbSst}	0.19	0.08	<0.25	6.1	3.2	<10	0.79	0.07	0.14

Table 4.2. Average porosity, permeability and mineral composition of the five homogeneous rock types for the CO2CRC's Otway Research Facility site (Mishra et al., 2019).

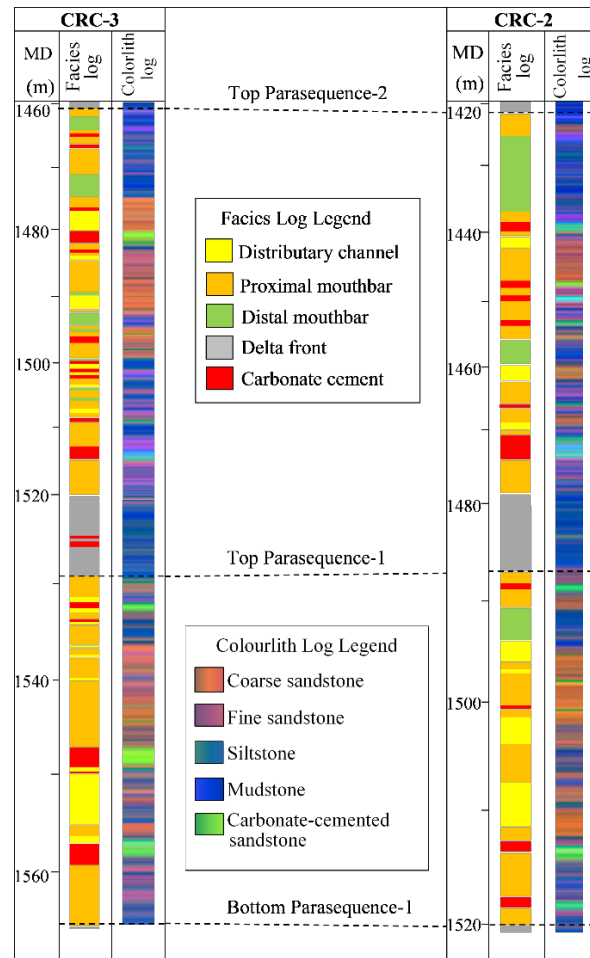


Figure 4.4. The available depositional facies and lithotype logs for the CO2CRC's Otway Research Facility site (Mishra et al., 2019).

4.2.2.4. Reservoir modelling

The workflow (Figure 4.1) is used to obtain the modified lithotype logs for the two wells at the CO2CRC's Otway Research Facility site and sedimentary heterogeneity characterised at 5 mm scale is integrated as composite lithological units at 5 cm scale. The original lithotype logs cannot be directly used to build reservoir

models due to the software's technical limitations in handling grid cell sizes of 5 mm. The two modified lithotype logs form the basis of the reservoir model which is built in SKUA-GOCAD™ modelling software.

First, a structural framework model is built. For this purpose, delta front and distal mouth bar facies are used as horizons as they have been demonstrated to be continuous between the two wells (Dance, 2018). Regional anisotropy, heterogeneity pattern and degree of spatial connectivity of facies and rock types is determined using the variograms of textural dissimilarity which is a seismic attribute. Texture is a stochastic measure of the acoustic heterogeneity in a seismic volume. It consists of group of GLCM (Gray –Level of Co-occurrence Matrix), one of which is dissimilarity (Chopra and Marfurt, 2007; Wackernagel, 2013). Seismic data used was shot using static sources before any CO₂ and gas injection and has a horizontal resolution of 8 m in each of the two directions. A triple nested variogram modelling approach is used as it helps in identifying nested neighbourhoods by comparing the difference in the sills and their respective correlation lengths. The approach allows a confident matching of the different levels of spatial stochastic structure of the data. The variogram models provide information on directional azimuths which are used to obtain the most appropriate variogram fits.

The facies and modified lithotype logs are imported and used as categorical variables. The combined dataset allows to determine the proportion of different rock types in each facies. This is an important downscaling step of the depositional facies model as each depositional facies is composed of multiple rock types. The proportions are honoured while building the reservoir model. Firstly, the five depositional facies are populated as categorical variables within the structural framework of the model. The regional directions of the depositional facies are honoured using the azimuths derived from the textural dissimilarity variograms, as described above. Subsequently, the facies model is downscaled by populating homogeneous and composite rock types within each facies region using the two lithotype logs. Hence, the presented workflow leads to an improvement in the downscaling approach used to build conventional reservoir models (Doyen, 2007).

The sampling for the facies and the lithotype logs was carried out at a step size of 5 cm vertically. For the population of facies and rock types in the model, the facies and lithotype logs are used to obtain the respective 1D vertical proportion curves. To account for the lateral variation in facies and rock types, 2D horizontal proportion maps are derived for both the properties using ordinary kriging (Cressie, 1990). The 1D proportion curves are combined with the 2D proportion maps by ordinary kriging as well. This results in 3D proportion cubes which are used to account for spatial variations in both the properties. The 3D proportion cubes for facies and rock types were used to condition the data for the population of the respective property in the reservoir model using Sequential Gaussian Simulation (SGS) approach.

The population of facies and rock types in the structural model framework is followed by the rock property population. This is done using normal distribution of porosity and log normal distribution for permeability data for each rock type. At the final step of conditional simulation, Gaussian Anamorphosis Transformation using CDFs (p-p transform) is used.

4.3. Results

4.3.1. The scale of discretization and the number and composition of composite rock types

When applying the workflow (Figure 4.1) to the colorliths available for the CO2CRC's Otway Research Facility site (Figure 4.4), the highest resolution of the two colorliths was found to be 1.25 cm while that of the five homogeneous rock types (Table 4.2) was found to be 2.5 cm. The property population algorithms of SKUA GOCAD™ are not built to handle this resolution. Hence, the algorithm was used to determine the next coarser scale of discretization which worked out to be 5 cm with a total of 15 rock types where 10 rock types were composite units and 5 were homogeneous. At this resolution, it was just possible to build the reservoir model in SKUA. Each of the heterogeneous rock types at 5 cm resolution is comprised of two distinct color shades indicating that they are essentially composites of two homogeneous rock types in equal proportions. This was further confirmed by observations made on heterogeneous cores which have similar dimensions as that of the composite rock types (Figure 4.3). The application of the remaining steps in the workflow are demonstrated at 5 cm resolution.

The constituent color shades of the composite rock types were used to deduce their composition while their sedimentary structures were determined from the core samples (Table 4.3). One composite rock type was composed of cross bedding with the composition being coarse and fine sandstones. As seen in the cores, maximum thickness of the cross bedding foresets was about 5 mm. Five composite rock types were composed of planar bedding with mudstone and siltstone comprising the lamina within coarse and fine sandstones. The minimum size of the lamina was 5 mm as observed in the core samples. The lithological boundary between the massive beddings of carbonated and the non-carbonated rock types (Figure 4.3(c1)) was accounted for in four composite rock types.

The properties of the homogeneous rock types were upscaled by averaging the properties of the two combined rock types to determine the properties of the heterogeneous composite units. Table 4.4 shows their averaged mineral composition, upscaled porosity, horizontal and vertical permeabilities. The minimum porosity and horizontal permeability were characteristic of the massive bedding rock types with mudstone as the non-carbonated lithology while the maximum porosity and vertical permeability were characteristic of the cross bedding rock types. The minimum vertical permeability was characteristic of the planar bedding rock types with mudstone and siltstone as constituent lithologies.

The maximum horizontal permeability was seen for the planar bedding rock types with siltstone lamina within coarse sandstone rock type. The highest proportion of clay content was seen for the rock types characterised by planar bedding with mudstone lamina while high carbonate content was characteristic of the composite units characterised by massive bedding interface between the carbonated and the non-carbonated lithologies.

Rock Type Composition	Sedimentary Heterogeneity	Abbreviation Used
Coarse sandstone and fine sandstone	Cross bedding	X_{CSst}^{FSst}
Mudstone and coarse sandstone	Planar bedding	P_{CSst}^{Mst}
Mudstone and fine sandstone	Planar bedding	P_{FSst}^{Mst}
Siltstone and coarse sandstone	Planar bedding	P_{CSst}^{Slt}
Siltstone and fine sandstone	Planar bedding	P_{FSst}^{Slt}
Mudstone and siltstone	Planar bedding	P_{Slt}^{Mst}
Carbonate-cemented sandstone and coarse sandstone	Massive bedding	M_{CSst}^{CbSst}
Carbonate-cemented sandstone and fine sandstone	Massive bedding	M_{FSst}^{CbSst}
Carbonate-cemented sandstone and siltstone	Massive bedding	M_{Slt}^{CbSst}
Carbonate-cemented sandstone and mudstone	Massive bedding	M_{Mst}^{CbSst}

Table 4.3. Composition and sedimentary structures as deduced from cores for ten heterogeneous rock types at 5 cm discretization scale.

Rock Type	Porosity (fraction)		Vertical Permeability (md)		Horizontal Permeability (md)		k_v/k_h	Mineral Composition (fraction)		
	Mean	SD	Mean	SD	Mean	SD		Framework	Clay	Carbonate
X_{CSst}^{FSst}	0.284	0.0081	386	131	386	131	1	0.8446	0.1470	0.0084
P_{CSst}^{Mst}	0.232	0.0152	1.32	0.81	1800	749	0.000733	0.6688	0.3161	0.0151
P_{FSst}^{Mst}	0.229	0.0130	1.29	0.78	226	85.2	0.00571	0.6382	0.3467	0.0151
P_{CSst}^{Slt}	0.233	0.0212	30.3	12.9	1830	748	0.0166	0.7510	0.2393	0.0096
P_{FSst}^{Slt}	0.229	0.0193	22.7	8.76	252	87.3	0.0901	0.7205	0.2700	0.0096
P_{Slt}^{Mst}	0.179	0.0249	1.1	0.61	27.9	11.9	0.0394	0.5447	0.4390	0.0163
M_{CSst}^{CbSst}	0.225	0.0268	5.58	2.49	1800	749	0.00309	0.8271	0.0998	0.0732
M_{FSst}^{CbSst}	0.222	0.0278	5.5	2.44	228	85.2	0.0241	0.7965	0.1304	0.0731
M_{Slt}^{CbSst}	0.172	0.0326	4.81	1.97	29.7	11.9	0.1619	0.6207	0.2994	0.0799
M_{Mst}^{CbSst}	0.171	0.0296	1.39	0.74	3.9	1.45	0.356	0.7030	0.2227	0.0744

Table 4.4. Upscaled porosity, permeability, ratio of vertical to horizontal permeability and averaged mineral composition for the ten composite rock types at 5 cm resolution.

4.3.2. Lithotype log generation and statistical analysis

The color shades were cross plotted against the available mineral composition from core samples for the corresponding depths with red, blue and green channel values cross-correlated against the averaged framework, clay and carbonate contents, respectively (Figure 4.5). The coefficients of determination for the three cross-

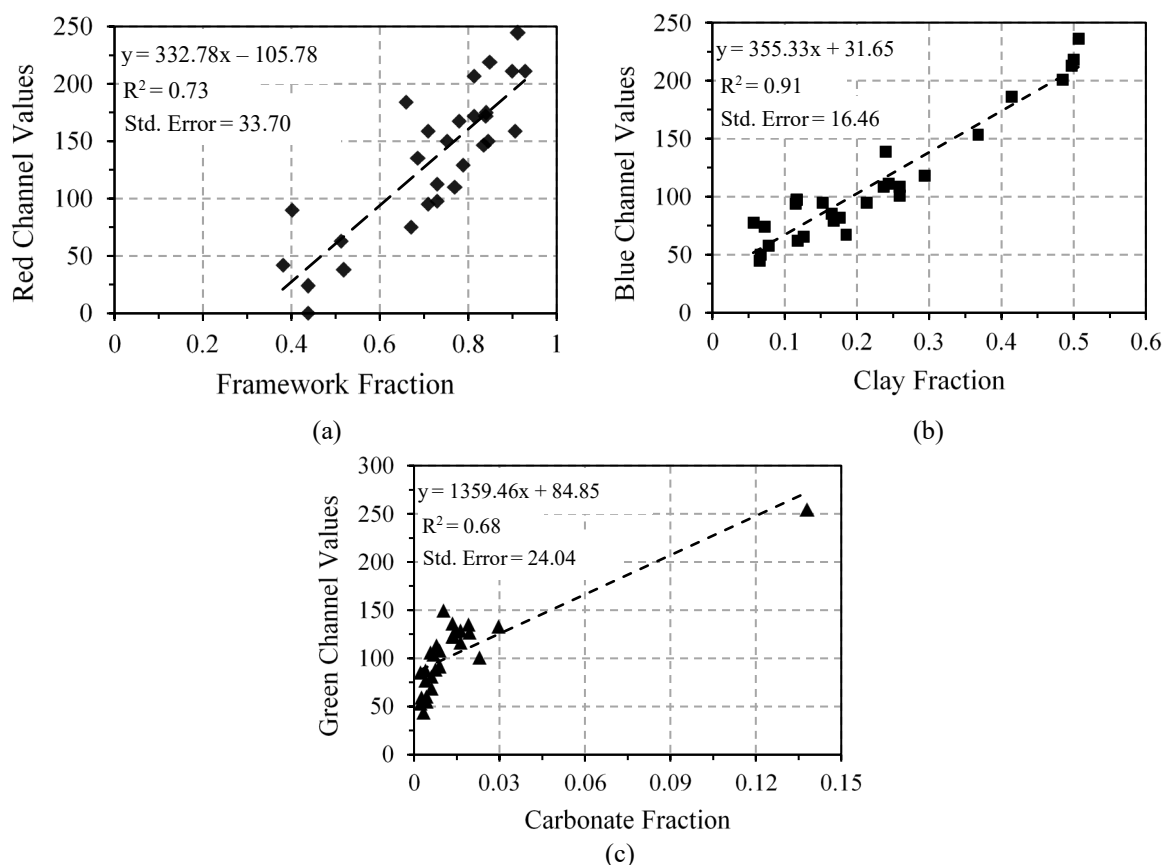


Figure 4.5. Cross correlation between (a) average red channel values and framework content, (b) average blue channel values and clay content, and (c) averaged green channel values and carbonate content for the 15 rock types defined at 5 cm discretization scale.

plots were 0.73, 0.91 and 0.68, respectively. The lower coefficient of determination associated with the cross-plot of green channel values against the carbonate content is due to the low number of samples with high carbonate content. The regression equation has been constrained in this cross-plot using the only core sample classified as carbonate-cemented sandstone. A t-test analysis was performed for the three correlations and showed that all the correlations were significant at 99% confidence level.

The color shade ranges for the 15 rock types are presented in Figure 4.6 and result in the lithotype logs for the two wells. Standard error associated with the regression fits was accounted for while determining the range of color shade values.

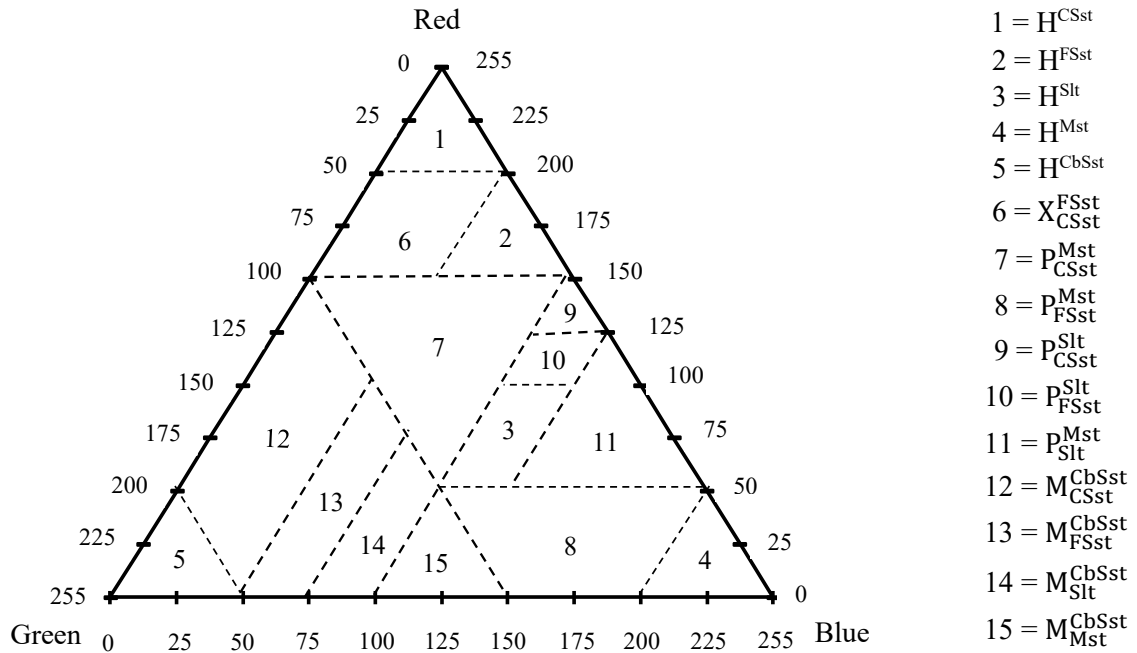


Figure 4.6. RGB color code ranges for the 15 rock types at 5 cm discretization scale.

The depth logs for facies and the derived rock types were compared to constrain the proportion of the rock types in different facies (Figure 4.7).

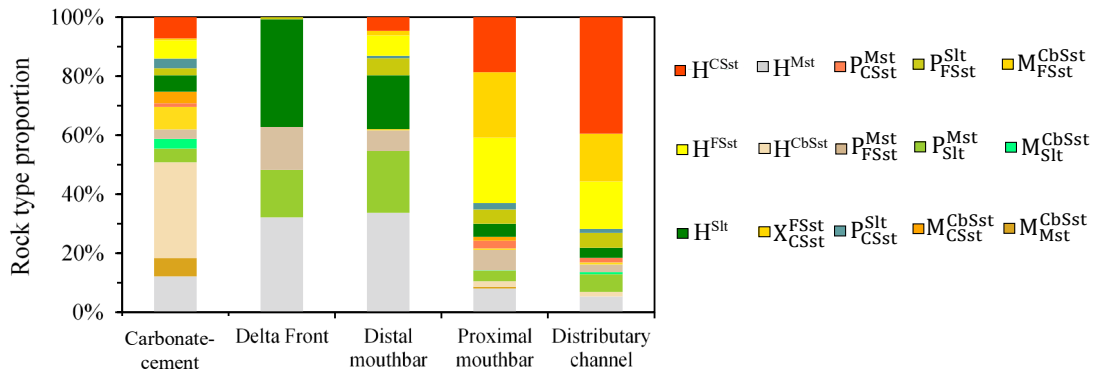


Figure 4.7. The proportion of different rock types in each of the five depositional facies.

4.3.3. High resolution reservoir model

The seismic scale geological anisotropy and the degree of spatial connectivity in facies and their associated rock types were incorporated from the available seismic data by analysing spatial variability of textural dissimilarity attribute (Figure 4.8).

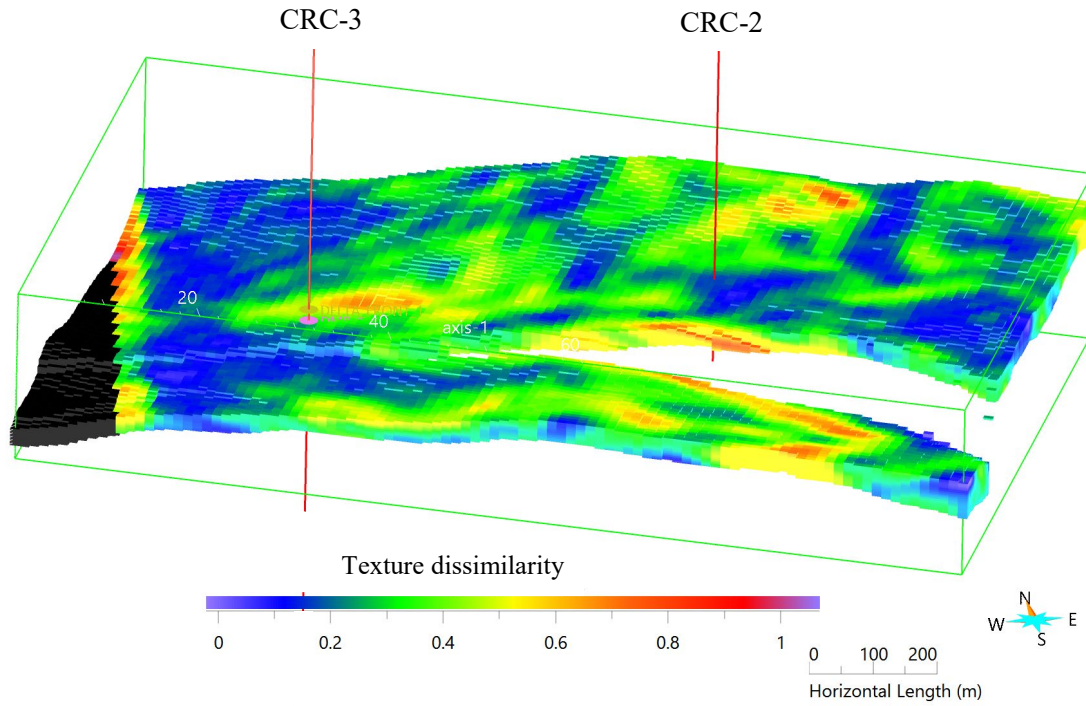


Figure 4.8. 3D variation of the seismic attribute texture dissimilarity for Parasequence-1, Paaratte Formation. The attribute is sensitive to variations in lithology and porosity at seismic scale. The seismic survey used is M0, which was the survey done prior to CO₂ injection. The black region represents an absence of seismic data while the gap in stratigraphic layer is due to the presence of a fault.

The derived triple nested variogram model (Figure 4.9) provided the best fitting to the input data. Three levels of anisotropy in heterogeneity pattern are evident (Figure 4.9b) which govern the spatial connectivity of rock properties in the geostatic model. Several realizations of the variogram models were developed. However, the final choice of the parameters was constrained by the correspondence between the subsequent distribution of depositional facies to those reported in literature (Dance et al., 2019).

Figure 4.10 shows the generated facies and rock type distributions. The model dimension is 760 m (horizontal) and 40 m (vertical). Grid cells had a horizontal resolution of 1 m for both the distributions while the vertical resolution of the facies distribution was 15 cm against the vertical resolution of 5 cm characteristic of the rock type model. The choice of lateral grid size resolution is based on the findings of previous studies where it has been shown that the depositional facies are continuous between the wells for at least a distance of 100 m (Dance et al., 2019). The 2D model had a total of 591,352 grid cells.

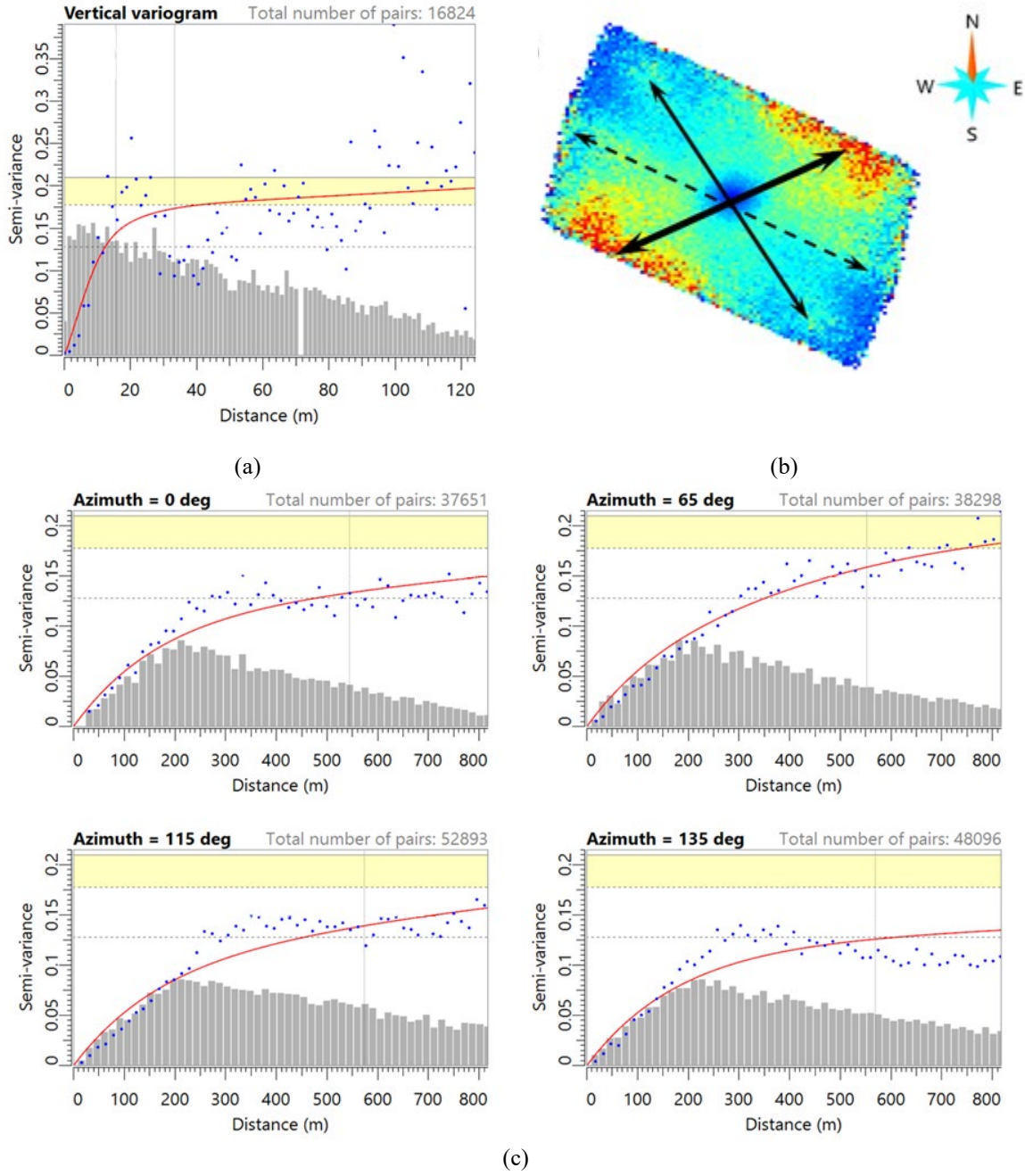


Figure 4.9. (a) Vertical variogram of texture dissimilarity. The dots represent experimental variograms while the red line indicates the fitted variogram models. (b) Variogram map of the seismic attribute with the directions of spatial anisotropy indicated by arrow. (c) Horizontal variograms of texture dissimilarity at 0, 65, 115 and 135 degree azimuth. The dots represent experimental variograms while red lines indicate the fitted variogram models. The fitted variogram models are triple nested combined Gaussian and Exponential Variograms.

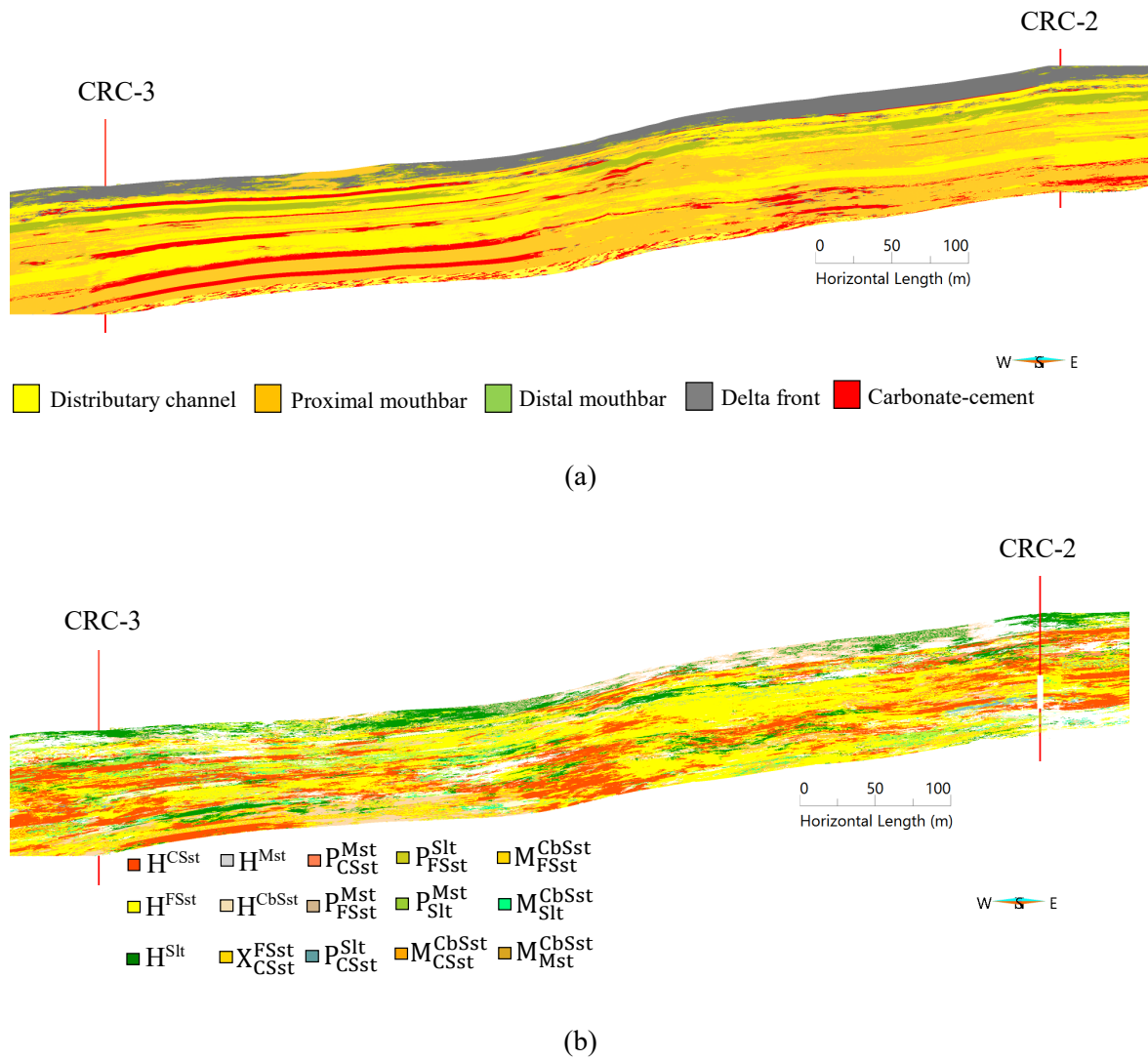
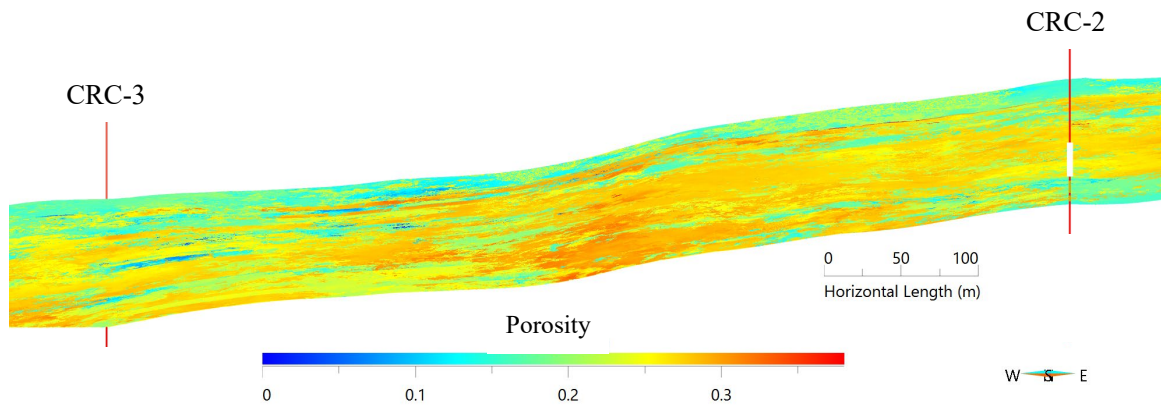


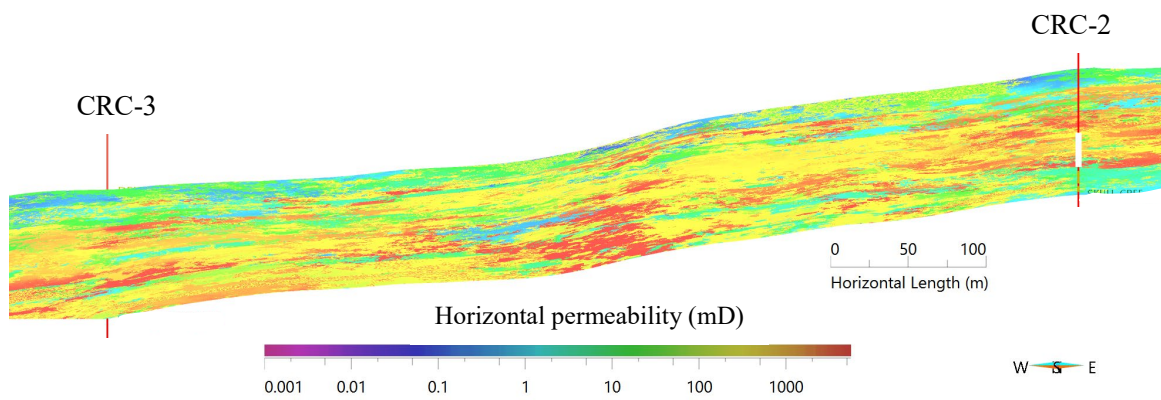
Figure 4.10. 2D reservoir model for Parasequence-1, Paaratte Formation with (a) facies distribution, and (b) rock type distribution. The figures have a vertical exaggeration of 2x.

The depositional facies model indicated that the distributary channels and the carbonate-cemented zones exist as discontinuous bodies in contrast to the delta front facies which exists as a continuous geobody (Figure 4.10a). The rock type model (Figure 4.10b) is a downscaled version of the depositional facies model (Figure 4.10a) where the distribution of the 15 rock types in each of the five depositional facies can be seen. The downscaling is useful in capturing the mm-scale sedimentary heterogeneity while also integrating regional anisotropy in rock properties. The facies model, in contrast, captures only the regional scale sedimentary heterogeneity.

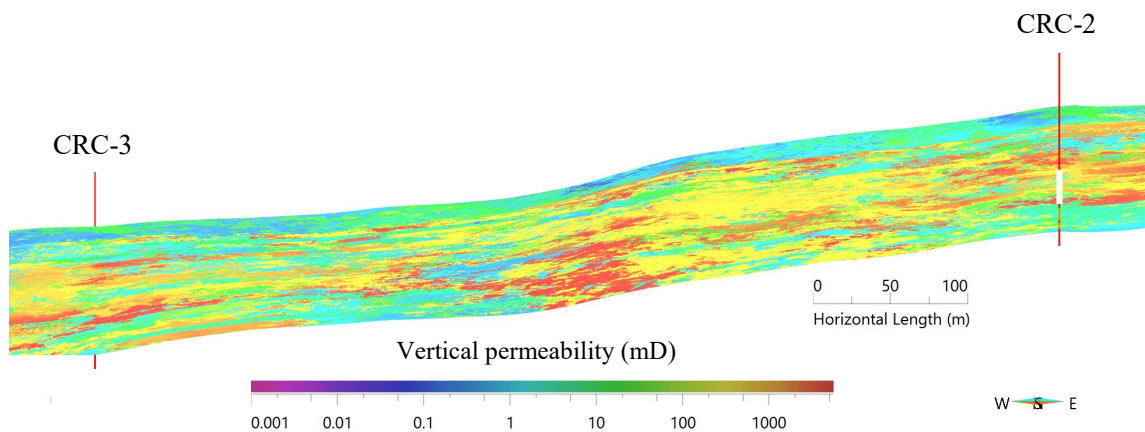
Porosity and permeability values (Tables 4.2 and 4.4) are populated in the rock type model (Figure 4.11). The distribution indicated the presence of lateral high porosity-high permeability streaks. The highest



(a)



(b)



(c)

Figure 4.11. 2D reservoir model for Parasequence-1, Paaratte Formation with the distributions of (a) porosity, (b) horizontal permeability, and (c) vertical permeability. The figures have a vertical exaggeration of 2x.

values of permeabilities were observed in the zone of flexural bending present in the middle portion of the model. The distribution of porosity and permeability values honours the regional heterogeneity in depositional facies. Higher porosity and permeability values are characteristic of distributary channels and proximal mouth bars while delta front and distal mouth bars comprise low porosity and permeability values. Overall there is a

good correspondence between the population of horizontal and the vertical permeability values. The zones with higher horizontal permeability also depict higher vertical permeability (Ringrose et al., 2005).

4.4. Discussion

4.4.1. Benefits of the presented workflow

The algorithm (Figure 4.1) presents an approach to obtain modified lithotype logs of the composite rock types. The modified logs serve as the means between the properties at mm-scale and the properties that are ultimately populated in the reservoir model, thereby bridging the gap between the two scales. The workflow overcomes the challenges associated with conventional reservoir modelling approaches where mm-scale heterogeneity is typically not accounted for (Avseth et al., 2010; Corbett et al., 1992). Usually, image based stochastic models are used to characterise sedimentary heterogeneity (Boeker et al., 2017; Colombero et al., 2012; Koltermann and Gorelick, 1996; Strebel, 2002). These models, however, suffer from a basic limitation. The statistically generated images are typically based on sedimentary structures observed in the outcrops, and while dynamic flow and reactive transport simulations based on these images may be useful for understanding the nature of fluid flow locally at the outcrop scale, the information cannot be confidently translated and utilised as a lithotype log. Hence their use in the reservoir scale studies is limited as there is no means to populate them in reservoir models in the absence of lithotype logs. The primary advantage of the presented workflow is that it guides the modification of lithotype logs and the associated homogeneous rock types such that they can be discretised at a scale which is feasible to implement in the reservoir models. The logs are further used to downscale the depositional facies model. The obtained rock type model sits nested within the larger depositional facies model thereby adding to the conventional geological modelling approaches. This allows the direct integration of mm-scale rock properties in the reservoir models.

Secondly, the workflow is used to determine the exact number and the composition of composite rock types using their color shade codes. This is essential for designing appropriate methodologies for upscaling different rock properties. A lack of this information might lead to a misinformed characterization and upscaling of the composite rock types which ultimately will lead to a loss of correspondence between the regional and sub-meter scale rock properties in the reservoir model.

Thirdly, the workflow can also be used to determine the maximum number of possible rock types that might be required to characterize a reservoir at various scales of discretization (Figure 4.12). For a reservoir composed of three homogeneous rock types at the highest resolution, the maximum number of rock types increases to six and nine at the next two coarsening scales. For a reservoir with five homogeneous rock types at the highest resolution, the coarse scale characterization would require a maximum of 15, 25, 30 and 31 rock types at the next four coarse scales, respectively. However, the actual number of rock types needed to characterise the reservoir might be less and can be determined on a case-by-case basis using the presented workflow. This implies that even though upscaling reduces the computational costs associated with dynamic simulations, a greater number of rock types are needed to characterise a coarsely discretised reservoir in the first place.

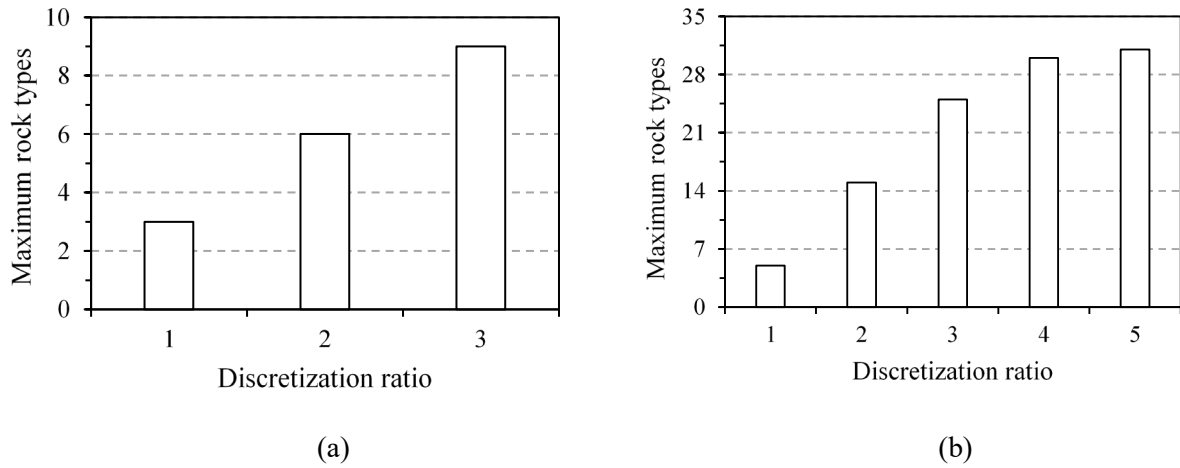


Figure 4.12. The maximum number of rock types required to cover the range of heterogeneity at different scales of coarsening for a heterogeneous reservoir with (a) 3 homogeneous rock types, and (b) 5 homogeneous rock types at the highest resolution. The discretization ratio is defined as the given reservoir resolution relative to the maximum reservoir resolution.

Fourthly, the rock types integrate various rock properties in one class. This reduces the need to build separate variograms for individual rock properties as is done in conventional geostatic modelling approaches (Ringrose and Bentley, 2015). The presented approach makes it possible to use only one variogram model for the population of all the rock properties in the reservoir while also preserving the spatial correlation of properties. Populating the properties separately increases the risk of generating unrealistic combination of rock properties in certain voxels. The presented approach overcomes this limitation and ensures that a given voxel has a realistic combination of different properties. This is evident from the presented models (Figures 4.10 and 4.11) where zones of high porosity are also zones of high permeability.

Finally, the downscaling of depositional facies model to rock type model (Figure 4.10) presents a more accurate representation of lithological heterogeneity as it allows to capture intra-facies variability in rock properties. The facies model forms the basis for rock property population in the conventional reservoir modelling approach. As can be seen from Figure 4.10, distributary channels facies are laterally extensive over hundreds of meters and are expected to serve as a preferential flow path. The rock type model (Figure 4.10b) enhances the facies model as it captures flow barriers within the distributary channel facies. It allows to account for the presence of low permeability rock types within the length of the channel. This is expected to lead to a discontinuity in the extent of high permeability streaks and has important implications in dynamic simulations as the lateral migration of fluid may be significantly impeded.

4.4.2. Limitations of the presented workflow

While the work flow has several advantages, there are also some inherent disadvantages. Firstly, the application of work flow is dependent on the availability of core and wireline log data. In the absence of core data, it is not possible to integrate the mm-scale heterogeneity in the lithotype logs using the presented approach. Secondly, it is beneficial to define the composite rock types such that their dimension is similar to that of the cores. This allows to easily determine the thickness of sedimentary units in the models used for rock

property upscaling. The dissimilarity in dimension of the two, if any, will increase the complexity of upscaling domains and needs to be accounted for in the characterization of the composite rock types.

4.4.3. The use of mineral composition in determining statistical significance

The study shows that the use of mineral group fractions to compute the significance of the composite rock type properties is statistically robust (Figure 4.5). Firstly, the use of mineral composition provides the convenience of validating each color channel contributing to the colorlith. This is especially important as no other rock property can be expressed as a combination of three end members which can then be correlated against the three color channel values. Secondly, the cross correlations are significant at 99% confidence levels with high values of the coefficients of determination. This gives confidence in using quantitative mineral composition data to characterize the composite rock types.

4.5. Conclusions

This study presents and demonstrates a new approach for systematically modifying the conventional lithotype logs in terms of composite rock types. This has two advantages: firstly, mm- to cm-scale lithological heterogeneity is accounted for in the definition of composite rock types and secondly, technical limitations associated with reservoir model discretization are overcome. The workflow determines the number of composite rock types and their composition in a structured manner. This step is important as it overcomes any bias associated with the choice of upscaling domains and leads to a correspondence of properties during the downscaling of the coarsely discretised depositional facies model. The upscaled properties are tied to the determined composite rock types and their depth logs are generated. The modified lithotype logs are useful in obtaining reduced yet confident variograms while accounting for the spatial correlation in the properties. The outcomes from the workflow are backed by core data which gives confidence in the utilizing and generalizing the presented approach.

Chapter 5

Quantification of the turning point saturation for cross bedded CO₂ storage reservoirs

5.1. Introduction

Geological carbon storage is deemed to be an effective technology mitigating global warming (Benson and Orr, 2008; Friedmann, 2007; Metz et al., 2005). As part of this scheme, CO₂ is injected into a geological reservoir where it is permanently stored via one or more of the four different trapping mechanisms: stratigraphic, structural, residual and mineral trapping (Friedmann, 2007; Metz et al., 2005). The storage capacity of the four trapping mechanisms has been well documented for different reservoirs (Bickle et al., 2007; Bradshaw et al., 2000; Metz et al., 2005; Pires et al., 2011; Steeneveldt et al., 2006). Most of these studies have focused on relatively homogeneous reservoirs in terms of lithology (Baklid et al., 1996; Ennis-King and Paterson, 2002; Korbøl and Kaddour, 1995; Pruess et al., 2003; Van der Meer, 1996).

However, CO₂ storage reservoirs are often lithologically heterogeneous (Doughty et al., 2001; Flett et al., 2005; Law and Bachu, 1996; Lindeberg, 1997). Reservoir heterogeneity can be characterized based on properties and scale of interest. In this study, we address heterogeneity in terms of flow and petrophysical properties like porosity, permeability and capillary pressure, at mm- to cm-meter scale. At such scales, lithological heterogeneity exists as intraformational baffles (Gibson-Poole et al., 2009; Yu et al., 2017), which are rock units with a higher capillary entry pressure due to their finer grain size compared to adjacent rock units. The baffles are usually interbedded within high-porosity and -permeability reservoir rocks to a varying extent (Flett et al., 2007). Due to their low porosity and permeability and high capillary entry pressure, the intraformational baffles control fluid flow pathways and act as flow barriers (Frykman et al., 2009; Green and Ennis-King, 2010a). This retards the migration of supercritical CO₂ to shallow depths rising under buoyancy and leads to capillary heterogeneity trapping in addition to residual trapping by a snap-off mechanism within the pore space (Gershenzon et al., 2017; Krevor et al., 2011; Li and Benson, 2015; Saadatpoor et al., 2010b; Trevisan et al., 2017). Lithologically heterogeneous reservoirs with higher volumetric proportions of intraformational baffles might trap a significant additional volume of CO₂ by local capillary forces compared to the homogeneous reservoirs by local capillary forces (Flett et al., 2007; Saadatpoor et al., 2010b).

In a heterogeneous siliciclastic reservoir, intraformational baffles exist as a part of different sedimentary structures such as cross bedding, flaser bedding and lenticular bedding (Miall, 2016). Out of these, cross bedding is one of the most prominent sedimentary structures characteristic of reservoir rocks, for example in the coastal to shallow marine deposits of the Paaratte Formation, Otway Basin (Australia) (Mishra et al., 2020). The cross bedding usually forms by the downstream migration of sediments along the flow direction within a distributary channel depositional facies environment. The sediment migration creates alternate dipping layers of coarse grained beds known as foresets and fine grained sediments known as lamina. The lamina layers have a

maximum thickness of 1 cm while the foresets are usually a few centimetres thick (Miall, 2016). In a cross bedded strata, lamina act as intraformational baffle while foreset beds act as reservoir rocks.

The cross bedded strata might significantly affect the migration of supercritical CO₂ and enhance capillary heterogeneity trapping (Corbett et al., 1992; Honarpour and Saad, 1994; Huang et al., 1996; Ringrose et al., 1993; Saad et al., 1995). This is mainly because of the geometry of intraformational baffles comprising cross bedding. The foreset beds typically have a lens like shape and are completely enveloped by mm- to cm-thick lamina layers (Miall, 2016; Reineck and Singh, 1975) (Figure 5.1a). The capillary heterogeneity trapping of supercritical CO₂ within the foreset beds is expected to be enhanced because of this specific geometry of cross beddings compared to baffles with other geometries such as planar laminations. The enveloping shape of lamina implies that under low fluid flow velocities, the CO₂ flow paths within the foreset are limited essentially to vertical direction due to buoyancy and the lateral migration of CO₂ will be restricted by the presence of dipping laminae. On the contrary, the planar bedded baffles are characterised by a limited lateral dip of laminae resulting in lateral fluid flow pathways allowing CO₂ to migrate around the baffle (Green and Ennis-King, 2010a; Green and Ennis-King, 2010b; Green and Ennis-King, 2013; Li and Benson, 2015; Saadatpoor et al., 2009a; Saadatpoor et al., 2010a; Saadatpoor et al., 2010b; Saadatpoor et al., 2013). Capillary trapping in such planar bedded reservoir rocks is higher than in homogeneous reservoirs (Ni et al., 2019), but could be significantly lower than in a cross bedded reservoir rock.

