

Reservoir-Condition Pore-Scale Imaging of Multiphase Flow

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A handwritten signature in purple ink, consisting of a stylized 'M' followed by a long, sweeping horizontal line.

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November 21th 2014

Declaration of Originality

I declare that this thesis, **Reservoir-Condition Pore-Scale Imaging of Multiphase Flow**, Is entirely my own work under the supervision of Dr Branko Bijeljic and Prof. Martin J Blunt. The work was performed in the Department of Earth Science and Engineering at Imperial College London. All published and unpublished material used in the thesis has been given full acknowledgment. This work has not been previously submitted, in whole or in part, to any other academic institution for a degree, diploma, or any other qualification.

A handwritten signature in purple ink, consisting of a series of loops and a long, sweeping tail.

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Abstract

This thesis presents the first method for the imaging of multiple fluid phases at conditions representative of subsurface flow by the use of X-ray micro-CT, focussing on four principal applications: (1) Capillary Trapping; (2) Ganglion Snap-off and remobilization; (3) Contact angle measurement; and (4) Dynamic phenomena associated with CO₂ drainage.

Firstly the pore-scale arrangement of CO₂ after drainage and imbibition was imaged in three carbonates and two sandstones. In each sample substantial amounts of CO₂ were trapped, showing that residual trapping can be used to locally immobilise CO₂. The size distributions of larger residual ganglia obey power law distributions with exponents broadly consistent with percolation theory, over two orders of magnitude.

To examine snap-off in more detail residual CO₂ was imaged at high resolution in a single carbonate. The capillary pressures of residual ganglia were found to be inversely proportional to the radius of the largest restriction surrounding each ganglion. The remobilization of residual ganglia was assessed using a reformulation of both the capillary and Bond numbers, finding the majority of ganglia in this system were remobilized at reformulated capillary numbers of around 1.

Thirdly this thesis presents the first method for the measurement of *in-situ* contact angle at realistic conditions by the use of micro-CT, applied to a single carbonate sample at 50°C and 10 MPa. Contact angles ranging from 35° to 55° were observed, indicating that the CO₂-brine-carbonate system is weakly water-wet.

Finally, we use fast synchrotron-based X-ray micro-CT to examine drainage into a brine saturated carbonate. The equilibrium capillary pressure change associated with drainage events is not sufficient to explain the accompanying snap-off, showing that dynamic forces can have a persistent impact on the pattern and sequence of the drainage process.

Extended Abstract

Geological carbon dioxide storage must be designed such that the CO₂ cannot escape from the rock formation into which it is injected, and often simple stratigraphic trapping is insufficient. CO₂ can be trapped in the pore space as droplets (ganglia) surrounded by water through capillary trapping. The processes governing trapping behaviour are fundamentally rooted in phenomena (such as wettability or capillary pressure) occurring at the pore-scale; however until now the experimental evaluation of flow at this scale under realistic conditions has remained out of reach.

This thesis presents the first method for the imaging at the pore scale of multiphase fluid arrangement and displacements at conditions representative of typical subsurface aquifers while maintaining chemical equilibrium between the CO₂, brine and rock by the use of the technique of X-ray microtomography (micro-CT). This method is then developed for four principal applications: (1) Capillary Trapping; (2) Ganglion Snap-off and remobilization; (3) Contact angle measurement; and (4) Dynamic phenomena associated with CO₂ drainage.

In the first of these applications micro-CT was used to image, at a resolution of 6.6 μm , the pore-scale arrangement of CO₂ after the injection of CO₂ (drainage) and after the injection of chase brine (imbibition), where the CO₂ is trapped as a residual phase, in three carbonates and two sandstones. Mutual chemical equilibrium was maintained between the fluid and rock phases, representing conditions far away from the injection site. In each sample substantial amounts of CO₂ were trapped, with the efficiency of trapping being insensitive to pore-morphology and chemistry, showing that residual trapping can be used to locally immobilise CO₂ in a wide range of rock types. Apart from one extremely well connected sample, the size distribution of residual ganglia larger than 10^5 voxel^3 ($2.6 \times 10^7 \mu\text{m}^3$) obey power law distributions with exponents broadly consistent with percolation theory, over two orders of magnitude. The value of the exponent correlates with the connectivity of

the rock, with better connected rocks having more large clusters relative to small clusters and vice-versa.

To examine the formation of residual ganglia by the process of snap-off in more detail residual CO₂ was imaged in a single carbonate sample at resolutions of 2 μm and 3.5 μm . The capillary pressure for each ganglion was found by measuring the curvature of the CO₂-brine interface, while the pore structure was parameterised using Euclidian distance maps of the pore-space. The formation of the residual clusters was examined by comparing the ganglion capillary pressure to local pore topography. The capillary pressure was found to be inversely proportional to the radius of the largest restriction (throat) surrounding the ganglion, which validates the imbibition mechanisms used in pore-network modelling. The potential mobilization of residual ganglia was assessed using a reformulation of both the capillary and Bond numbers, rigorously based on the balance of the pore-scale viscous (found using pore-scale modelling), buoyancy and capillary forces. The majority of ganglia in this system were remobilized at reformulated capillary numbers of around 1. Buoyancy forces were found to be small in this system, meaning the gravitational remobilization of CO₂ after residual trapping would be extremely difficult.

Thirdly we address contact angle, the measurement of which in systems other than ideal flat mineral surfaces has remained a challenge, even though it is a principal control of the flow of multiple fluid phases through porous media. This thesis presents the first method for the measurement of the contact angle between immiscible fluids at the pore scale at reservoir conditions by the use of micro-CT. It is applied to a super-critical CO₂-brine-carbonate system by resampling the micro-CT data onto planes orthogonal to the contact lines, allowing for vectors to be traced along the gain surface and the CO₂-brine interface. A distribution of contact angles ranging from 35° to 55° is observed, indicating that the CO₂-brine-carbonate system is weakly water-wet. This range of contact angles can be understood as the result of contact angle hysteresis and surface heterogeneity on a range of

length scales. Surface heterogeneity is examined by the comparison of micro-CT results with optical thin sections and SEM images.

Finally, we use fast synchrotron-based X-ray micro-CT to examine the process of CO₂ injection (drainage) into a brine saturated carbonate at representative subsurface conditions. The capillary pressure of both the connected and disconnected CO₂ was found by measuring the curvature of terminal menisci. Three individual dynamic drainage events were analysed, displaying the phenomena of equilibrium capillary pressure change and both local and distal (non-local) snap-off. The equilibrium capillary pressure change associated with drainage events is not sufficient to explain the accompanying snap-off as the disconnected CO₂ has a much lower capillary pressure than the connected CO₂ both before and after the event. Disconnected regions instead preserve the extremely low capillary pressures generated during the dynamic events. Local snap-off produced disconnected fluid configurations which were rapidly reconnected with the advancing connected CO₂, whereas non-local snap-off produced much more lasting configurations, showing that dynamic forces can have a persistent impact on the pattern and sequence of drainage events. Snap-off due to these dynamic forces is not only controlled by the pore tomography and throat radius, but also by the local fluid arrangement.

List of Publications

Journal Articles

1. **Andrew, M.G.**, H. Menke, M.J. Blunt, and B. Bijeljic, The imaging of dynamic multiphase fluid flow using synchrotron based x-ray microtomography. International Journal of Greenhouse Gas Control, 2014. Under Review.
2. Ott, H., **M.G. Andrew**, J. Snippe, and M.J. Blunt, Micro-scale solute transport and precipitation in complex rock during drying. Geophysical Research Letters, 2014. In Press.
3. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Pore by Pore Capillary Pressure Measurements using X-Ray Microtomography at Reservoir Conditions: Curvature, Snap-off and Remobilization of Residual CO₂. Water Resources Research, 2014, 50, DOI: 10.1002/2014WR015970
4. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Reservoir Condition Pore-Scale Imaging of Multiple Fluid Phases using X-Ray Microtomography Journal of Visualized Experiments, 2014. In Press.
5. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Pore-scale contact angle measurements at reservoir conditions using X-Ray microtomography. Advances in Water Resources, 2014. 68: p. 24-31.
6. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, New frontiers in experimental geoscience: X-ray microcomputed tomography and fluid flow. Microscopy and Analysis, 2014. March 2014: p. S4-7.

7. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Pore-scale imaging of trapped supercritical carbon dioxide in sandstones and carbonates. International Journal of Greenhouse Gas Control, 2014. 22: p. 1-14.
8. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Pore-scale imaging of geological carbon dioxide storage under in situ conditions. Geophysical Research Letters, 2013. 40(15): p. 3915-3918.

Conference Proceeding Papers

Presenting Author

1. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Micro-CT Imaging of Reservoir Condition CO₂ During Multi-phase Flow in Natural Rock, in International Conference on Greenhouse Gas Technologies 2014: Austin, TX, USA.
2. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Reservoir-condition pore scale imaging - contact angle, wettability, dynamics and trapping, in Gordon Research Seminar 2014: Lewiston, ME, USA.
3. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, In-situ condition pore-scale imaging: contact angle, wettability, dynamics and trapping, in Gordon Research Conference 2014: Lewiston, ME, USA.
4. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, In-situ condition pore-scale imaging: contact angle, wettability and trapping, in CCS In the Bigger Picture 2014: Cambridge, UK.
5. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Reservoir-Condition Pore Scale Imaging - Contact Angle, Wettability, Dynamics and Trapping, in EAGE Conference and Exhibition 2014: Amsterdam, the Netherlands.

6. **Andrew, M.G.**, H. Menke, B. Bijeljic, and M.J. Blunt, Reservoir condition pore-scale imaging of supercritical CO₂, in 1st Joint KFUPM-Zeiss Digital Rock Physics Workshop 2014: Dhahran, Saudi Arabia.
7. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, μ CT imaging of Multi-Phase Flow in Carbonates and Sandstones, in American Geophysical Union Fall Meeting 2013: San Francisco, CA, USA.
8. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Reservoir-Condition Pore-Scale Imaging of Super-Critical Carbon Dioxide – Uses and applications, in EAGE/SPE Joint Workshop - Beyond Closed Loop Integrated Monitoring 2013: Lisbon, Portugal.
9. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Reservoir-Condition Pore-Scale Imaging of Super-Critical Carbon Dioxide, in Workshop in 3D Imaging and Applications in Geosciences 2013: Abertay, UK.
10. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Reservoir-Condition Pore-Scale Imaging of Super-Critical Carbon Dioxide in Society of Petroleum Engineers Annual Technical Conference and Exhibition 2013: New Orleans, LA, USA.
11. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Multi-Scale Imaging of Multi-Phase Flow in Porous Media, in EAGE Conference and Exhibition 2013: London, UK.
12. **Andrew, M.G.**, B. Bijeljic, and M.J. Blunt, Multi-Scale Imaging of Multi-Phase Flow in Porous Media, in American Geophysical Union Fall Meeting 2012: San Francisco, CA, USA.
13. **Andrew, M.G.**, E. Boek, O. Gharbi, S. Shah, J. Crawshaw, and M.J. Blunt, Mutli-Scale Imaging of Multi-Phase Flow in Porous Media, in Nanofair 2012: Dresden, Germany.

Non-presenting author

1. Menke, H., B. Bijeljic, **M.G. Andrew**, and M.J. Blunt. Dynamic pore-scale imaging of reactive transport in heterogeneous carbonates at reservoir conditions, at EGU General Assembly, 2014.
2. Ott, H., **M.G. Andrew**, J. Snippe, M.J. Blunt, and A. Makurat. Capillary-driven solute transport and precipitation in porous media during dryout, at EGU general assembly, 2014.
3. Ott, H., **M.G. Andrew**, M.J. Blunt, and J. Snippe. Capillary-driven solute transport and precipitation in porous media during dry-out, at 6th International Conference on Porous Media, Interpore, Milwaukee, WI, USA, 2014.
4. Menke, H., B. Bijeljic, **M.G. Andrew**, and M.J. Blunt. Dynamic pore-scale imaging of reactive transport in heterogeneous carbonates at reservoir conditions, at EAGE Conference and Exhibition, 16-19 June 2014 Amsterdam, the Netherlands, 2014.

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1 Introduction

Multiphase fluid displacement in geological porous media is a process with a wide range of implications for the fields of energy and the environment. In order to produce oil and gas reserves, hydrocarbons are displaced in the pore-space of geological media with water. As this process of water imbibition proceeds, oil is trapped in the pore-space by capillary forces, stranding hydrocarbon resources as pore-scale droplets (or ganglia) in the subsurface. During hydrocarbon recovery this is a process that needs to be minimized, but during geological carbon capture and storage (CCS) it provides an important trapping mechanism for otherwise buoyant CO₂. Many of the processes governing the displacement of multiple fluids in a porous medium are rooted in interfacial phenomena, apparent at the scale of individual pores and throats. A rigorous experimental basis for these phenomena is therefore vital for an adequate holistic understanding of these processes.

In this thesis we develop new techniques for the imaging and analysis of multi-phase fluid flow at the pore scale by the use of X-ray micro computed tomography (micro-CT). These techniques include experimental development allowing for the first time reliable and repeatable micro-CT experiments to be performed at reservoir conditions, and a range of image analysis techniques for the extraction of key petrophysical parameters, such as contact angle, capillary pressure and capillary number. These methods are applied specifically to the CO₂-brine-rock system, of interest in the field of CCS. A range of novel results are presented, focussing on four principal applications of reservoir condition imaging:

- 1) Capillary trapping (section 6.1)
- 2) Ganglion Snap-off and remobilization (section 6.2)
- 3) Contact angle measurement (section 6.3)
- 4) Dynamic phenomena associated with CO₂ drainage (section 6.4)

In this introduction we shall describe some of the motivations behind this work. First we shall discuss some of the evidence for anthropogenic climate change and the role of that CO₂ storage can play in meeting this challenge (section 1.1). We shall then look at some of the issues associated with CO₂ storage, particularly different methods by which CO₂ can be trapped in the subsurface for over a wide range of time-scales (section 1.2). Finally, we shall examine how CO₂ phase behaviour changes with pressure and temperature, showing that in the subsurface CO₂ will exist as a super-critical fluid (scCO₂) (section 1.3).

1.1 Carbon Capture and Storage

Ice core data shows that, over the last 800,000 years, atmospheric CO₂ has been closely correlated with temperature. CO₂ concentration can be found by sampling air bubbles trapped in the ice column, and temperature can be estimated by looking at the isotopic variation in the ice, specifically in the deuterium concentration, as proposed by Craig [1]. By age correlating different Antarctic ice cores, the following curves are produced (figure 1.1.1).

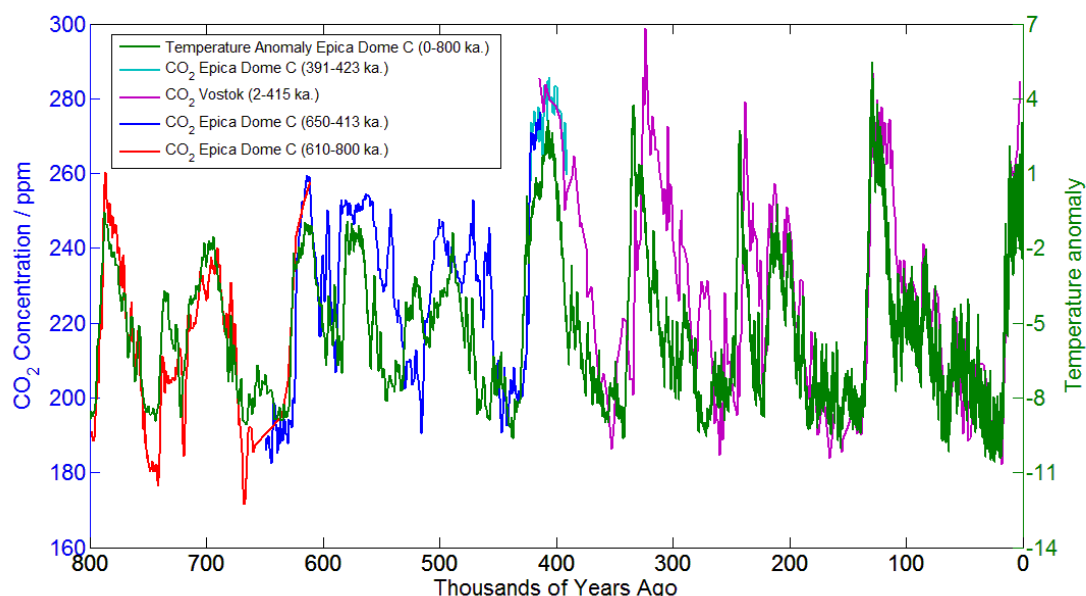


Figure 1.1.1: Atmospheric CO₂ concentration correlates well with temperature changes over the last 800,000 years. Data taken from [2-5]

We can see that the correlation between CO₂ and the independently measured temperature anomaly is remarkably strong, and that at no point does the CO₂ concentration exceed 300ppm. If we look at more recent atmospheric CO₂ concentration (as measured at the Mauna Loa observatory) we can see that CO₂ concentration has now far exceeded that of any previous time in the last 800,000 years.

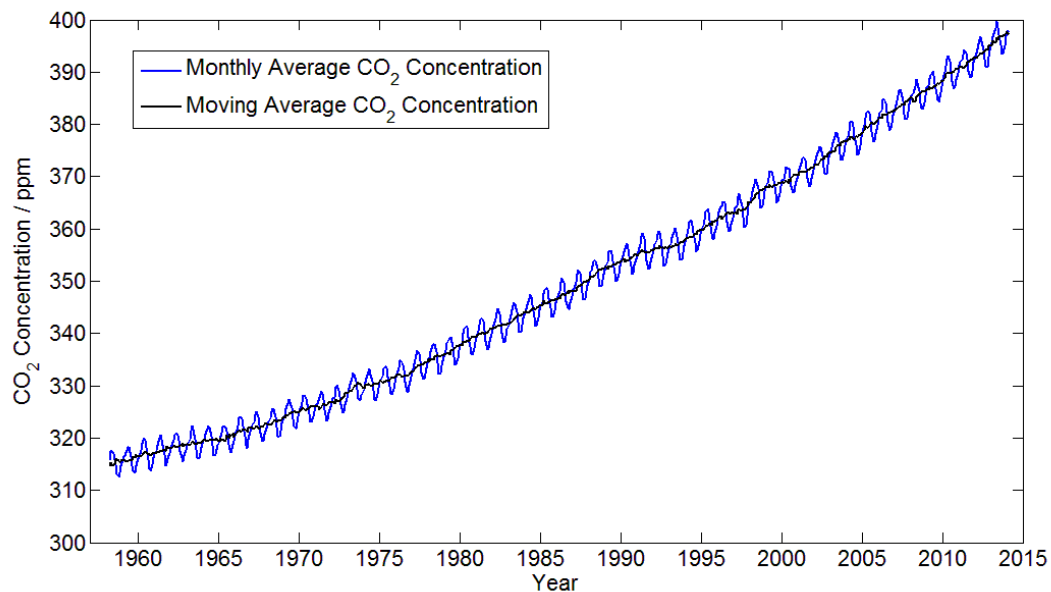


Figure 1.1.2: CO₂ concentration vs. time for the last 50 years, showing a steady dramatic increase in atmospheric CO₂. Data taken from [6].

This increase in atmospheric CO₂ is caused by an increase in world energy consumption propelled by an increasing reliance on relatively cheap and easily accessible fossil fuels, which currently account for 85% of primary energy production [7, 8]. Between 2010 and 2035 world population will likely increase from 6.8 billion to 8.6 billion, which, coupled with reductions in global energy poverty will increase world energy demand further by 35% [8]. Under currently proposed policies in 2035 it is predicted that oil, gas and coal will still account for 75% of the global energy mix, meaning energy related CO₂ emissions will rise from 31.2 Gt in 2011 to 37.0 Gt in 2035, which may cause a global temperatures rise of 3.6°C [8]. In order to stand a 50% chance of limiting temperature rise to 2°C in 2035, total CO₂ emissions need to be reduced to around 21.1 Gt, a 15.0 Gt reduction. CCS could

potentially contribute 2.5 Gt to this, the third largest single contributor, behind a growth in renewable energy sources and increased efficiency in electricity use and generation [8]. Geological CCS is the process where CO₂ is captured from large point sources and injected into rock formations, displacing resident brines such that the CO₂ remains underground on a time scale of hundreds to thousands of years. Of the geological formations of interest, such as depleted oil and gas reservoirs, saline aquifers, coal beds and salt deposits [9, 10], saline aquifers have the largest potential for storage and the widest geographical spread [11, 12].

1.2 Trapping Mechanisms

The sequestration of CO₂ in geological formations raises concern over storage effectiveness and safety. In all but the most overpressured situations, CO₂ is less dense than the brines resident in potential storage formations [13]. As the CO₂ is less dense there will be a tendency for the CO₂ to rise by buoyancy forces, creating a risk of CO₂ leakage into the atmosphere which, even over the scale of hundreds of years, would render any such scheme ineffective. It is therefore vital that a thorough understanding of trapping mechanisms in the subsurface is developed in order to minimize leakage risk. Trapping mechanisms can be divided into two groups, physical trapping and chemical trapping. Physical trapping consists of three distinct mechanisms; structural and stratigraphic trapping, hydrodynamic trapping and residual trapping. Chemical trapping also consists of three unique mechanisms; adsorption, dissolution and mineral precipitation.

1.2.1 Structural and Stratigraphic trapping

This refers to where permeable geological media are overlain by impermeable media, such as shales, whose structural arrangement precludes the upward and lateral motion of the CO₂. Structural traps, such as fault and fold structures, are formed by crustal movement whereas stratigraphic traps are formed by depositional or diagenetic processes. This trapping mechanism is thought to immobilize the vast majority of CO₂ during the period of CO₂ injection. Uncertainties in seal characterization and

seismic risk [10, 11, 14], especially in saline aquifers where effective seals have not already been demonstrated, mean that over long time scales this storage mechanism is the least secure. This is especially of concern as the increase in aquifer pressure during CO₂ injection, potentially creating local seal failure structures [15-17].

1.2.2 Hydrodynamic trapping

This trapping mechanism uses the very low regional flow rates in low permeability basins. In this case there is no need for closed stratigraphic or structural traps in regional formations, as the CO₂ residence time is long enough (thousands to millions of years) that it can be considered as effectively sequestered [18, 19]. It is, however, dependent on regional aquifer structures, and may not be an effective mechanism in all cases [20].

1.2.3 Adsorption

When CO₂ is injected into coal beds it diffusively adsorbs onto the surface of the coal, displacing attached methane, as CO₂ has a greater affinity to the coal than methane. This has been proposed as a potential immobilization mechanism when connected with enhanced methane recovery, however it is only applicable in coal bed CO₂ storage, which has a too small storage formation capacity worldwide to have a large impact on CO₂ emissions [21].

1.2.4 Dissolution

When carbon dioxide is injected into a saline aquifer, some of the CO₂ will dissolve in the resident aquifer brines as CO₂ is soluble in water. The CO₂ saturated brine is denser than the surrounding brine, which could potentially create convective fluid mixing, increasing dissolution rate by orders of magnitude [22-24]. This denser brine will then migrate deeper in the formation, increasing storage security, and slowly dilute through contact with unsaturated brines. Although convective mixing may even begin during CO₂ injection [25], its long term stability is uncertain, and the role of stratigraphic baffles on the creation of convection cells is uncertain.

1.2.5 Mineralization

On the longest time scales mineralization is an important mechanism, where carbonate ions dissolved in the resident brine react with the host rock, precipitating new carbonate minerals [26, 27]. The time scale of this form of trapping is many thousands of years, however, so it will not contribute significantly to storage security during the most sensitive period of CO₂ injection project in terms of the plume escape, which is during and immediately after injection [21].

1.2.6 Residual Trapping

CO₂ can be immobilized in the pore-space of the rock as small bubbles, surrounded by brine. This mechanism relies upon the fact (which will be confirmed in this thesis in Section 6.3) that the CO₂ is the non-wetting phase in the medium, and brine the wetting phase. Importantly it can occur over shorter time scales than all other non-stratigraphic trapping mechanisms. It has also been proven as a non-wetting phase trapping mechanism in oil fields where a significant proportion of the original oil in place cannot be produced, as it is rendered immobile during water flood. This combination of rapid action and proven effectiveness makes residual trapping an extremely attractive mechanism for CO₂ storage by which, under the right conditions, the vast majority of CO₂ can be immobilized [28].

Traditional trapping models, such as Land's model, relate the initial non-wetting phase saturation (S_i) and the residual non-wetting phase saturation (S_r) to the maximum non-wetting phase saturation (S_{imax}) and to the trapping seen at that saturation (S_{rmax}) [29]. In the Land model the efficiency of trapping can be expressed as

$$\frac{S_r}{S_i} = \frac{1}{1 + CS_i}$$

1.2.6.1

where C is the Land coefficient, defined as:

$$C = \frac{1}{S_{r,max}} - \frac{1}{S_{i,max}}$$

1.2.6.2

As well as the bulk saturation, models have been built to describe the cluster size distribution at residual saturation. The ingress of brine into a scCO₂ saturation core is an imbibition process where the wetting fluid invades each pore, displacing the non-wetting fluid. In a strongly water-wet rock we expect the water to fill areas of the pore space in order of size [30], trapping disconnected ganglia in the process called snap-off. As the disconnection of the non-wetting phase is associated with the formation of a connected wetting phase pathway through the rock, this process should be percolation like [31] so predictions can be made about the size distribution of trapped clusters. The number n of clusters of volume s should scale as

$$n(s) \sim s^{-\tau}$$

1.2.6.3

where τ is the Fisher exponent [32]. Network modelling has shown that in three-dimensional cubic regular lattices the value of this exponent is around $\tau=2.189$ [33]. This scaling exponent is useful when assessing storage security, as the higher the value of the exponent the higher the ratio of small ganglia to large ganglia, which has important implications for the security of the residual phase (Section 6.2).

1.3 CO₂ Phase Behaviour

An important factor during the injection of scCO₂ into the subsurface is its density and viscosity. The phase diagram for CO₂ is shown in figure 1.3.1.

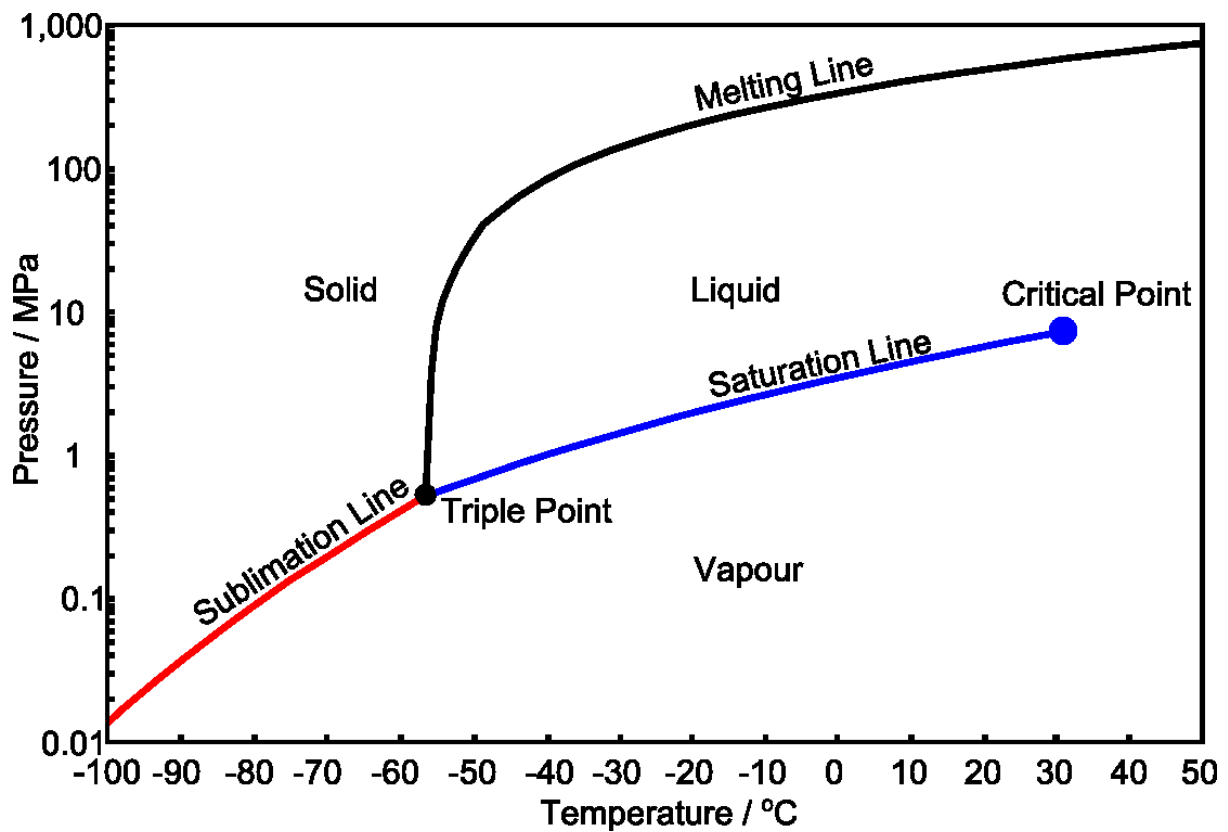


Figure 1.3.1: The phase behaviour of CO₂. Calculated using [34-37].

At low temperatures (above the triple point) CO₂ can exist as three distinct phases, solid liquid and gas, with chemical and thermophysical properties varying slowly and continuously within each phase field and discretely at the boundaries between them. Above the critical point (7.40 MPa, 304.25 K) [38], however, the distinction between a liquid phase and a gas phase disappears. Supercritical fluids tend to have densities similar to liquids, however have viscosities similar to those of gases [39]. Higher densities allow for a larger amount of CO₂ to be injected for a give increase in pressure, preventing rock hydrofracture and the possible compromise of seal formations [17, 40]. It is this phase, therefore, that most CCS projects envision CO₂ existing in the subsurface. As the petrophysical properties of scCO₂ are a strong function of temperature, pressure and salinity, experimental research into the subsurface behaviour of this CO₂ requires experiments to be taken at these realistic conditions.

2 Literature Review and Scientific Background

In this section we will introduce some of the scientific ideas behind multi-phase flow in porous media, and how these issues can be addressed experimentally. One of the most important phenomena governing flow behaviour in these systems is the surface force, arising from the fluid-fluid interface (section 2.1). Pressure differences between immiscible fluid phases (also known as the capillary pressure) will, at thermodynamic equilibrium, be resolved by the fluid-fluid interface forming a constant curvature shape, as examined in section 2.2. The relationship between the pressure difference and the interface curvature is given by the Young-Laplace equation (equation 2.2.9), which allows measurements of interface curvature taken directly on micro-CT images to be related to multi-phase pressure changes (sections 6.2 and 6.4).

Another phenomenon of critical importance in determining subsurface multi-phase flow behaviour is wettability, which is a measure of how readily one fluid adheres to a solid surface relative to another (section 2.3). At the pore-scale this is determined using a three-phase contact angle; however using traditional techniques measurements can only be made on pure mineral surfaces, limiting their descriptive utility in describing real systems. This issue is addressed, and a new method for the measurement of contact angle in real systems at realistic conditions is presented in section 6.3.

Much of work in describing multi-phase flow in porous media has focussed on the development of modelling techniques operating from the pore scale upwards. Although this thesis focusses on the experimental examination of multi-phase flow, elements of different modelling techniques were used to enhance and deepen experimental analysis, so the principles behind the mathematical description of flow and modelling are presented in section 2.4. The description of the dynamics of multi-phase displacement is of particular interest to the results acquired at synchrotron light sources (section 6.4), so are presented separately in section 2.4.1.

One way of dealing with the complex balance of forces in multiphase flow is by the use of dimensionless numbers, such as the capillary or Bond number (section 2.5). Although these have some success in describing resulting flow behaviour, they tend not to be rooted in the physics of the processes they attempt to parameterise, and so their predictive power is limited. The capillary and Bond number are reformulated to better represent these physical processes, and the results of this reformulation are presented in section 6.2.

CO₂ is highly soluble in brine, and this solubility is a major issue for designing experiments which intend to examine the CO₂-brine-rock system. In section 2.6 we present the chemical basis for this solubility, and how it depends on temperature and pressure. The solutions to the experimental problems presented by CO₂-brine solubility are presented in section 4.1.

Pore-scale information can be found using the technique of X-ray microtomography, or micro-CT. In section 2.7 the basis of micro-CT and its historical development is addressed, particularly in reference to geological systems. Micro-CT will be used for all the experimental results in this thesis (sections 5-6).

Finally in section 2.8 rock and pore classification systems are introduced. These techniques are useful for understanding how changes in geological setting can change pore topography and topology, which can in turn affect multi-phase flow behaviour. Although these geological classification techniques tend to be based on traditional 2D imaging (such as optical microscopy) or field studies, they can often be generalised to 3D, using micro-CT imaging to provide this information. This 3D generalisation of rock typing is presented in section 5.

2.1 Surface energy

When a liquid-liquid interface forms, intermolecular bonds are disrupted. This disruption is quantified by the surface energy. The surface energy for a specific liquid-liquid interface is defined in

terms of the surface energy density (also known as the interfacial tension) σ , with units of Nm^{-1} or Jm^{-2} . The variation in Gibbs free energy δG as we change a surface by area δA is therefore:

$$\delta G = \sigma \delta A \quad (2.1.1)$$

Many of the fundamental equations governing the behaviour of multiphase flow in porous media where capillary forces dominate can be derived by considering the fluid interface surface at thermodynamic equilibrium as a minimum free energy surface.

Two main methods for measuring surface energy density at elevated pressures are reported in the literature: the pendant drop method and the capillary rise method [41]. The pendant drop method can be used either with selected plane [42] or with drop shape analysis [43-45]. In the drop shape analysis methodology a small drop of one immiscible fluid is introduced into another, the shape of which can be measured, which is then compared to an analytical solution for the drop shape in terms of in terms of the surface energy density/surface tension. Measurements of the CO_2 -brine system have shown that the surface tension to range from around 25-65 mN/m , with lower surface tensions found at higher pressures (figure 2.1.1).

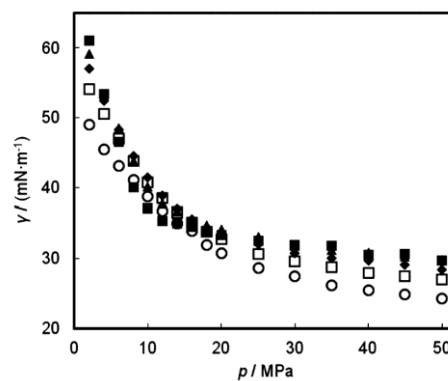


Figure 2.1.1: Reprinted (adapted) with permission from Li *et al.* [45]. Copyright 2012 American Chemical Society. Interfacial tension of $\text{CO}_2 + (0.864 \text{ NaCl} + 0.136 \text{ KCl})(\text{aq.})$, with a salinity of 1.98 mol.kg^{-1} , as a function of pressure at different isotherms: ■, $T=323.15 \text{ K}$; ▲, $T=343.15 \text{ K}$; □, $T=363.15 \text{ K}$; ○, $T=393.15 \text{ K}$; ◆, $T=423.15 \text{ K}$.

2.2 Capillary Pressure

Let us consider an interface with radii of curvature R_{11} and R_{12} displaced by some infinitesimal amount such that the new radii of curvature are R_{21} and R_{22} respectively. The normal displacement distance between the surfaces is δr , as shown in figure 2.2.1. The direction of R_{12} is in the plane of the page, as shown in figure 2.2.1.

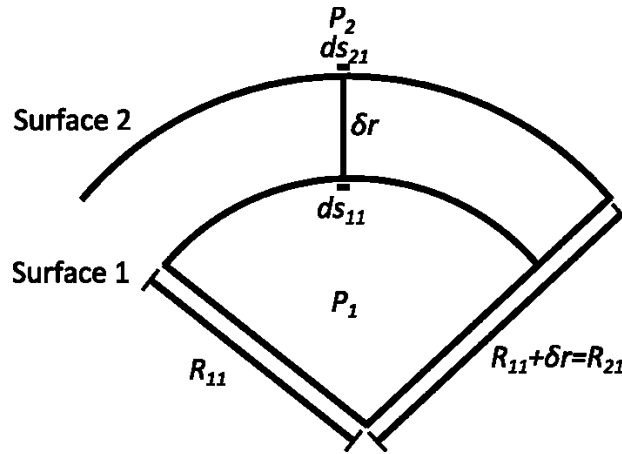


Figure 2.2.1: Schematic movement of a fluid-fluid interface.

A volume element between the two surfaces is

$$dV = \delta r dA$$

2.2.1

where dA is a surface element. If P_1 and P_2 are the pressures in the two media, and δr is positive if the displacement of the surface is towards medium 2, then the PV work (δW_{PV}) needed to bring about this change in volume is

$$\delta W_{PV} = \int (P_2 - P_1) dV = \int (P_2 - P_1) \delta r dA$$

2.2.2

The total work (δW) associated with this interface movement is however the sum of W_{pv} to the work connected with an increase in surface energy arising from a larger interface. This is the product of the difference in surface area (δA) with the interfacial energy density σ . The total work is therefore

$$\delta W = \int (P_2 - P_1) \delta r dA + \sigma \delta A$$

2.2.3

At thermodynamic equilibrium the total work is zero.

If surface 1 and surface 2 remain parallel, the orthogonal arc differentials along surface 2 (ds_{21} and ds_{22}) can be defined in terms of the arc differentials along surface 1 (ds_{11} and ds_{12}).

$$ds_{21} = \frac{(R_1 + \delta r) ds_{11}}{R_1} \text{ and } ds_{22} = \frac{(R_2 + \delta r) ds_{12}}{R_2}$$

2.2.4

The surface element dA before the interface displacement is $ds_{11}ds_{12}$, after interface displacement is equal to

$$ds_{11}(1 + \delta r/R_1)ds_{12}(1 + \delta r/R_2) \cong ds_{11}ds_{12}(1 + \delta r/R_1 + \delta r/R_2)$$

2.2.5

The change in surface area of each surface element is therefore:

$$\delta r dA \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

2.2.6

So the total change in surface area across the interface is therefore:

$$\delta A = \int \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta r dA$$

2.2.7

We can substitute eq. 2.2.7 into eq. 2.2.3, giving the equilibrium condition in the form

$$\int \delta r \left\{ (P_1 - P_2) - \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \right\} dA = 0$$

2.2.8

As this must hold for every infinitesimal displacement of the surface (for all δr) the expression inside the braces must be, at thermodynamic equilibrium, equal to 0. We therefore recover the Young-Laplace equation:

$$P_1 - P_2 = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

2.2.9

This pressure difference is, in porous media, called the capillary pressure (P_c), and is an inherently pore-scale phenomenon, as it arises from interface curvature defined by the topography of local pore walls. Traditionally phase 1 is considered to be oil or CO_2 and phase 2 considered to be water or brine. If we consider a simple capillary tube geometry the mean interfacial curvature can be related to the contact angle (θ) and tube radius (r), such that the capillary pressure in this system is

$$P_c = \frac{2\sigma \cos \theta}{r}$$

2.2.10

In real systems, however, curvature cannot be determined analytically, as it is a combined effect of an arbitrarily complicated pore morphology and contact angle. It can be seen, however, that given that the system is water wet, a vectorised representation of this capillary pressure can only be positive. That is the nonwetting-wetting phase interface must be convex over the non-wetting phase.

Capillary pressure has been examined at the macro-scale by assuming that it is a function of saturation only, arising from the viscous pressure drop across a certain length. This is an

oversimplification, leading to a non-unique solution of capillary pressure, specifically the hysteretic capillary pressure curve (figure 2.2.1).

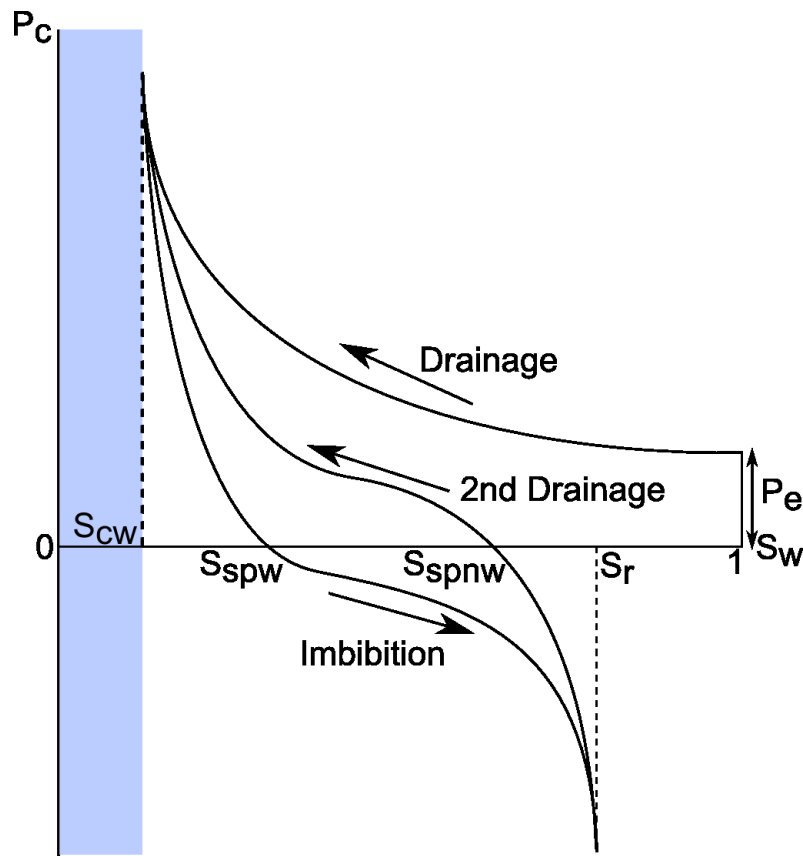


Figure 2.2.1: The hysteretic capillary pressure curve, showing the wetting phase saturation (S_w) as a function of capillary pressure (P_c).

In Figure 2.2.1, S_{spw} is the wetting phase saturation at zero macroscopic capillary pressure during imbibition, S_{spnw} is the phase saturation at zero macroscopic capillary pressure during the secondary drainage process, S_r is the residual oil saturation and S_{cw} is the connate wetting phase saturation. Multiple saturation values are achieved at each stage of the multi-phase flow process. This is because during initial non-wetting phase invasion, the pore-space is entirely saturated with the wetting phase, requiring a finite capillary entry pressure (P_e). During wetting phase invasion (imbibition) portions of the non-wetting phase resident in the pore-space are snapped off as pore-scale droplets. The macroscopic capillary pressure is therefore an average measure dependent on pore-scale fluid arrangement. In this representation, negative capillary pressure values may

represent a viscous pressure drop through the wetting phase in the opposite direction to the initial non-wetting phase invasion. In a water wet system this is completely divorced from the physical reality of capillary pressure at the pore scale, which remains positive in disconnected ganglia of the non-wetting phase. Continuum scale capillary pressure can be determined experimentally by the use of different core-flooding techniques, such as Mercury Injection Capillary Pressure (MICP) [46], porous plate coreflooding [47, 48] and quasi-steady state flooding [49].

These measurements of capillary pressure rely on external pressure measurements, so can only determine interface pressure differences around phase clusters connected to the pressure transducers. Also the fundamental pore-scale properties, such as interfacial configuration, interface curvature, contact angle and pore morphology are ignored. Although these continuum scale measurements can be illustrative and give a rough indication of pore topology, a more rigorous measure is needed.

It has been suggested [50-52] that capillary pressure at the macro-scale can be fully parameterized by adding an additional term for surface area between the fluids. Hassanizadeh and Gray [50] hypothesized that all possible static P_c values lie on a unique surface. In this formulation the hysteretic capillary pressure curve (figure 2.2.1) is an artefact of projecting 3D surface onto the P_c - S_w plane. Although some experimental and modelling evidence exists that for a specific pore morphology and wettability state a unique P_c - S_w - A_{nw} surface exists [53-58] some network modelling results have shown that hysteresis, even in the P_c - A_{nw} - S_w space can arise from contact angle hysteresis [59]. Contact angle hysteresis is discussed in section 2.3.

Recent developments in X-ray microtomography have allowed for capillary pressure to be measured directly on micro-CT images by measuring the non-wetting phase-wetting phase interfacial curvature, and equating this curvature with capillary pressure (equation 2.2.9). The first method for this was proposed by Armstrong *et al.* [60], and a modified version of this method is used in this study, and described here. Smoothed surfaces were generated for a non-wetting phase cluster using

a generalised marching cubes algorithm [61, 62]. The magnitude of smoothing across the ganglion surface can be altered by changing the size of the kernel of a modified Gauss filtered used to compute probability weights during the surface assignment. The curvature of this surface can be found by approximating the surface locally as a quadratic form:

$$ax^2 + by^2 + cz^2 + 2exy + 2fyz + 2gzx + 2lx + 2my + 2nz + d = 0$$

2.2.11

This form is then optimized locally such that it is the best fit for the existing surface. The eigenvalues and eigenvectors of this form then represent the principal curvature values and directions of principal curvature. A surface scalar field is produced, where the principal radii of curvature are averaged and assigned to each element across the interface. Armstrong *et al.* [60] correlated externally derived capillary pressure to this direct pore-scale measurement, validating it as an effective technique. In section 6.2 this method will be further developed to examine the details of the trapping process and how residual ganglia may be remobilized, and in section 6.4 it will be used to examine the dynamic processes associated with multi-phase displacement.

2.3 Wettability

Wettability is defined as the tendency of one fluid to adhere to a solid surface in the presence of other immiscible fluids [63] and is determined, at the pore scale, by the local contact angle (the angle that the fluid-fluid interface makes at equilibrium with the solid, usually measured through the denser phase). The fluid which adheres more readily to the surface is termed the wetting phase. The wetting phase will tend to reside in the smallest areas of the pore-space, such as small pores, the corners of larger pores and as well connected films residing in the roughness of the solid surface. Conversely, the fluid which adheres less readily, the non-wetting phase, occupies the largest areas of the pore-space, principally the centres of large pores.

Similarly to the Young-Laplace equation (equation 2.2.9), the Young wettability equation can be derived analytically [64] by thinking of the fluid interface as a minimum energy surface. Let us consider a drop wetting fluid on an ideally flat surface, where the solid-non-wetting phase tension is σ_{s-nw} , the solid-wetting phase tension is σ_{s-w} , and the non-wetting-wetting phase tension is σ_{nw-w} . If θ denotes the contact angle, the shape of the drop is a spherical cap with radius R , volume V and liquid-air surface area A (figure 2.3.1)

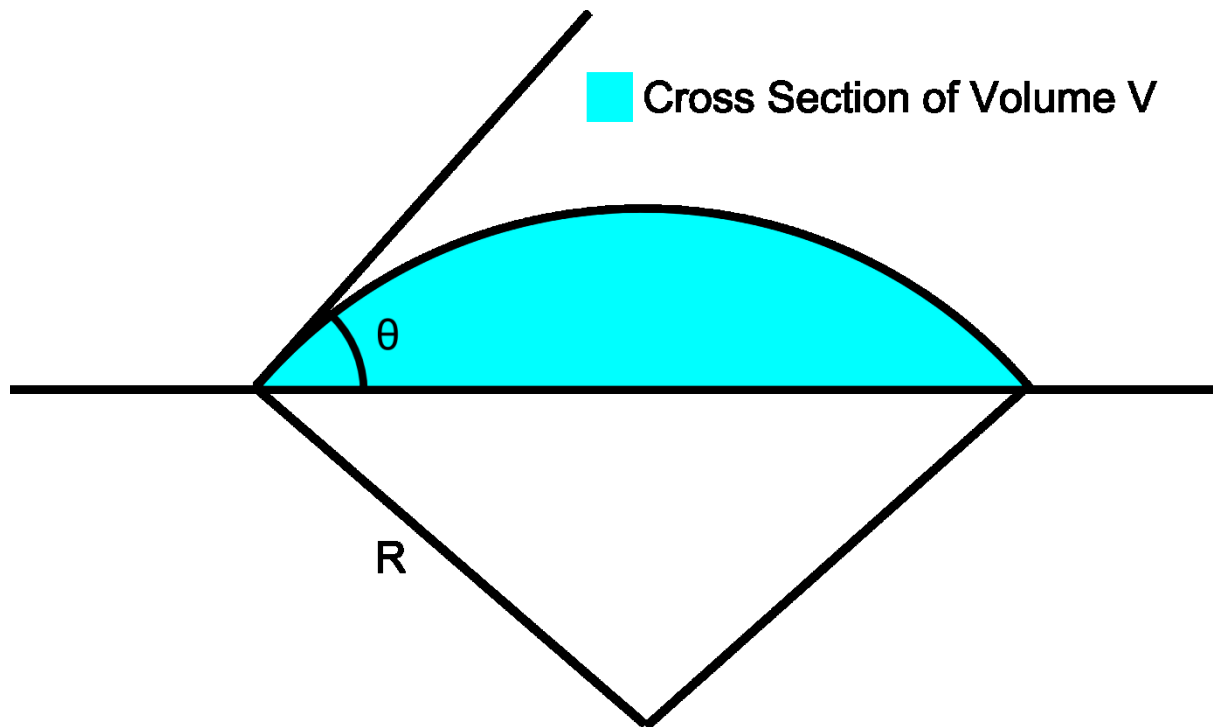


Figure 2.3.1: Schematic fluid arrangement used in the derivation of Young's equation (equation 2.3.7).

$$V = \frac{\pi R^3}{3} (1 - \cos\theta)^2 (2 + \cos\theta)$$

2.3.1

$$A = 2\pi R^2 (1 - \cos\theta)$$

2.3.2

The Gibbs free energy change of the drop is therefore:

$$G = \sigma_{nw-w}A + \pi(R\sin\theta)^2(\sigma_{s-w} - \sigma_{s-nw})$$

2.3.3

If the drop is of constant volume, we can substitute 2.3.1 and 2.3.2 into 2.3.3, giving:

$$G = \left(\frac{9\pi V^2}{(1 - \cos\theta)(2 + \cos\theta)^2} \right)^{1/3} (2\sigma_{nw-w} - (\sigma_{s-w} - \sigma_{s-nw})(1 + \cos\theta)) = G(\theta)$$

2.3.4

The Gibbs free energy is therefore a function of only one independent variable, the contact angle θ .

We can find the minimum free energy state by differentiating 2.3.4 and equating to zero:

$$\frac{dG}{d\theta} = \left(\frac{9\pi V^2}{(1 - \cos\theta)^4(2 + \cos\theta)^5} \right)^{1/3} 2(\gamma_{s-w} - \gamma_{s-nw} - \gamma_{nw-w}\cos\theta)\sin\theta = 0$$

2.3.5

The solutions to this equation occur at the trivial $\theta=0$ case (where drop volume is zero) and at

$$\sigma_{s-w} - \sigma_{s-nw} - \sigma_{nw-w}\cos\theta = 0$$

2.3.6

This gives us Young's equation:

$$\sigma_{s-nw} = \sigma_{s-w} + \sigma_{nw-w}\cos\theta$$

2.3.7

Equation 2.3.7 is more usually derived by a force balance at the contact line, however it is informative to realise that it is also a necessary result of having an equilibrium (and therefore a minimum free energy) interfacial surface.

Even in perfectly smooth surfaces, however, the system will adopt a distribution of contact angles, ranging from the advancing contact angle, as the wetting phase displaces the non-wetting phase, to

the receding contact angle, as the non-wetting phase displaces the wetting phase [65]. In non-ideal rough solid surfaces this is even more pronounced. It is caused by pinning of the contact line to a single spot on the rough solid surface. During wetting phase advance, small increases in the brine pressure, perturbing the fluid-fluid interface, will not move the contact line. The contact angle will increase until some threshold maximal contact angle (the advancing contact angle) is exceeded, where the contact line will start to move. Conversely, during the recession of the wetting phase the contact angle will approach a minimum (the receding angle) before contact line movement (Figure 5). The images are taken at the end of imbibition, during which the wetting phase swells displacing scCO_2 . During this process advancing contact angles will be present; however some rearrangement of the fluid interfaces after injection has finished is possible.

Surface roughness has long been recognised as modifying contact angle in real systems [66, 67] so the translation of these disparate values found on ideal, smooth surfaces, to the range of contact angles present in reservoir and aquifer rocks with heterogeneous surface roughness, mineralogical composition and pore topography remains unclear.

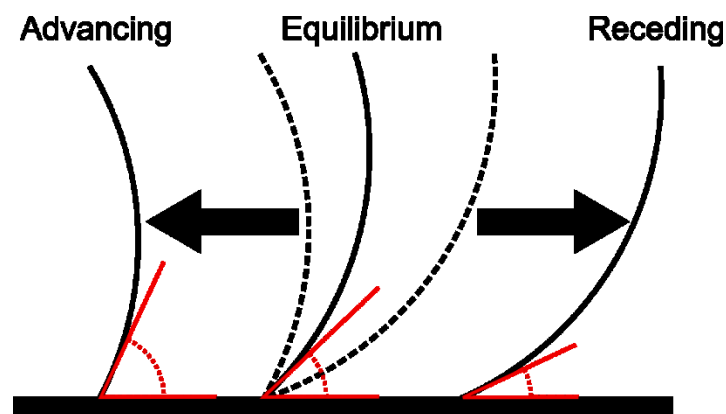


Figure 2.3.1: Hysteresis in the contact angle is expected. During wetting phase advance (imbibition) the contact angle will be larger than at equilibrium. During wetting phase recession (drainage) the contact angle will be smaller than at equilibrium. The grey arrows show the direction of interface movement. The dotted grey lines show the three different interface positions superposed on each other.

Various models have been proposed for the application of this to real systems with rough surfaces, such as the Cassie-Baxter [67] and the Wenzel [66] model. The Wenzel model describes the homogeneous wetting regime, where the entire of the rough surface is in contact with the non-wetting liquid. This corresponds to the situation shown in figure 2.3.2.

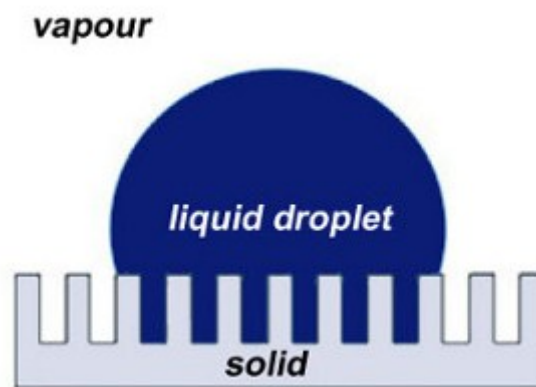


Figure 2.3.2: Fluid distribution according to the Wenzel model [66]. Taken from [68].

In this system an apparent contact angle θ_a is related to the intrinsic contact angle θ by

$$\cos\theta_a = r\cos\theta$$

2.3.8

where r is the roughness ratio, or the ratio of true area of a surface to the apparent macroscopic area. A more generalized picture is provided by the Cassie-Baxter model, where only part of the surface is in contact with the non-wetting phase (figure 2.3.3).

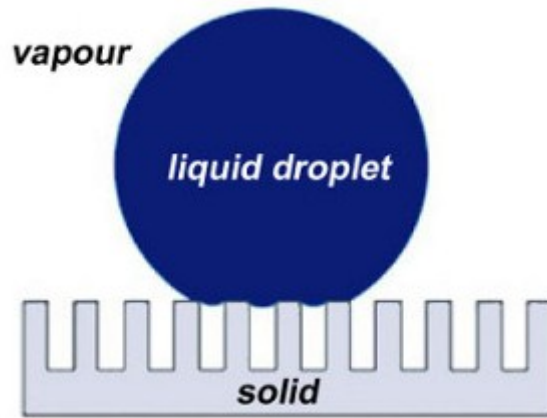


Figure 2.3.3: Fluid distribution according to the Cassie-Baxter model [67]. Taken from [68].

In this case the true contact angle is given by

$$\cos\theta_a = r_w f \cos\theta + f - 1$$

2.3.9

where r_w is the roughness ratio of the area of the surface in contact with the non-wetting phase, and f is the fraction of the surface in contact with the non-wetting phase. Once again these descriptions can be rigorously found from considerations of the interface as a minimum free energy surface, with derivations found in Whyman *et al.* [64]. They all, however, require a high degree of knowledge about the surface and fluid properties. In arbitrarily complex rock systems there is no way of knowing the roughness ratio, much less the fraction of the surface in contact with the non-wetting phase. They also assume an effective separation of length scales, that the surface is flat on the scale of the surface roughness. In more complex rock types this may not be the case.

As the contact angle controls the arrangement of fluids within the pore-space, its experimental evaluation is vital for a holistic understanding of multiphase flow in geological systems. Traditionally, however, this property could only be accessed directly on pure and flat mineral surfaces, by the use of the dynamic sessile drop method [69, 70], the captive bubble method [71] and in micromodel studies [72].

In the dynamic sessile drop method a small drop of the wetting fluid is placed on the solid surface. Increasing the drop volume causes the wetting phase to attempt to advance over the solid surface, giving the wetting phase advancing angle. Decreasing the drop volume causes the wetting phase to recede over the solid surface, giving the receding contact angle. Similarly in a captive bubble experiment a buoyant bubble of fluid is released onto the solid surface. If this surface is tilted the advancing face of the bubble gives the wetting phase receding angle and the receding face of the bubble gives the wetting phase advancing angle. In micromodel studies the angle can be directly measured from the micromodel image. These methods all provide measures more akin to the intrinsic contact angle dealt with by the Young equation (eq. 2.3.7). They then need to be applied to real systems, with complex surface topographies, which may be extremely difficult, as discussed above.

