Pore-scale Heterogeneity in the Mineral Distribution and Reactive Surface Area of Permeable Rocks

Peter Lai Ern Pinn
Abstract

This work was carried out within the Qatar Carbonates and Carbon Storage Research Centre to improve the characterisation of carbonate reservoirs.

3D images obtained using X-ray micro-tomography were used to characterise heterogeneity in surface area in one sandstone and five carbonate rocks. Surface area measured from X-ray imagery were 1 to 2 orders of magnitude lower than nitrogen BET measurements. Roughness factor, i.e. the ratio of BET surface area to X-ray based surface area, was correlated to the presence of clay or microporosity. Comparing statistical distributions of surface area to those in published modelling studies showed that the common practice of leaving surface area and pore volume uncorrelated in a pore led to unrealistic combinations of surface area and pore volume. In Berea sandstone, constraining ratios of surface area to pore volume to a range of values between that of quartz-lined and five times that of clay-lined spheres appeared sufficient. Statistical analysis suggest that at 600 µm, the observations do not yet form a representative elementary volume.

The development of dual-energy CT for phase identification is presented. Kaolinite, plagioclase, biotite, quartz, orthoclase, albite, dolomite, calcite, pyrite, magnetite, and hematite were scanned. The pairs: plagioclase-orthoclase, albite-quartz, biotite-orthoclase, and hematite-magnetite were not distinguished. Discrimination was possible for all other combinations. In Berea sandstone, kaolinite-smectite, quartz-albite, alkali feldspar-plagioclase, and pyrite-rutile were identified separately. Dual-energy CT has better contrast or capacity for larger samples than single-energy CT.

Finally, an adsorption isotherm was measured from batch experiments with quartz and aqueous caesium chloride. 0.755 M of caesium remained in solution while 0.995 mole of caesium was adsorbed per square metre of quartz. Adsorption was expected to increase average attenuation seven-fold and contribute to 86% of the average attenuation in the image. CT images were collected of an equivalent column experiment with quartz powder and aqueous caesium chloride. However, adsorbed caesium was measured to contribute less than 1% of the average attenuation.

This work has provided new capabilities to characterise pore-scale mineral and surface area heterogeneity and improve our understanding of CO₂ storage in carbonates.
Declaration of Originality

I declare that this thesis, Pore-Scale Reactive Surface Area Heterogeneity and Mineral Identification, is entirely my own work under the supervision of Dr Samuel Krevor. 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.

Peter Lai
Department of Earth Science and Engineering
Imperial College London
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Peter Lai
Department of Earth Science and Engineering
Imperial College London
July 2016
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List of Publications


This work was carried out within the Qatar Carbonates and Carbon Storage Research Centre to improve the characterisation of carbonate reservoirs. The thesis is organised into three chapters. The first chapter presents a study of mineral surface area and heterogeneity. Reactive surface area is an important control on interfacial processes between minerals and aqueous fluids in porous rocks. Spatial heterogeneity in the surface area can lead to complications in modelling reactive transport processes, but quantitative characterisation of this property has been limited. 3D images obtained using X-ray micro-tomography were used to characterise heterogeneity in surface area in one sandstone and five carbonate rocks. Measurements of average surface area from X-ray imagery were 1 to 2 orders of magnitude lower than measurements from nitrogen BET. A roughness factor, defined as the ratio of BET surface area to X-ray based surface area, was correlated to the presence of clay or microporosity. Co-registered images of Berea sandstone from X-ray and energy dispersive spectroscopy imagery were used to guide the identification of quartz, K-feldspar, dolomite, calcite and clays in X-ray images. In Berea sandstone, clay and K-feldspar had higher average surface area fractions than their volumetric fractions in the rock. In the Edwards carbonate, however, modal mineral composition correlated with surface area. By sub-sampling digital images, statistical distributions of the surface area were generated at various length scales of subsampling. Comparing these to distributions used in published modelling studies showed that the common practice of leaving surface area and pore volume uncorrelated in a pore has led to unrealistic combinations of surface area and pore volume in the models. It is suggested that these models adopt a moderate correlation based on observations. In Berea sandstone, constraining ratios of surface area to pore volume to a range of values between that of quartz-lined and five times that of clay-lined spheres appeared sufficient. Statistical analysis of fifteen images suggest that at the length scale of 600 µm, the observations do not yet form a representative elementary volume. There is scope for the development of the X-ray CT characterisation technique.

The second chapter is on the development of dual-energy CT for phase identification. A sample containing silicon and aluminium was prepared. Two X-ray CT scans were taken at 40kV and 150kV, from which the two elements were successfully discriminated. Further samples of kaolinite, plagioclase, biotite, quartz, orthoclase, albite, dolomite, calcite, pyrite, magnetite, and hematite were prepared. Scans were taken at 50kV and 150kV. It was not possible to discrimi-
inate the mineral pairs plagioclase-orthoclase, albite-quartz, biotite-orthoclase, and hematite-magnetite. Discrimination was possible for all other combinations. A sample of Berea sandstone was also scanned at 50kV and 150kV. Four groups of minerals: kaolinite-smectite, quartz-albite, alkali feldspar-plagioclase, and pyrite-rutile were identified separately. Comparison with the single-energy method indicated that the dual-energy method may have better effective contrast or the capacity to achieve the same contrast with larger samples. The dual-energy technique builds on the single-energy rock characterisation technique developed earlier.

The third chapter describes an exploratory study on the observation of aqueous adsorption. Aqueous adsorption is a physical process of major importance in topics such as groundwater remediation and water-rock chemical reactions. An adsorption isotherm was measured from a batch adsorption experiments with aqueous caesium chloride and quartz. The measurements were made after 3 hours in unbuffered conditions. At the highest concentration of caesium in solution, 0.755 M of caesium remained in solution while 0.995 mole of caesium was adsorbed per square metre of quartz. Based on this, the average attenuation of X-rays in a CT image of a column of quartz powder was calculated. With the adsorbed caesium, the average attenuation was expected to increase seven-fold from 3.03 cm\(^{-1}\) to 21.9 cm\(^{-1}\) or in other words, contribute to 86% of the average attenuation in the image. CT images were collected of a column of quartz powder injected with a similar concentration of aqueous caesium chloride. At the highest concentration, 0.759 M of caesium remained in solution. However, the adsorbed caesium was measured to contribute less than 1% of the average attenuation in the image. The investigation was unsuccessful in establishing X-ray CT as capable of observing adsorption. Two hypotheses were proposed for the disagreement between the model and experiment. The first is that there was a mistake in the adsorption isotherm measured. There were weak evidence to both support and reject this hypothesis. The second hypothesis is that diffraction fringes may be overwhelming the signal from the adsorbed component. However there was weak evidence to reject this hypothesis. The ability to observe adsorption in 3D at the pore-scale would allow chemical heterogeneity to be studied in a uniquely powerful way.

This work has provided new capabilities to characterise pore-scale mineral and surface area heterogeneity for reactive transport modelling. This will improve our understanding of how these rocks trap gas and fluids for the application of CO\(_2\) storage in carbonates.
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Chapter 1

Introduction

1.1 Motivation and Objectives

The coupling of chemical reactions and transport processes within porous rocks presents a significant challenge. The continuum formulation that underpins many reactive transport models considers that the properties are perfectly independent such that bulk behaviour of the coupled system can be modelled based on the average of its individual constitutive properties.

For example, assume there exist reactive and unreactive minerals distributed through a porous rock in a statistically homogeneous manner. Consider a case where an unreactive mineral lines a reactive grain and there exists a flow distribution that is statistically homogeneous but not microscopically homogeneous. In this case, if the reactive grain is in contact with a slightly higher than average fluid flux, then there will be a bulk reaction rate that is slightly lower than it might be predicted from average volume fraction of reactive grains and fluid flux. In other words, there exists a non-zero covariance between two or more constitutive properties of the system.

The macroscopic impact of this non-zero covariance is challenging to quantify and is a widely discussed hypothesis for explaining the laboratory-field discrepancy in reaction rate (White & Brantley 2003). Pore-scale heterogeneity in mineral distribution and the resulting average
chemical reaction rates that is not matched by continuum modelling has been a subject of increasing attention (Liu et al. 2015). This has been fuelled, in no small part, by the recent advancement in our ability to observe and measure pore-scale properties and processes (Steefel et al. 2015).

Characterising heterogeneity of important properties that drive chemical reactions such as reactive surface area may improve the prediction of field-scale reaction rates. Reaction rates measured in the laboratory are many orders of magnitude larger than those measured in the field. One explanation for this has been the heterogeneity in mineral distribution. It was initially suggested that reactive surfaces react first whilst more resistant sites remain, giving rise to complex spatial distributions of reaction rates (Lee & Parsons 1995).

More recently, mineral spatial distribution was shown to affect bulk chemical reaction rates. In one example using a pore network model, the rate and direction of kaolinite reactions, both dissolution and precipitation, were affected by their volume fraction and spatial distribution (Li et al. 2007b). Additionally, continuum models were shown to have large discrepancies in their bulk reaction rate predictions compared to pore network models. The pore network in this example was treated as the more accurate representation by including the mineral spatial distribution. When mechanistic models were used to interpret reaction rates in a natural system, there were still discrepancies between laboratory and field dissolution rates (Maher et al. 2006). Secondary mineral precipitation and incongruent reactions were proposed to explain the discrepancies. Transport limitations may also offer explanations (Bijeljic, Mostaghimi & Blunt 2013, Boon et al. 2015). In either case, it remains that field-scale reaction rates continue to challenge our modelling capabilities (Salehikhoo & Li 2015). It is not clear which of these possible explanations are most important and when. In one study, hydrodynamic conditions and field-scale heterogeneity were insufficient to explain the reaction rates calculated from fluid compositions sampled in the field Li et al. (2007b).

Bulk mineralogical characterisation techniques such as X-ray fluorescence spectroscopy and X-ray diffraction offer the capability to quantitatively measure mineralogical composition Williams & van Riessen (2010). However these techniques are not able to provide the spatial resolution
1.1. Motivation and Objectives

needed to study pore-scale mineralogical heterogeneity. The techniques that offer the spatial resolution required, such as optical petrography, scanning electron microscopy, and energy dispersive X-ray fluorescence analyses, provide 2-dimensional data. There are a variety of approaches to approximating surface area from 2-dimensional data but this is a limitation when investigating 3-dimensional properties such as surface area Crandell et al. (2012). 3-dimensional data can be extracted by combining energy dispersive X-ray fluorescence analysis with focused ion beam, but it is an extremely laborious for samples larger than a micrometer and it is impractical in effect.

The ability to characterise mineralogically heterogeneous rocks will be valuable for our current need to improve reactive transport modelling in the area of carbon storage. The injection of carbon dioxide into a carbonate system in the presence of brine results in an acidic fluid that is able to react with the host rock. The resulting weak acid is relatively reactive and affects the dissolution of aluminosilicates such as feldspars (Baines & Worden 2004). Clay and carbonate minerals are often precipitated as a result. The impact of heterogeneity on reaction rates is affected accordingly. The resulting changes to the pore structure can potentially exert a strong control on the distribution of preferential fluid pathways (Smith et al. 2013). Along with the existing permeability distribution, these geochemical reactions can serve to strengthen or weaken leakage pathways in the cap rock, existing fault, or along the wellbore, as well as affecting reservoir injectivity close to the wellbore (Gaus 2010). The evolution of relative permeability and porosity will be difficult to predict without an accurate understanding and model of the chemical reactions. The chemical reactions can be significantly impacted by existing mineral distributions (Kim et al. 2011).

At the larger scale, accurate transport characterisation will determine the maximum injection rates, as well as location and extent of the plume migration within the formation. These factors are important in predicting the timescales and efficacy of structural, residual and solubility trapping of the CO₂ gas, as well as the number of wells needed to achieve maximum CO₂ storage. All these factors combined determine the performance of a potential storage site in terms of storage capacity and the containment of the gas injected. In this way, the ability to characterise mineral heterogeneity is of value to the assessment of the economic viability and
long-term leakage risk of potential CO$_2$ storage projects.

Prediction of field reaction rates in reactive transport modelling might be improved if we can characterise pore-scale heterogeneity in key properties driving reaction, e.g., surface area, as a property of a given rock. Pre-existing high permeability flow paths arising from physical features such as microfractures and bedding planes are locations exposed to higher rates of chemical transport. The distribution of reactive minerals relative to the locations of higher rates of chemical transport therefore affect the locations of significant reaction rates (Smith et al. 2013). The combined effects of local mineral and flow heterogeneity therefore are important for accurate reactive transport modelling. Improved characterisation of pore-scale heterogeneity in mineral distribution and surface area are thus important for predictions of long-term CO$_2$ storage.

1.2 Qatar Carbonates and Carbon Storage Research Centre

This work was funded through major long-term support from Qatar Petroleum and Shell International for the Qatar Carbonates and Carbon Storage Research Centre (QCCSRC). This Centre is aimed in particular at reducing greenhouse gas emissions through advanced carbon capture and storage technologies. The programme was established to improve the characterisation of carbonate reservoirs and develop advanced computer modelling and simulations to establish an in-depth knowledge of rock structures and the way oil, water, natural gas and CO$_2$ move within them. This in turn will improve understanding of how these rocks trap gas and fluids. This work fits within the efforts to develop and use experimental methods and modeling for the characterization of reactive surface area and mineralogical heterogeneity. The use of these observations will be in the development of upscaling techniques for accurate and efficient modeling of chemical processes during flow in porous media.

The Centre is a collaboration between the Department of Earth Science and Engineering and
the Department of Chemical Engineering. This work is especially linked to the extensive mineral dissolution rates and pH data collected by Cheng Peng in another PhD project in the programme. The work also complements those from another PhD project by Benaiah Anabaraonye on the impact of fluid chemistry on dissolution rates. The work will have outstanding value when combined with the recent work by QCCSRC other researchers at visualising transport and trapping heterogeneity by Matt Andrew and Kamal Singh. Some of combined reactive transport experiments has begun to be investigated by Hannah Menke, also of QCCSRC and providing insights into the role diffusion-limited microporosity has in pore-scale reaction heterogeneity. These are all part of the efforts to characterise more complex systems that are more representative of natural rock structures in contact with a range of fluids.

1.3 Achievements

This work has succeeded in developing a practical tool to identify minerals using micro X-ray CT. A workflow was developed to characterise mineral-specific surface area distributions from X-ray CT scans. An advanced X-ray CT technique using two different X-ray energies was investigated. Dual-energy CT provides improvement in the size of specimen that can be characterised at comparable mineral identification performance.

1.4 Thesis outline

The major goal of this work is to investigate methods of characterising surface area and the associated mineralogy at the pore-scale in 3D. A major part will be in the development of the use of X-ray CT for this purpose. X-ray Computed Tomography or X-ray CT is the use of many X-ray images taken at different angles of an object to create a 3D image of the object. Two X-ray CT techniques were successfully developed and applied to characterising multimineral systems. The work has also led to a study on the application to observe aqueous adsorption. Aqueous adsorption is a fundamental physical process in both natural systems and
industrial applications. Unfortunately it was not successfully established that adsorption could be observed by this technique.