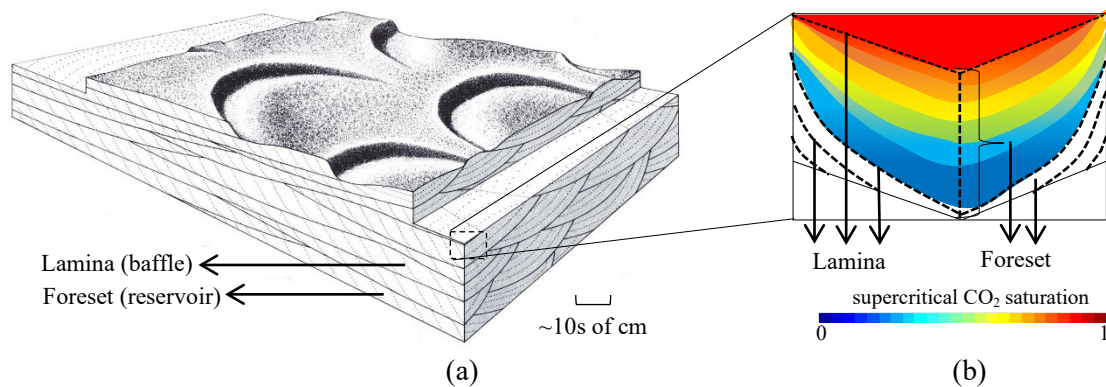


Figure 5.1. (a) Conceptual representation of the lens shaped, or convex, geometry of cross bedded strata in 3D (modified after Reineck and Singh, 1975). The black stippled lines represent lamina which act as intraformational baffle while the white space between the stippled lines represents foreset beds which acts as the reservoir rock; (b) A conceptual representation of a single foreset bed enveloped by lamina with distribution of turning point CO₂ saturations at the end of drainage before CO₂ migrates into the baffle.

Under a capillary limited flow regime, CO₂ injected below a cross bedded stratum rises under buoyancy during drainage and reaches the interface between the foreset rock and the overlying lamina. Due to higher capillary entry pressure characteristic of the lamina, the up-dip migration of CO₂ is impeded and it starts accumulating underneath the lamina. This increases CO₂ saturation below the foreset-lamina interface (Figure 5.1b). Additionally, the presence of dipping lamina layers around the foreset bed restricts lateral CO₂ migration. CO₂ saturation increases over time within the foreset bed resulting in an increase of buoyancy

pressure. Once the buoyancy pressure of CO₂ exceeds the entry pressure characteristic of the lamina, CO₂ migrates into the lamina (Bech and Frykman, 2018; Naylor et al., 2011). At this stage, CO₂ saturation below the foreset-lamina interface reaches its maximum, or turning point, value (Figure 5.1b) but is typically smaller than the end point CO₂ saturation value at irreducible water content post drainage. After the turning point saturation is reached, CO₂ saturation within the foreset layer decreases during imbibition.

Given the high volume proportion of cross beddings in sedimentary reservoir rocks and their potential for enhanced capillary heterogeneity trapping compared to other baffle geometries, it is important to explore the range of CO₂ turning point saturation within the foreset beds and the governing factors. The turning point saturations vary between a maximum value below the lithological interface and a minimum value at the bottom of the foreset layer (Figure 5.1b) (Bech and Frykman, 2018). A characterization of maximum turning point saturation in cross bedding is important as it provides a key parameter for the determination of the maximum expected amount of capillary trapping (Carlson, 1981; Jerauld, 1997; Kleppe et al., 1997; Land, 1968; Spiteri et al., 2008; Suzanne et al., 2003).

For heterogeneous reservoirs, several studies have focused on understanding fluid flow migration (Green and Ennis-King, 2010a; Green and Ennis-King, 2010b; Li and Benson, 2015; Saadatpoor et al., 2009a), the impact of hysteresis of relative permeability (Ataie-Ashtiani et al., 2002; Juanes et al., 2006; Honarpour et al., 1995) and capillary pressure curves (Bech and Frykman, 2018; Pini and Benson, 2017) on trapping and a quantification of capillary heterogeneity trapping (Green and Ennis-King, 2013; Krevor et al., 2011; Ni et al., 2019; Saadatpoor et al., 2013). Many of these studies are based on heterogeneous domains where intraformational baffles are planar and have limited lateral dip and extent (Green and Ennis-King, 2010a; Green and Ennis-King, 2010b; Li and Benson, 2015; Saadatpoor et al., 2009a). Hence, turning point saturation determined from these studies cannot be applied to reservoirs with cross bedding due to differences in the flow dynamics caused by the baffle geometry. Certain studies have considered cases with laminations perpendicular to flow (Bech and Frykman, 2018; Burnside and Naylor, 2014; Ni et al., 2019), thereby serving as approximations to cross bedding. However, a range of possible maximum turning point saturations expected for different rock types in cross bedded strata has not been determined (Burnside and Naylor, 2014). The rock types are expected to significantly impact the magnitude of maximum turning point saturation relative to CO₂ saturation corresponding to irreducible water saturation. Additionally, previous studies have shown that residual trapping is dependent on a range of rock properties (Chatzis and Morrow, 1984; Geistlinger et al., 2014; Holtz, 2009, 2002; Iglauder et al., 2011; Krevor et al., 2015; Ruspini et al., 2017) and have quantified the relative dependence of trapping (Ni et al., 2019) and plume speed (Li and Benson, 2015) on various rock properties and their associated heterogeneity. However, the impact of common rock properties and their heterogeneity on turning point saturation has not been quantified in absolute terms for a cross bedded strata. Also, the range of rock properties are usually implemented in a limited number of model domains (Bech and Frykman, 2018; Li and Benson, 2015; Ni et al., 2019). A limited range of simulations may mean the derived turning point saturation is not well constrained and introduces a larger uncertainty.

This study addresses the following three objectives in order to better understand and predict turning point saturation in cross-bedded sediments. Firstly, the range of maximum CO₂ saturation within the foreset layer during drainage is modelled for a time before CO₂ invades the lamina. The range is determined for different rock types and flow conditions typically characteristic of cross beddings. Secondly, the dependence of maximum turning point CO₂ saturation on different rock properties and their associated heterogeneity is quantified in absolute terms. Thirdly, regression models are derived determining the maximum turning point saturation directly from intrinsic rock properties.

5.2. Methodology

5.2.1. Geostatic modeling

The dimensions of cross bedding foresets and laminae have been determined using core sample data from the Paaratte Formation, Otway Basin (Australia), which is a heterogeneous siliciclastic sequence located in the state of Victoria, Australia (Dance, 2018). The cross bedded strata constitutes about 16% of the sequence (Mishra et al., 2020). The samples comprise coarse grained, lens shaped foresets with a thickness 2 to 3 cm enveloped by fine grained laminae with a thickness of 0.5 to 1.0 cm (Figure 5.2a) (Mishra et al., 2019). The variation of maximum turning point saturation within a single foreset layer is primarily an interfacial phenomenon due to the geometry of the dipping laminae restricting lateral CO₂ migration. Hence, lithological interfaces between the lamina and the foreset layers were represented in 1D and 2D geostatic models. The 1D models capture the lithological interface between the foreset and the lamina (Figure 5.2b) while the lens-like shape characteristic of foresets is implemented in the 2D models (Figure 5.2c). The models were constructed in PetraSim v5 (Alcott et al., 2006) and measured 5 cm horizontally and 3 cm vertically. A foreset layer of 2.5 cm thickness overlaid by a lamina with a thickness of 0.5 cm made up the 1D model (Figure 5.2b). The 2D models were composed of three layers of lamina each of 0.5 cm thickness and foreset deposits within and below the lamina (Figure 5.2c). The 1D model was discretized into grid cells with a length of 5 mm and a height of 1 mm resulting in a total of 300 cells (Figure 5.2b). The 2D model was discretized into 1 mm by 1 mm grid cells resulting in a total of 1500 cells (Figure 5.2c). The 1 mm resolution of models is the finest recommended resolution for the application of Darcy's law under the continuum scale assumption (Li and Benson, 2015).

2D models capture lithological heterogeneity of cross bedding better than 1D models, however, the computational time associated with dynamic simulations performed on 2D models is significantly larger and was deemed unreasonable for the large number of realizations. Also, the build-up of CO₂ underneath the lamina is a one dimensional process which takes place only along the vertical direction with the dipping laminae serving as flow barriers to the lateral migration of CO₂. Hence, 1D models with closed side boundaries were considered most suitable to determine the maximum turning point saturation before the entry of CO₂ into the lamina for a range of lithologies found in cross bedding structures. The 2D models are used to verify that there is no bias introduced in the estimates of maximum turning point saturation from 1D models due to a simplified representation of lithological heterogeneity.

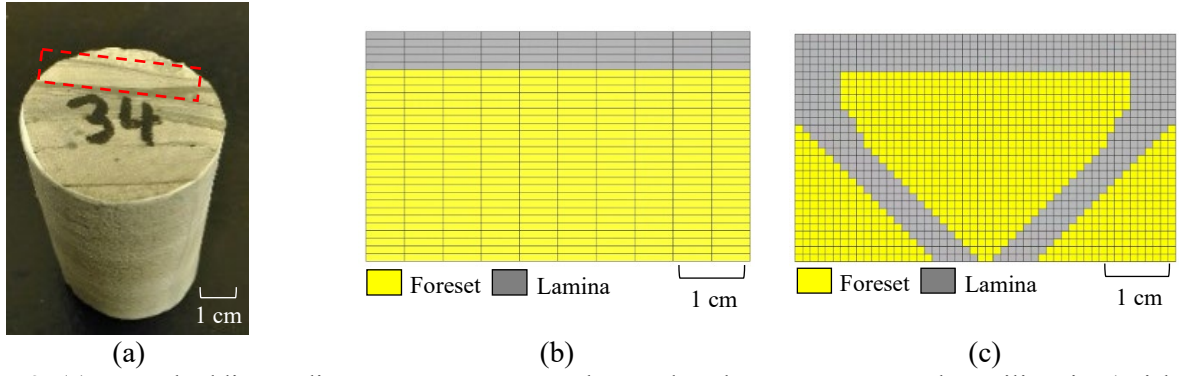


Figure 5.2. (a) Cross bedding sedimentary structure as observed at the Otway Research Facility site (Mishra et al., 2019). The area highlighted within the red box shows the lens shaped coarse grained foreset deposit in light grey shade enveloped by fine grained lamina in dark grey shade. (b) The implemented 1D model consisting of the interface between 0.5 cm thick lamina and 2.5 cm thick foreset. The model has a length of 5 cm and a height of 3 cm with a grid size resolution of 5 mm horizontally and 1 mm vertically. (c) The implemented 2D model characterized by lens shaped forest deposit enveloped by 0.5 cm lamina. The model has a length of 5 cm and a height of 3 cm with a grid size resolution of 1 mm along both the dimensions.

5.2.2. Implemented lithological properties

The geostatic model realizations were populated with four rock type classes characteristic of cross bedding structures according to a previous study (Mishra et al., 2019): coarse sandstone, fine sandstone, siltstone and mudstone. The rock types incorporate the range of heterogeneity in terms of porosity (ϕ), permeability (k_p) and capillary entry pressure (P_e) at cm-scale (Table 5.1). The drainage relative permeability-saturation curves for water and CO_2 phases were implemented using the van Genuchten-Mualem formulation (Mualem, 1976; Van Genuchten, 1980; Xu et al., 2004b):

$$k_{r,w} = s_{e,w}^{1/2} \left(1 - \left(1 - s_{e,w}^{1/m} \right)^m \right)^2 \quad (5.1)$$

$$k_{r,\text{CO}_2} = (1 - s_{e,w})^2 (1 - s_{e,w}^2) \quad (5.2)$$

where,

$k_{r,w}$ = water relative permeability,

k_{r,CO_2} = CO_2 relative permeability,

m = empirical parameter for the water relative permeability-saturation drainage curve,

$s_{e,w}$ = effective water saturation.

The effective water saturation is given as follows:

$$s_{e,w} = \frac{S_w - S_{w,\text{irr}}}{1 - S_{w,\text{irr}}} \quad (5.3)$$

where,

S_w = water saturation,

$S_{w,\text{irr}}$ = irreducible water saturation.

The transformed form of Brooks-Corey capillary pressure curve was used to incorporate the effect of entry pressure and entry-slope region in the van Genuchten capillary pressure formulation (Brooks and Corey, 1964; Li et al., 2013; Van Genuchten, 1980):

$$P_c = \begin{cases} Pe \left(\frac{S_w - S_{w,irr}}{1 - S_{w,irr}} \right)^{-1/\lambda} & \text{if } S_{w,irr} \leq S_w \leq 1 - S_{nt} \\ \frac{Pe}{S_{nt}} \left(\frac{1 - S_{nt} - S_{w,irr}}{1 - S_{w,irr}} \right)^{-1/\lambda} (1 - S_w) & \text{if } 1 - S_{nt} < S_w \leq 1 \end{cases} \quad (5.4)$$

where,

P_c = CO₂ capillary pressure (Pa),

Pe = capillary pressure scaling parameter (Pa),

S_{nt} = threshold CO₂ saturation corresponding to entry slope region, set to be 0.005 (Li et al., 2013),

λ = empirical parameter for drainage capillary pressure curve determined from pore size distribution and can be determined from the exponent m using the following relationship (Lenhard et al., 1989):

$$\lambda = \frac{m}{1-m} (1 - 0.5^{1/m}) \quad (5.5)$$

As the aim is to determine maximum turning point saturation, only the drainage curves have been implemented in the simulations. For implementation of the curves, the following parameters were required: m , $S_{w,irr}$ and Pe . Due to a lack of measured data, the representative range of the empirical exponent ‘ m ’ for each rock type was taken from literature (Cheng et al., 2017; Hermanson and Kirste, 2013). The implemented flow and petrophysical properties are shown in Table 5.1.

For each rock type, $S_{w,irr}$ values were calculated using the following empirical relation (Holtz, 2002):

$$S_{w,irr} = 5.159 \left[\frac{\log k_p}{\phi} \right]^{-1.559} \quad (5.6)$$

where ϕ and k_p are porosity and absolute permeability values for a given rock type.

Rock types	ϕ (fraction)	k_p (mD)	m	Pe (Pa)
Coarse sandstone	0.25-0.35	1000-7000	0.6-0.7	100-1000
Fine sandstone	0.25-0.35	100-1000	0.5-0.6	100-1000
Siltstone	0.1-0.25	10-100	0.4-0.5	1000-5000
Mudstone	0.1-0.25	1-10	0.3-0.4	5000-10000

Table 5.1. The range of porosity, permeability, capillary entry pressure and exponent m for each rock type class.

5.2.3. Model realizations

Coarse and fine sandstone rock types were used to represent the foreset layer while siltstone and mudstone rock types were used for the laminae layer in geostatic models (Figure 5.2). This resulted in four combinations of rock types covering the range of heterogeneity for lamina and foreset (Table 5.2). It is recommended that about 10-15 realizations are utilized for each independent parameter so that data overfitting can be avoided in

regression analysis (Babyak, 2004). The present study implements eight independent parameters: porosity, permeability, entry pressure and relative permeability exponent ‘m’ for lamina and foreset. Hence, the required number of realizations should be between 80-120. The values of different rock properties (Table 5.1) were varied randomly to generate 30 realizations for each of the four combinations, resulting in a total of 120 realizations for 1D models.

Constituent rock types		Abbreviation used	Realization number
Lamina	Foreset		
Mudstone	Coarse sandstone	I_{CSst}^{Mst}	1-30
Mudstone	Fine sandstone	I_{FSst}^{Mst}	31-60
Siltstone	Coarse sandstone	I_{CSst}^{Slt}	61-90
Siltstone	Fine sandstone	I_{FSst}^{Slt}	91-120

Table 5.2. Description of the four scenarios of lamina-foreset combinations implemented in 1D models.

Four 2D model realizations were generated using the rock property values corresponding to realization numbers 1, 31, 61 and 91. The generated values of different rock properties for each of the 120 realizations are shown in Figure 5.3. Differences in porosity values between the two lithologies have the same range across the four scenarios (Figure 5.3a). However, the differences in permeability (Figure 5.3b) and capillary entry pressure (Figure 5.3c) values are higher for scenarios with mudstone lamina (I_{CSst}^{Mst} and I_{FSst}^{Mst}) compared to scenarios with siltstone lamina (I_{CSst}^{Slt} and I_{FSst}^{Slt}). $S_{w,irr}$ values vary between 0.05-0.6 but the difference in values between foreset and lamina layers is lower for scenarios with siltstone lamina (Figure 5.3d). The distribution of ‘m’ (Figure 5.3e) and λ (Figure 5.3f) is similar though their numerical values differ for the same realization.

Relative permeability and capillary pressure curves for the 120 realizations were generated using equations 5.1, 5.2 and 5.4. A representative curve for each of the four scenarios is shown in Figure 5.4. CO_2 relative permeability for lamina was higher than for foreset layers (Figure 5.4a). The differences in relative permeability between the lamina and the foreset layers were higher at higher CO_2 saturation. There was an order of magnitude difference between lamina and foreset capillary pressures (Figure 5.4b and Figure 5.4c). The two scenarios with mudstone lamina (realization numbers 1 and 31) showed higher lamina capillary pressure for a given value of CO_2 saturation (Figure 5.4c). The height of the entry slope region represents capillary entry pressure and was small compared to capillary pressure values achieved at intermediate to high CO_2 saturations for the foreset (Figure 5.4b) and the lamina (Figure 5.4c).

The implemented rock properties are essentially layer averaged property values. Variations of rock properties within the foreset and the lamina have not been considered in the present study. Both the layers are implemented as homogeneous rock types with layer averaged values for a given realization. This is in agreement with visual observations made on core samples (Figure 5.2a) (Mishra et al., 2019). By implementing the two lithologies as homogeneous rock units, the maximum turning point saturation can be derived for all

rock type combinations and their respective differences in rock properties. The implementation of intra-rock type heterogeneity might lead to the generation of several interfaces at grid cell scale within the homogeneous rock types. Such interfaces will be characterized by limited lateral extent and dip resulting in the migration of CO₂ around the baffles (Li and Benson, 2015). Such a scenario is not representative of a cross bedding geometry.

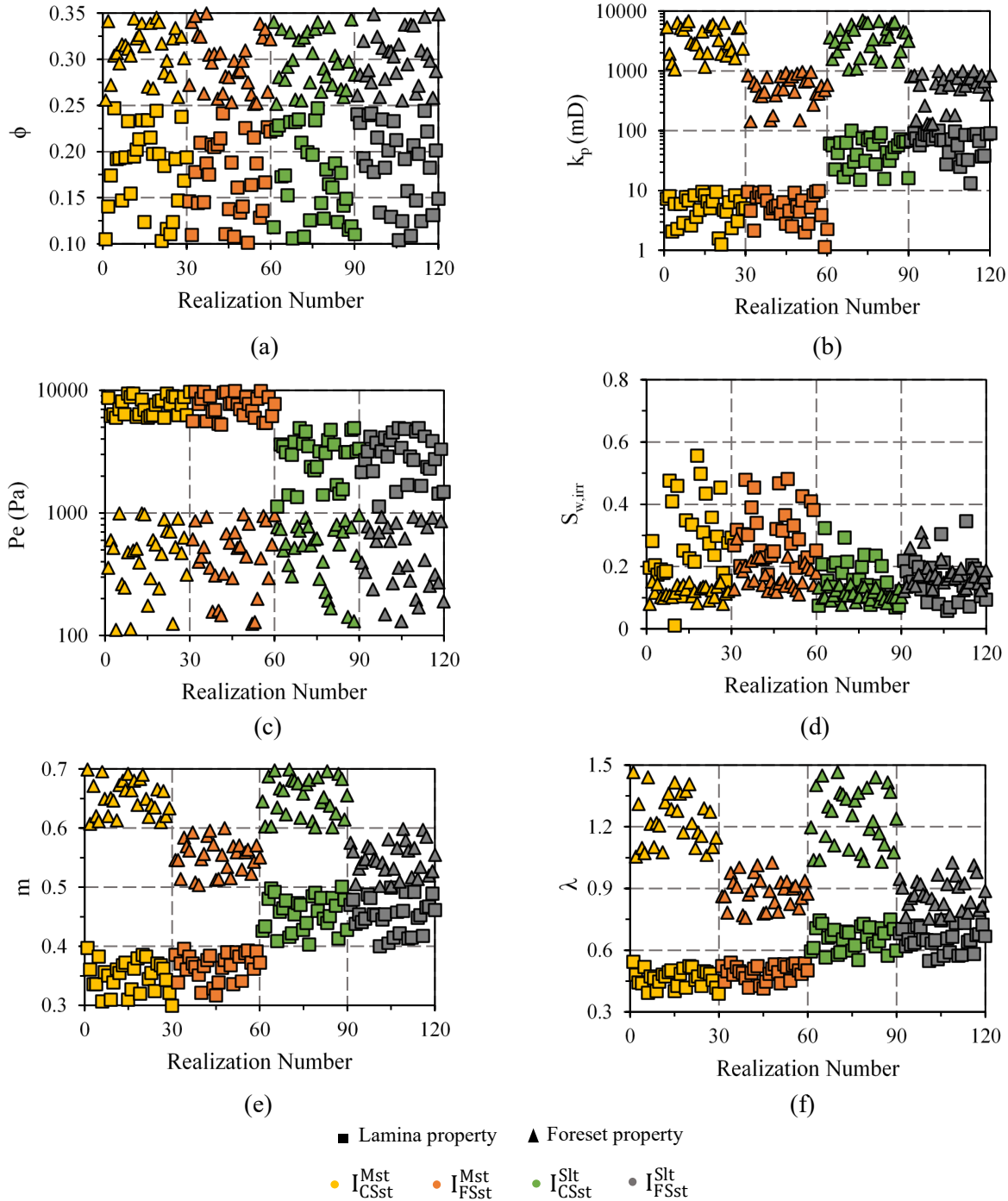


Figure 5.3. Property ranges used to populate foreset and lamina layers in 120 realizations for: (a) Porosity; (b) Permeability; (c) Capillary entry pressure; (d) Irreducible water saturation; (e) Empirical parameter m for relative permeability-saturation curve; (f) Empirical parameter λ for capillary pressure-saturation curve.

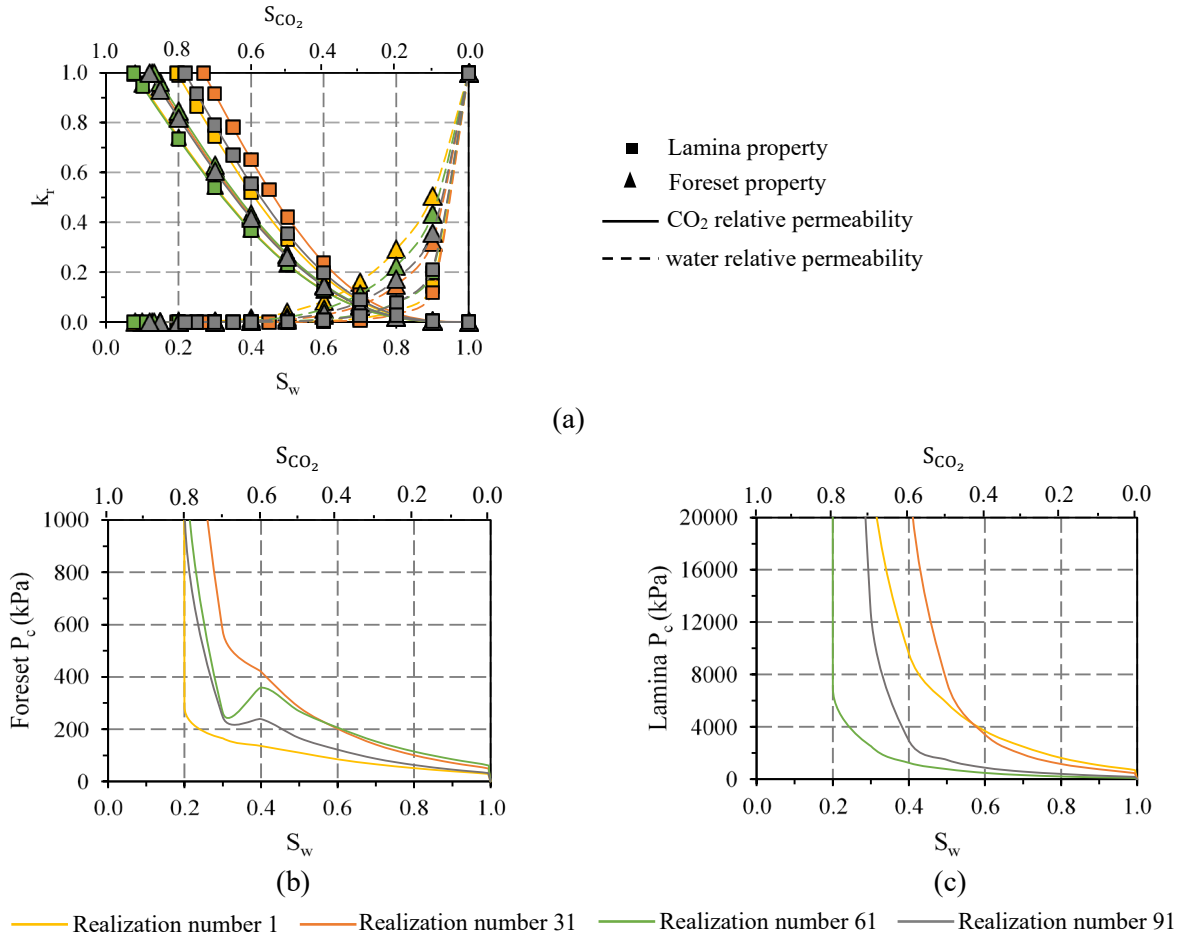


Figure 5.4. (a) Drainage relative permeability curves for CO₂ and water; (b) Drainage capillary pressure curves for foreset; and (c) Drainage capillary pressure curves for lamina for realization numbers 1, 31, 61, and 91.

5.2.4. Multiphase flow simulation set-up

Multiphase flow simulations were carried out on the constructed geostatic model realizations using the ECO2N equation of state module in TOUGH2 (Pruess, 2005). Supercritical CO₂ was injected from the base of the model at a rate of $1 \text{ g sec}^{-1} \text{ m}^{-2}$ for a duration of 30 minutes. The injection flux was used to calculate the conventional capillary number (N_c) using the following definition (Zhou et al., 2010):

$$N_c = \frac{u\mu}{\sigma} \quad (5.7)$$

where,

u = Darcy flow velocity, equal to $1.66 \times 10^{-6} \text{ m sec}^{-1}$ under the given injection flux,

μ = CO₂ viscosity, equal to $2.3 \times 10^{-5} \text{ Pa sec}$ (Chiquet et al., 2007),

σ = CO₂ water interfacial tension, equal to 35 mN m^{-1} (Espinoza and Santamarina, 2010).

The resulting capillary number is in the order of 10^{-9} indicating flow is dominated by the capillary force. This confirms that the entry of CO₂ into the lamina is not forced by high flow rates but rather occurs due to the build-up of buoyancy pressure. The accumulation of CO₂ underneath the overlying layer of lamina leads to an increase in its saturation until CO₂ enters the baffle. The side boundaries were closed to mass transport for 1D models while they were kept open for 2D models. The closed side boundaries in 1D models replicate the presence of dipping laminae characteristic of cross bedding. Simulations were carried out under a hydrostatic

pressure of 15 MPa and reservoir temperature of 60°C. CO₂ exists as a supercritical phase under these pressure-temperature conditions. The simulations were run for a period of 20 days as it was seen that CO₂ entered the baffle within this time period for all the realizations.

5.2.5. Dimensionless saturation

The values of irreducible water saturation vary over a range for both the lithologies (Figure 5.3d). In order to better understand the magnitude of maximum CO₂ turning point saturations obtained from simulation, the values are expressed in the form of dimensionless saturation, $\hat{S}_{CO_2,tp}^{max}$, defined as follows:

$$\hat{S}_{CO_2,tp}^{max} = \frac{S_{CO_2,tp}^{max}}{1 - S_{w,irr}} \quad (5.8)$$

where,

$S_{CO_2,tp}^{max}$ = maximum turning point CO₂ saturation within the foreset layer before the entry of CO₂ into lamina obtained from dynamic simulations,

$\hat{S}_{CO_2,tp}^{max}$ = dimensionless maximum turning point CO₂ saturation within the foreset layer before the entry of CO₂ into lamina.

$\hat{S}_{CO_2,tp}^{max}$ represents the ratio of maximum turning point saturation to end point CO₂ saturation at irreducible water content and varies between 0 and 1. Higher values of $\hat{S}_{CO_2,tp}^{max}$ indicate that the turning point CO₂ saturation within the foreset is relatively close to the end point CO₂ saturation value. For the cross bedding structures, this implies the presence of rock types that act as effective flow barriers and lead to a build-up of CO₂ saturation. The lower values of $\hat{S}_{CO_2,tp}^{max}$ indicate that CO₂ enters the laminae at turning point saturations which are much lower than end point saturation. This scenario is characteristic of rock types which are not effective flow barriers.

5.3. Results

5.3.1. Simulation results from 1D models

CO₂ injected at the base of the models rose under buoyancy through the foreset layer and accumulated underneath the lamina. The saturation built up until CO₂ entered the baffle. Figure 5.5 shows the evolution of CO₂ saturation profiles for one representative realization from each of the four scenarios: realization numbers 1 (Figure 5.5a), 31 (Figure 5.5b), 61 (Figure 5.5c) and 91 (Figure 5.5d). The initial CO₂ saturation distribution for the four realizations was similar. However, significant differences in the maximum CO₂ saturation at entry occurred for the four scenarios. Realization 1 (I_{CSst}^{Mst}) had the highest $S_{CO_2,tp}^{max}$ value of 0.8687 (Figure 5.5a), followed by realization 31 (I_{FSst}^{Mst}) with $S_{CO_2,tp}^{max}$ of 0.6967 (Figure 5.5b). $S_{CO_2,tp}^{max}$ derived from realizations 61 (I_{CSst}^{Slt}) (Figure 5.5c) and 91 (I_{FSst}^{Slt}) (Figure 5.5d) was relatively low, with $S_{CO_2,tp}^{max}$ values of 0.4261 and 0.5643, respectively. The time taken by CO₂ to enter the lamina was higher for realizations 1 and 31 compared to realizations 61 and 91. CO₂ entered into the lamina after 12 days for realization 1, 8 days for realization 31, 6 days for realization 61 and 7 days for realization 91.

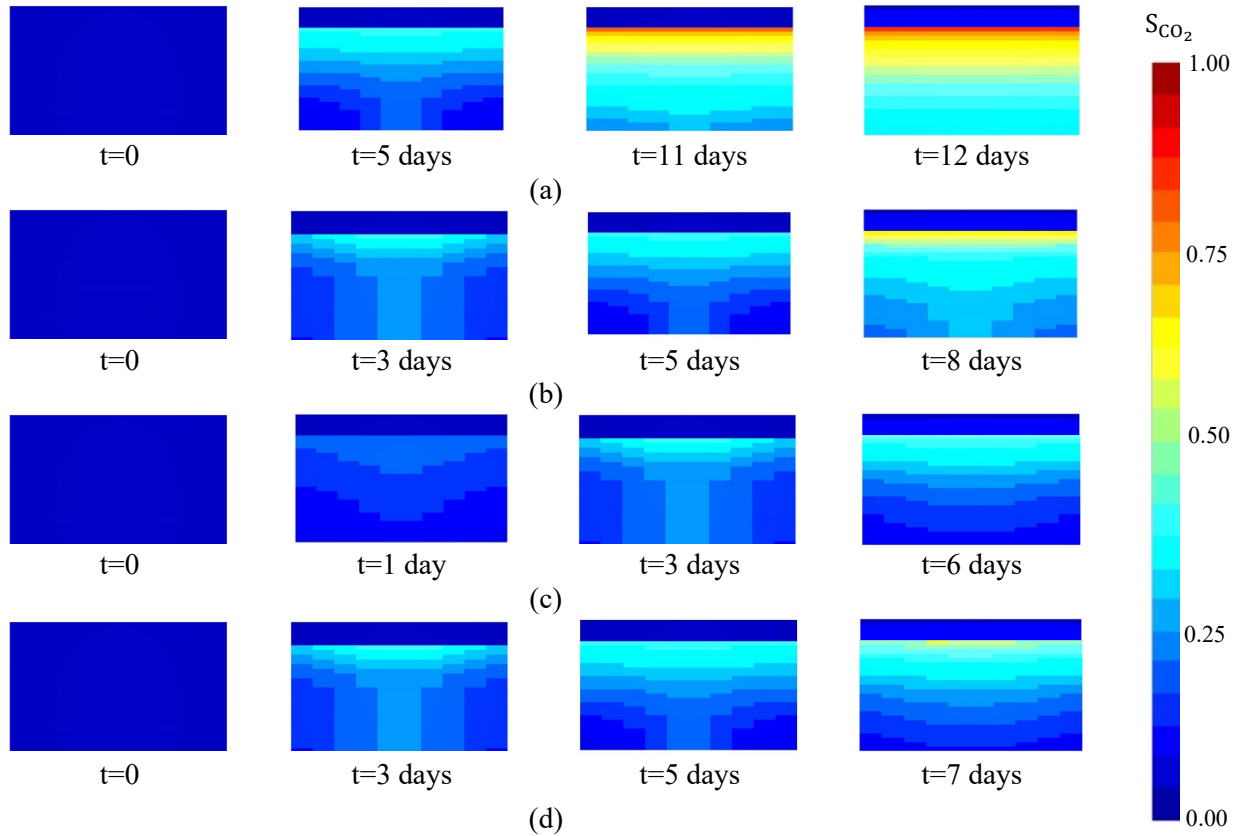


Figure 5.5. CO₂ saturation distribution in 1D models at four time steps from injection till entry of CO₂ into the lamina for: (a) Realization 1 (I_{CSSt}^{Mst}); (b) Realization 31 (I_{FSSSt}^{Mst}); (c) Realization 61 (I_{CSSt}^{Slt}); (d) Realization 91 (I_{FSSSt}^{Slt}). The last column for each case represents the distribution of turning point saturation before CO₂ migrates into the lamina.

5.3.2. Simulation results from 2D models

Figure 5.6 shows the temporal variation in CO₂ saturation profiles for the four 2D models corresponding to realizations 1 (Figure 5.6a), 31 (Figure 5.6b), 61 (Figure 5.6c) and 91 (Figure 5.6d). The evolution of CO₂ saturation for the four cases was similar to the corresponding 1D cases (Figure 5.5). Realization 1 (I_{CSSt}^{Mst}) showed the highest $S_{CO_2,tp}^{max}$ value among the four cases (Figure 5.6a). The maximum CO₂ saturation achieved for this case before the entry of CO₂ into the lamina was 0.8753. Realization 31 (I_{FSSSt}^{Mst}) showed the second highest $S_{CO_2,tp}^{max}$ value of 0.6527 (Figure 5.5b). Realizations 61 (I_{CSSt}^{Slt}) (Figure 5.6c) and 91 (I_{FSSSt}^{Slt}) (Figure 5.6d) resulted in relatively low $S_{CO_2,tp}^{max}$ values of 0.4531 and 0.5235, respectively. The time taken by CO₂ to enter the lamina was the same as that taken in the corresponding 1D cases. The only difference between results from 1D and 2D simulations was that the lateral extent of CO₂ in 2D models was restricted by the presence of dipping lamina layers while the lateral extent of CO₂ in 1D models was restricted by side boundaries of the model.

$S_{CO_2,tp}^{max}$ values obtained from 1D simulations were compared to the values obtained from 2D simulations (Figure 5.7). The maximum turning point saturations showed a close match from both the models indicating that the simplistic representation of heterogeneity in 1D models does not have any significant impact on the estimation of $S_{CO_2,tp}^{max}$.

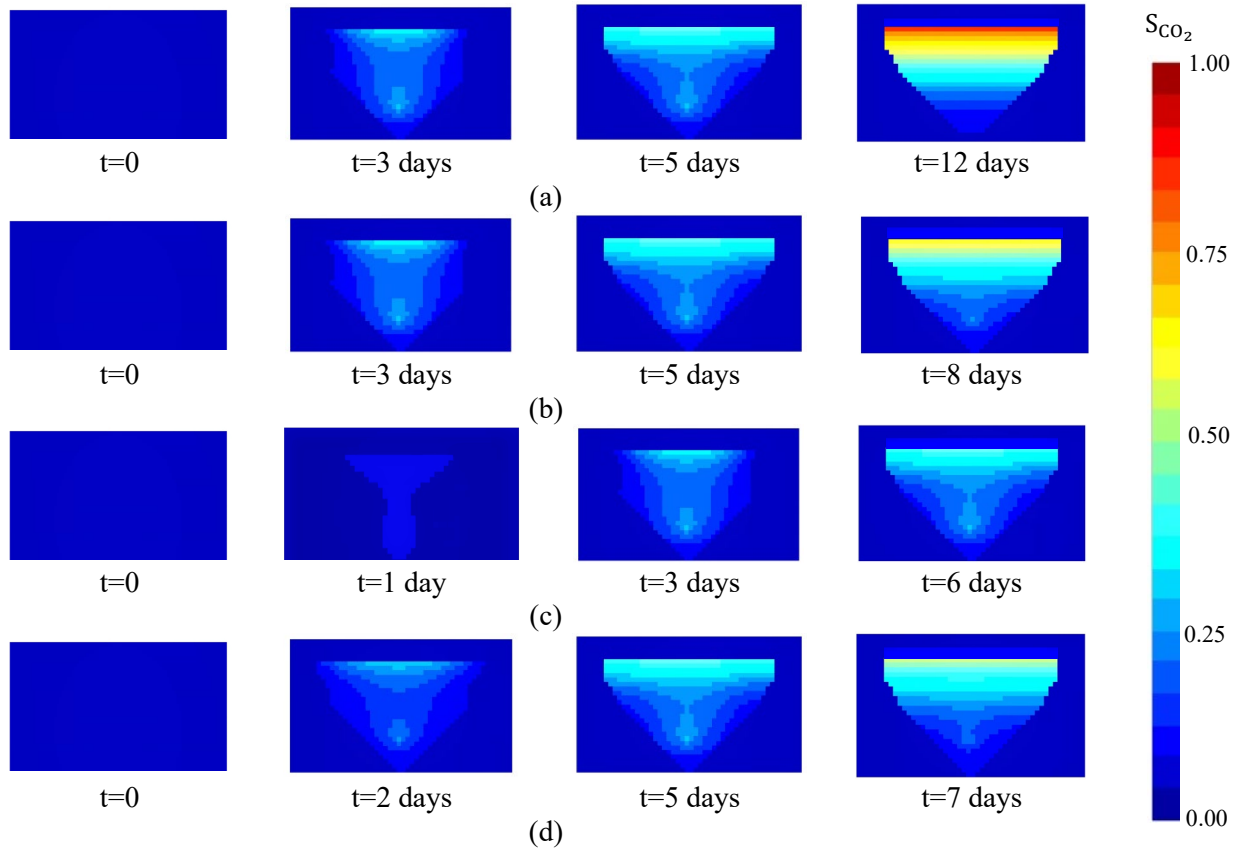


Figure 5.6. CO₂ saturation distribution in 2D models at four time steps from injection till entry of CO₂ into the lamina for: (a) Realization 1 (I_{CSst}^{Mst}); (b) Realization 31 (I_{FSst}^{Mst}); (c) Realization 61 (I_{CSst}^{Slt}); (d) Realization 91 (I_{FSst}^{Slt}). The last column for each case represents the distribution of turning point saturation before CO₂ migrates into the lamina.

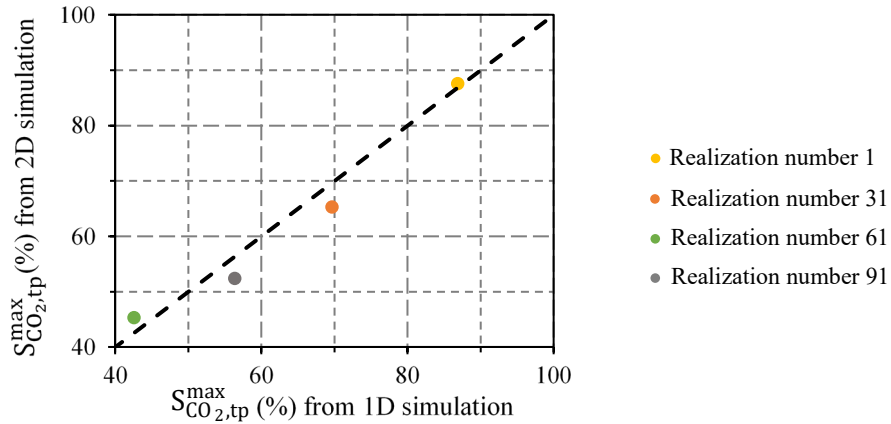


Figure 5.7. Comparison of maximum CO₂ saturation values obtained from 1D and 2D models. The stippled line is a unity slope line representing a 100% match in values of both the parameters.

5.3.3. Range of variation in maximum CO₂ turning point saturation for different rock types

The range of variation in $\hat{S}_{CO_2,tp}^{max}$ for the four scenarios is shown in Figure 5.8a and the corresponding probability density functions are shown in Figure 5.8b. Scenarios with mudstone lamina (I_{CSst}^{Mst} and I_{FSst}^{Mst}) were skewed towards higher $\hat{S}_{CO_2,tp}^{max}$ values and the maximum turning point saturation in these two scenarios reached about 87% and 77% of the end point CO₂ saturation values at irreducible water content on average, respectively

(Figure 5.8b). More specifically, about 53% of I_{CSst}^{Mst} realizations attained $\hat{S}_{CO_2,tp}^{max}$ values between 90-95% (Figure 5.8a). In contrast, scenarios with siltstone lamina (I_{CSst}^{Slt} and I_{FSst}^{Slt}) were skewed towards lower $\hat{S}_{CO_2,tp}^{max}$ values. The average $\hat{S}_{CO_2,tp}^{max}$ values for the two scenarios were 68% and 61%, respectively (Figure 5.8b). 13% of I_{CSst}^{Slt} realizations showed $\hat{S}_{CO_2,tp}^{max}$ values lower than 55% while 34% of I_{FSst}^{Slt} realizations had $\hat{S}_{CO_2,tp}^{max}$ values below 55% (Figure 5.8a). The spread of values for the scenarios with siltstone lamina was higher compared to scenarios with mudstone lamina (Figure 5.8b) indicating a larger uncertainty in the estimation of $\hat{S}_{CO_2,tp}^{max}$ for cross bedding with siltstone lamina.

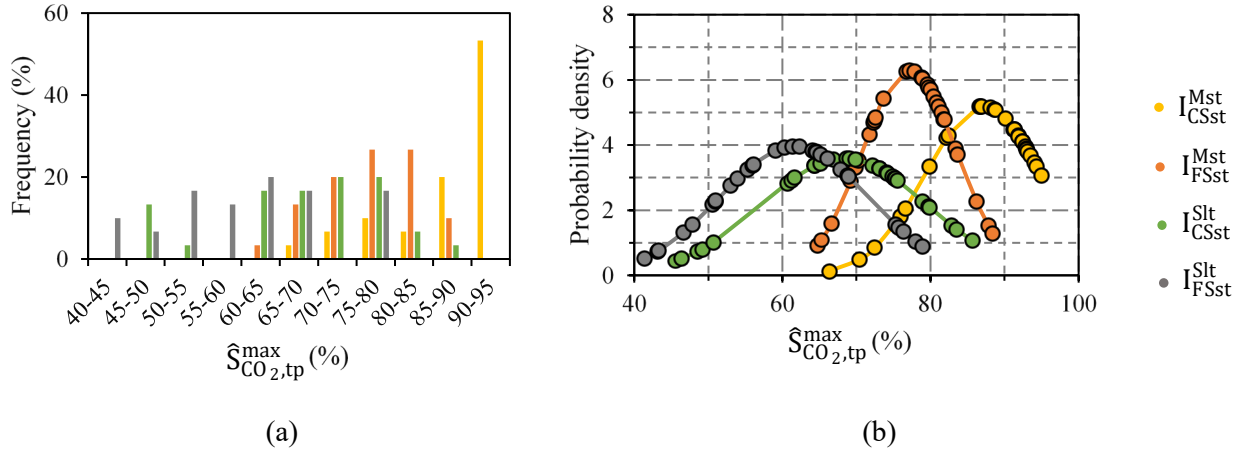


Figure 5.8. (a) Frequency and (b) probability density plots for the range of variation in maximum dimensionless CO₂ saturation for the four rock type scenarios.

Figure 5.9 shows the comparison between maximum turning point CO₂ saturations and end point CO₂ saturations at irreducible water content for the realizations 1, 31, 61 and 91. High values of turning point saturations were achieved for the scenarios with mudstone lamina (realizations 1 and 31) compared to scenarios with siltstone lamina (realizations 61 and 91). Especially for the scenario I_{CSst}^{Mst} (realization 1), the maximum turning point saturation was almost equal to end point saturation. On the contrary, maximum turning point saturation was much lower than its end point saturation value for the scenario I_{CSst}^{Slt} (realization 61).

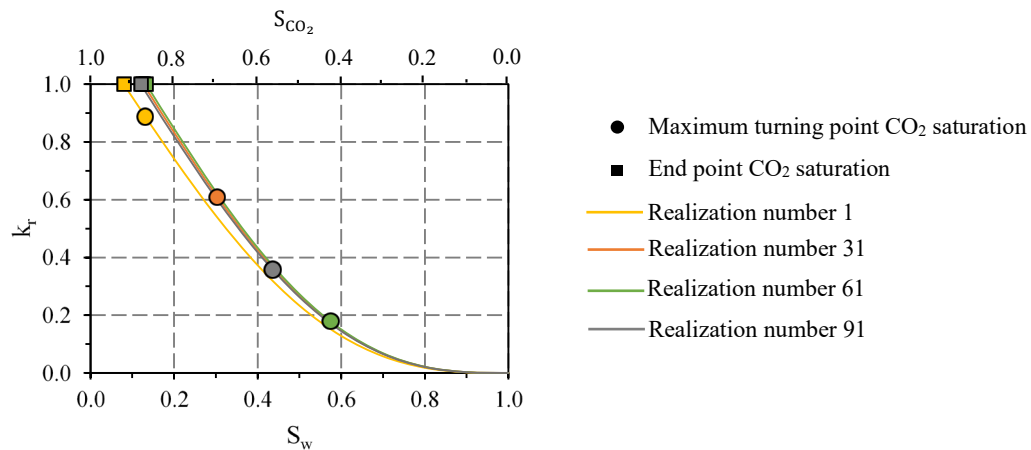


Figure 5.9. Comparison of maximum turning point CO₂ saturations and end point CO₂ saturations at irreducible water content on the CO₂ relative permeability curve for the realizations 1, 31, 61 and 91.

5.3.4. Dependence of maximum CO₂ saturation on lithological properties

$\hat{S}_{CO_2,tp}^{max}$ values varied across 120 realizations for the range of rock properties characteristic of the four rock types (Figure 5.10). $\hat{S}_{CO_2,tp}^{max}$ did not show any specific trend for the range of porosity implemented in the lamina (Figure 5.10a) and the foreset (Figure 5.10b). However, the trend was more pronounced for the range of permeability (Figure 5.10c) and capillary entry pressure (Figure 5.10e) characteristic of the lamina. $\hat{S}_{CO_2,tp}^{max}$ decreased with increasing lamina permeability (Figure 5.10c) and increased with increasing lamina entry pressure (Figure 5.10e). Scenarios with mudstone lamina (I_{CSst}^{Mst} and I_{FSst}^{Mst}) showed increasing $\hat{S}_{CO_2,tp}^{max}$ values with increasing foreset permeability (Figure 5.10d) and decreasing $\hat{S}_{CO_2,tp}^{max}$ values with increasing foreset entry pressure (Figure 5.10f). However, scenarios with siltstone lamina (I_{CSst}^{Slt} and I_{FSst}^{Slt}) did not show any specific trend with foreset permeability (Figure 5.10d) and foreset entry pressure (Figure 5.10f) and the data showed a wider spread indicating larger uncertainty. $\hat{S}_{CO_2,tp}^{max}$ showed a decreasing trend with increasing values of the empirical exponent 'm' characteristic of lamina (Figure 5.10g). However, no specific trend was observed for $\hat{S}_{CO_2,tp}^{max}$ with changes in 'm' characteristic of the foreset layer (Figure 5.10h) for the scenarios with siltstone lamina (I_{CSst}^{Slt} and I_{FSst}^{Slt}). The scenarios with mudstone lamina (I_{CSst}^{Mst} and I_{FSst}^{Mst}) showed an increasing trend with increasing 'm' values of the foreset (Figure 5.10h). Dependence of $\hat{S}_{CO_2,tp}^{max}$ is not explored separately with $S_{w,irr}$ and λ as both parameters are not strictly independent but have been derived from porosity, permeability and relative permeability exponent 'm' (equations 5.5 and 5.6).