Wettability can also be estimated on the core-scale by the use of the Amott wettability index [73, 74]. The Amott index for the wetting phase is defined using parameters from the hysteretic capillary pressure curve (figure 2.2):

$$A_i = \frac{S_{spw} + S_{spnw} - S_r - S_{cw}}{1 - S_{cw} - S_r}$$

2.3.10

Although this does provide some measure of the wettability in a real system it is only an indirect measure, divorced from the pore-scale physics. It is also extremely challenging to measure at realistic subsurface conditions, so its application to the scCO₂-brine-rock system remains an outstanding problem.

Even using simplified systems or indirect measures results are sparse and inconsistent, especially for scCO₂-brine-calcite systems. A single study [75] looked at this system using reservoir brines and samples, finding that system wettability was a strong function of system conditions such as temperature and pressure. They examined the CO₂-brine-calcite at 27°C and 58°C, and found that at

low temperatures the system seemed to be intermediate-wet at low pressures and CO₂-wet at high pressures. At higher temperatures the system was water-wet at low temperatures and intermediate-wet at higher pressures (figure 2.3.4).

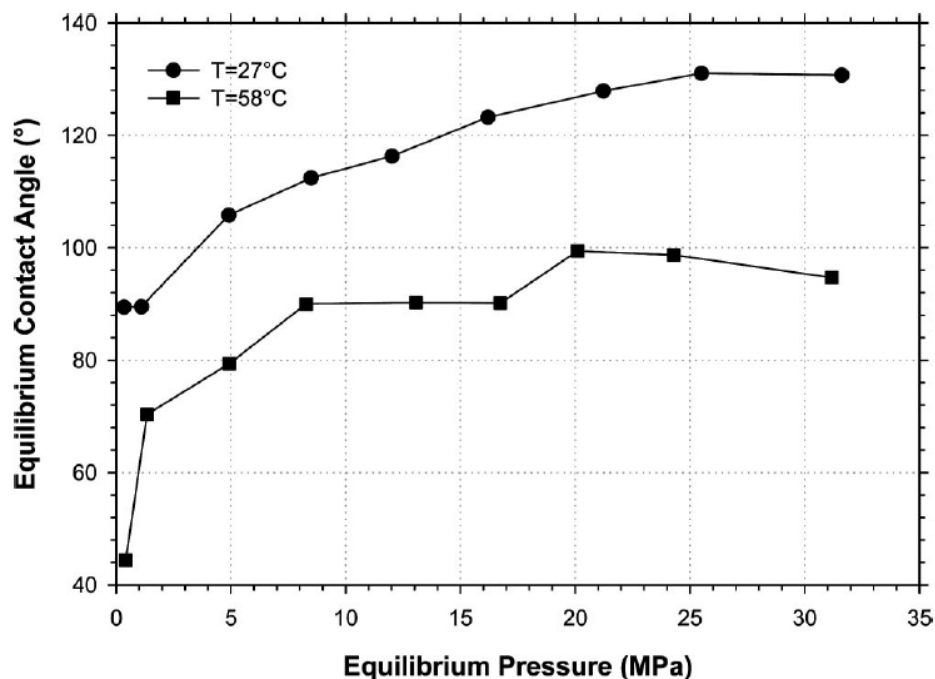


Figure 2.3.4: Change of equilibrium contact angle with pressure in the CO₂-brine-calcite system with pressure. Reprinted (adapted) with permission from Yang [75]. Copyright 2008 American Chemical Society.

More data is available with low salinity systems, which seem to be weakly water-wet. Three studies using the same sessile drop method and deionised water report differing angles for CO₂ on calcite. Espinoza and Santamarina [69] examined pressures ranging from 0-10 MPa and temperatures of 23.35°C and found a single angle of 30°. Bikkina [76] considered pressures ranging from 0-21 MPa and temperatures of 25°C and reported little hysteresis between the advancing and receding angle, with both in the range 40-55°. Broseta *et al.* [77], however, reported much more hysteresis, with advancing (imbibition) angles of 60-75° and receding (drainage) angles of 35-43° at 0.5-14 MPa and 35°C. Salinity has been observed to be a key control in the scCO₂-brine-quartz system, where much

more data are available. The system becomes less strongly water-wet as brine salinity is increased, with angles changing from 20° for pure water to 40° when 200 mg/l NaCl is used [69].

In section 6.3 we propose a new, direct method for the extraction of contact angle by the use of X-ray microtomography in real systems under in-situ conditions.

2.4 Flow and Modelling

The viscous motion of a fluid can be described by the Navier-Stokes equation:

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u}$$

2.4.1

where $\mathbf{u}$ is the flow velocity, ρ is the flow density and p is the pressure. In single phase flow, if the advective inertial forces are small compared with the viscous forces, such that the Reynolds number is much less than 1, and we assume no change in the flow field with time, this simplifies to the steady-state Stokes flow equation

$$-\nabla p + \mu \nabla^2 \mathbf{u} = 0$$

2.4.2

In this case, if the viscous forces are linear with flow rate, the medium is perfectly isotropic and fluid flow is only in one direction (x) this simplifies to Darcy's Law, which averages the Stoke's equation to find:

$$q = \frac{-k}{\mu} \frac{dP}{dx}$$

2.4.3

where q , the average fluid flow rate (volume per unit area per unit time), is related to the permeability (k), the viscosity (μ) and the pressure gradient (dP/dx). At the pore scale, where the medium is not perfectly isotropic, different approaches have been used to solve single and multi-phase fluid flow problems.

2.4.1 Multiphase Displacement

The description of multi-phase displacement is even more complex than that of single-phase displacement, as interfacial forces (sections 2.1-2.3) must be considered as well as the viscous pressure drop. One way of describing the flow in a complex porous medium is by the use of network modelling (starting in the 1950s with the use of electrical systems, due to a lack of computing facilities [78]), where the pore-space is represented as an idealized network of idealized pores. In this system rules can be formulated for non-wetting and wetting phase invasion so pore throats are filled in order of their size in accordance to the Young Laplace equation (equation 2.2.9). These early studies reproduced capillary pressure curves that had some of the same features as drainage capillary pressure curves obtained experimentally. Early network modelling did not fully capture the pore-space geometry of real rocks, so their predictive potential was limited. A suite of different statistical methods to extract realistic networks of ideally shaped pores and throats were then developed, mostly using multiple point statistics [79] or object based methods [80]. More recently more rigorous methods of network generation from micro-CT images have been suggested, such as that of maximum inscribed spheres [81]. In this technique spheres are grown at each point in the voxelized version of the pore-space and the pores are assigned where the largest spheres can be grown. Throats are assigned where pores touch each other. This technique of network extraction is used in section 6.1 to parameterise the pore-space of each rock type, allowing for the controls on measured flow behaviour to be better understood. A similar technique using the watershed catchment basins of a Euclidian distance map of the pore-space (section 3.3.3) is used in section 6.2 to parameterise the pore space in order to examine the details of ganglion snap-off. Different pore-space parameterisation techniques were used in different sections as each gave different information. The maximal ball technique was extremely effective at giving the bulk topological measures of connectivity used in section 6.1. The Euclidian distance mapping maintained the individual spatial relationship of each of the voxels within the micro-CT image, making it more appropriate for the pore-by-pore analysis presented in section 6.2.

The dynamic physics of drainage (non-wetting phase invasion) is traditionally described using a network based conceptualisation of the pore-space using invasion percolation theory, where process consists of a sequence of pore-scale events (Haines jumps) where the non-wetting phase displaces the wetting phase in a pore [82]. These events can be thought of as an irreversible change between two equilibrium states. As the old state becomes unstable and energetically unfavourable, surface energy is redistributed to a new local energy minimum. Using this description the event sequence can be deterministically predicted if pore entry pressures and connectivity are known. This geometric description, however, lacks any dependence on the dynamics of the process between the two equilibrium states and the change in capillarity associated with each of the events is assumed to be strictly local. Several authors have studied the drainage process in more detail [83-85], using rate controlled mercury injection or micro-model drainage and high speed 2D imaging to show the importance of cooperative pore filling events, showing that during pore body drainage, imbibition occurs in nearby throat regions. Section 6.4 shows results where fast synchrotron-based tomography is used to describe dynamic drainage pore-scale events at reservoir conditions. The results advance our understanding of these processes and help calibrate pore-scale network models [86, 87] and direct simulation approaches [88]. In particular, we observe persistent dynamically-controlled configurations of trapped non-wetting phase, which cannot be explained by capillary equilibrium concepts alone.

Another approach is to solve the flow equations directly in a voxelized representation of the pore space. There are a suite of different modelling tools to do this, including particle based methods such as Lattice-Boltzmann [57, 89-94] and smoothed particle hydrodynamics [95-97], or grid based computational fluid dynamics with fluid-fluid interface tracking/capturing and velocity-dependent contact angles [98], or through finite volume approaches [99]. A finite volume based method, implemented in OpenFOAM [100] where the pressure and velocity field are solved iteratively is used in section 6.2 to find the viscous pressure field through the wetting phase at residual state. This

allowed for viscous pressure drops across ganglia to be computed, allowing for the remobilization of residual ganglia and the reformulation of the capillary number to be addressed.

2.5 Dimensionless Numbers

In fluid mechanics flow behaviour tends to be classified in terms of dimensionless numbers representing the balance between different forces acting on the fluid. There is a large suite of these numbers, whose utility is determined by the important processes involved in a particular phenomenon. In non-reactive multiphase flow two of the most important of these dimensionless numbers are the capillary number, representing the ratio between viscous and capillary forces, and the Bond number, representing the ratio between gravitational and capillary forces.

2.5.1 Capillary Number

The ratio between viscous and capillary forces is critical in understanding the trapping process. Trapping can only occur if the capillary forces are dominant in a system, where the capillary number is very low. The capillary number is traditionally defined as

$$Ca = \frac{\mu q}{\sigma}$$

2.5.1.1

As the capillary number increases, the relative importance of viscous forces increase and the capillary forces immobilizing a particular ganglion in the pore-space are overcome, remobilizing the ganglion and reducing residual saturation. This process of capillary desaturation occurs at capillary numbers ranging from 10^{-7} to 10^{-3} (figure 2.5.1.1) [101-103].

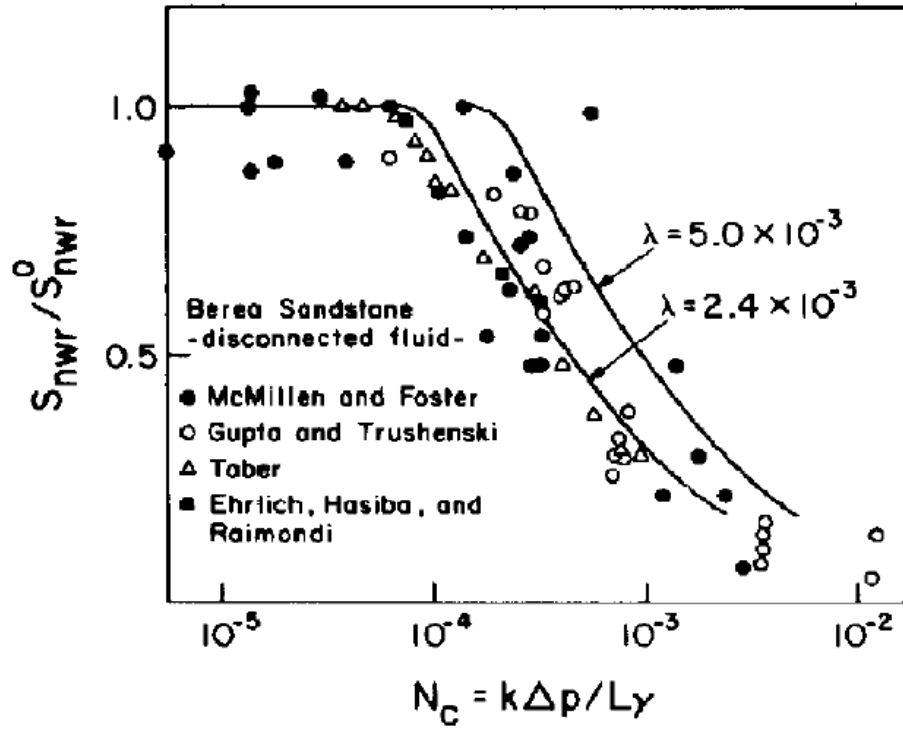


Figure 2.5.1.1: Compilation of capillary desaturation results on Berea sandstone. Taken from Larson [103]. Fluids are displaced from the core when viscous forces outweigh capillary forces, typically at traditional capillary numbers ranging from 10^{-7} to 10^{-3} . The capillary number shown here is equivalent to that given in equation 2.5.1.1 when Darcy's law (equation 2.4.3) is taken into account.

Unfortunately the result obtained in this way is unique to the tested rock type, unpredictable and unsatisfactory. If the capillary number is to reflect the balance between viscous and surface forces desaturation should occur at capillary numbers around 1. This inconsistency arises from the definition of capillary number. In equation 2.5.1.1 we define capillary number in terms of the viscous force and capillary forces at a specific point along the interface. It assumes that both viscous and capillary forces act over the same length scale. During the viscous remobilization of residual ganglia, however, viscous shear occurs over the entire length of the extended cluster interface, which can be potentially on the mm scale [104], whereas the capillary forces act over on the scale of a pore throat, which is typically a few micrometres. Newer formulations have incorporated this length

scaling by incorporating terms for the cluster length, with the first proposed by *Melrose and Brandner* [105] by incorporating Darcy's law into equation 2.5.1.2, resulting in

$$Ca_{critical} = \frac{k_{rw} K \Delta P}{\phi \gamma l_{cl}} \quad 2.5.1.2$$

where k_{rw} is the wetting phase relative permeability, K is the absolute permeability and ΔP is the pressure drop across a cluster of length l_{cl} . Hilfer and Øren [102] arrived at a similar definition using a rigorous dimensional analysis to connect the macroscopic and microscopic pictures of multiphase flow. The macro-scale capillary number capillary number they arrived at was

$$Ca = \frac{l_{cl} \mu q}{K P_b} \quad 2.5.1.3$$

where P_b is the capillary pressure at breakthrough. Finally Armstrong *et al.* [106] started with the averaging of measurements from pore-scale measurements, developing a capillary number definition as shown in equation 2.5.1.4.

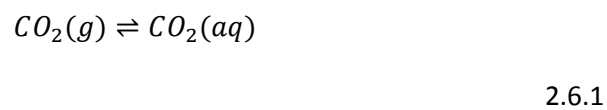
$$Ca = \frac{l_{cl} \mu q}{k_{rw} P_c} \quad 2.5.1.4$$

where P_c is the averaged capillary pressure and k_{rw} is the relative permeability, as calculated by pore-scale modelling through the wetting phase. Although this is the most realistic of all the capillary number definitions, and uses a quantitative measure of surface forces, it assumes that the viscous pressure drop across a ganglion at residual saturation is proportional to the ganglion length parallel to the flow. Although this seems like a reasonable assumption, and will be true in a uniform flow field, in a more heterogeneous flow field, such as those seen at residual saturation, it is likely to be

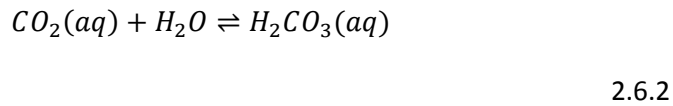
incorrect. For this reason a reformulation of capillary number, based on the pore-scale physics of displacement is proposed and discussed in section 6.2.

2.6 CO₂ solubility

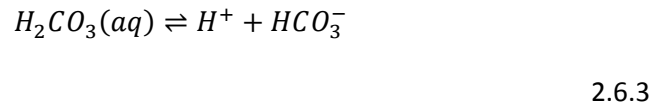
CO₂ will dissolve in aqueous fluids, forming a highly reactive carbonic acid. This process is the most common source of acidity, and starts with CO₂ entering the water through equilibrium with the atmosphere, as represented in equation 2.6.1.



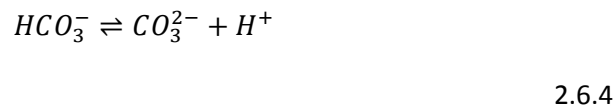
This CO₂ then reacts with the water to form carbonic acid:



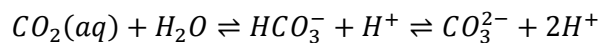
This then rapidly disassociates into a proton and a bicarbonate ion:



The bicarbonate species can then disassociate further, forming the carbonate ion and another proton:



These equilibria can therefore be written in the general form so as CO₂ partial pressure increases (either due to an increase in CO₂ concentration, or by increasing system pressure), CO₂ solubility increases, increasing the proton concentration of the resulting fluid, decreasing pH (figure 2.6.1).



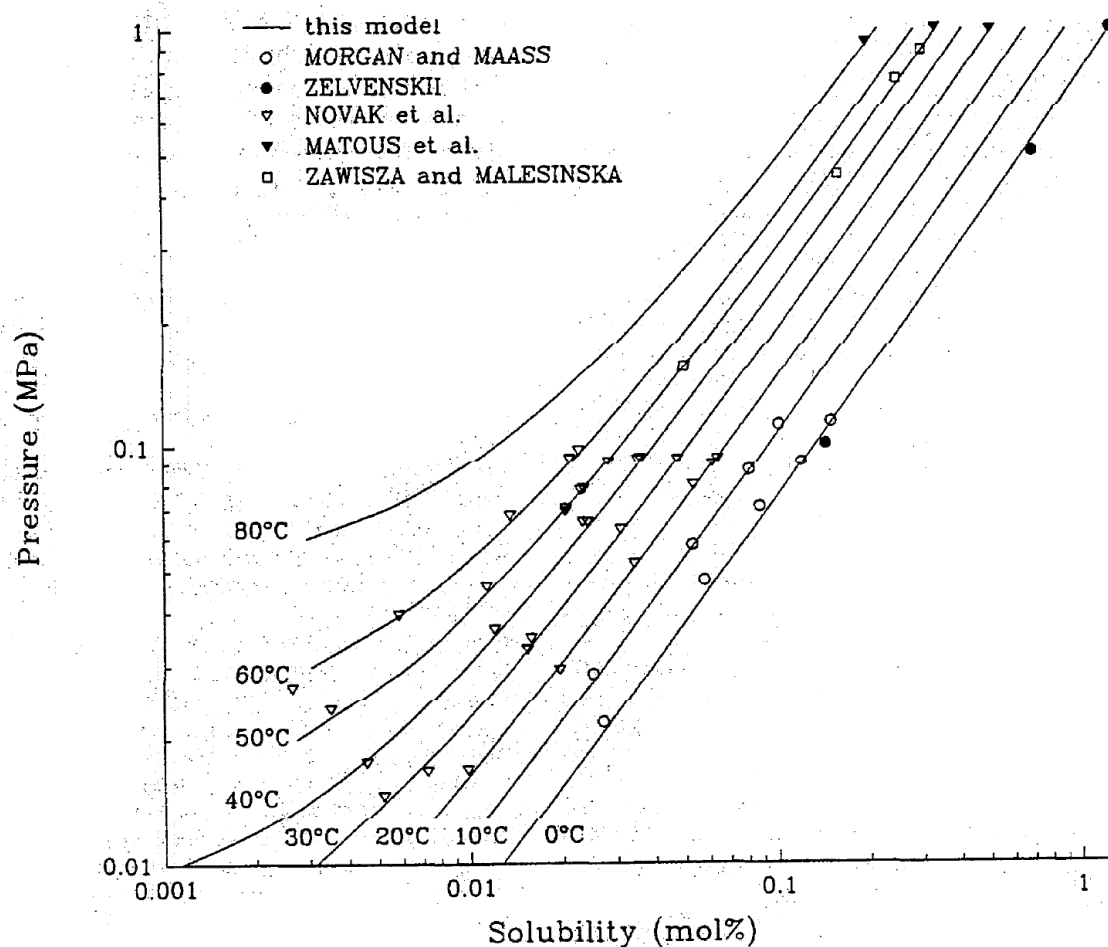


Figure 2.6.1: CO₂ solubility increasing with pressure. Taken from Carroll *et al.* [35].

Correspondingly, as temperature increases, solubility will decrease (figure 2.6.2), increasing pH [35].

Salinity is another important control on CO₂ solubility, decreasing solubility with increasing salinity.

For these reasons control of CO₂ solubility state, temperature and pressure were of vital importance when designing and developing the experimental methods used in this study (described in section 4).

2.7 Micro-CT imaging

“Tomos” is Greek for “cut” or “section”. Computed Tomography (CT) is a method for using X-rays to reveal the inner structure of materials as if we had “cut” or “sectioned” the material, but without

having to physically interfere with the sample. There are many different types of tomography, such as wave-speed inversion to find the structure of The Earth's mantle [107]; however X-ray computed tomography is by far the most heavily used and widespread in laboratory settings, from standard medical uses to micron scale scanning. In X-ray CT information is typically displayed as a series of two-dimensional images, each stacked on top of each other with an inferred spacing between each slice typically equal to the *pixel* (picture element) side length, thus transforming the two dimensional pixels into three dimensional *voxels* (volume element).

The intensity of each voxel in the CT slice is proportional the X-ray attenuation in that volume of the sample, representing X-rays that are either absorbed or scattered at that point. The linear attenuation of any object can be described using the Beer-Lambert law (equation 2.7.1).

$$I = I_0 e^{-\mu l}$$

2.7.1

where I is the transmitted intensity, I_0 is the incident intensity, μ is the linear attenuation coefficient and l is the optical length through the sample. The linear attenuation coefficient is primarily a function of three parameters; the density of the material, its atomic number, and the X-ray energy (higher energy X-rays tend to be more penetrating and absorbed less than low energy X-rays).

In order to obtain this 3D image, a series of projections are taken with a configuration shown below (figure 2.6.1). The value of each of the pixels on this series of projections usually corresponds to the transmission factor T :

$$T = \frac{I}{I_0} = e^{-\mu l}$$

2.7.2

This can mean that the materials with small attenuation coefficients are difficult to distinguish on reconstructed data, as their transmission factors are very similar for small objects.

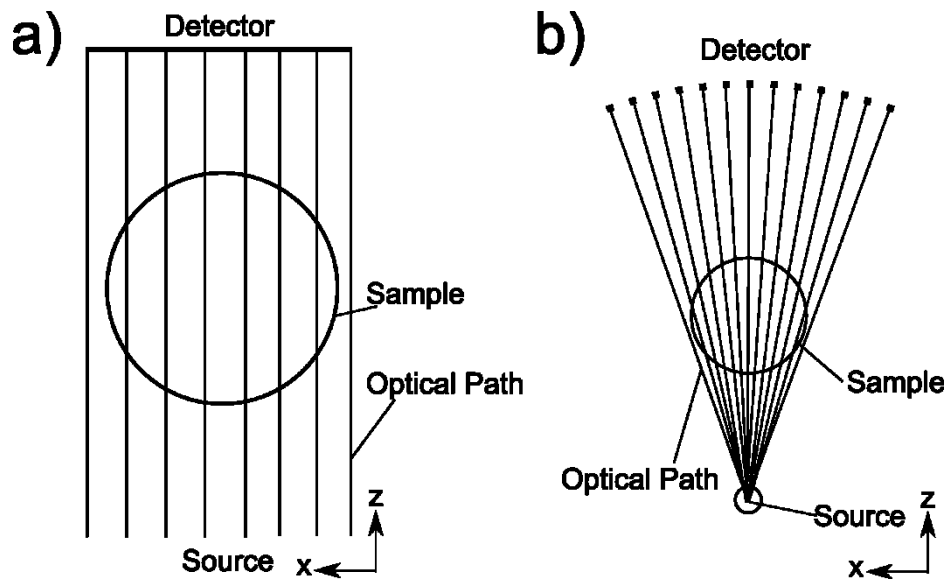


Figure 2.7.1 X-ray optical geometries. 2.7.1a shows a parallel beam used in typical synchrotron facilities, 2.7.1b shows a conical beam used in typical bench top systems. Detectors tend to be made of scintillating materials, the scintillations on which are converted into a digital image by a visible light CCD. Sources in synchrotron facilities tend to be the bending of a beam of high energy electrons, whereas sources in table top facilities tend to be Bremsstrahlung radiation from a (commonly tungsten) target hit by electrons accelerated using a small linear accelerator.

The simplest geometry to consider is shown above in figure 2.6.1a, but other geometries have exactly analogous procedures in place, but with simple geometrical transformations. The sample is rotated either through 180° or 360° to get a set of $[x, y]$ projections, changing sequentially in angle (θ). The series of projections is first converted into a series of sinograms, which are a series of $[x, \theta]$ images, changing sequentially in y . Each sinogram is then back projected into a 3D intensity map by a suite of different algorithms, discussion of which is beyond the scope of this thesis, but can be found in [108].

The most common use of CT imaging is in medicine, where it allows the non-invasive imaging of soft tissue and bone. In non-biological systems, however, we can make use of the fact that we can control sample movement, increase X-ray energy and dose (without any concerns over irradiating

the sample), decrease spot size and increase X-ray scan time, allowing us to go from the mm scale resolution of medical scanners to the μm resolution of micro-CT scanners.

2.7.1 Micro-CT instruments

The first X-ray producing device was the Crookes tube, an electrical discharge tube invented by William Crookes around 1869-1875. This was improved by William Coolidge in 1913, producing the Coolidge tube. The principle behind this system is the one still used by most X-ray sources today. In a Coolidge tube, electrons are produced under a very high vacuum ($10^{-6} - 10^{-4}$ Pa) by thermionic emission from a tungsten filament (the cathode), heated by an electric current. These electrons are accelerated by a high voltage towards a target, acting as an anode. The electrons will then impact on a target, typically made of tungsten, producing X-rays. X-rays are produced by two principal mechanisms. A continuous spectrum of radiation, called Bremsstrahlung, or breaking radiation, is produced by the deceleration of the electron as it is deflected by the atomic nucleus. On top of this high-intensity characteristic X-rays are produced when electrons are knocked out of inner-shells by the incident electron, causing outer shell electrons to fill the resulting vacancy in a process of self-neutralization. As the energy difference between these shells is fixed, the resulting X-rays are emitted at a single energy. The position of these peaks in the X-ray emission spectra (see, for example, figure 4.2.1.3) are only weakly dependent on the chemical structure within which the target atom is bound, showing that the resulting X-rays are the result of inner-shell interactions.

2.7.2 Origins of micro-CT

The first demonstration of X-ray micro tomography to look at geological samples was in 1987 [109] and used synchrotron sources in the United States to produce (by today's standards) poor-quality pictures of dry Coconino sandstone with a pixel size of around $10\ \mu\text{m}$ (figure 2.6.1.1), although the true optical resolution was much coarser.

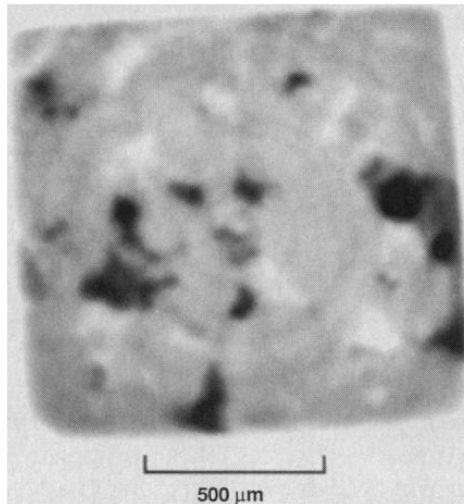


Figure 2.6.1.1 Tomographic reconstruction of Coconino sandstone from the original work on micro-CT imaging [109].

The ability of micro-CT to map the pore space of real, highly disordered porous media has since been used to predict both single-phase [110] and two-phase [111] porous media flow properties (section 2.3-2.5), with predictive success varying by the time of experiment, porous media type investigated and modelling method used. It has also been used to extract pore space statistical information, such as pore surface to volume ratios, average coordination numbers and aspect ratios used in core scale descriptions of sub-surface flow [112].

Although the potential of this technique for studies on “systems under conditions of temperature, pressure, and environment...which cannot be studied with conventional techniques” [109] was recognised early on, technological constraints held back progress for a long time until X-ray, computer and systems technologies had improved substantially in order to both acquire and process high-resolution data sets on representative sample sizes. Another problem has been the requirement for large expensive synchrotron facilities for high-resolution scanning, as only recently have table top scanners been able to produce images in the $<10\ \mu\text{m}$ resolution range. The limitations of micro-CT in the past have been reflected by the continuing usage of descriptions of the pore space found using statistical methods (section 2.3, [113-115]).

Dry scanning (to observe just the pore space, rather than resident fluids) has been useful as a tool for modelling. It provides a more rigorously defined space in which to run existing and new modelling techniques than statistical techniques ever could. However, in order to both verify the theoretical justification for the flow descriptions used, and also to push our physical understanding further (including the description of new physics to put into new generations of models required to describe flow in complex systems) it is necessary to do experiments using in-situ fluid flow. The first study to look at multi-phase flow under ambient conditions using micro-CT imaging, from 1993, [116] is shown below in figure 2.6.1.2.

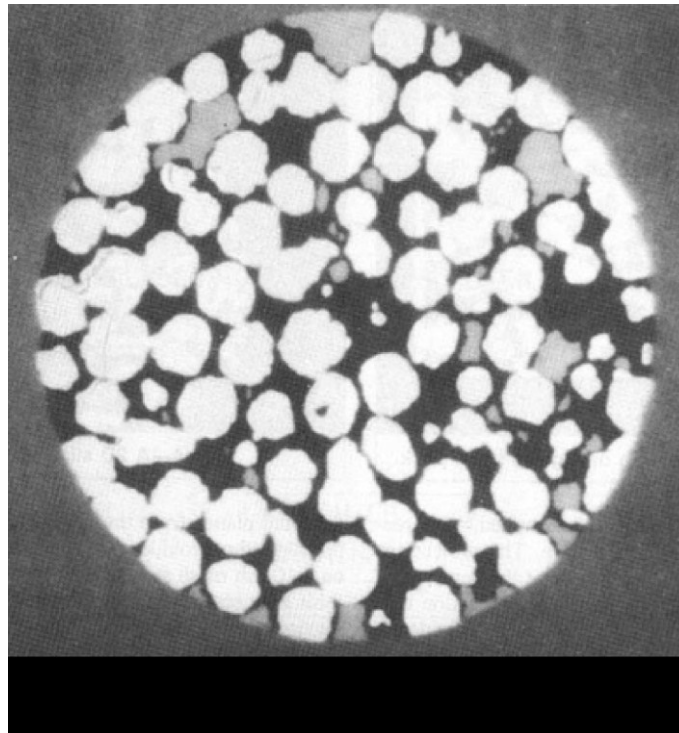


Figure 2.6.1.2 A 2D slice of a glass bead pack with oil (grey) and water (black). Taken from [116].

This qualitatively shows the potential for using micro-CT to identify multiple components in at least this simple pore space. The focus of research since then has tended to emphasise such simple systems (bead packs and well sorted sandstones at ambient pressures and temperatures with oil-brine systems), and has had many useful successes in coupling multiple modelling techniques (section 2.3-2.5) with experimental results [117]. Thin wetting layers (section 2.6.3) are, however,

not resolved even in the simple bead pack system. An excellent review of early applications, limitations and future views of micro-CT in hydrodynamic systems can be found in Wildenschild [117], and a more recent review in Wildenschild and Sheppard [118].

2.7.3 Moving to realistic conditions

Research into the use of carbon dioxide using micro-CT imaging has been limited due to the difficulties of working at super-critical conditions. The only group to successfully image scCO_2 using micro-CT imaging is at Imperial College [119, 120] (figure 2.6.2.1), and it is this study that this project hopes to consolidate and extend with new experimental techniques and into new systems (section 3.2).

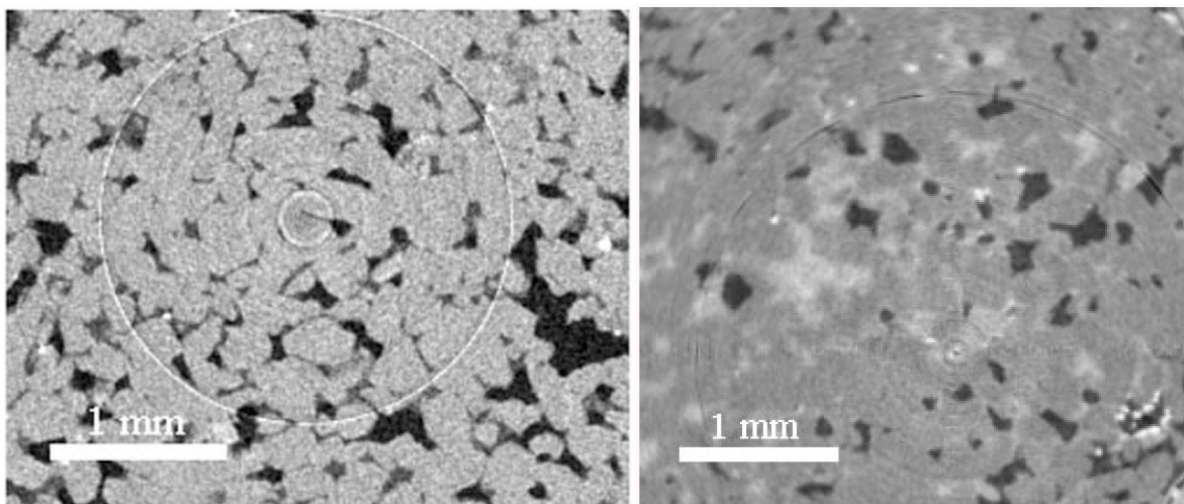


Figure 2.6.2: scCO_2 in Berea sandstone, imaged using micro-CT. The figure on the left shows the scCO_2 (dark), brine (dark grey) and grain (light grey) arrangement after drainage, or primary scCO_2 injection. The figure on the right shows the arrangement of multiple fluids after imbibition, or secondary water injection. Taken from [119].

One other study [121] has examined the behaviour of sub-critical high pressure gaseous CO_2 . As the properties of CO_2 vary so much between sub-critical and super-critical phases, this is not adequate to investigate genuine subsurface multiphase flow behaviour.

In section 6 we greatly extend the examination of realistic systems at realistic conditions, not only to the study of residual trapping in a wide range of rock types (section 6.1) but also to the processes of trapping and remobilization of residual ganglia (section 6.2) contact angle measurement (6.3) and the dynamic processes associated with multi-phase displacement (section 6.4).

2.8 Rock and Pore Classification Systems

In order to establish the rock types examined in this study in a wider context we briefly review existing rock and pore classification systems, used to classify the systems examined in this study in section 5.

2.8.1 Rock Classification Systems

As the depositional environment of sandstone and carbonate rocks can be extremely different, it often makes sense to classify them using different classification systems. A common method for carbonate classification is the Dunham system, based on depositional texture [122]. Carbonate rocks are composed of two components, grains and matrix. In the Dunham system the most important descriptive factor is the grain/matrix ratio, and how that impacts the texture of the rock. The grain origin is ignored (figure 2.8.1.1). This system has been expanded by Embry and Klovan [123]; however no rocks of the types identified by Embry and Klovan [123] were examined in this study.

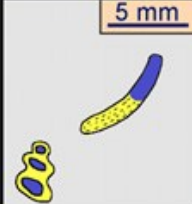
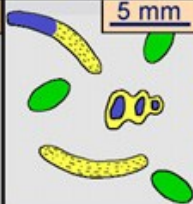
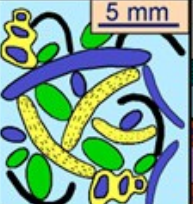
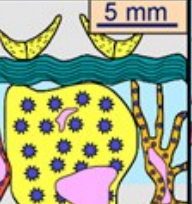
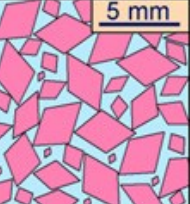
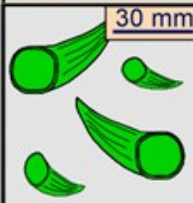
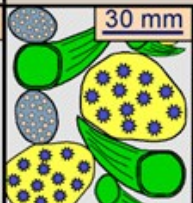
Depositional texture recognizable					Depositional texture not recognizable
Components not bound together during deposition				Components were bound together during deposition	
Contains carbonate mud (clay / fine silt)		Grain supported	Lacks mud and is grain supported		
Mud supported					
Less than 10% grains	More than 10% grains				
Mudstone	Wackestone	Packstone	Grainstone	Boundstone	Crystalline
					
Floatstone (large grains)		Rudstone (large grains)		Framestone	1m
				Bindstone	100 mm
				Bafflestone	100 mm

Figure 2.8.1.1: The Dunham rock classification system [122] with modifications by Embry and Klovan [123]. Used by permission of the University of Texas at Austin.

The primary sandstone classification was proposed by Krynine [124] and was updated by Dott [125].

The Krynine-Dott system classifies rocks in terms of mineralogical composition and matrix abundance (figure 2.8.1.2). In this case matrix is defined as any grains smaller than 30 μm in diameter.

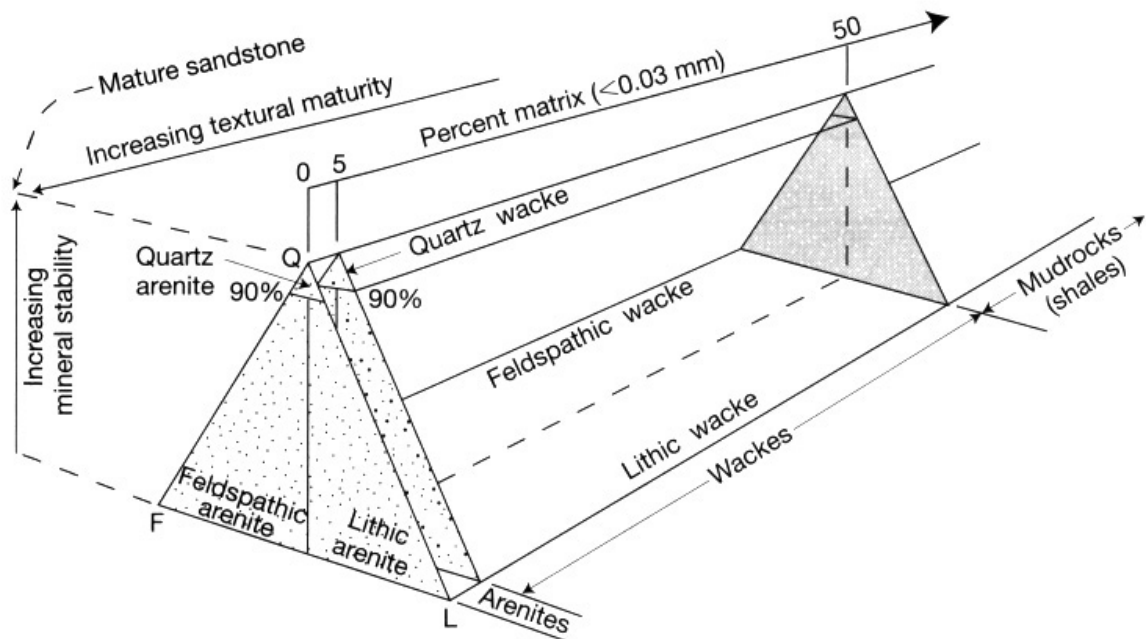


Figure 2.8.1.2: The Krynin-Dott rock classification system for siliciclastic rock types [124, 125]. Rocks with >95% quartz, feldspar or lithic fragments are termed arenites. Reproduced with permission from www.virtual-geology.info.

2.8.2 Porosity Classification Systems

Pore systems in carbonates are much more complex than those in siliciclastics. The classification systems used most widely by petroleum geologists working on carbonate systems is the Choquette and Pray system, based on rock fabric [126]. This method has some success in taking depositional setting and/or diagenetic evolution and prediction pore type evolution. This classification is summarised in figure 2.8.2.1. Petrophysicists and reservoir engineers tend to use classification systems more directly linked to pore geometries [127-129], which have more success in predicting single-phase porosity vs. permeability trends.

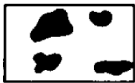
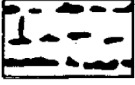
Fabric Selective Porosity		Nonfabric Selective Porosity	
Geometry	Genesis	Geometry	Genesis
 Interparticle	Diagenetic	 Fracture	Deformation
 Intraparticle	Depositional	 Channel	Dissolution
 Intercrystalline	Diagenetic	 Vug	Dissolution
 Moldic	Diagenetic	 Cavern	Dissolution
 Fenestral	Depositional		
 Shelter	Depositional		
 Growth or Framework	Depositional		

Figure 2.8.2.1: The Choquette and Pray [126] classification system, based on rock fabric. Reproduced with permission from www.wiki.aapg.org.

Microporosity occurs in both sandstones and carbonate aquifer rocks, and can affect their fluid flow properties and log responses [130]. Traditional approaches of pore classification attempt to fit microporosity as a subsection of other, genetically or texturally defined pore types. The only study which examines microporosity separately to the macroporosity divides microporosity observed in Middle Eastern carbonates into four different textural types [130]; microporous grains, microporous fibrous to bladed cement, microporous matrix and microporous equant cement.

2.8.3 Rock Sorting

A useful approach for quantifying grain sorting was proposed by Folk [131], where the grain size distribution was assumed to follow a log-normal distribution. The standard deviation of this distribution then gives an estimation of the grain sorting (table 2.8.3.1). A standard deviation of 1 means the grains vary over a range of approximately one order of magnitude.

Logarithmic Standard Deviation	Sorting Classification
0.00 – 0.35	Very well sorted
0.35 – 0.50	Well sorted
0.50 – 0.71	Moderately well sorted
0.71 – 1.00	Moderately sorted
1.00 – 2.00	Poorly sorted
2.00 – 4.00	Very poorly sorted
4.00 –	Extremely poorly sorted

Table 2.8.3.1: Sorting definitions according to Folk [131].

The logarithmic standard deviation was traditionally estimated using graphical techniques, such as the inclusive graphic standard deviation. This uses a quantity, ϕ , representing the natural logarithm of the grain size.

$$\phi = -\text{Log}_2 d$$

2.8.3.1

The inclusive graphic standard deviation (σ_i) is then

$$\sigma_i = \frac{\phi_{84} - \phi_{16}}{4} + \frac{\phi_{95} - \phi_5}{6.6}$$

2.8.3.2

where φ_5 , φ_{16} , φ_{84} and φ_{95} correspond to the 5th, 16th, 84th and 95th percentiles respectively. We can now estimate the standard deviation directly, however, by extracting the grain size distribution from a micro-CT image and then fitting a log-normal distribution to it (section 5).

3 Image Processing Techniques

Before images can be analysed, significant processing needs to be done on the image to increase the signal to noise ratio, remove any artefacts present, and segment the image. Here we will review some of the key existing techniques available for this process. These methods will not only be described, but also assessed using quantitative performance metrics. Techniques developed during this PhD will be described along with the results they were used to analyse in section 6.

3.1 Artefact Removal

Shortcomings in the image acquisition process can lead to artefacts being imposed upon the base signal of an X-ray scan (see, for example, [117]). These can include experimental failures, such as image noise due to a low count of incoming radiation, or image blur due to sample movement. The impact of these artefacts can be reduced using better experimental design, or the denoising techniques outlined in sections 3.2. Less trivial image artefacts include those arising from defects in the detector array (particularly ring artefacts), or the beam hardening of polychromatic beams (due to differential absorption of different X-ray frequencies), which manifests itself in the reconstructed image as streakings around high attenuation materials and intensity variation with distance to the sample centre. This intensity variation can either be such that the highest grey-scale for a particular material is found at the edge of an image (beam hardening), or that it is found in the centre, where it is caused by imperfect image reconstruction.

The impact of ring artefacts can be reduced experimentally by moving the sample slightly perpendicular to the beam direction by small known amounts on each projection in the process of dynamic ring removal. Prior to reconstruction these projections are then translated by the amount that the sample has been moved by. This has the effect of distributing the impact of any defects in the detector array across a wider area of the sample. Any ring artefacts will then be transformed

from sharp rings to more easily removed diffuse rings. Ring artefacts can also be removed numerically at the sinogram stage, as in this representation the rings appear as vertical lines, which can then be removed either using moving window normalization [132] or using Fourier filtering [133].

The removal of streaking artefacts due to beam hardening remains an unresolved problem [134]. The removal of intensity bias is, however, much easier and can be done by fitting some function to the intensity profile. This can be done iteratively, using exponential and trigonometric functions [135], or much more simply using a single quadratic function.

3.2 Denoising

As well as systematic artefacts, any experimentally derived image will also be subject to random noise. This noise will be homogenous through the sample, as opposed to the localised artefacts discussed above. Noise reduction algorithms typically act through a filter, where the grey-scale of a particular voxel of the reconstructed image is altered using some algorithm using a neighbourhood of local voxels. The simplest denoising algorithms act isotropically, including the mean and Gaussian filters. These replace the grey-scale value of a voxel with either the mean or the Gaussian weighted mean of the surrounding voxels within the local neighbourhood. Although this can be very effective at reducing noise, these methods tend to blur the interfaces between different phases. More complex filters which reduce noise levels while maintaining interface sharpness are called edge-preserving filters.

The simplest edge preserving filter is the median filter. In this algorithm the grey-scale of a voxel is replaced by the median value of the local neighbourhood (e.g. [136]). This keeps edges sharp, as the new grey-scale value is the value associated with an original voxel. The amount of denoising introduced is, however, small compared to other edge preserving filtering techniques, and if the amount of denoising is increased, the edge preserving ability of this algorithm can be degraded.

Another popular edge preserving denoising method is the anisotropic diffusion (AD) filter [137, 138]. The rationale behind this method is that areas of high average grey-scale gradient are likely to be the interfaces between materials, whereas the areas of low average grey-scale gradient are likely to be the central portions of phase regions. As the Gaussian distribution is the solution to the diffusion equation with a constant diffusion coefficient, a modified Gaussian smoothing with a strongly varying standard deviation can be applied such that the standard deviation of the Gaussian is inversely proportional to the grey-scale gradient in any particular direction. Areas of low grey-scale gradient (the interiors of phases) will be heavily smoothed, reducing noise, whereas the interfaces between phases are smoothed relatively little, retaining their sharpness.

A fairly recent development in image denoising is the non-local means filter [139, 140]. Unlike the previous edge preserving filters, this is a linear filter where the grey-scale of a certain voxel is replaced by the average of the grey-scales of other voxels. In contrast to the standard mean filter, however, each voxel within the search area is assigned a weight proportional to an index measuring the similarity of the weighted voxel to the voxel being replaced by the filter. Each voxel is essentially averaged with other voxels similar to it, including interface voxels, meaning that edges are preserved. It can potentially use the entire image for comparison, resulting in a large increase in the signal to noise ratio; however this tends to be extremely computationally costly. Usually the implemented algorithm uses a local search window and acts in 2D.

In order to assess the efficacy of these different denoising techniques in this thesis, a quantitative study of their effects on a Bentheimer sandstone image was undertaken, the results of which can be seen in figure 3.2.1.

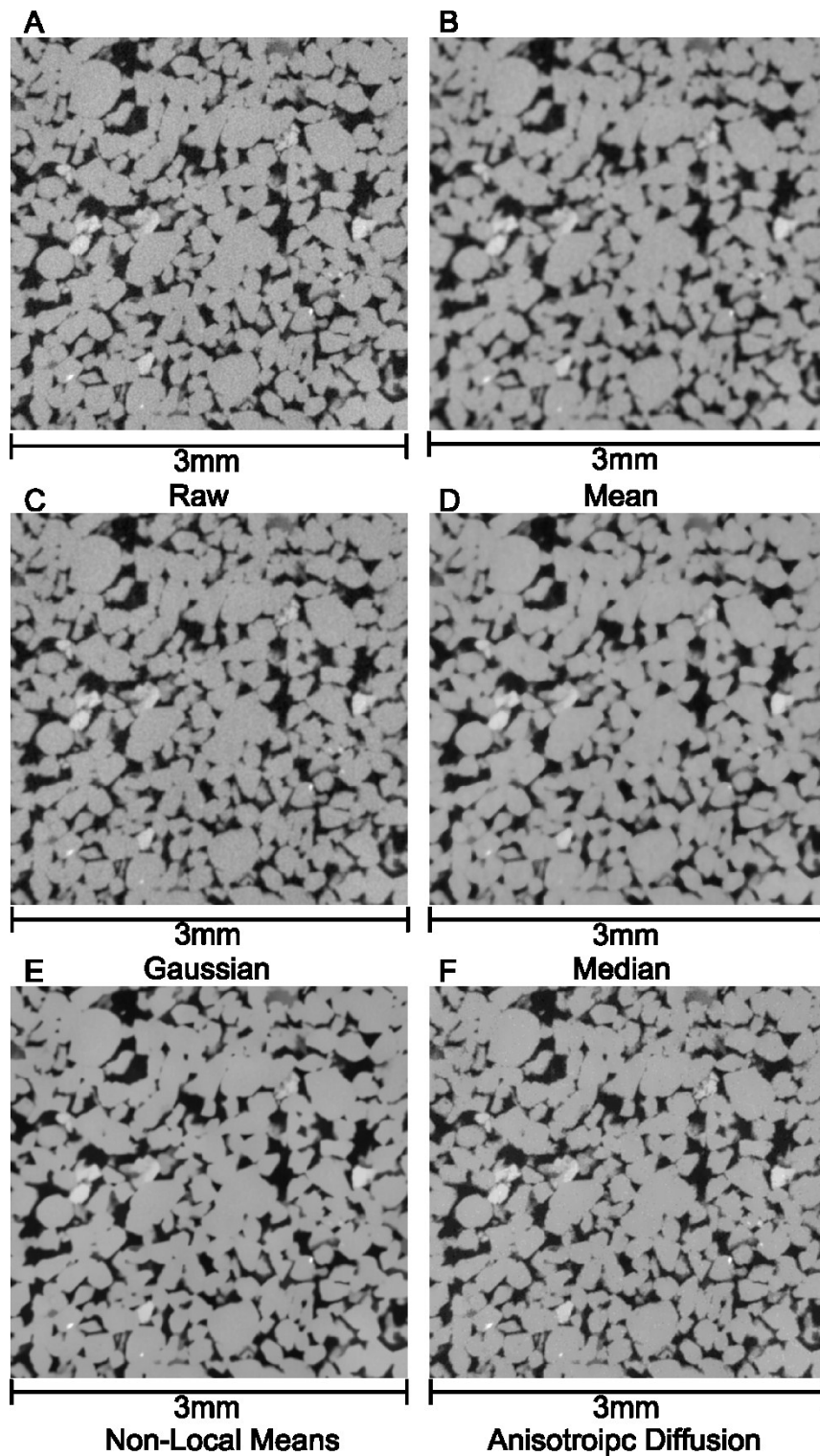


Figure 3.2.1: Graphical impact of different denoising methods on a dry Bentheimer micro-CT image.

A) The raw image. B) A mean filter. C) A Gaussian filter. D) A median filter. E) Non-Local Means. F) Anisotropic diffusion.

The signal to noise ratio and edge width was found both before and after each of the filtering mechanisms. The signal to noise ratio was found by first calculating the means (m_1 and m_2) and standard deviations (σ_1 and σ_2) of the grey-scale values within the rock and the pore-space respectively. The signal to noise ratio was then given by:

$$\text{Signal to noise ratio} = \frac{m_1 - m_2}{\frac{1}{2}(\sigma_1 + \sigma_2)}$$

3.2.1

and the edge width was estimated by finding the $\frac{1}{4}$ and $\frac{3}{4}$ intervals across a randomly chosen grain edge interface (as shown in figure 3.2.2).

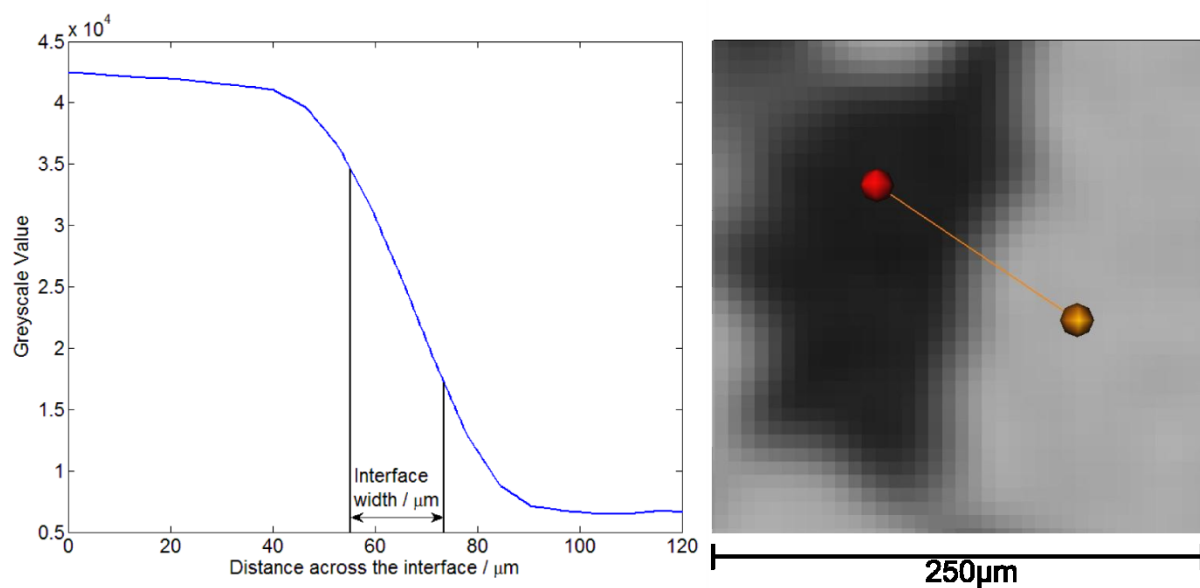


Figure 3.2.2: The definition the edge preservation metric used to assess the efficacy of different filtering techniques. A) Interface width was found by measuring the distance from the $\frac{1}{4}$ point across the interface to the $\frac{3}{4}$ point across the interface.

The results of this comparison are shown in table 3.2.1.

	Raw	Mean	Gaussian	Median	Anisotropic Diffusion	Non-Local Means
Signal to Noise Ratio	8.4	9.3	10.0	10.0	11.1	12.1
Interface Width / μm	11	18.1	14.2	10.8	9.9	10.5

Table 3.2.1: A comparison of the results from a metric based test of different denoising methods

The non-local means filter both increases the signal to noise ratio the most and does not increase the interface width from the raw image. For this reason it was the preferred image denoising technique used in this study (with the results of its use shown in section 6).

3.3 Image Segmentation

Once an image has been processed, and prior to any analysis, the image must be separated into the different phases present in the process of segmentation. It is a crucial step that affects all subsequent analyses.

3.3.1 Global Segmentation

The simplest segmentation technique is global thresholding, where any grey-scale below some globally defined threshold is assigned to one phase and any grey-scale above the threshold to another. The process of deciding the threshold to apply usually uses a histogram of the grey-scale values within an image, an example of which is shown in figure 3.3.1.1:

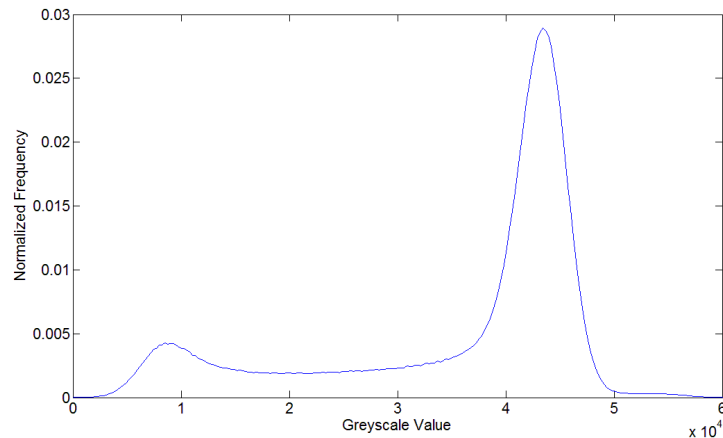


Figure 3.3.1.1: A histogram of the different grey-scale values for the raw Bentheimer scan shown in figure 3.2.1 A.

A threshold can then be applied at a minimum grey-scale value between the two phase end members. This can be problematic as, although the peaks in this distribution due to the pore and grain phases are clear, the distribution of grey-scale values are not entirely separated, and many voxels have intermediate grey-scale values between the two phase peaks. These voxels typically occupy the interface region between different phases and so suffer from partial volume artefacts. This is when a particular voxel is not entirely occupied by a single phase, giving it an effective attenuation intermediate between the two different phases. As the fraction of the voxel that is occupied by either phase varies continuously, the interface voxels can have any grey-scale between the two different end members. Any threshold applied here will misidentify certain voxels, particularly on the interface between different phase regions. Also the position at which to pick the threshold is arbitrary and prone to operator bias. Even in this relatively simple case, the threshold could be picked anywhere from 1.5×10^4 to 3×10^4 . A suite of techniques exist to remove operator bias and objectively estimate threshold position, such as multi-Otsu maximum variance thresholding [141] and maximum entropy segmentation [142]. Although these techniques remove operator bias, the issue of partial volume artefacts and voxel misidentification remains. For multiple fluid images this problem is even more severe (figure 3.3.1.2), and the segmentation of images containing a

partial saturation of multiple fluids is significantly more difficult than the segmentation of dry images [143].