The thesis is organised into three parts. In Chapter 2, the work on mineral surface area and heterogeneity is presented. Chapter 3 discusses the development of a more advance technique, dual-energy CT, for phase identification. Finally, Chapter 4 describes the investigation into the use of X-ray CT to observe aqueous adsorption. Chapter 5 reviews the main conclusions of the thesis.
Chapter 2

Mineral surface area and heterogeneity in sandstone and carbonate rocks

2.1 Introduction

The flow of aqueous fluids through porous rocks concurrent with chemical reactions is a dominant feature of many natural and engineered processes. These include the formation of karst zones, the evolution of snow packs during melting, CO$_2$ subsurface injection, nuclear waste remediation, near-surface contaminant transport and remediation and the transport of magma through the mantle. Reviews of reactive transport processes can be found in Steefel et al. (2005), Steefel & Maher (2009). Such processes are particularly difficult to model due to the coupling of chemical reactions, reactant transport through the pore space and at times the evolution of the pore space itself through rock dissolution and mineral precipitation (Haggerty & Gorelick 1995, Lichtner & Kang 2007, Dentz et al. 2011, Boso & Battiato 2013). As a result, there are longstanding difficulties with the use of laboratory scale characterisation of rock samples for modelling of transport and reaction at the field scale (Velbel 1985, Malmström et al. 2000, White & Brantley 2003, Zhu 2005, Maher et al. 2006, Navarre-Sitchler & Brantley 2007).

Recent investigation at pore and pore-network scales have begun to reveal the dominant underlying physical processes giving rise to the macroscopic manifestation of reaction at the
pore-scale. Laboratory scale observations of dissolution and precipitation reactions at mineral surfaces are precise and rate laws that include correlations with fluid chemistry and temperature are repeatable. Thus, Flukiger & Bernard (2009) and Molins et al. (2012) have accurately modelled upscaled reactive transport processes, fully resolving processes of flow, chemical component transport and reaction throughout a three-dimensional pore space. Computational power, however, limits direct modelling combining flow with heterogeneous chemical reaction to spatial domains of a few millimetres.

Statistical descriptions of rock properties - porosity, mineral composition, reactive surface area - that are heterogeneous at the pore scale provide a link between those processes at the pore-scale that can be directly modelled and the larger scale characterisation of reactive transport relevant to the field. They provide a description of the heterogeneity that gives rise to the complex reaction dynamics and deviations from continuum scale descriptions.

Several groups have made use of such statistical descriptions of a porous medium for pore-network models of reactive transport processes (Li et al. 2007a, Peters 2009, Nogues et al. 2013, Raoof et al. 2013). It is possible that such descriptions could also be used to parameterise multi-continuum models or single continuum models with more appropriate effective parameters (Lichtner & Kang 2007). In general these approaches have been limited, however, in their ability to base the statistical properties on direct observations of the properties in the rock material themselves.

In this work, we have focused on creating statistical descriptions of reactive surface area heterogeneity from X-ray microtomography observations of one sandstone and five carbonate rocks. Many studies have shown the important role of the surface area of reacting minerals - the fluid-solid interface - in determining rates and extents of reaction in porous rocks (Helgeson et al. 1984, Velbel 1985, Haggerty & Gorelick 1995, Kieffer et al. 1999, Colón et al. 2004, Noiriel et al. 2009, Luquot & Gouze 2009, Gouze & Luquot 2011, Navarre-Sitchler et al. 2013). For example, Navarre-Sitchler et al. (2013) showed that they were able to improve predictions of global basalt weathering rates by incorporating a roughness fractal dimension. This roughness fractal dimension was used to rescale weathering rates at varying spatial scales to BET surface
area-normalised rates. Variation in weathering rates were reduced to within one to two orders in magnitude and this remaining variation could be attributed to factors such as changes in erosional regime, parent lithology, mechanism, climate, composition of reacting fluid, and biological activity. They concluded that the largest source of variation in weathering advance rates across spatial scales is attributed to the inability to measure comparable surface area at different scales thereby demonstrating the importance of characterising reactive surface area correctly.

The observation of surface area, and its distribution among specific mineral phases in a porous medium, however, has been complicated by the difficulty in interrogating the interior properties of a rock. There are difficulties limitations to assuming idealised geometries based on grain sizes Bolourinejad et al. (2014). Conventionally, the approach for characterising surface area in field settings has been to measure overall surface area using, e.g. $N_2$-BET, and correlate mineral specific surface area to modal composition (Helgeson et al. 1984, Velbel 1985, Zhu 2005, Kampman et al. 2009). Observations of the rates of reactions in rock cores with simple mineralogy - pure quartz, calcite - and well established rate laws have also been used in Kieffer et al. (1999), Colón et al. (2004), Noiriel et al. (2009), and Luquot & Gouze (2009) to infer the evolution of surface area in sandstone and carbonate rocks. Neutron scattering has been used by Navarre-Sitchler et al. (2013) to characterise surface area heterogeneity and its evolution with reaction in low porosity igneous rocks. That technique had the advantage that features with length scales from microns to nanometers are simultaneously characterised across a sample domain with a length scale of order 1 cm.

Recent work by Peters (2009), Landrot et al. (2012), Golab et al. (2013) and Hezel et al. (2013) have described the distribution of surface area from observations of rocks using X-ray and electron imaging. In those works they pioneered the combined use of these observations, registering 3D X-ray imagery of rocks at the microscopic scale with 2D electron image mapping of minerals to produce 3D maps of the mineral distribution within a rock. The success of these techniques suggested that there was an opportunity to derive these statistical descriptions of the pore space from direct imagery of the mineral phases in situ of the rocks themselves. X-ray CT is able to provide mineral identification based on the material dependent attenuation
property of X-ray. Crucially, this is can be carried out at the pore-scale and in 3-dimensions. This means that 3-dimensional properties such as surface area and mineral volumes can be directly characterise. Perhaps more importantly, their spatial properties and correlation can also be characterised.

In this work we endeavoured to apply those techniques to develop a statistical description of the heterogeneity in the mineral surface area available for reaction from direct observations of a Berea sandstone and five carbonate rocks. The rock samples were dominated by pore-network structures, absent fractures, dissolution features, and vuggy conduits for flow. The description of these structures will be key to a full description of reactive processes in porous media, but are outside the scope of this work.

This chapter is organised as follows. In §2.2 the materials and methods employed for the research are reviewed. This includes brief summaries of the use of conventional petrological characterisation tools - thin sections, X-ray diffraction, fluorescence, electron microscopy, BET surface area characterisation and mercury porosimetry. This concludes with two sections, §2.2.5 and §2.3.1, in which more detail is given about the techniques used for processing X-ray images - identification of surfaces and mineral groups, and the generation of the statistical descriptions of the surface area that are the focus of this work.

The results are presented in §2.4. This includes detailed comparison between rock properties observed from conventional techniques to the same properties calculated from the digital X-ray imagery. Statistical descriptions of the mineral surface area are summarised using histograms and box plots, including analysis of mineral specific distributions. The results conclude with a comparison of the statistical properties assumed in the network modelling study of (Li et al. 2007a) to those observed in this work.

A significant utility of this work is the data itself and extensive supplemental information has been included with this chapter. This includes further detail about the techniques, tables of data used in the work and digital copies of all of the X-ray imagery used in this work.
2.2 Materials and Methods

2.2.1 Rock samples

The rocks studied are shown in scanning electron microscope images in Figure 2.2. The samples included two types that have been used extensively in petrophysical research applications, Berea sandstone (Khilar & Fogler 1983, Churcher et al. 1991, Shaw et al. 1991) and Estaillades limestone (Cadoret et al. 1995, Bijeljic, Mostaghimi & Blunt 2013). In addition, four quarry limestones, Ketton, Indiana, Guelph and Edwards, were chosen to explore the impact of pore structure on heterogeneity in the surface area.

The Berea sandstone and the Edwards and Guelph carbonates had significant fractions of at least two mineral types. For this reason mineral-specific characterisation was performed for the Berea and Edwards and not on the Estaillades, Ketton and Indiana carbonates. These were nearly entirely calcite and they were treated as mono-mineralogical systems in the analysis of surface area.

Figure 2.1: Thin-section micrographs in cross-polarized visible light of the rocks investigated in this study.
2.2.2 Average chemical and mineral composition

Observations made with X-ray diffraction (XRD) were used to identify the major minerals present in the samples and X-ray fluorescence spectrometry (XRF) was used to deduce approximate mineral fractions from the bulk chemical composition. The specimens for XRD and XRF were taken separately from the same sample blocks. The instrument used for XRD analysis was a PANalytical X’Pert Pro MPD. Quantitative XRF was performed on 38 mm diameter, 10 mm thick, solid disc specimens using a wavelength dispersive XRF spectrometer, Bruker AXS S4 Explorer. The elemental compositions from the XRF measurements were used to produce an estimate of mineral mass fractions based on the minerals identified by XRD in a procedure detailed in Appendix A.1.
### 2.2.3 Specific surface area and porosity

Surface area quantification from micro CT imagery was compared with parallel observations on the same samples using nitrogen adsorption and the Brunauer-Emmett-Teller (BET) method. Since the introduction of the concept of reactive surface area by Helgeson et al. (1984), a more nuanced understanding of the reactive surface area has developed. The use of BET surface areas, however, is still the observation of choice for calculating and modelling field scale water-rock interactions (Zhu 2005, Kampman et al. 2009). It has also been shown to be a useful proxy for effective surface area in far from equilibrium reaction processes (Hänschen et al. 2007). Normalisation of surface areas calculated from X-ray images in this work by those observed using N₂ BET also allows for comparison with past studies and wider application in the use of the observations in modelling.

The specific surface area of cylindrical pieces of each rock was measured, with samples sized so that they could also be imaged in the micro X-ray CT. The dimensions of the samples were approximately 5 mm diameter and 20 mm length. The analysis was performed with a Micromeritics Tristar 3000 using nitrogen as the working gas.

A nitrogen porosimeter was used to measure the average porosity of samples. The instrument was a Vinci Technologies PoroPerm Production 2. The samples were right cylinders, 1 inch (2.54 cm) each in diameter and length.

Mercury intrusion porosimetry (MIP) was used to characterise the pore throat and size

<table>
<thead>
<tr>
<th>Compound</th>
<th>Khilar &amp; Fogler (1983)</th>
<th>Shaw et al. (1991)</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>76</td>
<td>82.5</td>
<td>89.5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>7</td>
<td>9.7</td>
<td>4.8</td>
</tr>
<tr>
<td>Dolomite</td>
<td>4</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>9</td>
<td>3.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 2.1: Mineral volume fractions of Berea sandstone found in this study are comparable to those found in past studies.
distribution of the rock samples. The pore throat distribution was used to estimate the fraction of the total pore space below the resolution of the X-ray CT images (Knackstedt et al. 2008). This resolvable porosity was then used to back calculate the expected resolvable porosity from CT imagery at 1 μm resolution for evaluation of the segmentation process. The measurements were made on an AutoPore IV 9500 (Micromeritics Instrument Corp., Norcross, GA, USA) using 1-2g of rock fragments. The pressure ranged from 0.5 psi to 33,000 psi. The intrusion volume was normalised to the maximum intrusion volume at 33,000 psi to obtain saturation. Pore radius, \( r \) was calculated as a function of capillary pressure, \( P_c \) according to Equation 2.1, where the interfacial tension, \( \sigma_{hg-air} \) is 485 dynes/cm, and the contact angle, \( \theta_{hg-air} \) is 140° for sandstone and 130° for carbonate (Ethington 1990).

\[
P_c = \frac{2\sigma_{hg-air}\theta_{hg-air}}{r}
\]  

(2.1)

The radius in Equation 2.1 does not refer to a pore body radius, but rather a limiting radius for mercury intrusion - a pore throat. Thus to approximate 1μm pore bodies we use a value of \( r = 0.1μm \) from the mercury intrusion data, assuming that pore bodies are approximately an order of magnitude larger than pore throats.

### 2.2.4 Electron imaging and spectroscopy

Electron microscopy and spectroscopy were used to provide two-dimensional chemical and mineral phase maps of the Berea sandstone and Edwards carbonate. This provided a guide for segmenting mineral groups in X-ray images in these rocks, the samples where multiple mineral groups were analysed. Images were taken on a JEOL JSM-6400 SEM. The mineral composition of Berea sandstone, and Edwards and Guelph carbonates were investigated using the backscattered electron (BSE) imaging mode. Energy dispersive spectroscopy (EDS) was used to generate elemental maps for the identification of mineral groups, chlorite, clay, and feldspar. Previous efforts (Peters 2009, Landrot et al. 2012) have used thresholded BSE and EDS maps
2.2. Materials and Methods

The mineral-volume, and surface area fractions were estimated from the elemental maps. The phases present in the Berea sandstone were divided into five broad groups: pore, clay minerals, quartz, feldspars, and others to correspond with groups that could be identified in the X-ray images, discussed in the following §2.2.5. Specific parameters used for segmenting the electron images are provided in Appendix A.2.

2.2.5 X-ray imaging and image processing

In an image reconstructed from X-ray tomography, the value assigned to each volume pixel, or voxel, represents the average X-ray attenuation property of the material in that volume. The degree of attenuation is determined by the elemental composition and bulk density of the material and this gives the potential for limited mineral phase identification in X-ray images. Work in Uesugi & Tsuchiyama (1999), Tsuchiyama et al. (2000, 2005, 2013) showed that quantitative measurements of X-ray linear attenuation coefficients (LAC) were possible with both mono- and poly-chromatic X-ray beams. Based partly on these principles, several groups have recently made use of laboratory micro CT devices in application to mineral identification in rocks, including Peters (2009), Landrot et al. (2012), Golab et al. (2013) and Hezel et al. (2013).

The general procedure for segmentation - both between pore and solid, and of the mineral groups in the case of the Berea sandstone and Edwards carbonate - is described here and detailed information is provided in Appendix A.3. For all rocks, the X-ray image was denoised using the "non-local means neighbourhood" filter in Avizo Fire 8.0. The watershed segmentation module in Avizo Fire 8.0 was used for both binary and multiphase segmentation. Grey scale thresholds for the seeds were selected by eye and the specific parameters for each rock are provided in Appendix A.3. Additionally, the digital image after denoising is provided so that others may repeat the segmentation or implement their own procedures.

With the Berea sandstone and Edwards carbonate, the solid phase was further segmented into mineral groups. The work reported in Latham et al. (2008), Sok et al. (2010), and Golab et al. (2013) demonstrated the value of simultaneous analysis by backscattered electron imaging...
(BSE), energy dispersive spectroscopy (EDS), and micro-computed X-ray tomography for the use of X-ray CT for mineral phase and rock structure characterisation. We employed a similar approach, comparing data from X-ray imagery, BSE imaging, and 2D elemental composition maps to guide and evaluate the effectiveness of mineral identification using X-ray imagery. To create co-registered images, a Berea sandstone specimen was imaged in the X-ray microscope using the parameters described in Appendix A.3. Then, the sample was cut to expose a section of the rock that was imaged, and the remaining sample impregnated with epoxy and polished for BSE and EDS analysis as described in Section 2.2.4. The cut sample was imaged again to establish the location of the exposed surface. The alignment and registration of both X-ray images was performed in Avizo Fire 8.0. A range of grey scale values were associated with each mineral grouping based on an identification of those minerals in a particular 2D section of the 3D CT image. These were used to identify the seeds for the watershed segmentation process.