5.4. Discussion

5.4.1. The importance of rock types in cross bedding controlling the maximum CO₂ saturation

The present study quantifies the variation of maximum CO₂ saturation during drainage within the foreset beds of cross bedding sedimentary structures. The results show that the maximum CO₂ saturation varies between 40-95% of the end point saturation values at irreducible water content depending on the rock types of the foreset and the lamina (Figure 5.8a). This is a large range and can have important implications on the amount of capillary trapping within reservoir rocks with cross bedding.

The trapped CO₂ saturation at the end of imbibition ($S_{trapped}$) can be calculated in terms of the turning point saturation at the end of drainage using the Land trapping model (Land, 1968) given as:

$$S_{trapped} = \frac{S_{CO_2,tp}}{1 + CS_{CO_2,tp}} \quad (5.9)$$

where, C is the Land trapping coefficient which is a function of end point CO₂ saturations at the end of drainage and imbibition. The saturation of trapped CO₂ is a direct function of the turning point CO₂ saturation. Hence, it is desirable to have turning point saturation values equal to end point saturation values for maximizing capillary trapping. This is only possible when the laminae in the cross bedding sedimentary structures are impermeable. This scenario has been implemented in several studies (Green and Ennis-King, 2010a; Green and Ennis-King, 2010b; Green and Ennis-King, 2013). However, field data shows that laminae might have a low permeability and a capillary entry pressure allowing for CO₂ invasion at elevated

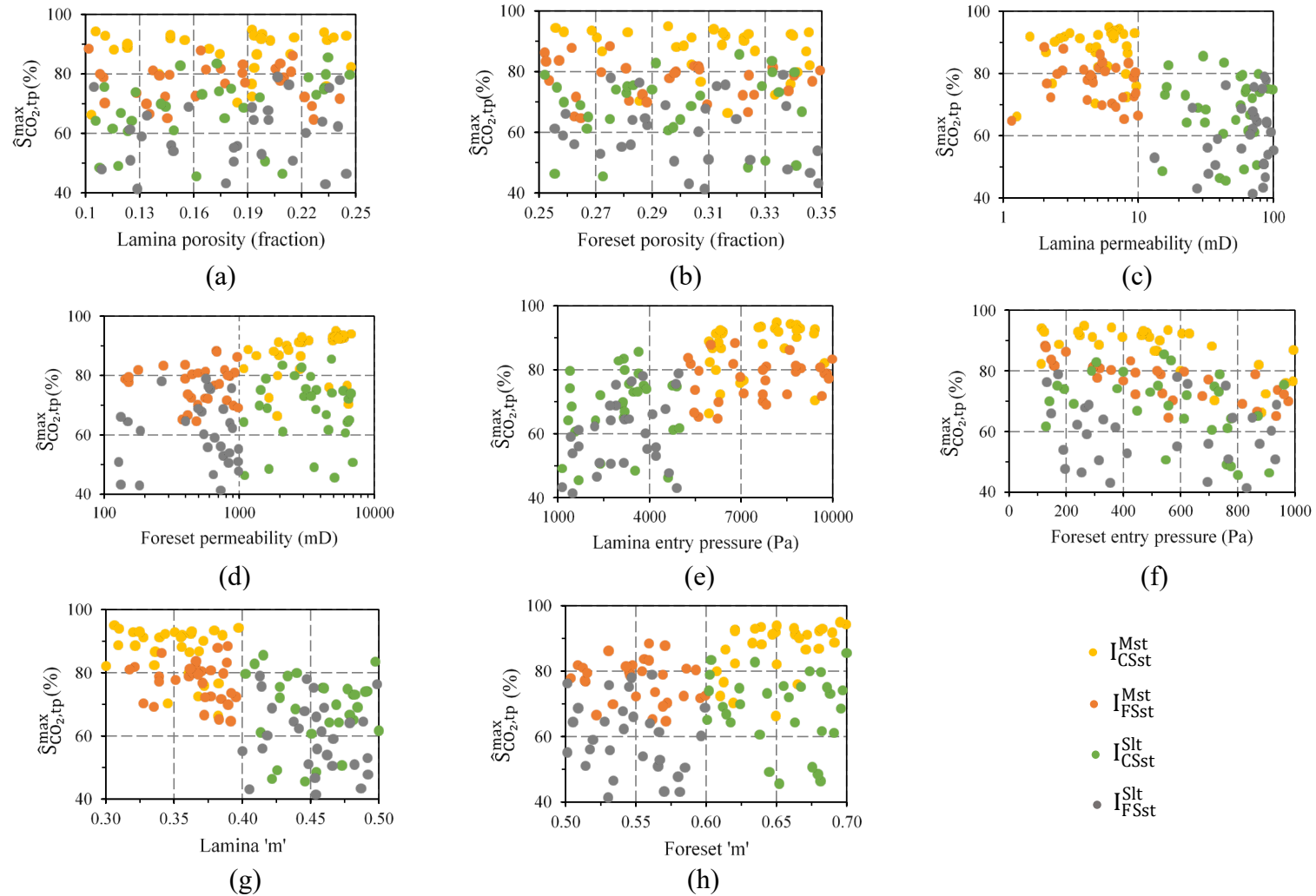


Figure 5.10. Range of variation in maximum CO_2 saturation prior to entry as a function of (a) lamina porosity; (b) foreset porosity; (c) lamina permeability; (d) foreset permeability; (e) lamina entry pressure; (f) foreset entry pressure; (g) lamina 'm'; (h) foreset 'm'.

buoyancy pressure. This reduces the ability of laminae to completely restrict the flow of CO₂ through them. Consequently, turning point saturation can be lower than end point saturation and results from studies assuming impermeable laminae may grossly overestimate the capillary trapping capacity. The present study accounts for field data, specifically for rock types forming laminae in cross bedding structures to provide a more realistic estimate of post drainage CO₂ saturation distribution. Other studies using realistic rock properties have mostly focused on the estimation of capillary trapping capacities and plume spreading for a range of reservoir rocks (Bech and Frykman, 2018; Doughty, 2010; Gershenzon et al., 2017; Ni et al., 2019; Ren et al., 2014; Ruprecht et al., 2014). The results presented here complement these studies by also quantifying the possible range of maximum CO₂ saturation before imbibition for representative rock types in cross bedding sedimentary structures.

The study shows that the presence of mudstone rich lamina and coarse sandstone rich foreset beds significantly favour the restriction of CO₂ within the foreset resulting in maximum CO₂ saturation values as high as 95% of their end point saturation values at irreducible water content (Figure 5.8a and Figure 5.9). Hence, such geological settings may be favorable targets for enhanced capillary heterogeneity trapping. The presence of mudstone lamina is likely to occur towards the downstream side of distributary channel reservoirs where depositional energy is low (Miall, 2016). On the other hand, laminae and foresets composed of siltstone and fine sandstone, respectively, are less effective as baffles and maximum CO₂ saturations may be as low as 40% of the end point saturation values at irreducible water content in some cases (Figure 5.8a and Figure 5.9). Siltstone rich lamina are characteristic of upstream sections of distributary channels where sediment deposition takes place under higher flow energy (Miall, 2016). The results also show that cases with siltstone lamina are characterized by a wider spread of maximum CO₂ saturation values compared to cases with mudstone lamina (Figure 5.8). This indicates that the presence of siltstone lamina might result in higher uncertainties associated with maximum turning point saturations. Thus, the results provide important insights regarding the favorable depositional environments for enhanced capillary trapping. In order to achieve turning point saturations comparable to end point saturation values at irreducible water content, it is important to ensure that cross bedded lithologies with mudstone rich lamina are preferentially utilized as potential targets for capillary heterogeneity trapping.

The results obtained from simulations based on 1D models are matched with results from 2D models for four cases (Figure 5.7). The comparison of results shows a good agreement between the two approaches and suggests simplified 1D models provide accurate results for the maximum CO₂ saturation and the saturation distribution (Figure 5.5 and Figure 5.6). The good agreement is a result of the lens shaped geometry of foreset bed and the lamina draped over the foreset bed in three dimensions. The geometry is characteristic of cross bedded strata and restricts the lateral migration of CO₂ around the lamina. It is for this reason that the simplified 1D models with lateral boundaries closed to mass

transport can replicate the estimates of maximum CO₂ saturation obtained from simulations based on 2D models. However, the use of 1D or 2D models might not be sufficient to calculate the amount of capillary heterogeneity trapping within the foreset beds and a complete 3D resolution of strata might be required for confident estimates.

5.4.2. Which rock properties control maximum turning point saturation and what is their impact?

The maximum CO₂ saturation varies significantly for the range of different lithological properties (Figure 5.10). Saturation shows a strong trend for permeability (Figure 5.10c), entry pressure (Figure 5.10e) and the empirical exponent m (Figure 5.10g) characteristic of the lamina. The trends are less well constrained for other rock properties. While these observations provide an initial idea on the importance of these properties on $\hat{S}_{CO_2, tp}^{max}$ it is also important to quantify the impact of rock properties and their associated heterogeneity in absolute terms.

The difference in rock properties between lamina and foreset is quantified in terms of a parameter referred to in this paper as interfacial anisotropy ratio (IAR). The ratio is a dimensionless number that accounts for the difference in a given rock property between the lamina and the foreset. For porosity, the anisotropy ratio, IAR_ϕ , is defined as the ratio of the porosity of the foreset (ϕ_f) to the porosity of lamina (ϕ_l) (Eq. 5.10). The anisotropy ratio for permeability, IAR_k , is defined as the natural logarithm of the ratio of foreset permeability (k_f) to lamina permeability (k_l) (Eq. 5.11). Similarly, the anisotropy ratio for capillary entry pressure, IAR_{Pe} , is defined as the natural logarithm of the ratio of the entry pressure characteristic of foreset (Pe_f) to the entry pressure characteristic of lamina (Pe_l) (Eq. 5.12). The anisotropy ratio for the empirical parameter ‘ m ’ (Eq. 5.13) is defined as the ratio of the foreset property, m_f , to the respective lamina property, m_l , and is referred to as IAR_m .

$$IAR_\phi = \phi_f / \phi_l \quad (5.10)$$

$$IAR_k = \ln(k_f / k_l) \quad (5.11)$$

$$IAR_{Pe} = \ln(Pe_f / Pe_l) \quad (5.12)$$

$$IAR_m = m_f / m_l \quad (5.13)$$

For a homogeneous stratum, the rock properties of the lamina and the foreset are equal. In that case, the IAR for permeability and capillary entry pressure are equal to 0 and the IAR for porosity and ‘ m ’ are 1. The greater the heterogeneity, the greater is the deviation of anisotropy ratios from these values. For lithologies found in cross bedding reported in this study, IAR_ϕ varies between 1 and 3.5; IAR_k varies

between 0 and 8.85; IAR_{Pe} varies between 0 and -4.6; and IAR_m varies between 1 and 2.3. With the above definitions, each model realization has unique values of the four dimensionless anisotropy ratios.

The impact of each anisotropy ratio on $\hat{S}_{CO_2,tp}^{max}$ is shown in Figure 5.11. While IAR_ϕ does not have any specific impact on $\hat{S}_{CO_2,tp}^{max}$, the other three anisotropy ratios show trends for the range of $\hat{S}_{CO_2,tp}^{max}$. The greater the deviation of IAR_k , IAR_{Pe} and IAR_m from a homogeneous case ($IAR_k=0$, $IAR_{Pe}=0$, $IAR_m=1$), the greater is the value of $\hat{S}_{CO_2,tp}^{max}$. Also, the scenarios with mudstone lamina and coarse sandstone foreset (I_{CSst}^{Mst}) are characterized by greater difference in the anisotropy ratios from homogeneity while the scenarios with siltstone lamina and fine sandstone foreset (I_{FSst}^{Slt}) are characterized by minor to moderate difference to the homogeneous case.

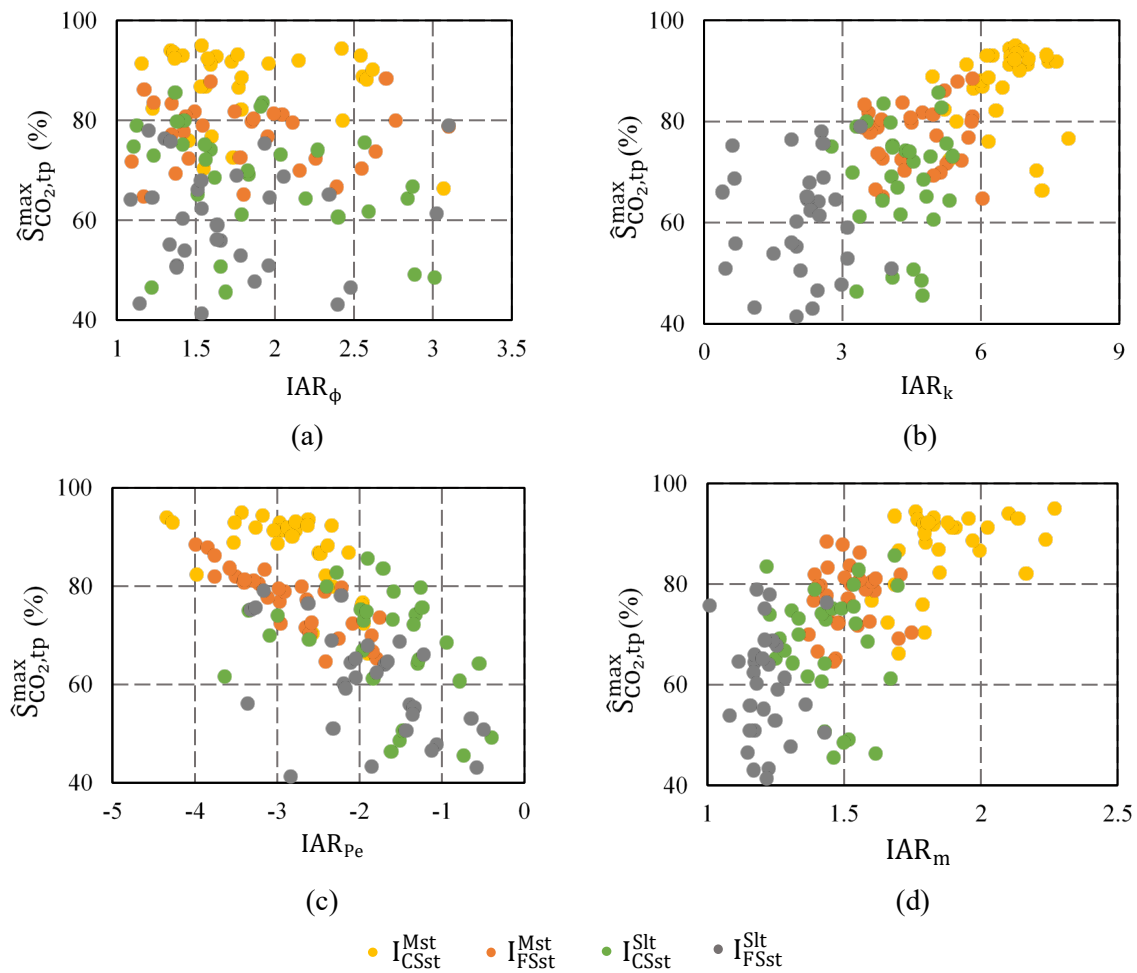


Figure 5.11. The impact of anisotropy in (a) porosity; (b) permeability; (c) capillary entry pressure; (d) exponent ‘m’ between foreset and lamina on maximum dimensionless CO₂ turning point saturations.

Multivariable linear regression was carried out to quantify the relationship between each of the eight rock properties and $\hat{S}_{CO_2,tp}^{max}$ and between the four interfacial anisotropy ratios and $\hat{S}_{CO_2,tp}^{max}$. The coefficient of determination (R^2) was 0.6678 for the former regression relationship and 0.6504 for the

latter regression equation. The confidence levels derived from t-test analysis for both regressions are shown in Figure 5.12. A confidence level greater than 95% is considered to be significant. Apart from porosity, the other six rock properties showed confidence level above 95%. Similarly, anisotropy ratios in permeability, entry pressure and the exponent ‘m’ had a confidence level of more than 95% while the porosity anisotropy ratio was statistically insignificant.

The impact of each of the eight properties and the four anisotropy ratios on $\hat{S}_{CO_2, tp}^{max}$ was quantified in absolute terms using step-wise multivariable regression analysis (Judd et al., 2011; Puranik et al., 2016). In this statistical approach, one independent variable is excluded from the multivariable regression model at a given step. This leads to a reduction in the value of R^2 obtained from multivariable regression analysis and the difference between the two values is referred to as marginal R^2 . The marginal R^2 values are a measure of the impact of each independent variable on the dependent parameter. The values are normalized to obtain the absolute impact of each of the independent variables.

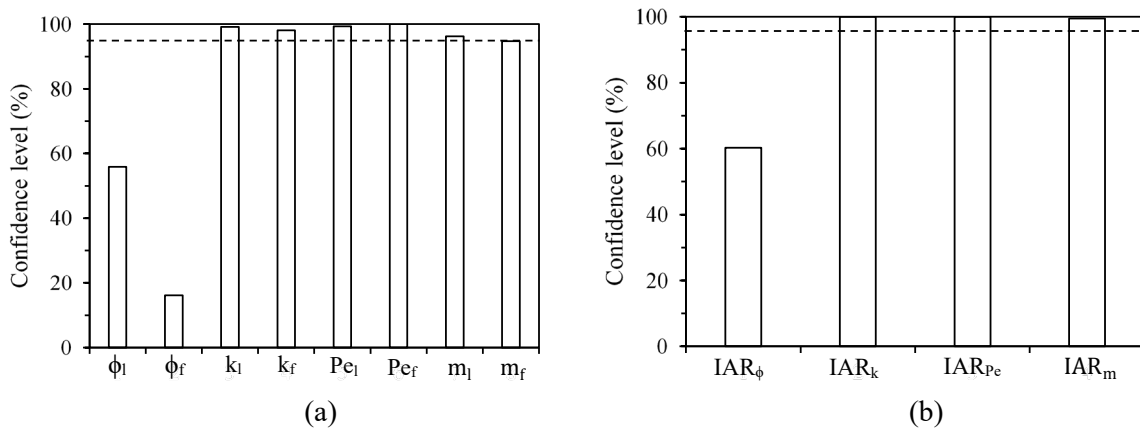


Figure 5.12. Confidence levels associated with the multivariable linear regression of (a) each rock property; and (b) each anisotropy ratio on $\hat{S}_{CO_2, tp}^{max}$. The stippled line shows 95% confidence level.

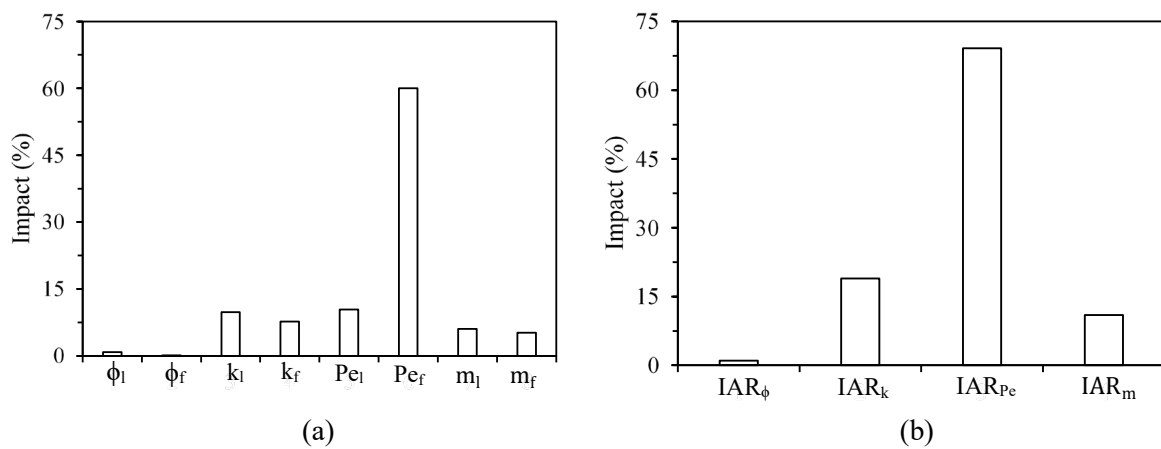


Figure 5.13. Absolute impacts of (a) the eight rock properties; and (b) four anisotropy ratios on the range of variation in $\hat{S}_{CO_2, tp}^{max}$.

The impacts of the eight rock properties on the variation in $\hat{S}_{CO_2, tp}^{max}$ are shown in Figure 5.13a and the impacts of the four anisotropy ratios on the variation in $\hat{S}_{CO_2, tp}^{max}$ is shown in Figure 5.13b. The analysis shows the capillary entry pressure of the foreset has the greatest influence on $\hat{S}_{CO_2, tp}^{max}$, with an absolute impact of 59.99% (Figure 5.13a) and possibly results from the fact that foreset entry pressure dictates the ease of CO₂ accumulation underneath the lamina which in turn controls buoyancy pressure at the interface of the two lithological units. The entry pressure and permeability characteristic of lamina influence the range of $\hat{S}_{CO_2, tp}^{max}$ by 10.38% and 9.79%, respectively, while foreset permeability has an impact of 7.7%. The impact of the empirical exponent 'm' varies between 5.21% and 6.03% for the two lithologies making up the cross bedding structure. The combined impact of porosity of both the lithologies on the variation in $\hat{S}_{CO_2, tp}^{max}$ is less than 2%. The six rock properties with significant influence on $\hat{S}_{CO_2, tp}^{max}$ also have confidence levels greater than 95% (Figure 5.12a). In terms of anisotropy ratios, IAR_{Pe} has the highest impact of 69.14% on the variation in $\hat{S}_{CO_2, tp}^{max}$ (Figure 5.13b). IAR_m and IAR_k have impacts of 10.94% and 18.93%, respectively while the impact of IAR_ϕ on $\hat{S}_{CO_2, tp}^{max}$ is less than 1%. Again, the confidence levels in the three significant anisotropy ratios, IAR_{Pe} , IAR_k and IAR_m are above 95% (Fig. 12b). Hence, the study shows that not only the values of individual rock properties influence maximum turning point saturation, but also the interfacial anisotropy in rock properties has a significant impact.

5.4.3. Regression models for the estimation of maximum turning point saturation from intrinsic rock properties

The results can be used to develop simple regression models for determining maximum turning point saturation directly from different rock properties and their associated interfacial anisotropy. The large number of simulations provide confidence in avoiding the issue of data overfitting in regression analysis. The analysis suggests six rock properties of the cross bedding structure (k_f , k_l , Pe_f , Pe_l , m_f , m_l) account for over 98% of the variation in $\hat{S}_{CO_2, tp}^{max}$ (Figure 5.13a) and are significant at 95% confidence level (Figure 5.12a). A multivariable linear regression between these six properties and $S_{CO_2, tp}^{max}$ results in the following relationship:

$$S_{CO_2, tp}^{max} = (1 - S_{w, irr})(77.53 - 0.094k_l + 0.001k_f + 0.001Pe_l - 0.019Pe_f - 53.982m_l + 34.250m_f) \quad (5.14)$$

The coefficient of determination (R^2) for the above relationship is 0.67 and the standard error is 8.09%. All the independent variables in the above relationship are significant at 99% confidence level. Additionally, the three interfacial anisotropy ratios: IAR_{Pe} , IAR_k and IAR_m account for over 99% of the variation in $\hat{S}_{CO_2, tp}^{max}$ (Figure 5.13b) and can be used to derive a multivariable linear regression equation:

$$S_{CO_2, tp}^{max} = (1 - S_{w, irr})(27.812 + 2.361IAR_k - 6.791IAR_{Pe} + 12.715IAR_m) \quad (5.15)$$

The coefficient of determination (R^2) for the above relationship is 0.65 and the standard error is 8.19%. All the independent variables in the above relationship are significant at 99% confidence level.

The rock property values in the above regression models are essentially layer averaged values. Equations 5.14 and 5.15 provide a preliminary estimate of maximum turning point saturation for each type of lamina-foreset interface in a cross-bedded strata directly from intrinsic rock properties of the two lithologies. Both the equations are dependent on six rock properties. Additionally, relative difference in the rock properties of foreset and lamina expressed as dimensionless numbers can be used to directly determine maximum turning point saturation using equation 5.15. The associated uncertainty in maximum turning point saturations for the cases with siltstone baffle largely contributes to standard errors of the two regression models.

5.5. Conclusions

The present study quantifies the range of maximum turning point CO_2 saturation during drainage for cross bedding sedimentary structures in CO_2 storage reservoirs. The maximum CO_2 saturation below the foreset-lamina interface at the time of CO_2 entry into the lamina is derived for 120 scenarios and the results are used to develop insights into rock types and depositional environments favorable for heterogeneity enhanced capillary trapping. The results show that maximum turning point saturation can vary between 40% and 95% of the end point CO_2 saturation at irreducible water content. Higher turning point saturation is achieved for cross bedding structures where the lamina is composed of mudstone rather than siltstone. This indicates that downstream sections of distributary channels in coastal to marine depositional environments have more potential for achieving high CO_2 turning point saturation under buoyancy driven conditions compared to the upstream sections. Stepwise multivariable analysis is used to quantify the absolute impact of various rock properties on the maximum turning point saturation. The results show that capillary entry pressure of the foreset layer has the highest influence (about 60%) on the variation in maximum turning point saturation amongst all rock properties while porosity has the least influence. The capillary entry pressure and permeability of the lamina layer have only a minor influence on the maximum turning point saturation of about 10% each. This study further shows that not only rock properties influence maximum turning point saturation, but also the anisotropy in rock properties across the lithological interface between the lamina and the foreset. The anisotropy in properties of the two lithologies has been expressed in terms of interfacial anisotropy ratios which quantify the extent of lithological heterogeneity by means of dimensionless numbers. The impact of anisotropy in entry pressure between the two lithologies on maximum turning point saturation is about 69%. The anisotropy in the relative permeability exponent and absolute permeability between foreset and lamina can influence maximum turning point saturation by only about 11% and 19%, respectively. Simulation results have been used to derive multivariable regression models for the direct estimation of maximum turning point saturation using different rock properties.

Chapter 6

Conditions and processes controlling carbon mineral trapping in intraformational baffles

6.1. Introduction

Carbon mineralization is the most secure of the four trapping mechanisms by which CO₂ is trapped geologically (Metz et al., 2005). Carbon mineral trapping has been well documented for different reservoirs (Baklid et al., 1996; Ennis-King and Paterson, 2002; Korbøl and Kaddour, 1995; Pruess et al., 2003; Spycher et al., 2019; Van der Meer, 1996; Xu et al., 2004a), yet there is uncertainty with its quantification due to the neglect of fine scale heterogeneity in reservoir models (Doughty et al., 2001; Flett et al., 2005; Law and Bachu, 1996; Lindeberg, 1997; Yang et al., 2014). Any form of heterogeneity is property and scale dependent. This study focuses on lithological heterogeneity at cm-scale which exists in the form of intraformational baffles and has been shown to be zones of high carbon mineral trapping (Gibson-Poole et al., 2009; Yu et al., 2017).

Baffles are rock units enriched in fine grained lithology and are interbedded within the coarser grained reservoir rocks to varying proportions (Flett et al., 2007). Intraformational baffles control fluid flow pathways and act as flow barriers due to low porosity and permeability and high capillary entry pressure (Frykman et al., 2009; Green and Ennis-King, 2010). Additionally, these baffles are enriched in clay minerals such as chlorites. At the interface of a reservoir rock and an intraformational baffle, the presence of CO₂ enriched water reduces the pH which triggers the dissolution of minerals. Clay minerals such as smectites and chlorites are enriched in divalent cations like Ca²⁺, Fe²⁺ and Mg²⁺ which are mobilized as the clays dissolve. The divalent cations may react with carbonate ions resulting from CO₂ dissolution and lead to the precipitation of carbonate minerals such as ankerite, dolomite and siderite. Consequently, CO₂ becomes permanently trapped as carbonate minerals (Matter and Kelemen, 2009; Hermanson and Kirste, 2013; Higgs et al., 2015; Watson, 2012; Watson and Gibson-Poole, 2005). It is therefore important to account for the presence of baffles in reservoir scale simulations in order to improve trapping capacity estimates.

While fluid flow behaviour and CO₂ capillary trapping has been well quantified at lithological interfaces between baffles and reservoir rocks (Green and Ennis-King, 2010; Saadatpoor et al., 2013), the geochemical processes associated with carbon mineralization at these interfaces and their impact on mineral trapping are only qualitatively understood. Furthermore, the impact of cm-scale lithological heterogeneity on carbon mineralization is rarely accounted for in reservoir scale simulations due to a lack of reduced geochemical parameters such as averaged reaction rates and mineral compositions.

In order to characterise the geochemical reactivity across cm-scale lithological interfaces and quantify carbon mineral trapping over an extended period of time (1000 years), the following three questions are addressed in this study. Firstly, which geochemical processes and conditions across the baffle-reservoir rock interface control geochemical reactions? Secondly, what is the range in the amount of mineralized carbon forming within the baffle-reservoir rock system by accounting for homogeneous and heterogeneous rock properties? Thirdly, can time dependent averaged reaction rates be derived for averaged mineral compositions? The averaged geochemical parameters are important to correctly assess mineral trapping in coarser scale simulations where cm-scale lithological heterogeneity and its impact on carbon mineralization is typically neglected.

6.2. Methodology

6.2.1. Geostatic model realizations

In heterogeneous siliciclastic reservoirs, the baffle-reservoir rock interfaces typically exist as a repetitive pattern of mm- to cm- thick lithological layers (Figure 6.1a) (Dance, 2018; Mishra et al., 2019; Mishra et al., 2020). This field observation was used to implement one of the interfaces as a 2-D geostatic model for this study (Figure 6.1b). The 2D model captures the lithological heterogeneity across the interface and was found sufficient to address the aims of this study. The model was constructed in PetraSim v5 (Alcott et al., 2006) and measured 10 cm horizontally and 2 cm vertically. The baffle was represented by a 1 cm thick layer and was overlaid above the reservoir rock layer of same thickness. The model was discretized into grid cells with a length of 2 cm and a height of 1 mm resulting in a total of 100 cells. The model and grid dimensions capture the heterogeneity across the interface while keeping the run-time of the simulations manageable. An additional geostatic model of

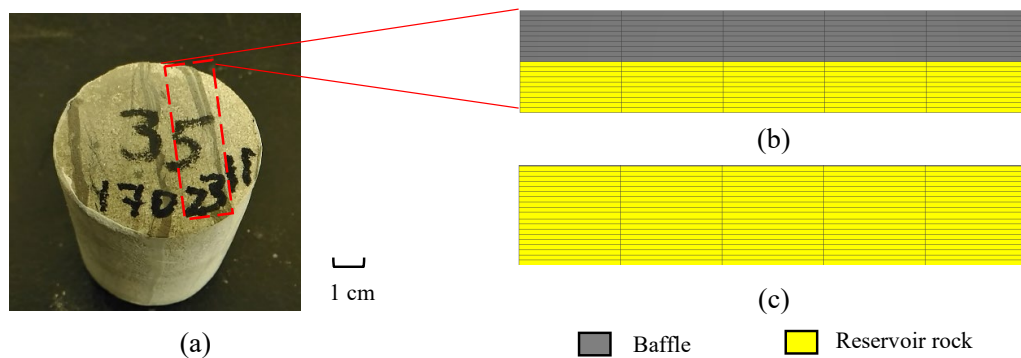


Figure 6.1. (a) Baffle-reservoir rock interfaces as observed in cores (Mishra et al., 2019). Baffle exist as 5mm-1cm thick lamina (dark gray) between reservoir rock types (light gray); (b) Implemented lithological interface as a 2D static model; (c) A model realization with homogeneous reservoir rock. The static models measure 10 cm horizontally and 2 cm vertically. The thickness of each layer in (b) is 1 cm.

same size was constructed with homogeneous reservoir rock making up the entire model domain in order to compare the simulation results obtained from homogeneous and heterogeneous models. The static model had a thickness of 1 cm in the third dimension with a single cell used to discretize it.

6.2.2. Rock property population

The flow and mineralogical properties of the reservoir and the baffle layers are derived from the coastal to shallow marine deposits of the Paaratte Formation at the CO2CRC Otway Research Facility. The site is located 300 kms southwest of Melbourne in Victoria, Australia. Porosity, permeability, CO₂ capillary entry pressure and mineral composition data are available for the five rock types identified at the site: coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone (Mishra et al., 2019). The relative permeability-saturation curves and capillary pressure-saturation curves for the five rock types were implemented using the van Genuchten-Mualem and the van Genuchten functions, respectively (Mualem, 1976; Van Genuchten, 1980; Xu et al., 2004b):

$$k_{r,w} = s_{e,w}^{1/2} \left(1 - \left(1 - s_{e,w}^{1/m_r} \right)^{m_r} \right)^2 \quad (6.1)$$

$$k_{r,CO_2} = \left(1 - s_{e,CO_2} \right)^2 \left(1 - s_{e,CO_2}^2 \right) \quad (6.2)$$

$$P_c = P_o \left(s_{e,w}^{-1/m_c} - 1 \right)^{1-m_c} \quad (6.3)$$

where,

$k_{r,w}$ = water relative permeability,

k_{r,CO_2} = CO₂ relative permeability,

P_c = CO₂ capillary pressure (Pa),

P_o = capillary strength parameter pressure (Pa),

m_r = empirical parameter for the relative permeability-saturation curve,

m_c = empirical parameter for the capillary pressure-saturation curve,

$s_{e,w}$ = effective water saturation,

s_{e,CO_2} = effective CO₂ saturation.

The effective water and CO₂ saturations are given as follows:

$$s_{e,w} = \frac{S_w - S_{w,irr}}{1 - S_{w,irr}} \quad (6.4)$$

$$s_{e,CO_2} = \frac{S_w - S_{w,irr}}{1 - S_{w,irr} - S_{CO_2,r}} \quad (6.5)$$

where,

S_w = water saturation,

$S_{w,irr}$ = irreducible water saturation,

$S_{CO_2,r}$ = residual CO₂ saturation.

For the implementation of the two curves, five van-Genuchten parameters were required: m_r , m_p , $S_{w,irr}$, $S_{CO_2,r}$ and P_o . P_o was calculated assuming that the curve passes through entry pressure at a

threshold CO₂ saturation of 0.005 (Li et al., 2013). For each rock type, $S_{w,irr}$ and $S_{CO_2,r}$ values were calculated using the following empirical relations (Holtz, 2002):

$$S_{w,irr} = 5.159 \left[\frac{\log k_p}{\phi} \right]^{-1.559} \quad (6.6)$$

$$S_{CO_2,r} = -0.969 \phi + 0.5473 \quad (6.7)$$

where ϕ and k_p are porosity and permeability values for a given rock type.

Due to a lack of measured data, the two empirical exponents were taken to be equal and their representative values were derived from literature (Cheng et al., 2017; Hermanson and Kirste, 2013). The implemented flow and petrophysical properties are shown in Table 6.1.

Rock types	Abbreviation used	Porosity (fraction)	Permeability (mD)	$S_{w,irr}$ (fraction)	$S_{CO_2,r}$ (fraction)	m	P _o (kPa)
Coarse sandstone	CSst	0.2857	3148.5	0.104	0.270	0.7	3.2
Fine sandstone	FSst	0.2801	406.5	0.159	0.276	0.6	6.3
Siltstone	Slt	0.1914	44.6	0.180	0.362	0.5	27.1
Mudstone	Mst	0.1754	8.3	0.390	0.377	0.4	51.1
Carbonate-cemented sandstone	CbSst	0.1873	6.1	0.552	0.366	0.4	84.6

Table 6.1. The values of flow and petrophysical properties for each of the five rock type classes (Mishra et al., 2019).

Coarse and fine sandstone rock types are characterized by high porosity, high permeability and low CO₂ capillary entry pressures and are hence populated in the reservoir rock layer of the static model. Mudstone and carbonate-cemented sandstone are characterized by low porosity, low permeability and a high entry pressure. Therefore, these two rock types have been populated in the baffle. Siltstone has intermediate values of flow properties and has been utilized as a baffle as well as a reservoir rock. This

Constituent rock types		Acronym used
Baffle	Reservoir rock	
Mudstone	Coarse sandstone	I ^{Mst} _{CSst}
Mudstone	Fine sandstone	I ^{Mst} _{FSst}
Mudstone	Siltstone	I ^{Mst} _{Slt}
Siltstone	Coarse sandstone	I ^{Slt} _{CSst}
Siltstone	Fine sandstone	I ^{Slt} _{FSst}
Carbonate-cemented sandstone	Coarse sandstone	I ^{CbSst} _{CSst}
Carbonate-cemented sandstone	Fine sandstone	I ^{CbSst} _{FSst}
Carbonate-cemented sandstone	Siltstone	I ^{CbSst} _{Slt}
-	Coarse sandstone	CSst
-	Fine sandstone	FSst
-	Siltstone	Slt

Table 6.2. Composition of the 11 geostatic realizations used for dynamic simulations.

leads to a total of 8 realizations for the static model with an interface. Additionally, three realizations are based on homogeneous static models with coarse sandstone, fine sandstone and siltstone as constituent rock types. The composition of the 11 realizations are described in Table 6.2.

The mineral composition of the five rock types were determined earlier and grouped into framework, clay and carbonate mineral fractions (Haese et al., 2019; Mishra et al., 2019). The framework minerals comprised albite, K-feldspar and quartz. Minerals of the clay fraction comprised chlorite, illite, kaolinite, muscovite and smectite. The group of carbonate minerals comprised ankerite, calcite, dolomite, magnesite and siderite. The mineral proportions of the five rock type classes are shown in Table 6.3.

Mineral	Coarse sandstone	Fine sandstone	Siltstone	Mudstone	Carbonate-cemented sandstone
Albite	0.0121	0.0195	0.0262	0.0254	0.0186
Ankerite	0.0019	0.0013	0.0000	0.0000	0.0992
Calcite	0.0000	0.0000	0.0000	0.0000	0.0008
Chlorite	0.0233	0.0515	0.0599	0.0900	0.0144
Dolomite	0.0004	0.0003	0.0000	0.0000	0.0206
Illite	0.0086	0.0214	0.0437	0.0824	0.0099
K-Feldspar	0.0760	0.0654	0.0591	0.0691	0.0512
Kaolinite	0.0415	0.0466	0.1237	0.1539	0.0331
Magnesite	0.0060	0.0056	0.0098	0.0180	0.0172
Muscovite	0.0097	0.0131	0.0337	0.0526	0.0112
Quartz	0.7870	0.7292	0.5417	0.3679	0.7092
Siderite	0.0001	0.0011	0.0010	0.0039	0.0001
Smectite	0.0334	0.0450	0.1014	0.1368	0.0145

Table 6.3. Mineral proportions (volume fraction of solid) in the five rock type classes (Mishra et al., 2019).

The thermodynamic data was used from the thermXu4.dat database available from TOUGHREACT. Transition state theory (Lasaga, 2014) was used to model dissolution and precipitation reactions using the following rate law:

$$R = \frac{\partial M}{\partial t} = \pm kA(1 - SI) \quad (6.8)$$

where,

R = reaction rate at time t (mol sec⁻¹),

M = amount of the given mineral at time t (mol),

k = rate constant (mol cm⁻² sec⁻¹),

A = specific surface area of the given mineral (cm² gm⁻¹),

SI = saturation index of the given mineral at time t.

Positive values of R indicate mineral dissolution while negative values indicate mineral precipitation. The reaction rate constant, k, can further be expressed as (Palandri and Kharaka, 2004):

$$k = k_{25}^n \exp \left[\frac{-E_a^n}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^a \exp \left[\frac{-E_a^a}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_H} \quad (6.9)$$

where,
 k_{25} = rate constant at 25°C ($\text{mol cm}^{-2} \text{sec}^{-1}$),
 E_a = activation energy (J mol^{-1}),
 R_g = universal gas constant, taken to be $8.31 \text{ J mol}^{-1} \text{K}^{-1}$,
 T = absolute temperature (K),
 a_H = activity of H^+ ion,
 n_H = reaction order.

Superscripts ‘n’ and ‘a’ denote corresponding values for neutral and acidic mechanisms. In the present study, the values of k_{25} and E_a have been taken to be the same for the dissolution and precipitation reactions.

Formation water composition of the site is shown in Table 6.4 (Vu et al., 2017) while mineral composition, reaction kinetic parameters (Palandri and Kharaka, 2004) and specific surface areas (Table 6.5) (Haese et al., 2014; Xu et al., 2004b; Yang et al., 2014) for each mineral are shown in Table 6.5.

Formation Water Ionic Composition	Speciated concentration ($\times 10^{-3} \text{ mol kg}^{-1} \text{H}_2\text{O}$)
Na^+	24.5
K^+	1.4
Ca^{2+}	3.1
Mg^{2+}	4.2
SiO_2	0.7
Fe	0.4
AlO_2^-	1.0
HCO_3^-	4×10^{-8}
pH	8.02

Table 6.4. Formation water chemistry modified after Vu et al., 2017.

Mineral	Composition	E_a (kJ mol^{-1})	k_{25} ($\text{mol m}^{-2} \text{sec}^{-1}$)	A ($\text{cm}^2 \text{gm}^{-1}$)
Albite	$\text{NaAlSi}_3\text{O}_8$	65	6.92E-11	10.0
Ankerite	$\text{CaMg}_{0.3}\text{Fe}_{0.7}(\text{CO}_3)_2$	14.4	5.012E-01	0.001
Calcite	CaCO_3	14.4	5.012E-01	0.001
Chalcedony	SiO_2	87.7	1.26E-14	10.0
Chlorite	$\text{Al}_2\text{Mg}_{2.5}\text{Fe}_{2.5}^{\text{II}}\text{Si}_3\text{O}_{10}(\text{OH})_8$	88.0	7.76E-12	70.0
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	36.1	6.46E-04	0.001
Illite	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$	23.6	1.05E-11	70.0
K-Feldspar	KAlSi_3O_8	51.7	8.71E-11	10.0
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	65.9	4.90E-12	70.0
Magnesite	MgCO_3	14.4	4.16E-07	0.001
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	22.0	1.41E-12	70.0
Quartz	SiO_2	87.5	1.26E-14	10.0
Siderite	FeCO_3	14.4	5.01E-01	0.001
Smectite	$\text{Ca}_{0.145}\text{Mg}_{0.26}\text{Al}_{1.77}\text{Si}_{3.97}\text{O}_{10}(\text{OH})_2$	23.6	1.04E-11	70.0

Table 6.5. Reaction kinetic parameters (Palandri and Kharaka, 2004) and specific surface area (Haese et al., 2014; Xu et al., 2004b; Yang et al., 2014) for each mineral implemented in the model realizations.

Chalcedony was included to account for the low pressure-temperature precipitation of silica.

6.2.3. Dynamic simulation set-up

Multiphase reactive transport simulations were run using the ECO2N equation of state module in TOUGHREACT v1.2 (Xu et al., 2011). Supercritical CO₂ was injected at the base of the models (Figures 6.1b, 1c) with a flux of 0.001 kg sec⁻¹ m⁻² for a duration of 30 minutes and allowed to rise under buoyancy. The top, left and right boundaries of the model were open to allow the lateral migration of supercritical CO₂ underneath the baffle. Simulations were carried out under a hydrostatic pressure of 15 MPa and reservoir temperature of 60°C which corresponds to a depth of approximately 1500m in the Otway Basin. CO₂ exists in supercritical and dissolved phases under these pressure-temperature conditions. Simulations were run for a period of 1000 years. Dissolved CO₂ together with all other ions were allowed to diffuse with a diffusion coefficient of 2x10⁻⁹ m² sec⁻¹ (Parkhurst and Appelo, 2013). Ankerite, dolomite, calcite, magnesite, siderite, illite, kaolinite, smectite and chalcedony were allowed to precipitate as secondary minerals.

6.2.4. Quantification of mineral dissolution and precipitation

The results from the reactive transport simulations were analyzed to develop insights into the factors governing carbon mineral trapping at cm-scale. For this purpose, the changes in the volume fractions of different minerals and the dissolved concentration of H⁺, Ca²⁺, Mg²⁺ and Fe²⁺ were calculated over the period of simulation to quantify the extent of precipitation and dissolution and the changes in formation water chemistry. The calculation was done separately for the baffle and the reservoir rock for each model realization in order to understand the dependencies between diffusive transport and dissolution/precipitation reactions across the interface.

6.2.5. Calculation of the mass of mineralogically trapped carbon

The mass of carbon mineralized per unit rock volume was determined from the volume fractions of five carbonate minerals using the principles of stoichiometry (Eq. 10).

$$M_{\min,t}^C = M_M^C \sum_{j=1}^5 \left(\frac{n_S^j V_{f,t}^j}{V_M^j} \right) \quad (6.10)$$

where,

$M_{\min,t}^C$ = mass of carbon in the mineral phase per unit whole rock volume at a given time t (gm cm⁻³),

M_M^C = molar mass of carbon (gm mole⁻¹),

$V_{f,t}^j$ = volume fraction of the carbonate mineral j at time t,

V_M^j = molar volume of the carbonate mineral j (cm³ mole⁻¹) (Robie and Bethke, 1962),

n_S^j = stoichiometry of carbon in one formula unit of the carbonate mineral j.

First, the molar volumes of five carbonate minerals (ankerite, calcite, dolomite, magnesite and siderite) were used to determine the moles of carbon at each time step for each mineral. The difference in the values at the beginning and the end of the simulation was then summed for the five minerals to

obtain the gain or loss of solid phase carbon (expressed in moles). The value is multiplied by the molar mass of carbon to obtain the amount of carbon mineralized (expressed in grams). Positive values of $M_{\min,t}^C$ signify carbon mineralization while negative values signify a net carbonate dissolution. The two scenarios are henceforth referred to as positive and negative mineral trapping, respectively.

6.3. Results

6.3.1. Distribution of supercritical and dissolved CO₂

The injected supercritical CO₂ accumulated within the reservoir rock layer below the lithological boundary (Figure 6.2a). The high entry pressure of the baffles restricted the entry of supercritical CO₂ across the lithological interface. The open boundaries on the right and left allowed the transport of CO₂ laterally underneath the baffle. This results in snap-off residual trapping of supercritical CO₂ rather than capillary heterogeneity trapping within the reservoir rock layer (Trevisan et al., 2017). Hence, the open boundary conditions help in replicating the flow behaviour characteristic of a real 3D rock. The distribution of residual CO₂ stabilized within the first hour of simulation. CO₂ saturation varied between 25-30% in the reservoir rock. The advection was accompanied by the dissolution of supercritical CO₂ into the formation brine. The diffusion of dissolved CO₂ and H⁺ ions into the baffle occurred within the first six months of simulation (Figure 6.2b). The amount of dissolved CO₂ varied between 2.734-2.739% of the total moles and did not change any further during the 1000 year period. This translates to a concentration of 1.561 to 1.564 moles of dissolved CO₂ per kg water. Dissolved CO₂ was enriched in reservoir rock layer while its concentration decreased into the baffle and was governed by diffusion. The concentrations of other ionic species in brine are at least 3 orders of magnitude smaller than the amount of dissolved CO₂. The solubility of supercritical CO₂ into formation brine is a function of temperature, pressure and salinity (Doughty, 2010). The three parameters were held constant in the

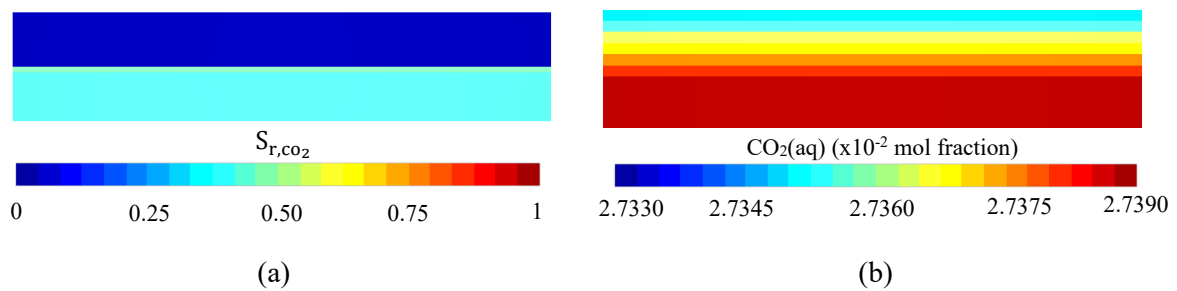


Figure 6.2. (a) Steady state residual CO₂ saturation distribution for a representative realization, I_{FSSt}^{Slt} , which was achieved within 1 hour of injection; (b) Steady state dissolved CO₂ concentrations across the lithological interface for the same realization was reached within the first 6 months after injection. The dissolved concentration of CO₂ was observed to be similar for all eight realizations with a lithological interface. The model dimensions are 10 cm horizontally and 2 cm vertically.

simulations as accounting for the variation in dissolved CO₂ was not in the scope of this paper. The implemented values of temperature, pressure and salinity lead to an excess amount of dissolved CO₂

within the reservoir rock which was sufficient to drive geochemical reactions until equilibrium during the 1000 year period.