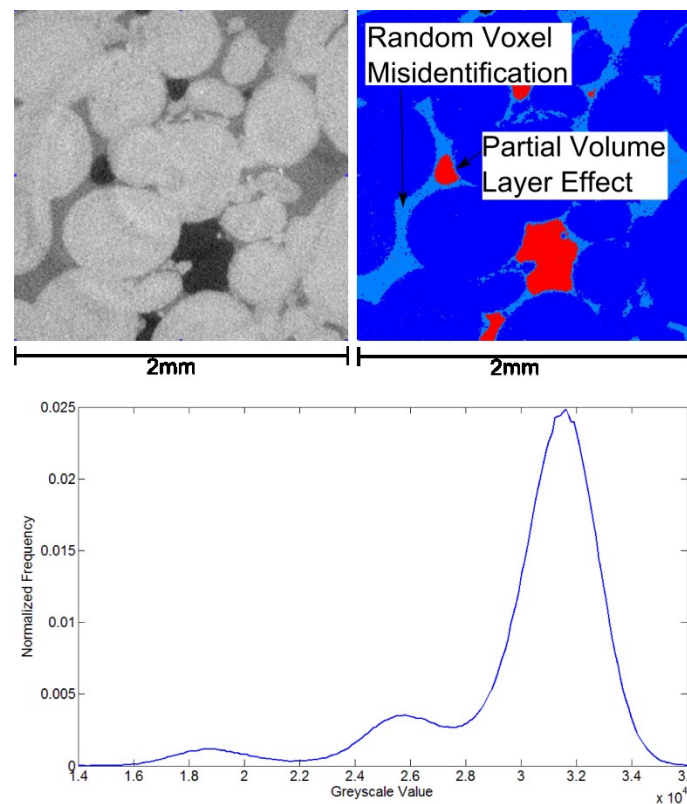


Figure 3.3.1.2: Some of the issues associated with simple universal thresholding on a multiphase image. A) The raw dataset. B) Different issues associated with thresholding, including random voxel misidentification and the partial volume layer effect. C) A histogram from the multiphase image.

The histogram can be improved significantly using the process of histogram bias correction.

Although many techniques exist for this, one key technique is gradient masking. As mentioned above in section 3.2, the interface regions tend to have high grey-scale gradients. By only measuring the voxels below some threshold gradient, we are essentially taking a histogram of only the centres of phase regions. A resulting histogram can be seen in figure 3.3.1.3.

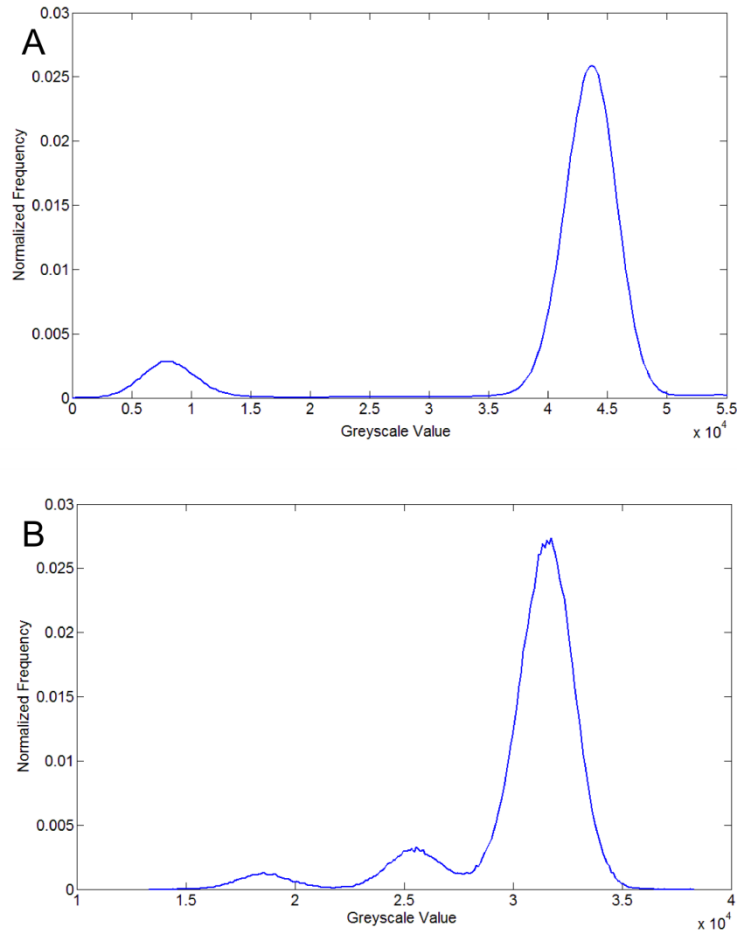


Figure 3.3.1.3: Histograms for the low gradient areas of a dry Bentheimer image ((A), figure 3.2.1) and a wet Ketton image ((B), figure 3.3.1.2).

Although the resulting histograms are now much less ambiguous, with very few voxels with grey-scale values between the two end members, any threshold applied universally from these images will still encounter the partial volume effects and voxel misidentification described above. Another approach is to use these histograms to segment the voxels from which they were generated, however in this case only a fraction of the image will be segmented, essentially the centres of each phase region. These images can then be used as the seeds for region growing algorithms, used to assign segments to the rest of the image, as described below.

3.3.2 Region Growing – Local Segmentation

Whereas global, histogram-based thresholding, relies on a single uniform threshold to completely assign voxel labels, region growing or local segmentation algorithms also account for local properties in label assignment. Once again there is a suite of different techniques available, including bilevel segmentation [144] and indicator kriging [145], and a full review of these techniques can be found in Schluter *et al.* [134]. One key technique used heavily in this thesis is the watershed algorithm, which is outlined below.

3.3.3 The Watershed algorithm

A watershed algorithm works by finding the catchment basins of a hypothetical three-dimensional topography defined by the intensity map in an image. This intensity map can be any of the attributes associated with an image, and the algorithm is very versatile and can be applied to a number of different problems. Two applications of this algorithm used in this study are watershed on the grey-scale gradient, used during segmentation (section 5-6), and watershed on the Euclidian distance map of a label image, used during pore classification (section 6.2 and 6.4) [118, 146]. The generic watershed algorithm is outlined below.

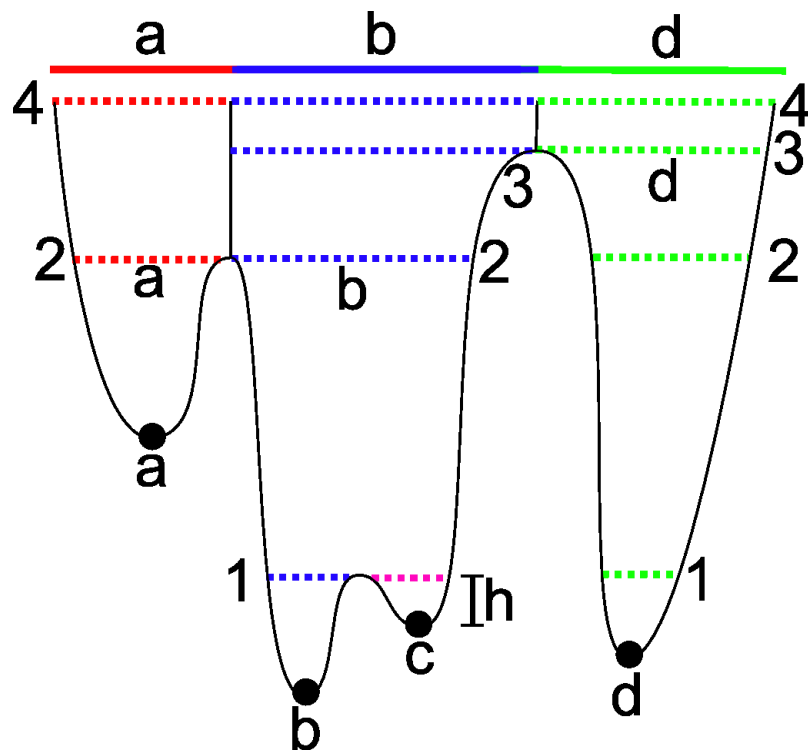


Figure 3.3.3.1: The generic watershed algorithm.

First local minima are located in the intensity function. This can be seen in figure 3.3.1.1 as the points a, b, c and d. These minima are then grown progressively up the contours in the intensity function, defining progressively larger proportions of the total number of voxels into different basins. Certain thresholds can be applied such that small local minima (such as basin c at position 1 in figure 3.3.3.1) do not create many spurious basins, but instead are merged into the basins associated with larger regional minima. These basins progressively grow up through the intensity map until they reach maxima in the intensity function, where they come into contact with neighbouring basins. At this point the interface stops moving, as all the voxels along that interface (the interface between basins a and b at position 2 in figure 3.3.3.1) are now classified. This process proceeds until all the voxels in the parameter space are classified.

This generic watershed algorithm is extremely useful, when conducted on a Euclidian distance map, for separating connected objects, such as grains in a consolidated rock (section 5). A Euclidian distance map is constructed from a label image, such that the grey-scale within each voxel

seed, as explained in section 3.3.1 above. Another method is to use a 2D histogram to describe the full distribution in both the grey-scale and the gradient of the grey-scale [147]. Such a 2D histogram is shown in figure 3.3.3.2.

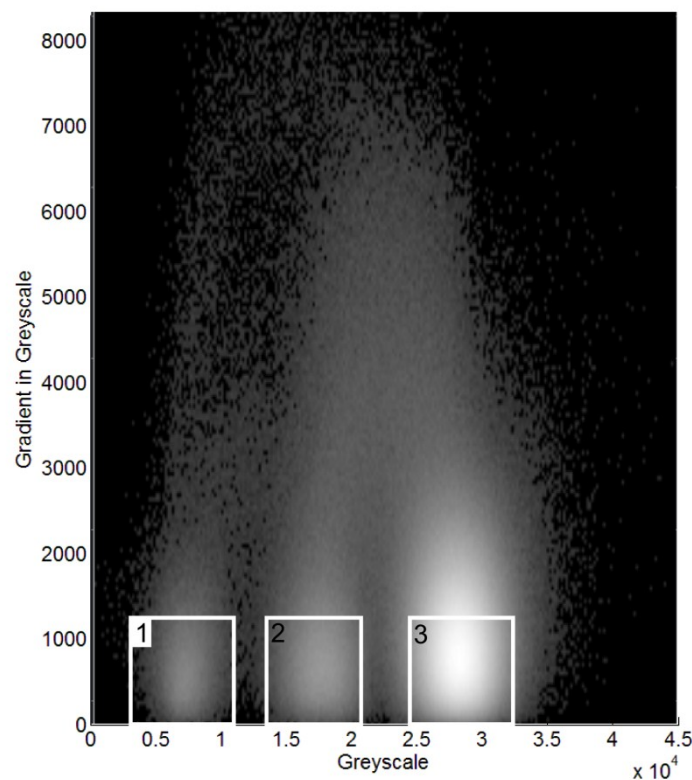


Figure 3.3.3.2: A 2D histogram used to describe seeds used in watershed segmentation, described in Jones *et al.* [147]. Each pixel on the plot represents a bin of specified grey-scale (x-axis) and grey-scale gradient (y-axis). The brighter the pixel, the more voxels fall within that bin. Seed regions can be described at low gradient areas where each phase region is unambiguously described. Three different phases can be identified, denoted by region 1, 2 and 3 on the figure.

Seed regions can be defined interactively in this way to get the best possible seed assignment. It is also possible to iterate between seed generation and watershed progression in order to get the best possible segmentation result. Once seed regions are assigned, they grow to areas of progressively higher grey-scale gradient, corresponding to the interfaces between phase regions. As different

regions of the seed can be assigned to different phases a-priori, when two basins of the same phase come into contact, they merge (as seen in figure 3.3.3.2, position one, where basins a_1 and a_2 merge), forming a larger connected phase cluster. When two basins of different phases come into contact (as in position 2, with phase a and phase b) this position defines the phase boundary. This process progresses until the entire of the image is assigned to different regions for each phase.

3.3.4 Simple Thresholds vs. Watershed

To compare the different segmentation techniques in this work a sensitivity study was conducted, for which a synthetic image was required. This provided a “ground truth” by which the efficacy of different techniques could objectively tested. The synthetic image was created by taking a segmented label image of real data and transforming it such that each label value corresponded to the mean grey-scale value within each phase of the real data. Gaussian noise was then created in the data, with the grey-scale standard deviation of the noise equal to the average internal grey-scale standard deviation within each phase of the original image. To simulate partial volume artefacts, a mean filter was passed over the sample, blurring the interface between different phases. Finally a ring artefact was introduced, creating a final synthetic image (figure 3.3.4.1).

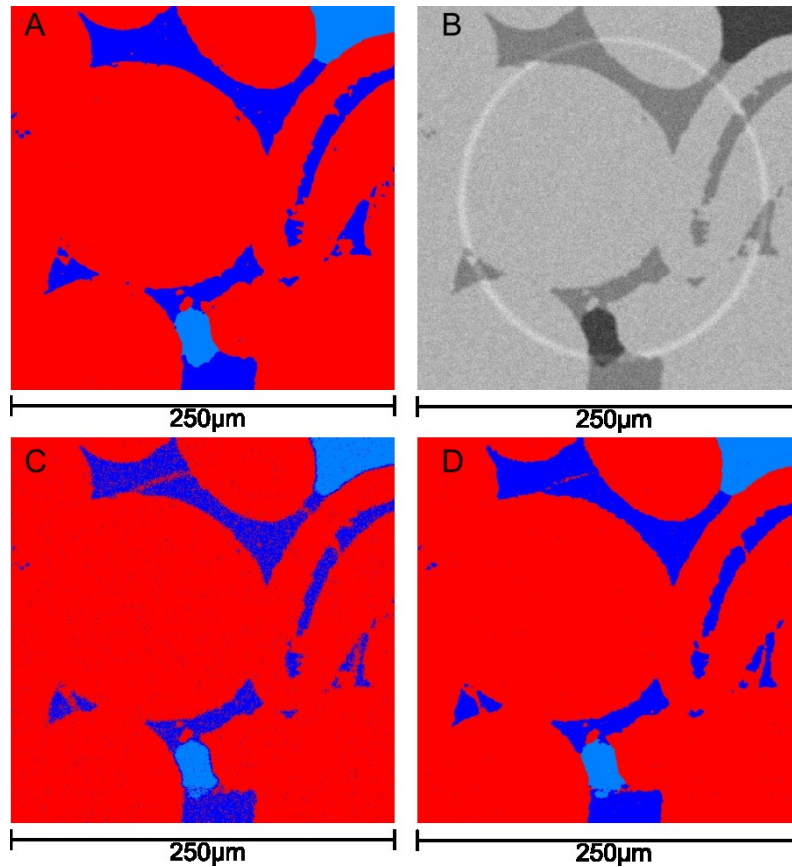


Figure 3.3.4.1: A synthetic image (B) was created from a label image (A) then resegmented using both simple grey-scale based segmentation (C) and watershed segmentation (D), seeded using a 2D histogram.

This image was then segmented using simple global thresholding and watershed segmentation, using a 2D histogram to generate the image seed, and the resulting segmented images compared to the original label image from which the synthetic image was generated (table 3.3.4.1). The watershed segmentation outperformed the global thresholds on multiple quantitative metrics, and on qualitative visual inspection. Qualitatively watershed segmentation did not produce voxel misidentification associated with the partial volume layer effect (section 3.3.1, figure 3.3.1.2). It also dealt with the ring artefact much better.

	Mislabeled Voxels - total	Mislabeled Voxels – high gradient
Simple Thresholding	4.99×10^6	2.15×10^6
Watershed Thresholding	1.71×10^6	1.10×10^6

Table 3.3.4.1: Results from the comparison between simple and watershed thresholding.

Quantitatively watershed segmentation produced approximately $\frac{1}{3}$ the number of mislabelled voxels that the global thresholding method produced, and approximately $\frac{1}{2}$ the number of mislabelled voxels in the high gradient regions, corresponding to phase interfaces. Although using synthetic images can be problematic, as doubts can remain about the applicability of artificial noise to real systems, watershed segmentation appears to be the best choice for the segmentation of challenging, multiphase images. For this use it was the preferred 2 phase and 3 phase segmentation technique used in this study, with the results of its use shown in section 6.

4 Experimental Methods

In this section we shall examine the techniques used in the acquisition and analysis of micro-CT images at reservoir conditions common to all the different experimental applications. The techniques unique to each application are discussed separately at the beginning of the discussion of each of the results associated with each application.

4.1 Experimental Technique Development

To successfully image the in-situ arrangement of scCO_2 and brine a novel and highly sensitive experimental apparatus was created, primarily focussed on use in the Versa XRM 500 X-ray microscope (section 4.2). The requirements for conducting experiments at elevated temperatures and pressures (HPHT) are very stringent, and require recent developments in materials, micro-CT facilities and computing resources. The key requirements that have to be fulfilled are that any core/sample holder needs to be able to withstand HPHT conditions while remaining sufficiently X-ray transparent to allow for effective imaging. Lab-based instruments impose an additional constraint, in that the core-holder must be small enough such that geometric magnification is effective. Although this constraint has been relaxed somewhat with the advent of newer lab-based micro-CT machines with the introduction of secondary optics, it has not been completely removed. Although resolution may be maintained at larger source-sample and sample-detector distances, the intensity of the X-ray beam still decreases with the square of the distance between the source and the detector. This means that longer exposure times must be used for a given signal/noise ratio, increasing overall scan acquisition time. Increasing acquisition time not only reduces the scanner's effective productivity, but means that the sample is more likely to move during image acquisition, causing blurring in the reconstructed images.

Experiments with soluble fluids are an additional challenge when using lengthy acquisition times. As CO₂ will diffuse through the plastic portions of the experimental assembly, and keeping the in-situ saturation constant is a challenge. All these issues meant that scan times longer than around 2 hours were impractical. In order to keep scan times below this stringent requirement, the core-holder must be around 1 cm in diameter.

The flow cell used in these experiments was based on a traditional Hassler cell design, built around a carbon fibre sleeve (Airborne Composites, The Hague, Netherlands). Two cell designs have been produced, for different applications. The first sleeve design is similar to that used by Iglauer *et al.* [119], with two significant alterations:

- 1) The sleeve has been elongated from 212 mm to 262 mm allow the sample source and detector to be as close to the sample as possible.
- 2) The carbon fibre composite used in the sleeve manufacture were changed from T700 fibres, with a stiffness of 230 GPa, to M55 fibres, with a stiffness of 550 GPa. This not only reduced the amount of sample movement during tomography acquisition, but also increased the maximum working pressure of the cell from 20 MPa to 50 MPa.

The second flow design is intended for use at synchrotron light sources. It is also made of the new M55 fibres, but is much shorter at 110 mm, in order to reduce sample motion during rapid tomographic rotation. This was enabled by the use of a parallel beam, removing the requirement for the source and detector to be extremely close to the sample.

A major experimental shortcoming in the first study to use micro-CT to examine CO₂ at reservoir conditions was the use of metal lines to control the flow to and from the core-holder. As the sample is rotated relative to the pumps, the flow lines also need to be rotated. Stiff flow lines can cause the sample to move, reducing image resolution or making some or all of the dataset unusable. To prevent this we replaced all the flow lines close to the rotation stage with flexible polyether ether

ketone (PEEK) tubing (Kinesis, St. Neots, UK, Part Number: 1560xL). These flow lines were flexible, providing very little lateral load to the core-holder during acquisition. We also attached the flow lines to valves attached to the sample stage, rather than attaching the flow lines to the coreholder. This meant that any existing flow-line load was transmitted directly to the stage, rather than to the sample, reducing the probability of sample motion.

A major disadvantage of using the PEEK tubing was that CO₂ was able to slowly diffuse through it, over a timescale of around 24 hours. This meant that CO₂ saturated brine left in the flow lines would gradually desaturate. This was avoided by careful planning of the experimental protocol.

Another major experimental shortcoming of the first study to image CO₂ at reservoir conditions [119] was inaccurate control of temperature. This can impact results in a number of ways. Firstly, temperature is a strong control on both interfacial tension and contact angle (sections 2.1 and 2.3 respectively). Furthermore, the solubility of both CO₂ and carbonate rock in brine is also highly temperature dependent. When scCO₂ is injected into a saline carbonate aquifer it will dissolve into the resident brine, forming a highly reactive carbonic acid, which will in turn start to dissolve any calcite present. To prevent this, and represent conditions in the aquifer far away from the injection site, the brine was pre-equilibrated with scCO₂ by vigorously mixing the two fluids together with small particles of the host rock in a stirred and heated reactor (Parr Instruments Co., IL, USA). The higher the temperature the less soluble both calcite and CO₂ are in the brine (Carroll *et al.* [35], section 2.6), so if the core and the reactor where equilibration takes place are not at exactly the same temperature, departure of CO₂ from equilibrium can lead to either the dissolution or exsolution (where dissolved CO₂ comes out of the brine due to the solubility state of the brine changing) of CO₂.

Previous studies used a heated confining fluid to heat the coreholder; however this was problematic. It has the disadvantages of the difficulty of accurately maintaining a constant confining pressure using a recirculating water supply, requiring extra heating baths for that supply, only having accurate

control of temperature at the point of the heating bath (not at the point of the core holder, as the confining fluid would cool between the water bath and the core holder). It would also require both an inlet and an outlet port for the confining fluid, increasing the number of fluid lines attached to the core-holder and so increasing flow line load.

Instead, a flexible heating jacket was used to surround the core holder. This very simple heating method resulted in very little coreholder load, and allowed for the precise and accurate heating. An extremely thin polyimide (Kapton) heating film was used (Omega Engineering, www.omega.co.uk), in order to minimize sample size. The construction of this film consists of an etched copper foil element 0.0127 mm thick, encapsulated between two layers of 0.0508 mm polyimide film. The copper elements present in the jacket did not noticeably affect image quality. Temperature was measured using a thermocouple sitting in the confining annulus of the cell (Omega Engineering, www.omega.co.uk). It was positioned on the outside of the confining sleeve, as close as possible to the core, ensuring an accurate, reliable and stable reading of the pore-fluid temperature. The thermocouple and heating film were connected to a custom build Proportional Integral Derivative (PID) controller, and temperatures were controlled to within $\pm 1^{\circ}\text{C}$.

High pressure syringe pumps were used to maintain pressure and control flow in the pore-space of the rock and in the reactor (Teledyne Isco, Lincoln, NE, USA, Model: 1000D), with a displacement resolution of 25.4 nl.

4.1.1 Lab-based Micro-CT Experiments

The experimental apparatus used in this study is shown in figure 4.1.1.1 – 4.1.1.3.

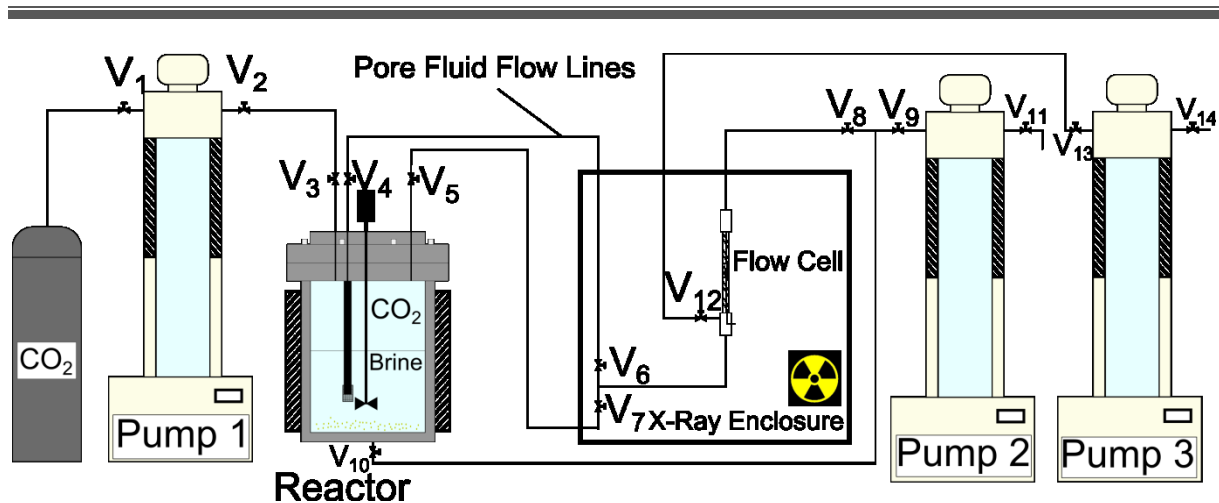


Figure 4.1.1.1: The pumps and valve arrangement used to control fluid flow, and the seating of the cell within the micro-CT enclosure.

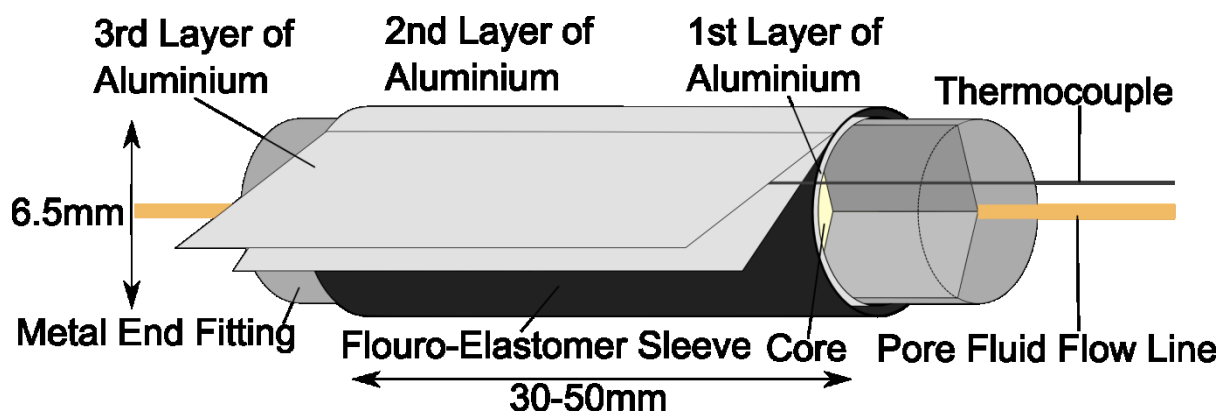


Figure 4.1.1.2: Detail of the core-assembly within the flow cell, showing a triple aluminium wrap around the core, preventing diffusive CO_2 exchange across the Viton sleeve.

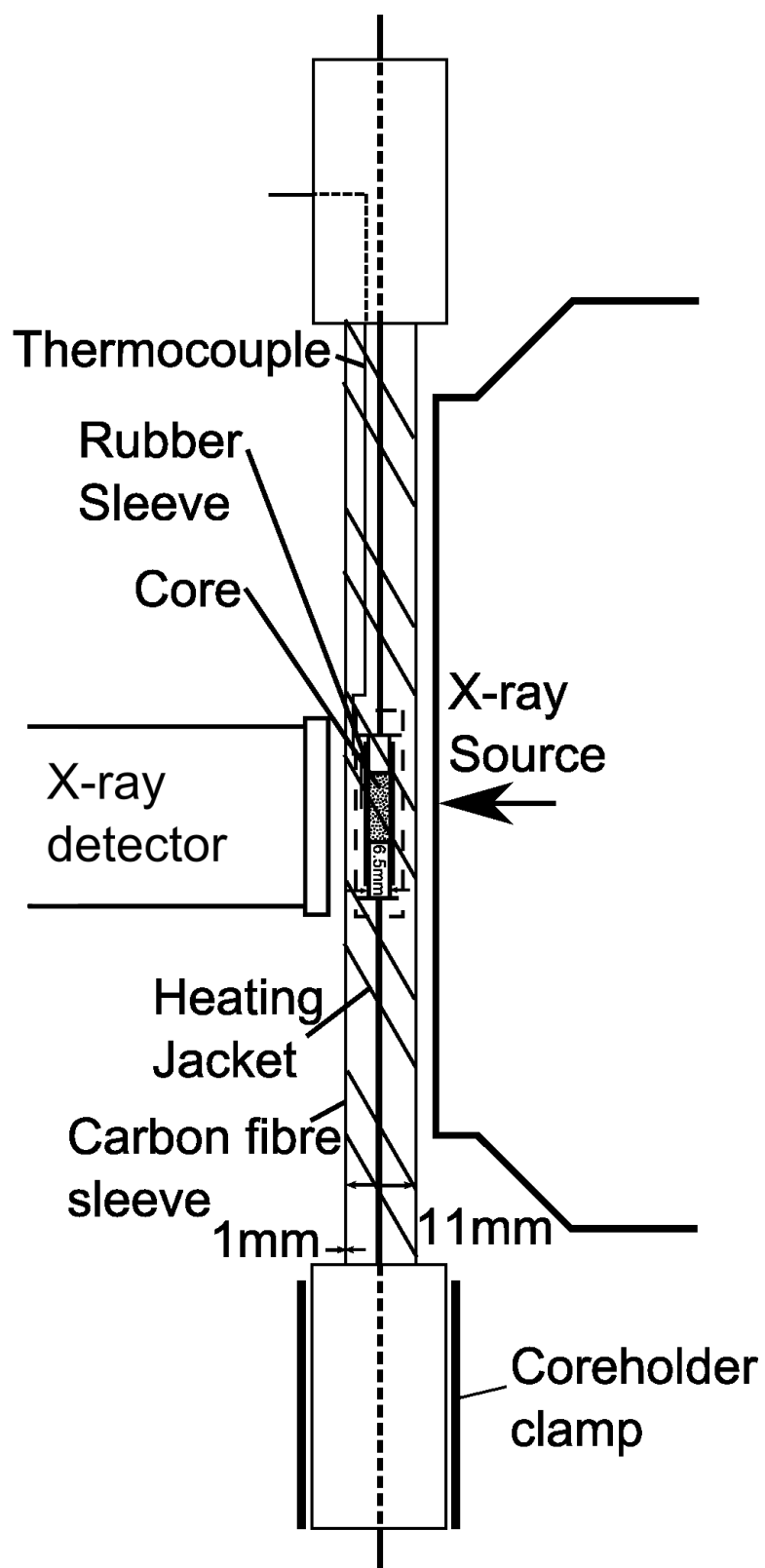


Figure 4.1.1.3: Detail of the flow cell, heating apparatus and the siting of the core assembly.

The samples were drilled into cylindrical cores 4-6.5 mm in diameter and 30 mm to 50 mm in length. These cores were then placed within a fluoro-polymer elastomer (Viton) sleeve, which was attached to metal fittings connecting the core to the pore-fluid flow lines (figure 4.1.1.2). This assembly was then placed within the high-temperature high-pressure flow cell described above (figure 4.1.1.3). To prevent diffusive scCO_2 exchange across the elastomer sleeve, the core assembly was wrapped three times in aluminium foil, once between the core and the sleeve, once between the Viton sleeve and the thermocouple, and once outside of the thermocouple.

4.1.1.1 Experimental Protocol

The basic protocol for each experiment conducted in the Versa lab-based micro-CT is given here. Slight differences in protocol for different experiments used for different analyses are given at the beginning of each of the results descriptions in section 6. Fluids were injected under conditions analogous to the “unsteady state” conditions used in larger scale core-flood experiments. The objective of these experiments is to image fluid distributions at the pore scale after drainage (CO_2 injection) and imbibition (brine injection) at representative conditions.

Each experiment consisted of the following steps:

- 1) Place the brine in the base of the reactor and seal the reactor. Brine composition is discussed in section 4.2.1.
- 2) Close all valves apart from valve 1, 2 and 3, as defined in figure 4.1.1.1. Load CO_2 from the cylinder into pump 1 and the reactor then close valve 1.
- 3) Slowly the temperature and pressure within the reactor to that desired for the pore fluid during the experiment.
- 4) Vigorously mix the reactor for at least 12 hours to ensure all phases are in chemical equilibrium prior to injection.

-
- 5) Open valve 13 and load the confining fluid into pump 3. Close valve 14. Open valves 12 and 13. Pressurize the confining annulus of the cell to at least 10% higher than the proposed pore fluid pressure.
 - 6) Open valve 11. Load brine into pump 2. Close valve 11 and open 9, 8 and 6.
 - 7) Slowly pressurize the pore-space of the rock until it is at the desired pore-fluid pressure, filling the pore-space of the sample with brine that has not been equilibrated with scCO₂.
 - 8) Open valve 4. Flush more than 1,000 pore volumes of equilibrated brine through the core by refilling pump 2 at a constant flow rate. This will miscibly displace un-equilibrated brine, ensuring 100% initial brine saturation and creating conditions in the core akin to the subsurface conditions in an aquifer at a point slightly ahead of the front of a scCO₂ plume. Pore volume is found by multiplying the core volume by the porosity found using helium porosimetry.
 - 9) Pass through 10 pore volumes (around 1ml) of scCO₂ through the core at very low flow rates ($1.67 \times 10^{-9} \text{ m}^3/\text{s}$), ensuring a low traditional capillary number (equation 2.5.1.1) of around 10^{-6} . Continually take 2D projections in order to accurately measure the total injected volume by observing the point when scCO₂ displaces the brine in the pore-space.
 - 10) Pass through 10 pore volumes (around 1ml) of equilibrated brine through the core at the same low flow rate, causing scCO₂ to become trapped as a residual phase in the pore-space.
 - 11) After steps 9 or 10 take tomographies of the sample to image the fluid distribution after drainage or imbibition respectively. Use a voxel size such that the entire diameter of the core fits within the field of view.
 - 12) Reconstruct the scans using proprietary software on the versa system. To scan the entire length of the core while retaining a small voxel size, reconstruct composite volumes by stitching together multiple overlapping sections, acquired sequentially.

4.1.2 Synchrotron Tomography Experiments

A variant of the experimental equipment described in section 4.1.1 was used at Diamond Light Source, a synchrotron based in Didcot, UK, to examine dynamic processes using fast tomography. Although the arrangement of the pumps in the system were not changed from those described in section 4.1.1 and shown in figure 4.1.1.1, the flow boundary conditions and core assembly were changed. The new core assembly is shown below in figure 4.1.2.1

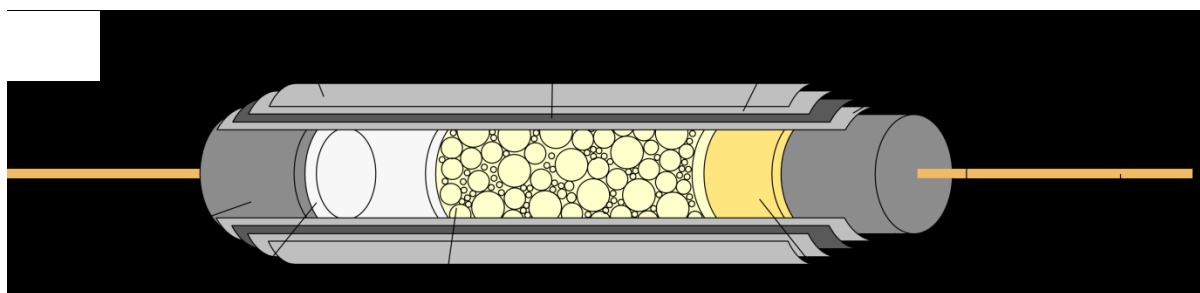


Figure 4.1.2.1: Detail of the core assembly showing a triple aluminium core wrap, a low permeability porous plate used for flow control and the plastic spacer used to monitor the CO₂-brine interface during system pressurization.

The principal challenges when imaging the dynamic displacement of fluids at representative subsurface flow conditions, apart from the challenges of equipment dealt with in section 4.1, are associated with dead volume. Previously published ambient condition experiments [85, 106, 148] used small volume low pressure integrated fluid pumps located extremely close to the rock core, meaning that the experimental assembly had a small dead volume relative to the pore volume. Working at high pressures and temperatures, however, requires large high pressure syringe pumps, which are connected to the core using long lengths of flexible tubing (figure 4.1.1.1). The dead volume of the system (defined as all the volume of fluid outside the rock core) is many orders of magnitude larger than the internal pore volume of the core. Small changes in ambient temperature can result in changes in the fluid volume within the dead space of the apparatus, which can then change the fluid pressure.

Boundary conditions used in traditional core-flooding experiments (typically constant injection rate on the inlet of the core and constant pressure, or back-pressure, at the outlet) are applied externally using connected pumps, so any small change in internal volume on the inlet (constant flow) side of the core will be compensated for by the outlet (constant pressure) side, causing unwanted fluid flow through the core. This is not an issue in core-scale experiments due to pore volumes and fluid flow rates orders of magnitude larger than those used in pore-scale experiments.

When using reactive fluids (such as CO₂ and brine), requiring equilibration in a reactor prior to fluid injection, dead volume issues are further exacerbated for three reasons. Firstly, the dead volume of the system is increased even further, as the reactors used can be around 1 l, whereas the core pore volume is <0.1 ml. Secondly, actively controlling temperature within the reactor introduces another temperature error, independent from changes in ambient temperature. Finally, the compressibility of CO₂ also presents an issue, as temperature errors are associated with larger changes in volume than relatively incompressible fluids like oil or brine.

At the relatively high fluid flow rates used in static end-point experiments (sections 4.1) these issues can be compensated for by reversing the boundary conditions to constant flow on the outlet face of the core and constant pressure on the inlet face. Any changes in the dead space fluid volume on the inlet side of the core (such as due to changes in reactor temperature) are now compensated for by the injection pump, rather than through the core. The outlet face of the core has a much smaller dead volume, as there is no reactor, and is mostly saturated with incompressible brine, so changes in ambient temperature do not result in significant undesired fluid flow.

At the very low flow rates required for the examination of dynamic flow even the changes in boundary condition described above are not sufficient. The changes in volume on the production side of the core become significant relative to the extremely slow flow rate. To better constrain the flow boundary conditions for the core we propose a new micro-flow arrangement. A constant pressure drop is applied across a low permeability porous plate on the outlet face of the core. This

plate has a much lower permeability than the rock, with a permeability ratio of around 200,000, so essentially the entire pressure drop is across the plate. For this a hydrophilic modified semi-permeable disk (aluminium silicate, Weatherford Laboratories, Stavanger, Norway) with a permeability of $14 \times 10^{-16} \text{ m}^2$ ($14 \times 10^{-6} \text{ D}$) was used.

During the initial phase of non-wetting phase injection (before non-wetting phase reaches the outlet of the core) fully-saturated flow through the porous plate applies a constant flow boundary condition at the outlet face of the core. This is not susceptible to the issues of externally applied constant flow boundary conditions discussed above, because this boundary condition is applied directly to the outlet face of the core, eliminating the impact of any changes in the volume of fluid within the dead space of the apparatus. The minimum flow rate attainable using this method is limited by the minimum pressure drop resolvable across the porous plate; however flow rates can be made smaller just by using thicker porous plates.

When the non-wetting phase impacts the porous plate, the pressure drop is still maintained across the porous plate, and the system starts to move towards a constant capillary pressure state. As the plate is strongly water-wet and has an extremely high capillary entry pressure (around 1.5 MPa), simple saturated flow stops and capillary pressure increases, draining the smaller pores that remained fully saturated with wetting phase at lower capillary pressures. This has the added benefit of allowing the system to attain much higher initial saturations than would otherwise be available using small micro cores. Drainage finally finishes when the pressure drop across the porous plate is equal to the capillary pressure in the core.

4.1.2.1 Experimental Protocol

The experimental methodology and protocol for the experiments in section 6.4 is presented here.

This represents a modified version of the protocol presented in section 4.1.1.1.

A 4 mm outer diameter polymeric tube was placed at the inlet face of the core so that the CO₂-brine interface could be easily monitored during pressurization prior to drainage. The core was then placed within a fluoro-polymer elastomer (Viton) sleeve, which was attached to metal fittings connecting the core to the pore-fluid flow lines. A thermocouple was mounted near the base of the core outside the Viton sleeve, which was then wrapped twice more with aluminium foil placed and placed within a high-temperature high pressure Hassler type flow cell. The thermocouple was connected to a custom PID temperature controller, which heated the cell using an external Kapton insulated flexible heater. The position of the thermocouple is crucial for accurate temperature control, and by siting it within the confining annulus by the base of the core it is possible to have a constant temperature within the cell throughout the experiment.

The brine used was Potassium Iodide (KI) with a salinity of 1.5 M, well within the range of aquifer salinities [149]. KI was chosen as a solute as it has a high atomic weight, and so a high X-ray attenuation coefficient, allowing for it to be used as a contrast agent, causing a large grey-scale difference between the brine and the CO₂ on the reconstructed tomographies. In order to prevent reaction between the carbonate rock and carbonic acid formed when scCO₂ is mixed with brine, the three phases were mixed together prior to injection in a heated reactor (Parr Instruments Co., IL, USA). High pressure syringe pumps were used to maintain system pressure and control the flow of fluids (Teledyne ISCO, Lincoln, NE, USA, Model: 1000D) with a displacement resolution of 25.4 nl.

Each experiment at the synchrotron light source would consist of the following steps:

1. Raise the pressure and temperature in the reactor to that desired for the pore fluid during the experiment (50°C and 10 MPa) and vigorously mix.
2. Load the core into the coreholder without the flowlines connected to the pumps, and establish a confining pressure of 1 MPa within the cell. This represents the same conditions

of differential pressure (with the confining pressure 1 MPa above the pore pressure) as during the experiment.

3. Image the core along its entire length using a large number of projections (3600). This step is to create a high quality unsaturated image from which the pore-space can be analysed in detail and to which saturated images can be compared.
4. Dismount and disassemble the coreholder, and remove the outlet end-piece from the Viton sleeve. The flowlines were connected to pump 3 and brine was injected, displacing the air in the lines until the end-piece is fully saturated with brine.
5. Re-connect the end-piece to the Viton tube, reassemble the coreholder and remount the coreholder onto the stage.
6. Bring the temperature of the coreholder up to reservoir temperature.
7. Apply a confining pressure of 2 MPa. Increase the pressure in the production line until it reaches 1.5 MPa, keeping the pressure in the core and the injection line at ambient pressure. This will cause brine to flow through the porous plate, gradually saturating the core.
8. When the CO₂-brine interface moves above the core into the polymeric tube, gradually increase the pressure in the injection line and core, keeping the pressure drop across the porous plate around 1.5 MPa, the confining pressure at least 0.5 MPa higher than both the pressure in the production line and the injection line and the CO₂-brine interface within the polymeric tube. This will compress and dissolve any CO₂ in the core until it is fully saturated with brine and bring the core up to reservoir pressure, at which point the pressure in pumps 1 and 3 should be around 10 MPa and in pump 2 (the confining pump) should be around 11 MPa.

-
9. At reservoir conditions there may be some constant offset between the readings in pumps 1 and 3, even if they were correctly calibrated at ambient conditions. In order to find this difference stop pump 3 while running pump 1 in constant pressure mode. Close valves 6, 7 and 8 then open valve 9. The difference between the pressure readings in pumps 1 and 3 will then be the pressure offset between the two pumps.
 10. Close valve 9 and open valves 6, 7 and 8. Reduce the pressure in pump 3, considering the transducer offset between pump 1 and 3, until there is a pressure drop of 0.5 – 1 MPa across the porous plate.
 11. The CO₂-brine interface (located in the plastic spacer before the inlet face of the core) will start to move. Monitor radiographs of the interface until it reaches the inlet face of the core. This can be done either by looking at the raw radiographs or looking at changes in the radiographs relative to the fully saturated state.
 12. Move the core until the region of interest is within the field of view.
 13. Monitor radiographs the core until CO₂ enters the field of view.
 14. As soon as CO₂ enters within the field of view reduce the pressure drop across the porous plate from 500 - 1,000 kPa to 5 kPa (the smallest resolvable pressure drop).
 15. Begin taking tomographies. Exposure time and the number of projections per tomography will depend specifically on the detector and synchrotron light source used. The representative results were acquired using 800 projections with an exposure of 0.04 s.
 16. The qualitative progress of the drainage process can be monitored without stopping the tomography sequence by monitoring changes in the first projection from each tomography.
 17. After no further change can be seen in the CO₂ saturation over the course of 30 minutes stop taking tomographies.

Each of these tomographies was reconstructed using a filtered back projection algorithm [150].

Reconstruction centre was found for the first and last tomography of the sequence and linearly interpolated between these two values. Each reconstructed tomography consisted of around 2200^3 voxels with a voxel size of $1.82\text{ }\mu\text{m}$. Each tomography took around 45 seconds to acquire, with 32 seconds spent taking projections and around 13 seconds spent returning to the initial state and preparing for the next tomography.

4.2 Imaging Strategy Design

4.2.1 Imaging in the Versa scanner

For all applications apart from the dynamic imaging (sections 4.1.2 and 6.4) 3D images were acquired using proprietary software on the Versa XRM 500 system. The Versa system incorporates optical magnification after the scintillator in order to increase resolution while maintaining larger source-sample and sample-detector distances, allowing for high pressure equipment to be incorporated without losing resolution (figure 4.2.1.1).

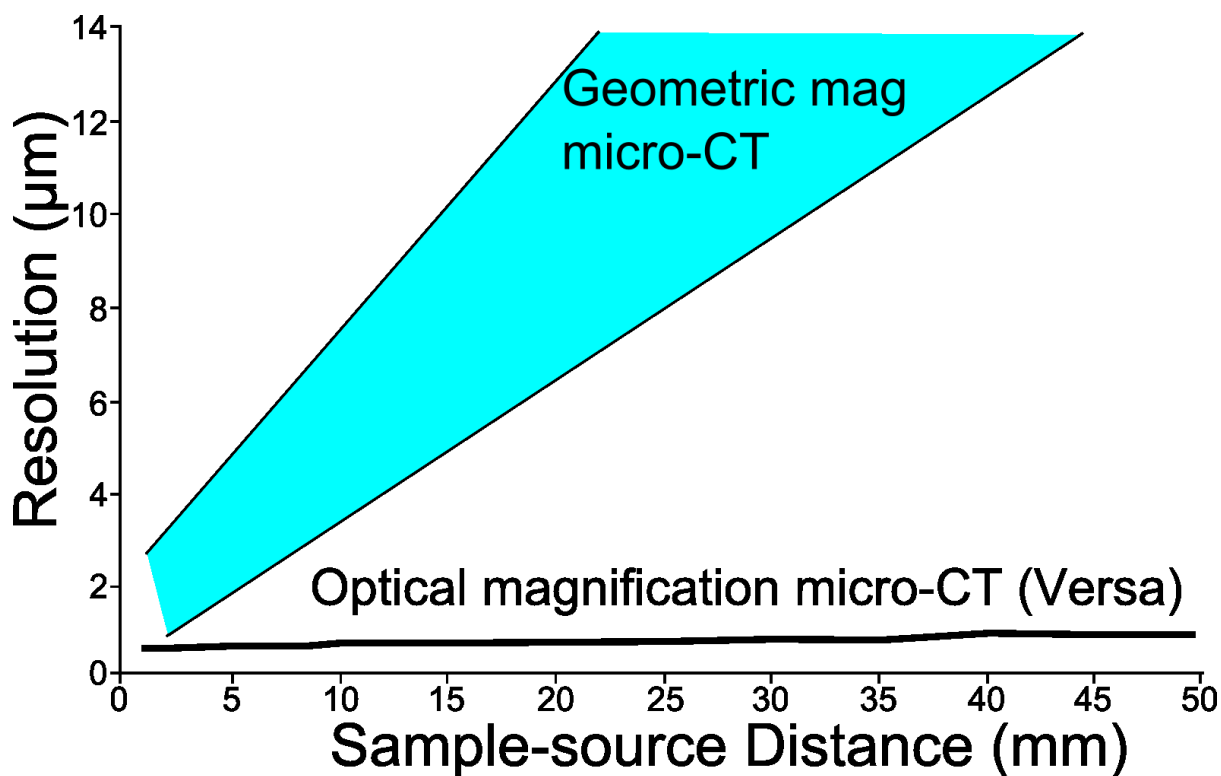


Figure 4.2.1.1: The resolution of the Versa XRM-500 with sample-source distance. High resolutions (small voxel sizes) can be maintained at relatively large sample distances. Figure modified from <http://www.xradia.com/>

For all the areas examined using the micro-CT scanner, including capillary trapping (sections 4.1.1 and 6.1), contact angle measurement (section 6.3) and all the applications related to capillary pressure (section 6.2) the imaging conditions were kept constant, with electron acceleration voltages of 80 kV and currents of 7 mW. The resulting X-ray emission spectra is shown in figure 4.2.1.2, calculated using SpekCalc [151-153].

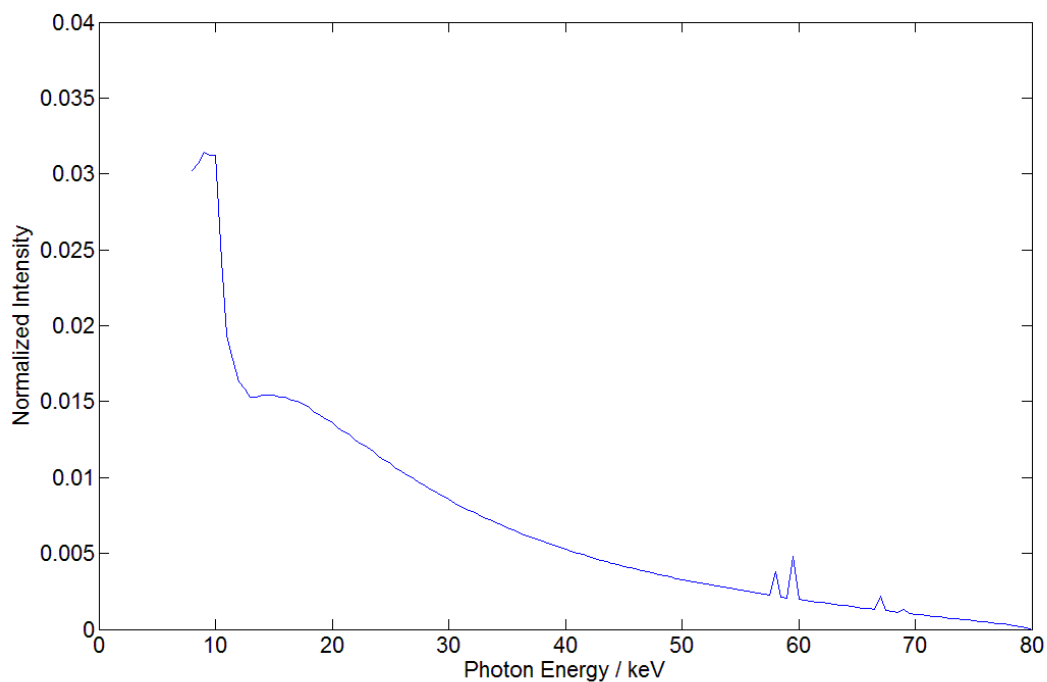


Figure 4.2.1.2: X-ray spectra emitted by the source.

The spectrum as it comes out of the X-ray source is dominated by very weak low-energy X-rays. If these were incident on an imaged area these would be quickly absorbed, changing the transmitted X-ray spectrum, resulting in beam hardening artefacts. These are usually corrected by adding in-line filters to absorb these low energy X-rays. In the high-pressure system, however, the coreholder acts as a filter, meaning additional filters are redundant. The modified spectrum incident on the core inside the coreholder is shown in figure 4.2.1.3.

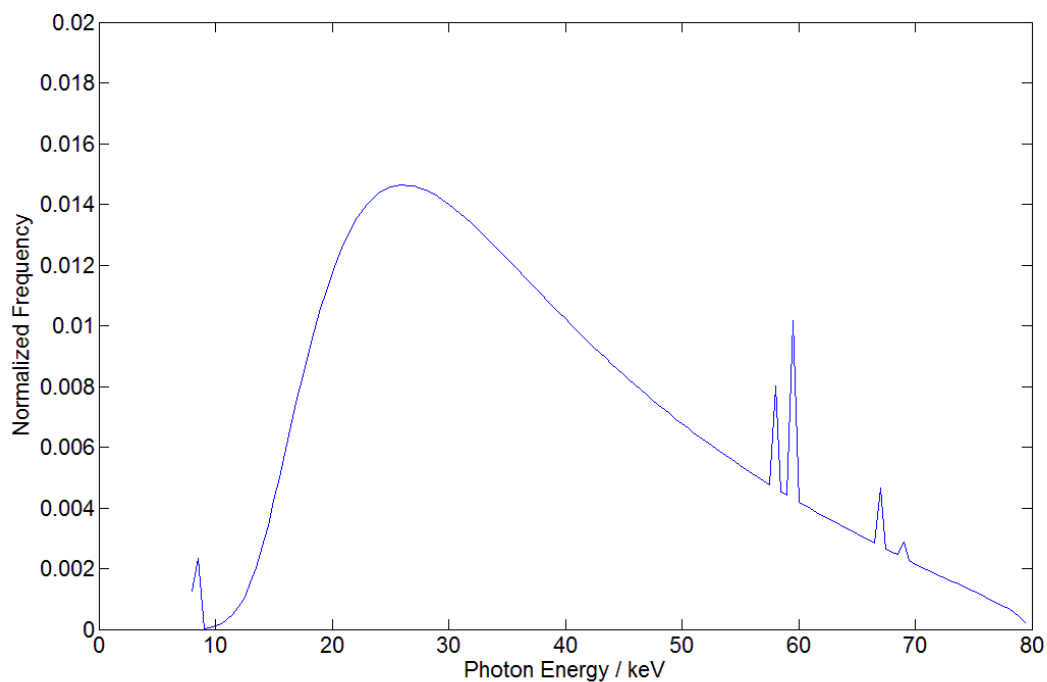


Figure 4.2.1.3: X-ray spectra incident on the sample, filtered by intervening air and core holder assembly.

The incident X-rays range from 15-80 keV. The sharp peaks in the spectrum are characteristic X-rays from the target emission spectra. The distribution peaks at around 30 keV. The absorption spectra for the various species used in this study are shown in figure 4.2.1.4. As salinity is an important control on interfacial tension, representative reservoir salinities should be maintained in the brines used.

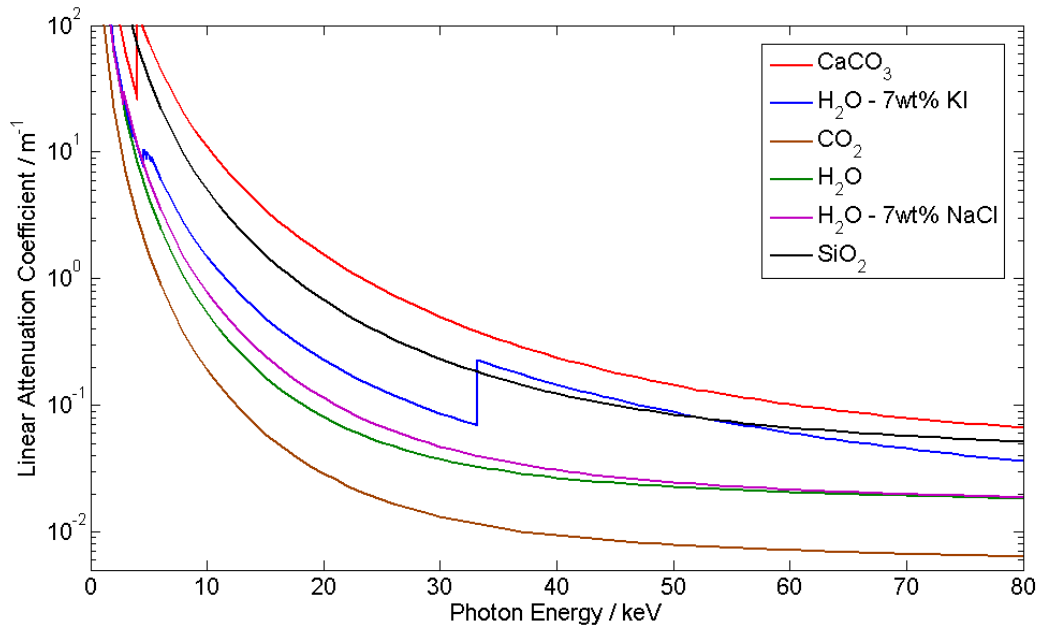


Figure 4.2.1.4: Density adjusted linear attenuation coefficients for the different species of interest in this study.

Both CO_2 and NaCl have low mass attenuation coefficients over the range of energies present in the incident X-rays. Although significantly different, as the sample is small, they will both equate to similar (large) effective experimental transmission factors (equation 2.7.2). To examine the effect of changing attenuation coefficients on inter-phase contrast, the X-ray behaviour of a 6 mm diameter sample with a porosity of 0.2 was simulated under the imaging conditions described above (source acceleration voltages of 80 kV). In order to compare the impact of different brine dopants on phase contrast, six different system states were considered; when the pore-space was filled with a vacuum, CO_2 , H_2O , a 7 wt% NaCl brine, a 7 wt% KI brine and a hypothetical case where pore-space was filled with solid rock. Inter-phase contrast arises from relative differences in transmitted X-ray intensity between difference system states. Figure 4.2.5 shows the normalized differences in transmitted X-ray intensity as a function of photon energy relative to the case where the pore-space of the sample is at a vacuum.