Table 2.2 summarises the definition of the segmentation groups. The feldspar group mostly consists of alkali feldspars but plagioclase, illite, and muscovite were also included in this group. Kaolinite and smectite comprised the bulk of the clay mineral group. The quartz group consisted of quartz and albite which has similar attenuation properties to quartz. Calcite, oxides and sulphides such as hematite and pyrite, and remaining micas, including biotite, formed the others group. Phase contrast effects at the grain boundaries in the Berea sandstone often resulted in misidentification of quartz as small pieces of feldspar. The feldspar volumes were sorted by size and feldspar labels below a size threshold were relabelled as quartz. The central $600^3$ of $1000^3$ voxels were extracted from the centre of the image for further analysis. The mineral groups identified in the Edwards rock were quartz, dolomite, and others.
2.3 Parameters used for X-ray imaging and segmentation

The contrast in X-ray light attenuation, represented as greyscale contrast in the reconstructed images, was the predominant differentiator for identifying mineral groups in the X-ray images. Other information, such as local grain textures, could potentially be used but was not in this work with the exception of the identification of clearly mislabeled feldspar groups. Generally using low energy settings increased contrast in light attenuation but there was an inverse relationship between absorption contrast and noise in the images as a result of low photon flux. At low X-ray energies, the current was reduced to maintain the micrometer scale focal spot size of the electron beam on the X-ray source target, and preserve the voxel resolution of the imaging. This meant that as X-ray flux was reduced, scan time increased. The mineral groups such as quartz, feldspar and clays were generally distinguished by their relative amounts of silicon and aluminium, elements that are separated by a single atomic number. With many groups of scanning parameters, the greyscale contrast between mineral groups was found to be within the order of magnitude of impertinent influences, such as source stability, sample stage drift, refraction at density boundaries, partial volume effect, insufficient X-ray counts, byte scaling and beam hardening. An empirical search of the scanning parameter space was employed, comparing the contrast to noise ratio in our images using the ratio of the modal separation to their combined spread to identify optimised parameters. Large uniform regions

<table>
<thead>
<tr>
<th>Group name</th>
<th>Major mineral</th>
<th>Minor minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feldspar</td>
<td>alkali feldspar</td>
<td>plagioclase, illite, muscovite</td>
</tr>
<tr>
<td>Quartz</td>
<td>quartz</td>
<td>albite</td>
</tr>
<tr>
<td>Clay</td>
<td>kaolinite</td>
<td>smectite</td>
</tr>
<tr>
<td>Other</td>
<td>calcite</td>
<td>hematite, pyrite, mica</td>
</tr>
</tbody>
</table>

Table 2.2: Description of the X-ray segmentation groups for the Berea sandstone. Minor minerals constituted less than 10% of a given segmentation group.
of quartz grains and dry pore space in Berea sandstone were sampled. It was found that given an optimised setup, the noise in the images was sensitive largely to the parameters of energy, specimen dimension, and byte scaling. Ultimately, operating the beam at 40kV and 3W, at a resolution of 1 μm on the Xradia VersaXRM-500 produced images useable for mineral identification. This set of parameters was used for both the Berea sandstone and Edwards carbonate. The specimens were cut to less than 2 mm to reduce unnecessary beam hardening, and the reconstructed data scaled to the range, 0 to 7000 byte. The scanning parameters included 2500 projections, 40s exposure time, and camera binning of 2, to collect a $1 \times 10^9$ voxel image.

Figures 2.3 and 2.4 show the results of the segmentation of X-ray images for the Berea sandstone and Edwards carbonate respectively.
2.3. Parameters used for X-ray imaging and segmentation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Berea 1 Plug 1</th>
<th>Berea 1 Plug 2</th>
<th>Berea 1 Plug 3</th>
<th>Berea 1 Plug 4</th>
<th>Edw</th>
<th>Gue</th>
<th>Ket</th>
<th>Ind</th>
<th>Est</th>
</tr>
</thead>
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<tr>
<td>No.phases</td>
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<td>5</td>
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<td>4</td>
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Table 2.3: Segmentation parameters used for image processing
Figure 2.3: Segmentation process in the mineral phase identification of Berea sandstone sample: (a) Gradient mask, initial labels for (b) clay, (c) quartz, (d) feldspar, (e) other minerals, and (f) first segmentation result. (g) Mislabelled feldspar, and (h) final segmented Berea
2.3. Parameters used for X-ray imaging and segmentation

2.3.1 Quantifying surface area heterogeneity

In this work we have focused on describing spatial heterogeneity in the surface area of a rock through the construction of distributions in the local surface area to pore volume ratio. There are a number of ways in which surface area heterogeneity could be quantified (we note that the data, available as supporting material, can be used to generate these). This metric reflects a contribution to the local reactivity of the solid in this system per unit volume of fluid.

We have used this metric for a number of reasons. The amount of surface area available in a sub-region of a rock is influenced both by the presence of porosity and the shape of the pore-solid boundary. In other words, a given cubic millimetre of rock may have more surface area than a comparative sub-volume in a separate location because it has more pore volume, or it may have more surface area because the geometry of the pore itself is more tortuous. The comparison of the surface area to pore-volume ratio disentangles these and provides a measure of solid reactivity due to surface area morphology alone.

It is also evident that reactive transport processes are strongly affected by feedbacks between the changing composition of the fluid and reaction rates at the fluid-solid boundary (Colón et al. 2004, Noiriel et al. 2009, Dentz et al. 2011, Gouze & Luquot 2011). The surface area to
pore (fluid) volume ratio provides some measure of the extent to which local reactive processes will influence the local chemical composition of the fluid - there is less fluid chemistry change in a large body of fluid compared with a smaller body for a given reaction rate (Lichtner & Kang 2007).

To build the distribution from an X-ray image, first an image was sub-sampled at a chosen length scale. From this subsample the surface area to pore volume ratio was calculated following a procedure detailed in Appendix A.4. Then the process was repeated for every unique location throughout the X-ray image and a frequency histogram was constructed from the values. For example, an X-ray image cube with dimension 600 µm on each side contained 216 unique sub-cubes with dimension 100 µm on each side. Frequency histograms were generated for each rock type using sub-sample sizes ranging from 50 µm to 300 µm. For all of the rocks, initially this process was performed using a binary segmentation of the images into pore space and rock. Subsequently, the distributions for the Berea sandstone and Edwards carbonate were separated into their individual mineral constituents.

![Sub sampling from a 600 µm data set for a 100 µm cube.](image)

**Figure 2.5:** Sub sampling from a 600 µm data set for a 100 µm cube.

### 2.4 Results and Discussion

#### 2.4.1 Porosity and surface area

Figure 2.6 shows the pore throat size distribution estimated from mercury intrusion porosimetry. The corresponding estimate of the fraction of the total pore space below the resolution of the
X-ray CT images is shown in Figure 2.7. It was estimated that the X-ray imagery could capture 80-85% of the porosity for the Berea sandstone and Edwards and Guelph carbonates whereas significant amounts of unresolvable “microporosity” was present in the Estaillades, Ketton and Indiana carbonates. In the case of the Ketton carbonate, Figure 2.6 shows a clear bimodal distribution of the pore throats with approximately 40% of the porosity accessed through pore throats greater than 10 µm and another 40% below 10^{-1} µm. The Guelph and Indiana carbonates have multiple modes with porosity more evenly distributed across the length scales.

Figure 2.6: Mercury saturation as a function of pore radius for sandstone and carbonate samples used in this study. Each measurement was repeated on two separate specimens.
Figure 2.7: Resolvable porosity in CT images for the sandstone and carbonate samples used in this study estimated from mercury intrusion porosimetry.

Figure 2.8 shows the porosity estimate from the steady-state nitrogen gas porosimetry data compared with micro CT imagery, before and after correcting the micro CT based calculation for the sub-resolution porosity. The corrected values are simply the uncorrected values divided by the fraction of resolvable porosity shown in Figure 2.7. In all cases the porosity calculation based on CT imagery alone underestimates the porosity relative to porosimetry as expected. In the case of one of the Berea sandstone samples, and the Edwards, Ketton and Indiana carbonates the correction reconciles much of the difference.

The vast difference in size scale between samples used in each measurement (0.2 mm$^3$ in the X-ray imagery as compared with about 100 cm$^3$ for the porosimetry observation) means that discrepancies were to be expected. An indication of the variability in the porosity measurement for the Berea sandstone is shown for the Berea 2 sample. For this sample 20 X-ray images were generated and the corresponding porosity variation is shown as whiskers from the mean value in Figure 2.8. A range of porosity values varying over 0.10 porosity units was observed due to natural heterogeneity in the rock at the size scale of the X-ray images, apparently below the representative elementary volume for porosity. Porosity from nitrogen gas porosimetry and the pore throat size distributions measured from mercury intrusion porosimetry, on the
other hand, showed little variation due to the larger volume of the samples. It is known from statistical tests described in the Results section of this Chapter that the micro-CT images used are not yet of a representative elementary volume size. However, there has been some evidence that the representative elementary volume size for porosity occurs around the mm-scale (Dongxiao Zhang 2007). Hence it was speculated that the cm-scale samples used in the nitrogen gas porosimetry measurements are at the representative elementary volume size whilst the micro-CT were not.

The advantage of using porosity measurements made by nitrogen gas porosimetry is that it includes pore space down to mm$^{-7}$. When chemical transport is dominated by diffusion, the pore space that can be accessed by diffusion can be accounted for by nitrogen gas porosimetry. However it was observed that in carbonate rocks with heterogeneous pore structures, the pore space that are limited by diffusion transport experience effectively zero solute transport velocities relative to the advection dominated and larger pore spaces (Bijeljic, Raeini, Mostaghimi & Blunt 2013). Indeed, as observed experimentally with Ketton, a rock with both micro- and macro-porosities, in the larger macro-pores where chemical transport was dominated by advection, the correct reaction rates was predicted when the micro-pores was not included (Menke et al. 2015). In other words, measurements that include micro-pores such as nitrogen gas porosimetry may be inappropriate when characterising the rock for reactive transport modelling when chemical transport and reaction are dominated by the advection dominated macro-pores. In this case, then it is more accurate and therefore an advantage to use the measurements from micro-CT imagery that are unable to resolve microporosity and thus discount the diffusion limited pore spaces.
Chapter 2. Mineral surface area and heterogeneity in sandstone and carbonate rocks

Figure 2.8: Comparison of porosity measured from nitrogen gas porosimetry and micro CT imagery at 1 µm resolution, before and after correction.

Figure 2.9 shows that the BET surface area of the rocks ranged nearly two orders of magnitude, from .08 $m^2 g^{-1}$ for the Guelph carbonate up to 4.3 $[m^2 g^{-1}]$ for the Edwards carbonate. The surface area of Berea sandstone samples varies within the range of 0.7-1.4 $m^2 g^{-1}$, similar to values that can be found in the literature, e.g., Sen et al. (1990).

In the work of (Kerbrat et al. 2007) it was shown that the calculation of specific surface area from X-ray CT images converges to adsorption based measurements when the roughness of the surfaces is above the resolution of the X-ray imagery. For the minerals studied in this work it was expected that a significant fraction of surface area would be below the resolvable threshold.
of the 1 $\mu$m resolution micro CT imagery. Figure 2.10a shows pairs of BET and micro CT based surface area measurements obtained from a single sample. The values are provided in tabular form in Appendix A.5. The BET surface areas were 1-2 orders of magnitude higher than the values calculated from the X-ray imagery. There was a weak correlation among the entire dataset. This is primarily due to the varying degrees that specific mineral groups and microporous regions contribute to the discrepancy between the two observations for a given rock. This is discussed in further detail here.

The comparison of X-ray imagery to surface adsorption measurements leads to a variation of the concept of the roughness parameter. The roughness parameter is an empirical factor conventionally used to reconcile the difference between surface areas measured with adsorption and those calculated based on the assumption of a simplified mineral grain geometry, e.g., a sphere (Helgeson et al. 1984, White & Peterson 1990). In the case of this work, the X-ray image provides the geometrical simplification. On the one hand X-ray imagery can provide more morphological information than, e.g., the assumption of spheroid grains, because more complex shapes are resolved in the imagery. On the other hand, there is no limit to the grain or pore size considered in the purely geometrical framework (one can assume spheres as small as is known to be appropriate) whereas with the X-ray imagery micro porous regions can only be accounted for with the roughness parameter.

In Figure 2.10b the ratio of the two surface areas, the roughness parameter, is plotted as a function of the BET surface area. As expected, the roughness of the samples generally increase with increasing total surface area. Roughness factors based on geometrical shapes alone have been observed to range from 5-200 for unpolished mineral grains in rocks (White & Peterson 1990) similar to the range obtained in this work. The coincidence may reflect the competing effects of increased geometrical complexity balanced by the lack of the resolved microporosity.

A comparison of the roughness parameter plot (Figure 2.10b) with the MIP based analysis of resolvable porosity (Figure 2.7) provides insight into the nature of the roughness for the various rocks. The Ketton carbonate has the highest roughness factor and also the most sub-resolution pore space, nearly 40% of the pore volume was expected to be below the resolution of the X-
ray imagery. This is followed by the Edwards carbonate in both roughness and microporosity. In these cases, microporosity is thus likely to be a major contributor to the roughness ratio. Following this, the Berea sandstone has the next highest roughness factor but among the most resolvable porosity. Over 90% of the pore space was estimated to be above the X-ray image resolution. In this case the roughness must be primarily attributed to the high clay content of the rock. The Guelph and Indiana carbonates have minor amounts of microporosity, no clay and correspondingly low roughness factors. The Estaillades has the least amount of microporosity of the carbonates and has the lowest roughness ratio of the group, despite having an equal or higher BET surface area compared with the Guelph and Edwards carbonates. This further underscores the role that microporosity plays in the discrepancy between the X-ray images and the BET measurements for the carbonate minerals. In other words, with the carbonate rocks, high specific surface areas in the absence of microporous regions were well captured by the X-ray imagery.
2.4. Results and Discussion

Figure 2.10: (a) Surface area inferred from CT observations is plotted against the measurement using N$_2$ BET (b) The roughness ratio (BET surface area : CT calculated surface area) plotted against BET surface area. This shows that roughness increases as expected with total BET surface area. Variation among sample types at a constant BET surface area reflects differences in microporosity between e.g., the Edwards and Ketton or the Indiana and Estaillades.

2.4.2 Chemical and mineral composition

The minerals identified by XRD in the rocks are shown in Table 2.4, the bulk chemical compositions are shown in Table 2.5 and the inferred mineral compositions are shown in Table 2.6.
Table 2.4: Minerals identified from X-ray diffraction in the rock samples used in this work

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Table 2.5: The major elemental composition of sandstone and carbonate rocks measured using X-ray fluorescence spectroscopy

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## 2.4. Results and Discussion

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</table>

Table 2.6: Mineral composition by mass fraction of Berea sandstone and carbonate samples inferred from the XRF data

Results showing details of the image processing of the BSE and X-ray imagery are reported in Appendix A.2 and A.3. To guide the X-ray image processing for the Berea sandstone, segmentation was performed on locations in the rock that had been imaged using BSE. The comparative segmentation is shown in Figure 2.11. The volume and area fractions of minerals in the images derived from BSE and X-ray observations for the same location in the rock are summarised in table 2.7. The porosity and specific surface area inferred from the co-registered images are recorded in Table 2.8. The segmentation of the X-ray image identified quartz, K-feldspar and most clays well. In this particular location there was significant albite (cyan in the BSE image in Figure 2.11) which was included in the quartz segmentation group because it cannot be distinguished in the X-ray images from grey-scale segmentation. At the bottom centre of the 2D section, there is a large orthoclase grain that has been partially weathered.
to illite and was identified as feldspar and quartz in the X-ray image. In this rock, the illite and albite minerals constitute less than 10% of the total segmentation grouping (see Table 2.6) implying that this location saw a larger impact than would be typical for the image as a whole.