6.3.2. Changes in mineral content

The amount of different minerals changed at different rates in the two rock types for the range of realizations. The changes in mineral volume fractions for the reservoir rock layer, baffle layer and homogeneous models are shown in Figures 6.3, 6.4 and 6.5, respectively. Figure 6.3 illustrates that all minerals in the reservoir rock layer, except kaolinite (Figure 6.3e), showed dissolution. Albite (Figure 6.3a) and K-feldspar (Figure 6.3b) showed dissolution. The results suggest that within the reservoir rock layer: (i) carbonate minerals such as ankerite (Figure 6.3g), calcite (Figure 6.3h), dolomite (Figure 6.3i) and siderite (Figure 6.3k) dissolved completely within the first year of simulation (ii) magnesite showed a slower dissolution rate compared to other carbonate minerals (Figure 6.3j) and (iii) kaolinite was the only clay mineral which precipitated (Figure 6.3e) while chlorite (Figure 6.3c), illite (Figure 6.3d) and smectite (Figure 6.3f) dissolved.

Figure 6.4 illustrates changes in the mineral content for the baffle layer. Different dissolution and precipitation responses were observed for carbonate-cemented (I_{CSst}^{CbSst} , I_{FSst}^{CbSst} and I_{Slt}^{CbSst}) and carbonate-depleted (I_{CSst}^{Mst} , I_{FSst}^{Mst} , I_{Slt}^{Mst} , I_{CSst}^{Slt} and I_{FSst}^{Slt}) rock types. For the realizations with mudstone and siltstone baffles, illite (Figure 6.4d) and dolomite (Figure 6.4i) precipitated while the other minerals dissolved. For the realizations with carbonate-cemented baffles, dissolution of all minerals except for kaolinite (Figure 6.4e) and calcite (Figure 6.4h) was observed. Calcite (Figure 6.4h) and dolomite (Figure 6.4i) showed net precipitation in the first year of simulation followed by dissolution in the realizations I_{CSst}^{CbSst} and I_{FSst}^{CbSst} . Ankerite (Figure 6.4g) showed slower dissolution as compared to dissolution in the reservoir rock layer (Figure 6.3g).

All minerals except for kaolinite dissolved in simulations using homogeneous realizations (Figure 6.5). The rate of dissolution of carbonate minerals such as ankerite (Figure 6.5g), calcite (Figure 6.5h), dolomite (Figure 6.5i) and siderite (Figure 6.5k) was significantly higher as they completely dissolved within the first year of simulation.

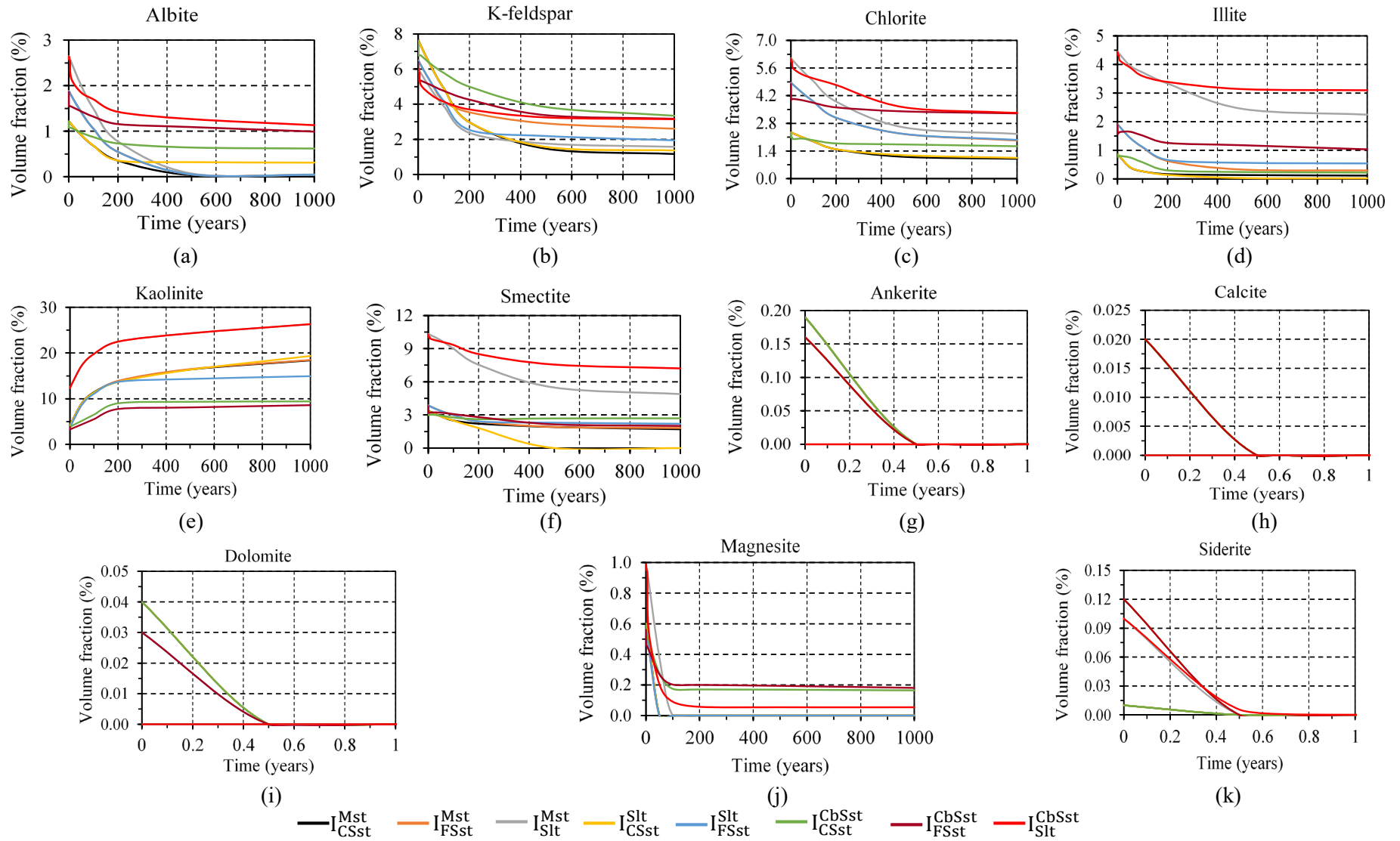


Figure 6.3. Change in the solid volume fraction of different minerals in the reservoir rock layer.

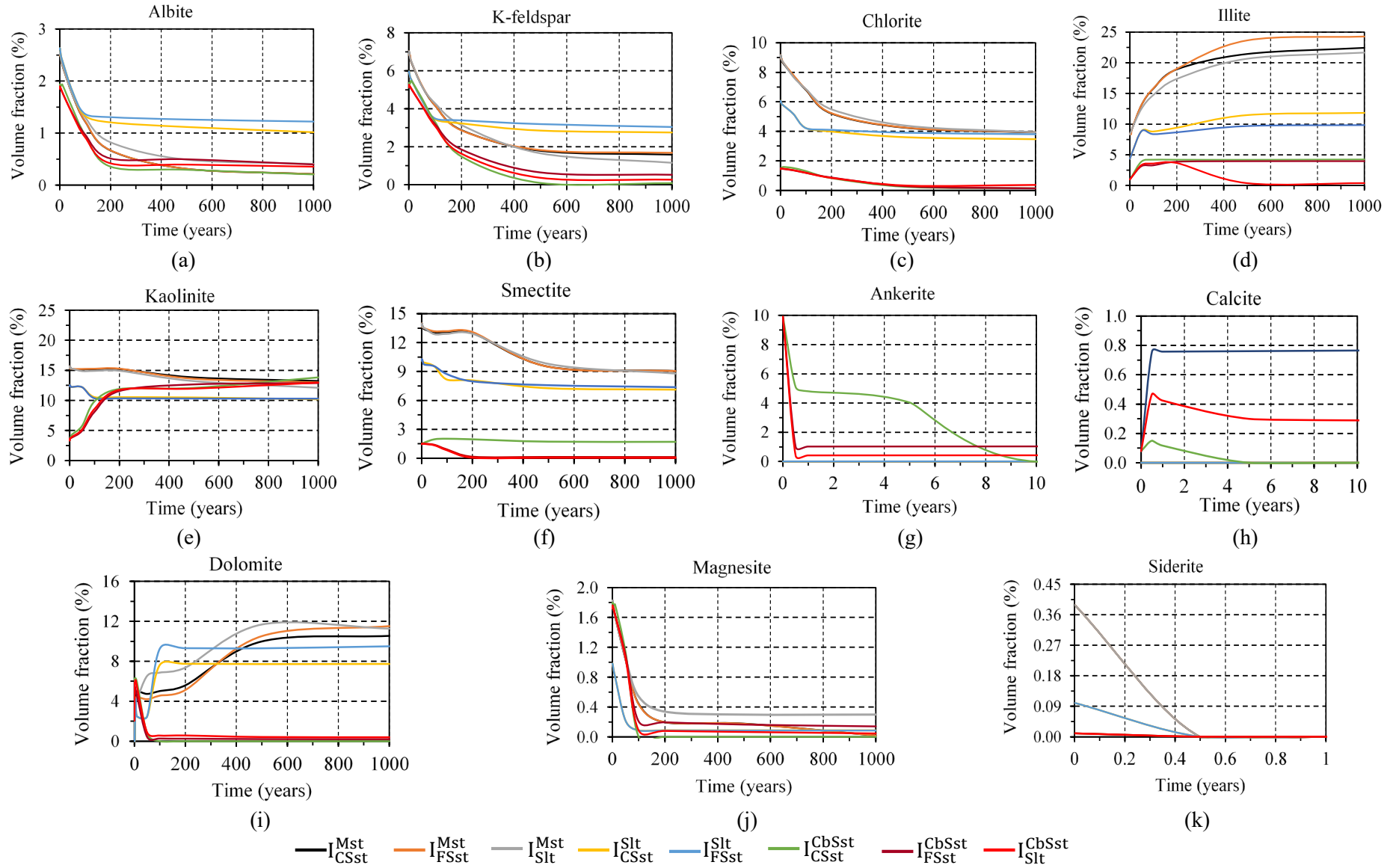


Figure 6.4. Change in the solid volume fraction of different minerals in the baffle layer.

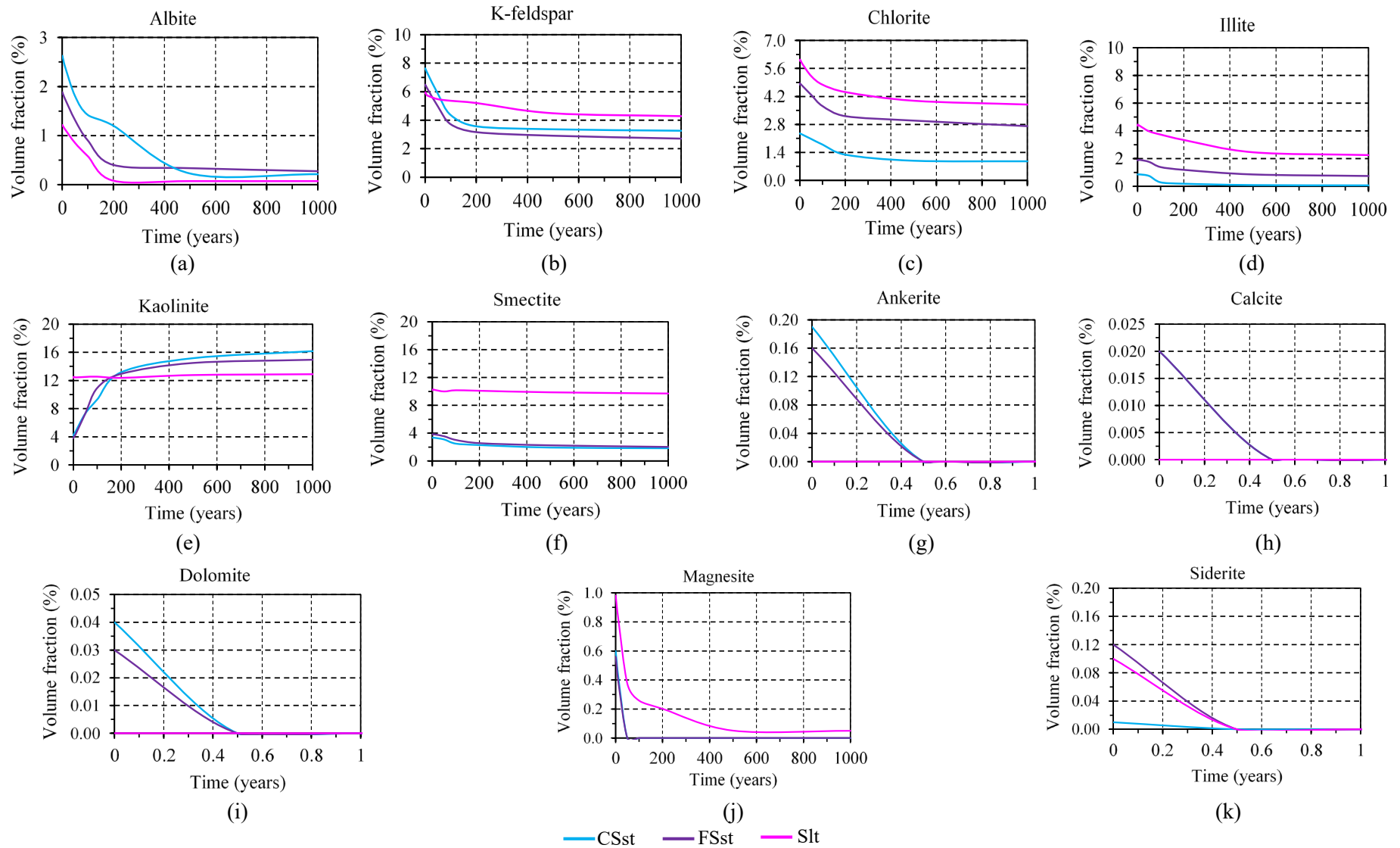


Figure 6.5. Change in the solid volume fraction of different minerals in the three homogeneous realizations.

Dolomite was the only carbonate mineral to precipitate for the realizations with mudstone and siltstone baffles (Figure 6.4i). The precipitation of dolomite was observed at the interface within the baffle layer (Figure 6.6). The precipitation amount showed a gradient with the highest amount of precipitation observed at the interface which decreased further away from the interface into the baffle.

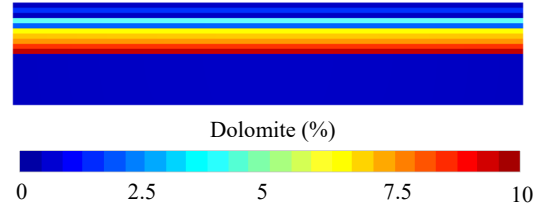


Figure 6.6. Amount of dolomite in the solid phase for the representative realization I_{FSst}^{Slt} after a period of 1000 years. Similar distribution profiles were observed for the realizations with carbonate depleted baffles.

6.3.3. Changes in pH and dissolved Ca^{2+} , Fe^{2+} and Mg^{2+} concentrations

The pH evolution varied for the different realizations (Figure 6.7). For the reservoir rock layer of the heterogeneous realizations (Figure 6.7a), pH showed a sharp decline from the initial value of 8.02 to approximately 3.5 in the first six months of simulation. Over time, pH gradually increased for the realizations with carbonate depleted baffles (I_{CSst}^{Mst} , I_{FSst}^{Mst} , I_{Slt}^{Mst} , I_{CSst}^{Slt} and I_{FSst}^{Slt}) but did not exceed 4.5. The pH dropped from 8.02 to 4.5-5.25 for the baffle layer within the first year of simulation (Figure 6.7b). Initial buffering of pH was observed for the realizations with carbonate-cemented baffles (I_{CSst}^{CbSst} , I_{FSst}^{CbSst} and I_{Slt}^{CbSst}) where the dissolution of carbonate led to a rise of pH to 5-5.5. pH gradually increased to 6-6.25 over a period of 200-500 years for the realizations with mudstone and siltstone baffles. On the

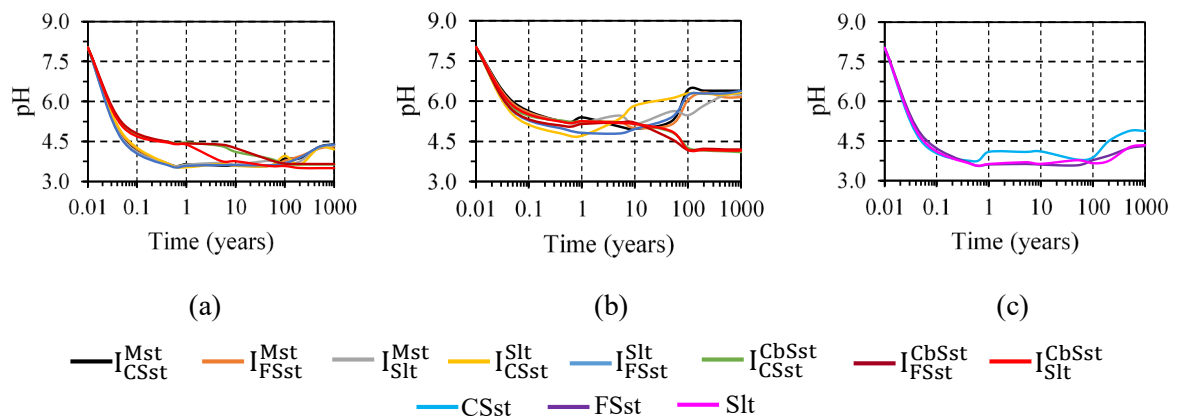


Figure 6.7. Changes in the pH for the (a) reservoir rock layer of the heterogeneous realizations; (b) baffle layer of the heterogeneous realizations; and (c) homogeneous realizations.

other hand, pH eventually reduced to 4-4.5 for the realizations with carbonate-cemented sandstone. The homogeneous rock types showed an initial decrease of pH from 8.02 to 3.5-4 within the first year of

simulation. Subsequently, the pH slightly increased over the period of simulation but did not exceed a value of 5.

Changes in pH were different for carbonate-cemented (I_{CSst}^{CbSst} , I_{FSst}^{CbSst} and I_{Slt}^{CbSst}) and carbonate-depleted (I_{CSst}^{Mst} , I_{FSst}^{Mst} , I_{Slt}^{Mst} , I_{CSst}^{Slt} and I_{FSst}^{Slt}) baffles. Figure 6.8 shows the pH evolution profiles for a representative realization with carbonate-depleted baffle, I_{FSst}^{Slt} (Figure 6.8a) and for a representative realization with carbonate-cemented sandstone baffle I_{CSst}^{CbSst} (Figure 6.8b). Similar pH evolution profiles

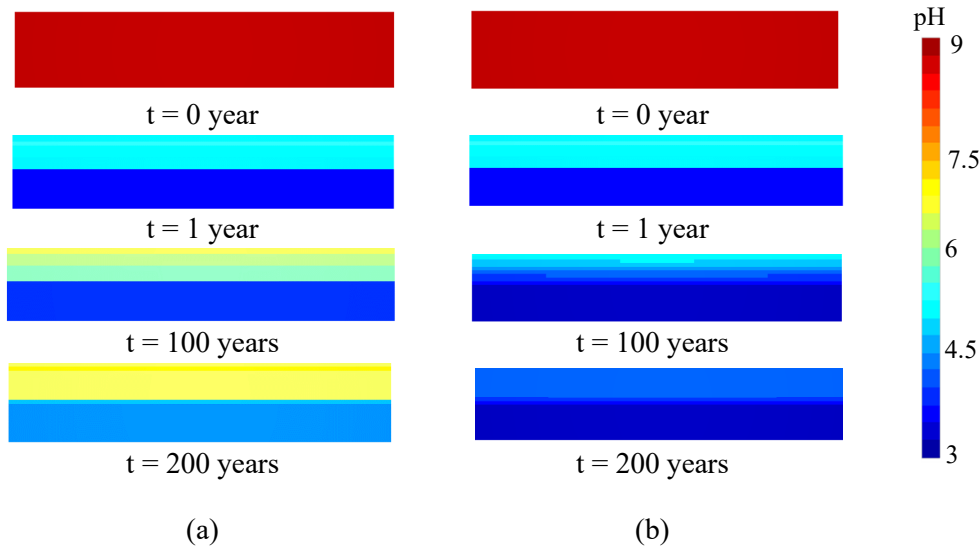


Figure 6.8. Evolution of pH profiles in simulations with (a) carbonate-depleted baffle (I_{FSst}^{Slt}); (b) carbonate-cemented sandstone baffle (I_{CSst}^{CbSst}). The other realizations in the two categories showed similar pH evolution profiles.

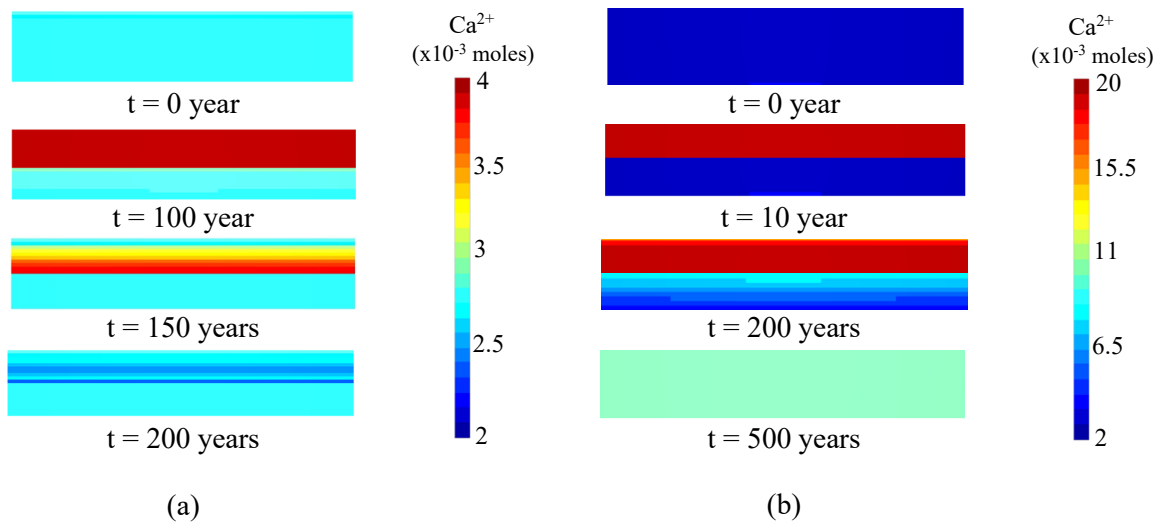


Figure 6.9. Ca^{2+} concentration (mol kgw^{-1}) evolution profiles for the realization with (a) carbonate depleted baffle (I_{FSst}^{Slt}); (b) carbonate-cemented sandstone baffle (I_{CSst}^{CbSst}). The other realizations in the two categories showed similar Ca^{2+} evolution profiles.

were observed for other realizations as well. For the former, pH was always lower in the reservoir rock layer as compared to that in the baffle. The pH within the baffle layer showed a gradual increase and stabilized at a value of 6-6.5 after 200 years of simulation. For I_{CSst}^{CbSst} , a similar profile was observed initially, followed by a gradual decrease of pH in the baffle over the same period of simulation. Apart from pH, the precipitation of carbonate minerals is governed by the amount of dissolved Ca^{2+} (Figure 6.9), Fe^{2+} (Figure 6.10) and Mg^{2+} (Figure 6.11) ion concentrations. The amount of the three ions showed an initial increase in the baffle as compared to the reservoir rock layer after 50-100 years of simulation.

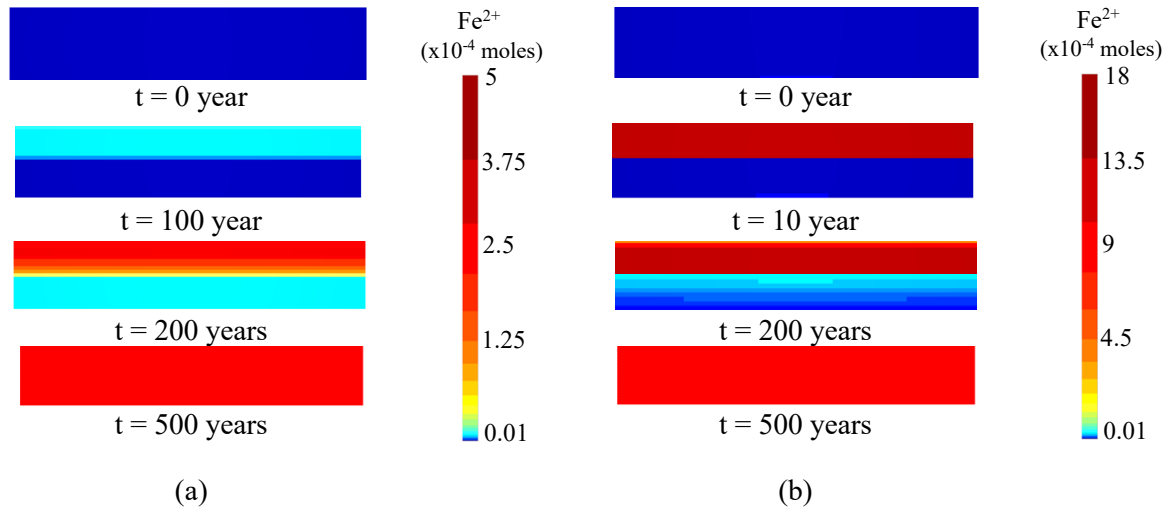


Figure 6.10. Fe^{2+} concentration ($mol\ kgw^{-1}$) evolution profiles for the realization with (a) carbonate depleted baffle (I_{FSst}^{Slt}); (b) carbonate-cemented sandstone baffle (I_{CSst}^{CbSst}). The other realizations in the two categories showed similar Fe^{2+} evolution profiles.

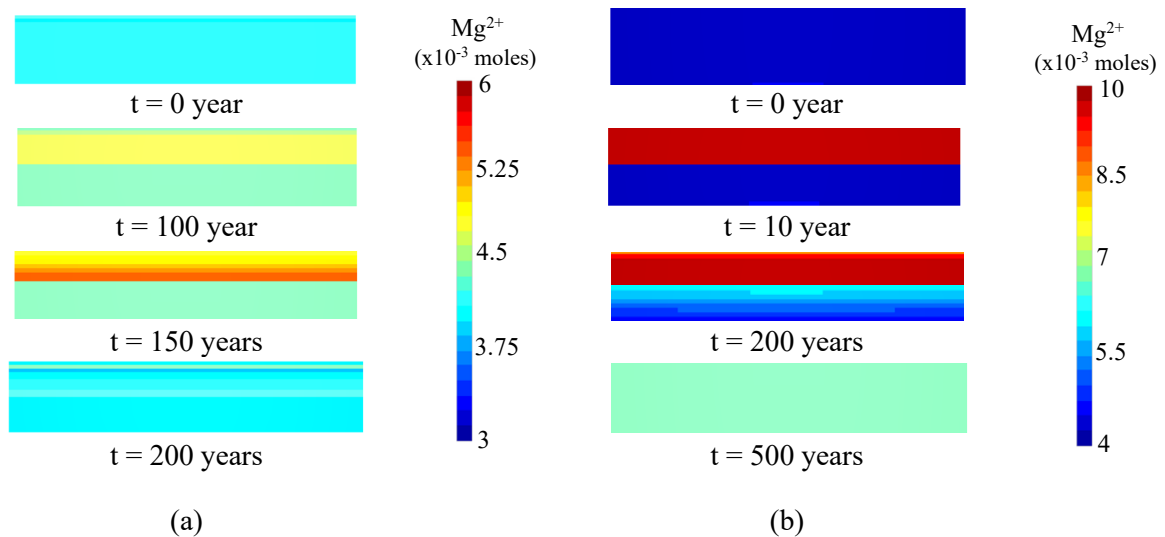


Figure 6.11. Mg^{2+} concentration ($mol\ kgw^{-1}$) evolution profiles for the realization with (a) carbonate depleted baffle (I_{FSst}^{Slt}); (b) carbonate-cemented sandstone baffle (I_{CSst}^{CbSst}). The other realizations in the two categories showed similar Mg^{2+} evolution profiles.

This was followed by their diffusive transport towards the reservoir rock layer. Consequently, Ca^{2+} (Figure 6.9a) and Mg^{2+} (Figure 6.11a) concentrations for the realizations with mudstone and siltstone baffles decreased between 100 and 200 years. The concentration of the three ions in the realization with carbonate-cemented sandstone baffle (Figure 6.9b, 10b and 11b) underwent diffusive transport into the reservoir rock layer before reaching steady state conditions after about 500 years of simulation.

6.3.4. Amount of carbon trapped mineralogically

The net change in the volume fraction of carbonate minerals was used to calculate the total mass of carbon trapped mineralogically for each realization (Figure 6.12). The change in the amount of carbon mineralized varied rapidly during the first 200 years of simulation after which the rate of change declined. Three distinct types of behavior with respect to carbon mineralization were observed (Figure 6.12). The first group showed a net increase in the mass of carbon mineralized and is characteristic of the realizations with mudstone and siltstone baffles ($I_{\text{CSst}}^{\text{Mst}}$, $I_{\text{FSst}}^{\text{Mst}}$, $I_{\text{Slt}}^{\text{Mst}}$, $I_{\text{CSst}}^{\text{Slt}}$ and $I_{\text{FSst}}^{\text{Slt}}$). The second group showed slight decrease in the mass of carbon in solid phase representing a net dissolution of carbonate minerals. This is characteristic of the homogeneous realizations (CSst, FSst and Slt). The third group depicted significant decrease in the mass of carbon mineralized and is characteristic of the realizations with carbonate-cemented sandstone baffles ($I_{\text{CSst}}^{\text{CbSst}}$, $I_{\text{FSst}}^{\text{CbSst}}$ and $I_{\text{Slt}}^{\text{CbSst}}$).

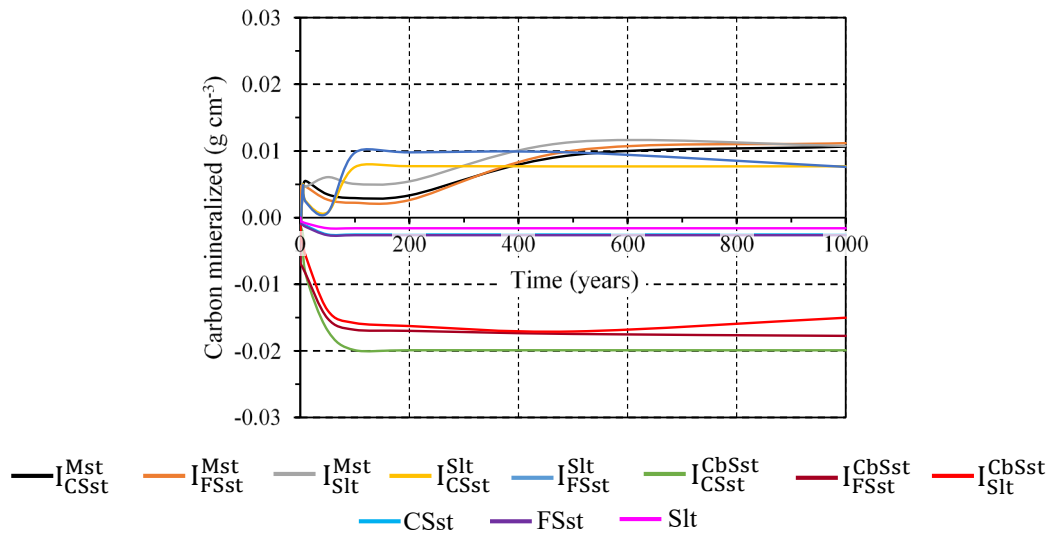


Figure 6.12. Total carbon mineralized per unit rock volume in each realization over 1000 years. Positive values indicate a net gain in the amount of carbon in the mineral phase while negative values indicate a net loss of carbon from the mineral phase.

6.4. Discussion

6.4.1. Processes and conditions governing carbon mineralization

6.4.1.1. Mechanism of carbon mineralization at cm-scale lithological interfaces

The dissolution of supercritical CO₂ into the formation brine (Figure 6.2b) lowers the pH of the reservoir rock to values between 3.5-4.5 (Figure 6.7a). Dissolved CO₂ and H⁺ diffuse from the reservoir rock into the baffle (Figure 6.2b) lowering its pH from 8.02 to 4.5-5.25 (Figure 6.7b). The acidic conditions in both the lithologies leads to mineral dissolution. Reservoir rocks are enriched in framework minerals (quartz and feldspar) relative to clay and carbonate minerals (Table 6.3). The dissolution of albite (Figure 6.3a) and K-feldspar (Figure 6.3b) releases aluminium and silica ions which stimulate the precipitation of kaolinite (Figure 6.3e). Clay minerals such as chlorite (Figure 6.3c), illite (Figure 6.3d) and smectite (Figure 6.3f) (<10 volume% of solid phase, Table 6.3) undergo dissolution. The minor fraction of primary carbonate minerals (Figures 6.3g-k) (<1 volume% of solid phase) completely dissolves.

On the contrary, carbonate-depleted baffles are enriched in clay minerals compared to framework (quartz and feldspar) and carbonate minerals (Table 6.3). The acidic conditions in these baffles lead to partial dissolution of chlorite (Figure 6.4c), kaolinite (Figure 6.4e) and smectite (Figure 6.4f) and precipitation of illite (Figure 6.4d). Consequently, H⁺ ions are consumed, pH increased from 4.5-5.25 to 5.5-6.5 in the baffle and dissolution rates slow down (Figures 6.7b, 6.8a, 6.9a, 6.10a and 6.11a) during the first 100 years. The rise in pH suggests the rate of H⁺ consumption by chemical reactions exceeds the diffusive flux of H⁺ from the reservoir rock into the baffle. Concurrently, dissolved Ca²⁺, Fe²⁺ and Mg²⁺ become enriched in the baffle mainly due to the dissolution of smectite, chlorite and a combination of chlorite and smectite, respectively.

The enrichment of dissolved Ca²⁺, Fe²⁺ and Mg²⁺ in the baffle leads to a concentration gradient and associated diffusion of those cations from the baffle towards the reservoir rock layer. An enrichment of these ions near the interface of the two lithologies but within the baffle layer was observed (Figures 6.9a, 10a and 11a). The enrichment of the ions along with a rise of pH favors the precipitation of a carbonate mineral, primarily dolomite near the interface (Figures 6.4i and 6.6). This leads to a depletion of Ca²⁺ and Mg²⁺ ions from the brine (Figures 6.9a and 11a) while Fe²⁺ diffuses into the reservoir rock (Figure 6.10a). The realizations with carbonate-depleted baffles undergo a net increase of carbon in the mineral phase (Figure 6.12). This is because the conditions slowly become conducive for the precipitation of secondary carbonate minerals which is in turn driven by the balance between the supply of H⁺ ions by diffusion from the reservoir rock and their consumption by clay minerals.

However, the processes occurring in carbonate-cemented baffles evolve differently as they are enriched in primary carbonate minerals (>10 volume% of total solid phase) compared to clay minerals (<10 volume% of total solid phase) (Table 6.3). The initial drop in pH due to the diffusion of H⁺ from the reservoir rock to the baffle leads to the dissolution of primary carbonate minerals (Figures 6.4g-k). This increases the concentration of dissolved Ca²⁺, Fe²⁺ and Mg²⁺ ions. The released carbonate reacts with H⁺ to form bicarbonate. This quickly buffers the pH of the baffle to 5.25-5.75 within the first year

of simulation (Figures 6.7b and 6.8) (Newell et al., 2008) and slows down the dissolution of clay minerals. The rise in pH favors the precipitation of a minor amount of secondary calcite (Figure 6.4h). The dissolved Ca^{2+} , Fe^{2+} and Mg^{2+} ions diffuse towards the reservoir rock (Figures 6.9b, 6.10b and 6.11b). However, contrary to the case of carbonate-depleted baffles, the minor fractions of chlorite (Figure 6.4c) and illite (Figure 6.4d) in carbonate-cemented baffles are not sufficient to increase the pH within the baffle. Hence, the low pH as well as the low concentration of Ca^{2+} , Fe^{2+} and Mg^{2+} ions prevents the precipitation of secondary carbonates (Figures 6.4g-k) and the dissolved Ca^{2+} , Fe^{2+} and Mg^{2+} ions diffuse into the reservoir rock over time (Figures 6.9b, 6.10b and 6.11b). Also, the H^+ ions diffuse from the reservoir rock into the baffle (Figure 6.8b) and leads to further acidification of brine within the baffle layer (Figure 6.8b). Hence, the realizations with carbonate-cemented baffles undergo an overall loss of carbon from the mineral phase (Figure 6.12) as the primary carbonates dissolve while conditions do not favor the precipitation of secondary carbonates.

For simulations with homogeneous reservoir rocks, the entire volume is in contact with supercritical CO_2 trapped residually. This leads to a drop in pH from 8.02 to values of 3.5-4.5 within the first year of simulation (Figure 6.7c). A lack of sufficient clay minerals and the contact with supercritical CO_2 throughout the pore volume do not lead to a significant increase in pH, unlike in realizations with mudstone and siltstone baffles. Therefore, the homogeneous reservoir rocks do not experience the precipitation of secondary carbonates (Figures 6.5g-k). pH increases slightly over a period of a few hundred years due to the dissolution of the minor fraction of chlorite (Figure 6.5c). The dissolution of a minor fraction of primary carbonate minerals (Figures 6.5g-k) leads to an overall, but insignificant, loss of carbon from the mineral phase (Figure 6.12).

Previous field and simulation studies have confirmed the diffusion of dissolved CO_2 across the lithological interface resulting in comparatively higher dissolution of chlorites (Gherardi et al., 2007; Higgs et al., 2015; Xu et al., 2005) and precipitation of secondary carbonate minerals such as dolomite (Heinemann et al., 2013). The present study further extends our knowledge by providing a detailed understanding of the mechanisms governing carbon mineralization at the cm-scale lithological interfaces.

6.4.1.2. Factors governing carbon mineral trapping in intraformational baffles

The results suggest variable carbon mineralization in different realizations (Figure 6.12) which differ from each other in terms of flow properties and mineral composition. While flow properties primarily govern capillary trapping of supercritical CO_2 , it is the mineral composition that exerts a dominant control on positive or negative carbon mineral trapping. The mineralogy of reservoir rocks has very little impact on carbonate precipitation reactions while clay and carbonate content of the baffle influence the evolution of pH and the supply of bivalent cations (section 6.4.1.1). The impact of varying baffle

mineralogy on the amount of carbon mineralized is shown in Figure 6.13. It can be seen that the extent of mineral trapping is insensitive to the clay and carbonate content of the reservoir rock. However, an increase in the carbonate content of the baffle reduces the amount of mineral trapping (Figure 6.13a). A high carbonate content in baffle can lead to a loss of carbon from the mineral phase. On the other hand, higher chlorite concentrations in the baffles can enhance mineral trapping (Figure 6.13b).

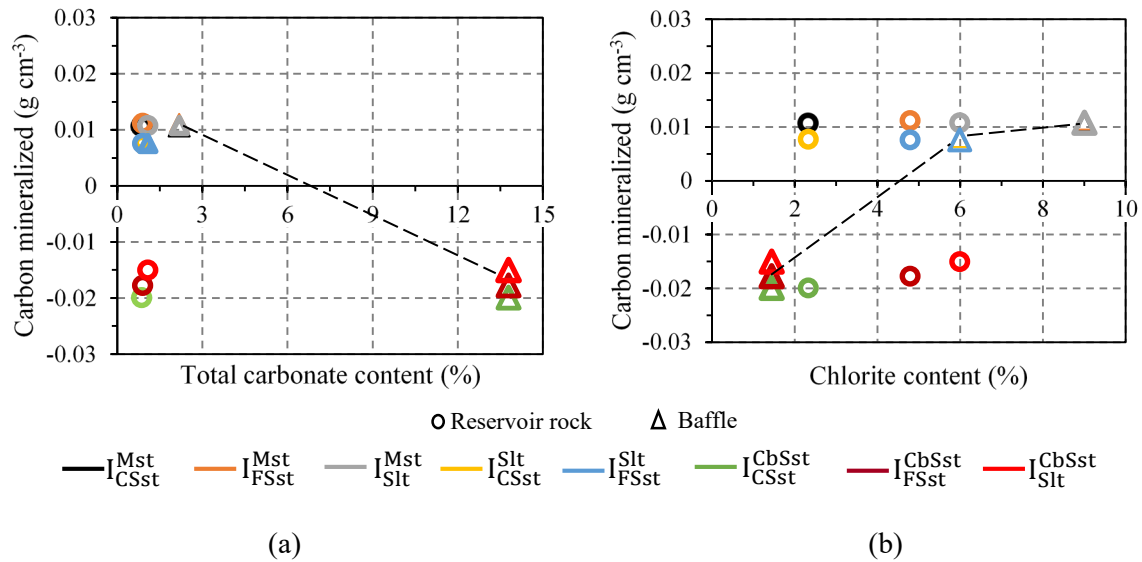


Figure 6.13. Dependence of carbon mineralization on (a) total carbonate content; and (b) chlorite content of the two lithologies.

The present study only takes into account a single reservoir-baffle interface of a given thickness. The understanding of the processes developed in this study can be used to qualitatively understand the impact of multiples interfaces and thicker beds on carbon mineralization. The presence of multiple lithological interfaces will lead to the precipitation of secondary carbonate at each interface boundary. However, the amount of carbon mineralized is expected to be the same for each baffle layer with similar thickness and mineral composition. The amount of carbon mineralized is expected to differ for thicker beds where the result will be controlled by the diffusion length scale relative to bedding thickness. For beds with a thickness greater than diffusion length scale, the minerals in proximity to the interface will contribute to mineral trapping while the minerals further away from the interface might not react. The mineral trapping capacity also depends on whether CO₂ enters the baffle or not. If supercritical CO₂ enters the baffle, then the presence of residual CO₂ will supply H⁺ ions to the baffle faster than their consumption by chlorite dissolution and illite precipitation resulting in acidic conditions over 100s of years, thereby inhibiting the precipitation of secondary carbonate minerals.

6.4.2. Variations in the amount of carbon mineralized

The range of constituent rock properties of the baffle and the reservoir rock leads to large differences in the amount of CO₂ mineralized (Figure 6.14). Homogeneous reservoirs are characterized by a complete loss of mineralized carbon due to the long term (500-1000 years) acidic conditions created by the presence of supercritical CO₂. However, the presence of mudstone and siltstone baffles might significantly enhance the mineral trapping capacity. On the other hand, the presence of carbonate-cemented rock types might lead to a significant loss of carbon from the mineral phase. The net amount of carbon mineralized at reservoir scales will depend on the proportion of different types of baffles. Significant mineral trapping (as much as 250-400% higher than in homogeneous reservoirs) can be expected in heterogeneous reservoirs comprising mudstone and siltstone baffles depleted in carbonates (Figure 6.14). On the other hand, a net loss of carbon from the mineral phase occurs where carbonate cements are abundant. In this case, almost the same amount of carbon is lost from the mineral phase compared to homogeneous reservoirs, though the absolute amount will be significantly higher (Figure 6.14). The large range of variation in the impact of different types of baffles on carbon mineralization highlights the need for a careful reservoir characterization. A lack of appropriate characterization of cm-scale lithological heterogeneity or its neglect in reservoir modelling studies might lead to conclusions that mineral trapping is insignificant (Czernichowski-Lauriol et al., 2006; Gilfillan et al., 2009; Heinemann et al., 2013; Li and Pang, 2015; Pang et al., 2012). This is true for homogeneous reservoirs and reservoirs with carbonate-cemented lithologies. However, in reservoirs with significant mudstone and siltstone baffles, carbon mineral trapping may be significantly enhanced.

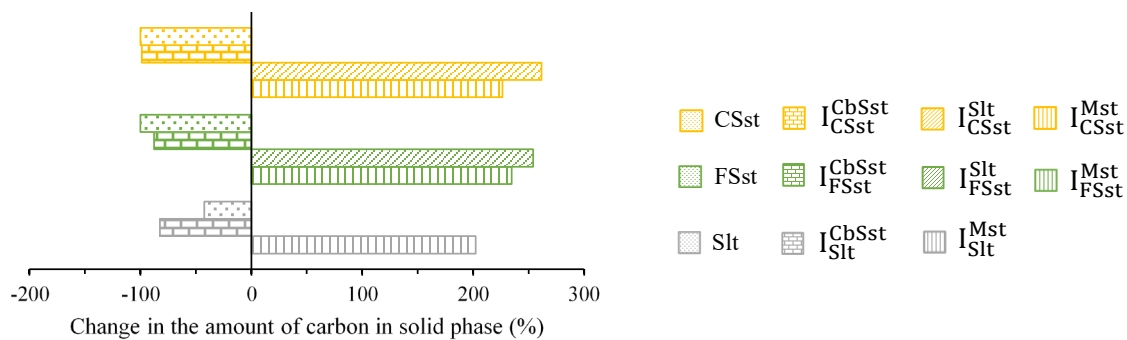


Figure 6.14. Variation in the amount of carbon mineralized over 1000 years for different reservoir and baffle rock types.

6.4.3. Reduced geochemical parameters

The results show that carbon mineral trapping can be significant under certain lithological conditions. Hence, it is important to account for potentially enhanced trapping in coarser scale models in order to improve the estimation of carbon trapping capacity. However, cm-scale interfaces are typically neglected in coarser models due to the computational limitation posed by grid size resolution and the assumption of negligible carbon mineralization. To overcome this problem, it is necessary to

obtain averaged geochemical parameters such as reaction rate and mineral composition based on results from fine scale simulation. The averaged parameters incorporate the impact of baffles and can further be used in reduced geochemical systems at coarser scale where resolving mm- and cm-scale lithological heterogeneities is not practical.

6.4.3.1. Averaged mineral specific reaction rates

The results show that the amount of a given mineral changes at different rates in the baffle and in the reservoir rock layer for any given realization (section 6.3.2). Hence, the mineral specific reaction rates in the baffle and in the reservoir rock can be averaged to obtain mineral specific reaction rates for the reduced model. For a given realization, the net amount of a mineral is the sum of its amount in the baffle and the reservoir rock at any point in time. The net mineral content was used to formulate an averaged rate for each mineral using the following equation:

$$\bar{R} = \frac{\Delta \bar{M}}{\Delta t} \quad (6.11)$$

where,

$\bar{R}$ = averaged reaction rate for the given mineral (mol sec⁻¹),

$\Delta \bar{M}$ = change in the total amount of a mineral in baffle and in reservoir rock at over time Δt (mole),

Δt = time interval (sec).

The calculation was done for all the minerals in each realization and the temporal variations of $\bar{R}$ are shown in Figure 6.15.

The averaged mineral specific reaction rates take into account the evolving volume fractions of each mineral in each realization for the period of simulation. These reaction rates can further be used in coarse scale geochemical simulations addressing carbon mineralization. This is especially important to account for the precipitation of secondary carbonate minerals within the baffles (Figures 6.15g,h,i,j,k). Also, the evolution of clay minerals is different in a homogeneous rock compared to a heterogeneous rock (Figures 6.15c,d,e,f). If the averaged reaction rates are ignored, the evolution of clay and carbonate minerals will in coarser scale simulations be different and may result in an underestimation of carbon mineral trapping capacity. The approach used here has been utilized in previous studies (Kim et al., 2011; Wen and Li, 2017; Wen and Li, 2018) and was modified in the context of the present study. However, previous studies focused on simple geochemical systems with up to two or three constituent minerals. In case of this study, the approach has led to the derivation of nearly a hundred averaged mineral specific reaction rates. Hence, the implementation of averaged reaction rates in reduced models at coarser scales might be impractical as the large number of rate equations will add to computation time.