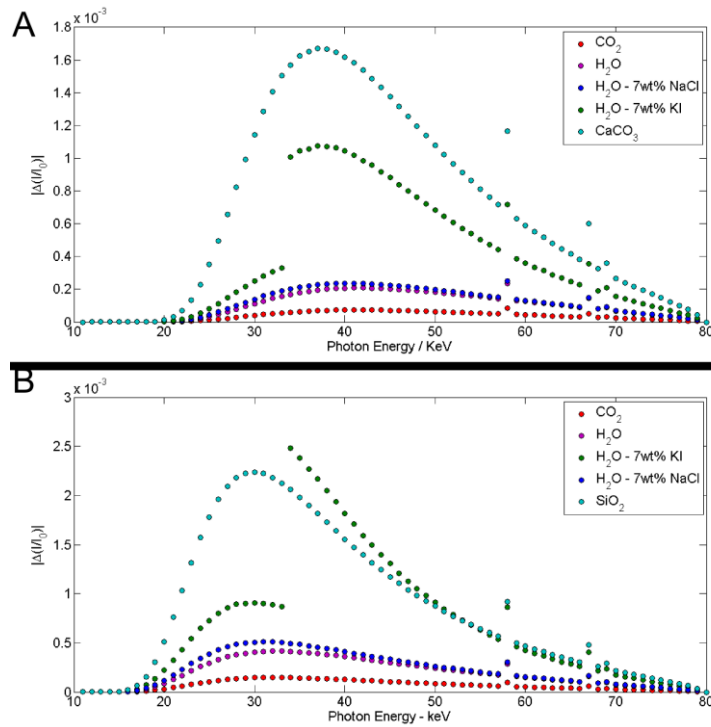


Figure 4.2.5: Normalized changes in attenuation as a function of energy when the pore-space of a modelled carbonate (A) and sandstone (B) are saturated with different fluids. Differences are taken relative to the case when the pore-space is filled with vacuum.

The overall transmission factor was then calculated by integrating this over the entire X-ray spectrum. The result of this is shown in table 4.2.1.

Material	Vacuum	CO ₂	H ₂ O	H ₂ O –	H ₂ O –	Solid (CaCO ₃
Filling				7wt% NaCl	7wt% KI	or SiO ₂)
Porosity						
Sandstone	0.413	0.408	0.400	0.397	0.365	0.353
Carbonate	0.250	0.247	0.243	0.242	0.224	0.202

Table 4.2.1: Integrated attenuation coefficient for the modelled system at with different porosity saturating fluids.

We can see that filling the pore-space with water or NaCl doped brine has very little impact on the X-ray intensity compared to filling the pore-space with CO₂, meaning there will be little difference in the reconstructed grey-scale value of CO₂ and brine in a multiphase system using these fluids. This will be extremely difficult to segment. Salinity could be increased using this solute to increase attenuation, but this would compromise the realistic nature of the fluids used. This means that NaCl is a poor choice of salt for the brine used during these experiments. KI doped brine, however, shows a much larger impact on the attenuation factor. What is more, at these salinities the attenuation associated with KI brine is approximately half the attenuation associated with CaCO₃, so the reconstructed grey-scale value of KI brine would be approximately half way between the grey-scale value of CO₂ and of CaCO₃, the optimum situation for three phase segmentation. For this reason it was chosen as the preferred brine solute for these experiments.

Quartz (SiO₂) has a smaller linear attenuation coefficient than calcite, similar to that of the KI doped brine (figure 4.2.5); however the dopant was kept the same in order to ensure comparability between the results with calcite in the capillary trapping study. As the application where results from sandstones and carbonates are compared required only the separation of the CO₂ from the other phases, not three-phase segmentation, so the similarity in the attenuation coefficient between quartz and doped brine did not affect the results.

One of the critical parameters when designing an imaging strategy is the number of projections to use in a single tomography. The larger the projection number, the more information is available for the reconstruction process and the larger the signal to noise ratio will be. The scan acquisition time is, however, directly proportional to the projection number. While this might not be a significant issue for dry scanning, scanning at reservoir conditions is time sensitive, as the CO₂ will eventually diffuse through the confining sleeve and the saturation in the core will drop. The experiments must take place on a much shorter time scale than this process, so the projection number used must be

an optimized solution accounting for the trade-off between the desire for quick experiments and the desire for a high signal to noise.

In order to make this decision, a study was conducted into the effects of projection number on signal to noise in this system. A rock core was loaded into the flow cell and imaged fully saturated with CO₂. The signal is defined as the difference between the average grey-scale value of each phase, and the noise is defined as twice the mean of the standard deviation of both phases.

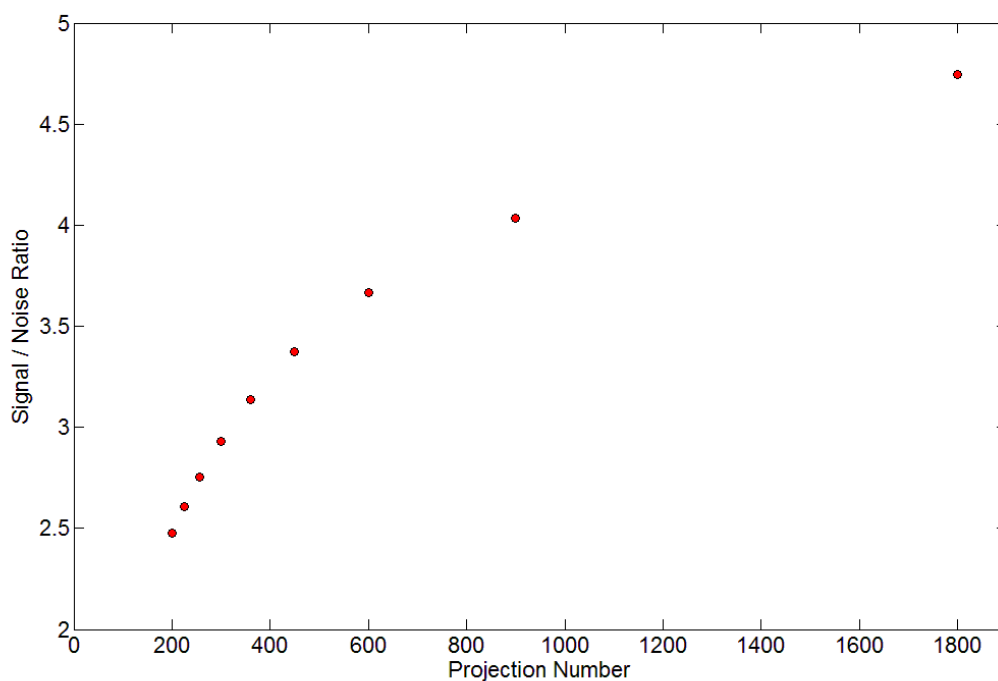


Figure 4.2.6: The impact of projection number on reconstructed signal to noise ratio between CO₂ carbonate grains.

For successful segmentation between phases a signal to noise of at least 3 is required. For the examination of capillary trapping (section 6.1), simple bulk properties of the CO₂ will be used, meaning that all that is required is for the CO₂ to be separated from the rest of the image. In this case figure 4.2.6 accurately represents the signal/noise ratio of the examined system, meaning that a projection number of just 400 can be used, meaning that image acquisition times for each volume are around 15-20 minutes.

For more complex analysis, such as the extraction of capillary pressure and contact angle (sections 6.2 and 6.3 respectively) the effective signal level is much lower, as CO₂, brine and rock need to be effectively distinguished for three-phase segmentation. This means that the projection number used during acquisition needs to be much higher, with 1,600 projections used for both these studies.

Images acquired at Diamond Light Source tend to have lower signal to noise ratios than those acquired using the Versa XRM 500, due to the difference in the respective spectra.

5 Rock and Pore Typing

We used the Krynin-Dott classification scheme for the sandstones examined (Doddington and Bentheimer) and the Dunham classification scheme for the carbonates (Ketton, Estailades and Mount Gambier). We also include a Choquette and Pray description of the pore-space and a Cantrell description of the micro-pore space. For rock types with low aspect ratio grains (Ketton, Bentheimer and Doddington) individual grains were found by first calculating the Euclidian distance map of a segmented micro-CT image. Grain seeds were found by finding the local minima in the Euclidian distance map. Grain voxels were then assigned by growing these seeds progressively up the distance map surface (figure 3.3.3.1). The boundaries between each grain were defined by the boundaries between each of these regions, and represent the saddle points in the three dimensional Euclidian distance map. Although the grain identification is imperfect, the vast majority of grains in simple granular samples (Ketton Oolite, section 5.1, Bentheimer sandstone, section 5.4 and Doddington sandstone, section 5.5) are the same as would be identified visually. For more complex pore topographies, such as those seen in bioclastic carbonates (Estailades, section 5.2 and Mt. Gambier, section 5.3) this approach could not be used, as the centres of grains were not accurately determined by the local maxima in the Euclidian distance map.

The samples of the different rocks used in for the generation of the optical thin section images, micro-CT scans and SEM images examined in this section were taken from cores extracted from the same block and no more than 5cm from the samples used for the multiple fluid imaging used in section 6, minimizing the potential impact of structural heterogeneity.

5.1 Ketton

Ketton Oolite is taken from the Upper Lincolnshire Limestone member, quarried in Ketton, Rutland, UK, and was deposited 169-176 years ago. It is chemically almost universally calcitic, with a minor quartz component (table 5.6.2). It is a medium grained oolitic grainstone, with a bimodal allochem

population, divided between large spherical to elliptical ooliths and a population of smaller peloids and grain fragments (figure 5.1.1).

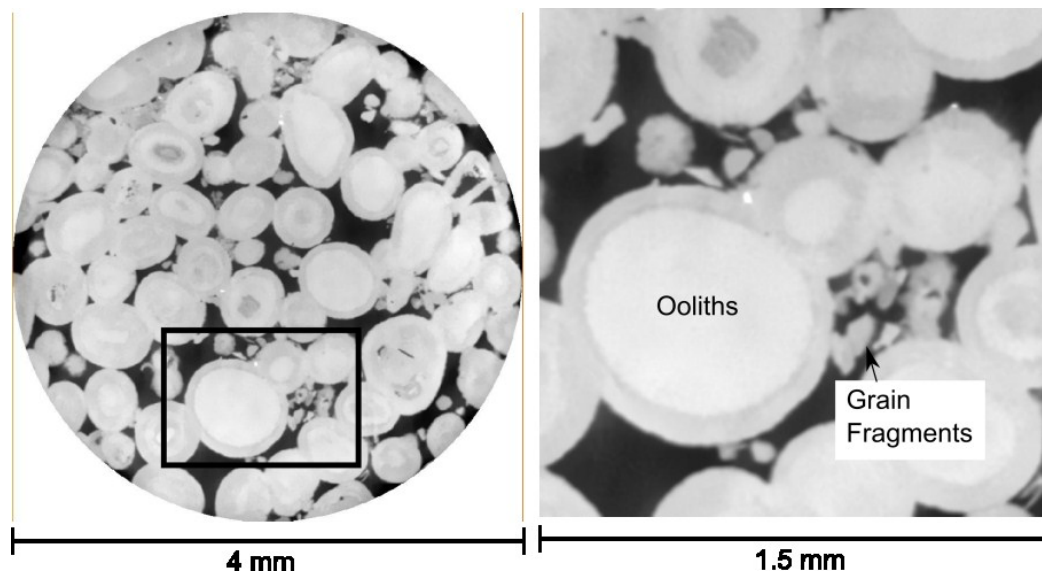


Figure 5.1.1: Slices from a micro-CT scan of Ketton Oolite with a voxel size of 4 μm .

The total grain population is shown in figure 5.1.2.

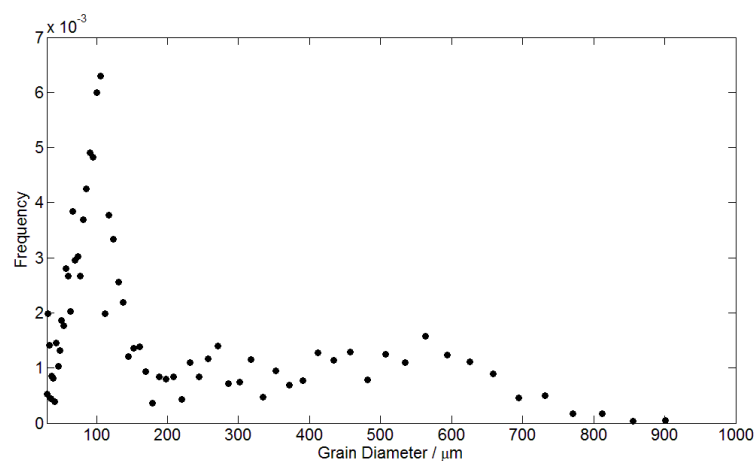


Figure 5.1.2: Grain size distribution and sorting with Ketton Oolite.

The larger oolith population dominates the rock volumetrically. The rock is moderately to poorly sorted, with a logarithmic standard deviation of 1.06. They display concentric layering, marked by differences in the level of micritization, and are heavily recrystallized. The oolith nuclei are

principally micritic peloids, but can also be bioclast fragments or sub-angular calcitic grains (figure 5.1.3). Some (approximately 10%) of the oololiths' nuclei have been dissolved and are no longer apparent.

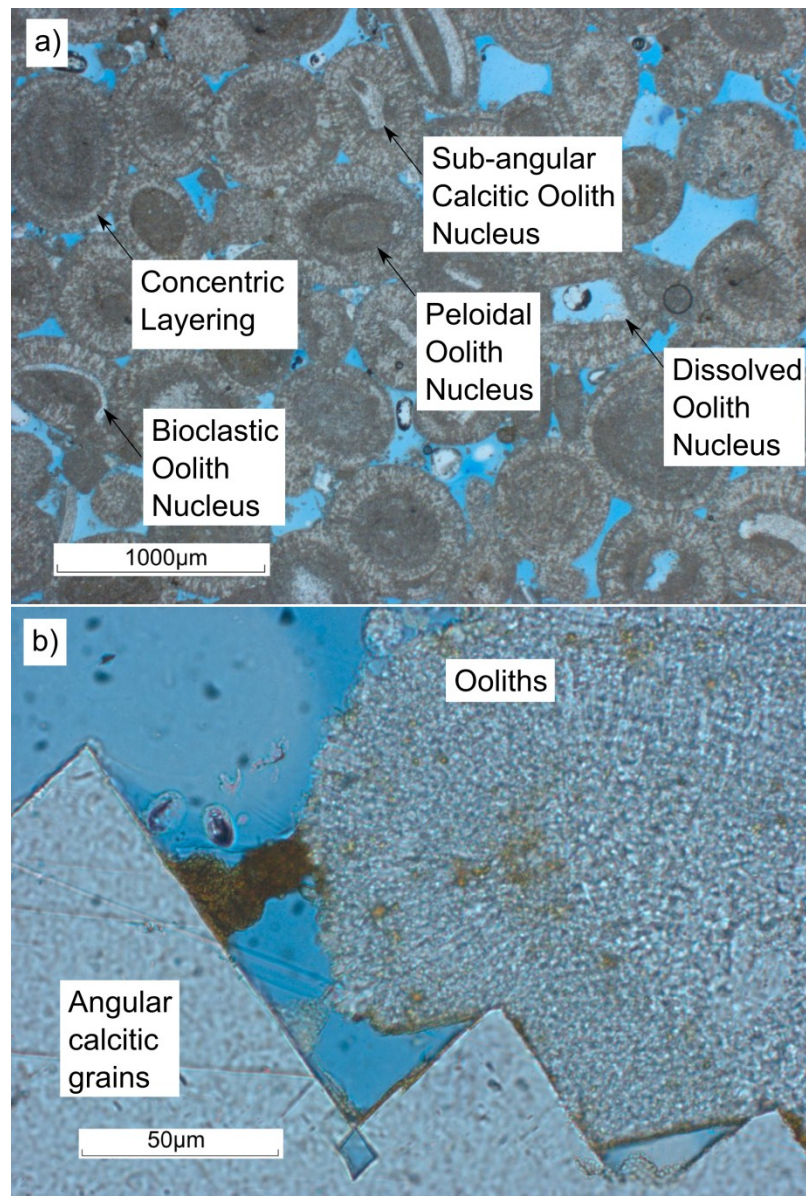


Figure 5.1.3: Thin section images of Ketton Oolite, showing grain nuclei and concentric layering (a) and the presence of angular calcitic grains along with Oololiths (b).

The Mercury Intrusion Capillary Pressure (MICP) curve for this rock demonstrates two distinct populations of pore throats (figure 5.1.4). Capillary entry pressures were converted to effective throat radii using equation 5.1.1.

$$P_c = \frac{2\sigma}{r}$$

5.1.1

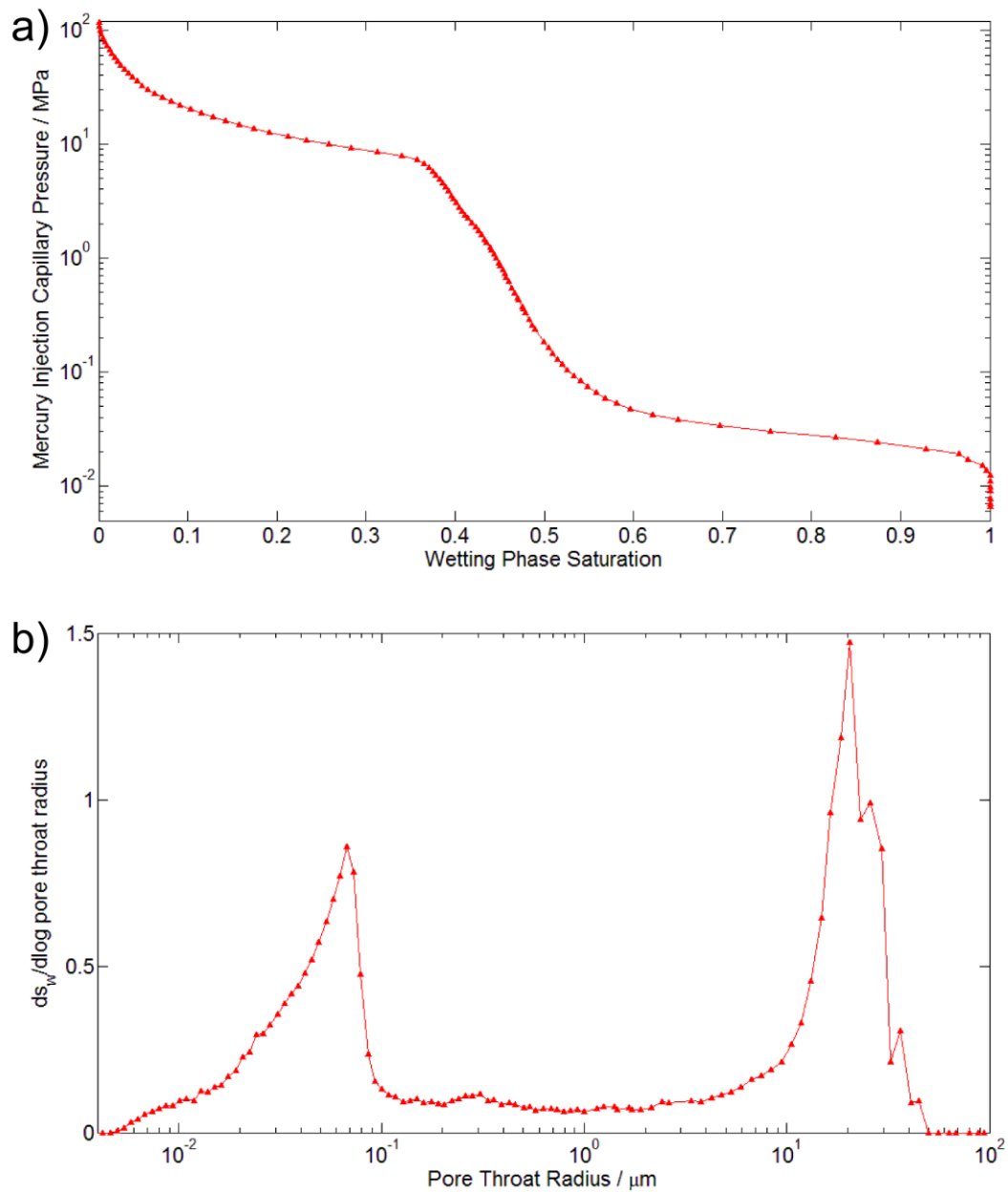


Figure 5.1.4: A) MICP curve for Ketton Oolite. B) Throat size distribution, showing two clear distinct populations.

The larger pore throats are associated with the large interparticle pores, and contribute 50-60% of the total porosity. The remainder of the porosity resides in the microporosity present in the

microporous oolitic grains. This micro-porosity can be seen on scanning electron microscope (SEM) images (figure 5.5.5).

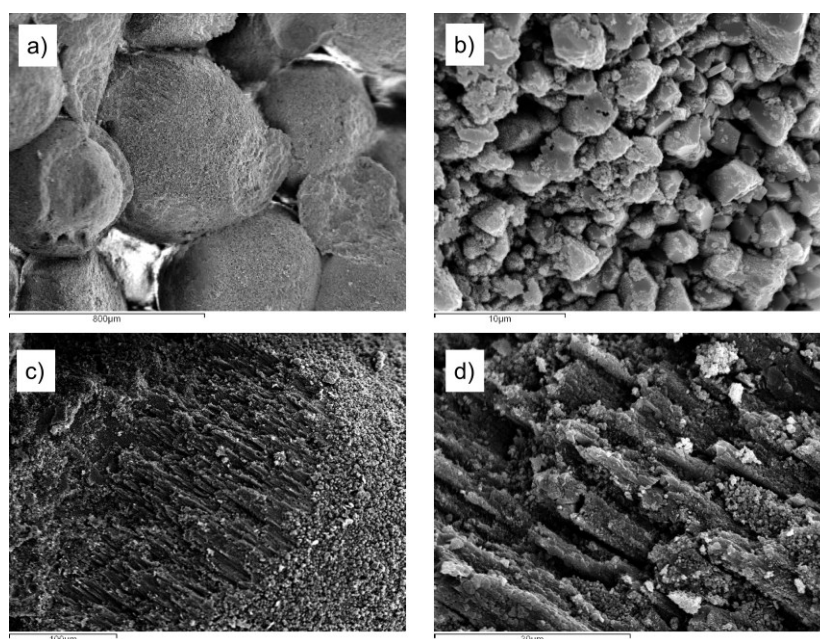


Figure 5.1.5: SEM images of Ketton Oolite, showing changes in surface texture.

The microporosity can be classified as either a standard micritic texture (figure 5.5.5 b) or an intra-grain bladed texture (figure 5.5.5 c-d), similar to the bladed cement described by Cantrell [130]. The depositional environment of this rock is most likely a high energy tropical sea. It has a helium porosity of 0.2337 and a permeability of $2.807 \times 10^{-12} \text{ m}^2$ (measured at Weatherford Laboratories, East Grinstead, UK).

5.2 Estailades

Estailades limestone was taken from the Estailade formation, quarried in Oppede, France, and was deposited 22 million years ago. It is a medium to coarse grained moderately sorted bioclastic grainstone, which is chemically almost universally calcitic with a minor quartz component (table 5.6.2). The allochem population is principally bioclasts (70%) with a significant population of angular to subangular calcitic grains. The bioclast population consists of bivalve molluscs, bryozoa and coral fragments (figure 5.2.1).

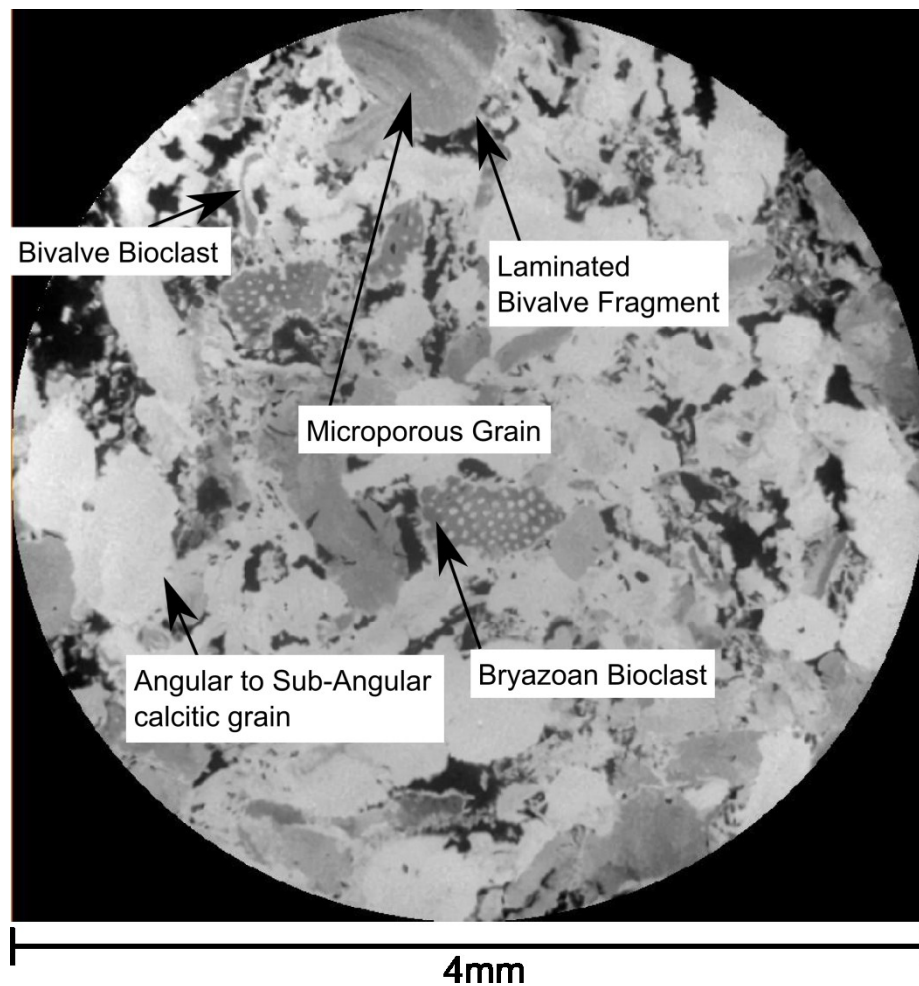


Figure 5.2.1: A slice taken from a dry micro-CT scan of Estailades limestone with a voxel size of 4 μm , showing a complex bioclastic grain population with both microporous and non-microporous grains.

Some bivalve grains preserve their original foliated and multilayer microstructure. Bryozoa fragments retain their original zooid wall structure. Extensive selective recrystallization of the bioclasts suggest heterogeneity in the mineralogical composition of the bioclasts during deposition. Layered bivalve and bryozoa bioclasts appear to be the most heavily recrystallized, with bryozoa zooid interiors consisting of sparry calcite and bryozoa walls consisting of micrite.

The MICP curve shows two different populations of pore throats (figure 5.2.2). The larger population of pore throats are associated with larger interparticle pores, contributing around 50% to the total porosity.

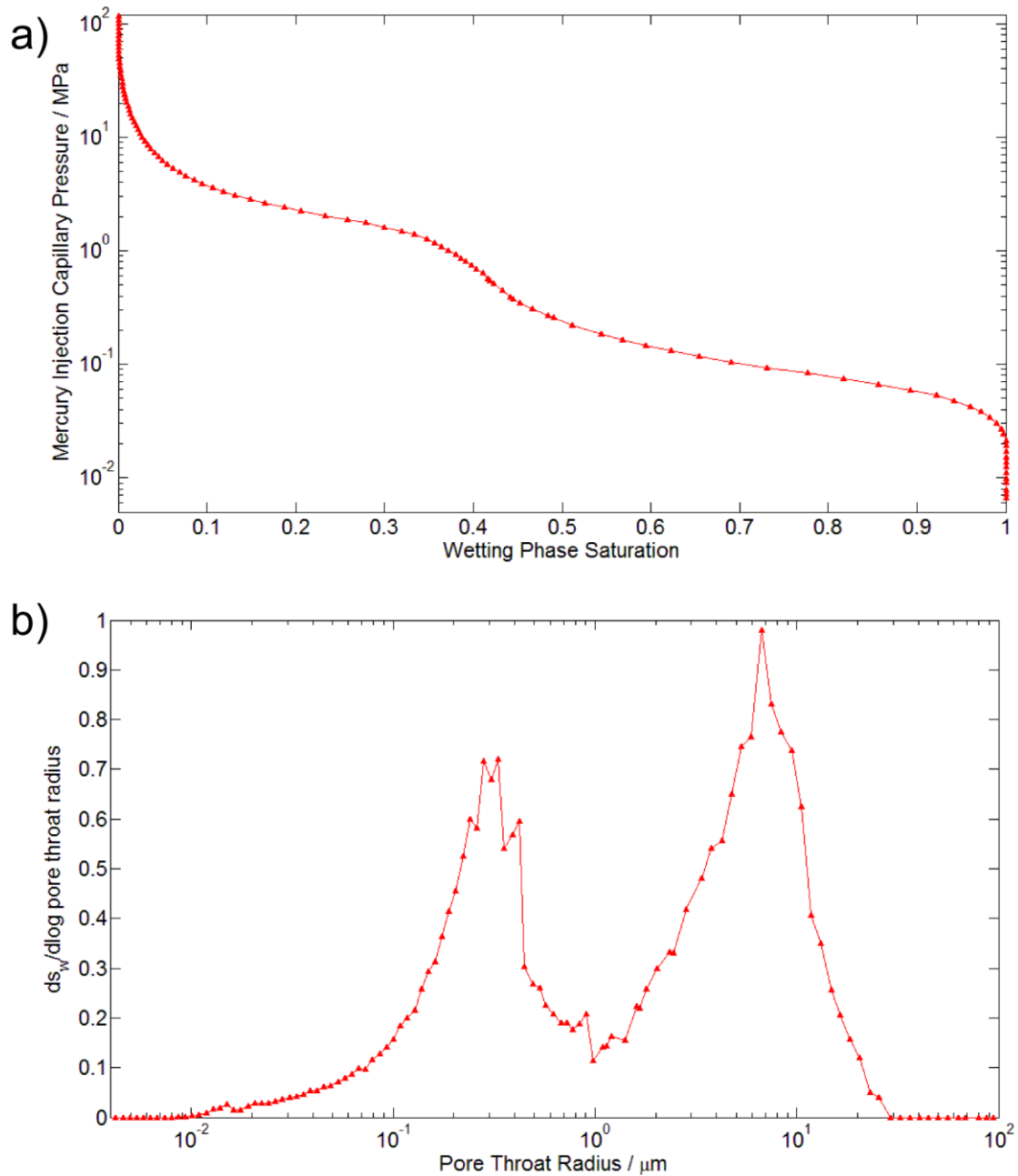


Figure 5.2.2: A) MICP curve for Estailades Limestone. B) Throat size distribution, showing two clear distinct populations.

The remainder of the totally porosity resides in the microporous grains (figure 5.2.1). The microporosity resides uniquely in microporous bioclasts. The difference between microporous and non-microporous grains can be seen on SEM (figure 5.2.3).

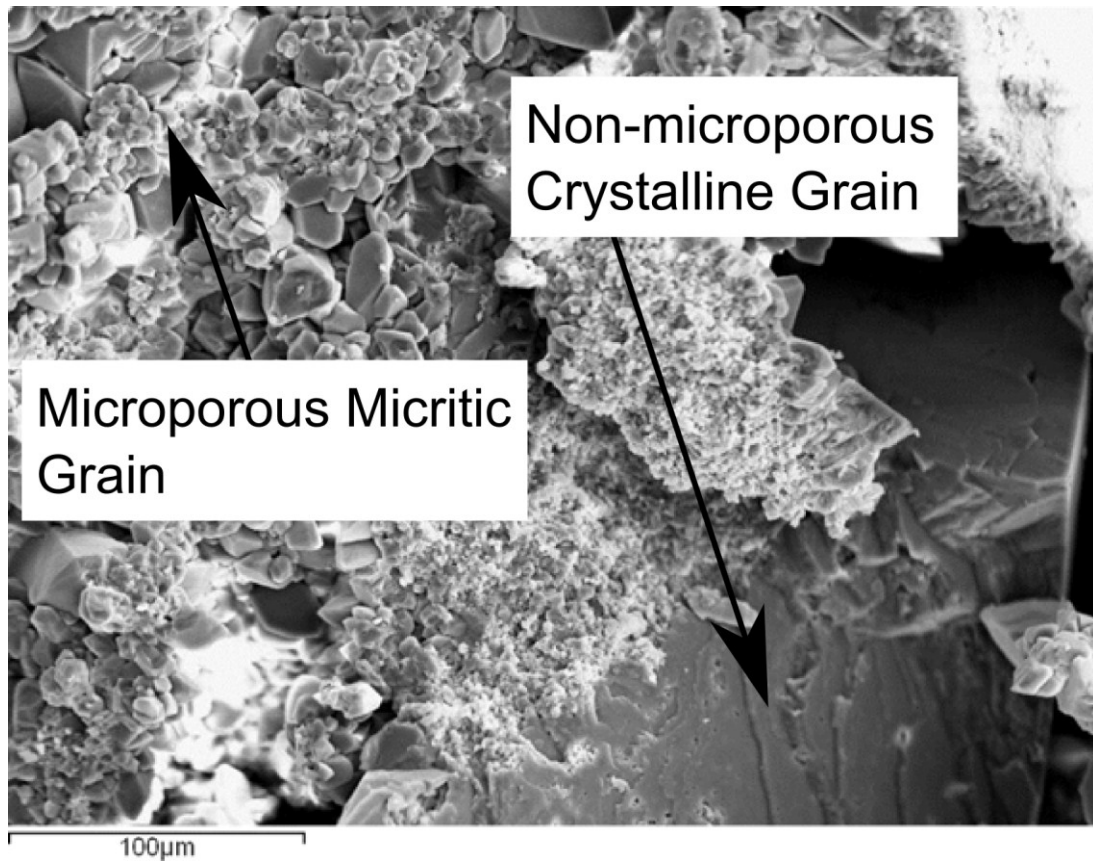


Figure 5.2.3: Microporous and non-microporous grains in Etailades limestone imaged using SEM

This rock has a porosity of 0.295 and a permeability of $1.490 \times 10^{-12} \text{ m}^2$ (measured at Weatherford Laboratories, East Grinstead, UK).

5.3 Mount Gambier

Mount Gambier Limestone was taken from the Heytesbury group, deposited between 15-38 million years ago, and quarried in Mount Gambier, Australia. It is a coarse grained, extremely high porosity exclusively bioclastic grainstone. It is chemically uniformly calcitic. The bioclast population is principally coral fragments (80%) and gastropod shells (20%). The coral fragments are extremely well preserved, high aspect ratio grains, typically greater than 1 mm in length. At least two, morphologically distinct coral species are evident in this sample (figure 5.3.1).

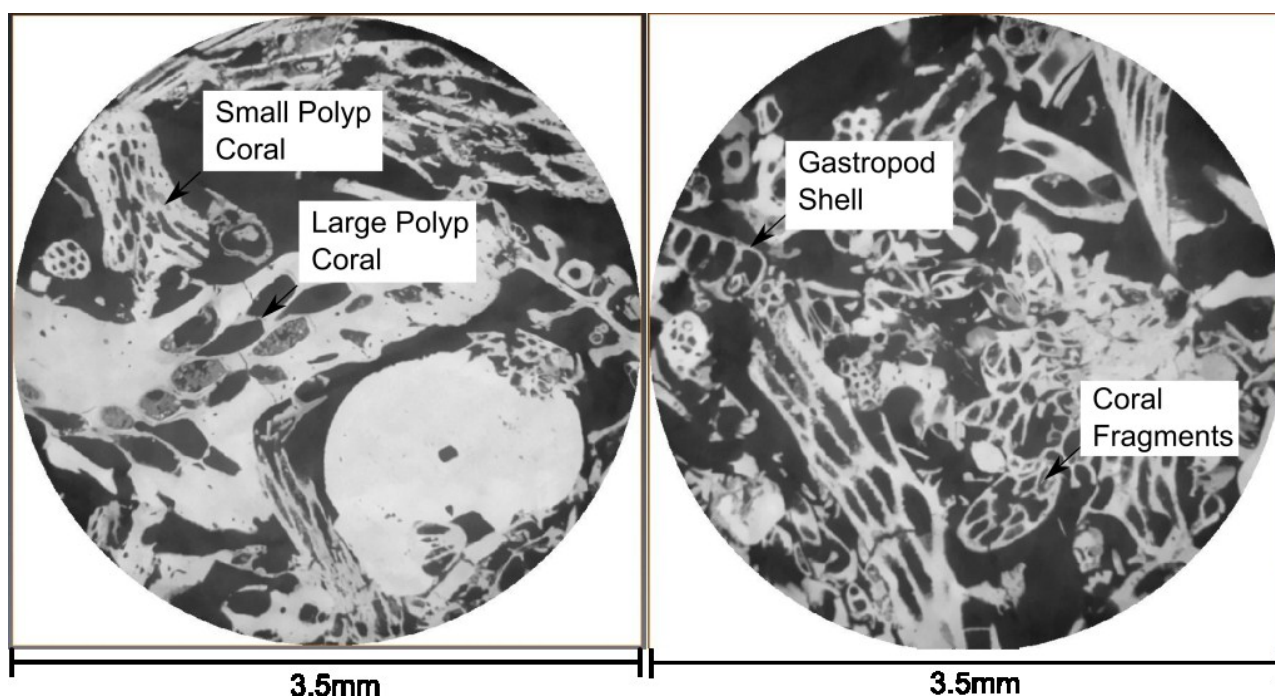


Figure 5.3.1: Slices taken from a micro-CT of Mt Gambier limestone, showing a bioclastic grain population consisting of coral fragments and gastropod shells.

The MICP curve shows a well-defined unimodal pore throat size distribution with a large tail towards smaller pore throats (figure 5.3.2).

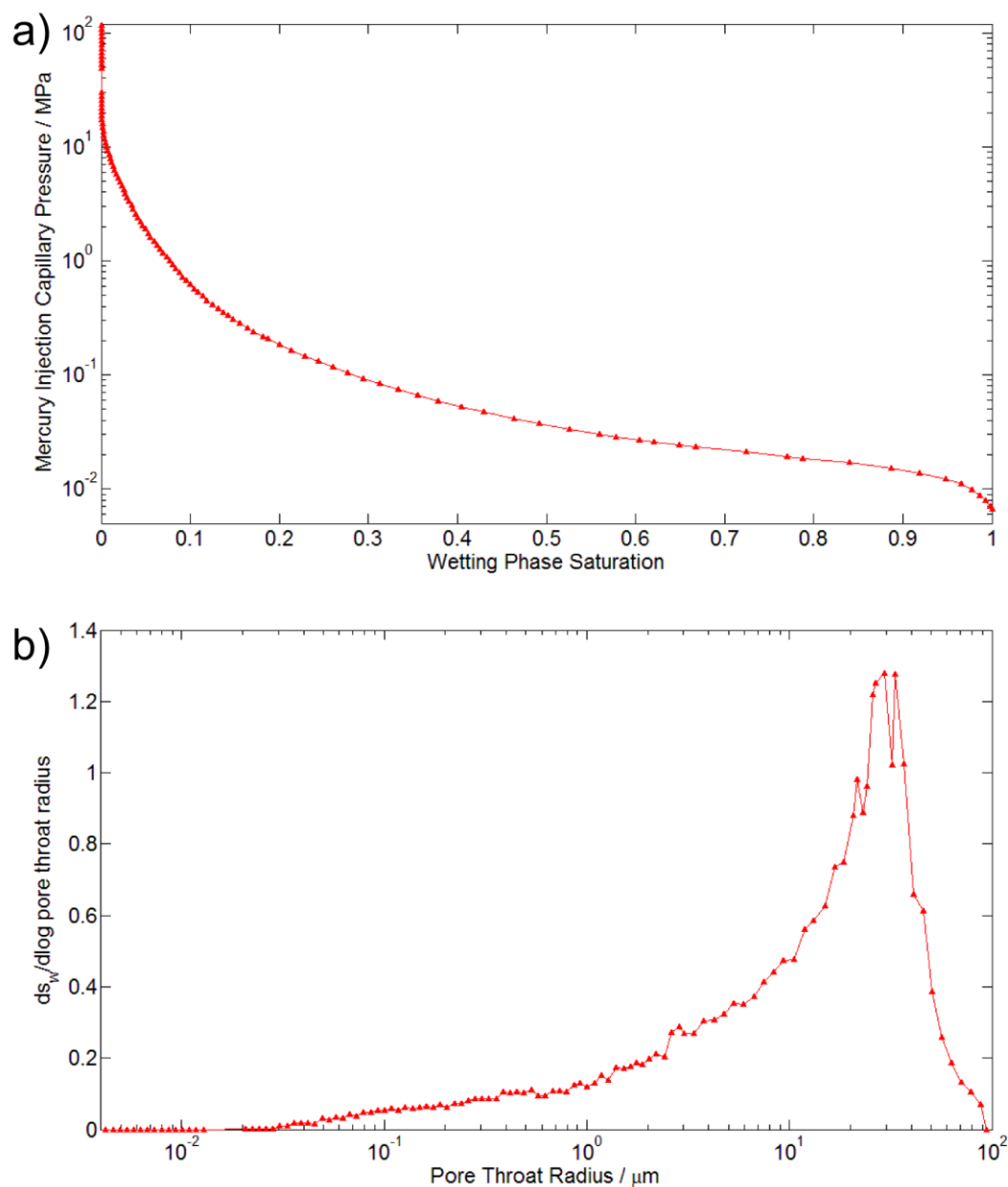


Figure 5.3.2: A) MICP curve for Mt Gambier limestone. B) Throat size distribution, showing a single well defined population with a long tail towards smaller pore throat radii.

The well-defined peak in pore throat size corresponds to the large, interparticle pores. The tail in the pore throat size distribution can be explained by the extensive recrystallization of the bioclasts, evident on SEM images of this rock type (figure 5.3.3), creating a significant amount of otherwise absent microporosity.

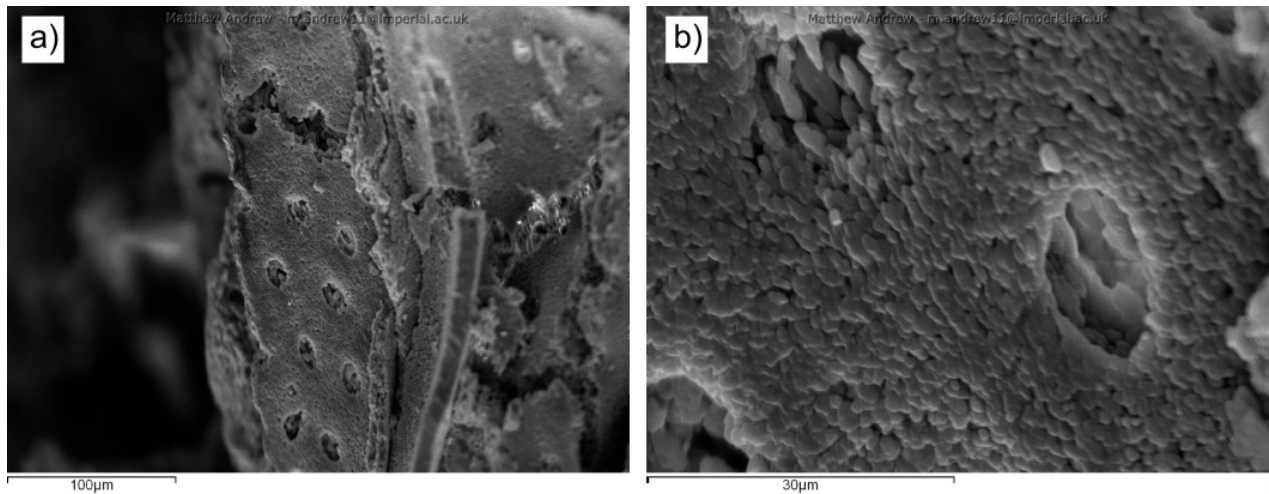


Figure 5.3.3: SEM images of Mt Gambier showing extensive recrystallization of the bioclast population.

This rock has a porosity of 0.552 and a permeability of $6.676 \times 10^{-12} \text{ m}^2$ (measured at Weatherford Laboratories, East Grinstead, UK).

5.4 Bentheimer

Bentheimer sandstone was taken from the Bentheim Sandstone member, quarried in Bad Bentheim, Germany and was deposited 133-140 million years ago. It is a medium grained, very well sorted, angular quartz arenite (figure 5.4.1).

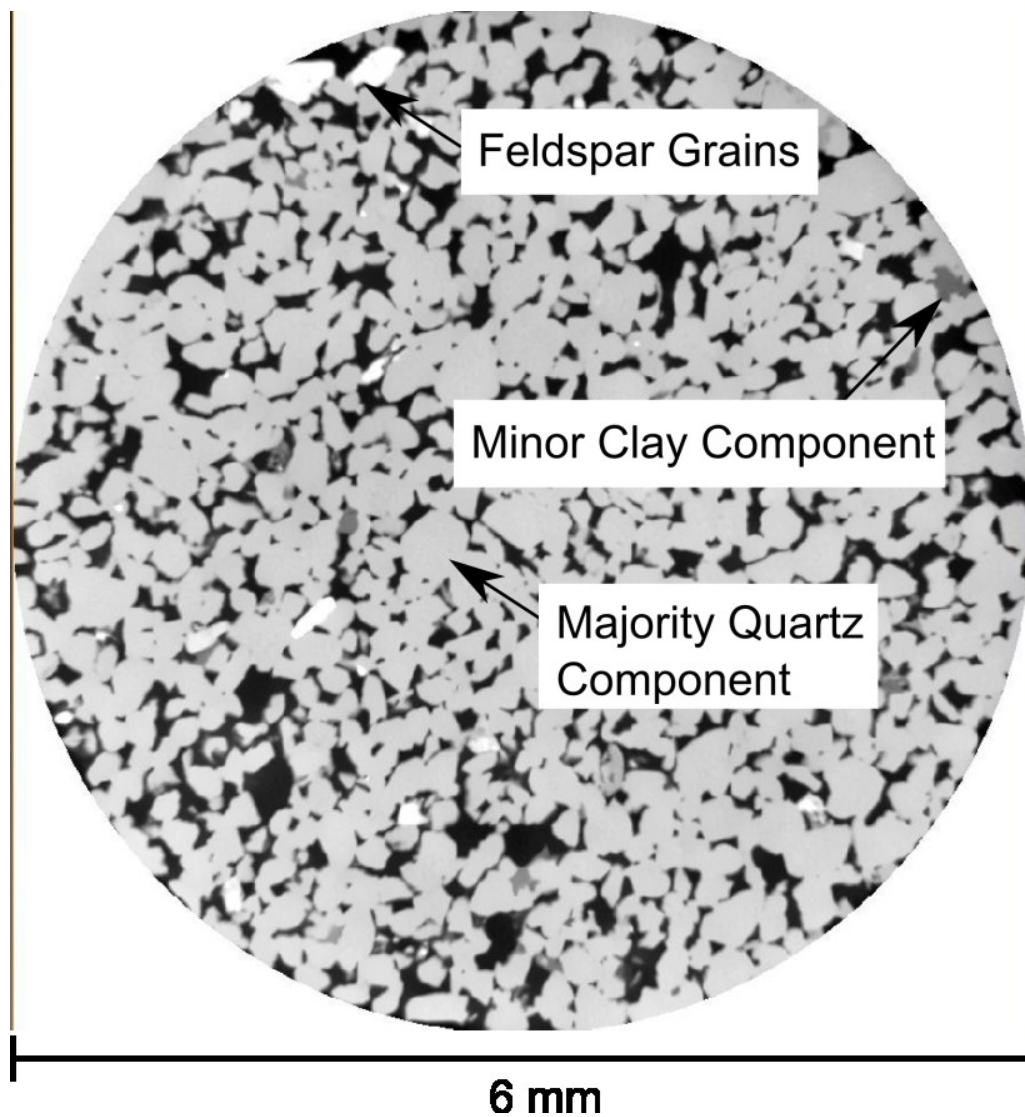


Figure 5.4.1: Slice taken from dry micro-CT scan of Bentheimer sandstone with a voxel size of 6 μm .

It has a 95% quartz composition, 4% feldspar composition and around 1% fine clay (table 5.6.2). The grain size distribution is shown in figure 5.4.2.

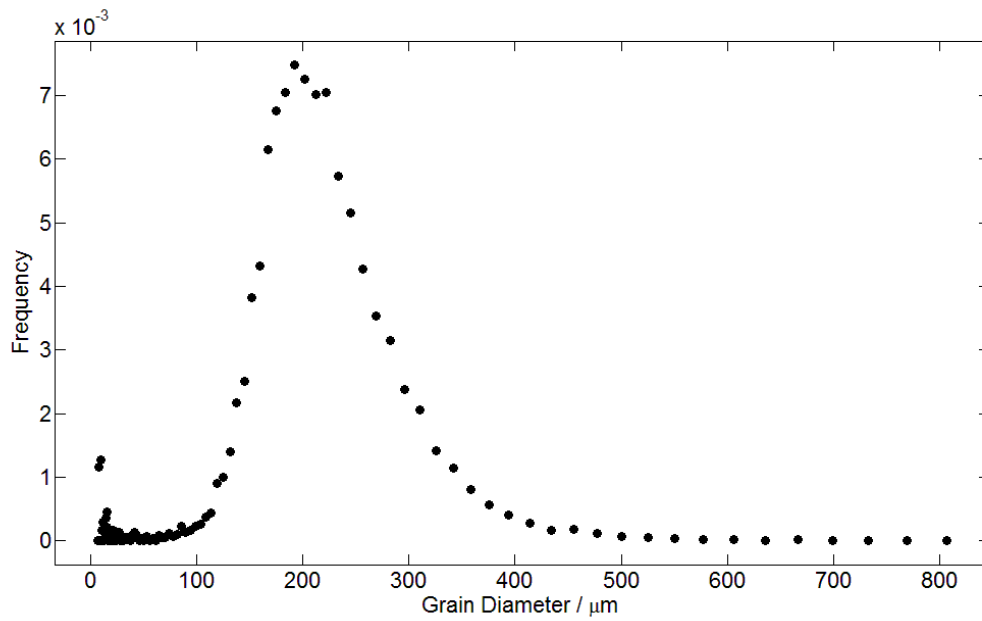


Figure 5.4.2: Grain size distribution and sorting of Bentheimer sandstone.

The mean grain diameter is 227 μm and the logarithmic standard deviation of this sample is 0.32.

The MICP curve (figure 5.4.3) shows a single, well defined peak in the pore size distribution, indicating that the entire of the connected porosity resides in the macroporosity with very little microporosity.

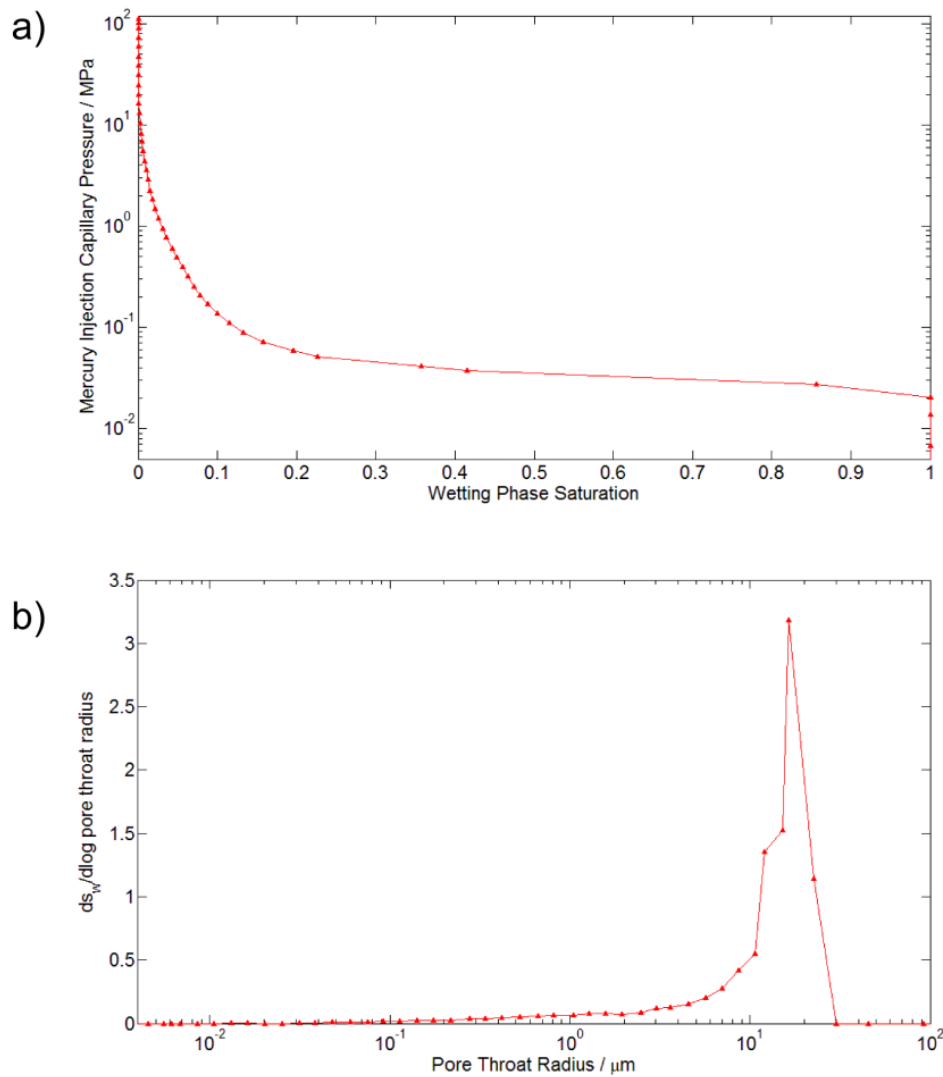


Figure 5.4.3: A) MICP curve for Bentheimer sandstone. B) Throat size distribution, showing a single well defined population.

This sandstone was probably deposited in a coastal (deltaic) to marine setting. Elsewhere in the member sponge spicules and glauconite are found, indicating an open marine setting, however coarser clasts and lignitic matter are found, pointing to a more proximal, coastal setting. It has a porosity of 0.20 and a permeability of $1.875 \times 10^{-12} \text{ m}^2$ (measured at Imperial College London, London, UK).

5.5 Doddington

Doddington sandstone is taken from the Fell Sandstone formation, quarried in Doddington, Northumberland, UK. It was deposited between 343-339 million years ago. It is a well sorted, well sorted, angular quartz arenite (figure 5.5.1).

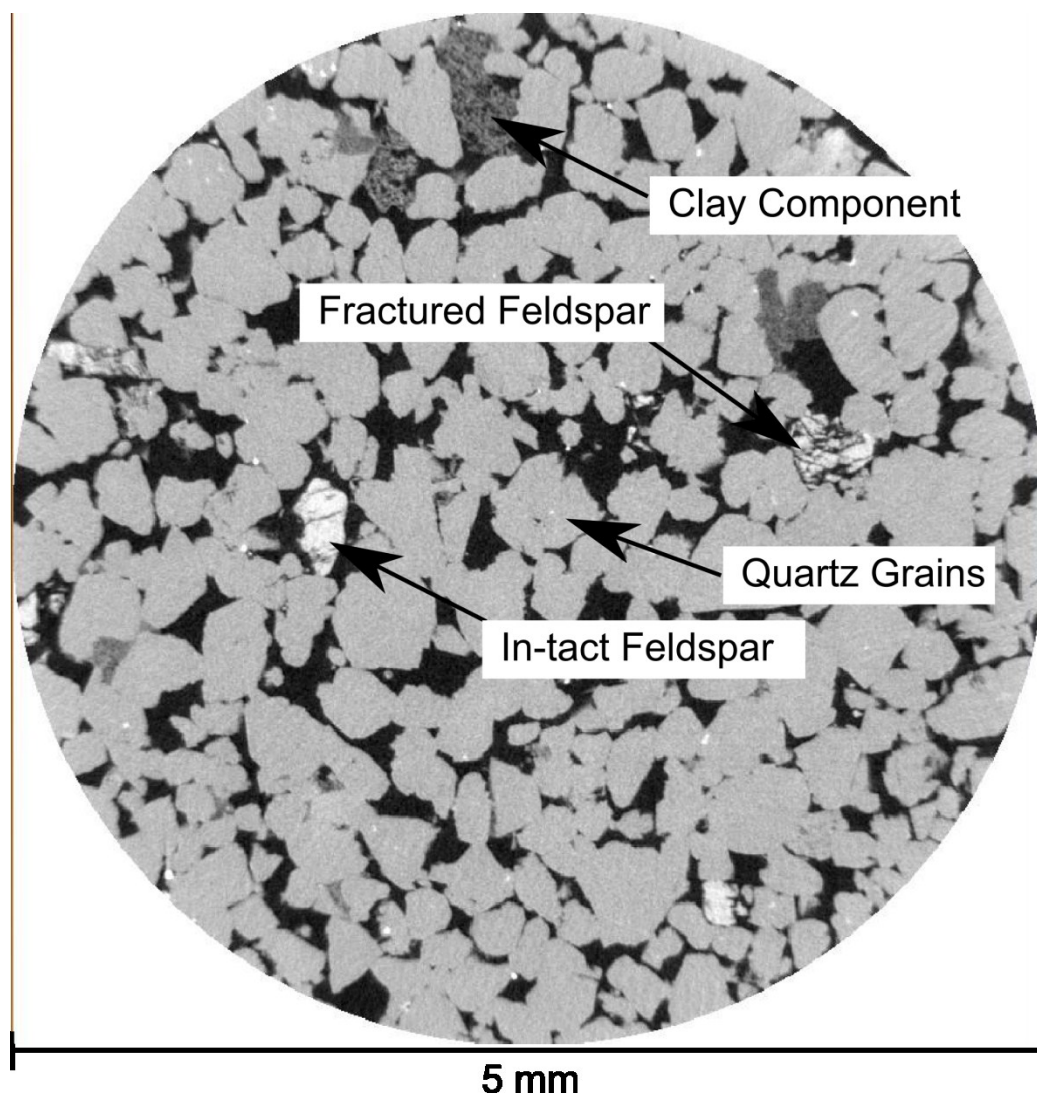


Figure 5.5.1: Slice from micro-CT scan of Doddington sandstone, showing a grain population of quartz, feldspar and clay.