Figure 2.11: On the left is the BSE image (top), and micro CT (bottom) of a Berea sandstone. On the right is the segmented BSE (top), and segmented micro CT image (bottom). In the segmented BSE image, sodium feldspar is in cyan, distinct from the potassium feldspars in green.
2.4. Results and Discussion

<table>
<thead>
<tr>
<th></th>
<th>Volume fraction</th>
<th>Area fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CT</td>
<td>SEM</td>
</tr>
<tr>
<td>Clay</td>
<td>0.07</td>
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<tr>
<td>Quartz</td>
<td>0.85</td>
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<td>Feldspar</td>
<td>0.08</td>
<td>0.12</td>
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<tr>
<td>Others</td>
<td>0.01</td>
<td>0.01</td>
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</table>

Table 2.7: Mineral volume and area fraction from co-registered CT and SEM 2D section of Berea sandstone (see Figure 2.11)

<table>
<thead>
<tr>
<th></th>
<th>CT</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.148</td>
<td>0.226</td>
</tr>
<tr>
<td>Total surface area / pore volume [µm²/µm³]</td>
<td>0.234</td>
<td>0.658</td>
</tr>
</tbody>
</table>

Table 2.8: Porosity and surface area per pore volume from co-registered CT and SEM 2D sections of Berea sandstone (see Figure 2.11)

The volumetric composition of the entire Berea sandstone and Edwards carbonate X-ray images in terms of the segmentation mineral groups are provided in Table 2.9 along side the surface area fraction calculated from the images. This can be compared with the volumetric fraction of the mineral groups measured by XRF in Table 2.6. For the sandstone, the inferences from X-ray imagery appear to underestimate the feldspar group minerals and overestimate the quartz group minerals while the clay group is consistent. For the Edwards carbonate, the X-ray imagery appears to overestimate the amount of quartz at the expense of the carbonate minerals.

Comparing the volumetric fraction and surface area fraction of the minerals from the X-ray imagery of the Berea sandstone shows that there was little correlation between the two. In all of the samples, the clay and feldspar group demonstrated far higher surface area fractions compared with the bulk mineralogy, whereas quartz showed less. In this case, using the modal mineral composition of the rock as a proxy for surface area is a poor assumption. On the other hand, the Edwards carbonate showed a strong correlation between the modal mineral
composition and the surface area. This suggests that the nature of a correlation, or lack thereof, will be rock specific. Further work is needed to see if these correlations can be related to the formation and diagenetic history of the rock.
### 2.4. Results and Discussion

<table>
<thead>
<tr>
<th>Specimen/ Porosity+</th>
<th>Group</th>
<th>Volume fraction</th>
<th>Surface area/ bulk volume $[m^2/m^3]$</th>
<th>Area fraction</th>
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</thead>
<tbody>
<tr>
<td>Berea 1</td>
<td>Clay</td>
<td>4.8%</td>
<td>$1.56 \times 10^4$</td>
<td>37.5%</td>
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<tr>
<td>Plug 1</td>
<td>Quartz</td>
<td>89.5%</td>
<td>$2.17 \times 10^4$</td>
<td>52.2%</td>
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<tr>
<td>16.0%+</td>
<td>Feldspar</td>
<td>3.5%</td>
<td>$3.63 \times 10^3$</td>
<td>8.8%</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>2.3%</td>
<td>$6.61 \times 10^2$</td>
<td>1.6%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>100.0%</td>
<td>$4.16 \times 10^4$</td>
<td>100.0%</td>
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<tr>
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<td>Clay</td>
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<td>$5.50 \times 10^3$</td>
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<tr>
<td>Plug 2</td>
<td>Quartz</td>
<td>77.4%</td>
<td>$1.93 \times 10^4$</td>
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<tr>
<td>11.4%+</td>
<td>Feldspar</td>
<td>6.7%</td>
<td>$6.28 \times 10^3$</td>
<td>19.4%</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>13.4%</td>
<td>$1.33 \times 10^3$</td>
<td>4.1%</td>
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<tr>
<td><strong>Total</strong></td>
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<td>100.0%</td>
<td>$3.24 \times 10^4$</td>
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<td>Clay</td>
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<tr>
<td>Plug 3</td>
<td>Quartz</td>
<td>74.7%</td>
<td>$1.87 \times 10^4$</td>
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<td>9.8%+</td>
<td>Feldspar</td>
<td>7.5%</td>
<td>$4.53 \times 10^3$</td>
<td>16.7%</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>16.6%</td>
<td>$1.09 \times 10^3$</td>
<td>4.0%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
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<td>100.0%</td>
<td>$2.71 \times 10^4$</td>
<td>100.0%</td>
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<tr>
<td>Berea 1</td>
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<td>$9.76 \times 10^3$</td>
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<tr>
<td>Plug 4</td>
<td>Quartz</td>
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<tr>
<td>16.2%+</td>
<td>Feldspar</td>
<td>9.5%</td>
<td>$5.09 \times 10^3$</td>
<td>11.2%</td>
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<tr>
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<td></td>
<td>0.4%</td>
<td>$1.85 \times 10^2$</td>
<td>0.4%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
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<td>$4.56 \times 10^4$</td>
<td>100.0%</td>
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<td>Edwards</td>
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<td>37.6%+</td>
<td>Dolomite</td>
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<td>$7.61 \times 10^4$</td>
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<tr>
<td><strong>Total</strong></td>
<td></td>
<td>100.0%</td>
<td>$1.01 \times 10^5$</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

Table 2.9: Mineral volume and specific surface area from X-ray CT. The porosities tabulated here are uncorrected for resolution. The heading Area/bulk means surface area per bulk volume of the sample.
2.4.3 The spatial distribution of surface area

For each rock five frequency histograms of the surface area distributions were generated. The histograms are provided for the Berea sandstone in Figure 2.12. The carbonate rocks, Ketton and Indiana, are also shown in Figures 2.13 and 2.14. Ketton and Indiana represent carbonate rocks with a less heterogeneous and more heterogeneous pore-structure respectively. The other carbonate rocks are included in Appendix A.6.

Each histogram represents the distribution at a particular sub-sample size, 50, 75, 100, 200 and 300 $\mu$m respectively. Best fit log-normal curves are also shown on the histograms with their parameters, mean and standard deviation. The sixth graph in each figure shows box plots summarising the histogram data at each sub-volume length scale. On each box plot the central mark is the median, an x denotes the mean, the edges of the box are the 25th and 75th percentile, the whiskers mark 2.7 standard deviations and the red diamonds indicate outliers.

As the sampling size decreases the distributions broaden reflecting the expected increase in heterogeneity at smaller sampling length scales. The distribution in the Berea sandstone and Estaillades carbonate are well described by a log-normal distribution whereas the remaining carbonates have more complex distributions. Multiple modes appear in the Guelph, Ketton, and Indiana carbonates.

Images of the digital rock subsamples at a length scale of 100 $\mu$m that have low, median and high values of the surface area to pore volume ratio are shown in Figures 2.15 for samples of the Berea sandstone, and others are shown Appendix A.6. In all cases higher surface area to pore volume ratios are associated with more and smaller pores within the subvolume. Those subvolumes that are dominated by a single pore tend to have low surface areas. This is the kind of trend that is captured by simplified representations of surface area, e.g., the assumption of spheroid pores or mineral grains.

This description of surface area heterogeneity is less meaningful if the sub volume being used is smaller than a significant number of pores in the rock. This threshold can be seen clearly in Figure 2.12 for the Berea sandstone where the mean in the surface area to pore volume ratio
begins to deviate, generally increasing, when sub-sample length decrease below the character-
istic pore size of those rocks. The Berea sandstone and Estaillades carbonate have a single
characteristic pore size and the distributions of surface area are not generally useful at size
scales below this pore size. This issue is complicated, however, for rocks such as the carbonates
in this work that have several modes or a continuous range of pore sizes across length scales.
In this case surface area heterogeneity at small spatial scales in some locations in the rock may
indeed be important simultaneous with regions of large spatial scale where the metric is mean-
ingless because it is encompassed within a single pore body. In this case the multi-continuum
formulation proposed by Lichtner & Kang (2007) may be appropriate.

A separate issue tied to the limitations in image resolution is that at small pore sizes, ap-
proaching single voxels, the marching cubes algorithm has trouble accurately interpolating and
meshing the surfaces. As the sub volume scale decreases to 20 µm there is a large increase in
surface area not accounted for. Thus statistics using the sub-volume sizes less than 50 µm were
not included.
Figure 2.12: Mono-mineralogical surface area distribution for Berea sandstone 1 plug 1
Figure 2.13: Mono-mineralogical surface area distribution for Ketton carbonate
Figure 2.14: Mono-mineralogical surface area distribution for Indiana carbonate
2.4. Results and Discussion

Figure 2.15: Sub volume of Berea 1 plug 4 rock with binary segmentation showing from top to bottom: least, typical, and greatest surface area per pore volume.
The distributions shown in Figure 2.12 and in Appendix A.6 of the Berea sandstone and Edwards carbonate were further separated into the mineral groups obtained from the segmentation of the X-ray images. These rocks had significant fractions of multiple mineral groups, whereas the others were primarily calcite. These histograms are shown in Figure 2.16 and in Appendix A.6 for the same range of sub-sample sizes with colours delineating each mineral group. Box plots summarising the mineral specific distributions at various sub volume sizes are also provided in Appendix A.6.

The plots shown on a logarithmic scale showed that approximating the distributions as log normal appears to be appropriate for the Berea sandstone minerals and to a lesser degree with Edwards carbonate minerals. The natural log plots also show peaks at zero indicative of sub-volume samples that have no surfaces associated with a given mineral. For example, in Figure 2.16 at 200 µm, 7% of the sub-volume sample cubes do not have any of the feldspar group minerals in them. This information is also provided in the legend of each graph. A summary of the statistics is contained in tabular form in Appendix A.6.

Figure 2.17 shows examples of 100 µm sub-volumes with the lowest, median and highest surface area to pore volume ratios obtained for the feldspar group. Images showing examples of the other groups are provided in Appendix A.6. Their respective surface area to pore volume measurements are included in the images. For the clay, feldspar and other group minerals of the Berea sandstone the most important factor determining the available surface was the overall abundance of the mineral itself in the sub-volume, rather than the geometry of the pores. For the quartz, the most important factor was the absence of other minerals and particularly clay. Thus the overall distribution of minerals at the scale of 100 µm generally determines the heterogeneity in surface area in the Berea sandstone. For the Edwards the mineral groups were distributed more evenly at the scale of 100 µm, with nearly every sub-volume containing quartz and dolomite. In this case the surface area within a sub volume for a given mineral was the most important factor determining the mineral-specific surface area.
Figure 2.16: Multi-mineralogical surface area distribution for Berea 1 plug 1
Figure 2.17: Sub volumes of the Berea sandstone with 5 phase segmentation showing from top to bottom: least, typical, and greatest feldspar surface area per pore volume. Similar images focused on the other mineral groups and for the Edwards carbonate are included in Appendix A.6.
2.4.4 Analysis of the impact of surface area heterogeneity on reactive transport modelling

Some insight into the impact of the observed heterogeneity on reactive transport processes can be obtained from the comparison of the observations presented here with the statistical properties assumed in past simulations focused on understanding the impact of surface area heterogeneity (Li et al. 2007a, Peters 2009, Nogues et al. 2013, Raoof et al. 2013). In particular, the pore network model simulations presented in Li et al. (2007a) provide the best point of comparison because the mineralogical composition assumed in that work was broadly similar to the Berea sandstone in this study.

In that work, simulations were performed on a sandstone rock model composed of quartz, clay and anorthite, with the clay and anorthite constituting 6-50% of the volume fraction of the rock. The models with the lower fractions of reactive minerals (6.25 and 12.5%) were similar to the Berea sandstone used in this work. It was found that heterogeneity in the distribution of reactive surface area in the pore space could give rise to large deviations in effective reaction rates as compared with what would be predicted using continuum models with average parameters. At that time pore-scale observations of the surface area properties were not available and the distributions were based on reasonable assumptions inferred from published values for $\approx 1 \text{ cm}^3$ scale samples of various rocks, including Berea sandstone. The distribution of the surface area to pore volume in Li et al. (2007a) was recreated and is shown in Figure 2.18.

To make the comparison, the distributions of the Berea sandstone at the 100 $\mu$m subvolume size obtained in this study were used. The distributions had to be converted to values representative of those that would have been measured by BET adsorption to be comparable to the values used in Li et al. (2007a), originally measured using BET. An accurate conversion depends on a characterisation of correlations between the geometric area of a mineral measured in the X-ray images and the observations with gas adsorption specific to those minerals which were unavailable for this work. Rather, we provide a first order estimate of what this conversion might look like based on surface area measurements of various mineral groups reported in the literature.
The average roughness ratio, $\beta$, of BET surface area, $A_{BET}$, to X-ray CT derived geometric surface area for Berea sandstone, $A_{geom}$, or

$$A_{BET} = \beta A_{geom}, \quad (2.2)$$

was found to be $\beta = 39$ as reported in Figure 2.10. This roughness factor can be thought to be made up of contributions from the surfaces of specific minerals,

$$\beta = f_{qtz}\beta_{qtz} + f_{clay}\beta_{clay} + f_{fsp}\beta_{fsp} + f_{other}\beta_{other}, \quad (2.3)$$

where $f_i$ is the fraction of the geometric surface area made up of mineral group $i$, $\sum_i f_i = 1$ and $\beta_i$ are roughness ratios following the same relationship as shown in Equation 2.2.

A first order estimate was made for this work from compiled literature values reported in White et al. (1996). Those observations show that weathered quartz, feldspar, oxides and carbonates (these last two constituting the other grouping in this study) tend to have specific surface areas that are of the same order of magnitude while clays are a factor of 10 or more greater. Using the geometric surface area fractions of each mineral as the average from all datasets reported in table 2.9, $\beta = 39$, and the constraints

$$\beta_{fsp} = \beta_{other} = \beta_{qtz} \quad (2.4)$$
$$\beta_{clay} = 10\beta_{qtz}, \quad (2.5)$$

Equation 2.3 is reduced to an expression in $\beta_{qtz}$. Solving for this results in the roughness ratios, $\beta_{fsp} = \beta_{other} = \beta_{qtz} = 13$ and $\beta_{clay} = 130$.

The geometric surface area fraction of each mineral group is shown in a stacked bar plot in Appendix A.7. There was no apparent correlation between the total amount of surface area and the surface area abundance of each mineral group, e.g., clay was not more or less abundant at the pore surfaces of those sub volumes with higher or lower surface area to pore volume.
ratios. Using the roughness ratios and the mineral surface composition, a roughness factor for each sub volume was calculated and used to convert the geometric surface area distribution to a BET equivalent surface area distribution.

A compilation of histogram plots is shown in Figure 2.18 which includes the distribution of $\beta$ values for all of the sub volumes, the surface area to pore volume distribution observed in this work before and after normalisation to BET equivalent values, and the distribution assumed in Li et al. (2007a), based on observations made with BET adsorption. The distribution in $\beta$ reflects the range of modal composition of the pore-solid interface of the sub volumes, generally dominated by quartz (low $\beta$ values) but with a significant number of pores where clay dominates the surface area composition. The conversion of the geometric surface area distribution to the BET equivalent results in a skew of the distribution giving it a more exponential character as compared to the lognormal shape of the geometric surface area distribution. The variance also increases relative to the value of the mean.

The distribution of the surface area to pore volume ratio implied in Li et al. (2007a) is more heterogeneous than what was observed in this work, with a variance an order of magnitude higher than the variance obtained in the BET equivalent distribution.