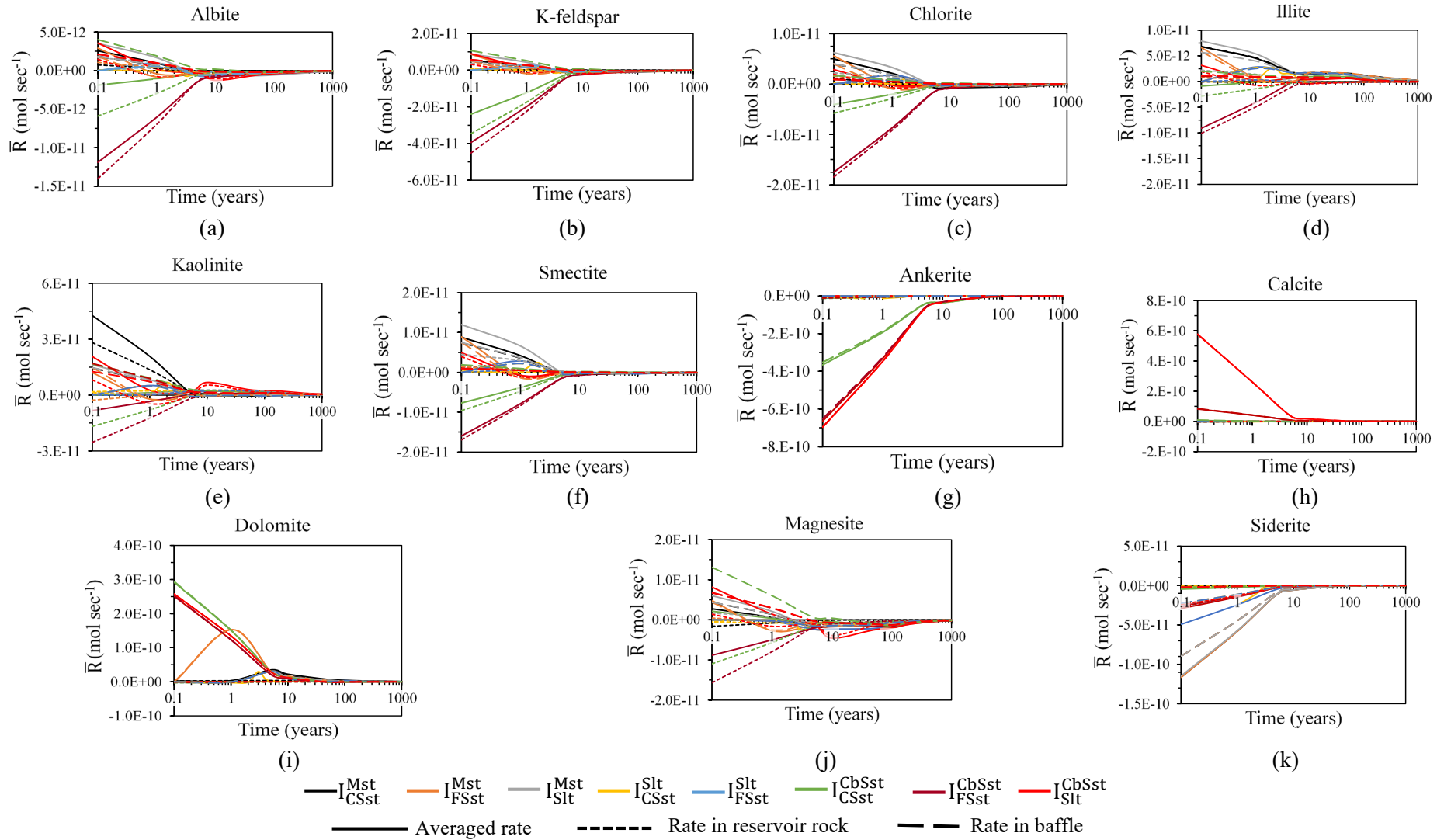


Figure 6.15. Mineral specific averaged reaction rates for all the minerals in different realizations. The reaction rate of the mineral in the baffle and the reservoir rock layer are also shown by two stippled lines.

6.4.3.2. Averaged mineral composition

Our results have shown that not all minerals contribute to carbon mineral trapping (section 6.4.1). Specifically, all the minerals present within the reservoir rock layer have an insignificant impact on carbon mineralization while the minerals present within the baffle layer govern mineral trapping. These observations can be utilized to formulate an averaged initial mineral composition such that the lithologies contributing to mineral trapping are accounted for in the reduced model at coarser scale while the lithologies not contributing to mineral trapping are neglected. Hence, the total mineral composition of the system can be modified as follows:

$$\bar{M}^{\text{initial}} = M_{\text{baffle}}^{\text{initial}} + f.M_{\text{reservoir rock}}^{\text{initial}} \quad (6.12)$$

where,

$M_{\text{baffle}}^{\text{initial}}$ = initial amount of a given mineral in the baffle (mole),

$M_{\text{reservoir rock}}^{\text{initial}}$ = initial amount of a given mineral in the reservoir rock (mole),

$\bar{M}^{\text{initial}}$ = total initial amount of a mineral in the given realization (mole),

f = a binary variable depending on the contribution of minerals in reservoir layer to carbon mineralization.

To derive the reduced mineral composition, the value of ‘ f ’ was set to zero for the realizations with carbonate depleted baffles ($I_{\text{CSst}}^{\text{Mst}}$, $I_{\text{FSst}}^{\text{Mst}}$, $I_{\text{Slt}}^{\text{Mst}}$, $I_{\text{CSst}}^{\text{Slt}}$ and $I_{\text{FSst}}^{\text{Slt}}$). This is because minerals in the reservoir rock do not contribute to the precipitation of secondary carbonate minerals. Only the minerals in the baffle contribute to carbon mineralization and are accounted for in the reduced models. For the realizations with carbonate-cemented sandstone baffles ($I_{\text{CSst}}^{\text{CbSst}}$, $I_{\text{FSst}}^{\text{CbSst}}$ and $I_{\text{Slt}}^{\text{CbSst}}$), the value of f was set to 1 resulting in the mineral content of both the layers to be taken into account. This is because these realizations show a net negative carbon mineral trapping which results from the dissolution of carbonate minerals in both the lithologies.

Except for the cases where f was set to 0, the values of $M_{\text{baffle}}^{\text{initial}}$ and $M_{\text{reservoir rock}}^{\text{initial}}$ are derived by converting the respective volume fractions from Table 6.3 to moles. The resultant amount of minerals, $\bar{M}^{\text{initial}}$, is further converted from moles to volume fraction and is shown in Table 6.6.

The use of averaged mineral composition in reduced geochemical models does not increase the number of reaction rate equations contrary to the use of averaged mineral specific reaction rates. The number of reaction rate equations remain 11, specific to each mineral. In other words, the rate equations are the same for a given mineral across all the realizations, only their amount varies. On the contrary, the first approach resulted in a total of 88 reaction rates, specific to 11 minerals, where the reaction rate of each mineral varied

across each of the 8 realizations. Hence, this approach yields nearly eight times fewer rate equations for the realizations of this study. Also, no simulations are required for the lithologies where there is no net change in the amount of carbon. In traditional approaches of averaging mineral compositions, the mineral content of both the lithologies is averaged. However, this might increase the content of clay and carbonate minerals in the reduced models which may lead to a wrong estimation of mineral trapping capacities. By neglecting the lithologies that do not contribute to carbon mineralization, it is ensured that the amount of carbon mineralized or dissolved in the reduced domain is the same as in the fine scale simulations. Note, flow and petrophysical properties of the two constituent lithologies must be taken into account when obtaining a reduced flow model. On the contrary, the mineral composition is averaged by selectively modifying the initial mineral composition of the two rock types.

Mineral	I_{CSst}^{Mst}	I_{FSst}^{Mst}	I_{Slt}^{Mst}	I_{CSst}^{Slt}	I_{FSst}^{Slt}	I_{CSst}^{CbSst}	I_{FSst}^{CbSst}	I_{Slt}^{CbSst}
Albite	0.0135	0.0135	0.0127	0.0139	0.0138	0.0155	0.0185	0.0223
Ankerite	0.0000	0.0000	0.0000	0.0000	0.0000	0.0537	0.0534	0.0497
Calcite	0.0000	0.0000	0.0000	0.0000	0.0000	0.0005	0.0005	0.0004
Chlorite	0.0482	0.0481	0.0454	0.0318	0.0317	0.0186	0.0301	0.0371
Dolomite	0.0000	0.0000	0.0000	0.0000	0.0000	0.0112	0.0111	0.0103
Illite	0.0445	0.0443	0.0419	0.0232	0.0231	0.0093	0.0141	0.0268
K-Feldspar	0.0370	0.0369	0.0349	0.0314	0.0313	0.0628	0.0573	0.0551
Kaolinite	0.0825	0.0822	0.0777	0.0657	0.0654	0.0370	0.0354	0.0783
Magnesite	0.0096	0.0096	0.0091	0.0052	0.0052	0.0120	0.0118	0.0135
Muscovite	0.0277	0.0276	0.0261	0.0170	0.0170	0.0100	0.0113	0.0214
Quartz	0.6531	0.6544	0.6731	0.7490	0.7499	0.7437	0.7254	0.6187
Siderite	0.0021	0.0021	0.0020	0.0005	0.0005	0.0001	0.0006	0.0005
Smectite	0.0735	0.0733	0.0693	0.0538	0.0536	0.0233	0.0255	0.0578

Table 6.6. The reduced mineral composition (volume fraction of solid) of the realizations.

The presented averaged geochemical parameters are limited in application to systems where the amount of reactive minerals in baffles is similar to that used in the present study. The reactive amount depends on the balance between diffusion length scale and baffle thickness. For baffles with increasing thickness, the fraction of minerals contributing to carbon mineralization within the baffles is governed by the diffusion distance by various ions into the baffles. On the contrary, the application of both the averaging approaches is not limited by the volume of reservoir rock. For reservoirs rocks with dimensions different from the present study, the averaged geochemical parameters can be derived by changing the relevant parameters in equations 6.11 and 6.12.

6.5. Conclusions

This study presents an improved understanding of conditions leading to carbon mineralization and quantifies carbon mineral trapping at lithological interfaces characteristic of cm-scale heterogeneity. Eight 2D multiphase reactive transport simulations were set up with a range of baffle and reservoir rock properties. The study shows that the balance in the supply of H^+ ions from the reservoir rock to the baffle by diffusion and their consumption by clay mineral dissolution in baffles controls carbon mineralization. The presence of chlorite and illite in the baffle contributes towards consuming H^+ ions faster than they can be supplied by diffusion. Thereby, the pH increases which in turn leads to the precipitation of secondary carbonate minerals at the lithological interface but within the baffle layer. The results highlight that the higher clay content of the baffles enhances carbon mineral trapping while the presence of carbonate-cemented rock types in baffles leads to an overall loss of carbon from the mineral phase. The clay and carbonate content of the reservoir rock do not have a significant impact on carbon mineralization as the presence of residually trapped CO_2 maintains highly acidic conditions within the reservoir rock layer, thereby inhibiting the precipitation of secondary carbonate minerals. The study establishes that the amount of carbon mineralized is highly variable and can be enhanced by as much as 250-400% compared to homogeneous rocks depending on the lithological properties of the baffle and reservoir rocks. A high chlorite and a low carbonate content of baffles favor a net positive mineral trapping. The results show that carbonate-depleted baffles enhance carbon mineral trapping while carbonate-cemented baffles lead to a net loss of carbon from the mineral fraction. Hence, the favourable geological targets for enhanced carbon mineral trapping should consist of siliciclastic intraformational baffles rather than carbonate-cemented intervals. Such zones are expected to occur within the depositional facies such as distributary channels where intraformational baffles in the form of cross bedding laminae result from fluctuating depositional energy conditions within a larger homogeneous sandstone dominated strata. Furthermore, averaged mineral specific reaction rates and averaged mineral composition are derived. These parameters can further be used in reduced models at coarser scale to incorporate the impact of baffles on carbon mineralization without a need to account for mm- to cm-scale lithological heterogeneity. The present study uses transition state theory derived kinetic rate laws to model fluid-rock reactions while other kinetic rate laws have not been explored. This is a limitation and the amount of secondary minerals might be influenced by the choice of kinetic rate laws. However, this will not affect the main conclusion of this study.

Chapter 7

Reservoir scale impact of intraformational baffles on carbon mineral trapping capacity

7.1. Introduction

Global warming is one of the major contemporary environmental concerns which is believed to be responsible for sea level rise, shrinking glaciers and ice caps and a threat to human health (Cline, 1992; Fowler and Hennessy, 1995; Hoel and Kverndokk, 1996; Houghton, 2009; Martens, 2013; Meehl et al., 2005; Tan and Shibasaki, 2003; Weart, 2008; Yafeng and Shiyin, 2000; Zhang et al., 2015). The rise in global temperature is attributed to the increase in the atmospheric concentration of CO₂ from anthropogenic sources (Joos and Bruno, 1996; Matthews et al., 2009; Zeebe et al., 2016). Several methods have been developed to control the atmospheric CO₂ concentrations (Beaumont et al., 2014; Bhattacharyya et al., 2008; Brown, 1992; Day et al., 2005; Ghommam et al., 2012; Mitra and Zaman, 2014; Ogawa et al., 2006; Rahman et al., 2017). Geological carbon storage is one such way which is considered effective, economical and safe (Bachu, 2002; Flett et al., 2005; Friedmann, 2007; Gunn et al., 2012; Oldenburg and Unger, 2003; Zhang and Song, 2014). In this approach, CO₂ is injected in the sub-surface to depths greater than 800 m in high porosity-high permeability storage reservoirs where it is permanently trapped (Benson et al., 2012; Benson and Orr, 2008; Metz et al., 2005).

The CO₂ storage reservoirs are lithologically heterogeneous at different scales (Flett et al., 2005; Flett et al., 2007; Law and Bachu, 1996). At km-scale, heterogeneity can exist in the form of depositional environments while at the micro-meter scale heterogeneity exists as a complex network of connected pores (Bernabé and Revil, 1995; Cross, 1991; Cross et al., 1993; Haggerty and Gorelick, 1995; Lai et al., 2015; Miall, 2016; Smith et al., 2013).

Lithological heterogeneity is known to significantly impact fluid flow and fluid rock reactions in the sub-surface (Downey, 1984; Gershenzon et al., 2017; Green and Ennis-King, 2010a; Hermanson and Kirste, 2013; Saadatpoor et al., 2009a; Sundal and Hellevang, 2019; Trevisan et al., 2017; Watson and Gibson-Poole, 2005). The impact has been well quantified at regional scales where the presence of certain depositional environments can either create preferential flow paths or completely block the flow (Christopher et al., 2006; Fulljames et al., 1997; Green and Ennis-King, 2010a; Green and Ennis-King, 2010b). The behaviour of fluid flow at pore scale is also fairly well understood (Blunt and King, 1991; Fourie et al., 2007; Meakin and Tartakovsky, 2009). However, the reservoir scale impact of heterogeneity

at mm- to cm-scales on fluid flow and fluid-rock reactions is less well understood (Frykman et al., 2009; Gibson-Poole et al., 2009; Hermanson and Kirste, 2013; Krishnamurthy et al., 2017; Li and Benson, 2015; Yu et al., 2017). At this scale, lithological heterogeneity exists in the form of sedimentary structures such as cross and planar bedding where low porosity, low permeability layers are embedded within the high porosity, high permeability reservoir rock. These beds are referred to as intraformational baffles (Gibson-Poole et al., 2009; Miall, 2016; Yu et al., 2017). In the context of geological carbon storage, the baffles retard buoyancy driven migration of fluid, increase the tortuosity of flow and enhance capillary heterogeneity trapping (Frykman et al., 2009; Green and Ennis-King, 2010a; Green and Ennis-King, 2010b; Green and Ennis-King, 2013; Krevor et al., 2011; Li and Benson, 2015; Ni et al., 2019; Saadatpoor et al., 2009b; Saadatpoor et al., 2010b; Saadatpoor et al., 2013). The baffles are also rich in clay minerals such as chlorites which dissolve in CO₂ rich, acidic water resulting from CO₂ injection and release cations such as Ca²⁺, Fe²⁺ and Mg²⁺. As the pH increases over 100s to 1000s of years, these cations react with carbonate ions (CO₃²⁻) resulting in the precipitation of secondary carbonate minerals, thereby storing carbon in the mineral phase (Hermanson and Kirste, 2013; Higgs et al., 2015; Matter and Kelemen, 2009; Watson, 2012; Watson and Gibson-Poole, 2005). Hence, the presence of intraformational baffles enhances not only capillary trapping but also mineral trapping.

However, baffles are typically not accounted for in the static reservoir models primarily due to a restriction posed by grid size resolution as the large number of grid cells increase computational costs (Doveton and Prensky, 1992; Mishra et al., 2020; Ruhovets et al., 1992). This leads to an underrepresentation of baffles in reservoir models and hence an underestimation of the carbon trapping capacity.

The described research gap is addressed in this study. The aim of this paper is to quantify the impact of intraformational baffles on carbon mineral trapping capacity at reservoir scale. For this purpose, reactive-transport simulations are run on a static reservoir model with a vertical resolution of 5 cm where the different rock properties at mm-scale are integrated in the model. The amount mineral trapping is calculated and compared with that obtained from a conventional reservoir model with a vertical resolution of 2 m where intraformational baffles are not accounted for. This allows for quantifying the degree of underestimation associated with mineral trapping capacity determined using conventional reservoir models. The study also explores the differences in the processes governing carbon mineralization resulting from the presence of intraformational baffles.

7.2. Study area and regional geology

7.2.1. Study area overview

The CO2CRC's Otway Research Facility site is located approximately 300 km southwest of Melbourne in Victoria (Figure 7.1) (Dance, 2013). The current study focuses on data from the wells CRC-2 ($38^{\circ}31'50.06''$ S, $142^{\circ}48'41.45''$ E) and CRC-3 ($38^{\circ}31'42.3''$ S, $142^{\circ}48'17.8''$ E), because of the abundance and type of data available. The two wells are located about 630 meters apart. The site is located within the Otway Basin and is a part of the Paaratte Formation in the subsurface.

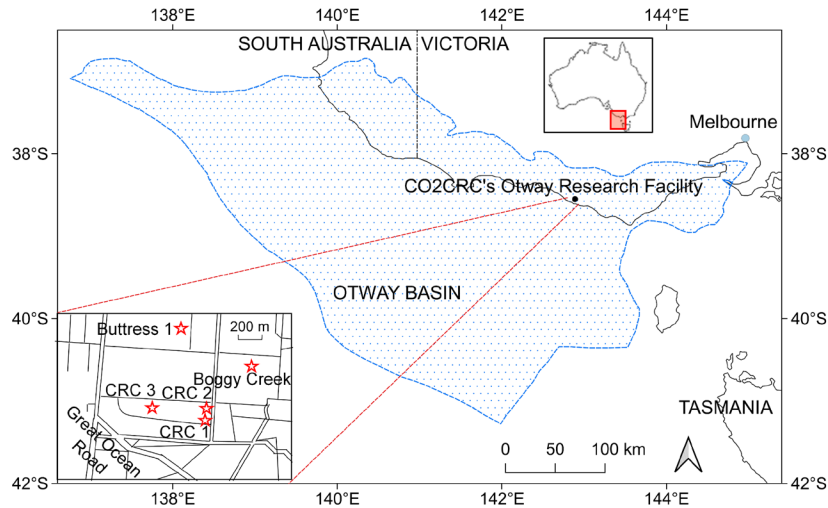


Figure 7.1. Location of the CO2CRC's Otway Research Facility showing the wells CRC-1, CRC-2, CRC-3, Buttress-1 and Boggy Creek. Major roads are shown as parallel solid lines while the footpaths are shown in solid lines. The present study is based on the data from CRC-2 and CRC-3 wells.

7.2.2. Geological setting

The Otway Basin is set in a rift-to-passive margin environment and occupies an area of 150,000 km² with a maximum thickness of 8 km (Dance, 2013; Exon and Lee, 1987; Miyazaki et al., 1990; Moore et al., 2000; Robertson et al., 1978). The Basin came into existence in Tithonian-Barremian with the rift between Australia and Antarctica (Dance, 2013; Holford et al., 2011; Krassay et al., 2004; Moore et al., 2000; Norvick, 2005; Willcox and Stagg, 1990). The rifting resulted in thermal subsidence followed by passive margin subsidence (Cande and Mutter, 1982; Dance, 2013). Further evolution of the basin was controlled by six major cycles of sea level change between Late Cretaceous and Quaternary and led to the formation of five Groups (oldest to youngest): Otway, Sherbrook, Wangerrip, Nirranda and Heytesbury. The development of the oldest formation, the Otway Group, was controlled by tectonic activity where the sediments ranged from volcanoclastic at the base to fluvial and shallow lacustrine at the top and comprised of interbedded carbonaceous shale and basalts to interbedded volcanoclastic sandstone, mudstone and coal (Morton et al., 1994; Woollands and Wong, 2001). The Sherbrook Group was deposited under marginal marine conditions within a low stand system tract at the base to upper deltaic plain environment within a

high stand system tract at the top (Boyd and Gallagher, 2001; Buffin, 1989; Woollands and Wong, 2001). Sedimentologically, the Group comprises shale, black pyritic mudstone, siltstone, interbedded calcareous sandstone and coarse grained sandstone (Hawkins and Dellenbach, 1971; Woollands and Wong, 2001). The Wangerrip Group consists of transgressive-regressive units (Morton et al., 1994) deposited under low energy conditions in a marginal marine environment at the base to a shallow-marine environment at the top and consists of carbonaceous claystone, mudstone and sandstone (Morgan, 1985; Morton, 1990; White, 1995; Woollands and Wong, 2001). The Nirranda Group developed under open marine conditions and consists of mixed carbonates and siliciclastic sediments (Krassay et al., 2004; O'Brien and Thomas, 2007). The topmost Heytesbury Group was deposited under inner shelf conditions at the base to mid-shelf conditions at the top. It is characterised by open marine carbonate sequences (Woollands and Wong, 2001).

For the current study, the stratigraphic interval of interest is a part of the Paaratte Formation belonging to the Sherbrook Group. The formation occurs between depths of 1120–1570m. Locally, the Paaratte Formation is a low dipping faulted anticline with dips ranging between 2° – 5° towards the north (Dance, 2012). The formation comprises three member units, Unit A, Unit B and Unit C. Unit A (lowermost) comprises three fourth order parasequences with Parasequence-1 at the bottom and Parasequence-3 at the top (Dance, 2018). The current study utilizes data from Parasequence-1 which is composed of four facies: delta front, distal mouth bar, proximal mouth bar and distributary channel (Boyd and Gallagher, 2001; Dance, 2018). Lithologically, the parasequence is comprised of sandstone, siltstone and mudstone with carbonate-cemented intervals (Geary et al., 2001; Geary and Reid, 1998; Woollands and Wong, 2001). The data depicts the presence of mm- to cm-scale lithological heterogeneity (Mishra et al., 2019).

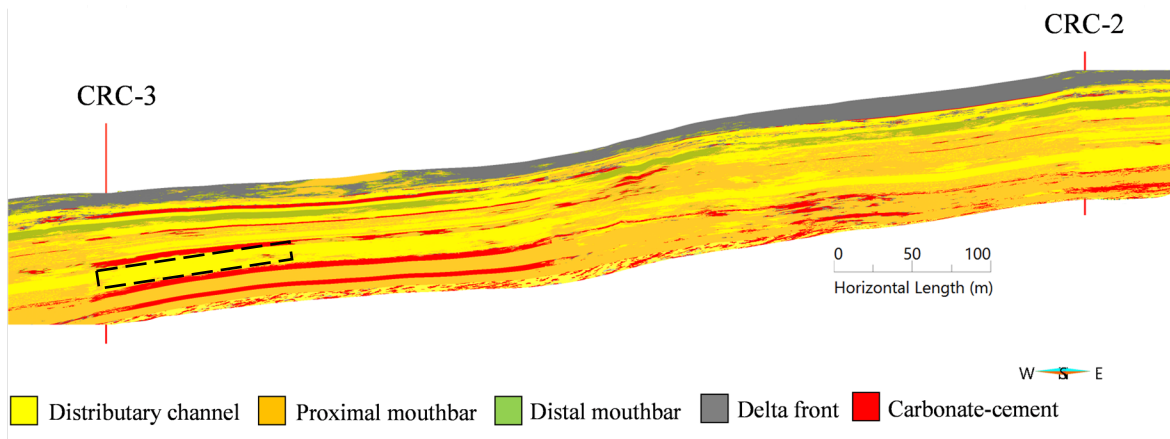
7.3. Methodology

7.3.1. Available static reservoir models

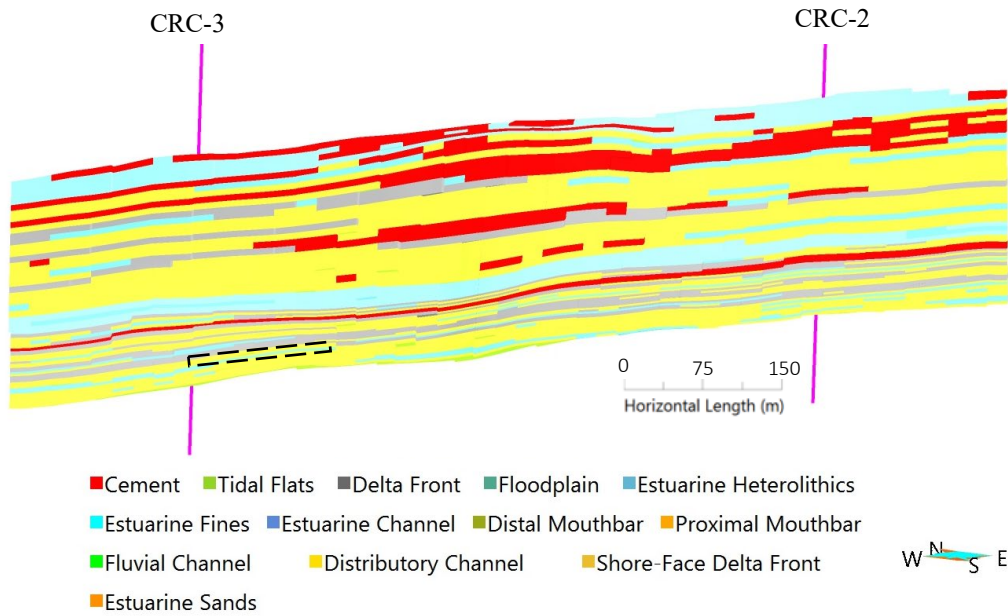
Two 2-D static reservoir models were used in this study: Model-A and Model-B (Figure 7.2). The models are aligned with the transect between CRC-3 and CRC-2 wells and are composed of Paaratte Formation. Model-A has a grid size resolution of 1 m horizontally and 5 cm vertically while Model-B has a resolution of 20 m horizontally and 2 m vertically. Hence, Model-A represents a higher resolution rendition of the section while Model-B is characterised by resolution characteristic of a typical reservoir model. Model-A was available from a previous publication (Mishra et al., 2020) while Model-B was provided by CO2CRC Limited. Parasequence-1 in both the models is composed of distributary channel, proximal mouth bar, distal mouth bar, delta front and carbonate-cemented facies environments.

To maintain computational feasibility, reactive transport simulations were performed on a sub-section each from both the reservoir models (Figure 7.2). The sub-sections measured 100 m horizontally and 6 m

vertically and are part of Parasequence-1 in both the models. The Model-A sub-section consisted of 12,000 cells while Model-B consisted of 15 cells. The left-most boundary of the sub-sections corresponded with



(a)



(b)

Figure 7.2. Distribution of depositional facies environments for (a) Model-A (modified after Mishra et al., 2020); and (b) Model-B. Both models measure 800 m horizontally. Model A measures 40 m vertically and captures Parasequence-1 of the Paaratte Formation while Model-B measures 150 m vertically and shows Parasequences-1, 2 and 3. The stippled lines show the location of the chosen sub-section for running the dynamic simulations. The sub-section is a part of Parasequence-1 in both the models and measures 100 m horizontally and 6 m vertically. Image (a) has a vertical exaggeration of 2x.

the location of the CRC-3 well which acts as CO₂ injection well. The top and bottom boundaries of both the sub-sections is parallel to the regional structural dip. In terms of depositional facies, the sub-section

from Model-A is composed of distributary channel while the sub-section from Model-B is composed of distributary channel and proximal mouth bar depositional facies in near equal proportions. Distributary channel facies acts as a reservoir rock with a significant amount of injected CO₂ expected to flow laterally within the unit (Dance et al., 2019). The sub-section dominated by distributary channel depositional facies was chosen as it contains mm- to cm-scale lithological heterogeneity in the form of intraformational baffles. The top-most layer of the sub-section from Model-A is comprised of carbonate-cemented facies which acts as the seal.

Sedimentary structure	Constituent rock types		Acronym used
	Baffle	Reservoir rock	
Homogeneous	-	Coarse sandstone	H ^{CSst}
Homogeneous	-	Fine sandstone	H ^{FSst}
Homogeneous	-	Siltstone	H ^{Slt}
Homogeneous	-	Mudstone	H ^{Mst}
Homogeneous	-	Carbonate-cemented sandstone	H ^{CbSst}
Cross bedding	Fine sandstone	Coarse sandstone	X ^{FSst} _{CSst}
Planar bedding	Mudstone	Coarse sandstone	P ^{Mst} _{CSst}
Planar bedding	Mudstone	Fine sandstone	P ^{Mst} _{FSst}
Planar bedding	Siltstone	Coarse sandstone	P ^{Slt} _{CSst}
Planar bedding	Siltstone	Fine sandstone	P ^{Slt} _{FSst}
Planar bedding	Mudstone	Siltstone	P ^{Mst} _{Slt}
Massive bedding interface	Carbonate-cemented sandstone	Mudstone	M ^{CbSst} _{Mst}
Massive bedding interface	Carbonate-cemented sandstone	Siltstone	M ^{CbSst} _{Slt}
Massive bedding interface	Carbonate-cemented sandstone	Fine sandstone	M ^{CbSst} _{FSst}
Massive bedding interface	Carbonate-cemented sandstone	Coarse sandstone	M ^{CbSst} _{CSst}

Table 7.1. Description of the 15 rock types represented in Model-A (Mishra et al., 2020).

upscaled from a resolution of 1 cm to 5 cm and the upscaled domains are referred to as composite rock types (Mishra et al., 2020). Hence, the five facies environments constituting Model-A have been downscaled to 15 rock types at 5 cm resolution, 5 of which are homogeneous rock types while 10 are composite rock types (Table 7.1) (Mishra et al., 2020).

In terms of rock properties, lithological heterogeneity for the Otway site has been classified into five homogeneous rock type classes: coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone (Mishra et al., 2019). The higher resolution of Model-A further allows to capture cm-

scale lithological heterogeneity which has been reported to exist as cross bedding, planar bedding and the interface of two massively bedded lithologies. Each of the sedimentary structures is known to consist of several 5 mm thick layers of lamina composed of baffle and reservoir rock. The core analysis revealed that the baffle layer is composed of siltstone, mudstone and carbonate-cemented sandstone while the reservoir rock layer consists of coarse sandstone, fine sandstone and siltstone in the sedimentary structures (Mishra et al., 2020; Mishra et al., 2019). The lithological properties of the sedimentary structures have been characterized (Mishra et al., 2019). On the contrary, the coarser resolution of Model-B does not allow a

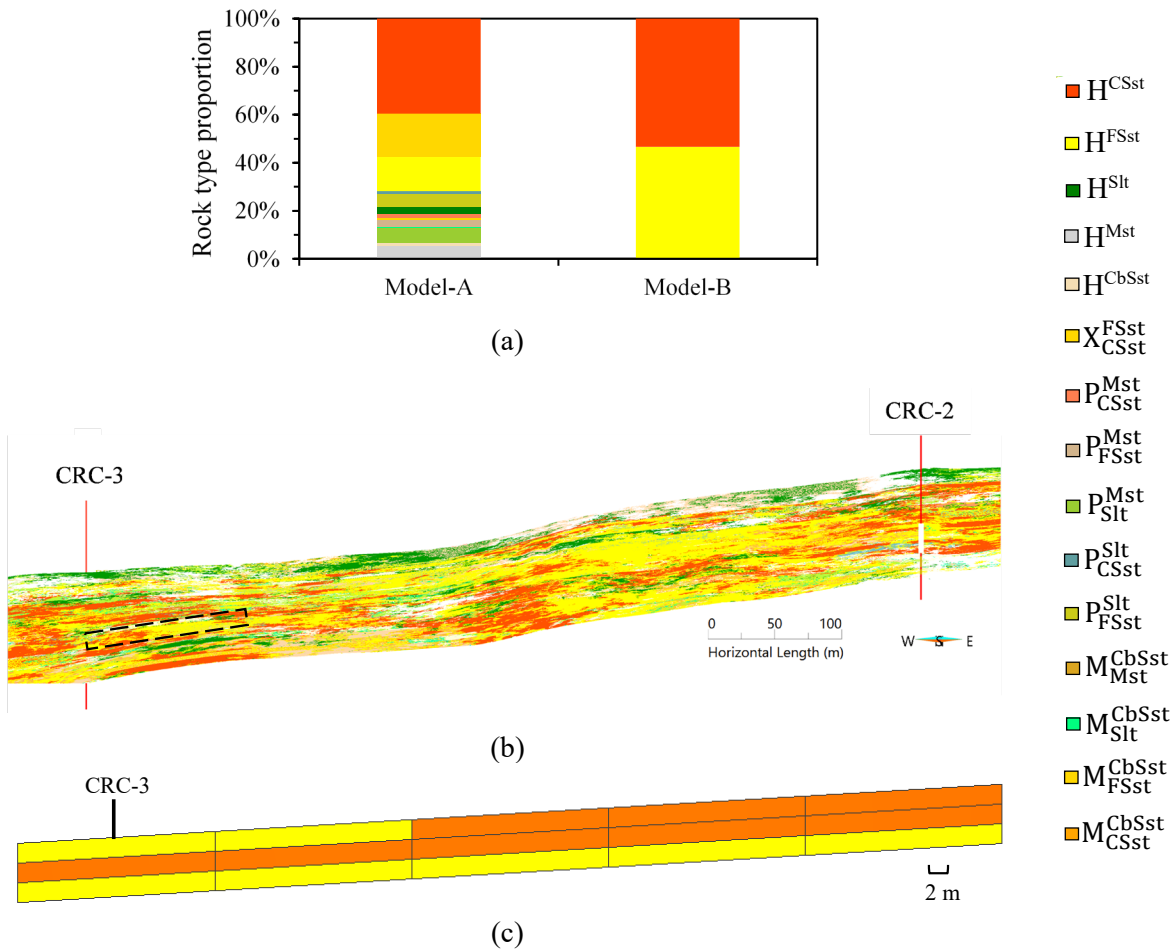


Figure 7.3. (a) Proportion of rock types in Model-A and Model-B (Mishra et al., 2020); (b) Rock type distribution in Model-A (modified after Mishra et al., 2020); (c) Rock type distribution in the sub-section from Model-B. The stippled lines in image (a) show the location of the chosen sub-section from Model-A. Image (a) has a vertical exaggeration of 2x.

further downscaling of the facies environments in terms of rock types. Therefore, each of the facies was assigned the properties of a single homogeneous rock type as the model is homogeneous at depositional environment scale due to the limitation posed by grid size resolution. Hence, coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone comprise distributary channel, proximal mouth bar, distal mouth bar, delta front and carbonate-cemented facies, respectively.

The proportion of rock types in the two sub-sections is shown in Figure 7.3a while Figures 7.3b and 7.3c show the distribution of rock types in Model-A (Mishra et al., 2020) and Model-B, respectively.

7.3.2. Property population

7.3.2.1. Available flow and petrophysical data

Porosity and permeability data for the 15 rock types have been taken from a previous publication (Mishra et al., 2020). The bounding and scanning relative permeability-saturation curves for water (wetting) and CO₂ (non-wetting) phases were implemented using the modified form of the van Genuchten relative permeability function to account for hysteresis (Doughty, 2006; Lenhard and Parker, 1987; Parker and Lenhard, 1987; Van Genuchten, 1980):

$$k_{r,w} = s_{e,w}^{1/2} \left[1 - \left(1 - \frac{s_{e,nwt}}{1-s_{e,wtp}} \right) \left(1 - (s_{e,w} + s_{e,nwt})^{1/m_r} \right)^{m_r} - \left(\frac{s_{e,nwt}}{1-s_{e,wtp}} \right) \left(1 - s_{e,wtp}^{1/m_r} \right)^{m_r} \right]^2 \quad (7.1)$$

$$k_{r,nw} = (1 - s_{e,w} - s_{e,nwt})^{1/3} \left(1 - (s_{e,w} + s_{e,nwt})^{1/m_r} \right)^{m_r} \quad (7.2)$$

where,

$k_{r,w}$ = relative permeability of the wetting (water) phase,

$k_{r,nw}$ = relative permeability of the non-wetting (CO₂) phase,

m_r = relative permeability empirical parameter, taken equal for drainage and imbibition,

$s_{e,w}$ = effective wetting phase saturation,

$s_{e,nwt}$ = effective trapped saturation of the non-wetting phase,

$s_{e,wtp}$ = effective turning point saturation of the wetting phase.

Exponent ‘m’ is taken to be the same for drainage and imbibition. The effective saturations can be obtained from the following relations:

$$s_{e,w} = \frac{s_w - s_{w,irr}}{1 - s_{w,irr}} \quad (7.3)$$

$$s_{e,wtp} = \frac{s_{w,tp} - s_{w,irr}}{1 - s_{w,irr}} \quad (7.4)$$

$$s_{e,nwt} = \frac{s_{nw,r}(s_w - s_{w,tp})}{(1 - s_{w,irr})(1 - s_{w,tp} - s_{nw,r})} \quad (7.5)$$

where,

s_w = wetting phase saturation,

$s_{w,irr}$ = irreducible wetting phase saturation,

$s_{w,tp}$ = turning point saturation of the wetting phase,

$s_{nw,r}$ = residual non-wetting phase saturation.

s_w and $s_{w,tp}$ are dynamically determined over the period of simulation. $s_{nw,r}$ is a function of turning point saturation of the wetting phase at the end of drainage and is determined using the following equation (Land, 1969):

$$s_{nw,r} = \frac{1-s_{w,tp}}{1 + \left[\frac{1}{s_{nw,max}} - \frac{1}{(1-s_{w,irr})} \right] (1-s_{w,tp})} \quad (7.6)$$

where,

$s_{nw,max}$ = maximum possible saturation of the non-wetting phase.

The modified form of van Genuchten capillary pressure function has been used to account for hysteresis (Doughty, 2006; Van Genuchten, 1980):

$$P_c = P_o \left[\left(\frac{s_w - s_{w,irr}}{1 - s_{w,irr} - s_{nw,r}} \right)^{-\frac{1}{m_c}} - 1 \right]^{(1-m_c)} \quad (7.7)$$

where,

P_c = capillary pressure (Pa),

P_o = capillary strength parameter for scaling the capillary pressure curve (Pa),

m_c = capillary pressure empirical parameter, taken equal for drainage and imbibition.

The van Genuchten capillary pressure curve is characterized by an entry slope region at low CO_2 saturations. The values of P_o and m_c have been derived such that the height of entry slope region corresponds to capillary entry pressure characteristic of each rock type at a threshold saturation of 0.005 (Li et al., 2013). The values of $s_{nw,r}$ and hence $s_{e,nwt}$ are zero for drainage and non-zero for imbibition in equations 7.1, 7.2 and 7.7. The formulation of relative permeability and capillary pressure curves for the two phases during drainage and imbibition requires five parameters: m_r , m_c , $s_{w,irr}$, $s_{nw,max}$ and P_o . These values were provided for the 15 rock type classes for capillary dominated flow regime (Dr. Maartje M. Boon, personal communication) and are shown in Table 7.2 along with porosity and permeability data (Mishra et al., 2020).

7.3.2.2. Available geochemical data

Transition state theory (Lasaga, 2014) was used to model dissociation and precipitation reactions using the following rate law:

$$R = \pm kA(1 - SI) \quad (7.8)$$

where,

R = reaction rate at time t (mol sec⁻¹),

k = rate constant (mol cm⁻² sec⁻¹),

A = surface area of the given mineral (cm²),

SI = saturation index of the given mineral at time t.

Rock Type	Porosity (fraction)		Vertical Permeability (md)		Horizontal Permeability (md)		m _r	m _c	S _{w,irr}	S _{nw,max}	P _o (kPa)
	Mean	SD	Mean	SD	Mean	SD					
H ^{CSst}	0.29	0.02	3149	2266	3149	2266	0.70	0.70	0.10	0.26	3.2
H ^{FSst}	0.28	0.01	406.5	200.9	406.5	200.9	0.60	0.60	0.16	0.23	6.3
H ^{Slt}	0.19	0.04	44.6	43.2	44.6	43.2	0.50	0.50	0.18	0.26	27.1
H ^{Mst}	0.18	0.03	8.3	3.8	8.3	3.8	0.40	0.40	0.39	0.34	51.1
H ^{CbSst}	0.19	0.08	6.1	4.1	6.1	4.1	0.40	0.40	0.55	0.13	84.8
X ^{FSst} _{CSst}	0.28	0.01	386	131	386	131	0.70	0.53	0.13	0.30	8.4
P ^{Mst} _{CSst}	0.23	0.02	1.32	0.807	1800	749	0.96	0.35	0.25	0.50	65.1
P ^{Mst} _{FSst}	0.23	0.01	1.29	0.782	226	85.2	0.78	0.36	0.27	0.45	62.6
P ^{Slt} _{CSst}	0.23	0.02	30.3	12.9	1827	748	0.88	0.40	0.14	0.52	37.8
P ^{Slt} _{FSst}	0.23	0.02	22.7	8.76	252	87.3	0.69	0.44	0.17	0.44	32.9
P ^{Mst} _{Slt}	0.18	0.02	1.10	0.610	27.9	11.9	0.49	0.41	0.29	0.30	54.6
M ^{CbSst} _{CSst}	0.23	0.03	5.58	2.49	1802	749	1.19	0.33	0.33	0.48	125.4
M ^{CbSst} _{FSst}	0.22	0.03	5.50	2.44	227.9	85.2	0.94	0.33	0.36	0.45	121.5
M ^{CbSst} _{Slt}	0.17	0.03	4.81	1.97	29.7	11.9	0.59	0.39	0.37	0.37	106.7
M ^{CbSst} _{Mst}	0.17	0.03	1.39	0.739	3.90	1.45	0.42	0.38	0.47	0.14	132.6

Table 7.2. The values of flow and petrophysical properties for each of the 15 rock types (Mishra et al., 2020; Dr. Maartje M. Boon, personal communication).

Positive values of R indicate mineral dissolution while negative values indicate mineral precipitation.

The reaction rate constant, k, can further be expressed as (Palandri and Kharaka, 2004):

$$k = k_{25}^n \exp \left[\frac{-E_a^n}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^a \exp \left[\frac{-E_a^a}{R_g} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H \quad (7.9)$$

where,

k₂₅ = rate constant at 25°C (mol cm⁻² sec⁻¹),

E_a = activation energy (J mol⁻¹),

R_g = universal gas constant, taken to be 8.31 J mol⁻¹ K⁻¹,

T = absolute temperature (K),

a_H and n_H = activity of H⁺ ion and reaction order, respectively.

Rock type	H^{CSst}	H^{FSst}	H^{Slt}	H^{Mst}	H^{CbSst}	X_{CSst}^{FSst}	P_{CSst}^{Mst}	P_{FSst}^{Mst}	P_{Slt}^{Mst}	P_{CSst}^{Slt}	P_{FSst}^{Slt}	M_{CSst}^{CbSst}	M_{FSst}^{CbSst}	M_{Slt}^{CbSst}	M_{Mst}^{CbSst}
Albite	0.0121	0.0195	0.0262	0.0254	0.0186	0.0154	0.0135	0.0135	0.0127	0.0139	0.0138	0.0155	0.0185	0.0223	0.0219
Ankerite	0.0019	0.0013	0.0000	0.0000	0.0992	0.0017	0.0000	0.0000	0.0000	0.0000	0.0000	0.0537	0.0534	0.0497	0.0492
Calcite	0.0000	0.0000	0.0000	0.0000	0.0008	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0005	0.0005	0.0004	0.0004
Chlorite	0.0233	0.0515	0.0599	0.0900	0.0144	0.0356	0.0482	0.0481	0.0454	0.0318	0.0317	0.0186	0.0301	0.0371	0.0525
Dolomite	0.0004	0.0003	0.0000	0.0000	0.0206	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0112	0.0111	0.0103	0.0102
Illite	0.0086	0.0214	0.0437	0.0824	0.0099	0.0137	0.0445	0.0443	0.0419	0.0232	0.0231	0.0093	0.0141	0.0268	0.0467
K-Feldspar	0.0760	0.0654	0.0591	0.0691	0.0512	0.0700	0.0370	0.0369	0.0349	0.0314	0.0313	0.0628	0.0573	0.0551	0.0602
Kaolinite	0.0415	0.0466	0.1237	0.1539	0.0331	0.0398	0.0825	0.0822	0.0777	0.0657	0.0654	0.0370	0.0354	0.0783	0.0939
Magnesite	0.0060	0.0056	0.0098	0.0180	0.0172	0.0057	0.0096	0.0096	0.0091	0.0052	0.0052	0.0120	0.0118	0.0135	0.0176
Muscovite	0.0097	0.0131	0.0337	0.0526	0.0112	0.0105	0.0277	0.0276	0.0261	0.0170	0.0170	0.0100	0.0113	0.0214	0.0314
Quartz	0.7870	0.7292	0.5417	0.3679	0.7092	0.7631	0.6531	0.6544	0.6731	0.7490	0.7499	0.7437	0.7254	0.6187	0.5213
Siderite	0.0001	0.0011	0.0010	0.0039	0.0001	0.0007	0.0021	0.0021	0.0020	0.0005	0.0005	0.0001	0.0006	0.0005	0.0020
Smectite	0.0334	0.0450	0.1014	0.1368	0.0145	0.0357	0.0735	0.0733	0.0693	0.0538	0.0536	0.0233	0.0255	0.0578	0.0763

Table 7.3. Proportion of constituent minerals (volume fraction of solid) for the 15 rock types.

Superscripts ‘n’ and ‘a’ denote corresponding values for neutral and acidic mechanisms. In the present study, the values of k_{25} and E_a have been taken to be the same for the two mechanisms as commonly done (Palandri and Kharaka, 2004).

To model geochemical reactions using the defined rate law (equation 7.8), the following data is required: mineral composition for each rock type, the temperature-corrected rate constant for each reaction, the mineral-specific surface area and the initial formation water composition. The proportion of minerals in the homogeneous rock types (Mishra et al., 2019) and the averaged mineral proportions characteristic of the composite rock types (Mishra et al., submitted; Appendix F) were available from previous publications and are shown in Table 7.3. Three major classes of minerals were accounted for as previously suggested (Haese et al., 2019): framework, clay and carbonates. The framework minerals comprised albite, K-feldspar and quartz. Clay minerals comprised chlorite, illite, kaolinite, muscovite and smectite. The carbonate minerals comprised ankerite, calcite, dolomite, magnesite and siderite. Chalcedony was included to account for the low pressure-temperature precipitation of silica.

Mineral	Composition	Activation Energy (kJ mol ⁻¹)	Rate constant at 25°C (mol m ⁻² sec ⁻¹)	Specific surface area (cm ² gm ⁻¹)
Albite	NaAlSi ₃ O ₈	65	6.92E-11	10.0
Ankerite	CaMg _{0.3} Fe _{0.7} (CO ₃) ₂	14.4	5.012E-01	0.001
Calcite	CaCO ₃	14.4	5.012E-01	0.001
Chalcedony	SiO ₂	87.7	1.26E-14	10.0
Chlorite	Al ₂ Mg _{2.5} Fe _{2.5} Si ₃ O ₁₀ (OH) ₈	88.0	7.76E-12	70.0
Dolomite	CaMg(CO ₃) ₂	36.1	6.46E-04	0.001
Illite	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂	23.6	1.05E-11	70.0
K-Feldspar	KAlSi ₃ O ₈	51.7	8.71E-11	10.0
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	65.9	4.90E-12	70.0
Magnesite	MgCO ₃	14.4	4.16E-07	0.001
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	22.0	1.41E-12	70.0
Quartz	SiO ₂	87.5	1.26E-14	10.0
Siderite	FeCO ₃	14.4	5.01E-01	0.001
Smectite	Ca _{0.145} Mg _{0.26} Al _{1.77} Si _{3.97} O ₁₀ (OH) ₂	23.6	1.04E-11	70.0

Table 7.4. Reaction kinetic parameters (Palandri and Kharaka, 2004) and specific surface area (Haese et al., 2014; Xu et al, 2004; Yang et al., 2014) for each mineral implemented in the model realizations.

Formation Water Ionic Composition	Speciated concentration (x10 ⁻³ mol kg ⁻¹ H ₂ O)
Na ⁺	24.5
K ⁺	1.4
Ca ²⁺	3.1
Mg ²⁺	4.2
SiO ₂	0.7
Fe	0.4
AlO ₂ ⁻	1.0
HCO ₃ ⁻	4x10 ⁻⁸
pH	8.02

Table 7.5. Formation water chemistry modified after Vu et al., 2017.

Mineral composition, reaction kinetic parameters (Palandri and Kharaka, 2004) and specific surface areas (Haese et al., 2014) for each mineral are shown in Table 7.4 while initial formation water composition of the Paaratte Formation is shown in Table 7.5 (Vu et al., 2017).

7.3.3. Multiphase reactive transport modelling set-up

Multiphase reactive transport simulations were run using the ECO2N equation of state module in TOUGHREACT v1.2 (Xu et al., 2011). Supercritical CO₂ was injected from the left boundary of the two models at a flux of 1E-4 g cm⁻² sec⁻¹ for a duration of 1 day for Model-A and 20 minutes for Model-B, given the accelerated numerical dispersion of CO₂ in Model-A. The injection flux was used to determine conventional capillary number (N_c) using the following definition (Zhou et al., 2010):

$$N_c = \frac{q\mu}{\sigma} \quad (7.10)$$

where,

q = Darcy flow velocity, equal to 1.66x10⁻⁶ m sec⁻¹ under the given injection flux,

μ = CO₂ viscosity, equal to 2.3x10⁻⁵ Pa sec (Chiquet et al., 2007),

σ = CO₂ water interfacial tension, equal to 35 mN m⁻¹ (Espinoza and Santamarina, 2010).