It has a chemical composition of 93.6% quartz, 1.7% feldspar, 0.2% calcite and 4.5% clay. The grain population is dominated by angular to sub angular quartz clasts. Although some of the feldspar clasts are in-tact, many are fractured, and this could be a source of intra-granular microporosity. The

clay component is significantly microporous. The grain size distribution is shown in figure 5.5.2, with a mean grain diameter of 250 μm and a logarithmic standard deviation of 0.50. The well-defined peak at large grain sizes is due to the large quartz grains, and the fractured feldspar and clay grains may be responsible for the other peak at the smallest grain sizes.

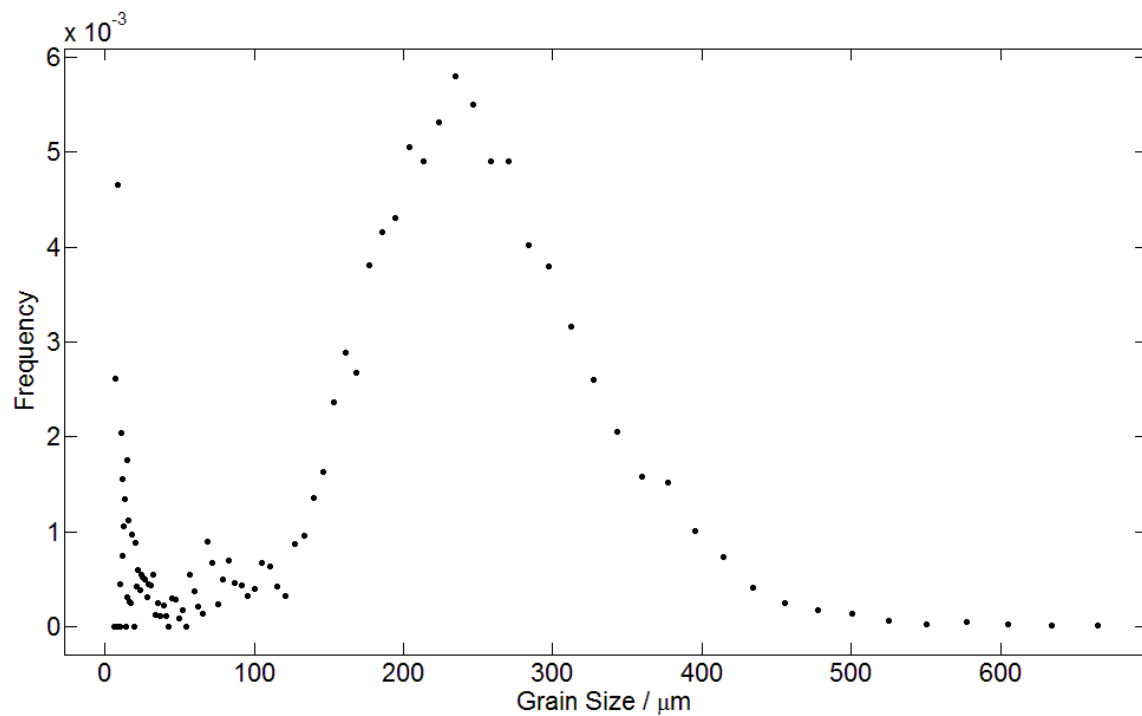


Figure 5.5.2: Grain size distribution and sorting of Doddington sandstone

The MICP curve shows a single, well defined peak, corresponding to the interparticle porosity (figure 5.5.3), with a very slight tail towards smaller pore throats. The clay and fractured feldspar components may be responsible for this tail.

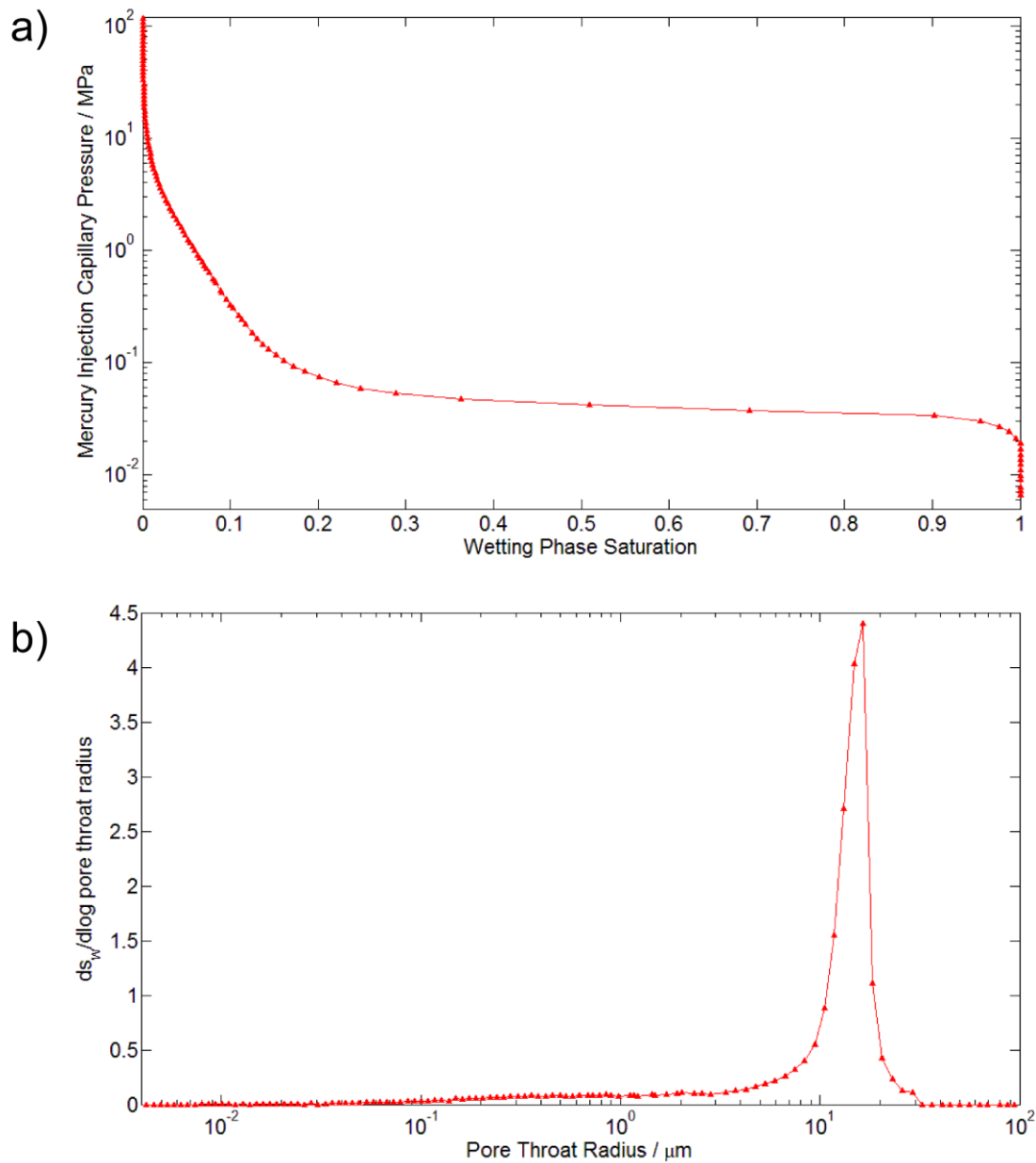


Figure 5.5.3: A) MICP curve for Doddington sandstone. B) Throat size distribution, showing a single well defined population with a long tail towards smaller pore throat radii.

This rock has a porosity of 0.192 and a permeability of $1.038 \times 10^{-12} \text{ m}^2$ (measured at Weatherford Laboratories, East Grinstead, UK). This rock was most likely deposited in a series of rivers and deltas.

5.6 Summary

The basic details about each rock type are summarised below in table 5.6.1, and the basic petrophysical properties and chemical composition of each rock type shown in table 5.6.2.

Sample	Rock Type	Geological Group	Place of Origin	Age / Million Years
Ketton	Carbonate	Upper Lincolnshire Limestone Member	Ketton, Rutland, UK	169-176
Mount Gambier	Carbonate	Heytesbury Group	Mount Gambier, Australia	15-38
Estailades	Carbonate	Estailade Formation	Oppède, France	22
Bentheimer	Sandstone	Bentheim Sandstone Member	Bad Bentheim, Germany	133-140
Doddington	Sandstone	Fell Sandstone Formation	Doddington, Northumberland, UK	343-339

Table 5.6.1: Basic details about each rock type.

Sample	Helium Porosity	Permeability / m ²	% Calcite	% Quartz	% Feldspar	% Clay
Ketton	0.2337 ^a	2.807×10^{-12a}	99.1 ^a	0.9 ^a	0 ^a	0 ^a
Mount Gambier	0.552 ^a	6.676×10^{-12a}	100 ^b	0 ^b	0 ^b	0 ^b
Estailades	0.295 ^a	1.490×10^{-13a}	97.9 ^a	2.1 ^a	0 ^a	0 ^a
Bentheimer	0.20 ^c	1.875×10^{-12c}	0 ^b	95 ^b	4 ^b	1 ^b
Doddington	0.192 ^a	1.038×10^{-12a}	0.2 ^a	93.6 ^a	1.7 ^a	4.5 ^a

^a Analysis conducted at Weatherford Laboratories (East Grinstead, UK)

^b Analysis conducted at the Natural History Museum (London, UK)

^c Analysis conducted at Imperial College (London, UK)

Table 5.6.2: Basic petrophysical properties and chemical composition of each rock type. Chemical

composition was found using X-ray diffraction.

6 Multiphase Flow Imaging

In this section we will describe the results of reservoir condition multi-phase micro-CT imaging in realistic systems. These results focus on four principal applications:

- 1) Capillary trapping (section 6.1)
- 2) Ganglion snap-off and remobilization (section 6.2)
- 3) Contact angle measurement (section 6.3)
- 4) Dynamic phenomena associated with CO₂ drainage (section 6.4)

Each of these applications shall be dealt with in turn, with short conclusions presented at the end of each results section. A more complete discussion of the conclusions arising from this thesis, along with considerations for potential future work is presented in section 7.

6.1 Capillary Trapping

The first application for the methodology described in section 4 was to examine capillary trapping over a wide range of rock types and mineralogies. These results were published in Andrew *et al.* [154].

6.1.1 Injection Strategy

The fluids were injected under conditions analogous to the “unsteady state” conditions used in larger scale core-flood experiments. The experimental parameters used for these experiments are given in table 6.1.1.1. Full experimental protocol is described in section 4.

Source Voltage / kV	Source Current / μA	Core size / mm	Voxel Size / μm	Brine Composition	Projection Number	Temperature / $^{\circ}\text{C}$	Pressure / MPa	Flow Rate / m^3/s
80	7	6.5	6.5	7 wt% KI	400	50	10	1.67×10^{-9}

Table 6.1.1.1: Experimental parameters used for partially saturated imaging in the capillary trapping study.

Experiments were conducted on the five different rock types described in section 5. For each rock type one experiment was run to image the initial saturation after drainage and five were run to image the residual saturation after imbibition. The initial non-wetting phase saturation was therefore only measured once, and was assumed to be the same for each experimental run in which imbibition was examined. This assumption was confirmed visually during each of the five experiments examining imbibition by comparing 2D projections taken during the drainage step to those taken during the drainage step during the experiment where initial saturation was imaged. Only one rock core was used for each rock type in order to minimise confounding effects of structural heterogeneity within a single rock type.

To scan the entire length of the core while retaining a small voxel size, composite volumes were constructed by stitching together five overlapping sections, acquired sequentially. Each individual section consisted of around 1000^3 voxels. The stitching was done using software proprietary to the Versa XRM-500 system. Each section took 15–20 min to acquire, meaning an entire composite volume took around 90 min. The image was then cropped to a cuboidal volume of around $900 \times 900 \times 3300$ voxels resulting in the image size of approximately $6 \times 6 \times 22$ mm; the quantitative analysis was restricted to this volume.

The dry scans were of 6 mm diameter cores that were drilled adjacent to the cores examined during wet scanning in order to minimise the effect of structural heterogeneity. They were then mounted on a kinematic stage and were single volumes reconstructed from a set of 1600 projections. They were processed and segmented using the same techniques as the wet scans, although the voxel

sizes – between 6.2 and 3.9 μm – were smaller. To facilitate comparison between dry and wet scanning dry scanning results were reported in units equal in volume to the wet scanning voxel size (6.6 μm).

6.1.2 Image Processing

After acquisition, the images were filtered using a non-local means edge preserving filter [139, 140] (section 3.2). The images were then segmented into two phases, with the scCO_2 being treated as one phase and the brine and the rock treated as the other phase. This was done as the segmentation of images containing a partial saturation of multiple fluids is significantly more difficult than the segmentation of dry images [143] (section 3.3). As simple grey-scale segmentation is insufficient, segmentation using a watershed algorithm computed off a seed generated using a 2D histogram was performed (section 3.3.3, [147]). This image processing work flow is shown for Bentheimer in Figure 6.1.2.1.

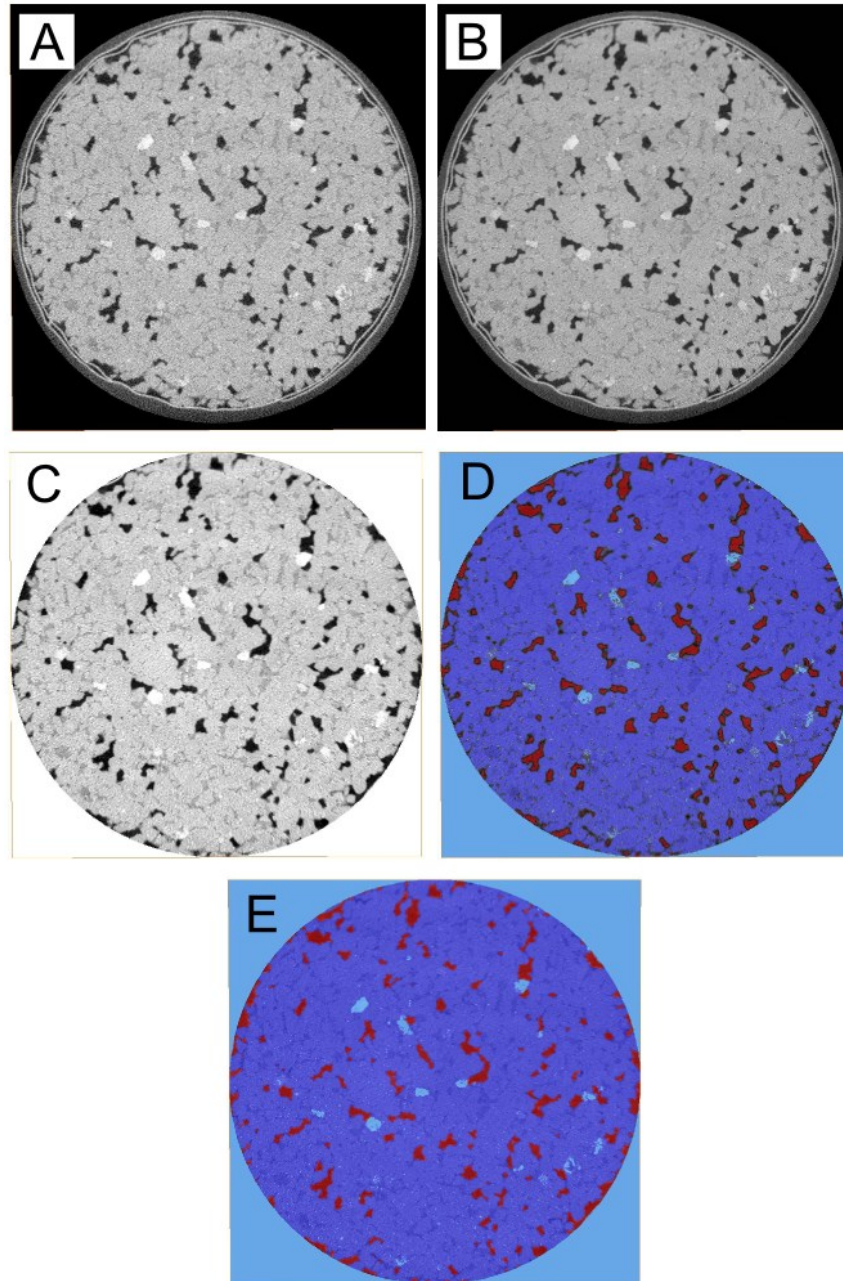


Figure 6.1.2.1: The segmentation of a wet image consisted of five steps, shown here for Bentheimer sandstone. A-B The image was filtered using a non-local means edge preserving filter [139, 140]. B-C The image was cropped so only the core was in the field of view. C-D A seed was generated using 2D histogram [147]. The red areas correspond to the scCO_2 portion of the seed and the dark blue areas to brine and grain, which are grouped together as a single phase. The light blue area corresponds to the area of the scan outside the core. D-E Each voxel outside the seeded areas was assigned to a phase using a watershed algorithm.

The segmented image was then analysed in 3D in order to identify and measure the volume of each unique disconnected ganglion, which was then labelled, as shown in Figures 6.1.2.2-6.1.2.6. All this process was conducted within the Avizo Fire 8.0 (Visual Sciences Group, www.vsg3d.com) and imageJ programs.

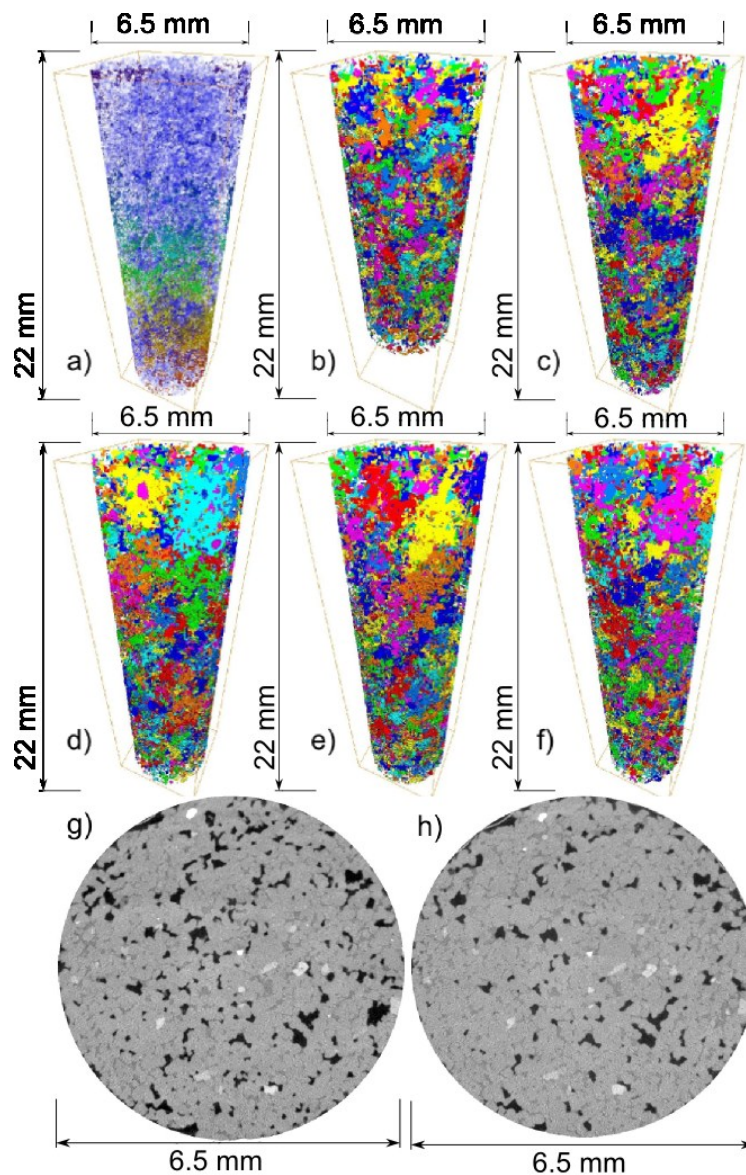


Figure 6.1.2.2: Images of Bentheimer after drainage and imbibition. A) A 3D rendering of the core after drainage where each non-wetting phase cluster is given a different colour. B-F) A 3D rendering of the core after imbibition coloured as described for A). The large range of colours indicates a poorly connected residual phase. G) A cross-section of the core after drainage. H) A cross-section of the core after imbibition.

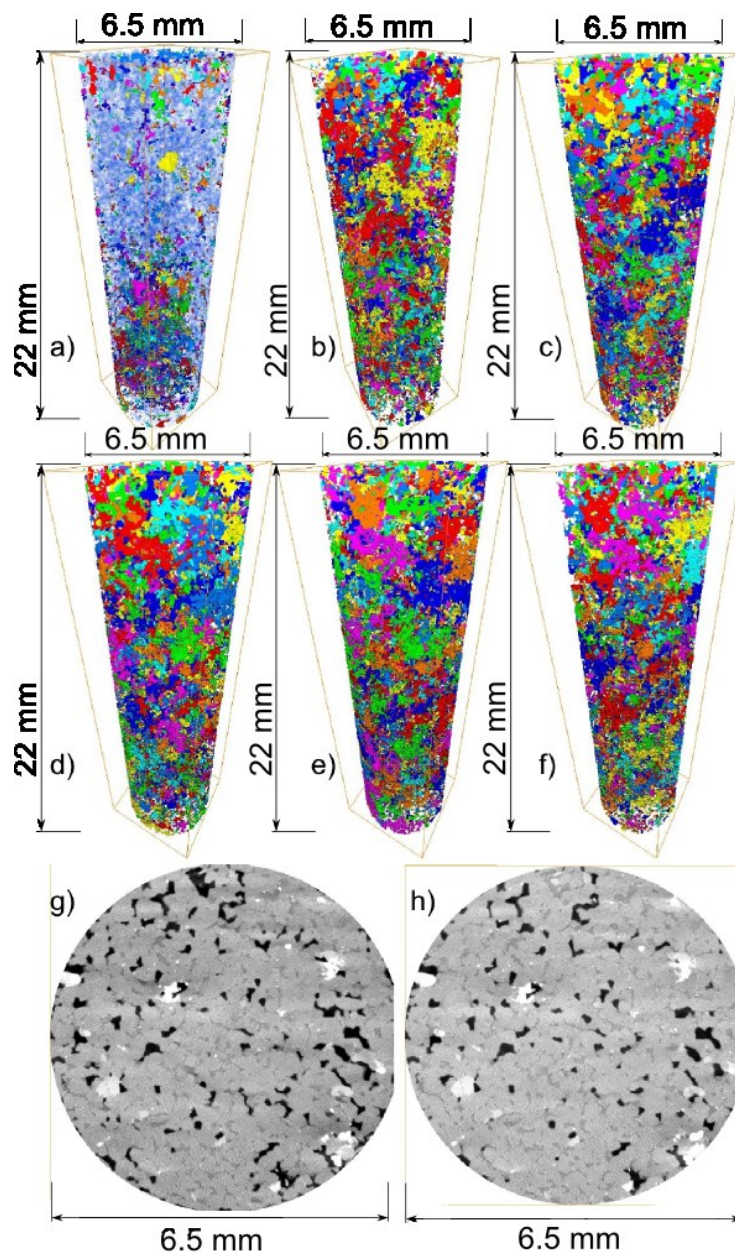


Figure 6.1.2.3: Image of Doddington after drainage and imbibition. A) A 3D rendering of the core after drainage where each non-wetting phase cluster is given a different colour. B-F) A 3D rendering of the core after imbibition coloured as described for A). The large range of colours indicates a poorly connected residual phase. G) A cross-section of the core after drainage. H) A cross-section of the core after imbibition.

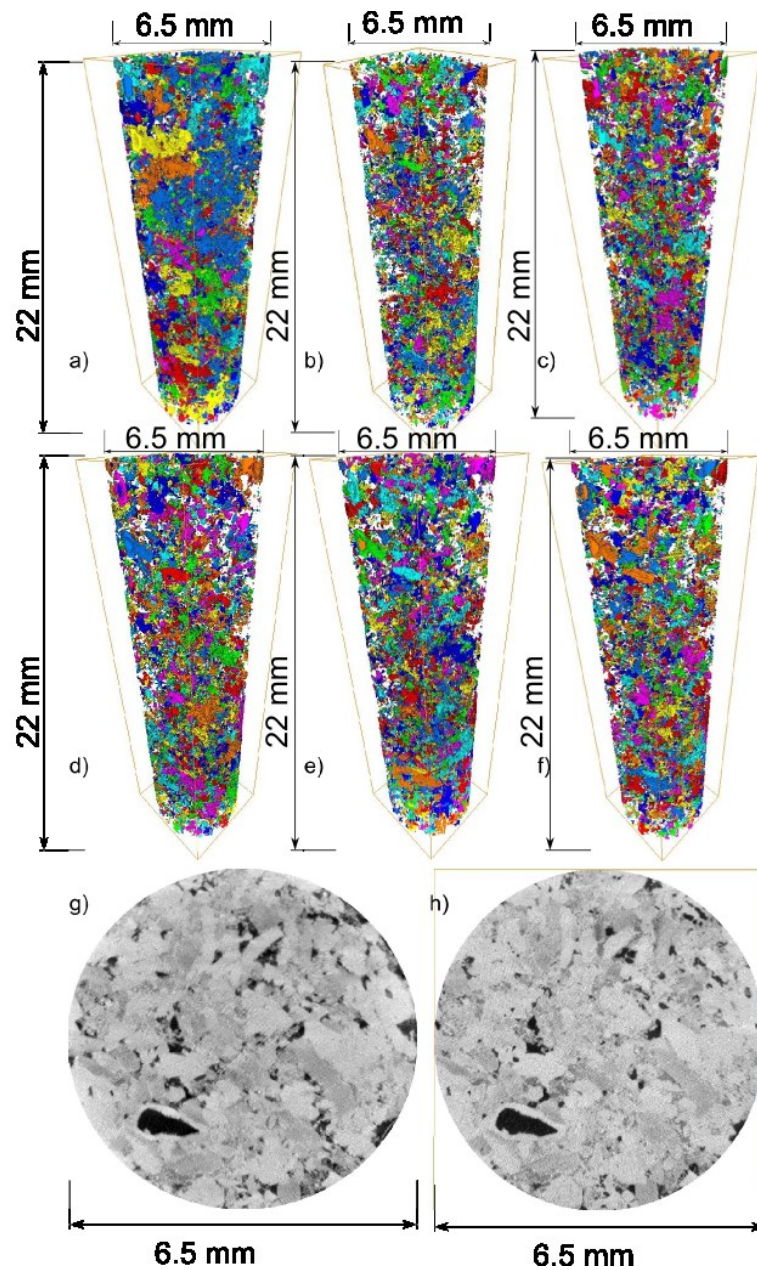


Figure 6.1.2.4: Image of Estailades after drainage and imbibition. A) A 3D rendering of the core after drainage where each non-wetting phase cluster is given a different colour. B-F) A 3D rendering of the core after imbibition coloured as described for A). The large range of colours indicates a poorly connected residual phase. G) A cross-section of the core after drainage. H) A cross-section of the core after imbibition.

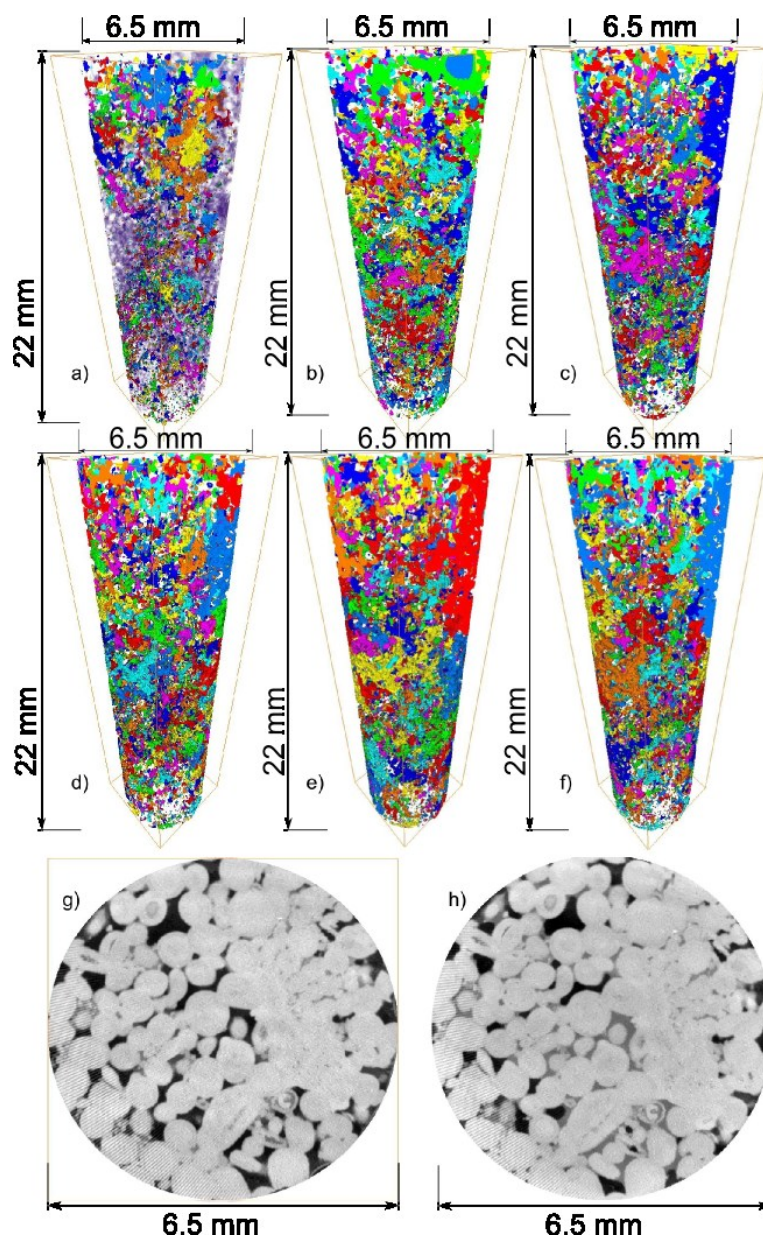


Figure 6.1.2.5: Image of Ketton after drainage and imbibition. A) A 3D rendering of the core after drainage where each non-wetting phase cluster is given a different colour. B-F) A 3D rendering of the core after imbibition coloured as described for A). The large range of colours indicates a poorly connected residual phase. G) A cross-section of the core after drainage. H) A cross-section of the core after imbibition.

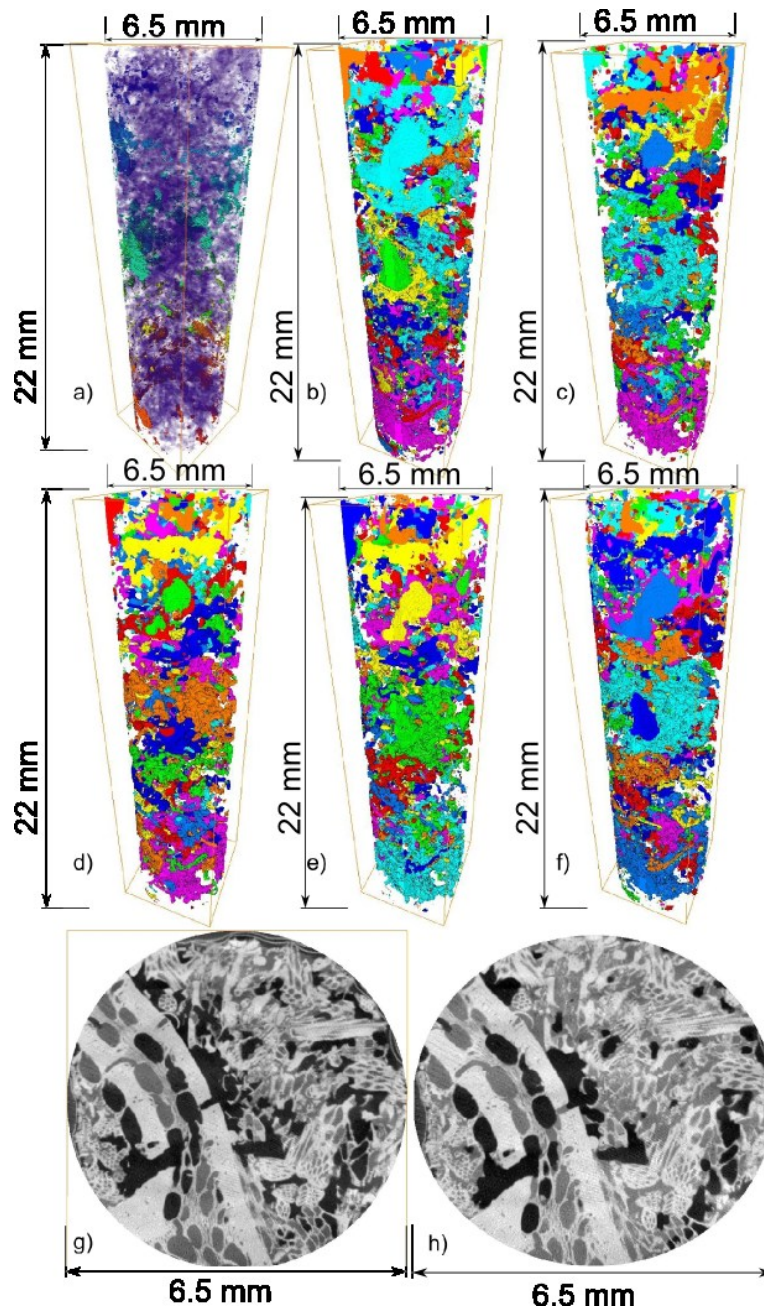


Figure 6.1.2.6: Image of Mount Gambier after drainage and imbibition. A) A 3D rendering of the core after drainage where non-wetting phase cluster is given a different colour. B-F) A 3D rendering of the core after imbibition coloured as described for A). The large range of colours indicates a poorly connected residual phase. G) A cross-section of the core after drainage. H) A cross-section of the core after imbibition.

The apparent porosity as evaluated from the dry μ CT images is shown in Table 6.1.2.1. For Bentheimer, Doddington and Mt Gambier: this is similar to that obtained using helium porosimetry (table 6.1.2.1); however for Estailades and Ketton the apparent porosity is significantly smaller. This is due to the presence, in these rock types, of significant sub-resolution microporosity, as discussed in section 5. These pores are apparent on mercury injection analysis described previously and have high capillary entry pressures (>0.1 MPa) compared to the maximum possible capillary pressures generated during these experiments (<0.01 MPa), so are assumed to remain saturated with brine for the duration of the experiment.

Pore networks were extracted from the dry scans by using a topological analysis of the pore space in which the largest voids are identified as pores by the method of maximal inscribed spheres, see section 2.4.1 [81]. Modal pore volumes were then found from this distribution by fitting a Gaussian distribution to the natural logarithm of the pore size distribution, as shown in Figure 6.1.2.7. The pore-volume weighted connectivity for each sample was calculated by weighting the coordination number of a pore (the number of other pores connected to it) with its volume, then calculating an overall average. This was used as a metric of the connectivity of the pore space, as straight statistical averaging hides the impact of very large, very well connected pores to the overall connectivity. It corresponds to the average connectivity of a hypothetical volumetric element within the network model. It can be seen from this analysis that Mount Gambier is much better connected than the other samples, as we might expect for a rock with such an extremely high porosity and permeability. The other two carbonates (Estailades and Ketton) were slightly less connected than the two sandstones; Bentheimer was better connected than Doddington. These differences are much smaller, however, than that between Mount Gambier and all other samples. These results are summarised in Table 6.1.2.1.

Sample	Voxel size / μm	Apparent Image-measured porosity	Helium Porosity	Modal Pore Size / Voxel ³	Pore-Volume Weighted Connectivity
Bentheimer	6.16	0.221	0.20 ^a	413	6.92
Doddington	5.39	0.198	0.192 ^b	577	5.68
Estailades	4.60	0.097	0.295 ^b	234	5.17
Ketton	4.44	0.129	0.2337 ^b	1756	5.30
Mt Gambier	3.93	0.517	0.552 ^b	1072	20.71

^a Measured at Imperial College (London, UK)

^b Measured at Weatherford Laboratories (East Grinstead, UK)

Table 6.1.2.1: Summary of the results of dry scanning and network extraction.

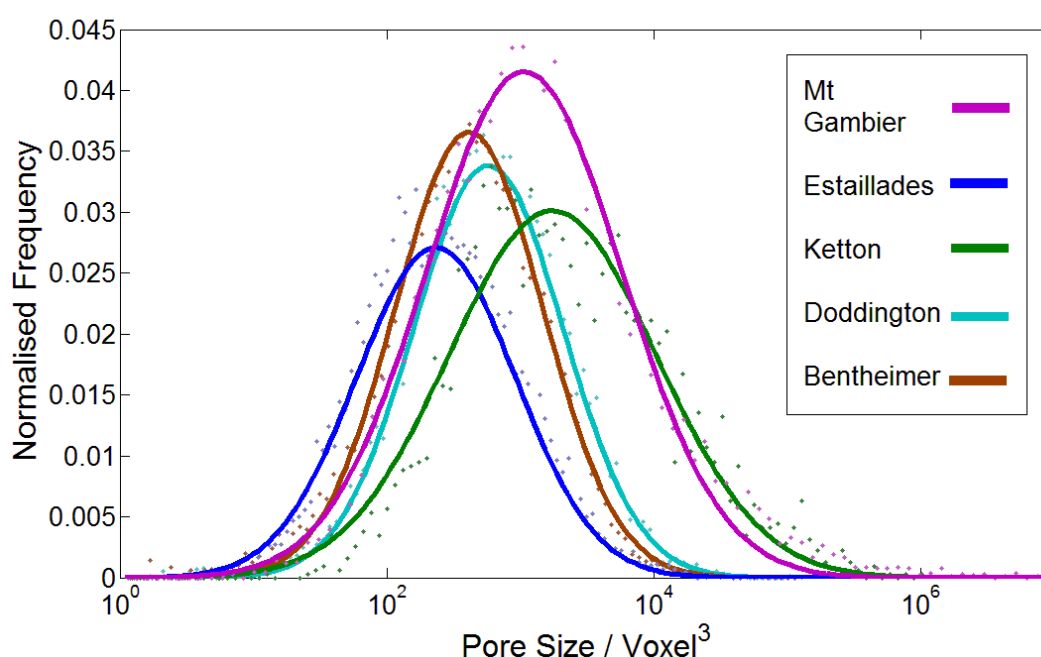


Figure 6.1.2.7: Pore size distributions for each rock type. Each binned distribution was fitted using a logarithmic Gaussian distribution in order to find modal pore sizes (Table 6.1.2.1) which would be used as a lower cut-off for the ganglia size distributions. The pore size units are the same as used in

Figure 6.1.3.1.

6.1.3 Results and Discussion

The segmented wet images were analysed by counting the number of voxels of residually trapped scCO_2 to find the proportion of the rock volume occupied by trapped scCO_2 – the capillary trapping capacity. This can then be converted to a residual saturation (S_r) by dividing this value by the

porosity as obtained using helium porosimetry. In all rock types, significant proportions of scCO_2 were trapped as a residual phase. Sandstones tended to have higher residual saturations than carbonates, and higher capillary trapping capacities. The exception to this trend was Mt Gambier, which had an extremely high capillary trapping capacity, yet a rather low residual saturation due to the extremely high porosity of this sample.

Sample	Volume (voxel)	Volume (mm)	Initial Saturation	Residual Saturation	Capillary Trapping Capacity	S_r/S_i	Largest Ganglion Contribution	Fitted Fisher Exponent
Bentheimer	927 ×	6.078 ×	0.453	0.320 ± 0.010	0.070 ± 0.002	0.706	0.06 ± 0.06	2.11
	908 ×	5.954 ×						
	3305	21.67						
Doddington	916 ×	6.006 ×	0.488	0.33 ± 0.04	0.064 ± 0.008	0.681	0.06 ± 0.06	2.17
	906 ×	5.941 ×						
	3306	21.68						
Estailades	927 ×	6.078 ×	0.238	0.155 ± 0.005	0.0458 ± 0.0014	0.646	0.0137 ± 0.0011	2.28
	904 ×	5.928 ×						
	3304	21.66						
Ketton	900 ×	5.901 ×	0.313	0.203 ± 0.013	0.047 ± 0.003	0.653	0.05 ± 0.02	2.29
	877 ×	5.750 ×						
	3314	21.73						
Mt Gambier	891 ×	5.842 ×	0.32	0.212 ± 0.009	0.116 ± 0.005	0.662	0.260 ± 0.013	1.83
	888 ×	5.823 ×						
	3296	21.61						

Table 6.1.3.1: Summary of results for trapped saturation. The largest ganglion contribution refers to the fraction of the total residual scCO_2 residing in the largest unique ganglion.

Larger core-scale studies of residual trapping in this rock type showed a lower residual saturation of 0.137 ± 0.012 [155]. Data was not available for direct comparison with the other samples; however, the behaviour of scCO_2 and brine has been studied in Berea, a consolidated sandstone similar to Doddington and Bentheimer. A residual saturation of 0.25 was found at the core scale [48], and 0.249 at the pore scale [119]. This compares to 0.320 ± 0.010 in Bentheimer and 0.33 ± 0.04 in Doddington in this study.

The variation of residual saturation between carbonates (with an average of 0.19) and sandstones (with an average of 0.325) can be explained by variations in the initial saturation (S_i) and variations in the ratio of microporosity to macroporosity in each sample. If, instead, we look at the efficiency of trapping (the fraction of the initial scCO_2 which is trapped in place after waterflood; S_r/S_i) then we find much less variation (0.65-0.71) over the rock types. The sandstones showed a slightly larger capillary trapping efficiency (with Doddington and Bentheimer showing efficiencies of 0.681 and 0.706 respectively) to the carbonates (with Mount Gambier, Estailades and Ketton showing efficiencies of 0.662, 0.646 and 0.653 respectively). This compares to a capillary trapping efficiency of 0.50 seen in larger core-scale experiments in Berea sandstone [48]. The micro-flow cell seems to show more trapping than seen in larger scale experiments, possibly due to the limited flow domain preventing displacement of some scCO_2 that would be mobile in a larger system.

The ingress of brine into a scCO_2 saturated core is an imbibition process where a wetting fluid (brine) invades each pore, displacing non wetting fluid (scCO_2). In a strongly water-wet rock we expect the water to fill areas of the pore space in order of size [30], trapping disconnected ganglia in the process called snap-off. This process should be percolation like [31] so predictions can be made about the size distribution of the isolated clusters (section). The number n of clusters of volume s (measured in voxels) should scale as $n(s) \sim s^{-\tau}$ (equation 1.2.6.1), where τ is the Fisher exponent [32] (see section 1.2.6). Network modelling has shown that in three-dimensional cubic regular lattices the value of this exponent is around $\tau=2.189$ [33]. This scaling exponent is useful when assessing storage security, as the higher the value of the exponent the higher the ratio of small ganglia to large ganglia. This increases storage security as small ganglia are less easy to mobilize by viscous or gravitational forces.

In real systems the distribution of ganglia sizes will be affected by two other effects; clusters can be neither smaller than a single pore, nor larger than the system size. The modal pore size, as found by the topological analysis of the pore space (Figure 6.1.2.7) was for each sample between 2×10^2

voxel³ and 2×10^3 voxel³. As a result 10^3 voxel³ was used as a lower cut-off for ganglion size.

Lowering the effect of the upper cut-off by increasing system size was the motivation behind examining stitched volumes of multiple scans, however it can never be totally ruled out.

One way to assess the effect of the system size on overall behaviour (or how close one is to the representative elementary volume, or REV, defined as the minimum volume for which a volume increase does not change system behaviour) is to look at the contribution that the largest unique ganglion makes to the overall residual saturation. If the total trapped volume is an order of magnitude or more larger than the largest single ganglion, we can be fairly confident that all ganglia are statistically well represented and the system size (approximately the same for each rock type) is above the REV. This is the case for all rock types apart from Mount Gambier (Table 6.1.3.1), where the extremely high porosity and connectivity of the pore-space (as discussed above) prevents complete trapping for small blobs and encourages the formation of extremely large ganglia. In this case 26% of the total residual scCO₂ resides in the largest single ganglion, contributing 0.055 ± 0.003 to the residual saturation. These results are different to findings for trapping in a bead pack for an oil-brine-rock system [156], underlining the importance of experiments at representative pressures and temperatures when assessing problems pertaining to scCO₂ storage.

One natural way of extracting the Fisher exponent from real data is to plot the binned quantity, as defined by Dias and Wilkinson [31].

$$N_s = \sum_{s'=s}^{2s-1} n_{s'}$$

6.1.3.1

which should scale as:

$$N_s \sim s^{-(\tau-1)}$$

6.1.3.2

This is then plotted on a log-log plot as a function of s (Figure 9), showing power-law behaviour for large ganglia, but an under-representation of smaller ganglia compared to the power law model. All the experiments for each rock type were put into a single graph. The exponents were then calculated by excluding ganglia smaller than 10^5 voxels (approximately the start of the power-law behaviour) and performing Levenberg-Marquardt regression [157, 158] using a least absolute residual robust fitting algorithm [159, 160]. This was performed using a commercial software package (MATLAB R2013a, The MathWorks Inc., Natick, MA, 2013).

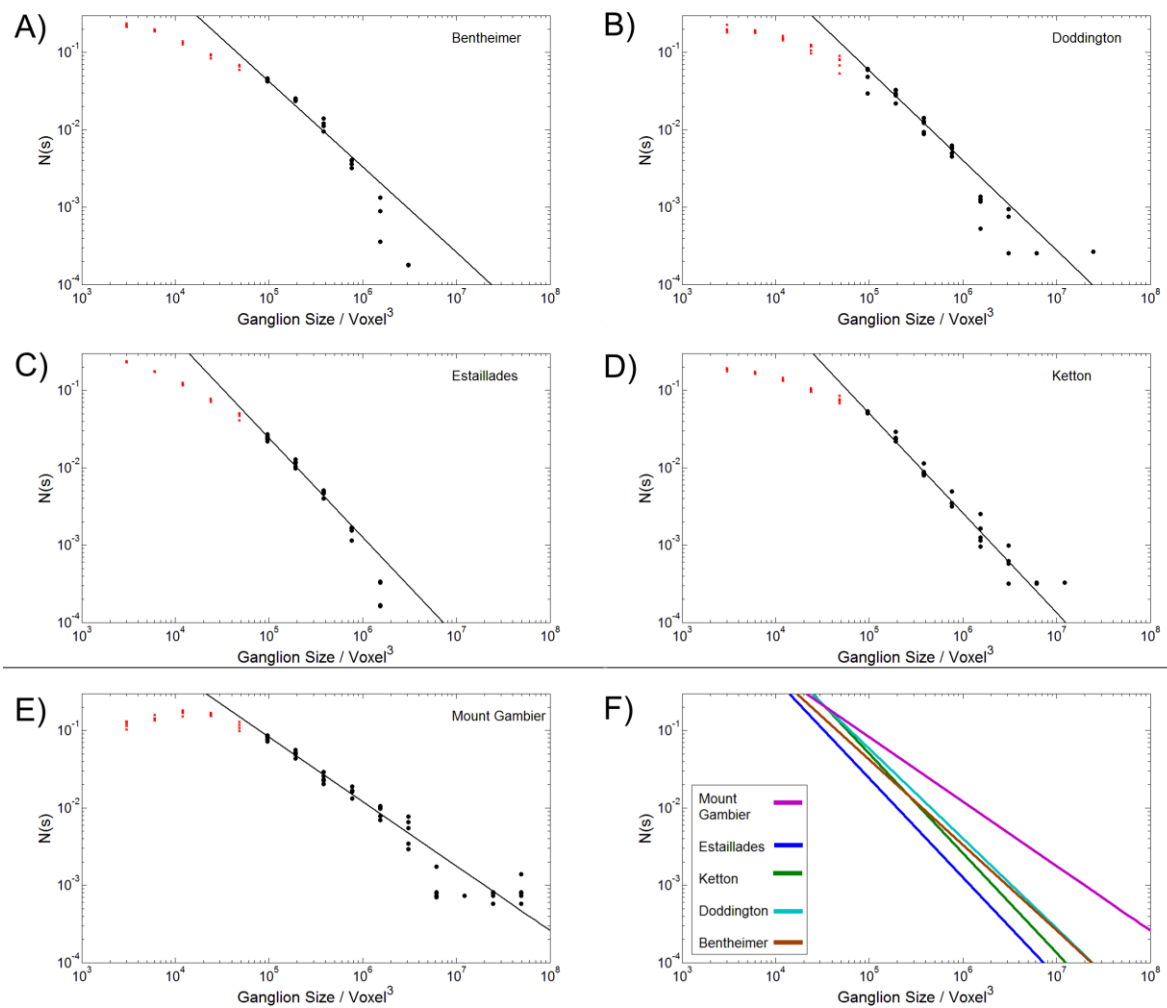


Figure 6.1.3.1: Ganglia size distribution (N_s), Equation (6.1.3.1), for all rock types. A) Bentheimer B) Doddington C) Estailades D) Ketton and E) Mount Gambier. F) Shows the fit lines all plotted together. Red data points are excluded from the percolation analysis.

The under-representation of smaller ganglia in all sample types may be explained by the fact that the scCO₂-brine-rock system is not strongly water-wet [69, 75, 161, 162]. This means that the exact nature of local pore filling and trapping may not be strictly percolation like, as cooperative pore filling or piston-like displacement may become more or less important compared to snap-off [113]. Larger (above 10⁵ voxel³) ganglia, however, see the system as a whole, averaging out local heterogeneity in the pore filling mechanism, so at this scale the trapping can only be fundamentally controlled the hierarchy of pore sizes, and so the behaviour is percolation like. These results are summarised in Table 6.1.3.1.

For all samples other than Mount Gambier, the calculated exponent fell in the range between 2.1 and 2.3, close to the theoretical value in three dimensions of 2.189. Mount Gambier had a significantly smaller Fisher exponent (1.83) which may be due to the extremely high connectivity of the pore space. This may lead to an inhibition of snap-off that disconnects the non-wetting phase, as piston like displacements or cooperative filling may come to dominate in these unusual pore geometries. During the dynamic imbibition process non-wetting ganglia in this pore-space will be substantially better connected, making it more difficult for wetting phase bypass and snap-off to strand regions of the CO₂ completely. The other carbonates have a slightly higher apparent Fisher exponent than the sandstones. This could, in turn, be explained by their slightly lower coordination numbers, as a greater proportion of the scCO₂ will reside in poorly connected portions of the pore space, which inhibit piston-like displacement compared to snap-off. Indeed there seems to be a general negative correlation between how well connected the pore space is and the fitted Fisher exponent (Figure 6.1.3.2). The trapping efficiency of each rock type (S_r/S_i) is, however, similar – in the range 0.65 -0.71 – meaning that the overall trapping behaviour appears to be fairly insensitive to pore structure.

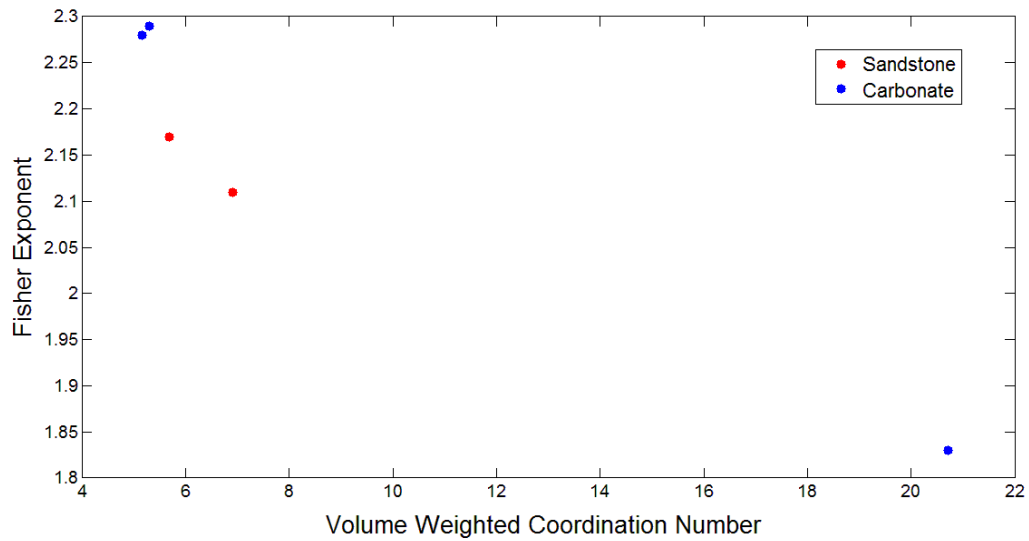


Figure 6.1.3.2: The correlation of pore-volume weighted connectivity with Fisher exponent.

More generally these results confirm conclusions in larger core-flood experiments [47, 48, 155, 163] that scCO_2 acts as the non-wetting phase in carbonates and sandstones, while brine acts as the wetting phase. This shall be further examined in section 6.3. It also shows that in the scCO_2 -brine-rock system differences in rock chemistry (at least under conditions of chemical equilibrium) matter less to the overall ganglion dynamics than differences in pore structure and connectivity. Significant residual saturations were observed in all samples, with two-thirds of the initial saturation was trapped in all cases, indicating that residual trapping is a viable local trapping mechanism in a wide range of rock types.

6.1.4 Conclusions

We have non-invasively imaged multiple fluid phases (scCO_2 and brine) at high resolution (voxel size $6.6 \mu\text{m}$) at pressures and temperatures representative of prospective subsurface storage sites in the pore-space of a suite of carbonate and sandstone rocks. In all cases, after brine injection significant proportions of the scCO_2 were trapped as a residual phase in clusters with sizes ranging over five orders of magnitude. In each case clusters larger than around 10^5 voxel^3 obeyed power law distributions consistent with percolation theory. Well-connected pore-spaces tended to have more

large clusters relative to small clusters, and vice-versa. The chemical composition of the rock had, however, comparatively little effect on the size distribution. This is encouraging for CCS, indicating that residual trapping can contribute to storage security for a wide range of rock types and compositions.

6.2 Pore by Pore Capillary Pressure Measurement: Curvature, Snap-off and Remobilization of Residual CO₂

For the next application, we used the methodology described in section 4 to use X-ray microtomographic imaging coupled with new interface curvature measurement tools to examine the capillary pressure distribution at the end point of the CO₂ trapping process. We relate these measurements to the local pore-space topography that is responsible for the snap-off of the non-wetting phase. Moreover, we use a combination of experiment and pore-scale modelling analysis to present a new methodology providing full information on how trapped CO₂ could be remobilized by either viscous or gravitational forces, with specific reference to the importance of local pore-space structure.

6.2.1 Materials and Methods

We examined samples of Ketton oolite, as fully described in section 4.1.1. The experimental parameters used in this study are shown in table 6.2.1.1.

Source Voltage / kV	Source Current / μ A	Core size / mm	Voxel Size / μ m	Brine Composition	Projection Number	Temperature / °C	Pressure / MPa	Flow Rate / m ³ /s
80	7	4-6	2 – 3.5	7 wt% KI	1,600	50	10	1.67×10^{-9}

Table 6.2.1.1: Experimental parameters used for the capillary pressure measurement study.

6.2.2 Flow Strategy and Image Acquisition

Scans were taken of residual scCO₂, which was achieved using the methodology described in section 4. Fluid rearrangement during the scan was minimised by allowing the system to re-equilibrate for 20 minutes before the scan. Two experiments were performed, one using a 4 mm diameter core imaged with a voxel size of 2.013 μ m and one with a 6.5 mm diameter core imaged with a voxel size of 3.533 μ m . The higher resolution experiment was used to test the impact of resolution on the curvature measurement, while the lower resolution experiment was used to examine the viscous

and gravitational remobilization of ganglia. The analysed volume for the lower resolution scan was more than five times larger than for the high resolution experiment, allowing for more ganglia to be examined and a more statistically representative sample to be collected, with very little change to the observed capillary pressure (section 6.2.4).

6.2.3 Image Processing and Analysis

After acquisition the images were filtered using a non-local means edge preserving filter [139, 140] before being corrected for any beam hardening or softening artefacts created during acquisition by subtracting a fitted second order polynomial surface, assumed to be constant in the Z direction, to the image. The segmentation of images containing a partial saturation of multiple fluids is significantly more challenging than the segmentation of dry images, so the use of simple grey-scale universal thresholding was insufficient [143]; see section 3.3. The image was segmented into three phases (rock grains, brine and scCO_2) by the use of a seeded watershed algorithm, where a seed was generated using a 2D histogram of both the grey-scale and the grey-scale gradient images [147]. This seed was then grown using a watershed algorithm on the grey-scale gradient image. The segmented image was then analysed in 3D to identify each unique disconnected ganglion, which was then labelled (figure 6.2.3.1).