Changing the roughness factor for clay can only moderately increase the variance due to the constraint that the bulk value for $\beta = 39$ as measured. This results in tradeoffs in roughness factors between minerals, as implied by the constraints of Equations 2.4 and 2.5. Increasing the clay roughness factor only does so relative to quartz, which is reduced to maintain the constraint $\beta = 39$. In other words, given the observations of bulk average specific surface area, bulk mineral composition at the surfaces of the pores and minimal porosity below the resolution of the X-ray images, there are important limits to the surface area that one could assume exists in, e.g., a completely clay lined pore. Additionally, values of $\beta$ cannot be reasonably assumed to be less than one, further limiting the range of roughness available.
Figure 2.18: (a) The distribution of roughness factors calculated for each specific 100 \( \mu m \) subvolume from all of the Berea sandstone samples (see Section 2.4.4). (b) The compiled surface area to pore volume distribution for the Berea sandstone observations calculated from X-ray imagery. (c) The conversion of the geometric surface area distribution to a BET equivalent surface area distribution using roughness factors shown in the top plot. (d) The distribution of surface area to pore volume used in the work of Li et al. (2007). (e) The distribution obtained from the observations in this work randomly associating the surface area of a subvolume to the pore volume of a subvolume. For the last two plots note that the horizontal axis of the final plot is cut off so as to provide a visual comparison. The variance and mean indicate the length of the tail and the distribution function with longer axes are shown in Appendix A.8.
The difference in the distributions appeared to originate predominantly in the assumption common to pore network model studies that surface area and pore volumes for a given pore are uncoupled. There was a weak positive correlation of surface area with pore volume shown in Figure 2.20a. The surface area to pore volume ratios fell between the bounds of the ratio that would be obtained for spheres with the quartz roughness factor ($\beta = 13$) and five times that of spheres with the clay roughness factor ($\beta = 130$). Note that the quartz boundary is a theoretical minimum limit whereas the clay boundary is not a theoretical upper limit.

Figure 2.20b shows an uncorrelated realisation of the plot - surface areas were plotted randomly against pore volumes from the set of subvolumes to evaluate the impact of this assumption. The ratio of surface area to pore volume falls well outside of the boundaries observed, with both very large surface areas and surface areas smaller than the theoretical minimum for a given pore volume. This resulted in a significant widening of the distribution of surface area to pore volume, shown in Figure 2.18e and in a cumulative distribution plot in Appendix H.
Chapter 2. Mineral surface area and heterogeneity in sandstone and carbonate rocks

Figure 2.20: This figure shows two plots of the BET normalised surface area calculated from the X-ray imagery against the pore volume for 900 subsamples ($10^6 \mu m^3$) of an X-ray image. (a) The observed properties - surface area and pore volume were obtained from the same subvolume. (b) The impact of removing the correlation in the properties - surface areas were plotted randomly against pore volumes from the set of subvolumes. The lines show the values that would be obtained for spheres with the five times the clay roughness factor ($\beta = 130$), the average roughness factor ($\beta = 39$), and the quartz roughness factor ($\beta = 13$) which is a theoretical minimum for these observations.

The relevant size scale for describing heterogeneity for modelling reactive processes depends ultimately on the length scale over which heterogeneity in the overall reaction rate may appear. Reaction rate heterogeneity may develop because of heterogeneity in the distribution of reactive surfaces, but heterogeneity in the fluid chemical composition, local flow rates and temperature can be of equal or greater importance depending on the specific setting (Li et al. (2007a), Flükiger & Bernard (2009) and Molins et al. (2012)). Further, the relative influences of these processes are coupled (surface area giving rise to reaction heterogeneity will lead to heterogeneity in local chemical composition and so on), and the relevant scale at which to characterise surface area heterogeneity will be highly process-specific. Depending on fluid flow rates, temperature and chemical composition, simply measuring the average surface area at the
millimetre scale as has been conventionally done may be sufficient; whereas at times, heterogeneity measured at a characteristic pore size (e.g., around 75-100 µm for the Berea sandstone) or some intermediate scale will be needed.

2.4.5 Statistical Significance

The reproducibility of the heterogeneity characterisation was investigated with the Berea sandstone rock. The spatial distribution of surface area that was obtained through sampling the X-ray CT images suggests a lognormal distribution of a certain mean and variance. The test was repeated on different specimens of Berea sandstone to evaluate if the observations reflect an invariable characteristic of the rock. Therefore the null hypothesis is that the observations are not significantly different. The 5% significance level chosen for the test means that the observed difference in 5% or less of the observations was due to random sampling error. A low p-value suggests that the observations are statistically different and the null hypothesis can be rejected.

One-Way Analysis of Variance was used to determine whether there were significant differences between the means of the observations. The assumptions of the test are that the variable is normally distributed in each observation set and that the variances in each observation are equal. The test also assumes that the observations are independent (Sokal & Rohlf 1969). The observations comprised the decimal logarithm of the surface area per pore volume. The observations were assumed to be normal, their variances equal and independent of each other.

X-ray CT images of fifteen different specimens of Berea sandstone were collected, each measuring 600³ µm and voxel resolution of 1 µm. Each image was divided into 100³ µm samples to populate one set of observation. The statistical test consists of fifteen such observations. For each image, each voxel was classified as rock or pore space. Based on this binarised image, the surface area and pore volume was calculated for each 100³ µm sample. The logarithm of the surface area to pore volume was taken and the difference in their means tested. The fifteen observations are shown in Figure 2.21.
Figure 2.21: The graph shows the distributions of surface area, $A$, to pore volume, $V$. The measurements are made on X-ray CT images of Berea sandstone with voxel resolution of 1 µm. Each distribution is lognormal and composed of 216 samples, each with a size of $100^3$ µm. The tops and bottoms of each "box" are the 25th and 75th percentiles of the samples, respectively. The line in the middle of each box is the sample median. The whiskers are lines extending above and below each box and correspond to approximately ±2.7σ. Observations beyond the whisker length are marked as outliers. The notches display the variability of the median between samples. Two medians are significantly different at the 5% significance level if their intervals do not overlap.

The difference between the observations were found to be statistically significant as determined by One-Way Analysis of Variance (Matlab R2012b). The result of the analysis was $F(14,3225) = 17.65$, $p = 0.05$. 14 and 3225 are the degrees of freedom between and within the observations.
2.5 Conclusions

respectively. If the null hypothesis is true, F-ratio should have a value close to 1. The large F-ratio means a larger difference between the distributions than expected from random sampling error. A post analysis test was performed to inspect where the differences were occurring. Because the variances were assumed to be homogeneous, Tukey’s honestly significant difference test (Matlab R2012b) was selected. The test is based on the results of the One-Way Analysis of Variance. Figure 2.22 shows the result of the Tukey’s test. Each observation mean is represented by a circle, and the comparison interval is represented by the line extending out from the circle. Two observation means are significantly different if their intervals are disjoint. The scatter between the groups are notable and supports the results of the One-Way Analysis of Variance test. Therefore the null hypothesis is rejected and the differences in repeated observations of surface area heterogeneity at the 100 µm scale are statistically significant.

Heterogeneity in the surface area to pore-volume rock property was characterised by sampling CT cubic images of Berea sandstone measuring 600 µm in side. Characterisation of fifteen different rock specimens produced log-normal probability distributions of varying means and variances. Statistical analysis of the fifteen probability distributions suggested that the differences were statistically significant. Further analysis verified the result. The results suggest that at the 600 µm scale of the images collected, the observations are below the representative elementary volume for the surface area to pore-volume property of the rock.

2.5 Conclusions

This work provides a statistical characterisation of pore-scale heterogeneity in the reactive surface area of minerals within permeable rocks based on direct observation of the pore morphology and mineral distribution in three dimensions.

Comparison of average specific surface area from BET measurements with those inferred from X-ray images showed that the two observations could be reconciled with a variation on the use of a roughness factor, $\beta$. Roughness factors ranged from $10 < \beta < 200$. Total BET surface area, the presence of clay, and microporosity were all associated with higher values of the roughness
Figure 2.22: The graph shows fifteen observations of surface area to pore volume distributions measured from X-ray CT images of Berea sandstone. Each observation mean is represented by a circle, and the comparison interval is represented by a line extending out from the circle. Two group means are significantly different if their intervals are disjointed. An example of how to interpret is shown for the first observation - the difference between group 1 and groups 2, 3, 11 and 12 is statistically significant.
factor for a given rock.

Average mineral composition computed from X-ray images corresponded well with the average composition obtained from segmented BSE images. In the Berea sandstone, clays preferentially coated quartz grains and resulted in no correlation between the modal mineral composition of the rock and the fraction of surface area made up by the mineral. In situations like this, using the mineral composition of the rock as a proxy for surface area would lead to significant error in reaction modelling. On the other hand, the volumetric composition and surface area fraction in the Edwards carbonate were strongly correlated. In cases like this, the assumption is reasonable.

Distributions of the surface area to pore volume ratio were presented as a measure of heterogeneity of the reactive surface area in the rocks. In sandstone and carbonate rocks high values of the ratio were associated with a larger number of volumetrically smaller pores. Locations in the rock with larger pores tended to have lower surface area to pore volume ratios.

Distributions of this ratio for specific mineral groups in Berea sandstone and Edwards carbonate were constructed. In the Berea sandstone, the most important factor determining abundance of the surface area of clay and feldspar group minerals in a location was the presence of the mineral in that location - increased feldspar led to increased feldspar surface area. For quartz, however, the presence or absence of clay was the most important factor. In the Edwards carbonate, the amount of total surface area within a sub volume was the most important factor controlling the abundance of the surface area of a given mineral group.

The information can be used directly in statistically-based models of reactive transport including the emerging group of pore network models focused on characterising reactive processes. Statistical analysis of fifteen images suggest that at the length scale of 600 µm, the observations do not yet form a representative elementary volume. In pore network models it will be important to put physically based constraints on combinations of properties for individual pores. In this work it was found combinations of pore volume and surface area for a specific pore were constrained to values ranging between five times those that would be obtained for clay lined spheres and those that would be obtained for quartz lined spheres.
Chapter 3

Dual-energy CT for mineral identification

3.1 Introduction

This chapter looks at the investigation into a variation of the X-ray CT method to identify minerals in porous rocks. The relevant principles of X-ray CT will be introduced briefly before the motivation for this investigation is discussed. CT number is the empirical measure of the degree by which the X-rays have been attenuated as it passed through that volume of material. X-ray attenuation is a function of the material’s electron density and effective atomic mass (Mull 1984, Chantler 2000). For the purpose of discriminating different minerals, the term contrast is used and refers to the magnitude difference in CT number between two minerals and is defined later in Equation 3.3. Since micro-CT equipment do not typically use the Hounsfield scale as medical CT equipment do, empirical measures of contrast are only appropriate within a single CT scan or between scans that have been reconstructed with the same scaling.

The 3D image produced from a micro-CT scan has a finite voxel resolution because of finite-sized X-ray detector elements. The finite resolution produces partial-volume artefacts when more than one phase is present in a voxel. For example, feldspar minerals in this study often exhibit a porous structure at the micrometre scale. As the voxels are also of the same scale,
so the voxels containing feldspar also often include porosity. Consequently, the CT number associated with each voxel reflects the mixture of pore space and feldspar. As the mixture varies in space, the voxels associated with feldspar exhibit a range of CT numbers. This variance in CT numbers mean that some of them may have similar CT numbers to voxels associated with quartz. In other words, partial-volume artefacts have a negative impact on contrast. Contrast is also reduced by Gaussian noise during X-ray emission from the source and interaction with the sample and detector. It has the same effect of causing the mineral to have a larger spread in CT value. This means that discrimination is possible for some but not all minerals in practice (Lai et al. 2015). These impacts also exist in the image segmentation process describe in §2.2.5.

3.1.1 Motivation

Recently pore-scale heterogeneity and the emergent behaviour produced has been a subject of increasing attention (Steefel et al. 2015, Salehikhoo & Li 2015, Egan et al. 2015, Anovitz & Cole 2015). This study on discriminating mineral phases at the pore-scale is relevant for geo-engineering applications where the distribution of surface chemistry is important, such as near surface contaminant transport, mixed-wet hydrocarbon systems, low-salinity flooding, carbon sequestration, and nuclear waste storage (Al-Menhali & Krevor 2016, Wang et al. 2013, Menke et al. 2015, Liu et al. 2015, Hezel et al. 2013, Landrot et al. 2012, Peters 2009).

The use of micro-CT to identify and discriminate minerals has been demonstrated (Ellis & Peters 2015, Lai et al. 2015, Golab et al. 2013, Tsuchiyama et al. 2000, Uesugi & Tsuchiyama 1999). Three principle techniques available for phase identification will be briefly reviewed here. The advantages and drawbacks of each variation will become clear. At the end of this subsection, it is hoped that the reader can conclude that there has not been a clear demonstration of a readily accessible technique to identify minerals in 3D at the pore-scale relevant to reactive transport problems, thereby providing the motivation for the investigation of dual-energy X-ray CT.

In the most common method, when optimising X-ray CT to discriminate rock forming minerals, three factors have been shown to be important: sample composition, size, and X-ray energies.
available. In standard X-ray CT, the contrast between two phases is maximised when their linear attenuation coefficients are most different. Contrast typically increases exponentially with decreasing energy. Once sufficient contrast is achieved, the energy choice dictates the optimum sample size (Grodzins 1983, Kinney & Nichols 1992, Reiter et al. 2012). For a number of X-ray CT systems, the optimal signal-to-noise is obtained when the average $\mu x$ of the sample is approximately 1 (Tsuchiyama et al. 2013), where $\mu$ is linear attenuation coefficient and $x$ the thickness of the sample.

For example, for sandstones with an average linear attenuation coefficient of 3.028, 1.024, and 0.5309 cm$^{-1}$ at energies of 20, 30, and 40 keV respectively, the optimum sample size would be approximately 1.6, 4.7, and 9.1 mm respectively (Xcom 2010, Dawson et al. 2015, Hilt et al. 1999). In this way, higher X-ray energies are required for larger samples. However higher X-ray energies means diminished contrast in the images and therefore a reduced range of minerals that can be discriminated. This balance of contrast and sample size was demonstrated with a sample of 2 mm sandstone (§2.2.5).

A variation to the standard micro-CT method is to use X-rays with energies above and below the binding energy of the K-electron shell of a specific chemical element. The attenuation coefficient of the material increases sharply at this energy and produces a dramatically different CT number according to the abundance of that element. The identification of minerals that contain that element is significantly improved (Schlomka et al. 2008, Dilmanian et al. 1997, Riederer 1977). However this comes at a cost to the sample size.

The third technique is the use of K-edge subtraction using monochromatic X-rays available at synchrotrons. It works particularly well for identifying heavier elements in a matrix of lighter elements (Egan et al. 2015, Cooper et al. 2012). It works well with heavier elements because heavier elements have higher K-edge energies. Therefore higher energy X-rays that have increased penetration are used. Increased penetration means larger samples can be used.

If we consider the identification of Ti, in a chondrite sample with a typical linear attenuation coefficient of 500 cm$^{-1}$, then at the K-edge of Ti of 4.966 keV, the optimum sample size is approximately 20 $\mu$m (Tsuchiyama et al. 2013). For silicate minerals in sandstones, the K-
3.1. Introduction

edges of Al, K, and Ca are 1.562, 3.607, and 4.034 keV respectively. For the largest sample at 4keV, for sandstones with typical linear attenuation coefficient of 490 cm\(^{-1}\), the optimum sample size would be a similar 20 µm.