The resulting capillary number is less than 10⁻⁸ indicating flow under a capillary dominated regime. CO₂ was allowed to rise under buoyancy and flow through the model domains. The right and bottom boundaries were open to fluid and mass transfer while the top boundary was closed to mass transfer due to the presence of an overlying layer of carbonate-cemented sandstone rock type. Along with advection, dissolution of CO₂ in formation brine and the diffusion of dissolved CO₂ along with other ionic species was allowed with a diffusion coefficient of 2x10⁻⁹ m² sec⁻¹ (Parkhurst and Appelo, 2013). Ankerite, calcite, chalcedony, dolomite, illite, kaolinite, magnesite, siderite and smectite were allowed to precipitate as secondary minerals. The thermodynamic database thermXu4.dat from TOUGHREACT was used to model dissolution and precipitation reactions. Simulations were carried out under a hydrostatic pressure of 15 MPa and reservoir temperature of 60°C. The hydrostatic pressure and temperature correspond to a depth of roughly 1500 m in sedimentary basins. Simulations were run for a period of 1000 years. The evolution of the reservoir geochemistry in terms of changes in mineral volume fraction and pH was analyzed. Long term changes in the amount of dissolved CO₂ are not in the scope of this study and have not been addressed.

7.3.4. Calculation of the mass of mineralogically trapped carbon

The amounts of ankerite, calcite, dolomite, magnesite and siderite were used to calculate the mass of carbon in the mineral phase per unit rock volume at each instance using the following equation:

$$M_{\min,t}^C = 1000M_M^C \sum_{j=1}^5 \left(\frac{n_s^j v_{ft}^j}{v_M^j} \right) \quad (7.11)$$

where,

$M_{\min,t}^C$ = mass of carbon in the mineral phase per unit whole rock volume at a given time t (kg m^{-3}),
 M_M^C = molar mass of carbon (g mole^{-1}),
 $V_{f,t}^j$ = volume fraction of the carbonate mineral j at time t ,
 V_M^j = molar volume of the carbonate mineral j ($\text{cm}^3 \text{mole}^{-1}$) (Robie and Bethke, 1962),
 n_S^j = stoichiometry of carbon in one formula unit of the carbonate mineral j ,
 j = index of the carbonate mineral.

The difference in mass of carbon in the mineral phase at a given time and that at the beginning of the simulation is the mass of carbon mineralized over that period. Positive values of $M_{\min,t}^C$ indicate carbon mineralization while negative values indicate an overall dissolution of carbonate minerals. The two scenarios are referred to as positive and negative mineral trapping, respectively.

7.4. Results

7.4.1. CO₂ saturation distribution

Supercritical CO₂ flooded the model domains from left to right and it ascended under buoyancy during drainage. The flow of CO₂ within the models was also governed by the structural dip. Post imbibition, the saturation distribution achieved steady state after a period of 1 year for Model-A and 1 week for Model-B. The steady state CO₂ saturation distribution of both the models is shown in Figure 7.4. For most of the area, Model-A showed residual saturation values between 25-30% (Figure 7.4a). However, saturations as high as 60-70% were seen in certain areas while some regions showed CO₂ saturations between 0-15%. Model-B shows saturations between 25-30% in the entire domain (Figure 7.4b).

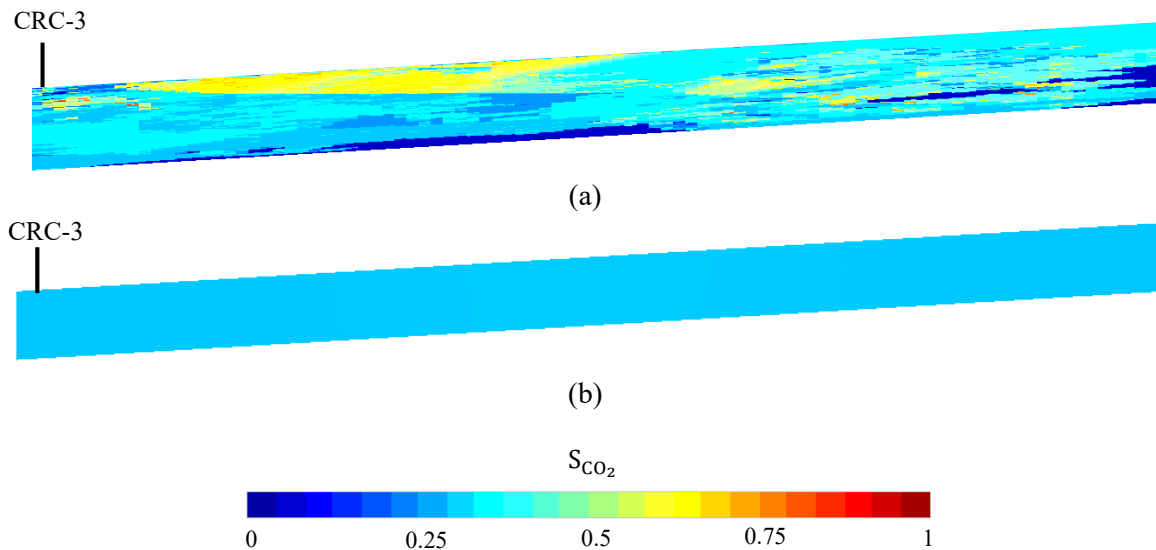


Figure 7.4. Steady state CO₂ saturation distribution for: (a) Model-A after 1 year; and (b) Model-B after 1 week.

7.4.2. Changes in mineral content

The changes in the contents of framework, clay and carbonate minerals were analysed for both the models (Figure 7.5). Albite, K-feldspar, chlorite and kaolinite underwent partial dissolution while smectite and illite underwent precipitation. The content of chlorite and kaolinite decreased by 3 and 2.5 vol %, respectively while that of illite and smectite increased by 9 and 1.5 vol %, respectively for Model-A (Figure 7.5b). For Model B, chlorite and kaolinite decreased by 1.5 and 4 vol %, respectively while illite and smectite increased by nearly 6 and 2 vol %, respectively (Figure 7.5b). The behaviour of these minerals was the same in both the models. However, the extent of dissolution and precipitation varied. The silicate minerals showed higher rates of dissolution and precipitation for the first 200 years of simulation after which the rates gradually declined (Figures 7.5a and 7.5b). Among the carbonate minerals, dolomite and siderite were seen to precipitate in Model-A in the first 100 years of simulation after which the rate of precipitation declined. The amount of dolomite increased by 1 vol % while that of siderite increased by 0.6 vol %. The other carbonate minerals in Model-A showed partial dissolution. The carbonate minerals in Model-B showed complete dissolution.

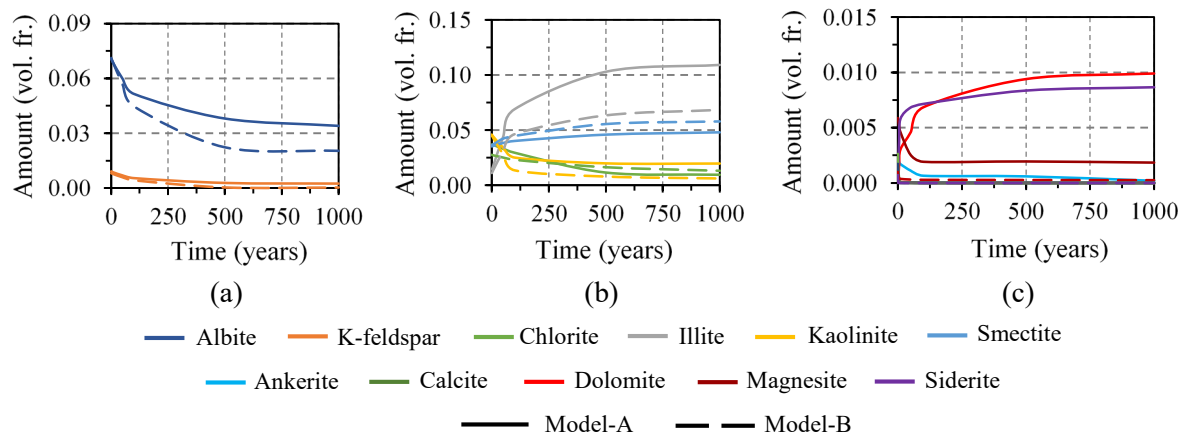


Figure 7.5. Changes in the solid volume fraction of: (a) framework; (b) clay; and (c) carbonate minerals over the simulation period for both the models. The solid lines represent minerals in Model-A while stippled lines represent minerals in Model-B.

The precipitation of secondary dolomite and siderite in Model-A was seen to occur at the interface between the reservoir rock and the baffle and within the baffles (Figure 7.6).

7.4.3. Changes in pH

The pH in both the models evolved differently (Figure 7.7). Both the models showed an initial drop in pH from 8.02 to 3.5-4 within the first year of simulation. However, pH in Model-A increased to values of 5-6 within and around the location of the baffles during the first 200 years of simulation. On the other hand, pH only slightly increased in Model-B to values of 4-4.5 during the same time. The pH did not show any changes after 200 years in both the models.

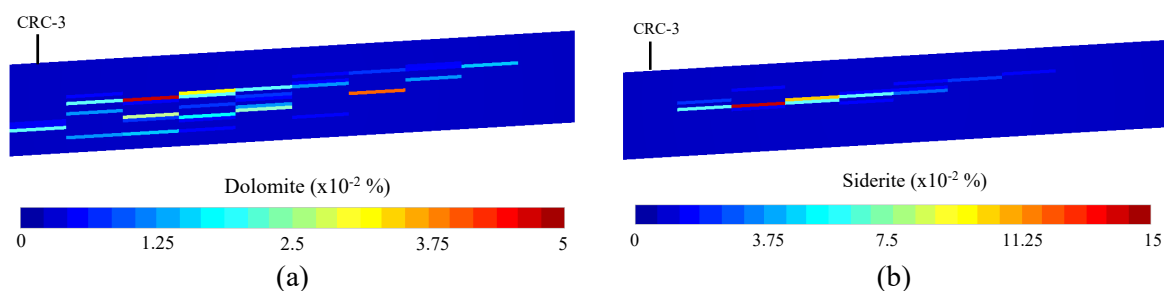


Figure 7.6. Spatial distribution of secondary: (a) dolomite; and (b) siderite after 1000 years in Model-A measured as solid volume fraction. The images represent a part of Model-A sub-section with a length of 10 m and a depth of 1 m.

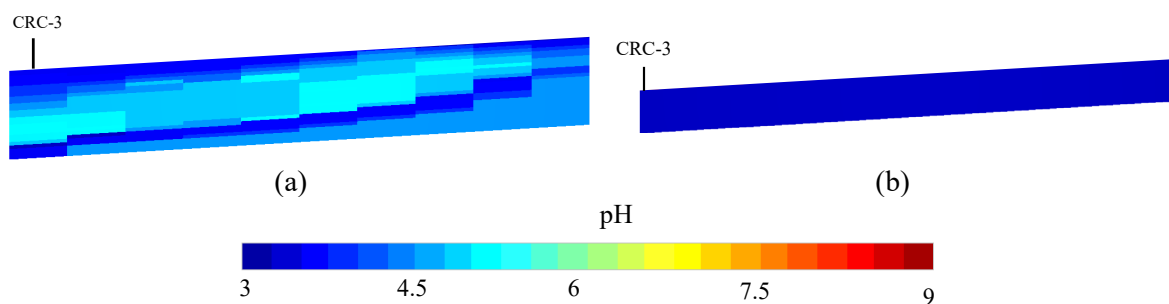


Figure 7.7. Spatial distribution of pH for (a) Model-A; and (b) Model-B after 200 years of simulation. Image (a) represents a part of Model-A sub-section with a length of 10 m and a depth of 1 m. Higher pH is observed around the location of baffles. Image (b) represents the entire Model-B sub-section with a length of 100 m and a depth of 6 m.

7.4.4. Amount of carbon mineralized

The amount of carbon mineralized was calculated for both the models (Figure 7.8). The models showed an initial decrease in the amount of carbon in the solid phase in the first year of simulation. However, the amount increased to 2.6 kg m^{-3} over 1000 years for Model-A. The rate of mineralization declined after 400 years of simulation. On the other hand, the amount of carbon in solid phase for

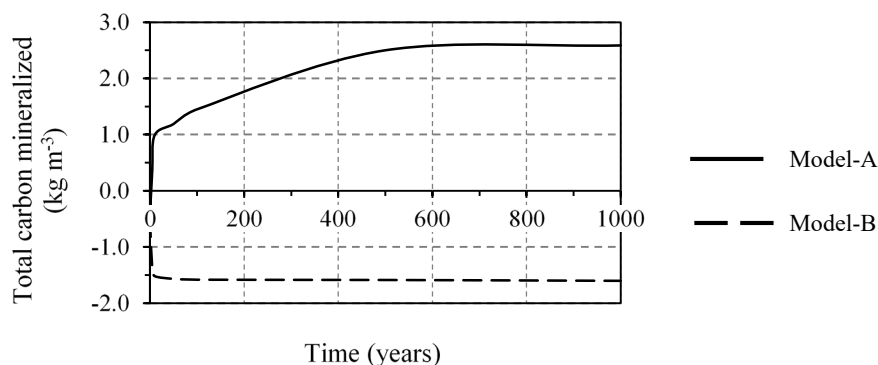


Figure 7.8. Amount of carbon mineralized in both the models.

Model-B did not show any further change after the first year of simulation and became constant at 1.6 kg m⁻³ lower than its initial value.

7.5. Discussion

7.5.1. Comparison of the processes governing CO₂ mineral trapping in the two models

Model-A shows capillary heterogeneity trapping in certain zones with high steady state CO₂ saturation values at the end of 1 year (Figure 7.4a). The rock types constituting the intraformational baffles (Table 7.2) act as flow barriers and prevent supercritical CO₂ from migrating vertically and laterally under buoyancy towards shallower depths (Figure 7.4a). The studies addressing residual trapping in heterogeneous reservoirs have reported enhanced capillary trapping (Green and Ennis-King, 2010a; Green and Ennis-King, 2010b; Green and Ennis-King, 2013; Krevor et al., 2011; Saadatpoor et al., 2009a; Saadatpoor et al., 2010a; Saadatpoor et al., 2013) supporting the results of this study. On the other hand, Model-B shows a near uniform CO₂ saturation distribution (Figure 7.4b) due to the absence of intraformational baffles. Consequently, Model-B does not show any capillary heterogeneity trapping.

A fraction of supercritical CO₂ in the reservoir rock dissolves in the in-situ brine resulting in a pH drop from 8.02 to 3.5-4 within the first year of simulation in both the models (section 7.4.3). The absence of supercritical CO₂ within the intraformational baffles in Model-A creates a sharp pH contrast between the reservoir rocks and the baffles. This leads to the diffusion of dissolved CO₂ and protons into the baffles. The acidic conditions within the baffles initiate the dissolution of chlorite and carbonate minerals and the precipitation of illite and smectite (Figure 7.5). This results in the mobilization of cations such as Ca²⁺, Fe²⁺ and Mg²⁺ (Table 7.4). The dissolution of chlorite and the precipitation of illite and smectite consumes protons resulting in an increase in pH within the baffles to values of 5-6 (Figure 7.7a). The increase in pH favours precipitation of secondary carbonate minerals such as dolomite and siderite in the baffles (Figures 7.5c and 7.6) and a decrease in the rate of dissolution and precipitation of silicate minerals (Figures 7.5a and 7.5b). The behaviour is different in Model-B where the uniform presence of supercritical CO₂ maintains acidic conditions for 1000 years throughout the domain preventing the precipitation of secondary carbonates (Figure 7.7b).

Hence, the presence or absence of intraformational baffles has a significant impact on processes governing carbon mineralization. Their presence in Model-A restricts supercritical CO₂, and hence permanent acidic conditions within the reservoir rock. On the other hand, baffles show an increase in pH over 200 years limited by the consumption of protons by chlorite, illite and smectite within the baffle and their slower diffusion from the reservoir. This affects net precipitation and dissolution of carbonate minerals in both the models (Hellevang, 2015; Hellevang et al., 2005). The observation of secondary carbonates precipitation at lithological interfaces in natural analogues (Heinemann et al., 2013; Higgs et al., 2015; Watson, 2012; Watson et al., 2005; Watson et al., 2003; Xi et al., 2019) further

supports the outcomes of this study. However, uncertainties regarding mineral specific surface areas, crystal nucleation and growth rates and kinetic models used to predict the type of secondary carbonate minerals have not been considered in this study (Hellevang, 2015; Hellevang and Aagaard, 2013; Hellevang et al., 2013).

7.5.2. Improved estimations of carbon mineral trapping capacity

The mineral trapping capacities for both the models were calculated using equation 7.11 (Figure 7.9). Model-A showed enhanced carbon mineral trapping compared to Model-B. The difference in trapping capacity between the two models is nearly 170% (Figure 7.9). Model-B showed negative mineral trapping due to highly acidic conditions over a period of 1000 years while Model-A showed positive trapping due to pH increase within the baffles. As such, the amount of carbon in the mineral phase in Model-A decreased by nearly 100%, indicating a loss of almost all the initial carbon due to the dissolution of primary carbonate minerals. However, Model-B showed a gain of 70% carbon in the solid phase resulting from the precipitation of certain secondary carbonate minerals. Hence, by accounting for intraformational baffles in reservoir scale models, the estimates of carbon mineralized can be improved by 170%. The enhanced trapping calculated in this study is characteristic of distributary channels with similar degree of heterogeneity. Specifically, for Parasequences-1 and -2 of the Paaratte Formation, the distributary channels have been reported to have a width of 50-300 m and a thickness of 0.5-7 meters (Dance, 2012; Dance et al., 2012; Dance et al., 2019). Assuming the length of the channel to be 1 km, the present study shows that 0.06-5 kT of carbon mineralized might be underestimated per distributary channel if the intraformational baffles are neglected in reservoir scale simulations. Hence, by appropriately accounting for intraformational baffles, the estimations of reservoir trapping capacities can be significantly improved. This is especially important for mineral trapping which otherwise might be estimated to be negative for reservoir rocks.

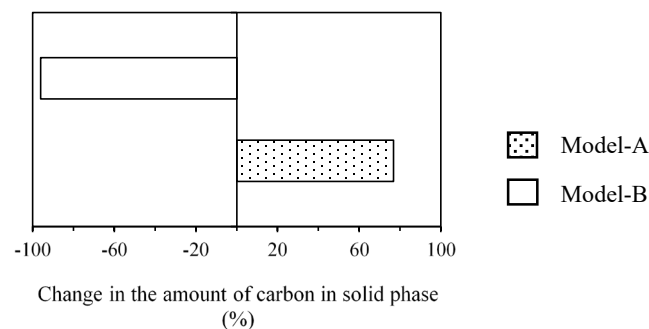


Figure 7.9. Change in the amount of carbon in solid phase in both models after a period of 1000 years.

7.6. Conclusions

The impact of intraformational baffles on carbon mineral trapping is quantified. For this purpose, multiphase reactive transport simulations are run on two models representing the same geological

section at different resolutions. The first model is a high-resolution model that captures intraformational baffles and the associated rock properties averaged from fine scale simulations. The second model is a conventional model in terms of grid size resolution and does not capture cm-scale lithological heterogeneity. The sub-sections were chosen from distributary channel facies as channels are not expected to significantly contribute to carbon mineral trapping. The results show that by appropriately accounting for intraformational baffles, estimations of mineral trapping capacity at reservoir scale can be significantly improved. Specifically for the Otway site, estimations show an improvement of about 2.5 times for mineral trapping. This implies that the mineral trapping capacity might be underestimated by 0.06-5 kT of carbon using conventional reservoir models. The enhanced mineral trapping results from the presence of intraformational baffles which leads to an increase in the pH within the baffles compared to reservoir rocks favouring the precipitation of secondary carbonate minerals. The conventional reservoir models do not account for intraformational baffles and hence pH remains acidic at values of 3.5-4 over 1000s of years inhibiting the precipitation of secondary carbonate minerals. The present study uses transition state theory derived kinetic rate laws to model fluid-rock reactions while other kinetic rate laws have not been explored. This is a limitation and the amount of secondary minerals might be influenced by the choice of kinetic rate laws. However, this will not affect the main conclusion of this study. Another limitation is associated with achieving the computation feasibility of running reactive transport simulations on the entire domain of a high-resolution regional scale reservoir model. This can be achieved by following a nested upscaling approach where the rock properties upscaled from mm-scale are used to derive cm-scale properties which are subsequently averaged to derive outcrop scale lithological properties. Another solution to address this issue can be developed by reducing a multi-mineral geochemical system to a mono-mineral system such that the latter provides the same estimates of carbon mineral trapping as the former.

Chapter 8

Conclusions and future work

8.1 Conclusions

Lithological heterogeneity at mm- to cm-scale in the form of intraformational baffles has been known to significantly influence fluid flow and geochemical reactions. However, baffles are often neglected in reservoir scale simulations. This is primarily because the property population algorithms of reservoir modelling softwares fail at the scale of intraformational baffles as it is below the resolution of wireline logs. Consequently, there is an under-representation of baffle and, hence, fluid flow and geochemical reactions in reservoir scale studies. Specifically for carbon storage reservoirs, this leads to an underestimation of CO₂ trapping capacities. The problem is addressed in this thesis through four research questions. The thesis is structured into a sequence of studies starting with the characterization of intraformational baffles and followed by a more accurate approach to quantify the carbon mineral trapping capacity at reservoir scale.

The first research question addressed the characterization of intraformational baffles is presented in Chapter 3. Field data from CO₂CRC's Otway Research Facility site was used for the characterization of lithological heterogeneity. It is important to use field data because many contemporary studies use synthetic rock type data to characterize intraformational baffles. While the approach is useful to qualitatively understand the impact of baffles on flow and reactions, the estimation of mineral trapping capacity at real CO₂ storage site remains uncertain. Porosity, permeability and capillary entry pressure data were available for the core samples from wells CRC-2 and CRC-3 at the site. Mineralogy data was analysed from 30 core samples using techniques such as QEMSCAN and hyperspectral reflectance analysis. The different datasets were combined and categorized into five rock type classes: coarse sandstone, fine sandstone, siltstone, mudstone and carbonate-cemented sandstone. The information was used to associate hyperspectral reflectance data from 78 depths with the rock type classes. Furthermore, a combination of neutron porosity, density and gamma ray logs were used to derive colourlith logs for the two wells. An association between the colour shades and the rock type classes was identified for the 78 depth points resulting in the translation of colourlith logs to lithotype logs.

The second research question addressed the integration of intraformational baffles in static reservoir models and is presented in Chapter 4. A new workflow was devised to systematically define and characterise composite rock types as a combination of homogeneous rock types derived in Chapter 3. The workflow was based on discretising the colourlith logs at various resolutions and coupling the constituent colour shades at coarser resolutions. The resultant colour shades were further correlated with the averaged rock properties of the composite rock types. Composite rock types serve to bridge the gap between the scale of intraformational baffles and the limiting resolution achievable by the

reservoir modelling software, SKUA, in terms of property population. Intraformational baffles often have a thickness of 5 mm (see Chapter 3) while the minimum vertical grid cell resolution is 5 cm. A total of 10 composite rock types were derived using the presented workflow and were confirmed from the available cores. This allowed the association of composite rock types with three sedimentary structures: cross bedding, planar bedding and the interfaces of two massive bedding surfaces. The flow and petrophysical properties of the composite rock types were obtained by upscaling the respective properties of the constituent homogeneous rock types. The composite rock types were then tied to the colourlith logs by associating red, blue and green shades with the amount of framework (quartz and feldspar), clay and carbonate minerals, respectively. The resultant lithotype logs were further used to build a static reservoir model. The approach allowed downscaling the depositional facies to rock types. The resolution of the reservoir model was 5 cm while integrating rock properties from 5 mm scale, thereby allowing an appropriate representation of intraformational baffles.

The third objective was aimed at understanding the processes governing flow and geochemical reactions at the lithological interface between the baffle and the reservoir rock. The objective was addressed in Chapters 5 and 6. Chapter 5 was focussed on understanding the impact of heterogeneity in porosity, permeability, capillary entry pressure and the van Genuchten relative permeability exponent on turning point CO₂ saturation in cross bedded strata. The objective was addressed through 120 multiphase flow simulations. The results showed that the entry of CO₂ into the baffles can occur at a range of turning point saturations between 40 and 95% of the end point saturation at a given irreducible water content. The range depends on the rock type composition of the cross bedded strata. This is an improvement in our understanding of CO₂ entry as baffles have been assumed to be impermeable barriers in several studies while the studies using realistic properties have not quantified the range of turning point saturations. The dependence of maximum turning point saturation on different rock properties has also been quantified. Chapter 6 aimed at understanding the processes controlling carbon mineral trapping at the lithological interface between the baffle and the reservoir rock for a range of rock properties. The objective was carried out using multiphase reactive transport simulations on eight realizations of lithological interfaces. The realizations covered the range of lithological heterogeneity characteristic of the composite rock types derived in Chapter 4. The results showed that carbon mineral trapping is significantly enhanced in the presence of carbonate-depleted baffles such as mudstone and siltstone and is significantly suppressed in the presence of carbonate-cemented baffles. A higher chlorite content and a lower carbonate content in the baffle were found to enhance carbon mineralization. The enhanced mineral trapping resulted from a rise of pH within the baffle which was caused by the consumption of protons by chlorites, illite and smectites faster than their diffusion from the reservoir rock. Two approaches were presented to derive averaged geochemical properties. The first approach involved deriving mineral specific averaged reaction rates while the second approach involved the

derivation of reduced mineral composition for each realization. The latter was later used in reservoir scale simulations in Chapter 7 due to its computational advantages over the former approach.

The fourth objective was the quantification of carbon mineral trapping capacity for a distributary channel and was addressed in Chapter 7. The distributary channel facies was chosen because distributary channels are not expected to significantly contribute to carbon mineral trapping. Two static reservoir models were used. The first model was taken from Chapter 4 and incorporated intraformational baffles along with their averaged rock properties derived in Chapters 4 and 6. The second model was provided by CO2CRC Limited and did not incorporate intraformational baffles. Multiphase reactive transport simulations were carried to estimate the changes in carbon mineral trapping over 1000 years. The results showed that mineral trapping capacity is 170% times higher than commonly estimated by appropriately accounting for intraformational baffles in distributary channels. The Chapter culminates the research undertaken and highlights the importance of incorporating intraformational baffles in reservoir models.

8.2 Limitations and future work

Some of the key limitations of the thesis are discussed. Firstly, the workflow used to derive composite rock types results in increasingly higher number of rock types at coarser discretization scales. The approach might result in an impractically high number of composite rock types if the target grid size in the reservoir model is 50 cm to 1 m. With the current workflow, 15 rock types were used in the reservoir model at a vertical grid size resolution of 5 cm. The high resolution increases the computational challenges of running dynamic simulations. Hence, it is important to further refine the workflow so that the number of composite rock types is manageable at coarser discretization scales.

Secondly, the large number of minerals for each rock type limits the dynamic simulations to only a smaller sub-section of the entire reservoir model. In order to run reactive transport simulations on the entire model domain, it is important to simplify the mineral composition of the system. Future studies can focus on developing a solution where a multi-mineral system can be reduced to minimal number of minerals with upscaled properties while still replicating the carbon mineral trapping capacity characteristic of the multi-mineral system.

Thirdly, Chapter 6 presents the geochemical processes at the interface between a baffle and a reservoir rock. However, the processes might be different at the interface of a thicker reservoir rock such as a seal rock. In this scenario, diffusion might be restricted to few 10s of cm within the seal rock and all the minerals within the seal might not participate in reactions. Future studies can look into such cases and the information can be helpful in improving the geochemical upscaling relationships.

Fourthly, the use of same diffusion coefficients for all the ionic species, empirically derived van-Genuchten parameters and mineral surface areas might lead to uncertainty in the results presented. The research outcomes can further be improved by using experimentally derived input parameters.

References

- Aghamoghanov, A., 2015. Influence of different modeling techniques on reservoir volume. University of Stavanger, Norway,
- Alcott, A., Swenson, D., Hardeman, B., 2006. Using petrasim to create, execute, and post-process TOUGH2 models, Proceedings of the TOUGH Symposium, Lawrence Berkeley National Laboratory, Berkeley, California, May, pp. 15-17.
- Andrews, T., 1869. Xviii. the bakerian lecture.—on the continuity of the gaseous and liquid states of matter. *Philosophical Transactions of the Royal Society of London*(159), 575-590.
- Arya, A., Hewett, T. A., Larson, R. G., Lake, L. W., 1988. Dispersion and reservoir heterogeneity. *SPE Reservoir Engineering*, 3(01), 139-148.
- Ataie-Ashtiani, B., Hassanizadeh, S.M. and Celia, M.A., 2002. Effects of heterogeneities on capillary pressure–saturation–relative permeability relationships. *Journal of contaminant hydrology*, 56(3-4), pp.175-192.
- Avseth, P., Mukerji, T., Mavko, G., Dvorkin, J., 2010. Rock-physics diagnostics of depositional texture, diagenetic alterations, and reservoir heterogeneity in high-porosity siliciclastic sediments and rocks—A review of selected models and suggested work flows. *Geophysics*, 75(5), 75A31-75A47.
- Ayling, B., Rose, P., Petty, S., Zemach, E., Drakos, P., 2012. QEMSCAN (Quantitative evaluation of minerals by scanning electron microscopy): capability and application to fracture characterization in geothermal systems. Paper presented at the Proc, Thirty-Seventh Workshop on Geotherm Reserv Eng. Stanford, California: Stanford University.
- Babyak, M.A., 2004. What you see may not be what you get: a brief, nontechnical introduction to overfitting in regression-type models. *Psychosomatic medicine*, 66(3), pp.411-421.
- Bachu, S., 2002. Sequestration of CO₂ in geological media in response to climate change: road map for site selection using the transform of the geological space into the CO₂ phase space. *Energy Conversion Management*, 43(1), 87-102.
- Bailey, A., King, R., Holford, S., Sage, J., Backe, G., Hand, M., 2014. Remote sensing of subsurface fractures in the Otway Basin, South Australia. *Journal of Geophysical Research: Solid Earth*, 119(8), 6591-6612.
- Baklid, A., Korbol, R., Owren, G., 1996. Sleipner Vest CO₂ disposal, CO₂ injection into a shallow underground aquifer. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Bear, J., 1972. Dynamics of fluids in porous materials. Society of Petroleum Engineers.
- Beaumont, N. J., Jones, L., Garbutt, A., Hansom, J., Toberman, M., 2014. The value of carbon sequestration and storage in coastal habitats. *Estuarine, Coastal Shelf Science*, 137, 32-40.
- Bech, N. and Frykman, P., 2018. Trapping of buoyancy-driven CO₂ during imbibition. *International Journal of Greenhouse Gas Control*, 78, pp.48-61.
- Benson, S. M., Bennaceur, K., Cook, P., Davison, J., de Coninck, H., Farhat, K., et al., 2012. Carbon capture and storage. *Global energy assessment-Toward a sustainable future*, 993.
- Benson, S. M., Cole, D. R., 2008. CO₂ sequestration in deep sedimentary formations. *Elements*, 4(5), 325-331.
- Benson, S. M., Orr, F. M., 2008 . Carbon dioxide capture and storage. *MRS bulletin*, 33(4), 303-305.
- Bernabé, Y., Revil, A., 1995. Pore-scale heterogeneity, energy dissipation and the transport properties of rocks. *Geophysical Research Letters*, 22(12), 1529-1532.
- Bhattacharyya, T., Pal, D., Chandran, P., Ray, S., Mandal, C., Telpande, B., 2008. Soil carbon storage capacity as a tool to prioritize areas for carbon sequestration. *Current science*, 482-494.
- Bickle, M., Chadwick, A., Huppert, H.E., Hallworth, M., Lyle, S., 2007. Modelling carbon dioxide accumulation at Sleipner: Implications for underground carbon storage. *Earth and Planetary Science Letters* 255, 164-176.
- Blunt, M., King, P., 1991. Relative permeabilities from two-and three-dimensional pore-scale network modelling. *Transport in porous media*, 6(4), 407-433.
- Boeker, U., Drews, M., Kurtev, K., Aplin, A., 2017. Core Image Property Logging for Rock Typing and Core-to-log Upscaling Purposes. Paper presented at the 79th EAGE Conference and Exhibition 2017.

- Boon, M.M. Benson Lab, Stanford University, personal communication.
- Boyd, G. A., Gallagher, S. J., 2001. The sedimentology and palaeoenvironments of the Late Cretaceous Sherbrook Group in the Otway Basin. In (pp. 475-484): Eastern Australian Basins Symposium.
- Bradshaw, J., Bradshaw, B., Spencer, L., Mackie, V., 2000. GEODISC Project 1- Regional Analysis Stage 2 Basins- Oerth Basin, Western Australia. In (Vol. Report No.: RPT06-0162): Australian Petroleum CRC.
- Bridge, J. S., Jalfin, G. A., Georgieff, S. M., 2000. Geometry, lithofacies, and spatial distribution of Cretaceous fluvial sandstone bodies, San Jorge Basin, Argentina: outcrop analog for the hydrocarbon-bearing Chubut Group. *Journal of Sedimentary Research*, 70(2), 341-359.
- Bridge, J. S., Tye, R. S., 2000. Interpreting the dimensions of ancient fluvial channel bars, channels, and channel belts from wireline-logs and cores. *AAPG bulletin*, 84(8), 1205-1228.
- Brooks, R. and Corey, T., 1964. HYDRAU uc properties of porous media. *Hydrology Papers*, Colorado State University, 24, p.37.
- Brown, A. R., 2011. Interpretation of three-dimensional seismic data: Society of Exploration Geophysicists and American Association of Petroleum.
- Brown, K., 1992. Carbon sequestration and storage in tropical forests: CSERGE.
- Buffin, A. J., 1989. Waarre sandstone development within the Port Campbell Embayment. *The APPEA Journal*, 29(1), 299-311.
- Buller, A. T., Bjørkum, P. A., Nadeau, P. H., Walderhaug, O., 2005. Distribution of hydrocarbons in sedimentary basins. *Research and Technology Memoir*, 15.
- Bunch, M., 2019. Quantified detection of carbonate cementation in sandstones using standard wireline log data, ASEG Extended Abstracts, 2019:1, 1-7, DOI: 10.1080/22020586.2019.12073185
- Burnside, N.M. and Naylor, M., 2014. Review and implications of relative permeability of CO₂/brine systems and residual trapping of CO₂. *International Journal of greenhouse gas control*, 23, pp.1-11.
- Caers, J., 2002. Geostatistical history matching under training-image based geological model constraints. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Caers, J., 2003. History matching under training-image-based geological model constraints. *SPE journal*, 8(03), 218-226.
- Caers, J., Li, L., Romary, T., 2014. Spatial Estimation Using Universal Kriging with Training Images.
- Cande, S. C., Mutter, J. C., 1982. A revised identification of the oldest sea-floor spreading anomalies between Australia and Antarctica. *Earth and Planetary Science Letters*, 58(2), 151-160.
- Cao, H., Aziz, K., 1999. Evaluation of pseudo functions. Paper presented at the SPE Western Regional Meeting.
- Carlson, F.M., 1981, January. Simulation of relative permeability hysteresis to the nonwetting phase. In SPE annual technical conference and exhibition. Society of Petroleum Engineers.
- Carman, P. C., 1937. Fluid flow through granular beds. *Trans. Inst. Chem. Eng.*, 15, 150-166.
- Carman, P. C., 1956. Flow of gases through porous media.
- Chatzis, I. and Morrow, N.R., 1984. Correlation of capillary number relationships for sandstone. *Society of Petroleum Engineers Journal*, 24(05), pp.555-562.
- Chen, Y., Durlofsky, L., 2006. Adaptive local-global upscaling for general flow scenarios in heterogeneous formations. *Transport in porous media*, 62(2), 157-185.
- Chen, Y., Durlofsky, L. J., Gerritsen, M., Wen, X.-H., 2003. A coupled local-global upscaling approach for simulating flow in highly heterogeneous formations. *Advances in water resources*, 26(10), 1041-1060.
- Cheng, C.-L., Perfect, E., Yu, T.E., Gragg, M.J., 2017. Impact of the capillary pressure-saturation pore-size distribution parameter on geological carbon sequestration estimates. 16, 67-72.
- Chiles, J.P., Delfiner, P., 1999. Modeling spatial uncertainty. *Geostatistics*, Wiley series in probability and statistics.
- Chiquet, P., Daridon, J.L., Broseta, D. and Thibeau, S., 2007. CO₂/water interfacial tensions under pressure and temperature conditions of CO₂ geological storage. *Energy Conversion and Management*, 48(3), pp.736-744.
- Chopra, S., Marfurt, K. J., 2007. Seismic attributes for prospect identification and reservoir characterization: Society of Exploration Geophysicists and European Association of Geoscientists and Engineers.

- Christie, M. A., 1996. Upscaling for reservoir simulation. *Journal of Petroleum Technology*, 48(11), 1,004-001,010.
- Christie, M. A., Blunt, M., 2001. Tenth SPE comparative solution project: A comparison of upscaling techniques. Paper presented at the SPE reservoir simulation symposium.
- Christie, M. A., Clifford, P., 1998. Fast procedure for upscaling compositional simulation. *SPE journal*, 3(03), 272-278.
- Christopher, C. A., Iliffe, J., Americas, B. P., 2006. Reservoir seals: How they work and how to choose a good one. Paper presented at the CO2SC Symposium, Lawrence Berkeley National Laboratory, Berkeley, California.
- Cipolla, C. L., Fitzpatrick, T., Williams, M. J., Ganguly, U. K., 2011. Seismic-to-simulation for unconventional reservoir development. Paper presented at the SPE Reservoir Characterisation and Simulation Conference and Exhibition.
- Cline, W. R., 1992. The economics of global warming. Institute for International Economics, Washington, DC, 399.
- CO2CRC Limited. Retrieved from <http://www.co2crc.com.au/otway-research-facility-2/>
- Coats, K., Dempsey, J., Henderson, J., 1971. The use of vertical equilibrium in two-dimensional simulation of three-dimensional reservoir performance. *Society of Petroleum Engineers Journal*, 11(01), 63-71.
- Coats, K., Nielsen, R., Terhune, M. H., Weber, A., 1967. Simulation of three-dimensional, two-phase flow in oil and gas reservoirs. *Society of Petroleum Engineers*, 7(04), 377-388.
- Collins, D. R., Doveton, J. H., 1986. Color images of Kansas subsurface geology from well logs. *Computers and Geosciences*, 12(4), 519-526.
- Colombera, L., Felletti, F., Mountney, N. P., McCaffrey, W. D., 2012. A database approach for constraining stochastic simulations of the sedimentary heterogeneity of fluvial reservoirs. *AAPG bulletin*, 96(11), 2143-2166.
- Combinable Magnetic Resonance Report. In: Schlumberger and CO2CRC Limited.
- Corbett, P. W. M., Ringrose, P. S., Jensen, J. L., Sorbie, K. S., 1992. Laminated clastic reservoirs: The interplay of capillary pressure and sedimentary architecture. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Cressie, N., 1993. *Statistics for Spatial Data* Wiley-Interscience.
- Cressie, N., 1990. The origins of kriging. *Mathematical geology*, 22(3), 239-252.
- Cross, T. A., 1991. Field-scale reservoir characterization. Lake LW, Carroll HB, Wesson T C. *Reservoir Characterization II*, 493-497.
- Cross, T. A., Baker, M. R., Chapin, M. A., Clark, M. S., Gardner, M. H., Hanson, M. S., et al., 1993. Applications of high-resolution sequence stratigraphy to reservoir analysis. *Collection Colloques et Seminaires-Institut Francais Du Petrole*, 51, 11-11.
- Czernichowski-Lauriol, I., Rochelle, C., Gaus, I., Azaroual, M., Pearce, J., Durst, P., 2006. Geochemical interactions between CO₂, pore-waters and reservoir rocks, *Advances in the geological storage of carbon dioxide*. Springer, pp. 157-174.
- Dance, T., 2012. Preliminary Static Modelling and Geological Uncertainty for Otway Project: Stage 3 Early Evaluate. Retrieved from CO2CRC Otway Project Stage 2. Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia:
- Dance, T., 2013. Assessment and geological characterisation of the CO2CRC Otway Project CO₂ storage demonstration site: From prefeasibility to injection. *Marine and Petroleum geology*, 46, 251-269.
- Dance, T. (CSIRO, Australia). Personal Communication, 2017.
- Dance, T., 2018. Characterisation of the Late Cretaceous Paaratte Formation, a heterogeneous saline aquifer, for an Australian CO₂ Storage Project. *J Petrol Geol*.
- Dance, T., Arnot, M., Bunch, M., Hortle, A., Lawrence, M., Ennis-King, J., 2012. Geocharacterisation and Static Modelling of the lower Paaratte Formation. Retrieved from CO2CRC Otway Project Stage 2. Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia:
- Dance, T., LaForce, T., Glubokovskikh, S., Ennis-King, J., Pevzner, R., 2019. Illuminating the geology: Post-injection reservoir characterisation of the CO2CRC Otway site. *International Journal of Greenhouse Gas Control*, 86, 146-157.

- Daniel, R., 2012. Containment/Injectivity results from MICP analysis for seals, intraformational barriers and reservoir samples, CRC-2, Otway Basin. Retrieved from Cooperative Research Centre for Greenhouse Gas Technologies, Melbourne, Australia:
- Daniel, R. F., Menacherry, S., and Bunch, M., 2012. Characterisation of dolomitic intraformational barriers, CRC-2B Injection Interval, Paaratte Formation. Retrieved from Cooperative Research Centre for Greenhouse Gas Technologies, Melbourne, Australia:
- Darcy, H. P. G., 1856. Les Fontaines publiques de la ville de Dijon. Exposition et application des principes à suivre et des formules à employer dans les questions de distribution d'eau, etc: V. Dalamont.
- Darman, N., Pickup, G. E., Sorbie, K. S., 2001. The calculation of pseudo functions using potential averaging methods. Paper presented at the SPE Reservoir Simulation Symposium.
- Day, D., Evans, R. J., Lee, J. W., Reicosky, D., 2005. Economical CO₂, SO_x, and NO_x capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy Conversion and Management*, 30(14), 2558-2579.
- De Rose, R. C., Stewardson, M. J., Harman, C., 2008. Downstream hydraulic geometry of rivers in Victoria, Australia. *Geomorphology*, 99(1-4), 302-316.
- Doughty, C., 2010. Investigation of CO₂ plume behavior for a large-scale pilot test of geologic carbon storage in a saline formation. *Transport in porous media*, 82(1), pp.49-76.
- Doughty, C., 2007. Modeling geologic storage of carbon dioxide: comparison of non-hysteretic and hysteretic characteristic curves. *Energy Conversion and Management*, 48(6), pp.1768-1781.
- Doughty, C., 2006. Modeling geologic storage of carbon dioxide: Comparison of non-hysteretic characteristic curves (No. LBNL-59435). Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA (US).
- Doughty, C., Pruess, K., Benson, S. M., Hovorka, S. D., Knox, P. R., Green, C. T., 2001. Capacity investigation of brine-bearing sands of the Frio Formation for geologic sequestration of CO₂. GCCC Texts and Reports.
- Doveton, J. H., Prensky, S. E., 1992. Geological applications of wireline logs: a synopsis of developments and trends. *The Log Analyst*, 33(3), 286-303.
- Downey, M. W., 1984. Evaluating seals for hydrocarbon accumulations. *AAPG bulletin*, 68(11), 1752-1763.
- Doyen, P., 2007. Seismic reservoir characterization: An earth modelling perspective (Vol. 2): EAGE publications Houten.
- Durlofsky, L., Milliken, W., Bernath, A., 2000. Scaleup in the near-well region. *SPE journal*, 5(01), 110-117.
- Durlofsky, L. J., 2003. Upscaling of geocellular models for reservoir flow simulation: a review of recent progress. Paper presented at the 7th International Forum on Reservoir Simulation Bühl/Baden-Baden, Germany.
- Durlofsky, L. J., 2005. Upscaling and gridding of fine scale geological models for flow simulation. Paper presented at the 8th International Forum on Reservoir Simulation Iles Borromees, Stresa, Italy.
- Dutton, S. P., Willis, B., White, C., Bhattacharya, J., 2000. Outcrop characterization of reservoir quality and interwell-scale cement distribution in a tide-influenced delta, Frontier Formation, Wyoming, USA. *Clay Minerals*, 35(1), 95-105.
- Earth System Research Laboratory. Retrieved from <https://www.esrl.noaa.gov/gmd/ccgg/trends/>
- Ennis-King, J., Bradshaw, J., Gibson-Poole, C., Hennig, A., Lang, S., Paterson, L., et al., 2005. Long-term numerical simulation of a portfolio of possible sites for geological storage of carbon dioxide in Australia. Paper presented at the Greenhouse Gas Control Technologies 7.
- Ennis-King, J., Paterson, L., 2002. Engineering aspects of geological sequestration of carbon dioxide, SPE Asia Pacific Oil and Gas Conference and Exhibition. Society of Petroleum Engineers.
- Erskine, W. D., Turner, L. M., Rose, T. A., 2016. Sedimentological and geomorphological effects of the 1997 and 1998 flood sequence on the Lower Snowy River, Victoria. *Proceedings of the Royal Society of Victoria*, 128(2), 25-43.
- Espinoza, D.N. and Santamarina, J.C., 2010. Water-CO₂-mineral systems: Interfacial tension, contact angle, and diffusion—Implications to CO₂ geological storage. *Water resources research*, 46(7).

- Exon, N. F., Lee, C. S., 1987. Seabed sampling off southeast Australia. In (Vol. 7, pp. 2-4): BMR Research Newsletter.
- Falivene, O., Arbues, P., Gardiner, A., Pickup, G., Munoz, J. A., Cabrera, L., 2006. Best practice stochastic facies modeling from a channel-fill turbidite sandstone analog (the Quarry outcrop, Eocene Ainsa basin, northeast Spain). *AAPG bulletin*, 90(7), 1003-1029.
- Finlayson, D., Johnstone, D., Owen, A., Wake-Dyster, K., 1996. Deep seismic images and the tectonic framework of early rifting in the Otway Basin, Australian southern margin. *Tectonophysics*, 264(1-4), 137-152.
- Flett, M., Gurton, R., Taggart, I., 2005. Heterogeneous saline formations: Long-term benefits for geo-sequestration of greenhouse gases. In *Greenhouse Gas Control Technologies 7* (pp. 501-509): Elsevier.
- Flett, M., Gurton, R., Weir, G., 2007. Heterogeneous saline formations for carbon dioxide disposal: Impact of varying heterogeneity on containment and trapping. *Journal of Petroleum Science and Engineering*, 57(1-2), 106-118.
- Fourie, W., Said, R., Young, P., Barnes, D. L., 2007. The simulation of pore scale fluid flow with real world geometries obtained from X-ray computed tomography. Paper presented at the Proceedings of the Boston COMSOL conference.
- Fowler, A., Hennessy, K., 1995. Potential impacts of global warming on the frequency and magnitude of heavy precipitation. *Natural Hazards*, 11(3), 283-303.
- Friedmann, S. J., 2007. Geological carbon dioxide sequestration. *Elements*, 3(3), 179-184.
- Frykman, P., Bech, N., Sørensen, A. T., Nielsen, L. H., Nielsen, C. M., Kristensen, L., Bidstrup, T., 2009. Geological modeling and dynamic flow analysis as initial site investigation for large-scale CO₂ injection at the Vedsted structure, NW Denmark. *Energy Procedia*, 1(1), 2975-2982.
- Fulljames, J. R., Zijerveld, L. J. J., Franssen, R. C. M. W., 1997. Fault seal processes: systematic analysis of fault seals over geological and production time scales. In *Norwegian Petroleum Society Special Publications* (Vol. 7, pp. 51-59): Elsevier.
- Gabrielsen, R. H., 2010. The structure and hydrocarbon traps of sedimentary basins. In *Petroleum Geoscience* (pp. 299-327): Springer.
- Gao, D., 2011. Latest developments in seismic texture analysis for subsurface structure, facies, and reservoir characterization: A review. *Geophysics*, 76(2), W1-W13.
- Garland, C. R., Haughton, P., King, R. F., Moulds, T. P., 1999. Capturing reservoir heterogeneity in a sand-rich submarine fan, Miller Field. Paper presented at the Geological Society, London, Petroleum Geology Conference series.
- Geary, G. C., Constantine, A. E., Reid, I. S. A., 2001. New perspectives on structural style and petroleum prospectivity, offshore eastern Otway Basin.
- Geary, G. C., Reid, I. S. A., 1998. Geology and prospectivity of the offshore eastern Otway Basin, Victoria - for the 1998 Acreage Release. In (Vol. Report 55). Victorian Initiative for Minerals and Petroleum: Department of Natural Resources and Environment.
- Geel, C., Donselaar, M., 2007. Reservoir modelling of heterolithic tidal deposits: sensitivity analysis of an object-based stochastic model. *Netherlands Journal of Geosciences, Geologie en Mijnbouw*, 86-4, 403-411.
- Geistlinger, H., Mohammadian, S., Schlueter, S. and Vogel, H.J., 2014. Quantification of capillary trapping of gas clusters using X-ray microtomography. *Water Resources Research*, 50(5), pp.4514-4529.
- Geoscience Australia. Retrieved from www.ga.gov.au/scientific-topics/energy/province-sedimentary-basin-geology/petroleum/offshore-southern-australia/otway
- Gershenson, N. I., Ritzi, R. W., Dominic, D. F., Mehnert, E., Okwen, R. T., 2017. Capillary trapping of CO₂ in heterogeneous reservoirs during the injection period. *International Journal of Greenhouse Gas Control*, 59, 13-23.
- Gherardi, F., Xu, T., Pruess, K., 2007. Numerical modeling of self-limiting and self-enhancing caprock alteration induced by CO₂ storage in a depleted gas reservoir. *Chemical Geology* 244, 103-129.
- Ghommam, M., Hajj, M. R., Puri, I. K., 2012. Influence of natural and anthropogenic carbon dioxide sequestration on global warming. *Ecological Modelling*, 235, 1-7.