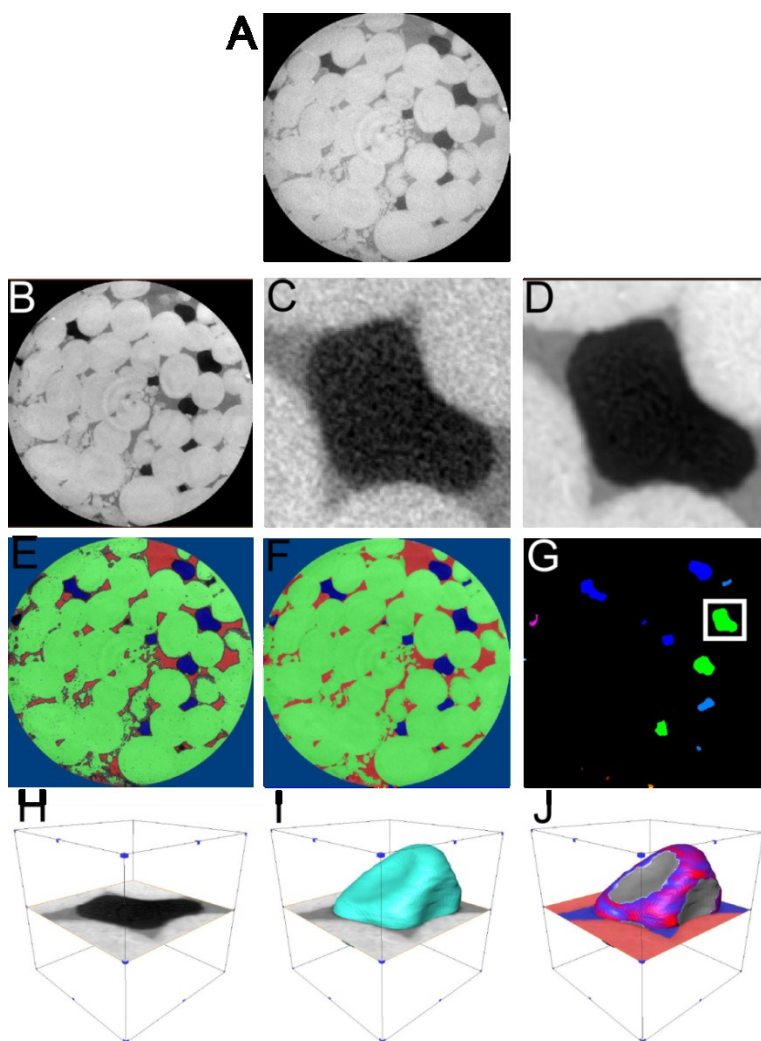


Figure 6.2.3.1: The image processing workflow. A: The raw reconstructed image. CO₂ is the darkest phase, rock grains are the lightest phase and brine is the intermediate phase. B: The raw image has been filtered using a non-local means edge preserving filter. C: A higher resolution subsection of the raw reconstructed image. The ganglion shown here is the same shown in figures 6.2.3.1H-J, figure 6.2.3.2 and figure 6.2.4.3. D: A high resolution subsection of the filtered image. E: The watershed seed image used for the initial segmentation step. F: The expanded label image, found by growing the labelled voxels in 2E using a watershed algorithm. G: A map of the ganglia present within the segmented image. H: A subvolume of the unsegmented filtered data, as shown by the white square in 6.2.3.1G. I: The data was resegmented using the same 2D seeded watershed algorithm, then a surface was generated using a generalized marching cubes algorithm. J: The curvature of this surface was found by creating best-fit quadratic surfaces across the interface.

A subvolume around each CO₂ ganglion was then extracted and re-segmented into three phases using the same 2D histogram-based watershed method detailed above. Local segmentation was likely to be more accurate than global segmentation as the artefact correction process described above may not remove all lateral variations in grey-scale across an image. The scCO₂ phase was then extracted and a smoothed surface was generated across it using a generalized marching cubes algorithm [61, 62]. The magnitude of smoothing across the ganglion surface could be altered by changing the size of the kernel of a modified Gauss filter used to compute probability weights during the surface assignment. The impact of the size of this kernel, and so the amount of smoothing, is examined later in section 6.2.4. The surface was labelled as either the CO₂-brine interface or the CO₂-grain interface by the use of the Sobel edge detection filter [164].

The curvature of this surface is found by approximating the surface locally as a quadratic form, equation 2.2.11. The eigenvalues and eigenvectors of this quadratic form represent the principal curvature values and the directions of principal curvature respectively. A surface scalar field is produced where the principal radii of curvature are averaged and assigned to each element across the interface. This method was originally described in Armstrong *et al.* [60]. The distribution of curvature seen across the CO₂-brine interface of a representative ganglion is shown in figure 6.2.3.2.

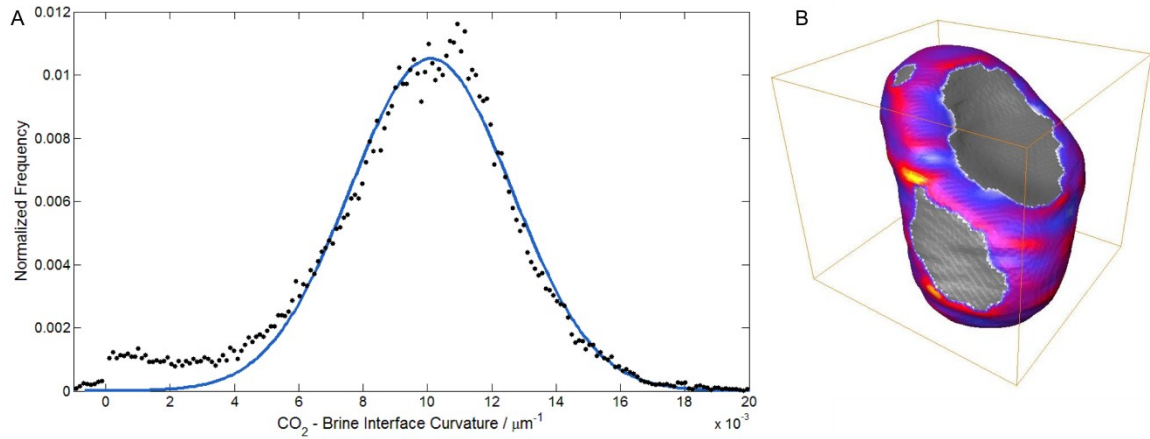


Figure 6.2.3.2: A: A histogram of the curvature of the CO₂-brine interface for a single ganglion. The blue line represents a fitted Gaussian distribution, giving an objective estimation of peak position. B:

The curvature map across a single ganglion. Blue colours represent low curvatures and yellow colours represent high curvature. Grey areas represent regions of the CO₂ ganglion which are in contact with the rock grain and which are ignored in the analysis.

The distribution clearly shows a single, well-defined peak, representing a single capillary pressure across the entire CO₂-brine interface. This distribution is then fitted using a trust region algorithm [165] in order to objectively estimate the peak position. From this peak position the pressure difference across the CO₂-brine interface – the microscopic capillary pressure – is calculated using the Young-Laplace equation (equation 2.2.9). The CO₂-brine interfacial tension is estimated by linearly interpolating between measurements found in [44, 45], for a given pressure, temperature and salinity, and a value of 0.0339 N/m was used in this study (see Table 6.2.3.1 for this and other fluid properties). Ganglion volume was measured by counting voxels and interfacial area was calculated measuring the area of the surface labelled as the CO₂-brine interface.

The CO₂ and brine labels of the whole segmented image were then joined together, so that the entirety of the pore-space could be analysed as a single unit. The pore-space was separated into individual pores by finding the watershed catchment basins of a Euclidian distance map of the pore-space (figure 6.2.3.3) [118, 146].

These pores were then individually labelled, and the interfaces between them defined as throats. Each throat was given a “radius” equivalent to the maximum of a Euclidian distance evaluated around the throat plane, equivalent to the radius of the maximum inscribed circle through the throat plane. The viscous remobilization criterion proposed in this work is stated as when the viscous pressure drop across a ganglion is larger than the difference between the static capillary pressure and the capillary pressure required to pass through the largest of the adjacent throats.

The viscous pressure drop was calculated by simulating incompressible viscous flow directly through the wetting phase. The volume conservation equation and the Navier-Stokes equation were solved using a finite volume method implemented in OpenFOAM [100]. The pressure and velocity field are solved iteratively based on the Pressure Implicit with Splitting of Operators (PISO) algorithm of Issa [166] (see Bijeljic *et al.* [167], Raeni *et al.* [99] and section 2.4 for more details). The viscous pressure drop across each ganglion was then calculated by finding the maximum and minimum pressure of the wetting phase voxels in contact with the ganglion (figure 6.2.3.3). The system was simulated at low Reynolds numbers; the pressure drop across a ganglion scaled linearly with the total pressure drop across the simulated volume, which in turn is proportional to the Darcy flow rate. Using Darcy’s law, the permeability was predicted when the image was fully-saturated with water. The wetting phase relative permeability was computed from the ratio of the pressure drop for fully-saturated flow to that with the imaged wetting phase occupancy at the end of the experiment – for the same Darcy velocity. The relative permeability of 0.28 (see Table 6.2.3.1) indicates that the ganglia restrict flow through some of the larger pore spaces, but that there is still significant connectivity of the wetting phase.

Darcy velocity (ms ⁻¹)	σ^a (Nm ⁻¹)	μ^b (Pa.s)	Permeability (m ²)	Wetting phase relative permeability
3.68×10^{-4}	0.0339	6.24×10^{-4}	3.59×10^{-12}	0.283

Table 6.2.3.1: List of key fluid and rock properties used in this study.

^a Taken from Li *et al.* [45].

^b Taken from Batzle & Wang [168].

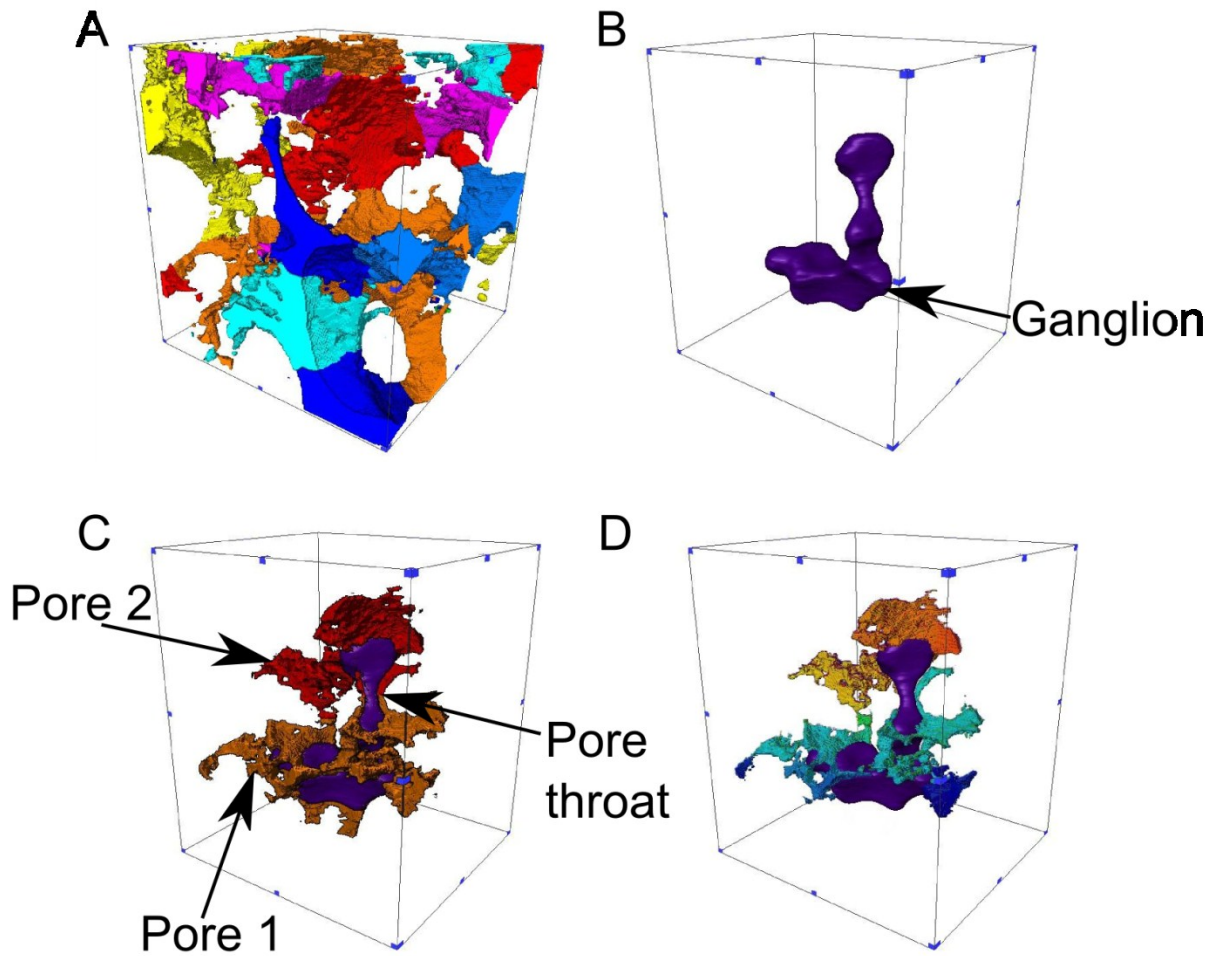


Figure 6.2.3.3: Ganglion occupying two pores. A: A rendering where each pore close to the ganglion shown in 4B-D, as found using the watershed basins of the distance map of the pore space, is rendered in a different colour. B: Shows the ganglion surface in purple. C: Shows that the ganglion is situated within two pores, with pore 1 coloured yellow and pore 2 coloured red. The narrow pore throat is indicated. D: Shows the pressure field calculated using finite volume method in OpenFOAM [99, 100, 167]. Blue regions represent low pressure and red regions represent high pressure. The maximum viscous pressure drop across the ganglion was found by finding the maximum and minimum pressure in the wetting phase adjacent to the ganglion.

6.2.4 Measurement Error

In order to quantitatively address potential measurement error for the image analysis process described above we conducted two sensitivity studies. First we address the impact that voxel size has on calculated ganglion curvatures, then we examine the impact that different amounts of smoothing during surface generation have on resulting curvature distributions. To examine the impact of voxel size on measured curvature, data from a high resolution experiment (with a voxel size of $2\text{ }\mu\text{m}$) was artificially coarsened to a voxel size of $4\text{ }\mu\text{m}$ by binning the data from around $1,000^3$ to 500^3 . The surface generation and curvature extraction procedure described above was then applied at both resolutions (figure 6.2.4.1).

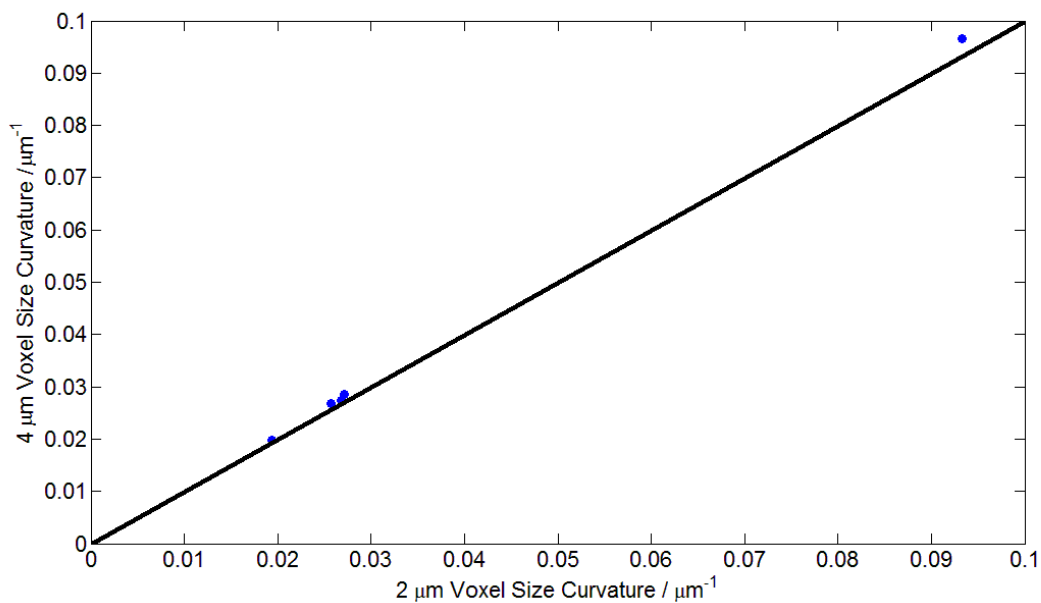


Figure 6.2.4.1: The variation of fitted curvature with voxel size. The peak curvature position measured at a $2\text{ }\mu\text{m}$ voxel size is indicated on the x axis, and the peak curvature position measured on a subsampled lower resolution image is shown on the y axis. The black line shows a 1:1 correspondence.

For this system, coarsening to a $4\text{ }\mu\text{m}$ voxel size has little effect on the peak curvature position, so the experiment with a larger voxel size ($3.533\text{ }\mu\text{m}$) was used, since many more ganglia could be

sampled. To examine the impact of smoothing on the calculated curvature, surfaces were generated across a representative ganglion multiple times using different smoothing kernel sizes (figure 6.2.4.2).

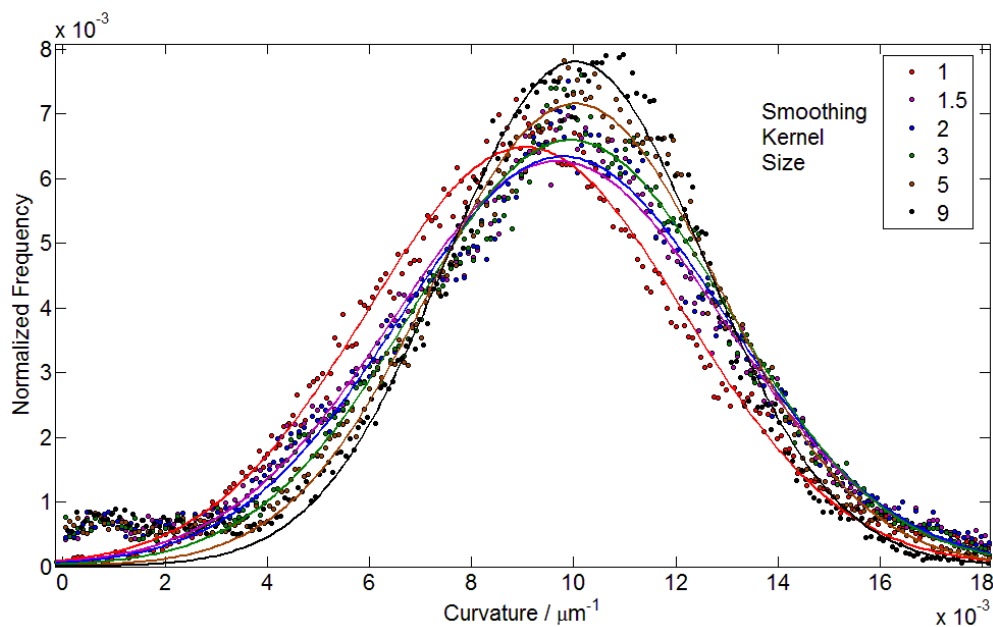


Figure 6.2.4.2: The impact of the smoothing kernel size on curvature distribution. The curvature peak position remains almost unchanged.

The peak curvature value changes very little with an increasing amount of surface smoothing (figure 6.2.4.3). As the magnitude of the principal radii of curvature of the CO₂-brine interface is around 100 times the voxel size, smoothing across these curvatures has a relatively small impact on their distribution.

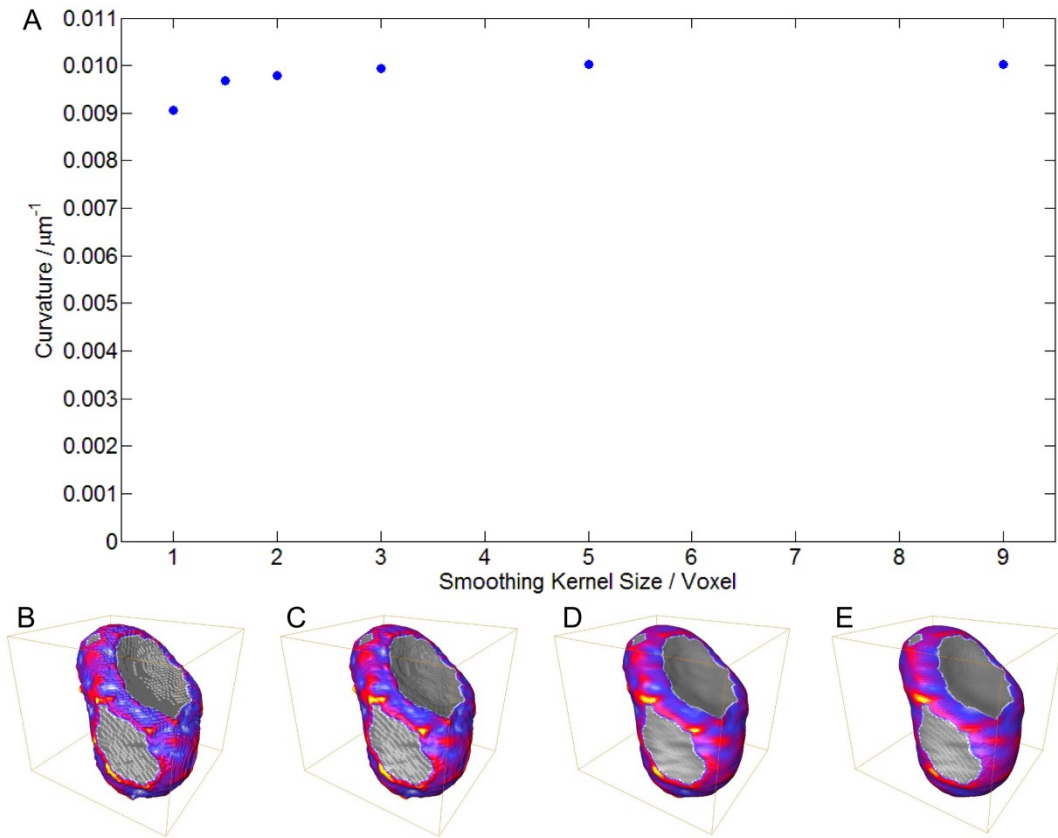


Figure 6.2.4.3: A: The variation of fitted curvature peak position with smoothing kernel size. Once more than a small amount of smoothing is applied, the curvature peak position remains unchanged.

B-E: The same ganglion rendered with different amounts of smoothing across the CO_2 -brine interface. B: 1 voxel kernel size. C: 1.5 voxel. D: 5 voxel. E: 9 voxel.

6.2.5 Results and Discussion

6.2.5.1 Snap-off

The interface curvature and the corresponding ganglion capillary pressure is observed to be a strong function of local pore topography, as measured by the maximum throat radius adjacent to the ganglion (figure 6.2.5.1.1). Ganglia that have smaller maximum adjacent throat radii are characterised by higher experimentally measured capillary pressures.

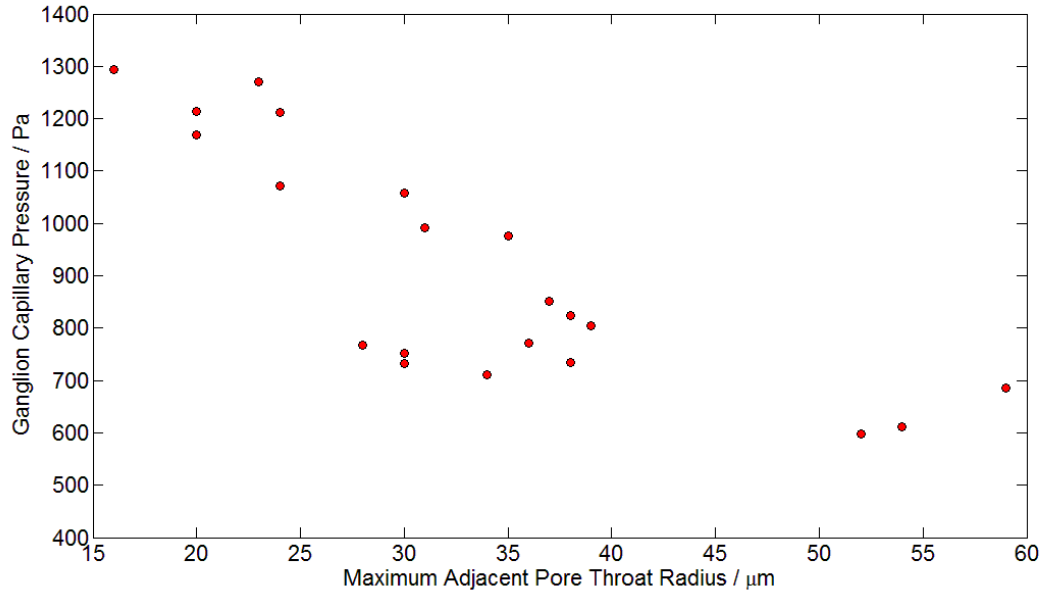


Figure 6.2.5.1.1: The variation of ganglion capillary pressure with maximum adjacent pore throat radius.

This is explained by the process of snap-off [30]. During capillary-driven wetting phase ingression (imbibition) the capillary pressure decreases along a hysteretic capillary pressure curve (see figure 2.2.1). As the capillary pressure decreases, the wetting phase (brine) layers in throat corners will swell until the CO_2 -brine interface becomes unstable, causing the throat to rapidly fill with water. If this throat is the only connection between a volume of CO_2 that may become isolated and the connected CO_2 phase, its filling will result in the formation of a disconnected CO_2 ganglion that preserves the capillary pressure at which it became immobilized. This process can be best understood by considering a set of throats surrounding a region of the pore-space filled with CO_2 . These throats can be represented by a set of hypothetical elements with cross-sections consisting of scalene triangles, with corner half angles β_1 , β_2 and $\beta_3 (=180 - (\beta_1 + \beta_2))$ (figure 6.2.5.1.2), defined such that $\beta_1 \leq \beta_2 \leq \beta_3 < \pi$ [169]. The elements maintain both the maximum inscribed radius, r , of the original throats with a shape factor G , such that $G = \frac{A}{P^2}$, where A is the cross-sectional area of the throat and P is its perimeter.

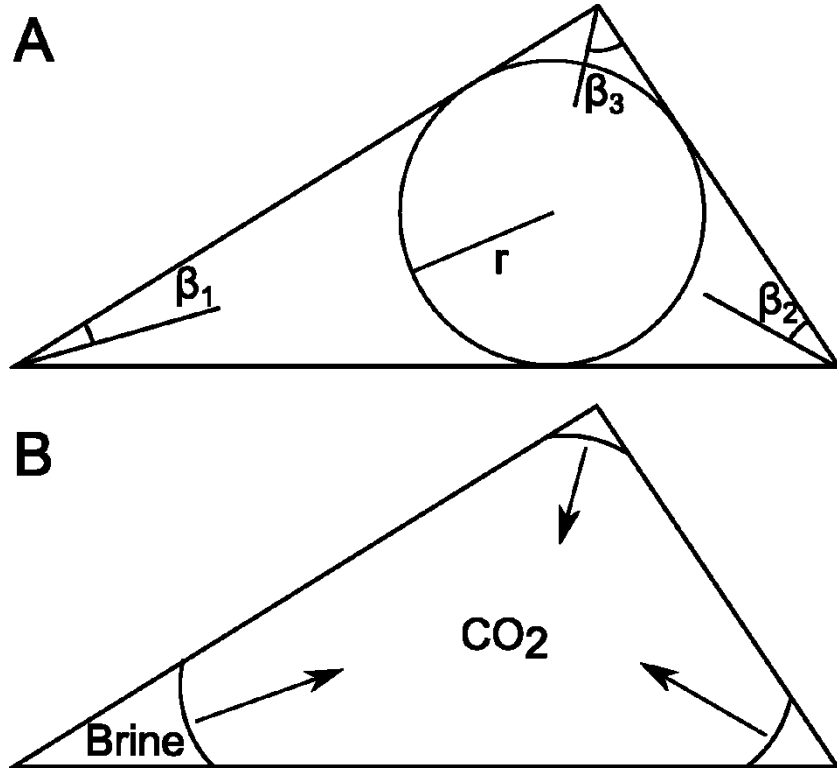


Figure 6.2.5.1.2: Throats can be represented as idealised triangular elements. A) The half angles and maximum inscribed circle for a pore throat. B) During imbibition the brine layers swell until two layers come into contact, making the CO₂-brine interface unstable and causing the throat to rapidly fill with brine in the process of snap off.

Snap off will occur when two of the wetting phase corner regions swell until they come into contact, after which the CO₂-brine interface becomes unstable and the throat rapidly fills with brine. If all three interfaces swell concurrently, this will occur between the interfaces in the two corners with the smallest half angles at a threshold capillary pressure [86]:

$$P_{c-so} = \frac{\sigma}{r} \left(\cos \theta_a - \frac{2 \sin \theta_a}{\cot \beta_1 + \cot \beta_2} \right)$$

6.2.5.1.1

As β_1 and β_2 are not uniquely defined by inscribed radius and shape factor, the snap off capillary pressure is also non-uniquely defined. It is therefore useful to consider the case where $\beta_1 = \beta_2 = \beta$, so equation 6.2.5.1.1 reduces to:

$$P_{c-so} = \frac{\sigma}{r} (\cos \theta_a - \sin \theta_a \tan \beta)$$

6.2.5.1.2

For a given shape factor and radius, the snap-off capillary pressure is now uniquely defined, and should scale approximately with the inverse of the inscribed throat radius. If local capillary equilibrium is maintained, and the throat half angle is constant, as capillary pressure decreases, connected throats will snap off in order of radius size. The final throat to snap off, disconnecting a residual ganglion, will therefore have the largest inscribed radius, and the resulting ganglion should preserve the capillary pressure at which this throat snapped off. As capillary equilibrium is maintained beyond a single pore, a CO₂ ganglion can span multiple pores. This occurs if snap-off in adjacent pores causes the ganglion to be isolated from the rest of the connected CO₂ phase before all the throats adjacent to a single pore have snapped off.

A correlation can be seen between the capillary pressure of a ganglion and the maximum inscribed radius of the adjacent pore throats (figure 6.2.5.1.3).

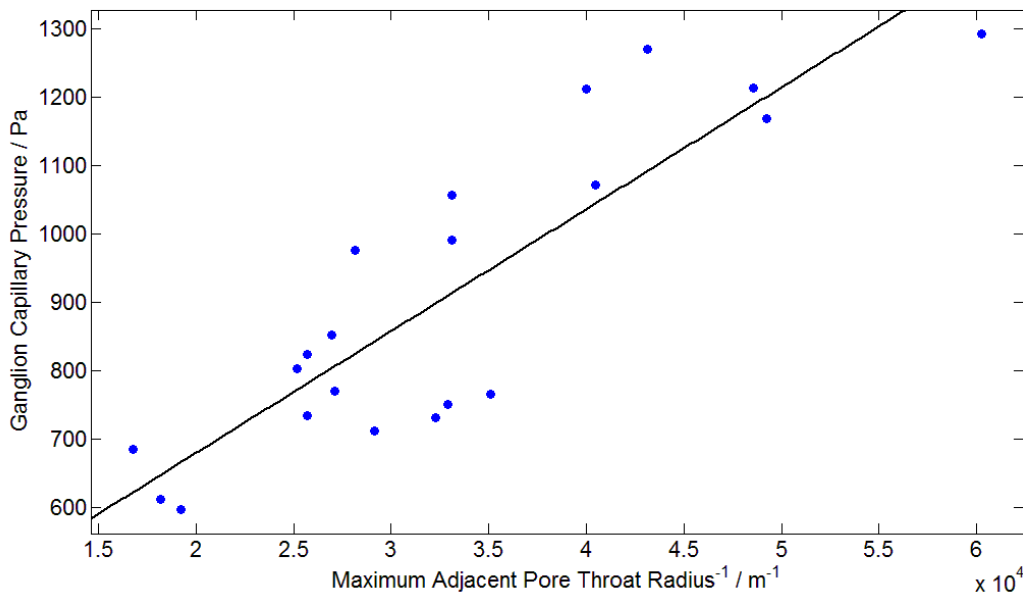


Figure 6.2.5.1.3: The variation of ganglion capillary pressure with the inverse of the maximum adjacent pore throat radius.

This correlation is only approximate as real throats may not maintain a constant shape factor with size, and even if they did, they may not be perfectly represented by idealised triangular elements. The contact angle in this system has been examined by Andrew *et al.* [170] (see section 6.3) finding a contact angle distribution of $45 \pm 10^\circ$. This variation in contact angle may contribute to any deviation from the inverse correlation between capillary pressure and adjacent throat radius. A linear model was fitted using a trust region algorithm [165], finding a coefficient of 0.017 ± 0.002 Pa.m, corresponding to a half angle of 15° for a contact angle of 45° , which can be used to assign the capillary pressure for snap off in network models.

6.2.5.2 Viscous Remobilization

The adjacent pore throats are a strong control on the viscous pressure drop required for ganglion remobilization (figure 6.2.5.2.1). The ganglion volume, however, is not well correlated to the adjacent pore throat radius. This is because ganglia can occupy multiple adjacent pores connected by relatively large pore throats which had not fulfilled the criteria for snap-off during wetting phase invasion.

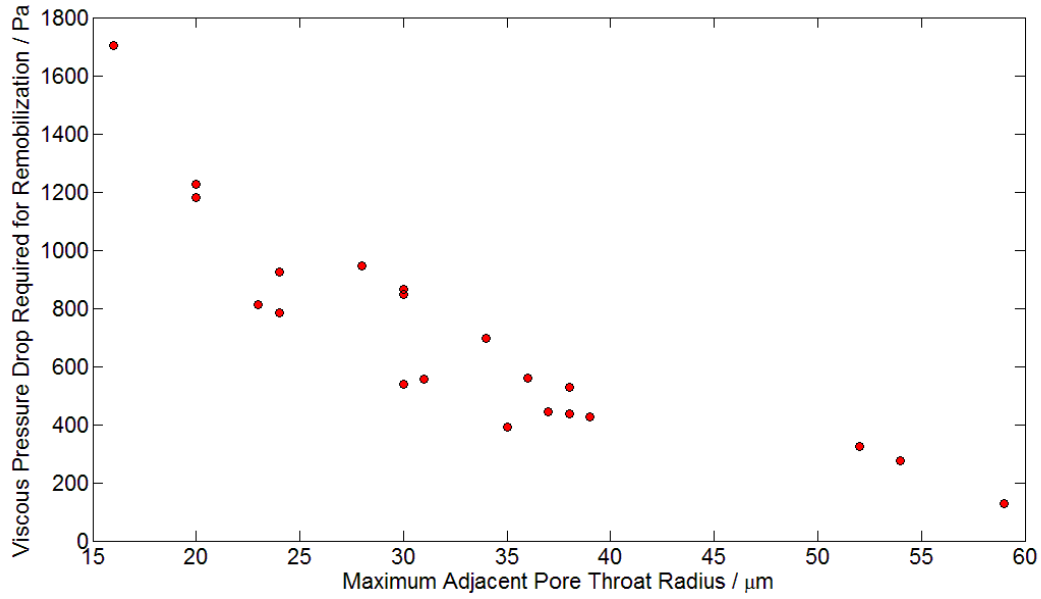


Figure 6.2.5.2.1: The variation of viscous pressure drop required for ganglion remobilization with maximum adjacent pore throat radius.

The ganglion volume is, nevertheless, important for cluster remobilization. Traditional examinations of capillary desaturation have focussed on the conventional capillary number where μ is the dynamic viscosity, q is the Darcy velocity and σ is the surface tension (also see equation 2.5.1.1):

$$N_c = \frac{\mu q}{\sigma}$$

6.2.5.2.1

With this representation of the relative effect of viscous forces versus surface tension, remobilization tends to occur above $N_c \sim 10^{-5}$ (e.g. [101]). This is unsatisfactory as, if the capillary number is to reflect the balance between viscous and surface forces, desaturation should occur at capillary numbers around 1. New formulations of capillary number [102, 105, 106] have incorporated the increased impact of viscous shear across an extended non-wetting-wetting phase interface by adding a term incorporating cluster length (as discussed in section 2.5.1). This is only valid if the pressure drop across any ganglion is proportional to the cluster length. In a uniform flow field this is the case; however the flow field through the wetting phase at residual saturation is

heterogeneous. These new formulations are also divorced from the direct physics of the remobilization process. In this study we propose a new definition for capillary number rigorously based on the pore-scale physics of the desaturation process.

The capillary number is defined as the ratio between viscous and surface forces, or the ratio between the viscous pressure drop across a ganglion and the capillary pressure, both acting over the ganglion interfacial area. Each ganglion is assigned a unique microscopic capillary number N_{cmicro} :

$$N_{cmicro} = \frac{\text{Viscous pressure drop across ganglion}}{\text{Capillary Pressure}} = \frac{\Delta P}{P_c}$$

6.2.5.2.2

The viscous pressure drop (ΔP) is computed directly by solving for flow in the wetting phase, as discussed previously in section 6.2.3 – this value is proportional to the imposed total Darcy velocity (flow rate). The capillary pressure (P_c), as described above in section 6.2.3, is found from the maximum curvature of the ganglion interface with the wetting phase.

This capillary number definition can then be upscaled to a macroscopic capillary number (N_{cmacro}) using a volume weighted average of the ratio of N_{cmicro} over k ganglia:

$$N_{cmacro} = \frac{\sum_{j=0}^k V_g^j N_{cmicro}^j}{\sum_{j=0}^k V_g^j}$$

6.2.5.2.3

where V_g^j is the volume of the j^{th} ganglion. Using this definition, the fraction of ganglia fulfilling the desaturation criterion is shown in figure 6.2.5.2.2 as a function of the macroscopic capillary number N_{cmacro} , equation (6.2.5.2.3) and N_c , equation (6.2.5.2.1). A ganglion is considered to be remobilized when the viscous pressure drop across it is equal to or greater than the difference between the ganglion's capillary pressure and the capillary pressure required to pass through the largest of the

adjacent pore throats, $N_{cmicro} > 1$. Remobilization is achieved through increasing the wetting phase flow rate.

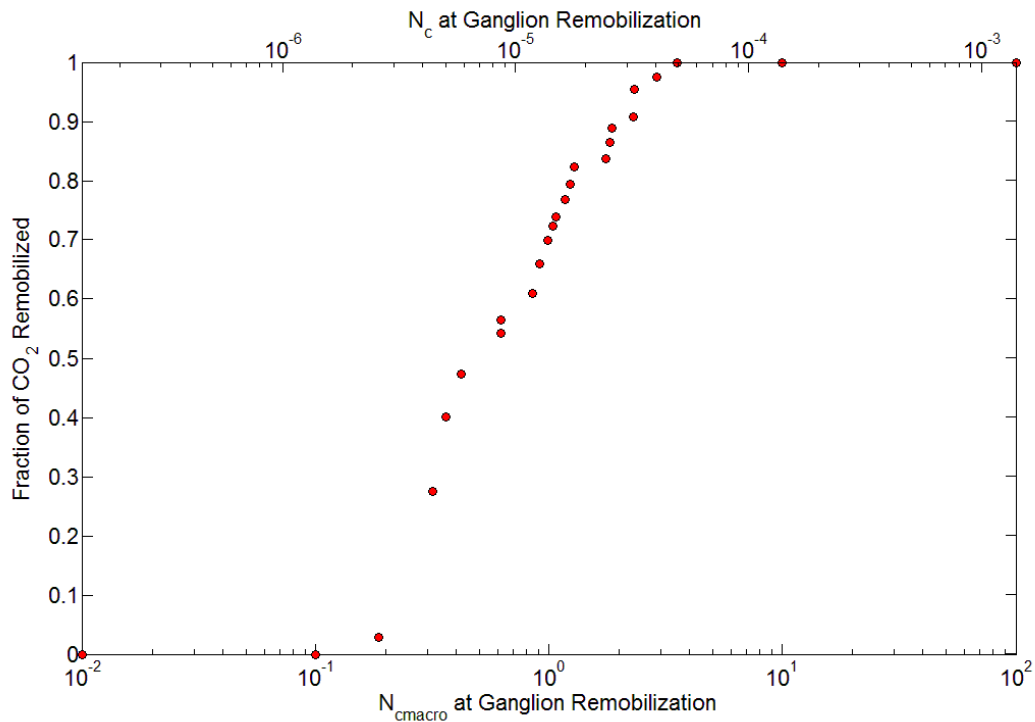


Figure 6.2.5.2.2: The fraction of CO_2 remobilized as a function of N_c and N_{cmacro} . Most ganglia fulfil the remobilization criteria around $N_{cmacro}=1$, and around $N_c=10^{-5}$.

The vast majority of the ganglia fulfil the remobilization criteria at N_{cmacro} around 1, and traditional capillary numbers (N_c) of around 10^{-5} . This demonstrates that this overall formulation for N_{cmacro} and the defined averaged parameters provide a reasonable representation of the local flow, whereas the traditional formulation for capillary number does not correctly represent the local balance between viscous and surface forces.

Our results on capillary trapping addressing a large range of rock types [154, 171], section 6.1, show that the distribution of ganglia sizes at residual saturation is controlled by pore-space structure and connectivity. Well-connected rocks tend to have more large clusters relative to small clusters and vice-versa. In this context it is interesting to examine the relationship between ganglion volume and remobilization. We would expect larger volume ganglia to have a larger cluster length along the

direction of the viscous pressure drop, and so should be easier to remobilize than smaller ones. This is the case with spherical ganglia, however as non-spherical ganglia (particularly long thin ganglia with high aspect ratios) may not be aligned with the direction of flow; hence any relationship between ganglion volume and remobilization of high aspect ratio ganglia would be inexact. Ganglion snap-off (as discussed above) is controlled by local pore topography, which is isotropic through the sample, so ganglia have no preferred orientation upon formation. On the other hand, remobilization is controlled by the viscous pressure field, which is highly directional. The relationship between the macroscopic capillary number (N_{cmacro}) required to remobilize each ganglion and the ganglion volume is presented in figure 6.2.5.2.3.

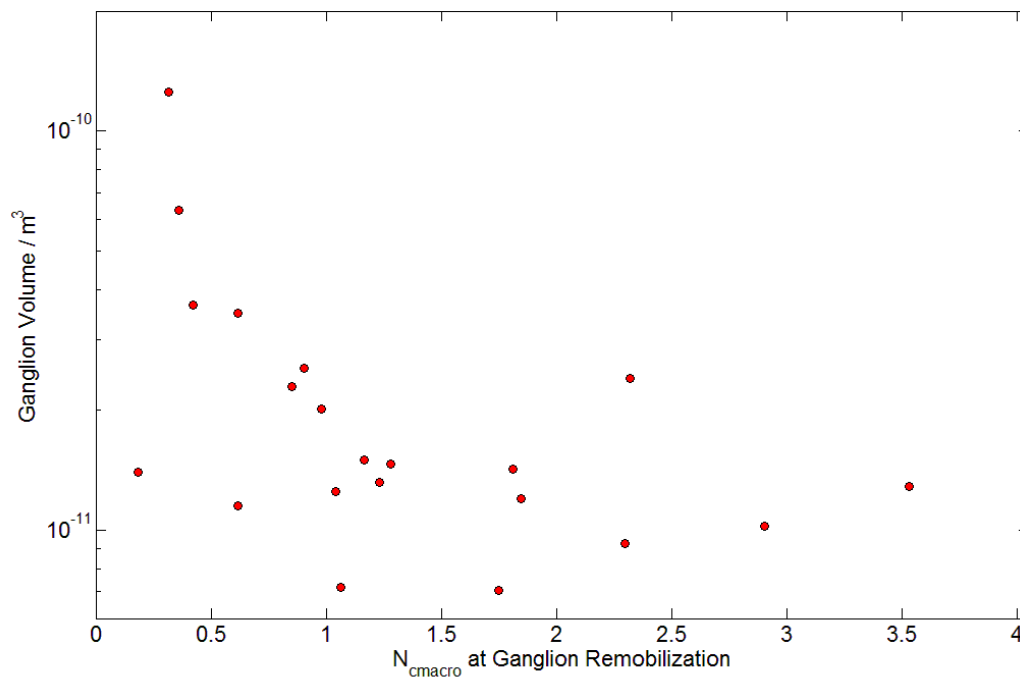


Figure 6.2.5.2.3: The relationship between the ganglion volume and the macroscopic capillary number N_{cmacro} required for remobilization of that ganglion.

Large ganglia tend to be remobilized at smaller N_{cmacro} than small ganglia. This is critical in understanding the differences between remobilization in different rock types as local pore

topography and connectivity are controlling factors in ganglia size distributions, section 6.1, [154], so they should be a controlling factor in viscous remobilization.

6.2.5.3 Gravitational Remobilization

Another potential mechanism for remobilization is the gravitational force arising from the density difference between the non-wetting phase and the wetting phase. This is traditionally defined using the Bond number (N_b), given by the ratio of gravitational forces to surface forces acting on some characteristic length scale L :

$$N_b = \Delta\rho g \frac{L^2}{\sigma}$$

6.2.5.3.1

where g is the acceleration due to gravity, $\Delta\rho$ is the density difference between the wetting and non-wetting phase and σ is the interfacial tension. Similarly to the analysis presented for the capillary number, it is possible to reformulate the Bond number to rigorously reflect the ratio between the buoyancy and capillary forces at the pore scale. Each ganglion of volume V_g has a buoyancy force acting on it equal to $\Delta\rho g V_g$ and capillary force equal to the capillary pressure acting on the interfacial area:

$$N_{b\text{micro}} = \frac{\text{Gravitational Forces}}{\text{Capillary Forces}} = \Delta\rho g \frac{V_g}{A_s \cdot P_c}$$

6.2.5.3.2

where A_s is the CO₂-brine interfacial area for an individual ganglion, computed by counting the number of faces between wetting and non-wetting phases in the segmented image.

The distribution of microscopic Bond numbers $N_{b\text{micro}}$ calculated from this experiment is relatively narrow ($5.2 \pm 1.4 \times 10^{-4}$) and shows that at residual saturation capillary forces are far stronger than gravitational forces. Ganglion volume to surface area ratios would have to increase, or capillary pressures decrease, by more than three orders of magnitude in order to start the gravitational remobilization of the residual CO₂. Although there are mechanisms for such a process, such as Ostwald Ripening [172], these rely on larger clusters having correspondingly lower surface energies,

due to lower surface areas at a given saturation. This can be examined in this system by looking at the ganglion volume to surface area ratio (V_g/A_s), which decreases with ganglion volume up to a certain point, as shown in figure 6.2.5.3.1. As ganglia span more and more pores, however, interfacial area increases almost linearly with ganglion volume, meaning their ratio V_g/A_s changes little, if at all. As larger clusters inside a porous medium are not as energetically favourable as they are in a free liquid (where volume to surface area ratios decrease as ganglion volume increases) there is no energy gradient to drive the process of Ostwald Ripening.

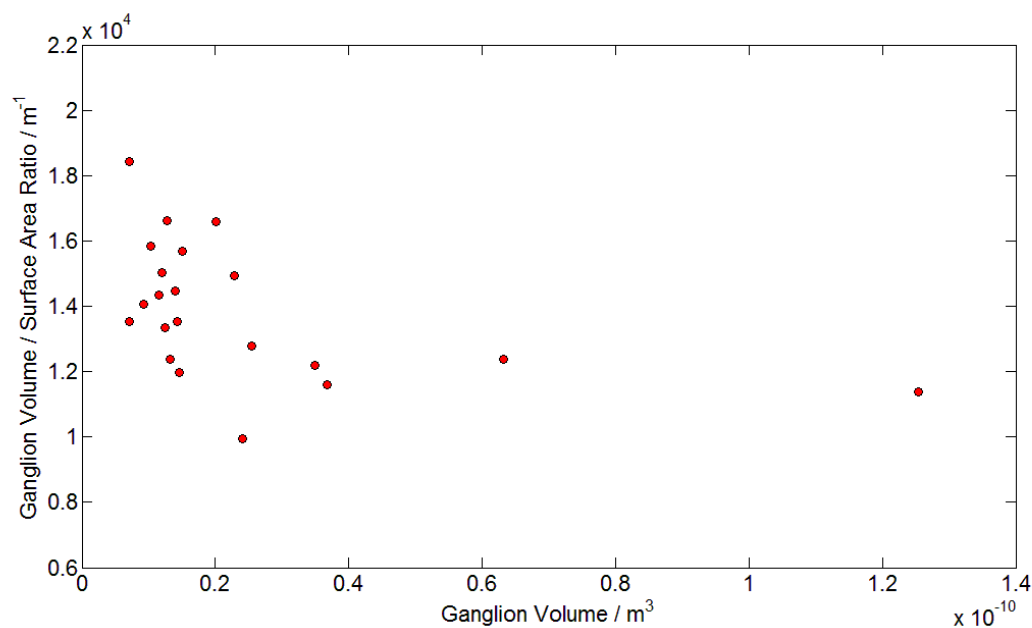


Figure 6.2.5.3.1: The variation of Ganglion Volume / Surface Area Ratio with ganglion volume. The smaller ganglia have higher volume/surface area ratios, while larger ganglia show relatively little variation.

If saturation were to increase, the non-wetting phase connectivity would correspondingly increase, decreasing total surface area. This would, however, require significant remobilization, which is difficult, as discussed above. As microscopic capillary pressure is unlikely to decrease by three orders of magnitude given fixed pore topographies and contact angles, the gravitational remobilization of

residual CO₂ seems extremely difficult, a positive result for capillary trapping efficiency in carbon capture and storage.

Following the approach of the previous section, this microscopic Bond number can be upscaled to a macroscopic Bond number by using a volume-weighted average:

$$N_{bmacro} = \frac{\sum V_g^j N_{bmicro}^j}{\sum V_g^j}$$

6.2.5.3.3

The upscaled Bond number in this system at residual saturation was 6.14×10^{-4} , confirming that gravitational remobilization for disconnected ganglia is extremely difficult.

6.2.6 Conclusions

We have presented a new method for measuring the curvature, formation, displacement and remobilization of a residual phase on a pore by pore basis at pressures and temperatures representative of flow in subsurface aquifers and oil and gas reservoirs (10 MPa and 50°C). At residual saturation capillary pressure was found by extracting interface curvature from the CO₂-brine interface surface. This was then compared to local pore topography by the use of a watershed algorithm on the distance map of the pore space in order to examine snap off, and viscous and gravitational remobilization of the residual CO₂. Capillary pressure was found to be a strong function of local pore topography, explained during imbibition by the timing of snap-off events, where small pore throats are snapped off early in the imbibition process and large pore throats are snapped off later. The viscous pressure drop across each ganglion was found by direct modelling of flow through the wetting phase, and this information was used to develop a new, physically based, capillary number definition. This showed that most ganglia fulfilled the remobilization criteria at capillary numbers around 1. Similarly a new formulation of the Bond number is proposed and it is shown that the gravitational remobilization of capillary trapped CO₂ is extremely difficult. This is an important

result for assessing the security of residual trapping as a mechanism for the long term immobilization of CO₂ in the subsurface.

The method for assessing fluid behaviour on a pore-by-pore basis has an application to a wide range of problems in porous media, and future work will focus on the application of this technique to dynamic (time resolved) tomographic systems (see section 6.4).

6.3 Contact angle measurement

The third application for the methodology described in section 4.1 is the measurement of contact angle, one of the fundamental controls on the macroscopic parameters for multiphase flow in porous media, such as capillary pressure and relative permeability (section 2). This in turn impacts the overall flow behaviour, such as oil and gas recovery [173, 174], methane production from hydrate bearing sediments [175-177] and the process of geological CO₂ storage [72, 178, 179].

6.3.1 Methods

The experimental apparatus is shown in figure 4.1.1.1, and described in section 4.1.1. Contact angle measurements were taken on images where the scCO₂ had been trapped as a residual phase, isolated as small droplets in the pore-space, as achieved in using the experimental protocol described in section 4.1.1. The experimental parameters used in this study are given in table 6.3.1.1.

Source Voltage / kV	Source Current / μ A	Core size / mm	Voxel Size / μ m	Brine Composition	Projection Number	Temperature / °C	Pressure / MPa	Flow Rate / m ³ /s
80	7	4	2.013	7 wt% KI	1,600	50	10	1.67×10^{-9}

Table 6.3.1.1: Experimental parameters used for partially saturated imaging in the contact angle study.

To reduce fluid re-arrangement the sample would be left for no more than approximately 20 minutes prior to image acquisition. The projections were binned from a 2000 $\times$ 2000 grid to a 1000 $\times$ 1000 grid on the camera. These projections were then reconstructed into a 3D volume using proprietary software on the Versa system, creating a reconstructed volume of 1,000³ voxels. The final examined field of view was 2 mm $\times$ 2 mm $\times$ 2 mm. A small voxel size (2.013 μ m) was used, so only a central portion of the core was within the field of view. Decreasing the voxel size would have increased image noise due to the effects of more material outside the field of view. It would have also greatly increased scan acquisition time, which would have increased the risk of interface movement during the scan, as discussed in section 4.1. On the other hand, larger voxels would lead

to less accurate identification of the phase interfaces. The ganglia examined in this study contained between 300,000 and 5,000,000 voxels, with a mean ganglion volume of 2,500,000 voxels.

6.3.2 Image Processing and Contact Angle Measurement

After acquisition the images were filtered using a non-local means edge preserving filter [139, 140] (section 3.2). They were then corrected for any beam hardening or softening artefacts created during image reconstruction by modelling these artefacts as radially symmetric Gaussian functions (section 3.1). The centre of this function was allowed to take any point in the x and y dimensions, but was assumed to be uniform in the z direction. As segmentation of images containing a partial saturation of multiple fluids is significantly more difficult than the segmentation of dry images [143], the use of simple grey-scale segmentation was insufficient. Instead a seeded watershed algorithm was used, with the seed generated by the use of a 2D histogram [147]. This segmented image was then analysed in 3D to identify each unique disconnected ganglion, which was then labelled.

A subvolume was then extracted around each unique ganglion and resegmented using the same 2D histogram-based watershed method detailed above, as the beam hardening and softening correction may not remove all lateral variations in grey-scale value across the image. Local segmentation was therefore likely to be more accurate than the primary global segmentation.

The edges of each phase were found on this new segmented image using a 3D Sobel filter [164]. The intersection of the edges of all three phases (scCO₂, brine and solid) was labelled as the contact line which could be traced in 3D. Finally a bilinear filter was applied to the resampled slice to eliminate possible angular quantisation due to the voxelized nature of the image. The contact angle was then measured by resampling the data onto a plane with a normal parallel to the contact line at a specific point (Figure 6.3.2.1). The measurement was taken according to the best interpretation of the tangential direction of the relevant surfaces at the contact line and no effort to “smooth” the surfaces was made. This can be seen in figure 6.3.2.1F, where the tangential direction on the grain

surface at the contact point is seen to be at a significant angle to the larger scale attitude of the grain surface. The resulting variation in contact angle was reported as part of the distribution shown in figure 6.3.4.1.

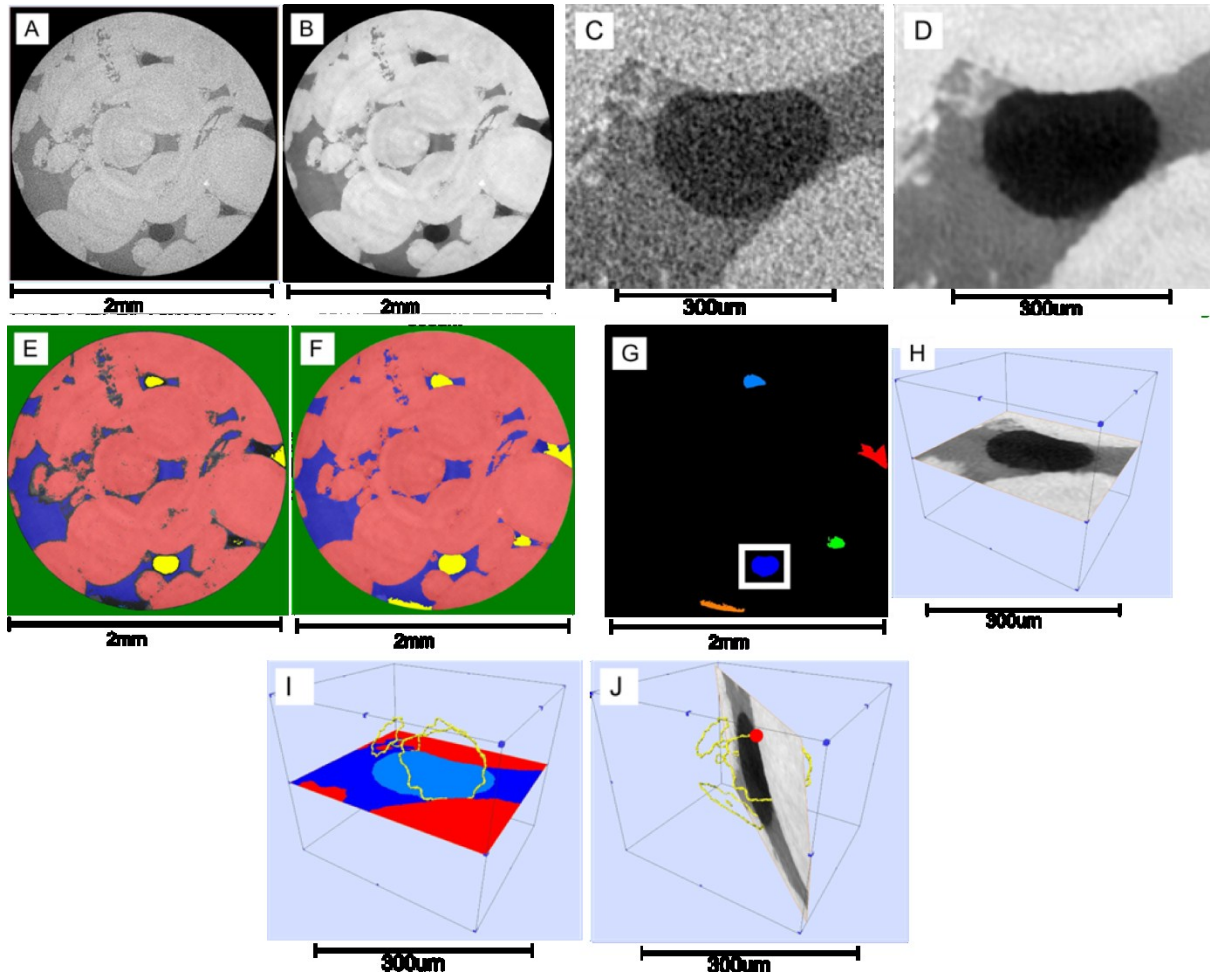


Figure 6.3.2.1: The image processing workflow. The darkest phase is scCO_2 , the intermediate phase is brine and the lightest phase is solid. A: The raw reconstructed image. B: The filtered image, filtered using a non-local means edge preserving filter and corrected for beam softening. C: A higher resolution subsection of the raw reconstructed image. D: This subsection filtered using a non-local means edge preserving filter. D: The watershed seed image, generated by labelling voxels using a 2D histogram. E: The expanded label image found by growing the seed shown in D with a watershed algorithm. F: A map of the ganglia present within the segmented image. H: A subvolume of the unsegmented data. The subvolume shown in H-J is shown as a white rectangle in G. H-J. The data were resegmented using a 2D histogram watershed segmentation. The contact line is shown as a yellow line rendered in 3D. J: The data were resampled onto a plane with a normal parallel to the contact line at a point indicated by the red dot.