For any technique, with all else being equal, monochromatic X-rays produce better contrast. When polychromatic X-rays are used, the linear attenuation coefficient, \(\mu\) (cm\(^{-1}\)) of a single material becomes the weighted average of the interactions at each energy. This typically reduces the achievable contrast in X-ray attenuation between mineral phases.

For polychromatic radiation which is characteristic of laboratory X-ray CT instruments, the linear attenuation coefficient, \(\mu\) is given by,

\[
\mu = \rho \sum_i \tau_i(E)w_i,
\tag{3.1}
\]

where \(\rho\) (g/cm\(^3\)) is density, \(\tau_i\) (cm\(^2\)/g) is the mass attenuation coefficient of element \(i\), which is a function of X-ray energy, \(E\), and \(w_i\) is the weight fraction of element \(i\) (Koch & MacGillavry 1962). Monochromatic radiation also provides an additional slight advantage in contrast resolution because of the absence of beam hardening artefacts (Adams et al. 1998). Monochromatic X-rays are available at large synchrotron facilities, however the limited access is often a considerable disadvantage.

3.1.2 Background on Dual-Energy X-ray CT

This study investigates a variation to the phase identification techniques described previously. In the dual-energy CT method, there are two dominant mechanisms by which the X-rays interact with the material. Two scans at distinct energy levels are taken in dual-energy CT. At the low and high energy, the dominant interaction mechanisms are the photoelectric effect and Compton scattering respectively (Clark et al. 2013, Graser et al. 2008, Granton et al. 2008, Alvarez & Macovski 1976). The different mechanisms are hypothesised to provide improved
ability to distinguish minerals. The potential applications of the dual-energy CT method are well recognised in medical applications (Lehmann et al. 1981, Brody et al. 1981, Hall et al. 1981, Engelke et al. 1989). This study looks at the application to discriminate minerals in rocks.

There has been work done on medical CT equipment (Möller et al. 2016, Van Abbema et al. 2015, Tatsugami et al. 2014, Van Abbema et al. 2012, Iovea et al. 2009), and micro-CT equipment (Lin et al. 2013, Van Geet et al. 2001, 2000) to accurately measure the effective atomic number, $Z_{\text{eff}}$ and electron density, $\rho_e$ of materials.

The energy of the X-rays is defined in units of keV for monochromatic X-rays or kV for polychromatic X-rays. For typical X-ray energies used in computed tomography, the linear attenuation coefficient, $\mu$ (cm$^{-1}$) can be represented empirically by,

$$\mu(E) = \rho_e Z_{\text{eff}}^m \alpha(E) + \rho_e \beta(E), \tag{3.2}$$

where effective atomic number, $Z_{\text{eff}}$ and electron density, $\rho_e$ (g/cm$^3$) are material properties, and $\alpha$, $\beta$ (cm$^2$/g) are empirical constants. Electron density, $\rho_e = \rho \left(\frac{2Z}{A}\right)$, where $\rho$ is bulk density, $Z$ is the atomic number and $A$ is the atomic weight (Bassiouni 1994).

At low X-ray energies, photoelectric absorption of X-rays is the dominant attenuation mechanism, and so attenuation can be approximated by $\mu \propto \rho_e Z^m$, where $m$ is an empirical fit. $m$ is approximately 3 for materials with small effective atomic number, $Z \leq 20$. At high X-ray energies, Compton scattering becomes the dominant mechanism and attenuation can be approximated by $\mu \propto \rho_e$ (Osipov et al. 2015, Heaven et al. 2010). The dependency of $\mu$ on the energy of the X-rays is specific to the material or mineral. In our application to sedimentary rocks, low X-ray energies refer approximately to the range 10 to 60keV and high X-ray energies to the range 60 to 300keV.

The threshold between low and high energies is defined as the energy at which the attenuation by photoelectric absorption equals the attenuation by Compton scattering. This threshold can
3.1. Introduction

Figure 3.1: Linear attenuation coefficient behaviour. a. Plot showing X-ray interaction mechanisms for sample containing silicon and aluminium particles. The order of attenuation swaps at high energy when Compton scattering dominates. b. Plot showing attenuation behaviour for several minerals commonly found in sedimentary rocks. The gradient change in attenuation indicates the threshold from photoelectric dominated to Compton dominated attenuation.

vary approximately $\pm 10$ keV for the materials investigated here. Thus, the attenuation profile is primarily a function of chemical composition, $Z_{eff}$, before the threshold, and bulk density, $\rho_e$, after the threshold.

In this investigation, scans were carried out at two X-ray energies such that photoelectric absorption and Compton scattering dominated in turn. Figure 3.1a shows the attenuation mechanisms for an example specimen composed of silicon and aluminium. Below the threshold, the higher atomic number of silicon determines its higher attenuation as compared with aluminium. However, at energies above the threshold, the lower electron density affects its lower attenuation. Figure 3.1b shows the use of the gradient change to identify the approximate energy threshold at 60 keV and therefore the energy range for which either photoelectric absorption or Compton scattering is the dominant attenuation mechanism for several mineral specimens.

Micro X-ray CT equipment typically output scans with arbitrary scalings, as compared to medical CT scanners which produce scans scaled according to the Hounsfield scale, where water and air are 0 and -1000 Hounsfield units respectively. In this study, the micro-CT scans were reconstructed with different scalings according to the specimen material. As such, contrast
between specimens were only evaluated where they were taken in the same scan. Different scans are presented in separate plots. Combining scans is appropriate if the materials are relatively similar in order to compare more specimens. Two scans (Figure 3.7a) were combined by using the same scaling. Modelling data were also scaled to enable comparisons with observations.

Chapter 3. Dual-energy CT for mineral identification

3.2 Materials and Methods

3.2.1 Samples and data collection

Three sets of samples with increasing complexity in composition were prepared: Si and Al, a set of known silicate and carbonate minerals, and a sandstone rock. The sandstone rock represents mineralogy typical of Arkosic sandstones, which are comprised of quartz mostly and relatively rich in feldspars. The Si-Al sample would allow us to observe the impact of atomic number and electron density and investigate separating the two most important elements in silicate minerals. Next, the hand specimens would allow us to examine minerals, in particular silicate minerals. Finally, the sandstone sample would allow the exploration of a multi-mineral system characteristic of natural sandstone rocks.

The Si-Al sample consisted of Al, Si, SiO$_2$ (fused silica), and CaF$_2$ particles that were suspended in an epoxy matrix inside a polyamide tube. The materials were chosen because Al and Si are normally difficult to separate using a single tomography. Different shaped particles were used for Al and Si to enable their identification. Figure 3.2 show that the Al particles are distinguishable from the Si particles as they are larger and more rounded. SiO$_2$ and CaF$_2$ are also observed to be clearly distinct in their CT numbers. As their segmentation is not particularly difficult, SiO$_2$ and CaF$_2$ will not be discussed in this study.

Hand specimens of known minerals commonly found in sedimentary rocks were procured from Northern Geological Supplies Ltd, Bolton, UK. This included kaolinite, quartz, plagioclase, orthoclase, albite, biotite, dolomite, calcite, pyrite, magnetite, and hematite. The specimens were attached to a hollow Kapton tube using epoxy. The minerals were scanned in four groups
3.2. Materials and Methods

Figure 3.2: Left showing a CT scan taken at 50kV of a sample containing silicon and aluminium. The silicon pieces are identifiable by their sharp edges while the aluminium pieces are more rounded. On the right is a bivariate histogram showing CT numbers from the scans taken at 50kV and 150kV. Colour scale indicate number of voxels in the image.

Table 3.1: Specimens

<table>
<thead>
<tr>
<th>Sample</th>
<th>Group</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Al</td>
<td>-</td>
<td>SiO$_2$,Si,Al,CaF$_2$</td>
</tr>
<tr>
<td>Minerals$^1$</td>
<td>1</td>
<td>Kao,Pl,Bt</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Qtz,Or,Ab</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Dol,Cal</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Py,Mag,Hem</td>
</tr>
<tr>
<td>Berea sandstone</td>
<td>-</td>
<td>Quartz, clays, feldspars</td>
</tr>
</tbody>
</table>

$^1$ Mineral abbreviations according to (Whitney & Evans 2009)

Energy-dispersive X-ray spectroscopy (EDS) was used to characterise the sample and identify the minerals present. Elemental maps were collected using Oxford Instruments X-Max Silicon Drift Detector with an active area of 150 mm$^2$ (Instruments 2015). The EDS system was installed on a ZEISS Auriga FIB-SEM which was operated at 15kV and 8 mm working distance. Table 3.2 shows the measured chemical compositions of the minerals. The elemental maps were used to derive the mineral identities.

Berea sandstone is a consolidated sandstone frequently used in petrophysical research. Its major mineral components are quartz, feldspars, and clays. A specimen was impregnated with
Table 3.2: Chemical composition of mineral phantoms.

| Mineral | Chemical composition
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Qtz SiO\textsubscript{2}</td>
<td>SiO\textsubscript{2}</td>
</tr>
<tr>
<td>Or KSi\textsubscript{3}O\textsubscript{8}</td>
<td>K\textsubscript{0.9}Na\textsubscript{0.1}Si\textsubscript{3}O\textsubscript{8}</td>
</tr>
<tr>
<td>Ab Na\textsubscript{0.5}Ca\textsubscript{0.5}Al\textsubscript{3}Si\textsubscript{3}O\textsubscript{8}</td>
<td>Na\textsubscript{0.8}Ca\textsubscript{0.1}Al\textsubscript{1.1}Si\textsubscript{3}O\textsubscript{8.3}</td>
</tr>
<tr>
<td>Pl Na\textsubscript{0.7}Na\textsubscript{0.4}Al\textsubscript{0.9}Si\textsubscript{3}O\textsubscript{8}</td>
<td>Na\textsubscript{0.1}Ca\textsubscript{0.1}Al\textsubscript{1.1}Si\textsubscript{3}O\textsubscript{8}</td>
</tr>
<tr>
<td>Kao Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}</td>
<td>Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}</td>
</tr>
<tr>
<td>Bt KMg\textsubscript{2.5}Fe\textsubscript{0.5}Al\textsubscript{3}Si\textsubscript{3}O\textsubscript{11.75}F\textsubscript{0.25}</td>
<td>K\textsubscript{1.1}Mg\textsubscript{2.4}Fe\textsubscript{0.3}Al\textsubscript{1.3}Si\textsubscript{3}O\textsubscript{11.4}</td>
</tr>
<tr>
<td>Dol CaMgO\textsubscript{6}</td>
<td>Ca\textsubscript{3}MgO\textsubscript{4}</td>
</tr>
<tr>
<td>Cal CaO\textsubscript{3}</td>
<td>CaO</td>
</tr>
<tr>
<td>Mag Fe\textsubscript{3}O\textsubscript{4}</td>
<td>FeO</td>
</tr>
<tr>
<td>Hem Fe\textsubscript{2}O\textsubscript{3}</td>
<td>FeO</td>
</tr>
<tr>
<td>Py FeS\textsubscript{2}</td>
<td>FeS\textsubscript{2}</td>
</tr>
</tbody>
</table>

1 Specimens of known minerals. Carbon and hydrogen is not included to make comparable with available measurements. Abbreviations according to Whitney & Evans (2009).
2 Mineral compositions used in estimations of X-ray CT response and contrast.
3 Mineral compositions based on EDS measurements at three locations on each mineral specimen.

epoxy and cut to a 2mm cylinder. Following the CT scans, the specimen was ground to expose an internal surface and EDS was performed. The mineral phases present in that surface of the Berea sandstone were identified in a similar way to the mineral samples.

For each of the three sample sets, CT scans were carried out using a ZEISS Xradia 520 Versa according to the parameters in Table 3.3. The X-ray source produces polychromatic radiation. Where 50kV low energy was applied to produce a low energy scan, the maximum spectral energy was 50kV and the average was approximately 25keV. Similarly, for the 150kV high energy scan, the average spectral energy was approximately 80keV.

Warmup scans were performed prior to the scans in order to stabilise the X-ray source. A stable source produces consistent flux of X-rays and reduces imaging artefacts. Each warmup consisted of operating the X-ray source, at the same energy and power as the intended scan, for an hour immediately prior to the scan.

Noise is higher when Compton scattering is the main attenuation mechanism. Therefore, the high energy scan was collected with four times the equivalent count of the low energy scan.
3.2. Materials and Methods

Table 3.3: Scan parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si-Al Phantom</th>
<th>Berea</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan</td>
<td>LE(^1)</td>
<td>HE(^2)</td>
<td>LE(^1)</td>
</tr>
<tr>
<td>Binning</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Voxel (µm)</td>
<td>4.0</td>
<td>4.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Voltage (kV)</td>
<td>40</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Power (W)</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Exposure (s)</td>
<td>10</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Projections</td>
<td>2001</td>
<td>2001</td>
<td>2001</td>
</tr>
<tr>
<td>Source (mm)</td>
<td>13</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Detector (mm)</td>
<td>13</td>
<td>120</td>
<td>190</td>
</tr>
<tr>
<td>Time (hrs:mins)</td>
<td>6:12</td>
<td>5:40</td>
<td>3:30</td>
</tr>
<tr>
<td>Filter</td>
<td>Air</td>
<td>HE(^6)</td>
<td>LE2</td>
</tr>
</tbody>
</table>

\(^1\) LE - low energy scan  
\(^2\) HE - low energy scan

Equivalent count is the number of projections multiplied by the number of X-ray hits on the detector per projection.

For the Berea sandstone, an additional scan was collected on an interior volume. This image was obtained by performing interior tomography using a 4X objective to produce 0.7 µm voxel resolution. This additional scan provides some textural information relative to the two lower resolution dual-energy scans. It may contribute to phase identification as a third degree of freedom but its use is not included in this study.

3.2.2 Data processing

Each dual-energy scan consists of a pair of images, one at low and one at high energy. They will be referred to as LE and HE respectively. The three sample sets described in the previous section are specified in Table 3.1.

The image of the Si-Al specimen was reconstructed (Zeiss 2015a). A single 16-bit image was reconstructed from 32-bit projections with the default adaptive global scaling. Figure 3.2 shows a typical cross-section of the image. The image was pre-processed with a noise reduction filter that was adjusted according to the noise in the image, given by the standard deviation of the air phase. The filter was applied once and twice on the LE and HE scans respectively. The
Chapter 3. Dual-energy CT for mineral identification

Figure 3.3: Typical section of a 3D CT image of K-feldspar mineral. The wall of the Kapton tube and epoxy are visible. The grayscale shown here is from least attenuating in dark colour to most attenuating in bright colour.

LE and HE scans were aligned using the Sub-Pixel Aligned tool and exported as 3D tiffs. The pre-processing was done using the manufacturer’s software (Zeiss 2015b).

A bivariate histogram renders the CT number from each voxel from both scans on a single plot. Figure 3.2 shows a bivariate histogram for the sample containing Si and Al. The Si and Al particles were identified and segmented based on the bivariate histogram.

The CT scans of the mineral samples were reconstructed and pre-processed in the same manner as the Si-Al sample. Figure 3.3 show a typical 2D section of the orthoclase specimen. Groups 1 and 2 were reconstructed using the same scaling and combined, resulting in three separately scaled groups. In each image, the mineral was cropped, re-registered between the LE and HE images, re-cropped to retain the overlapping volume, filtered using non-local means, and finally the solid and air phases identified using Watershed Segmentation (ZIB 2015).