- Gibling, M. R., 2006. Width and thickness of fluvial channel bodies and valley fills in the geological record: a literature compilation and classification. *Journal of Sedimentary Research*, 76(5), 731-770.
- Gibson-Poole, C., Svendsen, L., Underschultz, J., Watson, M., Ennis-King, J., Van Ruth, P., et al., 2006. Gippsland Basin geosequestration: a potential solution for the Latrobe Valley brown coal CO₂ emissions. *The APPEA Journal*, 46(1), 413-434.
- Gibson-Poole, C. M., Svendsen, L., Watson, M. N., Daniel, R. F., Ennis-King, J., Rigg, A. J., 2009. Understanding stratigraphic heterogeneity: A methodology to maximize the efficiency of the geological storage of CO₂. *AAPG Studies in Geology*, 59, 347-364.
- Gilfillan, S.M., Lollar, B.S., Holland, G., Blagburn, D., Stevens, S., Schoell, M., Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G.J.N., 2009. Solubility trapping in formation water as dominant CO₂ sink in natural gas fields. 458, 614.
- Gomez-Hernandez, J., Journel, A., 1990. Stochastic characterization of grid-block permeabilities: from point values to block tensors. Paper presented at the ECMOR II-2nd European Conference on the Mathematics of Oil Recovery.
- Green, C. P., Ennis-King, J., 2010a. Effect of vertical heterogeneity on long-term migration of CO₂ in saline formations. *Transport in porous media*, 82(1), 31-47.
- Green, C. P., Ennis-King, J., 2010b. Vertical permeability distribution of reservoirs with impermeable barriers. *Transport in porous media*, 83(3), 525-539.
- Green, C.P. and Ennis-King, J., 2012. Spatial grid correction for short-term numerical simulation results of carbon dioxide dissolution in saline aquifers. *Computational Geosciences*, 16(4), pp.1153-1161.
- Green, C.P., Ennis-King, J., 2013. Residual Trapping Beneath Impermeable Barriers During Buoyant Migration of CO₂. *Transport in porous media* 98, 505-524.
- Gunn, J. S., Ganz, D. J., Keeton, W. S., 2012. Biogenic vs. geologic carbon emissions and forest biomass energy production. *Gcb Bioenergy*, 4(3), 239-242.
- Haese, R.R., Black, J.R., Kirste, D., Watson, M., Singh, R., 2014. Otway Stage 2B extension project-initial science report. Cooperative Research Centre for Greenhouse Gas Technologies, Melbourne, Australia.
- Haese, R. R., Jiang, G., Ooi, S., Black, J. R., 2019. Enhanced reservoir characterization using hyperspectral core logging. *Journal of Sedimentary Research*, 89, 1-12.
- Haggerty, R., Gorelick, S. M., 1995. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resources Research*, 31(10), 2383-2400.
- Haldorsen, H. H., Damsleth, E., 1993. Challenges in reservoir characterization: Geohorizons. *AAPG bulletin*, 77(4), 541-551.
- Hawkins, P. J., Dellenbach, J., 1971. A review of Otway Basin. In M. A. Reynolds (Ed.), (Vol. 134, pp. 7-22): Bureau of Mineral Resources.
- Hearn, C., 1971. Simulation of stratified waterflooding by pseudo relative permeability curves. *Journal of Petroleum Technology*, 23(07), 805-813.
- Heinemann, N., Wilkinson, M., Haszeldine, R.S., Fallick, A.E., Pickup, G.E., 2013. CO₂ sequestration in a UK North Sea analogue for geological carbon storage. *Geology* 41, 411-414.
- Hellevang, H., 2015. Carbon capture and storage (CCS). In *Petroleum Geoscience* (pp. 591-602). Springer, Berlin, Heidelberg.
- Hellevang, H., Aagaard, P., 2013. Can the long-term potential for carbonatization and safe long-term CO₂ storage in sedimentary formations be predicted?. *Applied geochemistry*, 39, pp.108-118.
- Hellevang, H., Aagaard, P., 2015. Constraints on natural global atmospheric CO₂ fluxes from 1860 to 2010 using a simplified explicit forward model. *Scientific Reports*, 5, p.17352.
- Hellevang, H., Khattri, S.K., Fladmark, G.E., Kvamme, B., 2005. CO₂ storage in the Utsira Formation: ATHENA 3-D reactive transport simulations. Submitted to the journal of Basin Research.
- Hellevang, H., Pham, V.T., Aagaard, P., 2013. Kinetic modelling of CO₂-water-rock interactions. *International Journal of Greenhouse Gas Control*, 15, pp.3-15.
- Hermanson, J., Kirste, D., 2013. Representation of geological heterogeneities and their effects on mineral trapping during CO₂ storage using numerical modeling. *Procedia Earth and Planetary Science*, 7, 350-353.

- Hewett, T. A., 1986. Fractal distributions of reservoir heterogeneity and their influence on fluid transport. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Higgs, K. E., Haese, R. R., Golding, S. D., Schacht, U., Watson, M. N., 2015. The Pretty Hill Formation as a natural analogue for CO₂ storage: an investigation of mineralogical and isotopic changes associated with sandstones exposed to low, intermediate and high CO₂ concentrations over geological time. *Chemical Geology*, 399, 36-64.
- Hill, K. A., Durrand, C., 1993. The western Otway Basin: an overview of the rift and drift history using serial composite seismic profiles.
- Hoel, M., Kverndokk, S., 1996. Depletion of fossil fuels and the impacts of global warming. *Resource Energy Economics*, 18(2), 115-136.
- Holford, S., Hillis, R., Duddy, I., Green, P., Stoker, M., Tuitt, A., et al., 2011. Cenozoic post-breakup compressional deformation and exhumation of the southern Australian margin. *The APPEA Journal*, 51(1), 613-638.
- Holtz, M.H., 2009. Optimizing permanent CO₂ sequestration in brine aquifers: Example from the Upper Frio, Gulf of Mexico.
- Holtz, M.H., 2002. Residual gas saturation to aquifer influx: A calculation method for 3-D computer reservoir model construction, SPE Gas Technology Symposium. Society of Petroleum Engineers.
- Honarpour, M.M., Cullick, A.S., Saad, N. and Humphreys, N.V., 1995. Effect of rock heterogeneity on relative permeability: implications for scale-up. *Journal of Petroleum Technology*, 47(11), pp.980-986.
- Honarpour, M.M., Saad, N., 1994. Influence of small-scale rock laminations on core plug oil/water relative permeability and capillary pressure. In University of Tulsa Centennial Petroleum Engineering Symposium. Society of Petroleum Engineers.
- Houghton, J., 2009. Global warming: the complete briefing: Cambridge university press.
- Huntington, J., Whitbourn, L., Mason, P., Berman, M., Schodlok, M. C., 2010. HyLogging—Voluminous industrial-scale reflectance spectroscopy of the Earth's subsurface. Paper presented at the Art, Science and Applications of Reflectance Spectroscopy Symposium, ASD Inc., Boulder, Colo.
- Huang, Y., Ringrose, P.S. and Sorbie, K.S., 1996. The effects of heterogeneity and wettability on oil recovery from laminated sedimentary structures. *SPE Journal*, 1(04), pp.451-462.
- Hurst, A., Griffiths, C., Worthington, P. F., 1992. Geological applications of wireline logs II.
- Iglauer, S., Wüiling, W., Pentland, C.H., Al-Mansoori, S.K. and Blunt, M.J., 2011. Capillary-trapping capacity of sandstones and sandpacks. *SPE Journal*, 16(04), pp.778-783.
- Ito, M., Matsukawa, M., Saito, T., Nichols, D. J., 2006. Facies architecture and paleohydrology of a synrift succession in the Early Cretaceous Choyr Basin, southeastern Mongolia. *Cretaceous Research*, 27(2), 226-240.
- Jerauld, G.R., 1997. Prudhoe Bay gas/oil relative permeability. *SPE Reservoir Engineering*, 12(01), pp.66-73.
- Joos, F., Bruno, M., 1996. Pulse response functions are cost-efficient tools to model the link between carbon emissions, atmospheric CO₂ and global warming. *Physics Chemistry of the Earth*, 21(5-6), 471-476.
- Journel, A., Gunderso, R., Gringarten, E., Yao, T., 1998. Stochastic modelling of a fluvial reservoir: a comparative review of algorithms. *Journal of Petroleum Science and Engineering*, 21(1-2), 95-121.
- Juanes, R., Spiteri, E.J., Orr Jr, F.M. and Blunt, M.J., 2006. Impact of relative permeability hysteresis on geological CO₂ storage. *Water resources research*, 42(12).
- Judd, C.M., McClelland, G.H., Ryan, C.S., 2011. Data analysis: A model comparison approach. Routledge.
- Kaldi, J., Daniel, R., Tenthorey, E., Michael, K., Schacht, U., Nicol, A., et al., 2011. Caprock systems for CO₂ geological storage. IAEHGH Report, 1, 149.
- Kansas Geological Survey. Retrieved from <http://www.kgs.ku.edu/stratigraphic/KIMELEON/history.html>
- Kim, D., Peters, C. A., Lindquist, W., 2011. Upscaling geochemical reaction rates accompanying acidic CO₂-saturated brine flow in sandstone aquifers. *J. W. R. R.*, 47(1).

- Kleppe, J., Delaplace, P., Lenormand, R., Hamon, G. and Chaput, E., 1997, January. Representation of capillary pressure hysteresis in reservoir simulation. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.
- Knackstedt, M., Saadatfarm, M., Herring, A., Turner, M., Sok, R., Deakin, L., et al., 2018. Multiphase flooding dynamics of Otway core. Phase 1. Retrieved from Cooperative Research Centre for Greenhouse Gas Technologies, Melbourne, Australia:
- Koltermann, C. E., Gorelick, S. M., 1996. Heterogeneity in sedimentary deposits: A review of structure-imitating, process-imitating, and descriptive approaches. *Water Resources Research*, 32(9), 2617-2658.
- Korbøl, R., Kaddour, A., 1995. Sleipner vest CO₂ disposal-injection of removed CO₂ into the Utsira formation. *Energy Conversion and Management*, 36(6-9), 509-512.
- Kozeny, J., 1927. Über kapillare leitung der wasser in boden. *Royal Academy of Science, Vienna, Proc. Class I*, 136, 271-306.
- Krassay, A. A., Cathro, D. L., Ryan, D. J., Boulton, P. J., Johns, D. R., Lang, S. C., 2004. A regional tectonostratigraphic framework for the Otway Basin. In.
- Krevor, S., Blunt, M.J., Benson, S.M., Pentland, C.H., Reynolds, C., Al-Menhali, A. and Niu, B., 2015. Capillary trapping for geologic carbon dioxide storage—From pore scale physics to field scale implications. *International Journal of Greenhouse Gas Control*, 40, pp.221-237.
- Krevor, S.C., Pini, R., Li, B., Benson, S.M., 2011. Capillary heterogeneity trapping of CO₂ in a sandstone rock at reservoir conditions. *Geophysical Research Letters*, 38(15).
- Krishnamurthy, P.G., Trevisan, L., Meckel, T., 2017. Investigating the influence of geological heterogeneity on capillary trapping of buoyant CO₂ using transmitted-light flow visualization experiments. *Energy Procedia* 114, 4961-4966.
- Kyte, J. R., Berry, D., 1975. New pseudo functions to control numerical dispersion. *Society of Petroleum Engineers Journal*, 15(04), 269-276.
- Lai, P., Moulton, K., Krevor, S., 2015. Pore-scale heterogeneity in the mineral distribution and reactive surface area of porous rocks. *Chemical Geology*, 411, 260-273.
- Land, C.S., 1968. Calculation of imbibition relative permeability for two-and three-phase flow from rock properties. *Society of Petroleum Engineers Journal*, 8(02), pp.149-156.
- Lasaga, A. C., 1984. Chemical kinetics of water-rock interactions. *Journal of Geophysical Research: Solid Earth*, 89(B6), 4009-4025.
- Lasaga, A. C., 2014. *Kinetic theory in the earth sciences (Vol. 402)*: Princeton university press.
- Law, D. H. S., Bachu, S., 1996. Hydrogeological and numerical analysis of CO₂ disposal in deep aquifers in the Alberta sedimentary basin. *Energy Conversion and Management*, 37(6-8), 1167-1174.
- Lawrence, M. J. F., Arnot, M., Browne, G. H., Bunch, M., Dance, T., 2013. Geological interpretation of core and wireline data from Otway project wells CRC-1 and CRC-2. Retrieved from Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia.
- Lenhard, R.J. and Parker, J.C., 1987. A model for hysteretic constitutive relations governing multiphase flow: 2. Permeability-saturation relations. *Water Resources Research*, 23(12), pp.2197-2206.
- Lenhard, R.J., Parker, J.C. and Mishra, S., 1989. On the correspondence between Brooks-Corey and van Genuchten models. *Journal of Irrigation and Drainage Engineering*, 115(4), pp.744-751.
- Li, B., Benson, S. M., 2015. Influence of small-scale heterogeneity on upward CO₂ plume migration in storage aquifers. *Advances in Water Resources*, 83, 389-404.
- Li, B., Tchelepi, H.A. and Benson, S.M., 2013. Influence of capillary-pressure models on CO₂ solubility trapping. *Advances in water resources*, 62, pp.488-498.
- Li, J., Heap, A. D., 2008. A review of spatial interpolation methods for environmental scientists.
- Li, J., Pang, Z., 2015. Environmental isotopes in CO₂ geological sequestration. *Greenhouse Gases: Science and Technology* 5, 374-388.
- Liang, C., Cao, Y., Liu, K., Jiang, Z., Wu, J., Hao, F., 2018. Diagenetic variation at the lamina scale in lacustrine organic-rich shales: Implications for hydrocarbon migration and accumulation. *Geochimica et Cosmochimica Acta*, 229, 112-128.
- Lindeberg, E., 1997. Escape of CO₂ from aquifers. *Energy Conversion and Management*, 38, S235-S240.

- MacDonald, A. M., Bonsor, H. C., Dochartaigh, B. É. Ó., Taylor, R. G., 2012. Quantitative maps of groundwater resources in Africa. *Environmental Research Letters*, 7(2), 024009.
- Martens, P., 2013. *Health and climate change: modelling the impacts of global warming and ozone depletion*: Routledge.
- Matter, J.M., Kelemen, P.B., 2009. Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation. *Nature Geoscience* 2, 837.
- Matthews, H. D., Gillett, N. P., Stott, P. A., Zickfeld, K., 2009. The proportionality of global warming to cumulative carbon emissions. *Nature*, 459(7248), 829-832.
- Meakin, P., Tartakovsky, A. M., 2009. Modeling and simulation of pore-scale multiphase fluid flow and reactive transport in fractured and porous media. *Reviews of Geophysics*, 47(3).
- Meehl, G. A., Washington, W. M., Collins, W. D., Arblaster, J. M., Hu, A., Buja, L. E., et al., 2005. How much more global warming and sea level rise? *Science*, 307(5716), 1769-1772.
- Metz, B., Davidson, O., De Coninck, H., 2005. *Carbon dioxide capture and storage: special report of the intergovernmental panel on climate change*: Cambridge University Press.
- Miall, A. D., 2016. *Facies Models Stratigraphy: A Modern Synthesis*. In (pp. 161-214): Springer.
- Mikes, D., Barzandji, O. H. M., Bruining, J., Geel, C. R., 2006. Upscaling of small-scale heterogeneities to flow units for reservoir modelling. *Marine and Petroleum geology*, 23(9-10), 931-942.
- Mishra, A., Chaudhuri, A., Haese, R.R. (submitted). Conditions and processes controlling carbon mineral trapping in intraformational baffles. *International Journal of Greenhouse Gas Control*.
- Mishra, A., Kurtev, K.D. and Haese, R.R., 2020. Composite rock types as part of a workflow for the integration of mm-to cm-scale lithological heterogeneity in static reservoir models. *Marine and Petroleum Geology*, 114, p.104240.
- Mishra, A., Pajank, L., Haese, R. R., 2019. High Resolution Characterization of Lithological Heterogeneity of the Paaratte Formation, Otway Basin (Australia), a Coastal to Shallow-Marine Deposit. *Geosciences*, 9(6), 278.
- Mitra, A., Zaman, S., 2014. *Carbon sequestration by coastal floral community*: Energy and Resources Institute.
- Miyazaki, S., Lavering, I. H., Stephenson, A. E., Pain, L., 1990. Otway Basin, South Australia, Victoria and Tasmania. In (Vol. 6): Australian Bureau of Mineral Resources, Geology and Geophysics, Petroleum Accumulations Report.
- Moore, A. M. G., Stagg, H. M. J., Norvick, M. S., 2000. Deep-water Otway Basin: a new assessment of the tectonics and hydrocarbon prospectivity. *The APPEA Journal*, 40(1), 66-85.
- Morgan, R. P., 1985. Palynology review of selected oil drilling. Otway Basin, South Australia unpubl. rept, for Ultramar Australia MORGAN PALAEO ASSOCIATES.
- Morton, J. G. G., 1990. Revisions to stratigraphic nomenclature of the Otway Basin, South Australia. In: *Quart. geol. notes/South Australia*. Geol. survey.
- Morton, J. G. G., Hill, A. J., Parker, G., Tabassi, A., 1994. Towards a unified stratigraphy for the Otway Basin. Paper presented at the Finlayson, DM (compiler), NGMA/Petroleum Exploration Society of Australia Otway Basin Symposium, Melbourne.
- Mualem, Y., 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water resources research* 12, 513-522.
- Naylor, M., Wilkinson, M., Haszeldine, R.S., 2011. Calculation of CO₂ column heights in depleted gas fields from known pre-production gas column heights. *Marine and Petroleum Geology* 28, 1083-1093.
- Neglia, S., 1979. Migration of fluids in sedimentary basins. *AAPG bulletin*, 63(4), 573-597.
- Newell, D. L., Kaszuba, J. P., Viswanathan, H. S., Pawar, R. J., Carpenter, T., 2008. Significance of carbonate buffers in natural waters reacting with supercritical CO₂: Implications for monitoring, measuring and verification (MMV) of geologic carbon sequestration. *J. G. R. L.*, 35(23).
- Ni, H., Boon, M., Garing, C., Benson, S.M., 2019. Predicting CO₂ residual trapping ability based on experimental petrophysical properties for different sandstone types. *International Journal of Greenhouse Gas Control*, 86, pp.158-176.
- Norvick, M. S., 2005. Plate Tectonic Reconstructions of Australia's Southern Margins. In (Vol. 7). *Geoscience Australia*.

- O'Brien, G. W., Thomas, J. H., 2007. A Technical Assessment of the Yet-to-find Hydrocarbon Resource Inventory, Offshore and Onshore Otway Basin, Victoria, Australia: Department of Primary Industries.
- Ogawa, M., Okimori, Y., Takahashi, F., 2006. Carbon sequestration by carbonization of biomass and forestation: three case studies. *Mitigation adaptation strategies for global change*, 11(2), 429-444.
- Oldenburg, C. M., Unger, A. J., 2003. On leakage and seepage from geologic carbon sequestration sites. *Vadose Zone Journal*, 2(3), 287-296.
- Palandri, J.L., Kharaka, Y.K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. Geological Survey Menlo Park CA.
- Pang, Z., Li, Y., Yang, F., Duan, Z., 2012. Geochemistry of a continental saline aquifer for CO₂ sequestration: The Guantao formation in the Bohai Bay Basin, North China. *Applied geochemistry* 27, 1821-1828.
- Parker, G., 1995. Early Cretaceous stratigraphy along the northern margin of the Otway Basin, Victoria: Geological Survey of Victoria.
- Parker, J.C. and Lenhard, R.J., 1987. A model for hysteretic constitutive relations governing multiphase flow: 1. Saturation-pressure relations. *Water Resources Research*, 23(12), pp.2187-2196.
- Parkhurst, D.L., Appelo, C., 2013. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey.
- Perincek, D., Cockshell, C., 1995. The Otway basin: early Cretaceous rifting to Neogene inversion. *The AAPG Journal*, 35(1), 451-466.
- Pickup, G.E., 1998. Steady-state upscaling: from lamina-scale to full-field model. In *European Petroleum Conference*. Society of Petroleum Engineers.
- Pickup, G.E., Sorbie, K.S., 1996. The scaleup of two-phase flow in porous media using phase permeability tensors. *SPE journal*, 1(04), pp.369-382.
- Pini, R., Benson, S.M., 2017. Capillary pressure heterogeneity and hysteresis for the supercritical CO₂/water system in a sandstone. *Advances in Water Resources*, 108, pp.277-292.
- Pires, J. C. M., Martins, F. G., Alvim-Ferraz, M. C. M., Simões, M., 2011. Recent developments on carbon capture and storage: an overview. *Chemical Engineering Research and Design*, 89(9), 1446-1460.
- Pranter, M. J., Ellison, A. I., Cole, R. D., Patterson, P. E., 2007. Analysis and modeling of intermediate-scale reservoir heterogeneity based on a fluvial point-bar outcrop analog, Williams Fork Formation, Piceance Basin, Colorado. *AAPG bulletin*, 91(7), 1025-1051.
- Pranter, M. J., Hirstius, C. B., Budd, D. A., 2005. Scales of lateral petrophysical heterogeneity in dolomite lithofacies as determined from outcrop analogs: Implications for 3-D reservoir modeling. *AAPG bulletin*, 89(5), 645-662.
- Price, J., Smith, B., 2008. Geologic Storage of carbon dioxide—staying safely underground. *International Energy Agency Greenhouse Gas RandD Programme*.
- Pruess, K., 2005. ECO2N: A TOUGH2 fluid property module for mixtures of water, NaCl, and CO₂. Lawrence Berkeley National Laboratory Berkeley, CA.
- Pruess, K., Xu, T., Apps, J., Garcia, J., 2003. Numerical Modeling of Aquifer Disposal of CO₂. *SPEJ* 8 (1): 49–60.
- Puranik, S., Deshpande, P., Chandrasekaran, K., 2016. A novel machine learning approach for bug prediction. *Procedia Computer Science* 93, 924-930.
- Rabinovich, A., Itthisawatpan, K., Durlinsky, L.J., 2015. Upscaling of CO₂ injection into brine with capillary heterogeneity effects. *Journal of Petroleum Science and Engineering* 134, 60-75.
- Rahman, F. A., Aziz, M. M. A., Saidur, R., Bakar, W. A. W. A., Hainin, M., Putrajaya, R., Hassan, N. A., 2017. Pollution to solution: Capture and sequestration of carbon dioxide (CO₂) and its utilization as a renewable energy source for a sustainable future. *Renewable Sustainable Energy Reviews*, 71, 112-126.
- Reineck, H.E. and Singh, I.B., 1975. *Depositional sedimentary environments*. Berlin, etc.: Springer—Verlag.
- Ren, B., Sun, Y. and Bryant, S., 2014. Maximizing local capillary trapping during CO₂ injection. *Energy Procedia*, 63(Supplement C), pp.5562-5576.

- Reynolds, A. D., 1999. Dimensions of paralic sandstone bodies. AAPG bulletin, 83(2), 211-229.
- Reynolds, M., 1971. A review of the Otway Basin: Bureau of Mineral Resources, Geology and Geophysics.
- Rider, M., 1996. The geological interpretation of wireline logs. Whittles, Caithness, 1-175.
- Ringrose, P. S., Sorbie, K. S., Corbett, P. W. M., Jensen, J. L., 1993. Immiscible flow behaviour in laminated and cross-bedded sandstones. Journal of Petroleum Science and Engineering, 9(2), 103-124.
- Ringrose, P., Nordahl, K. and Wen, R., 2005. Vertical permeability estimation in heterolithic tidal deltaic sandstones. Petroleum Geoscience, 11(1), pp.29-36.
- Ringrose, P., Bentley, M., 2015. Reservoir model types. In Reservoir Model Design (pp. 173-231): Springer.
- Robertson, C. S., Cronk, D. K., Mayne, S. J., Townsend, D. G., 1978. A review of petroleum exploration and prospects in the Otway Basin region. In (Vol. 49): Canberra: Geoscience Australia.
- Robie, R.A., Bethke, P.M., 1962. Molar volumes and densities of minerals. Report TEI-822. United States Department of the Interior, Geological Survey, 1-37.
- Robson, A., King, R., Holford, S., 2016. 3D seismic analysis of gravity-driven and basement influenced normal fault growth in the deepwater Otway Basin, Australia. Journal of Structural Geology, 89, 74-87.
- Ruhovets, N., Rau, R., Samuel, M., Smith, H., Smith, M., 1992. Evaluating thinly laminated reservoirs using logs with different vertical resolution. Geological Society, London, Special Publications, 65(1), 99-121.
- Ruprecht, C., Pini, R., Falta, R., Benson, S. and Murdoch, L., 2014. Hysteretic trapping and relative permeability of CO₂ in sandstone at reservoir conditions. International Journal of Greenhouse Gas Control, 27, pp.15-27.
- Ruspini, L.C., Farokhpour, R. and Øren, P.E., 2017. Pore-scale modeling of capillary trapping in water-wet porous media: A new cooperative pore-body filling model. Advances in Water Resources, 108, pp.1-14.
- Ryan, S., Knight, L., Parker, G., 1995. The stratigraphy and structure of the Tyrendarra Embayment. Otway Basin, Victoria.
- Saad, N., Cullick, A.S. and Honarpour, M.M., 1995, January. Immiscible displacement mechanisms and scale-up in the presence of small-scale heterogeneities. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.
- Saadatpour, E., Bryant, S. L., Sepehrnoori, K., 2009a. Effect of capillary heterogeneity on buoyant plumes: A new local trapping mechanism. Energy Procedia, 1(1), 3299-3306.
- Saadatpour, E., Bryant, S. L., Sepehrnoori, K., 2009b. Upscaling local CO₂ trapping during buoyancy driven flow. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Saadatpour, E., Bryant, S. L., Sepehrnoori, K., 2010a. CO₂ leakage from heterogeneous storage formations. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Saadatpour, E., Bryant, S. L., Sepehrnoori, K., 2010b. New trapping mechanism in carbon sequestration. Transport in porous media, 82(1), 3-17.
- Saadatpour, E., Bryant, S. L., Sepehrnoori, K., 2013. Estimation of local capillary trapping capacity from geologic models. Energy Procedia, 37, 5501-5510.
- Schlumberger. Retrieved from www.glossary.oilfield.slb.com/en/Terms/e/elemental_capture_spectroscopy.aspx
- Schodlok, M. C., Whitbourn, L., Huntington, J., Mason, P., Green, A., Berman, M., et al., 2016. HyLogger-3, a visible to shortwave and thermal infrared reflectance spectrometer system for drill core logging: functional description. Australian Journal of Earth Sciences, 63(8), 929-940.
- Sheng, P., White, B., Nair, B., Kerford, S., 1987. Bayesian deconvolution of gamma-ray logs. Geophysics, 52(11), 1535-1546.
- Smith, M. M., Sholokhova, Y., Hao, Y., Carroll, S. A., 2013. Evaporite caprock integrity: An experimental study of reactive mineralogy and pore-scale heterogeneity during brine-CO₂ exposure. Environmental Science Technology, 47(1), 262-268.
- Spiteri, E.J., Juanes, R., Blunt, M.J. and Orr, F.M., 2008. A new model of trapping and relative permeability hysteresis for all wettability characteristics. Spe Journal, 13(03), pp.277-288.

- Spycher, N.F., Llanos, E.M., Vu, H.P., Haese, R.R., 2019. Reservoir scale reactive-transport modeling of a buoyancy-controlled CO₂ plume with impurities (SO₂, NO₂, O₂). *International Journal of Greenhouse Gas Control* 89, 40-51.
- Stacey, A., Mitchell, C., Nayak, G., Struckmeyer, H., Morse, M., Totterdell, J., Gibson, G., 2013. Geology and petroleum prospectivity of the deepwater Otway and Sorell basins: new insights from an integrated regional study. *The APPEA Journal*, 51(2), 692-692.
- Steefel, C. I., DePaolo, D. J., Lichtner, P. C., 2005. Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. *Earth and Planetary Science Letters*, 240(3-4), 539-558.
- Steefel, C. I., Lasaga, A. C., 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *American Journal of science*, 294(5), 529-592.
- Steenekveldt, R., Berger, B., Torp, T.A., 2006. CO₂ capture and storage: closing the knowing-doing gap. *Chemical Engineering Research and Design* 84, 739-763.
- Stone, H., 1991. Rigorous black oil pseudo functions. Paper presented at the SPE Symposium on reservoir simulation.
- Strebelle, S., 2002. Conditional simulation of complex geological structures using multiple-point statistics. *Mathematical geology*, 34(1), 1-21.
- Sundal, A., Hellevang, H., 2019. Using Reservoir Geology and Petrographic Observations to Improve CO₂ Mineralization Estimates: Examples from the Johansen Formation, North Sea, Norway. *Minerals*, 9(11), p.671.
- Suzanne, K., Hamon, G., Billiotte, J. and Trocme, V., 2003, January. Experimental relationships between residual gas saturation and initial gas saturation in heterogeneous sandstone reservoirs. In *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers.
- Tan, G., Shibasaki, R., 2003. Global estimation of crop productivity and the impacts of global warming by GIS and EPIC integration. *Ecological Modelling*, 168(3), 357-370.
- Thangarajan, M., 2007. *Groundwater: Resource evaluation, augmentation, contamination, restoration, modeling and management*: Springer Science and Business Media.
- Toth, J., 2009. *Groundwater in Igneous, Metamorphic, and Sedimentary Rocks*. *Groundwater-Volume I*, 67.
- Trevisan, L., Krishnamurthy, P. G., Meckel, T. A., 2017. Impact of 3D capillary heterogeneity and bedform architecture at the sub-meter scale on CO₂ saturation for buoyant flow in clastic aquifers. *International Journal of Greenhouse Gas Control*, 56, 237-249.
- Van der Meer, L. G. H., 1996. Computer modelling of underground CO₂ storage. *Energy Conversion and Management*, 37(6-8), 1155-1160.
- Van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal* 44, 892-898.
- Vu, H.P., Black, J.R., Haese, R.R., 2017. Changes in formation water composition during water storage at surface and post re-injection. *Energy Procedia* 114, 5732-5741.
- Wackernagel, H., 2013. *Multivariate geostatistics: an introduction with applications*: Springer Science and Business Media.
- Warren, J., Price, H., 1961. Flow in heterogeneous porous media. *Society of Petroleum Engineers Journal*, 1(03), 153-169.
- Watson, M. N., 2012. Natural CO₂ accumulations as analogues for CO₂ geological storage and CO₂-induced diagenesis in the Otway Basin, Australia.
- Watson, M. N., Daniel, R. F., Tingate, P. R., Gibson-Poole, C. M., 2005. CO₂-related seal capacity enhancement in mudstones: Evidence from the Pine Lodge natural CO₂ accumulation, Otway Basin, Australia. In *Greenhouse Gas Control Technologies 7* (pp. 2313-2316): Elsevier.
- Watson, M.N., Gibson-Poole, C.M., 2005. Reservoir selection for optimised geological injection and storage of carbon dioxide: a combined geochemical and stratigraphic perspective. In *The fourth annual conference on carbon capture and storage*. National Energy Technology Laboratory, US Department of Energy, Alexandria (pp. 2-5).
- Watson, N.M., Zwingmann, N., Lemon, N.M., Tingate, P.R., 2003. Onshore Otway Basin carbon dioxide accumulations: CO₂-induced diagenesis in natural analogues for underground storage of greenhouse gas. *The APPEA Journal*, 43(1), pp.637-653.

- Weart, S. R., 2008. The discovery of global warming: Harvard University Press.
- Wei, X., Lei, F., Xinye, Z., Pengfei, W., Xiaoli, Y., Xipu, Y., Jun, L., 2017. Object-based 3D geomodel with multiple constraints for early Pliocene fan delta in the south of Lake Albert Basin, Uganda. *Journal of African Earth Sciences*, 125, 1-10.
- Wen, H., Li, L., 2018. An upscaled rate law for mineral dissolution in heterogeneous media: The role of time and length scales. *Geochimica et Cosmochimica Acta*, 235, 1-20.
- Wen, H., Li, L., 2017. An upscaled rate law for magnesite dissolution in heterogeneous porous media. *Geochimica et Cosmochimica Acta*, 210, 289-305.
- White, C. D., Horne, R. N., 1987. Computing absolute transmissibility in the presence of fine-scale heterogeneity. Paper presented at the SPE symposium on reservoir simulation.
- White, M. R., 1995. Micropalaeontological analysis of 26 petroleum wells in the Gambier Basin, South Australia. In (Vol. 95): South Australia. Dept. of Mines and Energy, Report Book.
- Willcox, J. B., Stagg, H. M. J., 1990. Australia's southern margin: a product of oblique extension. *Tectonophysics*, 173(1-4), 269-281.
- Woollands, M. A., Wong, D., 2001. Petroleum Atlas of Victoria. In: Department of Natural Resources and Environment, State Government of Victoria.
- Xi, K., Cao, Y., Liu, K., Wu, S., Yuan, G., Zhu, R., Zhao, Y., Hellevang, H., 2019. Geochemical constraints on the origins of calcite cements and their impacts on reservoir heterogeneities: A case study on tight oil sandstones of the Upper Triassic Yanchang Formation, southwestern Ordos Basin, China. *AAPG Bulletin*, 103(10), pp.2447-2485.
- Xiaoqing, Z., Zhidong, B., Zongfei, L., Hua, Z., Qiuhui, C., 2013. An in-depth analysis of reservoir architecture of underwater distributary channel sand bodies in a river dominated delta: A case study of T51 Block, Fuyu Oilfield, Jilin. *Petroleum Exploration and Development*, 40(2), 194-201.
- Xu, T., Apps, J.A., Pruess, K., 2004a. Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers. *Applied geochemistry* 19, 917-936.
- Xu, T., Apps, J. A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a sandstone–shale system. *Chemical Geology*, 217(3-4), 295-318.
- Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., 2004b. TOUGHREACT user's guide: A simulation program for non-isothermal multiphase reactive geochemical transport in variable saturated geologic media.
- Xu, T., Spycher, N., Sonnenthal, E., Zhang, G., Zheng, L., Pruess, K., 2011. TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions. *Computers and Geosciences*, 37(6), 763-774.
- Yafeng, S., Shiyin, L., 2000. Estimation on the response of glaciers in China to the global warming in the 21st century. *Chinese Science Bulletin*, 7(45), 668-672.
- Yang, L., Xu, T., Yang, B., Tian, H., Lei, H., 2014. Effects of mineral composition and heterogeneity on the reservoir quality evolution with CO₂ intrusion. *Geochemistry, Geophysics, Geosystems*, 15(3), 605-618.
- Yu, C. W., Lei, S. C., Chiao, C. H., Hwang, L. T., Yang, W. H., Yang, M. W., 2017. Injection risk assessment for intra-formational seal geological model in a carbon sequestration application in Taiwan. *Greenhouse Gases: Science and Technology*, 7(2), 225-240.
- Zeebe, R. E., Ridgwell, A., Zachos, J. C., 2016. Anthropogenic carbon release rate unprecedented during the past 66 million years. *Nature Geoscience*, 9(4), 325-329.
- Zhang, D., Song, J., 2014. Mechanisms for geological carbon sequestration. *Procedia IUTAm*, 10(0), 319-327.
- Zhang, G., Yao, T., Xie, H., Wang, W., Yang, W., 2015. An inventory of glacial lakes in the Third Pole region and their changes in response to global warming. *Global Planetary Change*, 131, 148-157.
- Zhou, D., Fayers, F., Orr Jr, F., 1997. Scaling of multiphase flow in simple heterogeneous porous media. *SPE Reservoir Engineering*, 12(03), 173-178.
- Zhou, N., Matsumoto, T., Hosokawa, T., Suekane, T., 2010. Pore-scale visualization of gas trapping in porous media by X-ray CT scanning. *Flow Measurement and Instrumentation*, 21(3), pp.262-267.

Appendix A

This section presents the 30 core samples chosen for QEMSCAN and grain size analysis. The samples cover the range of lithological heterogeneity found in the different sedimentary facies. Table A1 provides a description of depth, depositional environment and all available flow data. Sample IDs are marked on the samples.



Figure A1. The core samples chosen for quantitative mineral analysis.

Sedimentary Facies	Core Sample ID	Sample Depth (m)	Porosity (%)	Permeability (mD)
Distributary Channel	#93	1477.20	26.9	7410.00
	#56V	1533.78	21.2	1.07
	#42	1549.75	28.4	1110.00
	#39	1551.25	26.5	615.00
	#37V	1552.82	29.6	1930.00
	#35	1553.48	21.2	130.00
	#34	1554.07	16.4	27.50
	#97	1464.80	28.5	141.00
Proximal Mouthbar	#92	1481.55	13.1	0.55
	#91	1484.45	29.7	1010.00
	#82	1502.90	24.0	357.00
	#79	1506.92	29.3	262.00
	#77	1508.80	26.6	353.00
	#75	1513.60	23.4	198.00
	#72	1518.45	27.1	109.00
	#59	1531.50	29.0	357.00
	#55	1533.86	12.6	33.40
	#51V	1539.50	26.8	407.00
Distal Mouthbar	#50	1540.30	28.3	4160.00
	#27	1560.95	28.0	249.00
	#25	1562.60	22.7	17.00
	#23	1563.60	29.1	535.00
	#98	1462.85	28.8	324.00
	#81	1505.00	14.1	0.90
	#71	1520.50	28.4	182.00
	#69	1523.90	17.2	0.08
	#67H	1524.65	21.5	0.64
	#67V	1524.65	21.5	NA
Delta Front	#66	1525.64	16.3	0.47
	#64	1526.05	27.6	268.00

Table A1. 30 core samples from CRC-3 well.

Appendix B

The following section presents the samples assigned to the five rock type classes (Table B1) and the analysis of Hylogger data (Table B2).

Rock Type Classes	Sample ID for QEMSCAN Analysis
Rock Type 1 (Coarse Sandstone)	#93, #50, #37V, #42, #91
Rock Type 2 (Fine Sandstone)	#23, #27, #39, #51, #64, #71, #72, #79, #82, #98, #59, #97, #77
Rock Type 3 (Siltstone)	#25, #34, #35, #55
Rock Type 4 (Mudstone)	#56V, #66, #67V, #69, #81, #92, #67H
Rock Type 5	#75
(Carbonate-cemented Sandstone)	

Table B1. 30 samples chosen for QEMSCAN analysis as assigned to different rock type classes.

	Distributary channel		Proximal mouthbar		Distal mouthbar		Delta front
Depth (m)	Porosity (Fraction)	Permeability (mD)	Framework (%)	Clay (%)	Carbonate (%)	Rock Type Class Assigned	
1462.85	0.29	324.00	78.47	0.00	21.53	Carbonate-cemented sandstone	
1464.80	0.29	141.00	86.91	9.53	3.56	Fine sandstone	
1466.80	0.20	1.03	62.66	18.56	18.78	Carbonate-cemented sandstone	
1470.80	0.20	2.25	83.66	16.34	0.00	Mudstone	
1474.55	0.15	0.06	74.83	18.40	6.77	Carbonate-cemented sandstone	
1477.20	0.27	7410.00	100.00	0.00	0.00	Coarse sandstone	
1481.55	0.13	0.55	76.10	0.00	23.90	Carbonate-cemented sandstone	
1484.45	0.31	4930.00	100.00	0.00	0.00	Coarse sandstone	
1484.45	0.30	1010.00	100.00	0.00	0.00	Coarse sandstone	
1488.70	0.23	10300.00	100.00	0.00	0.00	Coarse sandstone *	
1492.64	0.29	2810.00	100.00	0.00	0.00	Coarse sandstone	
1495.90	0.28	2040.00	100.00	0.00	0.00	Coarse sandstone	
1499.03	0.26	19.60	100.00	0.00	0.00	Unclassified	
1499.10	0.28	747.00	100.00	0.00	0.00	Fine sandstone	
1499.40	0.30	1140.00	81.74	8.73	9.53	Carbonate-cemented sandstone	
1501.00	0.13	0.83	59.60	3.65	36.75	Carbonate-cemented sandstone	
1502.90	0.24	357.00	100.00	0.00	0.00	Fine sandstone *	
1505.00	0.14	0.90	88.94	4.46	6.60	Carbonate-cemented sandstone	
1505.85	0.19	1.46	97.21	2.79	0.00	Mudstone	

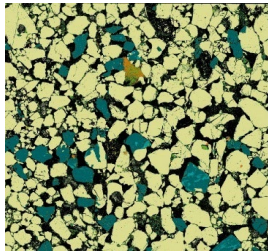
1506.92	0.29	262.00	100.00	0.00	0.00	Fine sandstone
1508.12	0.29	476.00	100.00	0.00	0.00	Fine sandstone
1508.80	0.27	353.00	100.00	0.00	0.00	Fine sandstone
1510.75	0.21	2.82	63.99	33.52	2.50	Mudstone
1513.60	0.23	198.00	92.75	0.00	7.25	Carbonate-cemented sandstone
1516.65	0.19	6.35	76.89	23.11	0.00	Mudstone
1517.80	0.29	205.00	95.03	3.23	1.74	Fine sandstone
1518.45	0.27	109.00	92.39	7.61	0.00	Fine sandstone
1522.75	0.15	0.02	63.96	36.04	0.00	Mudstone *
1523.90	0.17	0.08	76.62	23.38	0.00	Mudstone *
1524.60	0.19	0.55	77.62	22.38	0.00	Mudstone *
1524.65	0.22	0.64	85.38	14.62	0.00	Mudstone *
1525.64	0.16	0.47	78.63	21.37	0.00	Mudstone *
1526.05	0.28	268.00	91.46	8.54	0.00	Fine sandstone
1526.25	0.15	0.16	70.08	29.92	0.00	Mudstone *
1526.80	0.15	0.03	63.21	36.79	0.00	Mudstone *
1528.50	0.16	0.05	60.47	39.53	0.00	Mudstone *
1528.53	0.16	0.03	60.47	39.53	0.00	Mudstone *
1529.60	0.27	751.00	92.60	0.00	7.40	Carbonate-cemented sandstone
1529.65	0.27	814.00	100.00	0.00	0.00	Fine sandstone
1529.70	0.26	373.00	100.00	0.00	0.00	Fine sandstone
1531.50	0.29	357.00	94.40	5.60	0.00	Fine sandstone
1532.85	0.16	7.14	92.64	7.36	0.00	Mudstone
1533.23	0.28	1200.00	96.24	3.76	0.00	Coarse sandstone
1533.78	0.21	1.07	74.24	25.76	0.00	Mudstone
1533.86	0.13	33.40	61.99	38.01	0.00	Siltstone
1534.10	0.23	15.30	87.31	12.69	0.00	Siltstone
1534.82	0.12	0.15	71.41	28.59	0.00	Mudstone
1539.50	0.27	407.00	100.00	0.00	0.00	Fine sandstone
1539.60	0.28	1190.00	100.00	0.00	0.00	Coarse sandstone
1540.30	0.28	4160.00	100.00	0.00	0.00	Coarse sandstone
1540.55	0.29	1820.00	100.00	0.00	0.00	Coarse sandstone
1541.35	0.29	2200.00	100.00	0.00	0.00	Coarse sandstone
1542.35	0.30	2010.00	100.00	0.00	0.00	Coarse sandstone
1542.42	0.30	2410.00	100.00	0.00	0.00	Coarse sandstone
1543.75	0.28	2380.00	100.00	0.00	0.00	Coarse sandstone
1548.90	0.02	0.02	74.25	0.00	25.75	Carbonate-cemented sandstone
1549.25	0.17	1.05	82.93	17.07	0.00	Mudstone

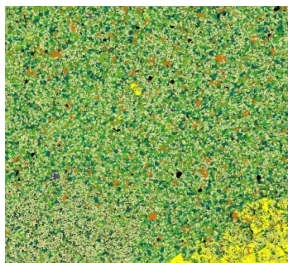
1549.75	0.28	1110.00	98.43	0.00	1.57	Coarse sandstone
1550.30	0.28	799.00	100.00	0.00	0.00	Fine sandstone
1550.75	0.23	1030.00	67.68	32.32	0.00	Unclassified
1551.25	0.27	615.00	96.91	3.09	0.00	Fine sandstone
1551.65	0.24	9670.00	97.44	0.00	2.56	Coarse sandstone *
1552.82	0.30	1930.00	100.00	0.00	0.00	Coarse sandstone
1552.95	0.30	2550.00	100.00	0.00	0.00	Coarse sandstone
1553.48	0.21	130.00	74.71	25.29	0.00	Siltstone *
1554.07	0.16	27.50	67.75	32.25	0.00	Siltstone
1554.12	0.16	0.03	67.75	32.25	0.00	Mudstone *
1554.25	0.27	5250.00	78.34	21.66	0.00	Coarse sandstone
1555.35	0.30	2840.00	91.57	8.43	0.00	Coarse sandstone
1556.42	0.29	556.00	100.00	0.00	0.00	Fine sandstone
1556.55	0.30	3420.00	100.00	0.00	0.00	Coarse sandstone
1559.57	0.28	195.00	89.59	10.41	0.00	Fine sandstone
1560.95	0.28	249.00	84.83	15.17	0.00	Fine sandstone
1561.02	0.29	318.00	100.00	0.00	0.00	Fine sandstone
1562.60	0.23	17.00	79.38	20.62	0.00	Siltstone
1562.64	0.28	89.10	69.62	30.38	0.00	Fine sandstone *
1563.35	0.29	380.00	100.00	0.00	0.00	Fine sandstone
1563.45	0.29	378.00	86.20	13.80	0.00	Fine sandstone
1563.60	0.29	535.00	76.04	23.96	0.00	Fine sandstone
1564.25	0.17	0.57	63.18	36.82	0.00	Mudstone *
1564.70	0.22	3.73	65.05	34.95	0.00	Mudstone
1565.39	0.17	0.15	77.95	22.05	0.00	Mudstone *

Table B2. Hylogger data from CRC-3 well and corresponding rock type classes. Rock type classes marked * do not strictly fall into the porosity and permeability range defined in Table 2.

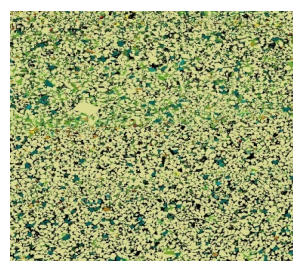
Appendix C

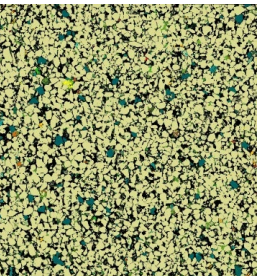
The following section presents the QEMSCAN results for the 30 samples from CRC-3 well.