Contact angles were measured manually on the unsegmented data by tracing two vectors tangential to the scCO₂-brine interface and the rock surface. The angle between these lines was then measured through the non-wetting phase with a 3D angle measurement tool (Figure 6.3.2.3). Measurements were performed at 300 points randomly selected along the scCO₂-brine-rock contact lines of different ganglia. The contact angle was not measured on the segmented data, as the angle measured was highly sensitive to the detail of segmentation close to the contact line, where we would expect the segmentation to be least accurate. In contrast, tracing the interface between the scCO₂ and the brine visually was relatively simple, making angle measurement more accurate and robust.

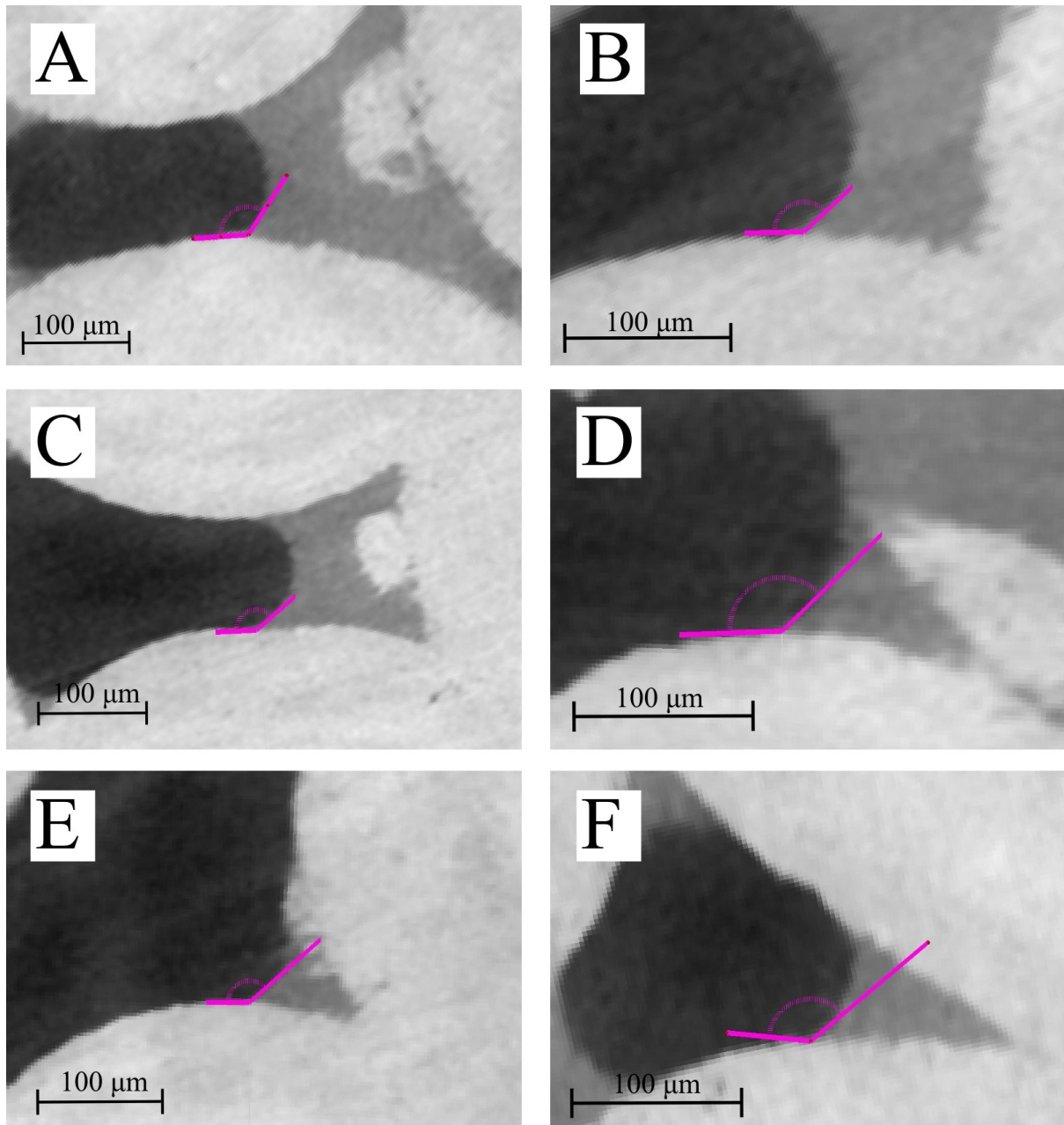


Figure 6.3.2.3: Six contact angles measured on the resampled data. The angles were measured through the dark non-wetting phase (the scCO_2), shown by the pink arc; however the quoted angles are the complement – measured through the wetting (denser - grey) phase. The angles measured in each of these cases are A 53° , B 42° , C 39° , D 41° , E 43° , F 46° .

All image processing was conducted within the Avizo Fire 8.0 (Visual Sciences Group, www.vsg3d.com) and imageJ programs.

6.3.3 Measurement Error

Finally measurement uncertainty cannot be eliminated. Two sources of measurement uncertainty can be identified: a misidentification of the resampling plane; and, once the resampling plane has been identified, the incorrect identification of the vectors tangential to the CO₂-brine interface and the rock surface. Although there may be some error in the identification of the triple point at any particular point along the contact line, a particular advantage of this approach is that the direction of the contact line will be well determined, as the positional error of the triple point is small compared to the length of the contact line. Any error in the determination of the triple point should be systematic, as the segmentation is always performed in the same way, so the direction of the contact line should be preserved. We estimate angular errors to the attitude of the resampling plane to be small, at most 5-10°. To quantify the impact this would have on measured contact angles, the resampling plane was rotated around two axes, perpendicular and parallel to the grain surface. Contact angles were measured at regular angular intervals, and the results can be seen in Figure 6.3.3.1. Large changes in the measured contact angle do not occur until angular errors of around 20-30° in the attitude of the resampling plane, so we would expect this error to be small.

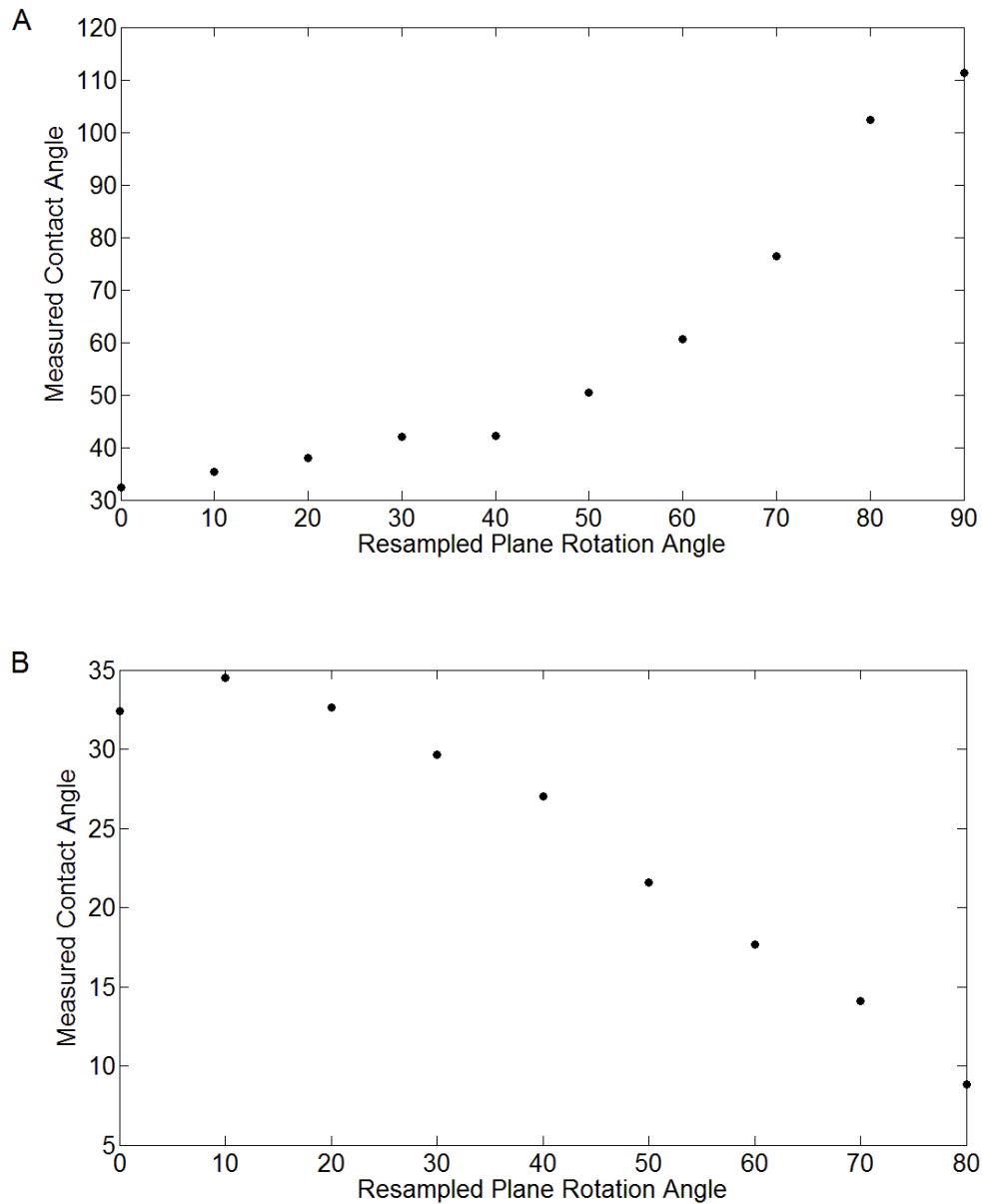


Figure 6.3.3.1: The sensitivity of contact angle to errors in the attitude of the resampling plane. A: the variation in contact angle as the resampling plane is rotated about a plane parallel to the grain surface. B: the variation in measured contact angle as the resampling plane is rotated about a plane perpendicular to the grain surface.

Another source of error is the incorrect identification of the CO₂-brine interface and the grain surface, an ambiguity which can be seen in Figure 6.3.2.3F. The primary control on this is the ratio of the spatial length scale for variation in the surface to the voxel size. The spatial length scale for variation of a particular interface can be quantified by fitting a surface to it and measuring its

curvature. This curvature can be determined by creating best fit quadratic surfaces, with well-defined curvatures, at each point along the generated surface, as detailed in [60] (section 6.2). A distribution of these curvatures for the CO₂-brine interface and the grain surface of a typical residual ganglion is shown in Figure 6.3.3.2. The curves represent Gaussian distributions fitted to each curvature distribution. The average radius of curvature for the CO₂-brine interface is 53 times the size of each individual voxel, and the average grain radius of curvature for the grain surface is 238 times the voxel size. As the typical length scale for spatial variation in the interfaces is orders of magnitude larger than the voxel size, errors in identification of the tangential vectors are correspondingly small. Furthermore, one of the principal advantages of this technique is that it allows for many measurements to be taken very rapidly, allowing for statistical distributions to be seen (Figure 6.3.4.1). The measurement error associated with taking each individual measurement manually should be random, therefore its relative impact should decrease inversely proportional to $\sqrt{n}$, where n is the number of measurements.

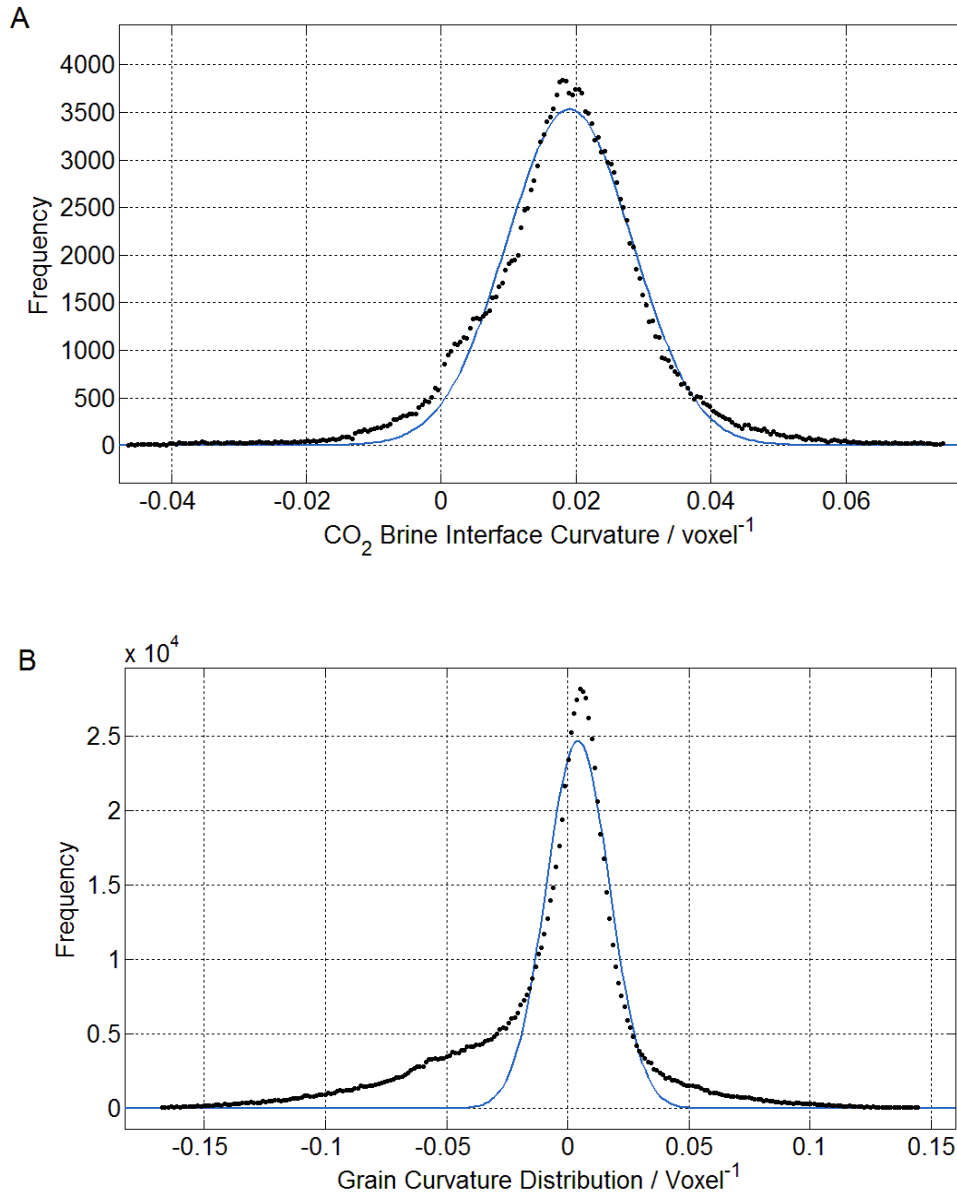


Figure 6.3.3.2: The spatial length scale for surface variation is estimated by calculating the surface curvature of a surface generated from grains and CO₂-brine interface around a representative ganglion. A shows the curvature distribution of the CO₂-brine interface. The typical radius of curvature is 53 times the voxel size. B shows the curvature distribution of the grain surface. The typical radius of curvature is 238 times the voxel size.

6.3.4 Results and Discussion

scCO₂ was universally seen to be the non-wetting phase in this system with a mean contact angle (as measured through the brine) of 45° and an approximately symmetric range around this mean of 10°: the standard deviation in the measured value is 6°. The distribution of contact angles as measured on all the ganglia in the image can be seen in figure 6.3.4.1.

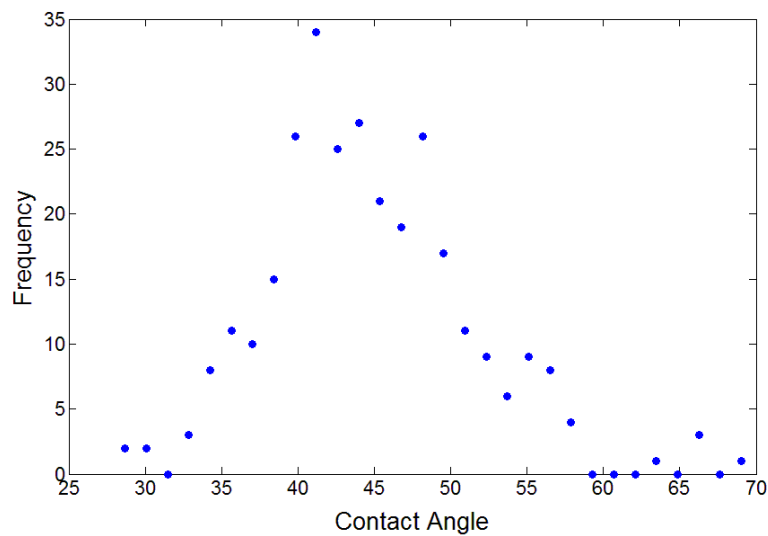


Figure 6.3.4.1: A histogram of the distribution of contact angles.

This distribution can be explained as the result of multiple contributing factors. Firstly, we would expect to see hysteresis between the advancing and receding contact angle. This is caused by pinning of the contact line to a single spot on the solid surface. During wetting phase advance, small increases in the brine pressure, perturbing the fluid-fluid interface, will not move the contact line. The contact angle will increase until some threshold maximal contact angle (the advancing contact angle) is exceeded, where the contact line will start to move. Conversely, during the recession of the wetting phase the contact angle will approach a minimum (the receding angle) before contact line movement (Figure 6.3.4.2). The images are taken at the end of imbibition, during which the wetting phase swells displacing scCO₂. During this process advancing contact angles will be present; however

some rearrangement of the fluid interfaces after injection has finished is possible: we discuss this in more detail later.

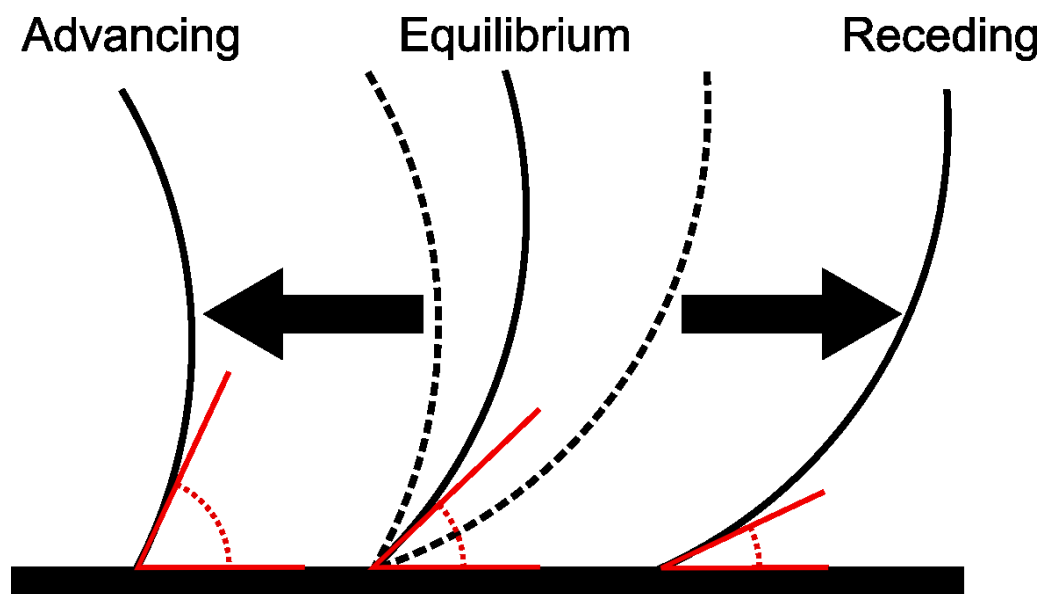


Figure 6.3.4.2: Hysteresis in the contact angle is expected. During wetting phase advance (imbibition) the contact angle will be larger than at equilibrium. During wetting phase recession (drainage) the contact angle will be smaller than at equilibrium. The grey arrows show the direction of interface movement. The dotted grey lines show the three different interface positions superposed on each other. Also see section 2.3.

The main sources of this hysteresis are roughness in the solid surface, adsorption effects and surface impurities [29, 34-36]. Even when contact angle is measured on crystal surfaces, moderate hysteresis is seen, with receding (drainage) contact angles ranging from 35-43° and advancing (imbibition) angles ranging from 60-75° for the scCO₂-calcite-water system, as mentioned previously [21]. As the grain surface in real rocks is heterogeneous we would expect this heterogeneity to cause a distribution in observed contact angles. Grain surface heterogeneity can be seen at larger scales, such that they are visible on the micro-CT scan, as small protrusions in the solid surface that can inhibit the movement of the contact line. This will effectively pin the contact line at a single point, causing the contact angle to change in response to changes in fluid pressure. The resulting

arrangement of fluids will then be dependent on these small details of the pore topography (Figure 6.3.4.3).

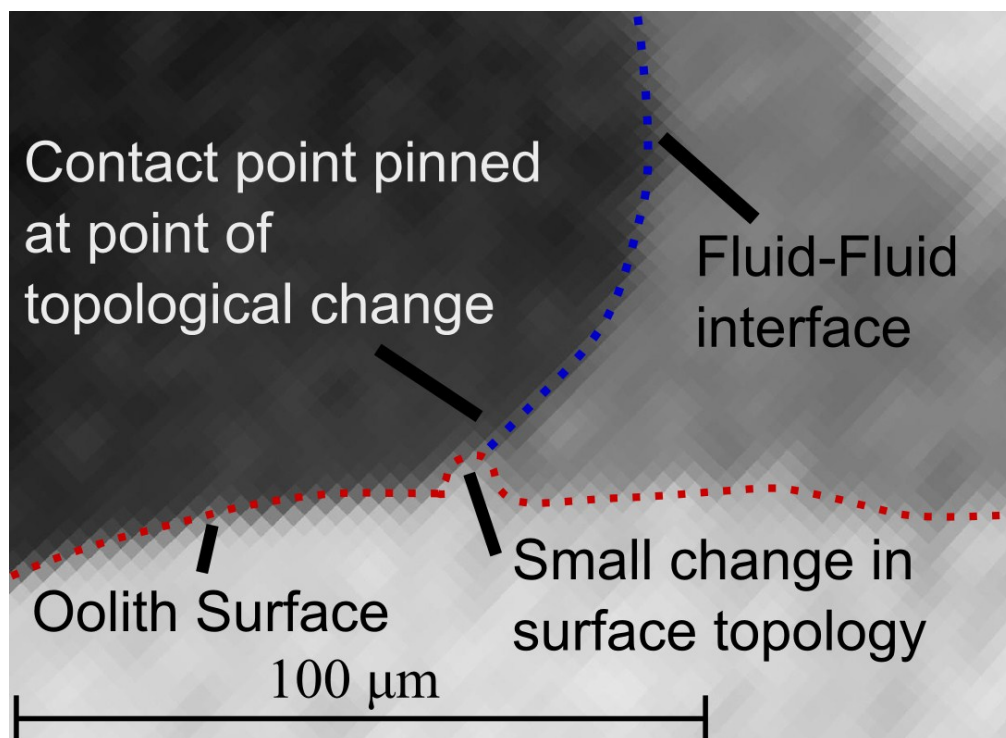


Figure 6.3.4.3: Small changes in the oolite surface can pin the contact line, changing the apparent contact angle as the fluid pressure changes.

At smaller scales, not visible on the micro-CT scan, changes in the surface roughness can be seen qualitatively in optical thin section (Figure 6.3.4.4) and scanning electron microscope (SEM) images (Figure 6.3.4.5). Optical thin sections show the interior structure of grains much more clearly than micro-CT images, making surface differences more obvious, whereas SEM images can be taken at a much higher resolution than either micro-CT or optical thin section images.

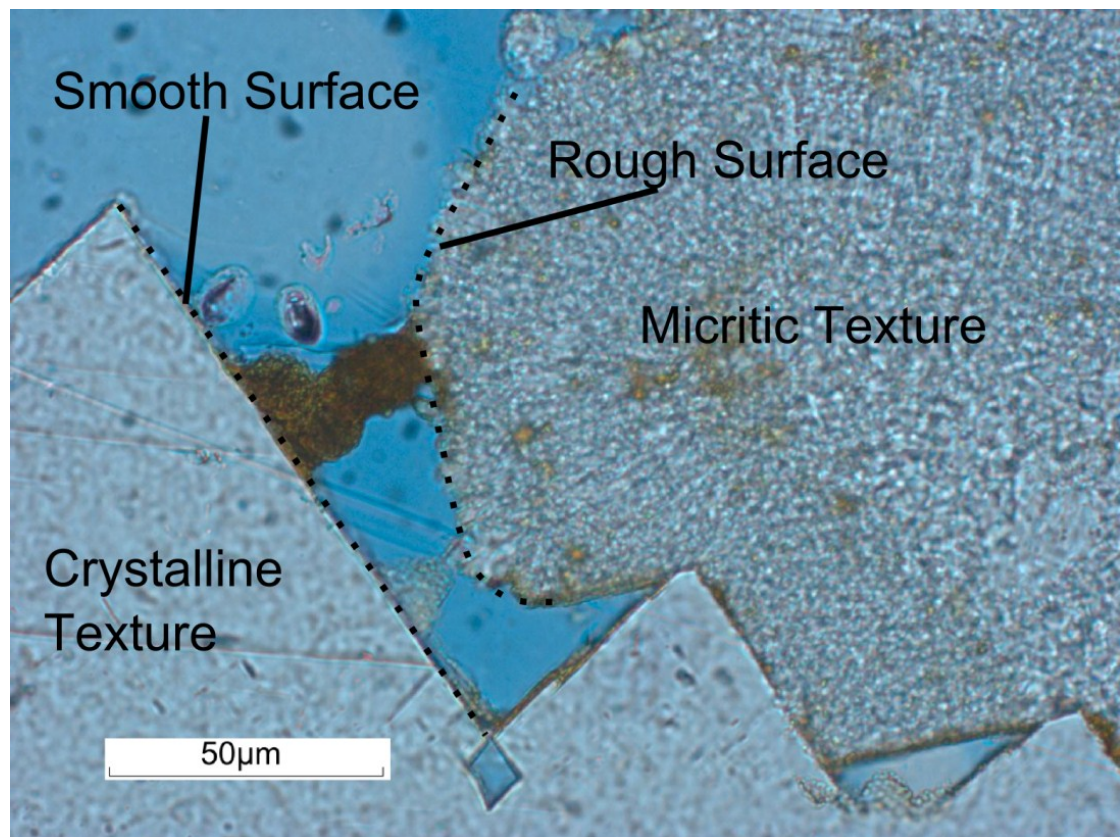


Figure 6.3.4.4: Surface roughness variations can be seen in optical thin section. The micritic texture is associated with a rough surface where crystalline texture is associated with a much smoother surface. See also figure 5.1.3.

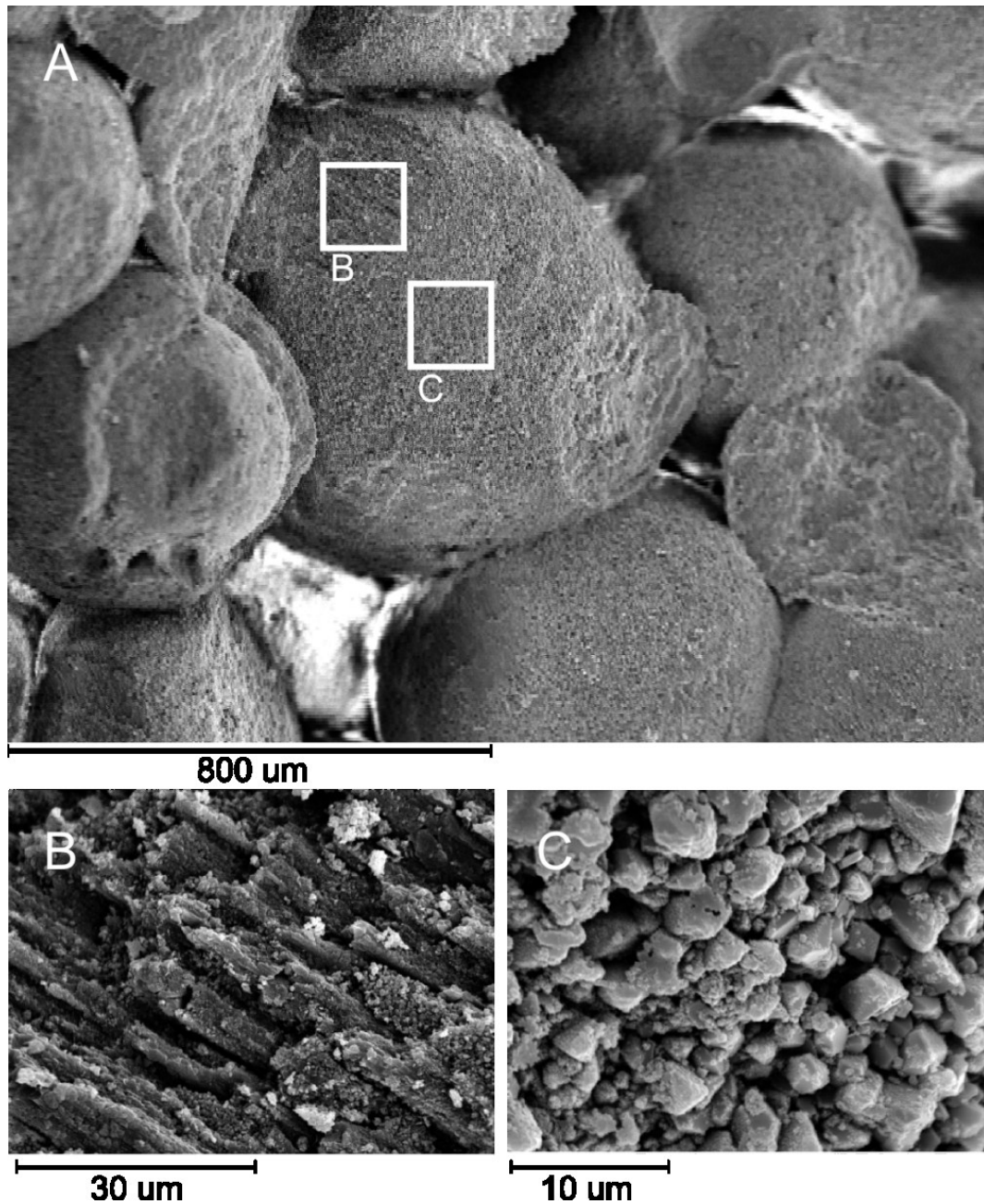


Figure 6.4.2.5: A) Spherical ooliths can be seen on low resolution SEM images. Zooming in on area B shows a relatively smooth surface texture, where zooming in on area C shows a much rougher surface texture.

Another contribution to the contact angle distribution, shown in Figure 6.4.2.6, is the relaxation of the advancing contact angle to the equilibrium angle. If the advancing or receding interfaces are allowed to come to rest, then the contact angle should approach a common equilibrium value over time [37, 38]. This process was observed in our study as an apparent intermediate phase appearing

on the interface near the contact point (Figure 9), caused by the interface moving during the scan. One interpretation of this interface movement is the relaxation of an advancing contact angle (after waterflooding) to an equilibrium position once injection has stopped and the fluids come to rest. This caused the reconstructed voxels to have a grey-scale intermediate between the grey-scale of the two fluid phases. The rate at which this occurs may be different at different points along the contact line, leading to a distribution of the apparent contact angle. It is possible that small changes in interface position, causing the presence of this apparent intermediate phase could also be caused by changes in ganglion volume due to small changes in temperature and solubility during the period of the scan.

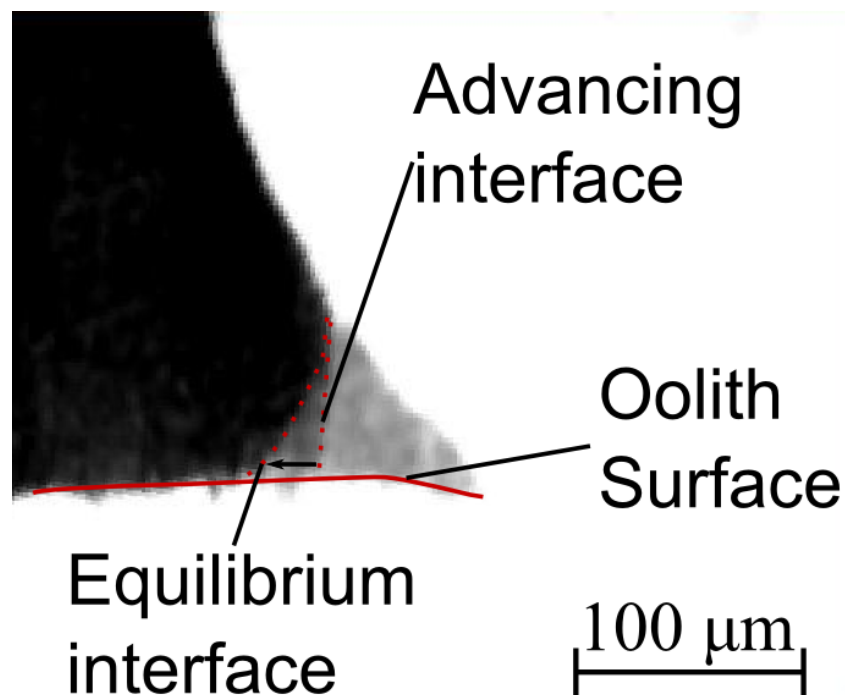


Figure 6.4.2.6: One factor contributing to the contact angle distribution is regression of the contact angle towards the equilibrium contact angle over time. The shaded region represents movement of the brine-scCO₂ interface during the scan. The arrow shows the direction of interface movement during the scan.

All of these processes contribute to the distribution of contact angle seen in Figure 6.3.4.1; the overall effect is to see a range of contact angles spanning approximately 30° . Larger impacts on the contact angle, such as the precipitation of asphaltenes on grain surfaces in oil reservoirs, or the use of surfactants for enhanced oil recovery, should be measurable and could be the target of further study. Although this method may not be applicable for rock types with pores that cannot be resolved by micro-CT scanning, for example shales, there is a wide range of systems for which it could be of great utility. The method for assessing the spatial length scale for variation of a surface outlined above could be extrapolated in future work to examine rocks with extremely complex pore topography, generating maps of surface roughness in order to target contact angle measurements to areas of interest, to describe the pore by pore impact of surface roughness on resulting contact angle distributions. This method could also be combined with recent developments in the generation of mineral mapping [180, 181] to examine the impact of mineral heterogeneity on the distribution of wettability.

This work contradicts some measurements of contact angle in the scCO_2 -brine-carbonate system, which was found to be intermediate-wet, with contact angles around 90° [75], but are consistent with trapping results on a scCO_2 -brine-limestone system, where significant proportions of CO_2 are trapped as a residual phase [154, 155, 171], section 6.1, indicating that the system is water-wet. This consistency supports this new method as a choice for wettability determination in specific systems, especially considering the difficulty in application of results from traditional methods such as the sessile drop. Furthermore, this measured distribution of contact angles could be input into pore-scale models to predict multiphase flow properties, such as capillary pressure and relative permeability [182].

6.3.5 Conclusions

We have presented a new method for measuring the contact angle of multiple immiscible fluids, applied to a scCO_2 -brine-carbonate system, at pressures and temperatures representative of flow in

subsurface hydrocarbon reservoirs and aquifers (10 MPa and 50°C) using micro-CT imaging. The micro-CT data are resampled onto a plane perpendicular to the contact line and then measured manually by tracing vectors tangential to the solid surface and the scCO₂-brine interface. This was done at 300 locations on an image of scCO₂ trapped as a residual phase in the pore-space of the scCO₂. This system was universally weakly water-wet with an average contact angle of 45±6°. The distribution of contact angles can be understood as the result of the multiple contributing factors of contact angle hysteresis and surface heterogeneity on a range of length scales. This measurement can be used as an input for pore-scale models. The technique has potential applicability to a wide range of problems in multiphase flow in porous media, from the development of mixed-wet reservoirs to the use of surfactants in contaminant transport.

6.4 The Imaging of Dynamic Multiphase Fluid Flow using Synchrotron Based X-ray

Microtomography

In this section the results of dynamic fluid flow measurements, acquired using synchrotron based fast tomography (as described in section 4.1.2) will be described. We focus on studying both local and non-local dynamic pore-scale events during drainage in which the injection of a non-wetting phase (scCO₂) into brine (wetting phase) is performed in a carbonate rock. We then demonstrate how the experimental method developed in this work can be used to describe and explain in detail three pore-scale phenomena during drainage: interface recession due to equilibrium capillary pressure change, Roof snap-off [30] and distal (non-local) snap-off.

6.4.1 Materials and Methods

We examine samples of Ketton oolite, as fully described in section 5.1. The experimental parameters used in this experiment are given in table 6.4.1.1.

Core size / mm	Voxel Size / μm	Brine Composition	Projection Number	Temperature / $^{\circ}\text{C}$	Pressure / MPa	Flow Rate / m^3/s
4	3.64	25 wt% KI	800	50	10	1.75×10^{-15}

Table 6.4.1.1: The experimental parameters used in the dynamic synchrotron experiments.

The experimental apparatus is shown in figure 4.1.1.1 and described in section 4.1.2.

6.4.2 Flow Strategy and Image Acquisition

A sequence of 134 tomographies were acquired during CO₂ injection at an effective flow rate of $1.75 \times 10^{-15} \text{ m}^3/\text{s}$. To control these extremely low flow rates the flow boundary conditions were changed from common constant flow – constant pressure boundary conditions to applying a constant pressure drop across an impermeable hydrophilic porous plate (aluminium silicate, Weatherford Laboratories, Stavanger, Norway) as described in section 4.1.2. The tomography time series was reconstructed using a filtered back projection algorithm [150] to create a 4D sequence of volumetric

images. The reconstruction centre was found for the first and last tomography in the sequence and linearly interpolated between these two values for the others. Each tomography took around 45 seconds to acquire with 32 seconds spent taking projections and around 13 seconds spent returning to the initial state and preparing for the next tomography.

6.4.3 Image Processing and Analysis

6.4.3.1 Partially Saturated Images

After reconstruction images were binned, so each $8 (2 \times 2 \times 2)$ voxel cube was averaged to a single voxel. They were then cropped around the core so each tomography consisted of around $1100 \times 1100 \times 1100$ voxels with a voxel size of $3.64 \mu\text{m}$. The images were then filtered using a non-local means edge preserving filter [139, 140] and transformed so that any small movement between tomographies was corrected by the process of registration. This was done by comparing each tomography to the first tomography in the sequence (the reference image) using a normalised mutual information metric [183, 184] in the process of registration. The registered images were resampled onto the same voxel grid as the first image using a Lanczos filter for voxel-wise interpolation [185]. This allowed for multiple transformed images in the displacement sequence to be compared on the same unique grid without concern about later voxel by voxel interpolation. The reference image was then subtracted from the resampled image, giving a difference image (figure 6.4.3.1.1 C). The difference images increased the contrast of displaced CO_2 , making local segmentation much easier.

Once individual events of interest were identified from the sequence, a small subvolume of the image set spatially and temporally located around that event could be extracted and a high quality local segmentation could be done at this location. This local segmentation used a watershed algorithm on the grey-scale gradient of the image, seeded using a 2D histogram [147], see section 3.3.3. The image processing workflow is shown in figure 6.4.3.1.1.

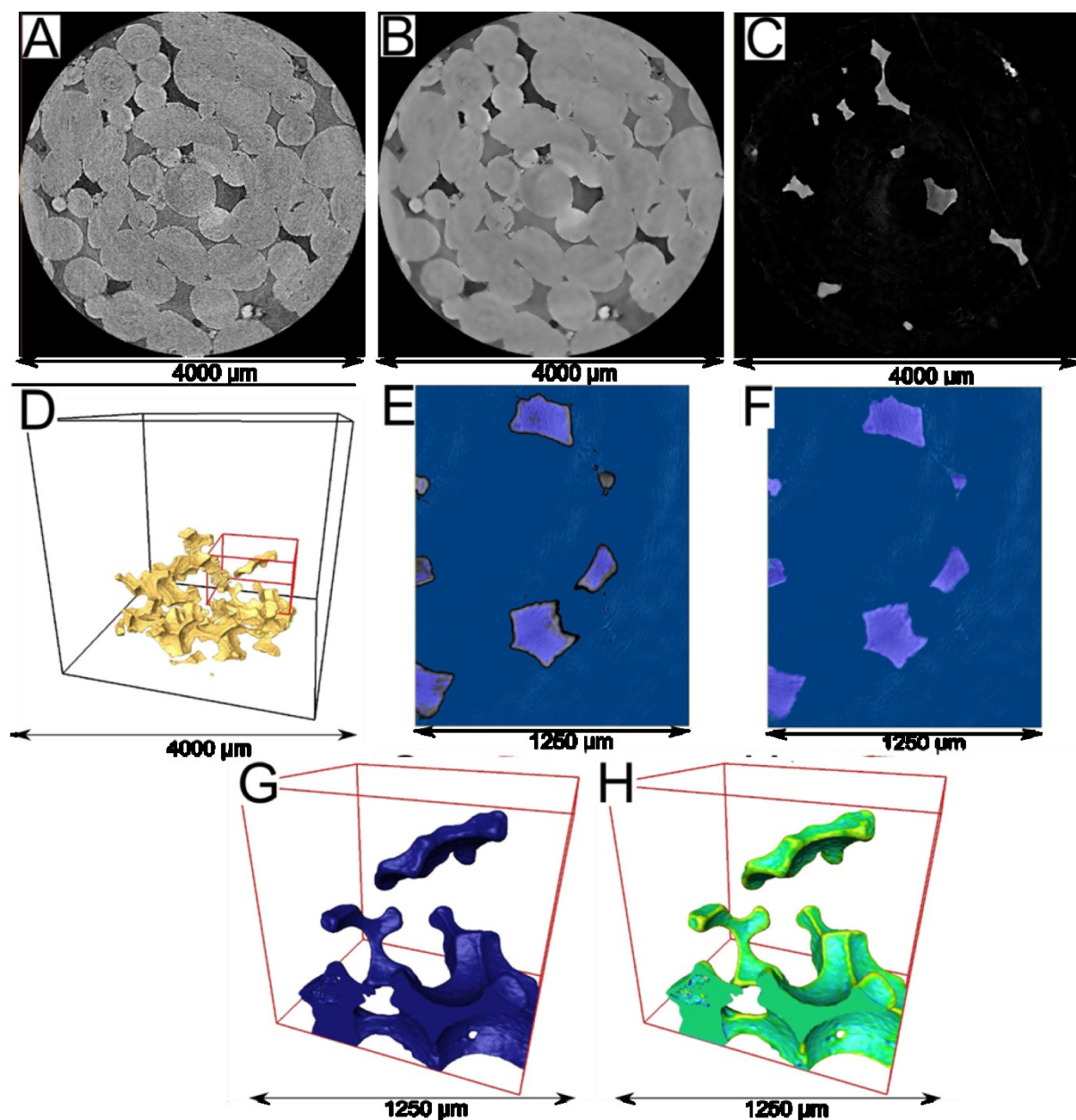


Figure 6.4.3.1.1: The image processing of partially saturated scans. A) The raw reconstructed image. CO₂ is the darkest phase, rock grains are the lightest phase and brine is the intermediate phase. B) The images were then filtered using a non-local means edge preserving filter. C) Difference images were created by finding the difference between each image and the reference image. This increases the contrast of CO₂, making segmentation easier and making it possible to view the progress of the drainage front without the need for segmentation of each individual image. D) These difference images were resampled using an $8 \times 8 \times 8$ kernel, allowing for the entire 4D dataset to be examined easily on a single computer. E) Individual events are identified and subsets of the data extract

information spatially and temporally located around the event. A local subvolume is shown here in the red box. F-G) Local segmentation can then be performed in this spatially and temporally located subset. Watershed segmentation was used, with the seed (F) for the watershed generated using a 2D histogram. G) A surface was generated for both the connected and disconnected CO₂ phase using a generalized smoothed marching cubes algorithm. H) Curvature was found on this surface by fitting a polynomial surface to each of the elements on the CO₂ surface. Each element was then assigned a curvature value from this best fit surface and an average interface curvature found from resulting distributions from selected areas of the interface surface.

In this study we determine one of the most important parameters describing multi-phase flow in porous media, capillary pressure, defined as the difference in pressure between a non-wetting and wetting phase in a porous medium (section 2.2). It is fundamentally a pore-scale phenomenon arising from the pressure difference across a curved interface with a defined surface tension separating two immiscible fluids. This relationship is described by the Young Laplace equation (also see equation 2.2.9).

$$P_c = 2\sigma C$$

6.4.3.1.1

where σ is the interfacial tension (section 2.1) and C is the mean interface curvature. Traditionally capillary pressure has only been accessible at the macro-scale, defined such that the values of capillary pressure uniquely define saturation values for a given displacement sequence for each given rock. This relationship between capillary pressure and saturation can be determined experimentally using techniques such as mercury injection capillary pressure [46], porous plate coreflooding [47, 48] and quasi-steady state flooding [49] (section 2.2). As these macroscopic measurements all rely on external pressure measurements, they can only determine interface pressure differences for phase clusters connected to an external pressure transducer.

Recent work has correlated externally derived capillary pressure measurements with direct pore-scale measurements of interface curvature; direct measurements of capillary pressure at the pore-scale can be made and so information from disconnected non-wetting phase clusters can be retrieved for real systems [60, 186], section 6.1. To measure local capillary pressure surfaces were generated across the segmented CO₂ ganglia using a generalized marching cubes algorithm [61, 62] (Figure 6.4.3.1.1 G and H). The curvature of this surface was found by approximating the surface locally as a best fit quadratic form, equation 2.2.11. The eigenvectors and eigenvalues of this form represent the directions of principal curvature and the principal curvature values respectively. A surface scalar field is then produced where the principal radii of curvature are averaged and assigned to each element across the surface. This method was originally described by Armstrong *et al.* [60] and errors in the protocol for the CO₂-brine-carbonate system addressed by Andrew *et al.* [186] (section 6.2).

Extending this technique to measure the capillary pressure during drainage in this system is, however, challenging. As drainage capillary pressures are much higher than those seen during imbibition – the radii of curvature are smaller – the technical measurement of curvature is much more difficult. The curvature assignment requires the fitting of quadratic surfaces over an extended region of the surface. The smaller radii of curvature means that the CO₂-brine interface are on average closer (as measured across the interface) to the three-phase contact line than at low capillary pressures. The curvature values measured at points on the interface close to the contact line are, however, less reliable than those measured far away from it. The non-continuous interface curvature change across the contact line affects the curvature any smoothed surface generated across it. To increase accuracy, curvature measurements were taken from regions of the CO₂-brine interface furthest away from the contact line, minimising this effect.

The CO₂-brine interface either resides as a corner meniscus, with its curvature pointing into the corners a pore (figure 6.4.3.1.2 A, region 2, figure 6.4.3.1.2 B, region 2), or it resides as a terminal

meniscus, with the curvature of the interface pointing into pore throats (figure 6.4.3.1.2 A, region 1, figure 6.4.3.1.2 B, region 1). At higher capillary pressures curvature measurements from corner menisci become unreliable as each surface element is very close to the contact line (as measured across the surface). Terminal menisci are, however, much better resolved, as their centres lie much further across from the contact line. Curvature discontinuities at the contact line therefore have a much smaller impact on the assigned interface curvature for terminal menisci, so these areas were selected for curvature measurement. Terminal menisci could be identified both as visually distinct regions of the CO₂ interface and by using the pore throat parameterisation described in section 3.3.3. When measurements are made on a sequence of tomographies around a specific event, the regions chosen for measurement occupy corresponding regions on each of the tomographies, occupying the same pore throats, reducing the impact of any potential sampling bias.

It is possible to quantitatively test this approach at low capillary pressures, such as those present in a ganglion disconnected from the rest of the CO₂ by local imbibition (section 6.4.4.3). At these low capillary pressures both corner and terminal menisci are sufficiently far away from discontinuities in interface curvature for global curvature measurements to give an accurate reflection of the equilibrium capillary pressure.

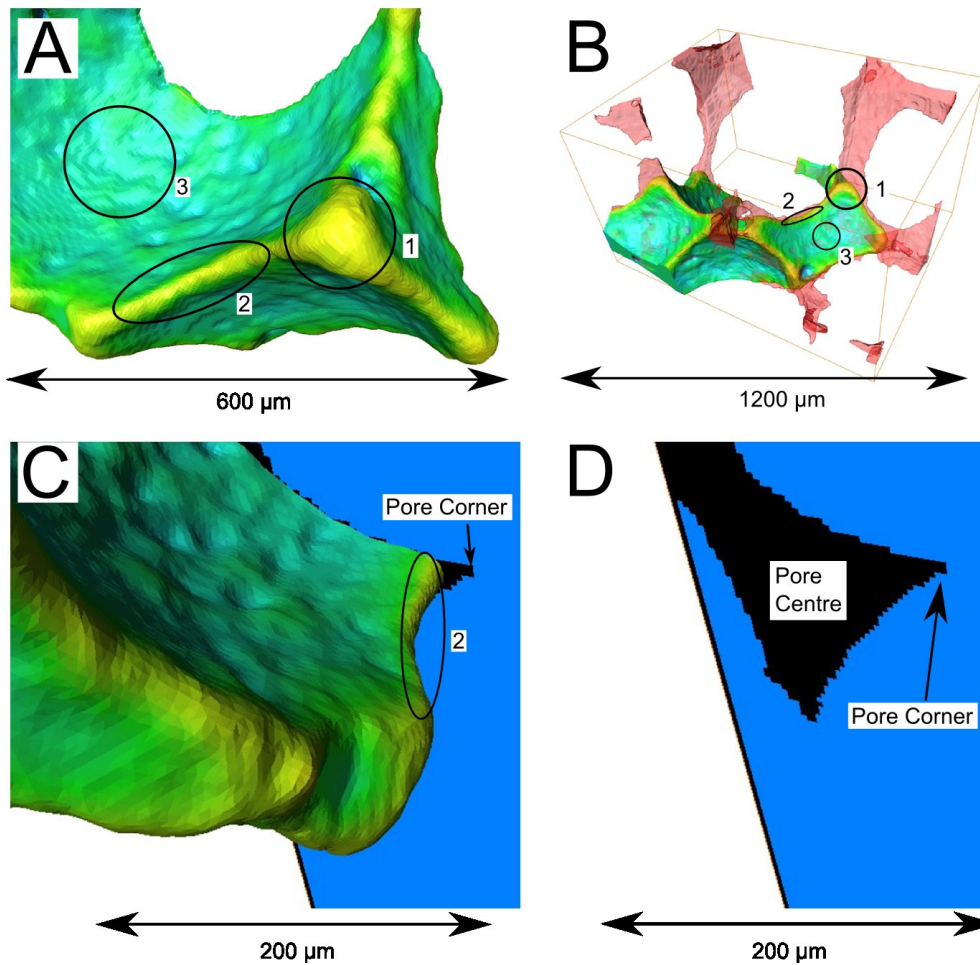


Figure 6.4.3.1.2: Curvature distributions across the CO₂ surface can be separated into three different areas, numbered in (A-C). Region 1 indicates the regions of the CO₂-brine interface residing in pore throats (terminal menisci), region 2 indicates the portions of the CO₂-brine interface residing in pore corners (corner menisci) and region 3 indicates the CO₂-grain interface. (B) shows a curvature map with the pore-space not occupied by CO₂ shown in red, showing the relationship between 1 regions on the interface and pore throats. (C-D) show the intersection of one of the 2 regions of the CO₂-brine interface with a slice of the segmented pore-space, showing the relationship between the corner menisci and pore corners.

The curvature distribution for the low capillary pressure ganglion clearly shows a bimodal distribution, with one negative peak corresponding to the CO₂-rock interface and one positive peak corresponding to the CO₂-brine interface (figure 6.4.3.1.3 C). If local regions of the CO₂-brine

interface are chosen for measurement (figure 6.4.3.1.3 B) the resulting distribution now only has one peak, due to the CO₂-brine interface, centred on the same point as the positive peak from the bimodal distribution. This shows us that the distributions generated using selective measurement faithfully recover the actual CO₂-brine interface curvatures. This allows us to use this technique at higher capillary pressures, removing the influence of the CO₂-rock interface and the CO₂-brine-rock contact line on the measured curvature distribution. This results in single well defined curvature peaks, allowing us to directly compare changes in the high capillary pressure connected CO₂ due to different aspects of the drainage process. To find an objective estimation of peak position and width these distributions were then fitted to a Gaussian model using a trust region algorithm [165]. This peak position was then converted to a pressure difference across the interface using the Young-Laplace equation (equation 2.2.9). The interfacial tensions in this system is estimated by linearly interpolating between measurements for a given pressure, temperature and salinity, and a value of 0.037 N/m was used in this study [44, 45]. This is the same as that used in section 6.3. Although measurement biases cannot be completely eliminated, as the regions chosen for measurement are spatially correlated during the evolution of each event, we can still draw conclusions about flow phenomena based on the relative changes in measured curvature.

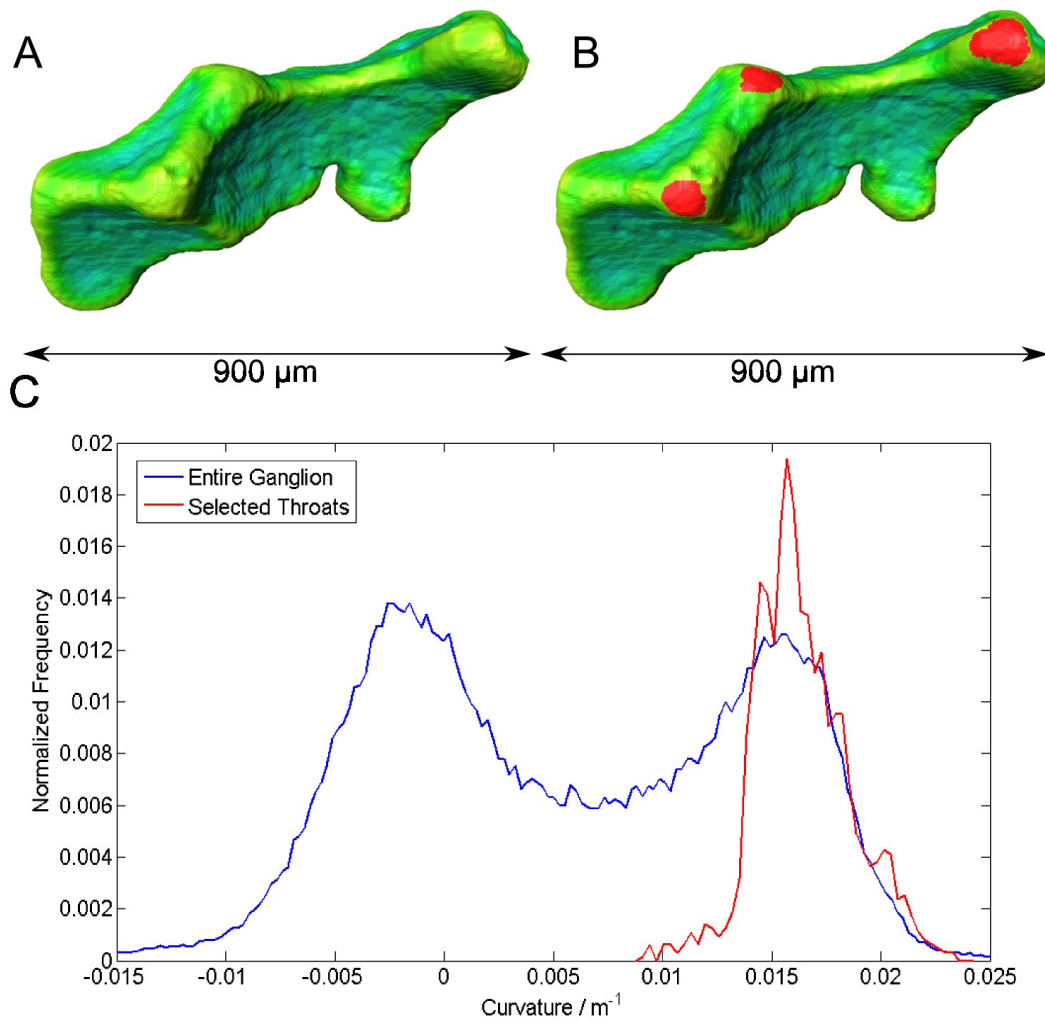


Figure 6.4.3.1.3: The selective measurement of interface curvature, only on regions of the pore-space residing in pore throats (as shown in figure 6.4.3.1.2 A, region 1) for a low capillary pressure disconnected ganglion. (A) shows the interface curvature distribution for an entire disconnected ganglion. (B) shows the selection sites for selective curvature measurement. (C) shows a comparison for the curvature distributions for measurements taken from the entire ganglion (blue) and only in selected throat sites (red). The measurement across the entire ganglion shows a clear bimodal distribution of curvatures, with the CO_2 -brine interface causing the peak at positive (convex) curvatures and the CO_2 -rock interface causing the peak at negative (concave) curvatures. Curvature measurements taken only from selected throats shows only one peak, representing the CO_2 -brine curvature, which is at the same position as the peak in the curvature distribution from the measurements taken across the entire disconnected ganglion.