The median CT numbers at low and high energy, $x$ and $y$ respectively, and standard deviation, $\sigma$ were measured according to Eqns. 3.3. The mean was not used because CT numbers are ordinal for the purpose of this work. Standard deviation is a measure of the noise of the system from X-ray generation, interaction, and detection, and variation in composition within the specimens.
3.2 Materials and Methods

In order to later discuss which phases can be uniquely identified, a measure of contrast is defined. The overlapping coefficient, $OVL$, between two minerals is given as the magnitude difference in median CT value, divided by the sum of their bivariate standard deviation values (adapted from Inman & Bradley (1989)). The bivariate standard deviation, $\sigma$ of a mineral is given as the geometric distance to the first standard deviation on the bivariate histogram.

$$
OVL = \frac{\sqrt{(y_2 - y_1)^2 + (x_2 - x_1)^2}}{\sigma_1 + \sigma_2},
$$

$$
\sigma_1, \sigma_2 = \frac{p \cdot q}{\sqrt{p^2 \sin^2(\theta) + q^2 \cos^2(\theta)}},
$$

$$
\theta = \arctan\left(\frac{y_2 - y_1}{x_2 - x_1}\right),
$$

where $x$ and $y$ are the median CT values of the LE scan and HE scan respectively. Subscripts 1 and 2 refer to specimen 1, and specimen 2 respectively. $\sigma_1$ and $\sigma_2$ are the bivariate standard deviation values for specimen 1 and specimen 2 respectively. Finally, $p$ and $q$ are the standard deviations of the LE scan and HE scan respectively.

In addition to contrast, it was also of interest to compare the monochromatic approximation of linear attenuation coefficients to the measured CT numbers, since the former is often used to predict relative CT numbers in order to estimate contrast. Therefore, the linear attenuation coefficient, $\mu$ (cm$^{-1}$) for each mineral specimen was calculated. The monochromatic energies 30keV and 80keV were chosen to represent the average spectral energies of the LE and HE scans at 50kV and 150kV respectively (Xcom 2010). The modelled compositions are described in Table 3.2.

The calibrations needed to back transform the linear attenuation coefficients from CT numbers were not performed. So instead, a custom scaling was performed based on the same principle as the Hounsfield unit scale. As Hounsfield scale is a linear transformation with air and water fixed to two arbitrary numbers -1000 and 0, so the model was scaled to the measured CT scale using two points. Air and the next least attenuation specimen (kaolinite, dolomite, pyrite) were used as the two points to scale the modelled CT numbers. The rescaled model is described as,
\[ \mu_{q,i} = \mu_{p,a} + (\mu_{p,i} - \mu_{p,a}) \cdot \frac{\mu_{b} - \mu_{a}}{\mu_{p,b} - \mu_{p,a}}, \] (3.4)

where \( \mu \) is linear attenuation coefficient. Subscripts \( q \) refers to the rescaled model, \( p \) to the unscaled model, \( i \) to specimen \( i \), \( a \) to air, and \( b \) to the specimen used as the second scaling point (kaolinite, dolomite, pyrite).

The scan of the Berea sandstone was reconstructed and pre-processed in the same manner as the Si-Al sample. The image was cropped, filtered, and the internal surface where elemental maps were collected was identified and registered (ZIB 2015).

### 3.3 Results and Discussion

#### 3.3.1 Sample containing Al and Si

At X-ray energies below the threshold, it was expected that the material’s \( Z_{\text{eff}} \) will have first order control on the order of their CT number. At energies above the threshold, \( \rho_e \) becomes the primary determinant. The \( Z_{\text{eff}} \) and \( \rho_e \) properties of Si are 14 and 2.32 g/cm\(^3\) and for Al, they are 13 and 2.62 (g/cm\(^3\)). Si has a higher \( Z_{\text{eff}} \) but lower \( \rho_e \) than Al. Figure 3.2b is a bivariate histogram of the sample containing Si and Al. So Si is expected to have a higher CT number than Al in the scan taken at 50kV, but a lower CT number in the scan taken at 150kV. The expected behaviour was observed in the dual-energy scans. Figure 3.4 shows all the phases identified correctly in 3D.

If a mineral pair has a larger percentage change in the magnitude of its \( Z_{\text{eff}} \) property than with Al-Si, then its magnitude difference in CT number would be proportionately larger. For example, kaolinite, quartz and orthoclase have \( Z_{\text{eff}} \) of 9.90, 11.15, and 12.39 respectively. These minerals have a greater percentage change in their magnitude of \( Z_{\text{eff}} \) than Si-Al, hence sufficient contrast in the CT scans of these minerals were expected. The values of \( Z_{\text{eff}} \) were calculated...
3.3. Results and Discussion

Figure 3.4: Phases identified in the sample containing silicon and aluminium. Silicon particles are in yellow and aluminium particles are in red. SiO$_2$ particles are in green and CaF$_2$ particles in grey. Only the silicon and aluminium phases are discussed in this study.

at 30keV to approximate a source with 50kV applied, according to the model composition in Table 3.2 using the database of photon interactions by Taylor et al. (2012).

### 3.3.2 Samples of known minerals

The samples of known minerals allow us to evaluate the contrast in dual-energy scans with minimum impact by voxel resolution. When the voxel resolution provided by the X-ray detectors is finite, CT images suffer from partial-volume artefacts. These artefacts occur when a voxel in the image represents the average attenuation of multiple phases such as air and a solid mineral. The impact of finite voxel resolution is only of practical interest with non-crystalline minerals such as kaolinite and biotite.

Figures 3.7a-c show the median and standard deviation of the mineral sample set. The overlapping coefficients, $OVL$ are tabulated in Table 3.5. According to Equation 3.3, $OVL$ values of 0 and 1 indicate that the CT values of the two minerals are up to 100% and 40% similar
Table 1: Overlapping coefficients

<table>
<thead>
<tr>
<th></th>
<th>Quartz</th>
<th>Kaolinite</th>
<th>Orthoclase</th>
<th>Albite</th>
<th>Plagioclase</th>
<th>Biotite</th>
</tr>
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<td>4.67</td>
<td>3.74</td>
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<tr>
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<tr>
<td>Plagioclase</td>
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<td></td>
<td></td>
<td></td>
<td>0</td>
<td>0.59</td>
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<tr>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

(a) Plagioclase specimen had a chemical composition more similar to albite.

(b) Albite specimen had a chemical composition more similar to plagioclase.

Dolomite Calcite

<table>
<thead>
<tr>
<th></th>
<th>Dolomite</th>
<th>Calcite</th>
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</thead>
<tbody>
<tr>
<td>Dolomite</td>
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<td>7.34</td>
</tr>
<tr>
<td>Calcite</td>
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Pyrite Magnetite Hematite

<table>
<thead>
<tr>
<th></th>
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<th>Magnetite</th>
<th>Hematite</th>
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</thead>
<tbody>
<tr>
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<td>3</td>
</tr>
<tr>
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</tr>
<tr>
<td>Hematite</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Figure 3.5: Overlapping coefficients, $OVL$, of known mineral samples. (a) shows the measured $OVL$ for the minerals quartz, kaolinite, orthoclase, plagioclase, albite and biotite. (b) shows the measured $OVL$ for the minerals dolomite and calcite. (c) shows the measured $OVL$ for the minerals pyrite, magnetite and hematite. The colour scale ranges from pink indicating smallest $OVL$ value, to blue indicating largest $OVL$ value. The colour scales apply within each data set and are not indicative of the relative scale between data sets. See main text and Figures 3.7a-c for details.

respectively. There is small chance of successful segmentation when $OVL = 0$. The likelihood of identifying unique minerals through greyscale based segmentation increases with increasing $OVL$ value.

$OVL$ values of 3.89 and 2.12 were observed for the quartz-kaolinite and quartz-orthoclase pairs respectively. Despite the better $OVL$, quartz-kaolinite was slightly more challenging to segment in the Berea sandstone specimen due to partial volume effects. This suggests that texture is a practical consideration in greyscale based segmentation.

The expected CT number of all the mineral specimens scanned were modelled and plotted alongside the measured values in Figure 3.7. There are several discrepancies between the modelled and measured values. The discrepancy may be due to simplifications of assuming monochromatic radiation and linear detector response. Additionally, the analysis of the minerals suggests that the chemical composition is also a factor. Table 3.2 shows the chemical composition of the minerals measured using EDS at three adjacent locations on the surface of each mineral specimen. The specimen known as albite had a chemical composition more similar to plagi-
clase and the albite specimen was more similar to plagioclase. So the order of the modelled CT numbers for albite and plagioclase in Figure 3.7 are not too different from expectations.

Apart from albite and plagioclase, there are some discrepancies with the relative contrast proposed by the model compared with the measured values for the remaining minerals kaolinite, orthoclase, quartz, and biotite. In the case of calcite and dolomite, there is a smaller contrast observed than expected from the model. This may be explained by the composition of the dolomite specimen which had more calcium than expected. When the measured chemical composition is used instead to calculate the expected CT numbers, the difference in CT number between the dolomite and calcite specimens was reduced by 48% compared to the 36% reduction that was observed experimentally. The monochromatic linear attenuation coefficient method used to calculate the expected CT numbers are loose approximations. The remaining discrepancy in the modelled and experimental CT numbers of the dolomite and calcite specimens can be attributed to the assumptions made in the model calculations. It is less clear in the case of pyrite, magnetite and hematite. This exercise highlights the limits of first order calculations to approximate expected contrast without taking into account more of the X-ray CT system and accuracy of chemical compositions.

The observations provide a useful picture of which minerals can be uniquely identified. Figure 3.5 suggests the relative order of ease in identification. There are three sets of data derived from four images. Each dataset has a different scaling where the contrast between the minerals between each dataset is better than within each dataset. Observations suggest that albite is difficult to separate from quartz. They also suggest that plagioclase is difficult to separate from orthoclase. In fact, when albite and plagioclase are present in Berea sandstone, it was not possible to effectively distinguish them from quartz and orthoclase respectively. Partial volume and beam hardening effects can easily obscure these weak differences in average CT numbers. Biotite posed some difficulty when paired with orthoclase. Hematite is also difficult to separate from magnetite. However the remaining combinations of quartz, kaolinite, orthoclase, plagioclase, albite, biotite, calcite, dolomite, pyrite, magnetite, and hematite appear to be amenable to greyscale based segmentation. While this conclusion is a function of X-ray system use, in particular, the X-ray energy; the relative order of contrast are material properties and
3.3.3 Sample of Berea sandstone

Figure 3.6 shows the internal surface from the CT scan and corresponding phase map. The phase map shows the mineral phases and was derived from the elemental maps (Instruments 2015).

The minerals identified from the CT scan, using the corresponding phase map were used to populate a bivariate histogram as shown in Figure 3.7d. Based on this histogram, a series of segmentation criteria as described in Table 3.4 was used to segment the CT scan. Eight phases including epoxy were picked out from the phase map. However, insufficient contrast in the CT scans meant that only five of the eight were distinguishable. For each mineral phase, their volume and interfacial area abutting the epoxy phase were calculated using the marching cubes algorithm after Lai et al. (2015).

The dual-energy scan of the Berea sandstone specimen enables a comparison between the dual-energy and single-energy results that were reported in Lai et al. (2015). Three similarities were found in both methods. In both, EDS proved useful in optimising the mineral identification.
3.3. Results and Discussion

Figure 3.7: Dual-energy histograms showing CT numbers at 50kV and 150kV for: a. kaolinite, quartz, plagioclase, orthoclase, albite, and biotite; b. calcite and dolomite; c. pyrite, magnetite, and hematite; d. Berea sandstone. In a-c, the cross and crosshair indicate the median and standard deviation respectively, and the circle indicates the calculated CT number according to the compositions in Table 3.2 using a database of photon interactions (Xcom 2010). See main text for details.
### Table 3.4: Segmentation thresholds for the CT scan of Berea sandstone.

Each set of x,y coordinates marks the vertices of a quadrilateral on the bivariate histogram shown in Fig. 3.7d. The regions outlined by the vertices define the segmentation groups according to CT numbers of the LE and HE scans.

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>$x_4$</th>
<th>$y_1$</th>
<th>$y_2$</th>
<th>$y_3$</th>
<th>$y_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>Epoxy</td>
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<td>16299</td>
<td>16299</td>
<td>13899</td>
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<td>16149</td>
<td>16141</td>
<td>18777</td>
</tr>
<tr>
<td>Kao</td>
<td>Kao</td>
<td>22587</td>
<td>26447</td>
<td>26447</td>
<td>22587</td>
<td>22896</td>
<td>22896</td>
<td>22896</td>
<td>26255</td>
</tr>
<tr>
<td>Ab</td>
<td>Qtz,Ab</td>
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<td>30320</td>
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<td>28828</td>
<td>27736</td>
<td>27736</td>
<td>27736</td>
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</tr>
<tr>
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<td>29645</td>
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<td>30894</td>
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<td>29293</td>
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<td>29293</td>
<td>30222</td>
</tr>
<tr>
<td>Ill</td>
<td>Ksp,III</td>
<td>34247</td>
<td>35001</td>
<td>35001</td>
<td>34247</td>
<td>31210</td>
<td>31210</td>
<td>31210</td>
<td>32099</td>
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<tr>
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<td>36730</td>
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<td>33484</td>
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<tr>
<td>FeO</td>
<td>Oxides</td>
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<td>51972</td>
<td>51972</td>
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<td>34664</td>
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<td>34664</td>
<td>39993</td>
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<td>TiO</td>
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<td>68425</td>
<td>68425</td>
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<tr>
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<td>62825</td>
<td>63361</td>
<td>63361</td>
<td>63361</td>
<td>67754</td>
</tr>
</tbody>
</table>

1 Initial and final refer to attempted and final segmentation groups respectively.

The effort and time required to collect the data were similar; each dual-energy scan took between 10 and 12 hours, taking about 24 hours in total, whereas the one single-energy scan took approximately 24 hours. Lastly, the groups of minerals that were identified were the same. Figure 3.8 shows that the dual-energy method was able to identify the same groups of minerals as single-energy X-ray CT.

Table 3.5 shows the volume and surface area fractions of the mineral groups identified from the dual-energy CT scan and EDS of the Berea sandstone specimen. The volume fractions of the quartz and oxides groups were almost identical between the CT and EDS data. The kaolinite and K-feldspar groups showed the most differences, with kaolinite being overestimated and K-feldspar underestimated in the CT scan. Overall, the mineral volume fractions measured using dual-energy X-ray CT was comparable to the measurements based on the data from EDS.

The table also shows the volume and surface area measurements adjacent to the surface where the EDS data was measured and further along the depth of the specimen. The mineral volume comparisons suggest that along the length scales of 30 μm and 425 μm, there is little difference and bulk mineral volume fractions stay relatively constant.

Figure 3.9 compares the dual-energy results with the single-energy scan of a similar specimen of Berea sandstone. The single-energy method demonstrated comparable volume estimations with its EDS benchmark (Lai et al. 2015). The single-energy method was unable to reliably
3.3. Results and Discussion

Figure 3.8: Quartz (Qtz), alkali feldspar (Ksp), kaolinite (Kao), rutile-pyrite (Oxides) and pore space (Pore) identified in Berea sandstone. Minerals identified from a. CT scans and b. energy dispersive X-ray spectroscopy. The mineral groupings are recorded in Table 3.4.

Table 3.5: Volume and surface area fractions for the mineral groups identified from EDS and CT scans.