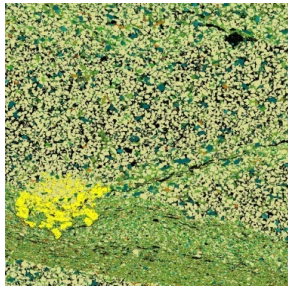
Sample ID: #93		
Minerals	Area %	Mineral map
Alkali		
Feldspar	11.14%	
Ankerite	0.00%	
Calcite	0.01%	
Chlorite	0.09%	
Dolomite	0.00%	
Illite	0.33%	
Ilmenite	0.01%	
Kaolinite	4.09%	
Magnesite	0.73%	
Muscovite	0.64%	
Palygorskite	1.68%	
Plagioclase	1.30%	
Pyrite	0.24%	
Pyrophyllite	0.07%	
Quartz	78.07%	
Rutile	0.01%	
Siderite	0.00%	
Smectites	1.58%	
Zircon	0.01%	
		2mm

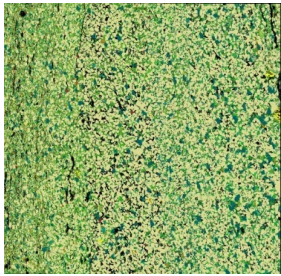
Sample ID: #56V		
Minerals	Area %	Mineral map
Alkali		
Feldspar	9.95%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	4.13%	
Dolomite	0.00%	
Illite	6.52%	
Ilmenite	0.04%	
Kaolinite	13.57%	
Magnesite	1.66%	
Muscovite	4.46%	
Palygorskite	2.32%	
Plagioclase	2.82%	
Pyrite	3.95%	
Pyrophyllite	0.08%	
Quartz	39.81%	
Rutile	0.18%	
Siderite	0.25%	
Smectites	10.22%	
Zircon	0.03%	
		2mm

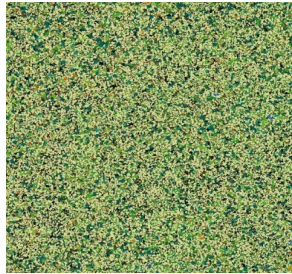
Sample ID: #42		
Minerals	Area %	Mineral map
Alkali		
Feldspar	12.08%	
Ankerite	0.50%	
Calcite	0.00%	
Chlorite	1.00%	
Dolomite	0.09%	
Illite	1.88%	
Ilmenite	0.02%	
Kaolinite	6.57%	
Magnesite	1.03%	
Muscovite	2.24%	
Palygorskite	2.47%	
Plagioclase	1.99%	
Pyrite	0.54%	
Pyrophyllite	0.13%	
Quartz	64.85%	
Rutile	0.05%	
Siderite	0.02%	
Smectites	4.52%	
Zircon	0.02%	
		2mm

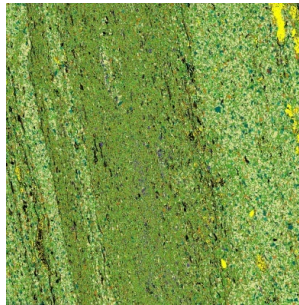
Sample ID: #39		
Minerals	Area %	Mineral map
Alkali		
Feldspar	4.41%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	0.74%	
Dolomite	0.00%	
Illite	1.26%	
Ilmenite	0.28%	
Kaolinite	5.72%	
Magnesite	0.40%	
Muscovite	0.54%	
Palygorskite	2.26%	
Plagioclase	1.12%	
Pyrite	0.37%	
Pyrophyllite	0.05%	
Quartz	79.82%	
Rutile	0.25%	
Siderite	0.01%	
Smectites	2.68%	
Zircon	0.09%	
		2mm

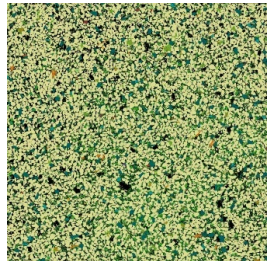
Sample ID: #37V		
Minerals	Area %	Mineral map
Alkali		
Feldspar	3.52%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	0.22%	
Dolomite	0.00%	
Illite	0.48%	
Ilmenite	0.18%	
Kaolinite	1.88%	
Magnesite	0.26%	
Muscovite	0.29%	
Palygorskite	1.69%	
Plagioclase	0.69%	
Pyrite	0.31%	
Pyrophyllite	0.02%	
Quartz	88.92%	
Rutile	0.12%	
Siderite	0.01%	
Smectites	1.39%	
Zircon	0.02%	
		2mm

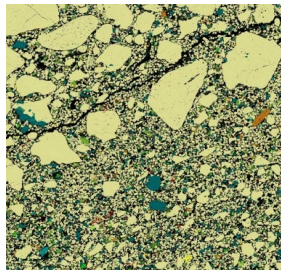
Sample ID: #35		
Minerals	Area %	Mineral map
Alkali		
Feldspar	5.77%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	3.07%	
Dolomite	0.00%	
Illite	4.30%	
Ilmenite	0.11%	
Kaolinite	8.34%	
Magnesite	1.32%	
Muscovite	3.05%	
Palygorskite	2.62%	
Plagioclase	1.82%	
Pyrite	3.24%	
Pyrophyllite	0.10%	
Quartz	60.40%	
Rutile	0.24%	
Siderite	0.14%	
Smectites	5.42%	
Zircon	0.06%	
		2mm

Sample ID: #34		
Minerals	Area %	Mineral map
Alkali		
Feldspar	6.79%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.27%	
Dolomite	0.00%	
Illite	2.49%	
Ilmenite	0.12%	
Kaolinite	6.59%	
Magnesite	0.74%	
Muscovite	1.44%	
Palygorskite	4.86%	
Plagioclase	2.83%	
Pyrite	0.31%	
Pyrophyllite	0.30%	
Quartz	62.76%	
Rutile	0.24%	
Siderite	0.05%	
Smectites	9.15%	
Zircon	0.05%	

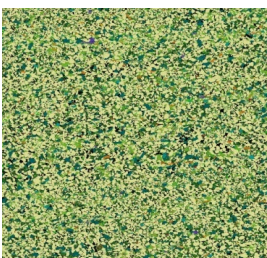
Sample ID: #97		
Minerals	Area %	Mineral map
Alkali		
Feldspar	7.65%	
Ankerite	0.09%	
Calcite	0.00%	
Chlorite	1.54%	
Dolomite	0.02%	
Illite	2.76%	
Ilmenite	0.31%	
Kaolinite	5.91%	
Magnesite	0.80%	
Muscovite	2.10%	
Palygorskite	4.25%	
Plagioclase	2.71%	
Pyrite	0.64%	
Pyrophyllite	0.04%	
Quartz	63.90%	
Rutile	0.30%	
Siderite	0.00%	
Smectites	6.82%	
Zircon	0.16%	

Sample ID: #92		
Minerals	Area %	Mineral map
Alkali		
Feldspar	4.94%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	7.45%	
Dolomite	0.00%	
Illite	8.00%	
Ilmenite	0.05%	
Kaolinite	19.64%	
Magnesite	4.13%	
Muscovite	7.95%	
Palygorskite	2.18%	
Plagioclase	1.56%	
Pyrite	3.65%	
Pyrophyllite	0.09%	
Quartz	28.44%	
Rutile	0.26%	
Siderite	1.62%	
Smectites	10.00%	
Zircon	0.04%	

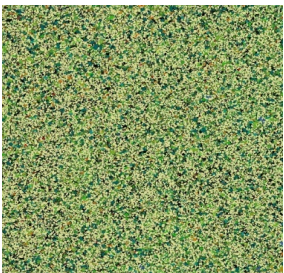
Sample ID: #91		
Minerals	Area %	Mineral map
Alkali		
Feldspar	4.96%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	0.29%	
Dolomite	0.00%	
Illite	1.10%	
Ilmenite	0.05%	
Kaolinite	4.62%	
Magnesite	0.20%	
Muscovite	0.69%	
Palygorskite	3.02%	
Plagioclase	1.18%	
Pyrite	0.10%	
Pyrophyllite	0.04%	
Quartz	75.83%	
Rutile	0.11%	
Siderite	0.01%	
Smectites	7.77%	
Zircon	0.03%	

Sample ID: #82		
Minerals	Area %	Mineral map
Alkali		
Feldspar	5.39%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.36%	
Dolomite	0.00%	
Illite	1.35%	
Ilmenite	0.26%	
Kaolinite	1.90%	
Magnesite	0.23%	
Muscovite	0.98%	
Palygorskite	0.63%	
Plagioclase	0.91%	
Pyrite	0.08%	
Pyrophyllite	0.01%	
Quartz	85.30%	
Rutile	0.20%	
Siderite	0.00%	
Smectites	1.25%	
Zircon	0.15%	

Sample ID: #79		
Minerals	Area %	Mineral map
Alkali		
Feldspar	7.46%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.79%	
Dolomite	0.00%	
Illite	2.00%	
Ilmenite	0.33%	
Kaolinite	3.05%	
Magnesite	0.43%	
Muscovite	1.35%	
Palygorskite	1.53%	
Plagioclase	2.65%	
Pyrite	0.02%	
Pyrophyllite	0.05%	
Quartz	75.69%	
Rutile	0.38%	
Siderite	0.02%	
Smectites	3.10%	
Zircon	0.15%	

Sample ID: #77		
Minerals	Area %	Mineral map
Alkali Feldspar	7.33%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	2.07%	
Dolomite	0.00%	
Illite	3.96%	
Ilmenite	0.07%	
Kaolinite	8.43%	
Magnesite	0.41%	
Muscovite	1.37%	
Palygorskite	6.96%	
Plagioclase	1.71%	
Pyrite	0.06%	
Pyrophyllite	0.05%	
Quartz	62.65%	
Rutile	0.12%	
Siderite	0.26%	
Smectites	4.52%	
Zircon	0.03%	

2mm

Sample ID: #75		
Minerals	Area %	Mineral map
Alkali Feldspar	7.65%	
Ankerite	0.09%	
Calcite	0.00%	
Chlorite	1.54%	
Dolomite	0.02%	
Illite	2.76%	
Ilmenite	0.31%	
Kaolinite	5.91%	
Magnesite	0.80%	
Muscovite	2.10%	
Palygorskite	4.25%	
Plagioclase	2.71%	
Pyrite	0.64%	
Pyrophyllite	0.04%	
Quartz	63.90%	
Rutile	0.30%	
Siderite	0.00%	
Smectites	6.82%	
Zircon	0.16%	

2mm

Sample ID: #72		
Minerals	Area %	Mineral map
Alkali Feldspar	7.58%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.59%	
Dolomite	0.00%	
Illite	1.80%	
Ilmenite	0.31%	
Kaolinite	4.38%	
Magnesite	0.59%	
Muscovite	1.37%	
Palygorskite	0.99%	
Plagioclase	2.53%	
Pyrite	0.11%	
Pyrophyllite	0.04%	
Quartz	75.02%	
Rutile	0.44%	
Siderite	0.29%	
Smectites	2.83%	
Zircon	0.13%	

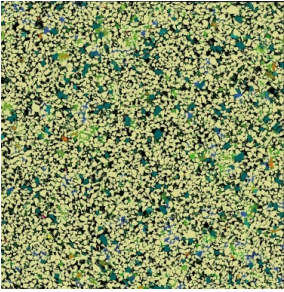
2mm

Sample ID: #59		
Minerals	Area %	Mineral map
Alkali Feldspar	5.89%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.02%	
Dolomite	0.00%	
Illite	2.33%	
Ilmenite	0.27%	
Kaolinite	8.14%	
Magnesite	0.40%	
Muscovite	1.09%	
Palygorskite	3.26%	
Plagioclase	1.75%	
Pyrite	0.11%	
Pyrophyllite	0.04%	
Quartz	66.15%	
Rutile	0.27%	
Siderite	0.00%	
Smectites	9.16%	
Zircon	0.11%	

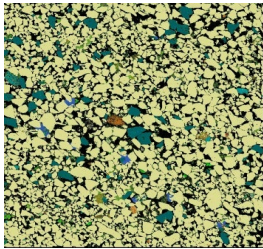
2mm

Sample ID: #55		
Minerals	Area %	Mineral map
Alkali Feldspar	5.19%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	4.15%	
Dolomite	0.00%	
Illite	7.60%	
Ilmenite	0.04%	
Kaolinite	24.36%	
Magnesite	1.29%	
Muscovite	6.86%	
Palygorskite	2.01%	
Plagioclase	2.36%	
Pyrite	0.19%	
Pyrophyllite	0.13%	
Quartz	29.53%	
Rutile	0.24%	
Siderite	0.17%	
Smectites	15.85%	
Zircon	0.03%	

2mm

Sample ID: #51		
Minerals	Area %	Mineral map
Alkali Feldspar	5.98%	
Ankerite	1.59%	
Calcite	0.02%	
Chlorite	0.39%	
Dolomite	0.33%	
Illite	0.68%	
Ilmenite	0.06%	
Kaolinite	2.14%	
Magnesite	0.98%	
Muscovite	0.54%	
Palygorskite	5.75%	
Plagioclase	0.93%	
Pyrite	0.09%	
Pyrophyllite	0.02%	
Quartz	77.46%	
Rutile	0.09%	
Siderite	0.04%	
Smectites	2.97%	
Zircon	0.11%	

2mm

Sample ID: #50		
Minerals	Area %	Mineral map
Alkali		
Feldspar	6.32%	
Ankerite	0.44%	
Calcite	0.01%	
Chlorite	0.21%	
Dolomite	0.09%	
Illite	0.50%	
Ilmenite	0.04%	
Kaolinite	3.59%	
Magnesite	0.80%	
Muscovite	0.62%	
Palygorskite	1.00%	
Plagioclase	0.89%	
Pyrite	0.12%	
Pyrophyllite	0.07%	
Quartz	83.81%	
Rutile	0.03%	
Siderite	0.02%	
Smectites	1.42%	
Zircon	0.02%	
		2mm

Sample ID: #27		
Minerals	Area %	Mineral map
Alkali		
Feldspar	7.10%	
Ankerite	0.02%	
Calcite	0.00%	
Chlorite	1.43%	
Dolomite	0.00%	
Illite	2.04%	
Ilmenite	0.36%	
Kaolinite	4.15%	
Magnesite	0.54%	
Muscovite	1.68%	
Palygorskite	1.11%	
Plagioclase	2.64%	
Pyrite	0.05%	
Pyrophyllite	0.04%	
Quartz	75.08%	
Rutile	0.52%	
Siderite	0.05%	
Smectites	2.87%	
Zircon	0.32%	
		2mm

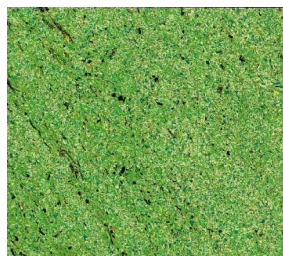
Sample ID: #25		
Minerals	Area %	Mineral map
Alkali		
Feldspar	5.90%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.66%	
Dolomite	0.00%	
Illite	3.09%	
Ilmenite	0.28%	
Kaolinite	10.17%	
Magnesite	0.58%	
Muscovite	1.47%	
Palygorskite	4.32%	
Plagioclase	3.45%	
Pyrite	0.01%	
Pyrophyllite	0.10%	
Quartz	58.31%	
Rutile	0.38%	
Siderite	0.03%	
Smectites	10.14%	
Zircon	0.10%	
		2mm

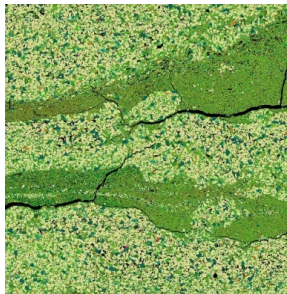
Sample ID: #23		
Minerals	Area %	Mineral map
Alkali		
Feldspar	5.94%	
Ankerite	0.01%	
Calcite	0.00%	
Chlorite	0.87%	
Dolomite	0.00%	
Illite	1.74%	
Ilmenite	0.17%	
Kaolinite	3.52%	
Magnesite	0.43%	
Muscovite	0.92%	
Palygorskite	4.03%	
Plagioclase	2.47%	
Pyrite	0.04%	
Pyrophyllite	0.12%	
Quartz	74.18%	
Rutile	0.34%	
Siderite	0.01%	
Smectites	5.04%	
Zircon	0.17%	
		2mm

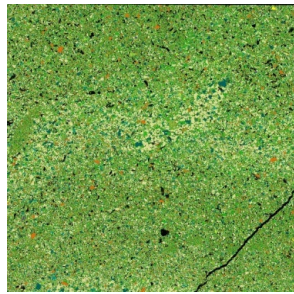
Sample ID: #98		
Minerals	Area %	Mineral map
Alkali		
Feldspar	7.77%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	2.23%	
Dolomite	0.00%	
Illite	2.64%	
Ilmenite	0.23%	
Kaolinite	4.91%	
Magnesite	0.56%	
Muscovite	2.22%	
Palygorskite	4.50%	
Plagioclase	1.93%	
Pyrite	0.21%	
Pyrophyllite	0.03%	
Quartz	68.14%	
Rutile	0.24%	
Siderite	0.01%	
Smectites	4.22%	
Zircon	0.13%	
		2mm

Sample ID: #81		
Minerals	Area %	Mineral map
Alkali		
Feldspar	6.27%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	4.98 %	
Dolomite	0.00%	
Illite	7.06%	
Ilmenite	0.08%	
Kaolinite	20.86%	
Magnesite	1.50%	
Muscovite	5.78%	
Palygorskite	2.49%	
Plagioclase	2.62%	
Pyrite	0.66%	
Pyrophyllite	0.16%	
Quartz	32.55%	
Rutile	0.23%	
Siderite	0.11%	
Smectites	14.61%	
Zircon	0.04%	
		2mm

Sample ID: #71		
Minerals	Area %	Mineral map
Alkali		
Feldspar	5.63%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	1.52%	
Dolomite	0.00%	
Illite	2.15%	
Ilmenite	0.42%	
Kaolinite	3.50%	
Magnesite	1.15%	
Muscovite	0.72%	
Palygorskite	10.18%	
Plagioclase	1.76%	
Pyrite	0.01%	
Pyrophyllite	0.03%	
Quartz	61.98%	
Rutile	0.34%	
Siderite	0.78%	
Smectites	8.48%	
Zircon	1.36%	

Sample ID: #69		
Minerals	Area %	Mineral map
Alkali		
Feldspar	7.40%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	6.68 %	
Dolomite	0.00%	
Illite	8.01%	
Ilmenite	0.06%	
Kaolinite	13.68%	
Magnesite	1.31%	
Muscovite	3.73%	
Palygorskite	3.39%	
Plagioclase	3.28%	
Pyrite	0.75%	
Pyrophyllite	0.08%	
Quartz	34.66%	
Rutile	0.23%	
Siderite	0.07%	
Smectites	16.65%	
Zircon	0.03%	

Sample ID: #67H		
Minerals	Area %	Mineral map
Alkali		
Feldspar	5.63%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	5.25%	
Dolomite	0.00%	
Illite	8.12%	
Ilmenite	0.08%	
Kaolinite	12.82%	
Magnesite	1.15%	
Muscovite	3.82%	
Palygorskite	3.85%	
Plagioclase	1.98%	
Pyrite	0.21%	
Pyrophyllite	0.07%	
Quartz	45.15%	
Rutile	0.20%	
Siderite	0.18%	
Smectites	11.42%	
Zircon	0.03%	

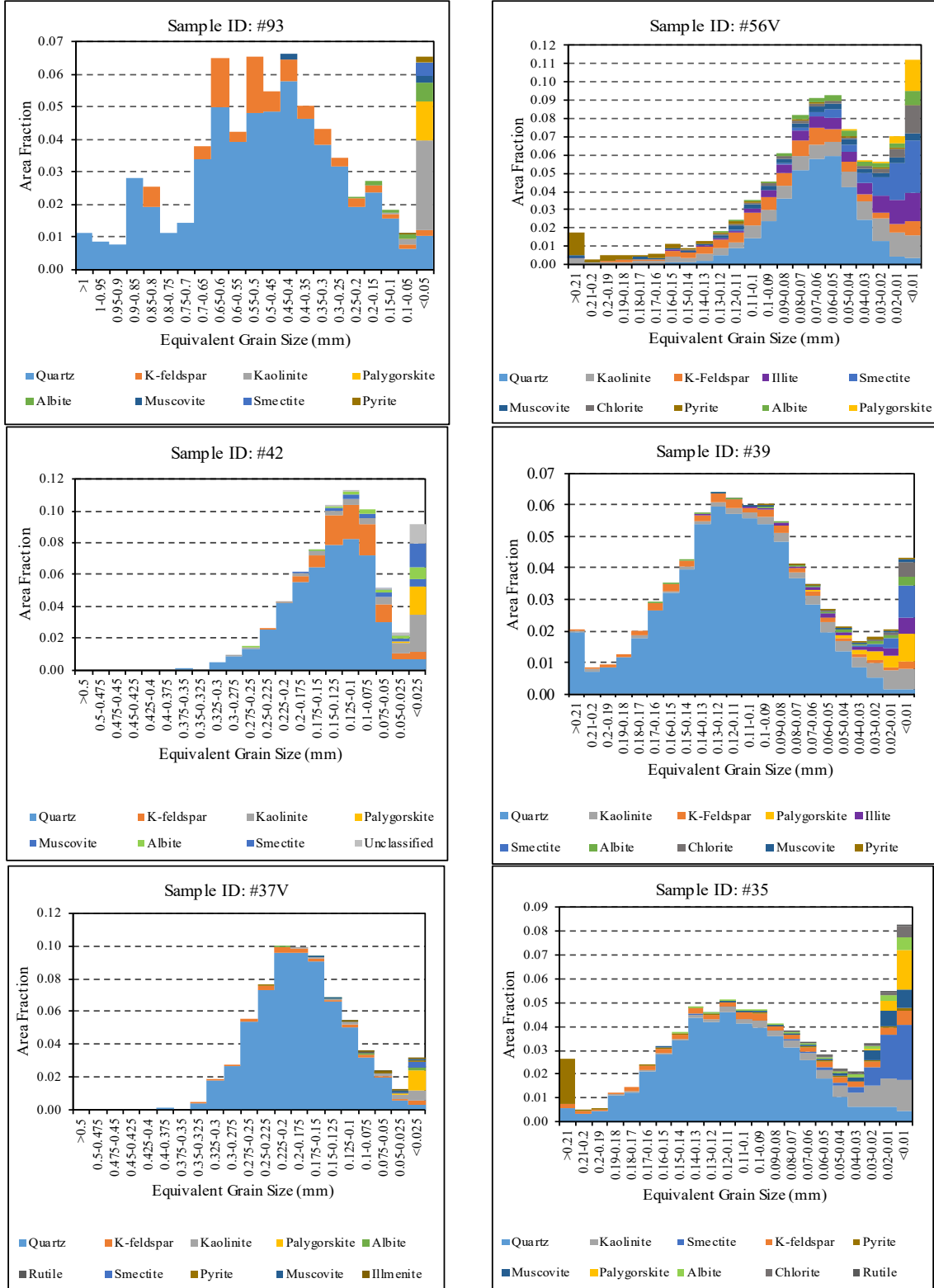
Sample ID: #67V		
Minerals	Area %	Mineral map
Alkali		
Feldspar	6.43%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	7.58%	
Dolomite	0.00%	
Illite	11.13%	
Ilmenite	0.08%	
Kaolinite	12.17%	
Magnesite	1.88%	
Muscovite	7.15%	
Palygorskite	3.78%	
Plagioclase	2.26%	
Pyrite	0.27%	
Pyrophyllite	0.04%	
Quartz	30.50%	
Rutile	0.25%	
Siderite	0.41%	
Smectites	15.99%	
Zircon	0.07%	

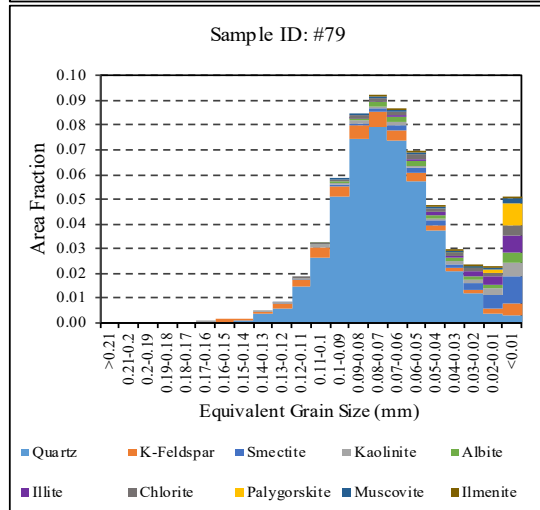
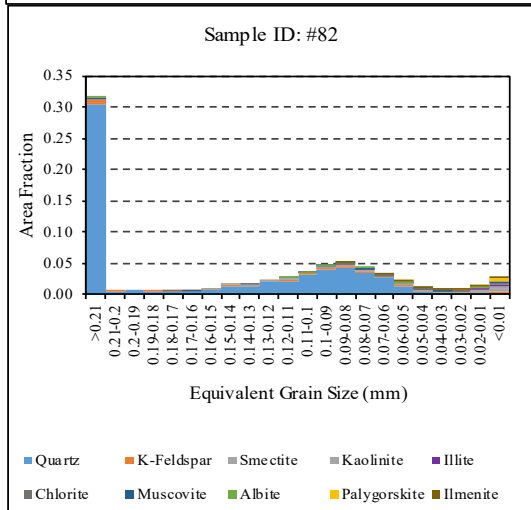
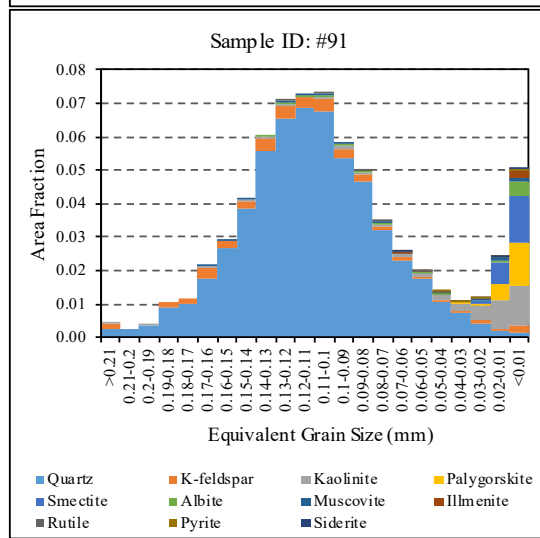
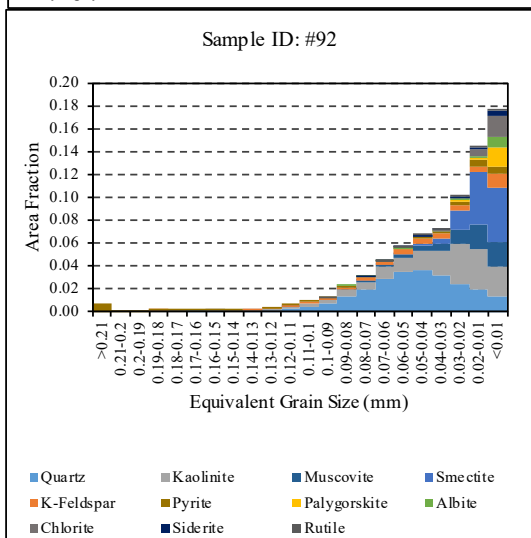
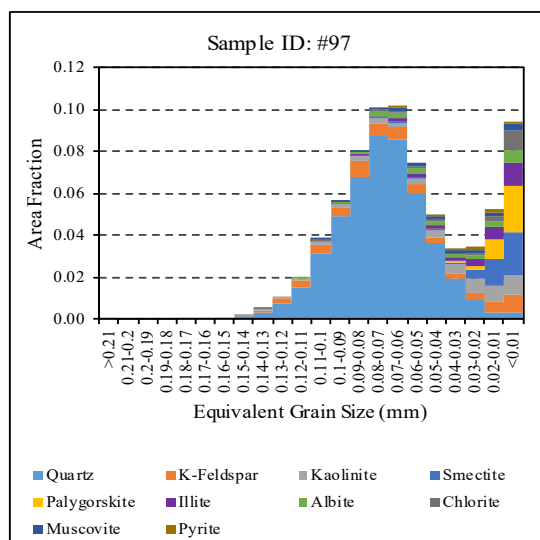
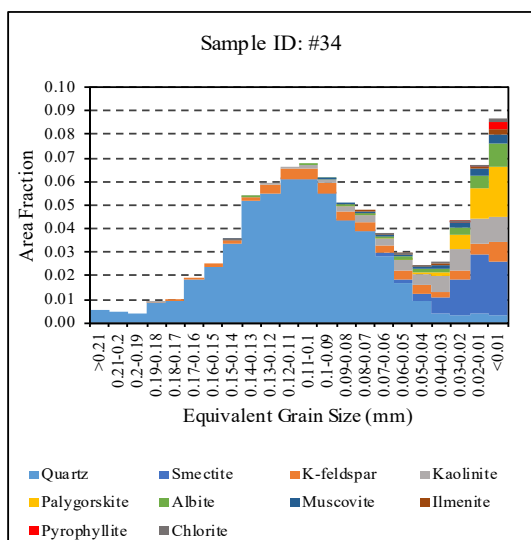
Sample ID: #66		
Minerals	Area %	Mineral map
Alkali		
Feldspar	7.75%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	6.39 %	
Dolomite	0.00%	
Illite	8.81%	
Ilmenite	0.06%	
Kaolinite	14.99%	
Magnesite	0.95%	
Muscovite	3.31%	
Palygorskite	2.56%	
Plagioclase	3.27%	
Pyrite	0.16%	
Pyrophyllite	0.10%	
Quartz	34.42%	
Rutile	0.23%	
Siderite	0.08%	
Smectites	16.88%	
Zircon	0.02%	

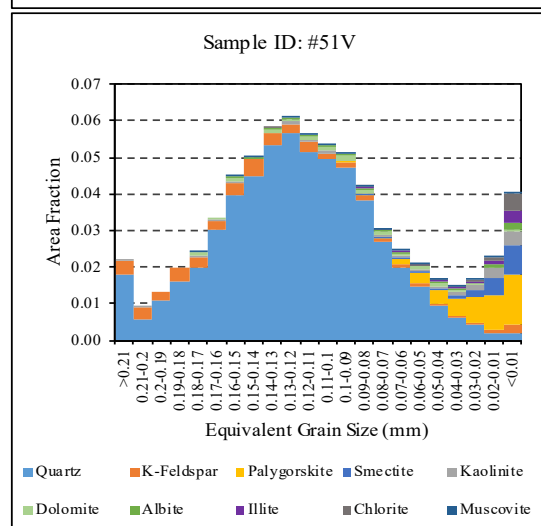
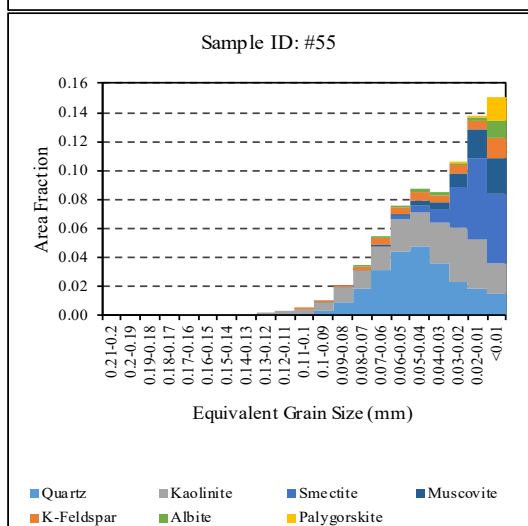
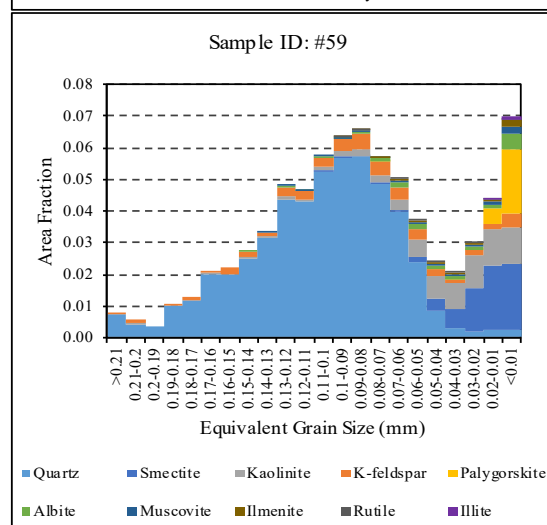
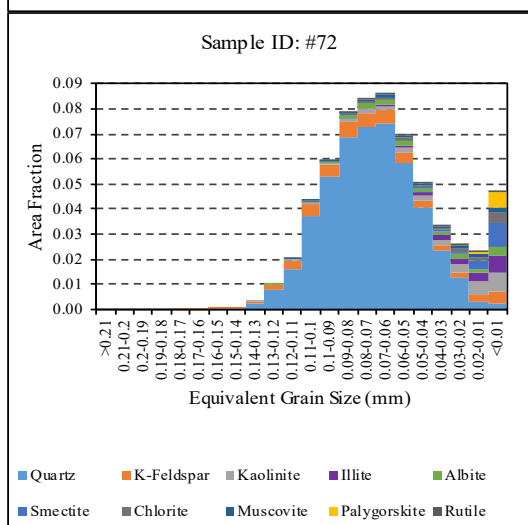
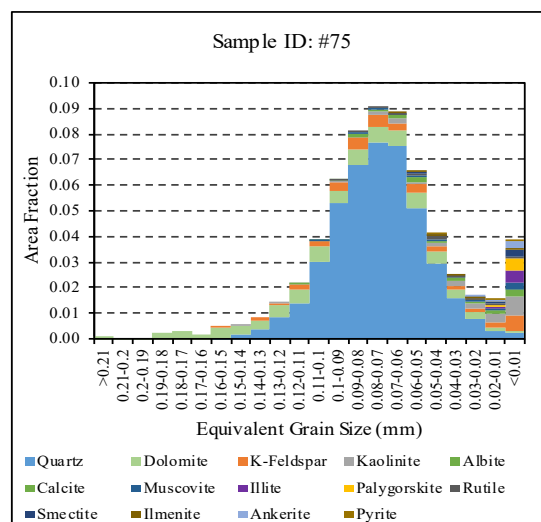
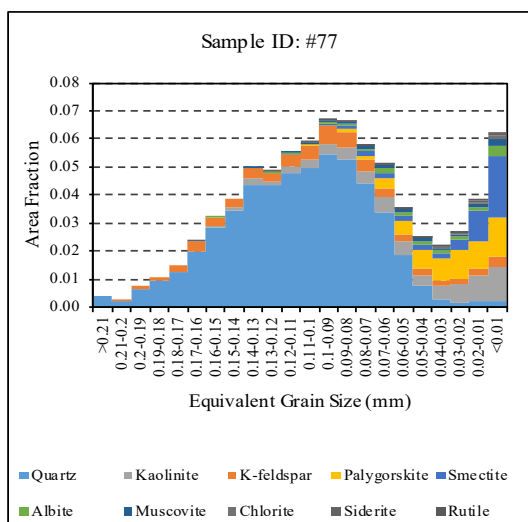
Sample ID: #64		
Minerals	Area %	Mineral map
Alkali		
Feldspar	6.86%	
Ankerite	0.00%	
Calcite	0.00%	
Chlorite	2.11%	
Dolomite	0.00%	
Illite	3.15%	
Ilmenite	0.14%	
Kaolinite	4.84%	
Magnesite	0.31%	
Muscovite	1.61%	
Palygorskite	3.00%	
Plagioclase	2.26%	
Pyrite	0.09%	
Pyrophyllite	0.04%	
Quartz	70.74%	
Rutile	0.24%	
Siderite	0.01%	
Smectites	4.55%	
Zircon	0.04%	

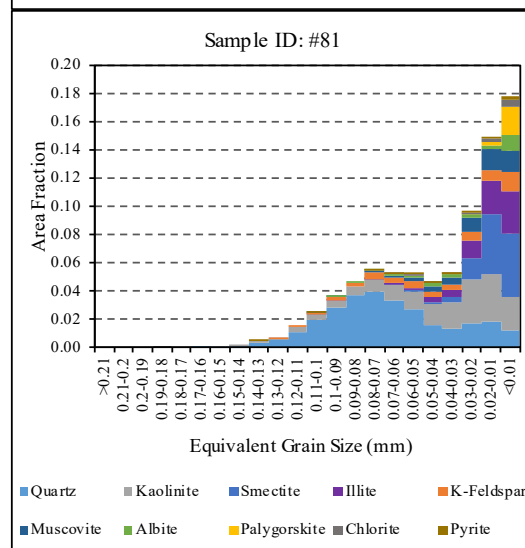
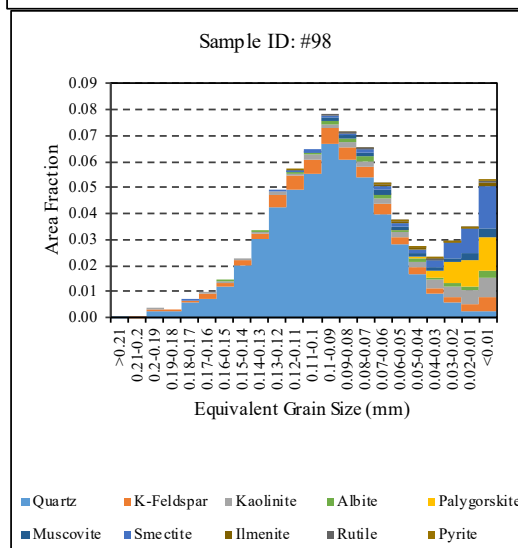
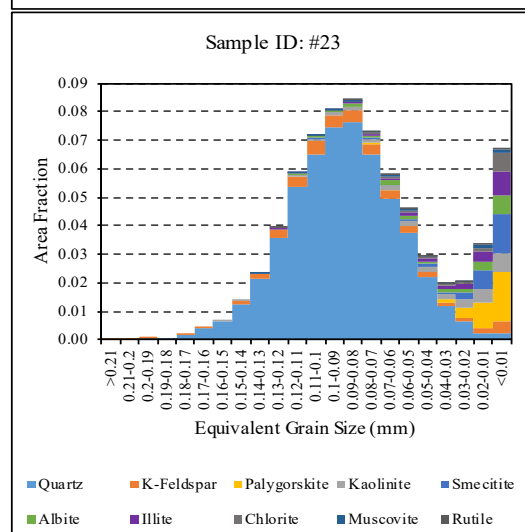
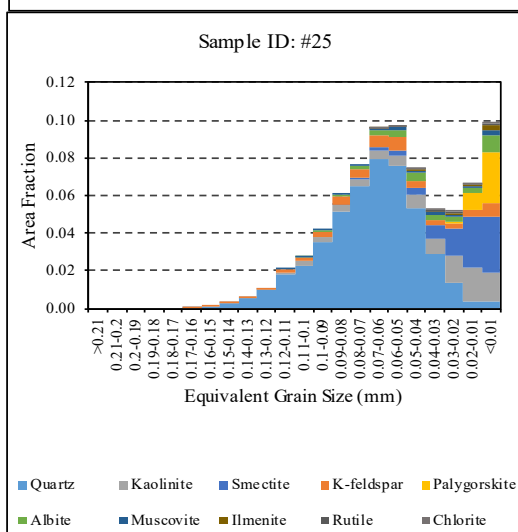
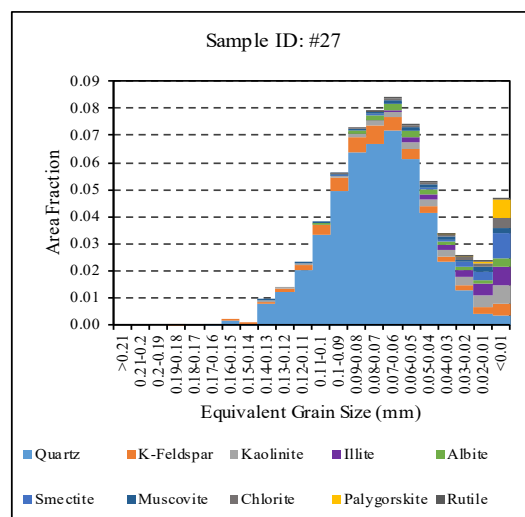
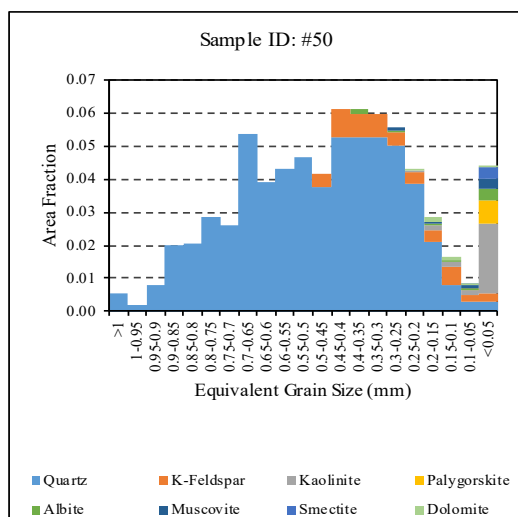
Appendix D

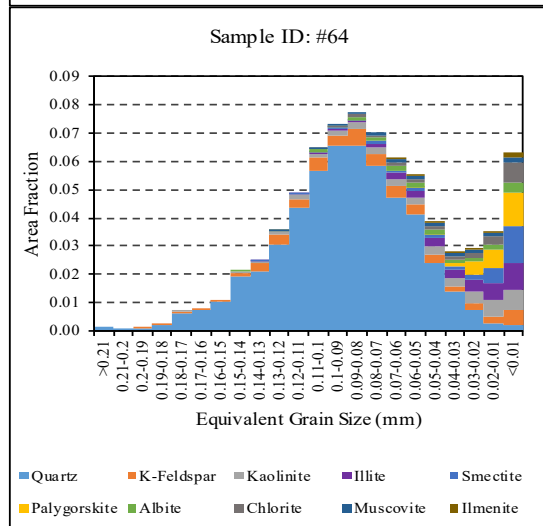
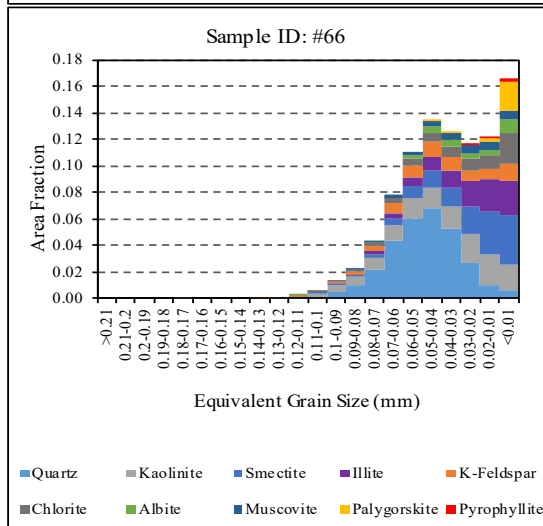
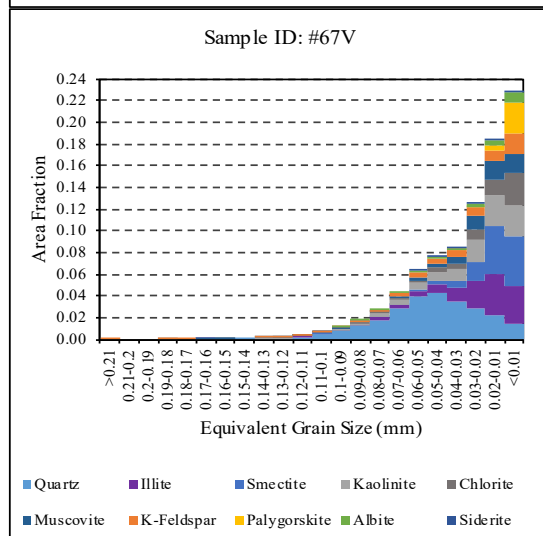
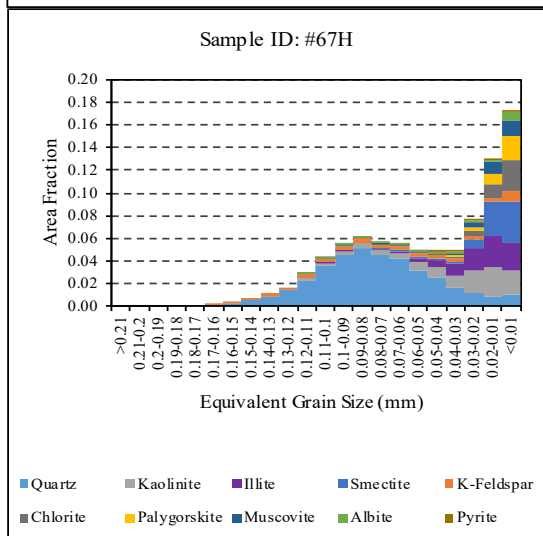
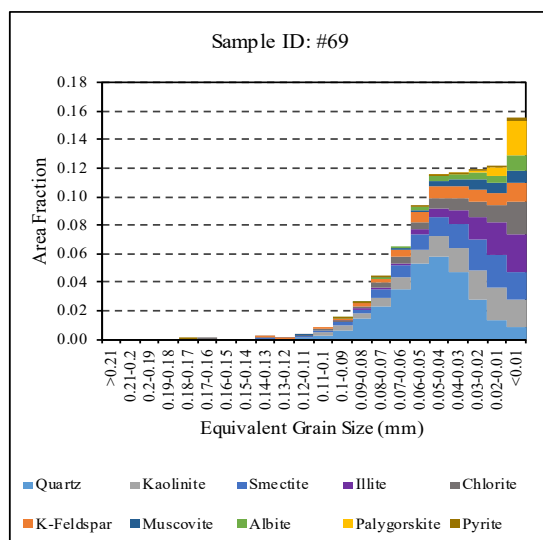
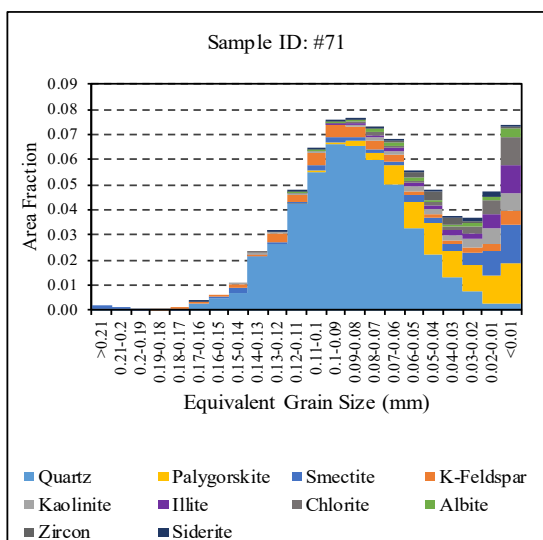
The following section presents the results of the grain size analysis of the 30 samples from CRC-3. The analysis is done in terms of area fraction covered on the minerals maps as a function of the equivalent grain size of different mineral phases.











Appendix E

This section presents the Python script used to discretise the colorliths.

```
import numpy as np
import cv2
from scipy import stats
import pandas as pd

#Read the image file
img = cv2.imread("img.png")

#Convert the image to RGB image
img = cv2.cvtColor(img, cv2.COLOR_BGRA2RGB)

#Collapse the width of the image to one pixel
img = stats.mode(img, axis=1)[0]

#If the bed thickness is I and the resolution is r,  $n = I/r$ 
# Initialize the elements of the numpy array
arr = np.zeros((n, 3), dtype=int)

#Let the number of pixels along the length of the image be p. p need not be always divisible #by n,
which means that we can have uneven number of pixels for every row in the final result. #In order to
balance it out as much as possible, we can find a pattern of close numbers whose #sum has a multiple
that is as close as possible to the p (without exceeding p). For example, #let's say  $p = 5110$  and  $n =$ 
 $900$ . n doesn't divide p. If we repeat (5, 6, 6) pattern over and over, #we reach 5100 which is 10 pixels
close to p. This is the approximation made. The whole image #will be split into the pattern 5, 6, 6, 5,
6, 6, 5, 6, 6, ... 300 times to fill all the 900 rows.

# Here, iterations = 300, pattern_length = 3,  $p_1=5$ ,  $p_2=6$ ,  $p_3=6$ 

j = 0
for i in range(iterations):
    for k in range(3):
        arr[i*pattern_length][k] = stats.mode(img[j:j+p1, 0, k])[0]
```

```

for k in range(3):
    arr[i*pattern_length+1][k] = stats.mode(img[j+p1:j+p1+p2, 0, k])[0]
for k in range(3):
    arr[i*pattern_length+2][k] = stats.mode(img[j+p1+p2:j+p1+p2+p3, 0, k])[0]

#Repeat the sequence for the pattern_length
j+=p1+p2+p3+..p(pattern_length)

#Write the results to an Excel file
df = pd.DataFrame(arr)
df.to_excel("results.xlsx", index=False)

```

Appendix F

This section presents reduced mineral composition for the two composite rock types: M_{Mst}^{CbSst} (interface between massive bedded carbonate-cemented sandstone and mudstone) and X_{FSst}^{CSst} (interface between cross bedded coarse and fine sandstones). The former is characterized by high capillary entry pressures for both the lithologies while the latter is characterized by low capillary entry pressures for both the lithologies. Consequently, supercritical CO₂ cannot enter the former composite while it floods the entire latter composite. This leads to no pH changes in M_{Mst}^{CbSst} while acidic conditions for 1000s of years in X_{FSst}^{CSst} . Hence, no net change in the amount of carbonate minerals is expected for both the composite rock types (given that the initial amount of carbonate minerals is nearly zero for X_{FSst}^{CSst}). Under this assumption, the reduced mineral composition for both the composites is the same as their volume averaged mineral composition (Table F1).

Mineral	M_{Mst}^{CbSst}	X_{FSst}^{CSst}
Albite	0.0219	0.0154
Ankerite	0.0492	0.0017
Calcite	0.0004	0.0002
Chlorite	0.0525	0.0356
Dolomite	0.0102	0.0004
Illite	0.0467	0.0137
K-feldspar	0.0602	0.0700
Kaolinite	0.0939	0.0398
Magnesite	0.0176	0.0058
Quartz	0.5606	0.7812
Siderite	0.0020	0.0007
Smectite	0.0763	0.0357

Table F1. Averaged mineral composition for the composite rock types M_{Mst}^{CbSst} and X_{FSst}^{CSst} .