6.4.3.2 Dry Scans

The dry scans were reconstructed, binned and filtered in a similar way to the partially saturated images. These scans were taken as multiple overlapping sections along the entire core. These were then reconstituted from 5 overlapping tomographies of around $1100 \times 1100 \times 1100$ voxels to a single long image around $1100 \times 1100 \times 3500$ voxels using registration with a normalised mutual information metric. After transformation individual sections were then merged using a Lanczos filter [185]. The long dry scan was then registered to the saturated reference scan using the same registration algorithm described above. Finally the reconstructed and registered dry scan was resampled onto the same grid as the partially saturated images using a Lanczos filter [185].

A subvolume of this dry scan was taken around the partially saturated images and the image was segmented into pore and void using a watershed algorithm seeded using a 2D histogram. The pore-space was then separated into individual pores by finding the watershed catchment basins of a Euclidian distance map of the pore space [118, 146], see section 3.3.3. These pores were then individually labelled, and the interfaces between them labelled as throats. In the case where more than two pores were connected across the same plane, the throat plane was split about the multi-pore intersection line such that each throat only connected two pores. Each throat was then given a “radius” equivalent to the maximum of the Euclidian distance function evaluated about the throat plane, the same as the radius of the maximum inscribed sphere centred on that throat plane. This allowed for the pore-space to be effectively parameterized while retaining both the spatial and topological relationship between the individual pores.

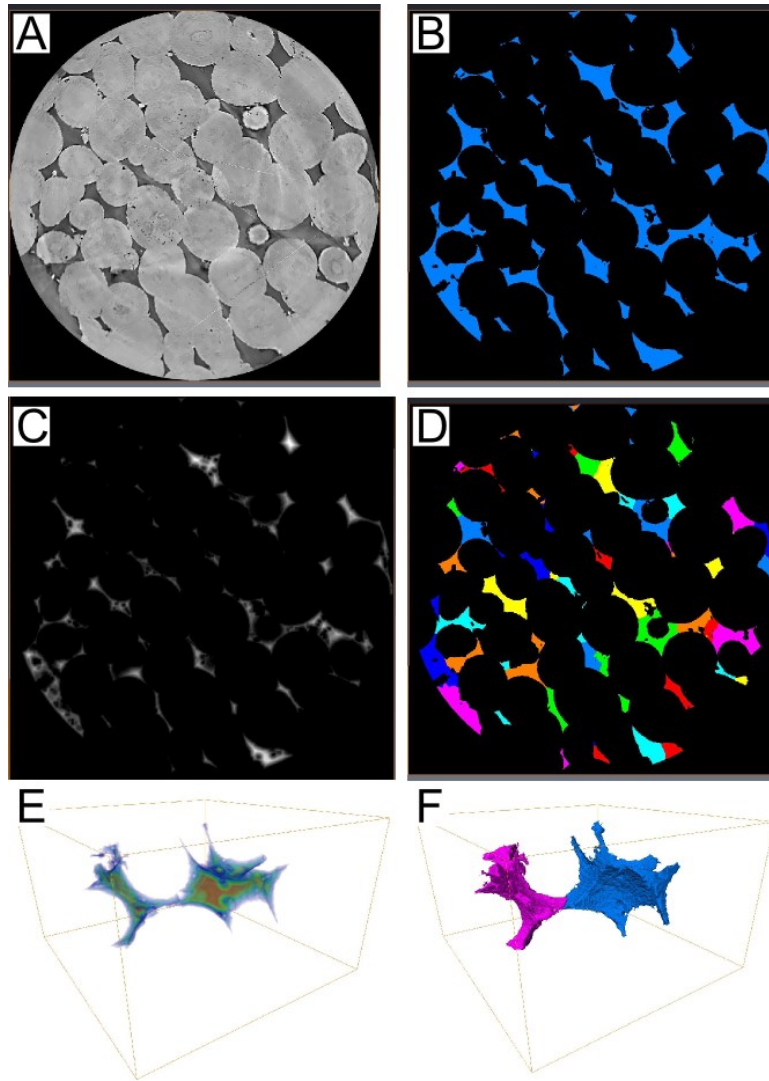


Figure 6.4.3.2.1: The image processing workflow for dry scans of the pore-space. (A) The image after reconstruction and filtering. (B) The image was segmented using a 2D histogram based watershed segmentation (figure 6.4.3.1.1). (C) A Euclidian distance map of the pore-space was calculated by assigning each voxel the distance from it to the nearest pore wall. (D) This was then used to separate the pore-space out into individual pores by calculating the watershed basins of this distance map.

Pore-throats are defined as the local minima in the Euclidian distance map, corresponding to constrictions in the pore-space and the centres of pore bodies represent the local maxima. (E-F) This separation process is shown for two example pores. (E) Regions of high Euclidian distances (shown in red) are defined as pore bodies and throats are defined as the regions connecting them. (F) The two separated pores from the distance map shown in (E).

6.4.4 Results

Drainage does not progress as a uniform front, but instead is quantized into a discrete set of events. The interface movement due to these jumps are not resolved with the temporal resolution available for this method (45 s); micro-model studies have shown that pores drain on millisecond time-scale regardless of the (externally imposed) capillary number [84, 85]. Each tomography then represents changes between two equilibrium states, before and after each of the non-wetting phase jumps. If a jump occurs during the acquisition period of a scan then the reconstructed grey-scale of the volume corresponding to the jump represents a time averaged value between the two fluid phases.

6.4.4.1 Equilibrium Capillary Pressure Change

Each of the jumps seen during this study is associated with an equilibrium capillary pressure reduction. This can be seen in figure 6.4.4.1.1.

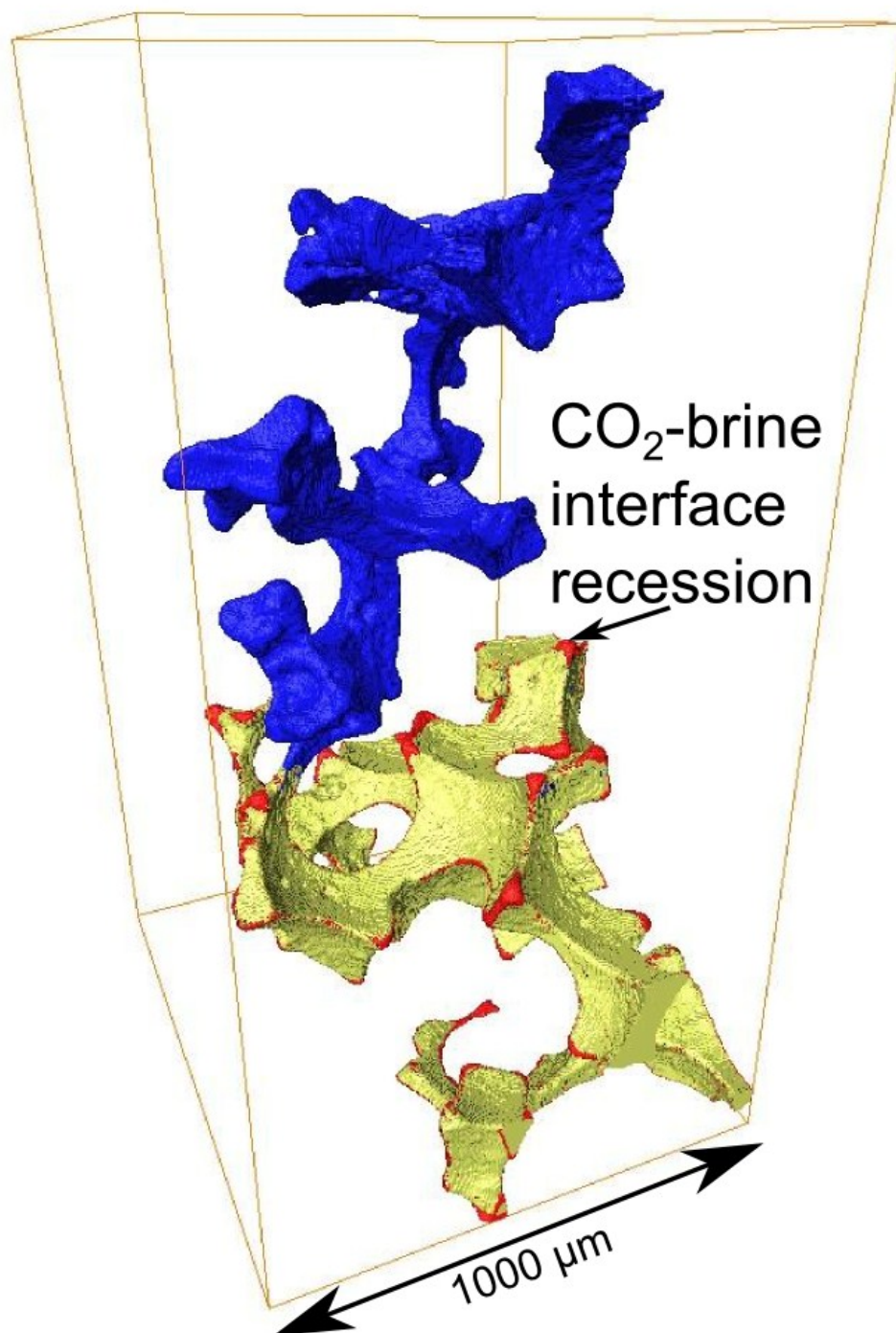


Figure 6.4.4.1.1: A volume rendering of the volume around a typical Haines jump. The region occupied by CO_2 after the jump but not before is shown in blue, the region occupied by CO_2 in both scans is shown in yellow and the region occupied by CO_2 before the jump but not after is shown in red. The quasi-static capillary pressure change associated with the event causes the CO_2 -brine interface to recede in pore-throats and the corners of pores.

The jump causes the interface residing in the corners of pores and pore throats to recede due to an equilibrium capillary pressure change. This recession provides the fluid required for the jump, allowing for a rapid pore filling without a quantized change in the bulk fluid volume. This shows that pore drainage events are cooperative and that the individual dynamics of an event depend not only on the local pore topography but also the fluid configuration in adjacent pores beyond the next neighbours. A schematic representation of this process is shown in figure 6.4.4.1.2, and the equilibrium change in capillary pressure due to the Haines jump can be seen in figure 6.4.4.1.3.

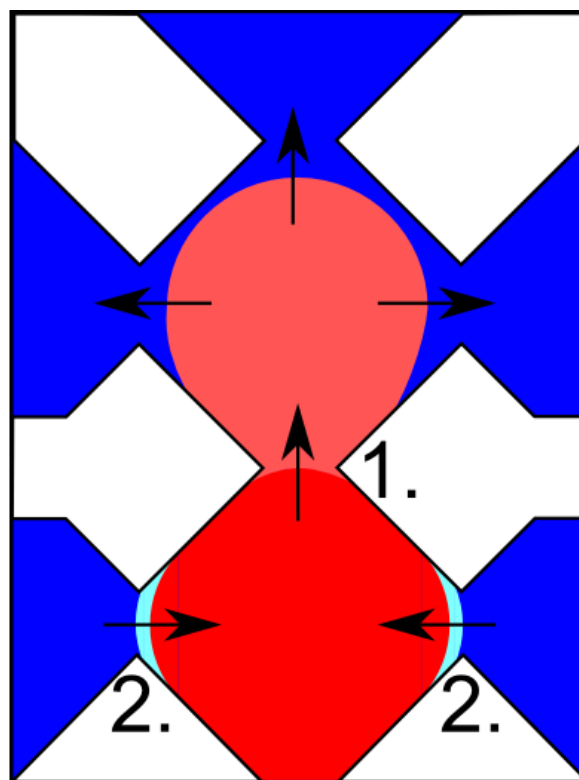


Figure 6.4.4.1.2: A schematic representation of a simple Haines jump. The non-wetting phase (CO_2) is shown in red, the schematic grains are white and the wetting phase (brine) is shown in blue. When the interface capillary pressure overcomes the threshold invasion capillary pressure for throat 1, the next pore is rapidly invaded, and a new capillary equilibrium established with the next pore saturated with non-wetting phase. The capillary pressure of the new equilibrium state will be lower than prior to the jump, causing the wetting-non-wetting phase interface to recede in the throats labelled 2.

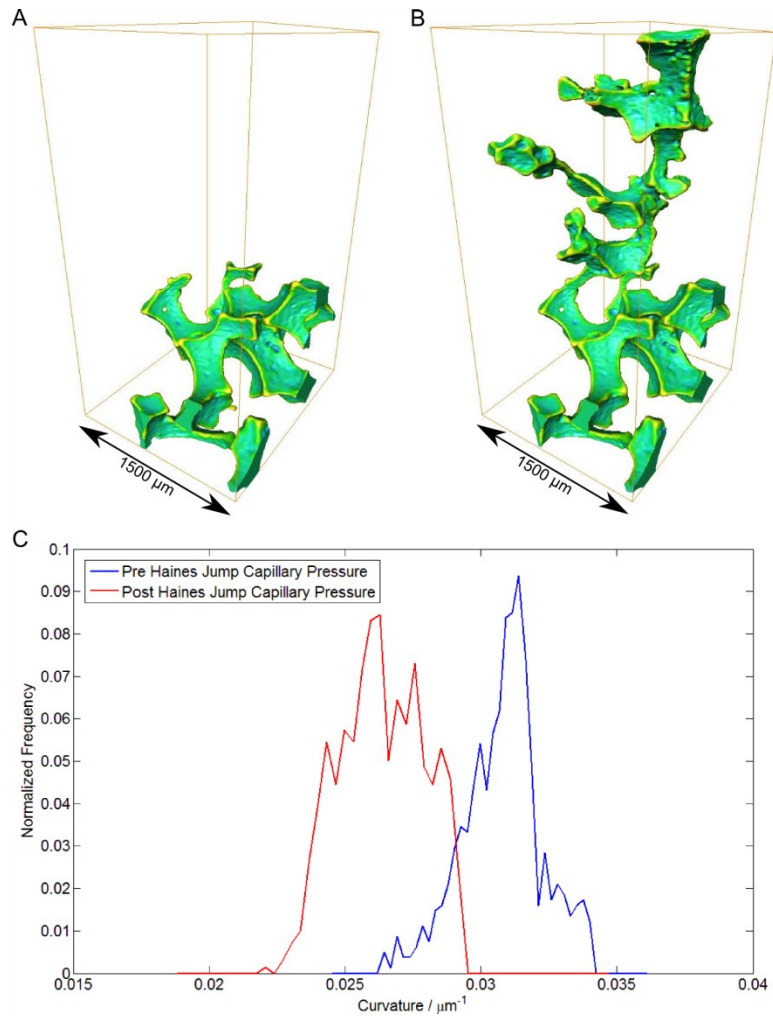


Figure 6.4.4.1.3: The capillary pressure maps for the connected CO₂ regions before a Haines jump (A) and after the jump (B). The resulting curvature distributions (C) show a clear decrease in interface curvature associated with the event. In the example displacement studied, the fitted curvature peak position prior to the jump is $0.0309 \pm 0.0012 \mu\text{m}^{-1}$ corresponding to a capillary pressure of $2.29 \pm 0.09 \text{ kPa}$ and after the jump is $0.0262 \pm 0.0017 \mu\text{m}^{-1}$, corresponding to a capillary pressure of $1.94 \pm 0.13 \text{ kPa}$. The non-wetting phase residing in pore-throats across the CO₂-brine interface supplies the fluid necessary for the drainage event. This fluid recession occurs across the entire of the interface as the surface reaches a new equilibrium. This observation is in agreement with work on rate controlled mercury injection experiments by Mason & Morrow [169] and Yuan [83] and micro-model studies by Armstrong *et al.* [85], providing the first evidence for this process by direct pore-scale observation in a real rock at reservoir conditions.

6.4.4.2 Roof Snap-off

Drainage events do not always proceed as a single Haines jump. When the non-wetting phase emerges from the pore throat, interfacial forces can be such that the leading portion of the non-wetting phase disconnects to form an isolated ganglion in the process of snap-off. Although this process is more commonly associated with macroscopic imbibition (wetting phase ingression) it was first described experimentally and analytically for the process of drainage by Roof [30], with further recent quantitative analysis using finite volume modelling by Raeini *et al.* [187]. The phenomenon occurs when the leading interface advances through the second pore, reducing its interfacial curvature. The surface will try to maintain capillary equilibrium, causing the wetting layer in the throat to thicken until it becomes unstable, at which point wetting phase will rapidly fill the throat, disconnecting a droplet of the advancing non-wetting phase from the rest of the connected non-wetting phase. After this the disconnected ganglion may rearrange, potentially changing its capillary pressure as it moves towards the centre of the pore in which it resides. This process can be seen schematically in figure 6.4.4.2.1.

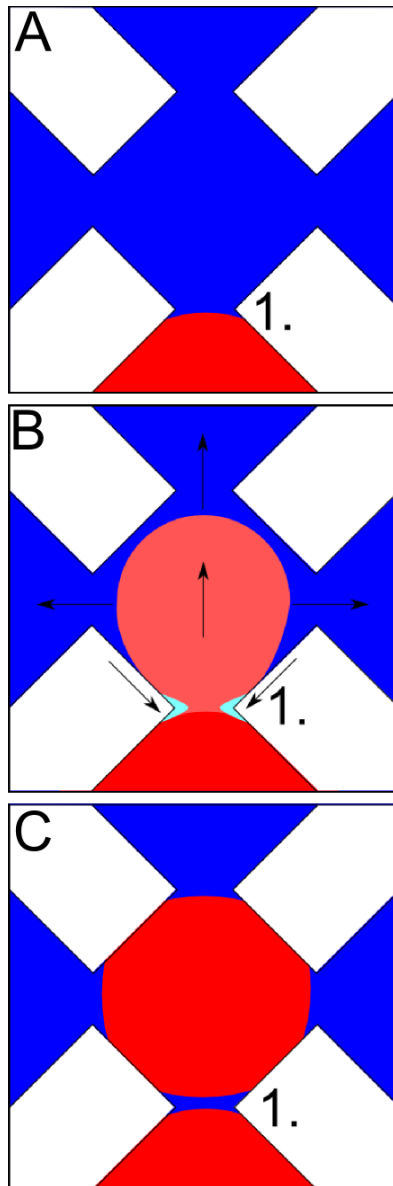


Figure 6.4.4.2.1: A schematic of the process involved in Roof snap-off, where a ganglion becomes disconnected immediately after throat invasion by snap-off of the throat through which the invasion took place. The colour scheme is the same as that is used for figure 6.4.4.1.1, and regions of wetting film growth are shown in light blue. (A) Shows the situation before the jump. During the event extremely low interface curvatures are generated locally around the event, causing the wetting layer in throat 1 to swell (B), eventually leading to its snap-off and the disconnection of non-wetting phase in an isolated ganglion (C). After the ganglion has become disconnected there may be some subsequent ganglion rearrangement as a local surface energy minimum is found.

This phenomenon can be seen in an example sequence of four tomographies within our dataset (figure 6.4.4.2.2). Surface curvature was measured, as described in section 6.4.3.1, for both the connected and disconnected CO₂ phase, and the results can be seen in figure 6.4.4.2.2.

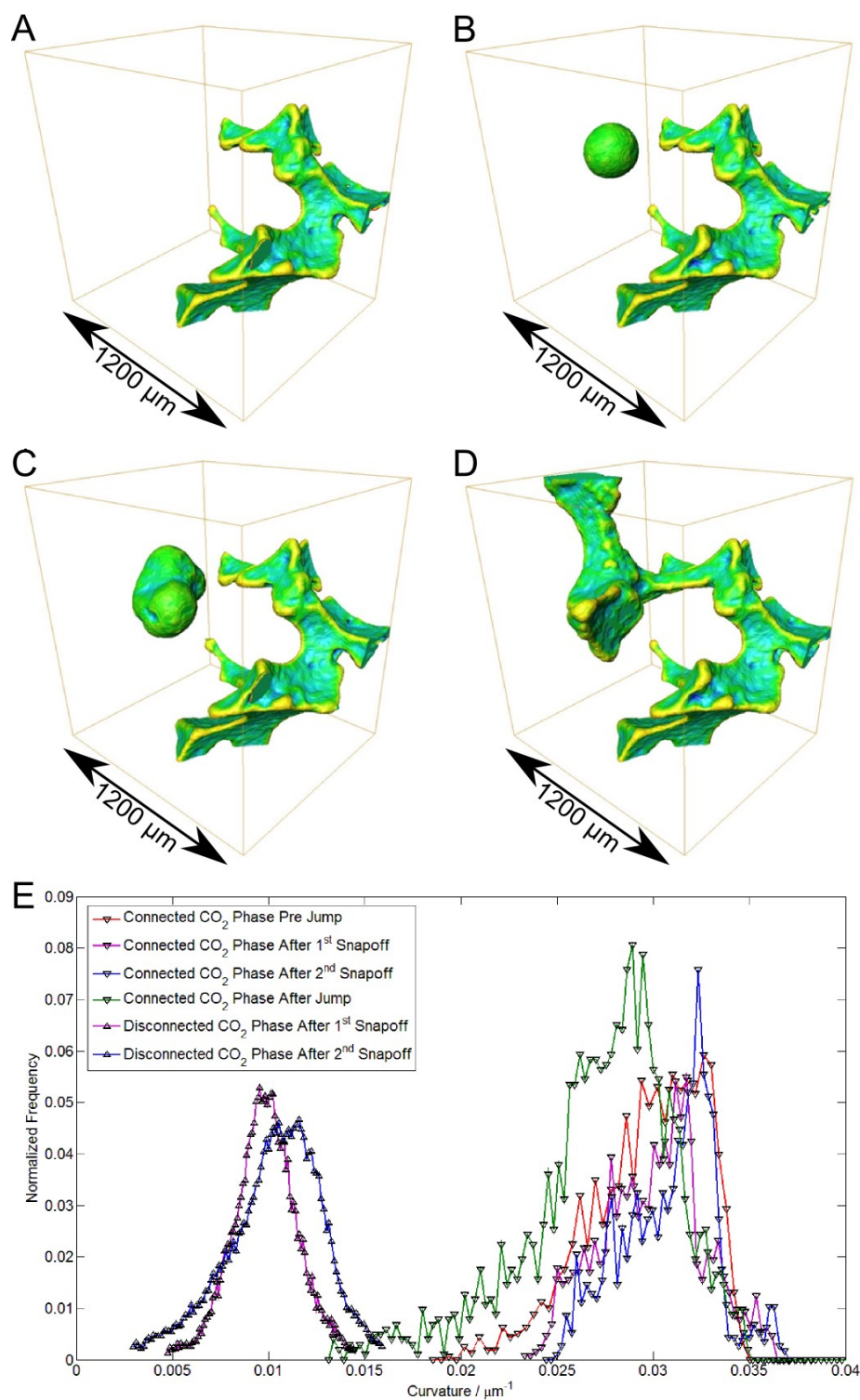


Figure 6.4.4.2.2: (A-D) Capillary pressure maps for the connected and disconnected CO₂ regions in a subvolume of four sequential tomographies during a Roof snap-off sequence. (E) The resulting capillary pressure distributions. Low capillary pressures in the disconnected phase region may be result of low transient capillary pressures generated during the drainage event.

Between steps 1 and 2 (figure 6.4.4.2.2 A-B) a small disconnected droplet of CO₂ with a volume of $4.33 \times 10^6 \mu\text{m}^3$ appears in the pore-space. Between steps 2 and 3 this ganglion has grown to a volume of $1.18 \times 10^7 \mu\text{m}^3$, presumably due to another cycle of drainage and local snap-off (multiple cycles of this process are not unexpected and were shown numerically in direct pore-space simulations by Raieni *et al.* [187]). Finally, by step 4 it is connected with the remainder of the CO₂ phase. The throat through which the ganglion is connected in step 4 is presumed to be the same one as the CO₂ moved through from the disconnected ganglia visible in steps 2 and 3.

This process must occur on a time frame shorter than the time required to take a tomography as no significant differences in reconstructed grey-scale can be seen in the space connecting this disconnected region to the remainder of the connected CO₂. Also the grey-scale across the disconnected ganglion is uniform with well-defined edges, whereas if interface movement occurred on the time scale of the tomography we would expect to see gradients in the grey-scale with poorly defined blurred edges. This supports the findings of [84, 106], that these events occur on millisecond timescales. A summary of the fitted curvature peak positions and corresponding capillary pressures can be seen in Table 6.4.4.2.1.

Step	Connected Curvature / μm^{-1}	Connected Capillary Pressure / kPa	Disconnected Ganglion Curvature / μm^{-1}	Disconnected Ganglion Capillary Pressure / kPa
1	0.030 ± 0.003	2.2 ± 0.2	N / A	N / A
2	0.030 ± 0.003	2.2 ± 0.2	0.0098 ± 0.0015	0.7 ± 0.1
3	0.031 ± 0.002	2.3 ± 0.1	0.011 ± 0.002	0.8 ± 0.1
4	0.028 ± 0.003	2.0 ± 0.2	N / A	N / A

Table 6.4.4.2.1: Summary of fitted curvature peaks and corresponding capillary pressures for both the connected and disconnected wetting phase during the event seen in figure 6.4.4.2.2.

From the curvature distributions of the connected and disconnected non-wetting phase we can see several interesting features. Firstly, the curvature of the disconnected ganglion after the first and second cycle of drainage and snap-off are very similar, with the capillary pressure of the ganglion present in step 3 (figure 6.4.4.2.2 C) slightly higher than that present in step 2 (figure 6.4.4.2.2 B). This indicates that the primary control on the capillary pressure of residual ganglia is not the rearrangement of the disconnected ganglion after snap-off, but the threshold snap-off capillary pressure, as defined by the local topography of the pore-throat, independent of ganglion volume. We would expect the impact of ganglion rearrangement on capillary pressure, however, to be different for ganglia of different volumes, with small ganglia rearranging more than large ganglia. Rearrangement could, therefore, be the cause of the slight change in interface curvature between the first and second step in the tomographic sequence (figure 6.4.4.2.2 E, table 6.4.4.2.1), but cannot be the first order control on disconnected ganglion capillary pressure. This supports the findings of Andrew *et al.* [186] (section 6.2) correlating the capillary pressures of a set of ganglia at residual saturation to the inverse of local throat radius (and so snap-off capillary pressure).

Secondly, the capillary pressures of the disconnected ganglia at both time steps are much lower than the capillary pressure of the connected CO_2 , even after the larger jump, which occurs between steps 3 (figure 6.4.4.2.2 C) and 4 (figure 6.4.4.2.2 D). We propose that this is due to significant dynamic capillary pressure gradients generated in the leading region of the non-wetting phase during the rapid drainage event. These cause the low capillary pressures required for throat snap-off, which are then preserved in the disconnected ganglion. Snap-off is not caused, therefore, by the equilibrium

capillary pressure change examined in section 6.4.4.1. After the event the rest of the connected CO₂-brine interface then equilibrates to capillary pressures close to those seen prior to the jump.

6.4.4.3 Distal Snap-off

Transient capillary pressures generated during a Haines jump can cause snap-off not only locally, in the throat invaded by the event, but also further away from this location. This non-local event is termed “distal snap-off”, and an example is shown in figure 6.4.4.3.1.

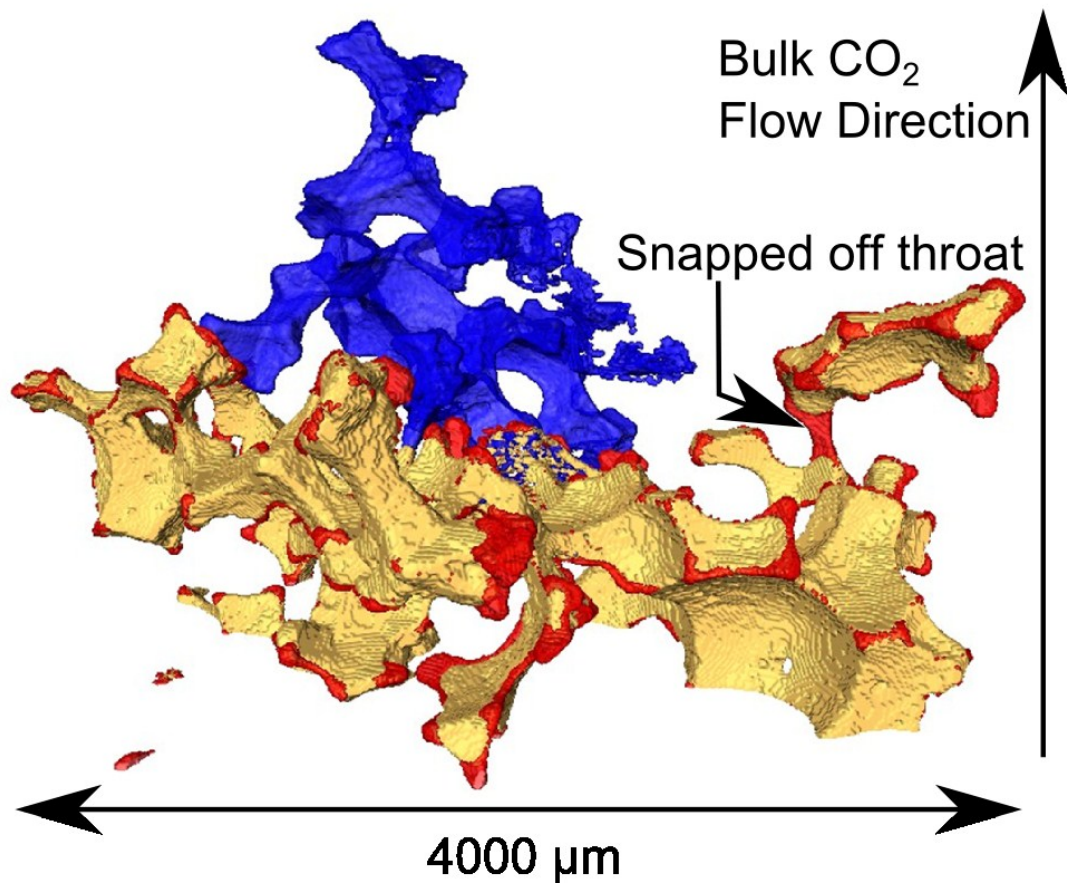


Figure 6.4.4.3.1: A rendering of a large Haines jump, coloured similarly to figure 6.4.4.1.1, with the regions occupied by CO_2 after the jump but not before shown in blue, the regions occupied by CO_2 both before and after shown in yellow and the regions occupied before but not after shown in red. This not only shows the interface recession resulting from the quasi-static capillary pressure change associated with the Haines jump, but also the snap-off of one of the throats occupied by CO_2 prior to the jump. Unlike the event analysed in section 6.4.4.2, this throat is not that through which the invasion occurred during the Haines jump.

Figure 6.4.4.3.2 shows local renderings of this snap-off event with the capillary pressure evolution for both the connected and the disconnected phase.

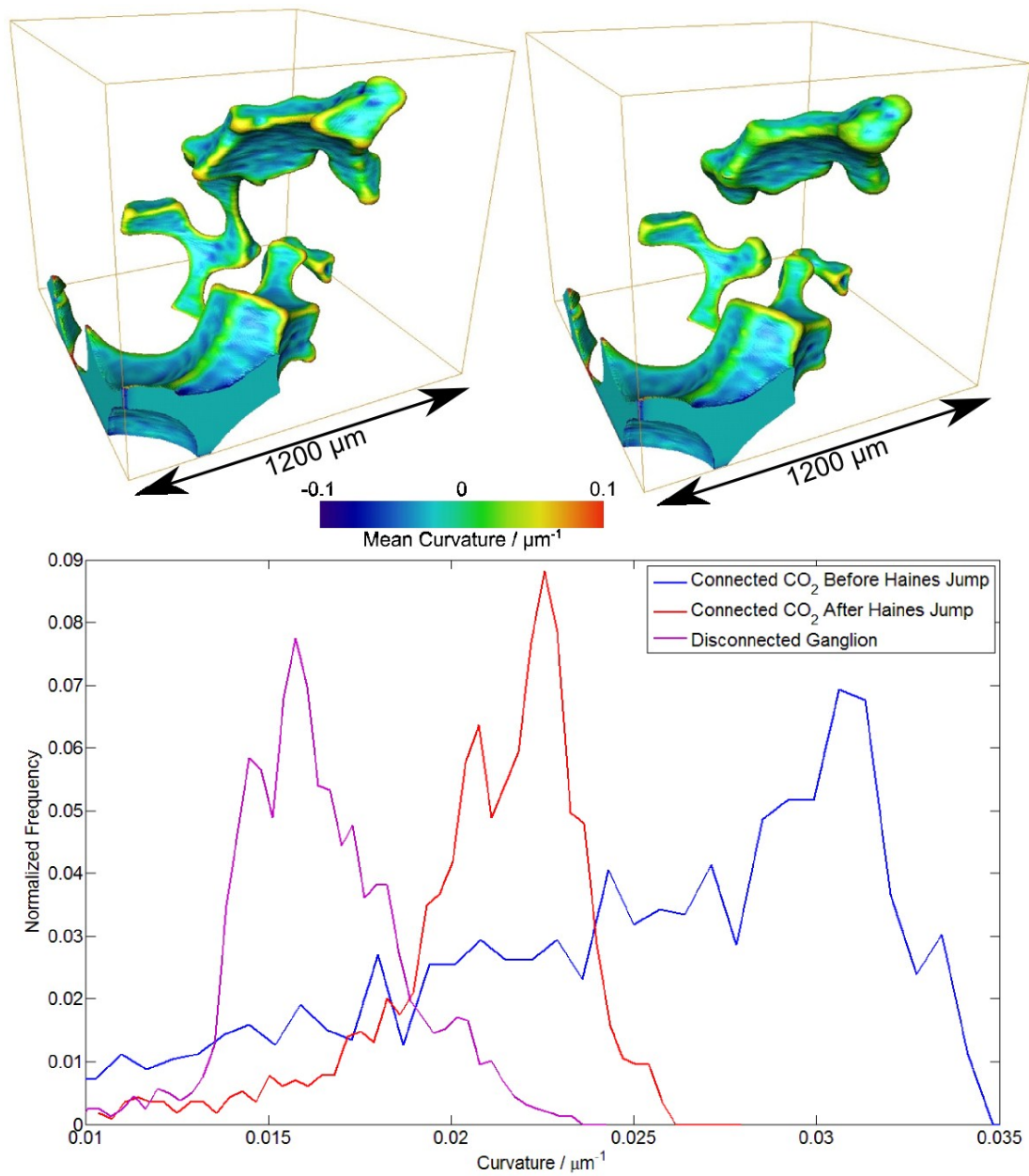


Figure 6.4.4.3.2: (A-B) non-wetting phase interface curvature maps of the volume surrounding the snapped off throat shown in figure 6.4.4.3.1 before the jump (A) and after it (B). (C) shows the resulting curvature distributions from these maps, showing that the ganglion capillary pressure is much lower than the capillary pressure of the connected CO₂ both before and after the event.

The low disconnected ganglion capillary pressure ($0.016 \pm 0.002 \mu\text{m}^{-1}$, corresponding to a capillary pressure of 1.1 ± 0.1 kPa) cannot be explained by the equilibrium change in capillary pressure associated with the drainage event, with the connected interface changing from a curvature of

0.030±0.002 μm⁻¹ (corresponding to a capillary pressure of 2.2±0.2 kPa) to a curvature of 0.022±0.002 μm⁻¹ (corresponding to a capillary pressure of 1.6±0.1 kPa). The disconnected ganglion must therefore preserve some transient low dynamic capillary pressure seen during interface movement. During a large jump, such as that seen here, the non-wetting and wetting phase are displaced and consequentially interface curvature is reduced, with these changes propagating away from the leading interface. This causes not only the interface to recede from the throats and corners and directly involved in the non-wetting phase invasion, but can potentially reduce the capillary pressure in throats a significant distance away. This can reduce the capillary pressure in these throats to below their snap-off capillary pressure, disconnecting regions of non-wetting phase.

Snap-off can be understood by considering the throats represented by a set of hypothetical elements with idealized triangular cross sections [86] (also see section 6.2). Snap-off occurs when the wetting phase in the corner regions of this element swells until they come into contact, causing the wetting-non-wetting phase interface to become unstable and the throat to rapidly fill with wetting phase. If all three interfaces swell concurrently (relying on the assumption that the wetting phase is well connected) then snap-off will occur at a capillary pressure of

$$P_{c-so} = \frac{\sigma}{r} (\cos \theta_a - \sin \theta_a \tan \beta)$$

6.4.4.3.1

where θ_a is the advancing contact angle and β is the effective throat corner half-angle [86] (also see equation 6.2.5.1.1, 6.2.5.1.2 and section 6.2.5.1). Snap-off capillary pressure is therefore a function of throat size and shape, with smaller throats snapping off at higher capillary pressures than larger ones, and throat radius is the primary control on pore-throat snap-off capillary pressure [186].

The rest of the throats occupied by non-wetting phase at the time of the jump remain occupied after the event has occurred. Although modelling the flow through each of the throats is computationally challenging, as the primary control on snap-off capillary pressure is throat radius (section 6.2.5.1) we

can use the throat radii (determined as described in section 3.3.3) to examine the behaviour of other throats within the connected CO₂ ganglion.

An example throat was identified which remained saturated with CO₂ throughout the event, despite having a smaller radius than that of the snapped-off throat (snap-off occurred in a throat of radius 26 μm, whereas a throat with a radius of 19 μm remained saturated with CO₂). As throat radius is the primary control on snap-off capillary pressure, and both were subject to the same dynamic forces during the drainage event, we might expect for snap-off to occur in both of these throats, or at least in the smaller one, rather than the other way round.

One possible explanation is proximity. We would expect the magnitude of dynamic changes in capillary pressure to decrease further away from any event; however the narrow throat which remained saturated with CO₂ was much closer to the event than that which snapped off, (440 μm as opposed to 1640 μm) so presumably is subject to the similar or larger dynamic forces than that experienced by the snapped off throat.

One critical difference may be the availability of wetting phase and how quickly it can invade the throat. The smaller throat which remains full of non-wetting phase after the event does not connect to any pores which are adjacent to pores saturated with wetting phase. The only path through which wetting phase can invade the throat is therefore through wetting films across grain surfaces.

Although these may be present, the rate at which wetting phase can move through these layers to a throat deep within the interior of the connected non-wetting phase may be insufficiently rapid to allow snap-off on the ms time scale associated with the jump. As the equilibrium capillary pressure change is not sufficient to cause snap-off these throats, they remain saturated with CO₂.

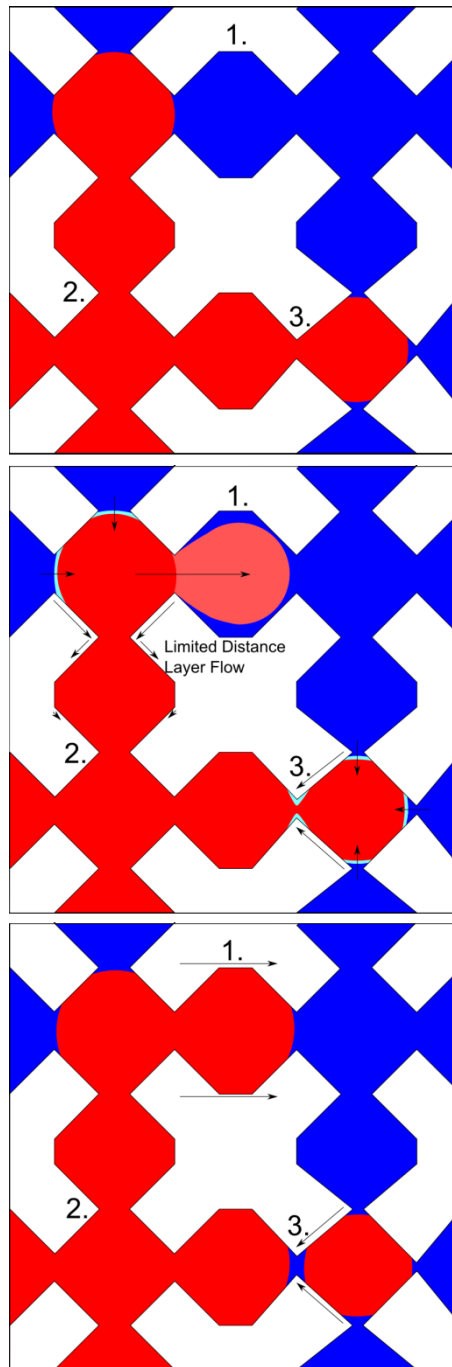


Figure 6.4.4.3.3: A schematic representation of the event shown in figure 6.4.4.3.1. Jump of fluid into pore 1 not only causes interface recession but the low dynamic pressures generated during the event is sufficient to cause snap-off in the throat 3. Although throats 2 and 3 have very similar snap-off capillary pressures, throat 2 does not snap-off as it is further away from available wetting phase, meaning that the wetting films could not grow sufficiently for snap-off to occur in the fast dynamic time scales involved in the jump process.

In contrast the throat that did snap-off connected to pores which were adjacent to pores filled with wetting phase, allowing more wetting phase flow during the event. This then allowed dynamic pressure gradients created during the event to be reflected by wetting layer growth within the throat, causing snap-off (figure 6.4.4.3.3, throat 3).

The process of distal snap-off is potentially more important for the long term evolution of the drainage sequence than local Roof snap-off (section 6.4.4.2) as the fluid configurations arising from distal snap-off are more persistent. The throat through which any specific Haines jump occurs is selected because it is the most energetically favourable; it has the lowest entry capillary pressure for any of those accessible to the wetting-non-wetting phase interface. If snap-off occurs through the throat through which the drainage event occurs without significant rearrangement in the connected non-wetting phase, then this throat will remain the most energetically favourable for a filling event. It will therefore be the site of the next event in the sequence. The disconnected ganglion volume will gradually increase due to a sequence of local invasion snap-off events until it becomes connected with the rest of the (connected) non-wetting phase. If, however, snap-off occurs in another throat unrelated to the throat through which the drainage event occurs, there is no reason that the snapped off throat should be re-filled until the equilibrium capillary pressure increases to above its invasion threshold. The disconnected ganglion can therefore remain disconnected for much longer in the drainage sequence, potentially impacting the wetting phase flow field and further dynamic events. This is seen by comparing the jump discussed in this section to that discussed in section 6.4.4.2. Whereas the disconnected ganglion formed due to the jump discussed in section 6.4.4.2 is reconnected fairly quickly with the rest of the connected CO₂ (within 4 tomographies, or around 3 minutes), the disconnected ganglion seen in figure 6.4.4.3.2 is not reconnected with the rest of the non-wetting phase for another 73 tomographies (around 55 minutes). This is much later in the drainage sequence, where the leading non-wetting phase interface had moved out of the field of view, meaning that this ganglion (preserving features associated with the dynamics of non-wetting

phase jumps) has a persistent impact on the wetting phase flow field and the sequence of subsequent drainage events.

6.4.5 Conclusions

We have used synchrotron-based fast X-ray microtomography to image the drainage process in a carbonate sample at representative subsurface conditions with a time resolution of around 45 s. Capillary pressure evolution around these events has been calculated using selective interface curvature mapping. By focussing on a small number of discrete drainage events (Haines jumps) in detail and comparing capillary pressure measurements to localised multi-phase fluid modelling we have observed dynamic drainage phenomena at representative reservoir conditions.

The quasi-static capillary pressure change associated with these events was found and measured. Snap-off was observed associated with these events, both in the throat through which non-wetting phase invasion occurred (Roof snap-off) and in throats far away from it (distal snap-off). It was found that distal (non-local) snap-off produced more persistent fluid configurations than Roof snap-off. Equilibrium capillary pressure changes associated with drainage events are not sufficient to explain the snap-off associated with these events, as the disconnected ganglia formed have lower capillary pressures than the connected non-wetting phase either before or after the jump. The snap-off may instead be due to significant dynamic pressure gradients generated during these events as fluid pressures and interface curvatures attempt to re-equilibrate after rapid fluid movement. Snap-off in these throats is not only controlled by throat radius and proximity to the event but also by the local fluid arrangement. A more mobile local wetting phase may lead to a greater likelihood for a throat to snap-off during an event.

The method described in this paper for controlling extremely low flow rates at subsurface conditions may be of use in future work using dynamic tomography to address a wide range of problems in multiphase flow in porous media.

7 Conclusions and Future Work

7.1 Conclusions

This thesis presents a novel methodology for the reliable and repeatable non-invasive imaging of multiple fluid phases inside porous rock at representative subsurface conditions by the use of X-ray microtomography. This research has established a platform for the examination of a range of pore-scale phenomena otherwise inaccessible to experimental interrogation. The four principal phenomena for scCO₂-brine-rock systems dealt with in this thesis are:

- 1) Capillary Trapping
- 2) Ganglion Snap-off and remobilization
- 3) Contact angle measurement
- 4) Dynamic phenomena associated with CO₂ drainage

For the interrogation of these problems a suite of image analysis and processing workflows were developed to allow for the measurement of key petrophysical properties (such as contact angle and capillary pressure), effective parameterization of the pore space and efficient data visualisation and manipulation.

Firstly, capillary trapping and ganglia size distributions were determined for five different rock types finding that in all cases a significant proportion of the CO₂ in place prior to brine injection was isolated and trapped as a residual phase. The size distribution of the larger of these residual ganglia obeyed power law distributions consistent with percolation theory; however smaller ganglia were under represented. This indicates that the exact nature of local pore filling and trapping may not be strictly percolation like, as cooperative pore filling or piston-like displacement may become more or less important compared to snap-off. Larger ganglia, however, see the system as a whole, averaging

out this local heterogeneity in the pore filling mechanism so at this scale the trapping can only be fundamentally controlled by the hierarchy of pore sizes. The exponent of the cluster size distribution was found to be correlated with pore connectivity, with better connected pore spaces having more large ganglia relative to small ganglia (smaller power law exponents) and poorer connected pore spaces having more small ganglia relative to large ganglia (larger power law exponents). This is because in poorly connected pore-spaces a greater proportion of the scCO₂ resides in poorly connected portions of the pore space, favouring snap-off over piston like displacement. In well-connected pore-spaces the opposite is true. The chemical composition of the rock had, however, comparatively little effect on the size distribution. This work is encouraging for CCS it shows that, locally, capillary trapping is a viable CO₂ storage technique and can contribute to storage security in a wide range of rock types and compositions.

Secondly, a new method was developed to understand the physics associated with the formation, displacement and remobilization on a pore by pore basis, applied to a sample of Ketton oolite, with experiments conducted at 50°C and 10 MPa. The capillary pressure distribution in the residual CO₂ was found by extracting interface curvatures from a set of ganglia by approximating the ganglion surface as a local quadratic form. The eigenvectors and eigenvalues of that form then respectively represented the directions and magnitudes of the principal curvature of each element on the CO₂-brine surface. Each of the elements on the surface was then assigned a mean curvature, and from the distribution across a specific disconnected ganglion a unique capillary pressure was assigned. Pore-space topography was parameterized using the watershed basins of a Euclidian distance map of the pore-space. As the snap-off capillary pressure is inversely proportional to the inscribed pore throat radius the last throat to snap-off adjacent to a ganglion during imbibition (disconnecting it from the remaining connected non-wetting phase) should be the throat with the largest inscribed radius. A linear correlation is found between the independently measured capillary pressures found in the set of residual ganglia and the inverse of the largest adjacent pore throat radius, supporting

both the pore-scale parameterization used in network modelling and our fundamental ideas about the physics of wetting phase invasion.

By combining the capillary pressures of the ganglia, the capillary pressures required to move through the largest of the adjacent pore throats and the viscous pressure drop through the wetting phase across each of the residual ganglia (as found using pore-scale modelling), I developed a new formulation of capillary number rigorously based on the pore-scale physics of remobilization.

Traditional capillary numbers indicate that ganglion remobilization should occur at capillary numbers of around 10^{-5} , whereas using the new reformulated definition remobilization should occur at capillary numbers of around 1. If the number is to represent the relative importance of capillary and viscous forces then remobilization around 1 is more satisfactory. The same approach was taken to gravitational remobilization, and a new reformulation of the bond number is presented. By looking at the microscopic bond numbers in the system and the trends seen in surface area to volume ratios of the residual ganglia, we can conclude that gravitational remobilization is extremely difficult in this system. This is a positive result for CCS, as it indicates that, in this system at least, projects using residual trapping should be safe from remobilization by gravitational forces.

Thirdly, a new method for the measurement of wettability and contact angle from multiple fluid phase micro-CT images was presented. Measurements were taken by resampling the data set onto a plane perpendicular to the fluid-fluid-rock contact line, as found using local three phase segmentation. Contact angle was measured on high resolution reservoir condition images of Ketton oolite taken at residual state at conditions of 50°C and 10 MPa. Measurements were taken at 300 points randomly selected from the contact line across multiple residual ganglia and a distribution of $45 \pm 6^\circ$ was found. A detailed and quantitative error analysis and sensitivity study for this system found that the measurement errors were not sufficient to explain the observed variation in angle. This error analysis also presented a method by which the applicability of this technique to a specific system could be assessed. The distribution can be explained as the result of multiple contributing

factors, including contact angle hysteresis and surface heterogeneity at a range of different length scales. This surface heterogeneity was visualized qualitatively using microtomography, visual light microscopy and electron microscopy.

Finally, fast synchrotron based microtomography was used to image the injection of scCO_2 under subsurface conditions into a brine saturated sample of Ketton oolite at the pore-scale with a spatial resolution of $3.64\text{ }\mu\text{m}$ and a temporal resolution of 45 seconds. Capillary pressure was measured from the images by finding the curvature of terminal menisci of both connected and disconnected CO_2 clusters. We provide an analysis of three individual dynamic drainage events at elevated temperatures and pressures, showing equilibrium capillary pressure change, and both local and distal (non-local) snap-off. The equilibrium capillary pressure change is not sufficient to explain snap-off in this system, as the disconnected CO_2 has much lower capillary pressure than the connected CO_2 both before and after the event. Disconnected regions instead preserve extremely low dynamic capillary pressures generated during the event. Snap-off due to these dynamic effects is not only controlled by the pore topography and throat radius but also by the local fluid arrangement. Whereas disconnected fluid configurations produced by local snap-off were rapidly reconnected with the connected CO_2 region, distal snap-off produced much more long lasting fluid configurations, showing that dynamic forces can have a persistent impact on the pattern and sequence of drainage events.

7.2 Future Work

Although the principal application of this work has been to look at pore-scale phenomena of interest for carbon capture and storage applications, the experimental platform which was built for the interrogation of these issues is applicable to a wide range of different issues associated with multi- and single-phase flow in porous media. What is more, the image processing and analysis workflows developed for the measurement of contact angle, measurement of capillary pressure, the effective parameterization of the pore space using Euclidian distance mapping and the visualisation tools developed for visualising and manipulating large 4D datasets in computationally efficient ways, can be used to interrogate a wide arrange of systems.

One issue not fully addressed in the examination of capillary trapping and cluster size distributions is the impact of low flow rate. There is some evidence (e.g. Georgiadis *et al.* [104]) indicating that in other systems , particularly the oil-brine-rock system at ambient conditions, much larger ganglia are formed. At low flow rates it is potentially possible that the restricted flow domain used in micro flow experiments may inhibit some of the displacement seen in larger samples, and the relative impact of the flow rate (and so viscous pressure gradient) and domain size could be investigated. This could be linked to further dynamic tomography work at synchrotron light sources to experimentally assess the dynamics of displacement using the same tools as were used in the capillary number reformulation presented in section 6.2.

The comparison of trapping behaviour to local rock structure parameterized on a pore by pore level provides a framework by which changes in a range of different flow phenomena can be correlated and understood over different rock types. Using the watershed basins of a Euclidian distance map of the pore space allows for the spatial arrangement of different pores and throats to be retained, in contrast to other network extraction algorithms where the pore space is abstracted as an array of perfect geometric objects. This experimental and conceptual framework can then be extended over a wider array of representative model systems or even to real rocks extracted from subsurface

reservoirs or aquifers to better understand the qualitative controls that pore topography and topology play on the behaviour of any specific flow phenomena (such as residual trapping) in a specific application.

The wettability characterization techniques presented in this thesis are perhaps the most exciting source of future work both inside and outside the field of CCS research. The rocks presented in this study were extremely mineralogically homogenous, composed of either quartz dominated arenites or purely calcitic carbonates. In more realistic systems we might expect significant additional mineralogical complexity and heterogeneity, leading to a much wider range of potential wettability states within aquifer. By coupling recent the wettability characterization tools presented in this thesis to new micro-CT mineralogical identification tools (e.g. Cnudde *et al.* [180]) it may be possible to start to generate a pore by pore and mineral grain by mineral grain understanding of how these processes work. By coupling this to dynamic tomography it may be possible to understand how these wettability differences impact changes in flow displacement processes.

Although saline aquifers present the most capacious and widely spread potential CO₂ storage sites, depleted oil and gas reservoirs are another highly attractive target due to existing infrastructure and low pore-space pressures prior to injection. The wettability state of these reservoirs is, however, complex, as, prior to their extraction, hydrocarbon reserves may have changed the wettability state of grain surfaces by the deposition of precipitates such as asphaltenes. This creates “mixed-wet” conditions, where part of the grain surface is water wet and part is oil (and potentially CO₂) wet. This system is an interesting target for future work as it would require a significant further development of experimental capabilities including four phase segmentation (oil, CO₂, brine and rock) and the incorporation of existing core-scale techniques such as sample aging (where oil is held in the rock in order to change the wettability state).

Mixed-wet systems are of interest not only in a CCS context but also when considering enhanced oil recovery (EOR) applications, where energy companies desire to increase the fraction of oil recovered

during a reservoirs lifetime. These techniques include surfactant flooding, low salinity flooding, temperature manipulation, CO₂ injection, water alternating gas (WAG) flooding and the instigation of reservoir hydrofracture. These techniques often lead to complex wettability states within the reservoir, and the pore-scale processes associated with them are often poorly understood. Reservoir condition pore-scale experimental evaluation of these processes could lead to not only a better holistic understanding of the physics behind them, but also a better understanding of how they should be best deployed in the field. This could be combined with rock aging technologies to track the evolution on the pore-scale at realistic conditions any specific reservoir of interest from the stage of hydrocarbon charging, through primary, secondary and tertiary resource recovery to potential storage of carbon dioxide.

Finally, the dynamic tomography techniques presented here are a fertile ground for further work, now that the method for both effective imaging of reservoir condition fluids under synchrotron light and the control of extremely low flow rates is established. The incorporation of time dependent behaviour could provide an unparalleled level of detail for the examination of pore-scale displacement processes. The first obvious extension of the work presented here is to look at the details of the time dependent phenomena associated with wetting phase ingression, imbibition and snap-off. This could use the existing techniques of pore-space parameterization and conceptual framework used in the correlation of maximum adjacent pore throat radius to ganglion capillary pressure. Further work could then focus on combining dynamic tomography techniques with the wettability characterisation tools to look at contact angle hysteresis and flow displacement processes in mixed wet or complex hydrocarbon systems.

In conclusion the existing applications and results presented in this thesis represent only the first of many low hanging fruit accessible from this experimental platform. Imaging technology and techniques are now sufficiently advanced that we can not only start finding new answers to existing questions, but new questions to ask. The ability to probe the pore-scale evolution of fluids could

potentially lead to not only developments in the way we find and measure key petrophysical parameters, but also a new and transformative holistic description of fluid flow in porous media.

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The screenshot shows the Copyright Clearance Center RightsLink interface. At the top, there are navigation links: Home, Create Account, Help, and Live Chat. The main content area displays the details of a request for permission for a book chapter titled "Superhydrophobicity, Learn from the Lotus Leaf" by Mengnan Qu, Jinmei He, and Junyan Zhang. The request is for a print and electronic format, and the permission is granted for a one-time use. The interface also includes a login section with fields for User ID and Password, and a "Log In" button. Below the request details, there is a section titled "PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE" with a list of conditions for the permission. At the bottom, there are buttons for "BACK" and "CLOSE WINDOW".

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Author: Xuesong Li, Edo Boek, Geoffrey C. Maitland, et al

Publication: Journal of Chemical and Engineering Data

Publisher: American Chemical Society

Date: Apr 1, 2012

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Engineering • Biomedical Engineering • "Biomimetics Learning from Nature", book edited by Amitava Mukherjee, ISBN 978-953-307-025-4, Published: March 1, 2010 under CC BY-NC-SA 3.0 license. © The Author(s).

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By Mengnan Qu, Jinmei He and Junyan Zhang

DOI: 10.5772/8789

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Publication: Science

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Author: Matthew Andrew, Branko Bijeljic, Martin J. Blunt

Publication: Water Resources Research

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Date: Nov 14, 2014

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Title: Pore-scale contact angle measurements at reservoir conditions using X-ray microtomography

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