<table>
<thead>
<tr>
<th></th>
<th>Volume fraction</th>
<th>Area fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDS₁ CT_EDS² CT³</td>
<td>EDS₁ CT_EDS² CT³</td>
</tr>
<tr>
<td>Kao⁴</td>
<td>0.08 0.11 0.12</td>
<td>0.16 0.26 0.28</td>
</tr>
<tr>
<td>Qtz⁵</td>
<td>0.80 0.81 0.80</td>
<td>0.61 0.66 0.66</td>
</tr>
<tr>
<td>Ksp⁶</td>
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<td>0.20 0.07 0.05</td>
</tr>
<tr>
<td>Oxides⁷</td>
<td>0.01 0.01 0.02</td>
<td>0.03 0.01 0.01</td>
</tr>
<tr>
<td>Total</td>
<td>1.00 1.00 1.00</td>
<td>1.00 1.00 1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>EDS₁ CT_EDS² CT²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.13 0.12 0.11</td>
</tr>
<tr>
<td>Area/pore volume (10⁴ m²/m³)</td>
<td>1.7 5.9 5.5</td>
</tr>
</tbody>
</table>

¹ Energy-dispersive X-ray.
² From a 30µm thick section of the CT image adjacent to the surface where EDS was performed.
³ From a 425µm thick section of the CT image adjacent to the surface where EDS was performed.
⁴ Kao - kaolinite group.
⁵ Qtz - quartz group.
⁶ Ksp - K-feldspar group.
⁷ Oxides - oxides group.
Figure 3.9: Comparison of mineral identification using a. single-energy, and b. dual-energy X-ray CT. Plots a and b are derived from two different specimens, but of the same Berea sandstone rock type. Five phases were identified: porosity and four mineral groups, kaolinite, quartz-albite, orthoclase-illite, and others that includes carbonates and oxides. The single-energy data and their volume and surface area fractions were calculated according to Lai et al. (2015).

identify kaolinite at the energy of the low contrast scan, 50kV, and needed the better contrast afforded by a lower energy of 40kV. This indicates that the dual-energy method may have an advantage of better contrast or $OVL$.

### 3.3.4 Analysis of the impact of contrast of known minerals and Berea sandstone on specimen size

When the linear attenuation coefficients of Si, Al, quartz, and orthoclase were modelled, it was observed that the contrast, or magnitude difference in their coefficients, of Si-Al and Qtz-Or were similar: $0.70\text{cm}^{-1}$, $0.76\text{cm}^{-1}$ respectively. The calculations were approximated at 25keV and 30keV respectively to represent the average spectral energy of the LE scans collected at 40kV and 50kV.

Based on the analysis of scans, it was observed that the contrast in the CT images of quartz and orthoclase was at least as good as those between silicon and aluminium. If we were to deduce the impact of natural composition variation within the crystalline minerals quartz and orthoclase, then there is some evidence that this natural variation is comparable to that of the silicon and aluminium particles. The scans of the Al-Si and Qtz-Or samples need to be
3.3. Results and Discussion

compared on the same CT scaling to obtain a robust conclusion. However, it is suggested that in practice, crystalline minerals are associated with relatively uniform CT responses and partial volume effects with the presence of non-crystalline minerals such as kaolinite. This is a useful assumption for advanced multi-label classifications that track multiple metrics such as variance in CT number (Wang 2008).

There may be an advantage of larger specimen sizes to be gained by using dual-energy in having the second degree of freedom in the CT measurement. A choice could be made to gain an increase of a factor of $\sqrt{2}$ in $OVL$, or an increase in specimen size.

The Qtz-Or pair represents the limit in contrast before unique identification becomes unreliable (Lai et al. 2015). Quartz and orthoclase have a difference in linear attenuation coefficients of 1.08 cm$^{-1}$ based on the database of photon interactions (Xcom 2010) and the model chemical compositions in Table 3.2. The attenuation coefficients were calculated at 20keV to represent the average spectral energy of a single-energy polychromatic scan with peak energy of 40kV. In order to achieve the same difference in linear attenuation coefficients, calcite and dolomite would need to be scanned at 35keV or approximately 70kV with polychromatic X-rays.

If the dual-energy method improves contrast by a factor of $\sqrt{2}$, then the difference in linear attenuation coefficient can be smaller by $\sqrt{2}$ and still identify the same minerals. So instead of 1.08 cm$^{-1}$, 0.76 cm$^{-1}$, which is smaller by $\sqrt{2}$, is sufficient. Consequently, the X-rays can be operated at higher energy of 38keV instead of 35keV. A CT scan with optimum signal-to-noise may be obtained when $\mu x \approx 1$ (Tsuchiyama et al. 2013), where $\mu$ and $x$ are linear attenuation coefficient and specimen thickness respectively. At 35keV and 38keV, a rock with no porosity and equal fractions of dolomite and calcite has an average $\mu = 3.17 cm^{-1}$ and $\mu = 2.52 cm^{-1}$ respectively. Therefore their optimum carbonate rock thickness, $x$ would be 3.2 mm and 4.0 mm respectively. As a result, operating at 38keV instead of 35keV would allow a larger sample to be scanned whilst maintaining the same degree of mineral identification. In other words, the $\sqrt{2}$ improvement in contrast gained through the dual-energy method may allow a 25% larger specimen, 4 mm thick instead of 3.2 mm, to be characterised with same contrast and signal-to-noise.
Finally, dual-energy X-ray CT may provide information at the voxel level. Vinegar & Wellington (1987) demonstrated the application of dual-energy CT to infer the volume fractions of a three phase system: oil, gas, and water, within a voxel. In a similar way, it could be applied to other ternary systems such as one composed of dolomite, calcite, and air.

Triple-energy or quad-energy would not lead to further improvements. The dual-energy method is based on the different attenuation mechanisms, photoelectric absorption and Compton scattering, dominating sequentially as energy is increased. This produces distinct attenuation response that forms the basis for a dual-energy attenuation response plot such as in Figure 3.7. For each attenuation mechanism, there is an optimum energy. For example, with photoelectric absorption, the best contrast occurs when transmission ratio and photoelectric absorption are optimised concurrently. The principles for optimum contrast are described in Grodzins (1983).

The next attenuation mechanism after Compton scattering is pair production, which starts to occur at X-ray energies greater than 1.02MeV and depending on the material, becomes the dominant mechanism around 10MeV. At those energies, transmission ratio is too far from optimal and the image contrast is too poor to matter. Hence there is insufficient motivation for triple-energy or quad-energy to be explored.

### 3.4 Conclusions

Dual-energy X-ray CT imaging was used to identify several minerals found in Arkosic sandstone. Analysis of the CT imagery of the specimen containing silicon and aluminium particles suggested that crystalline minerals produce relatively uniform CT responses. Non-crystalline minerals such as kaolinite exhibit greater variance in CT numbers. Scans of several specimens of known minerals revealed that albite may be difficult to separate from quartz, and plagioclase from orthoclase. The mineral pairs biotite-orthoclase and hematite-magnetite posed a similar difficulty. It was possible to uniquely identify pairs of the remaining combinations of minerals investigated: quartz, kaolinite, orthoclase, plagioclase, albite, biotite, calcite, dolomite, pyrite, magnetite, and hematite. This conclusion is specific to the X-ray CT setup. However
the relative order of contrast observed are material properties and independent of the X-ray system. Finally, a specimen of Berea sandstone was examined. The dual-energy method was able to identify the same groups of minerals as single-energy X-ray CT despite operating at less favourable X-ray energies, that is higher X-ray energies. The dual-energy method may yield better contrast, specimen size capacity or both.
Chapter 4

Visualisation of aqueous adsorption using X-ray CT

4.1 Introduction

Aqueous adsorption occurs when a solid surface is exposed to aqueous solutions. Adsorption is a physical process of major importance in many fields such as groundwater remediation and industrial catalysis. Organic contaminants can be persistent in the environment so their removal from aqueous solutions through the adsorption process is of special interest (Yu et al. 2014). Adsorption is also a precursor to water-rock chemical reactions (Rouquerol et al. 2013, Lu & Zhao 2004). The development of pore-scale imaging to characterise the distribution and degree of adsorption has a potentially valuable role in studies of chemical transport and reaction in porous rocks - particularly those with heterogeneous mineralogy (Schweich & Sardin 1981).

Observations of adsorption have been made using X-ray photoelectron spectroscopy (Castner et al. 1996) and atomic force microscopy (Lin et al. 1990). If it could be observed in 3D in a porous structure, it will be able to provide invaluable information on heterogeneity of the adsorption process itself, or potentially of liquid-solid chemical reactions in general.

X-ray computed tomography provides 3D images of solid structures such as a rock or porous
column which can be useful for characterising porosity or saturation states (Imhoff et al. 1995). Karacan & Okandan (2001) used calibrated dual-energy X-ray CT to quantify and visualise adsorbed gas in a coal sample. From the CT images, the authors were able quantify the amount of free gas in the pore spaces and stored gas that was adsorbed. This is because the CT number within an X-ray computed tomography image is a function of the molecular composition and density. In many CT systems, solid rock or grains produce clear differences in CT number with fluids, and are often sufficient for characterising gas and liquid saturations (Pini et al. 2012). More recently, Vandevoorde et al. (2013) used X-ray micro-CT to visualise the process of water adsorption inside stone based on changes in CT numbers. These works have all been carried out without resolving pore-scale structures, that is by measuring bulk density changes in volume averaged pixels. It would provide valuable insight to be able to relate differences in adsorption capacities and rates to pore-scale structures. It would of interest to understand adsorption heterogeneity and its spatial distribution relative to heterogeneity of fluid flow and chemical transport. This study attempted to develop the use of pore-scale imaging using X-ray CT to visualise and quantify aqueous adsorption in porous rocks.

In this study, the adsorption of caesium from a caesium chloride solution on micrometer sized quartz grains was investigated. The zero-point-charge of quartz is at approximate pH 2.8 (Churchill et al. 2004) and at pH values above this, the surface has a net negative charge and attracts cations such as caesium in an aqueous caesium chloride solution. Caesium has a mass attenuation coefficient eleven times greater than silicon dioxide. Consequently, caesium was selected for the prospect of observing caesium adsorbing onto quartz.

The investigation was exploratory in observing adsorption of caesium. The following sections describe the approach and results to obtain the CT imagery and adsorption isotherm. A column of quartz powder was set up and caesium chloride solutions were injected. Bench top X-ray CT and synchrotron X-ray CT were both used to obtain the imagery. The expected impact that adsorption would have on the CT numbers of the CT images was calculated. A comparable experiment was also carried out with a Berea sandstone and aqueous caesium chloride. Analysis is presented on the plausible hypotheses for the failure to observe adsorption.
4.2 Materials and Methods

4.2.1 Samples and data collection

Fine granular quartz sand was obtained from Merck Millipore. Surface area was measured using the BET method with nitrogen gas at 77K using a Micromeritics Tristar 3000. The measurement was carried out three times and the average surface area of the quartz powder was $0.0307 \pm 0.0011 \text{m}^2/\text{g}$. High purity (99.99%) caesium chloride from Sigma-Aldrich was used to prepare CsCl solutions.

A batch adsorption experiment of Cs on quartz were carried out. The solution was pH buffered and allowed to equilibrate for 3 hours. 5ml of 0.1M NaCl electrolyte solution with CsCl concentrations of 0.01M, 0.1M, 0.5M, and 1M were prepared. Then each solution was divided into equal portions of parent and reactor volumes. The parent volume was measured to determine the initial Cs concentration. Then 5g/L of quartz powder was suspended in the reactor volume and allowed to mix by continuous shaking for 24 hours. The solution was allowed to settle and the supernatant decanted through a 0.45 µm nylon syringe filter. The Cs concentration in the supernatant was measured using Agilent 7900 ICP-MS. The Cs adsorbed to the quartz was inferred by the difference in the initial and final concentrations of Cs in the reactor volume.

The results of the batch adsorption experiment are shown in Figure 4.1. The adsorbate concentration and pH condition are indicated. As the column experiment was conducted, the CT scans were found to take between 6 and 12 hours. In the shortest 6 hour scan, if adsorption rate was assumed to be linear, then the image captures the arithmetic average amount of adsorption equivalent to a batch adsorption experiment left to equilibrate for 3 hours. It was expected that the longer scans would capture even more adsorption, equivalent to a batch adsorption experiment left to equilibrate for 6 hours. So the batch experiment was carried out where the solution was allowed to equilibrate for 3 hours to determine a conservative estimate of adsorption that would be captured by CT imagery. The CT model was calculated according to the results of the expected amount of adsorption from the measurements of the batch adsorption experiment. However, it was observed that the results of the amount adsorbed from the CT
4.2. Materials and Methods

Figure 4.1: Batch adsorption experiment: Plot shows adsorption isotherm with a Langmuir fit. This data is given in Table 4.1.

Imaging of the column experiment were far less than predicted by the calculations based on the batch adsorption measurements. The following subsection describes the results of the column experiment. The results of the CT model are discussed at the end of Section 4.3.

The batch adsorption experiment results were fitted using a Langmuir isotherm. This is justified as the results are in the domain where available adsorption sites are not limiting. A Langmuir isotherm describes the empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The adsorbent concentration generally increases with decreasing rate with increasing solute concentration (Brunauer et al. 1940). The fitting parameters are indicated in Figure 4.1.

Higher concentrations of Caesium was not used because based on the calculations using the results of the batch adsorption experiment described in Section 4.2.4, there should be abundant change to CT attenuation using concentrations up to 0.8M. Furthermore, using higher concentrations of Caesium or cations with higher attenuation property would begin to introduce imaging artefacts such as streaking or local beam hardening in the images, making interpre-
tation more challenging. The alternative of using ions with diminished attenuation property would simply reduce the expected magnitude of change adsorption would have on the CT number, decreasing the probability of visualising adsorption.

Two sets of column experiments were performed and the column scanned using polychromatic and monochromatic X-ray CT. Figure 4.2 shows a schematic of the column apparatus. A column of quartz powder was packed into a Fluoroelastomer tubing 3mm and 5mm inner and outer diameter and 55mm long. The column is inserted into a carbon fibre holder and the space between the tubing and holder was filled with water and pressurised to 10bar. The confining fluid ensures injected fluid does not bypass the column. An image of the column was taken using X-ray CT. Following the scan, 30ml volumes of CsCl solution at 0M, 0.01M, 0.1M, 0.5M, and 1M were injected from the bottom of the column with images taken after each injection to collect a total of 6 scans - 1 image when the column was dry and 5 images with the column saturated. 0M refers to deionised water.

The X-ray CT scans were taken with a Zeiss Versa 500 at 50kV and power throughput of 4W. The X-rays were polychromatic and have a peak energy of 50keV. No source filter was used. A 4x objective was used to achieve a 3 μm voxel resolution. 2200 projections were taken as the sample was rotated through 180° around an axis perpendicular to the X-ray beam. The exposure length was set such that 9000 counts was obtained through the centre of the projection.

The same column experiment was duplicated with a Berea sandstone at the Diamond Light Source (Didcot, UK). The I13-2 Imaging beamline supply X-rays from 8 to 30 keV with a maximum photon flux of 4 10^9 Ph/s (Raua et al. 2011). The energy of the beam was filtered to 25keV ± 0.1 % by passing the X-rays through a double-crystal monochromator. 1800 tomograms with an exposure time of 5 s each were taken at 25keV as the sample was rotated 180°. A 250 μm thick CdWO4 scintillator was used with a 4X objective lens and a PCO 4000 camera with 4008 x 2672 pixels. The transmission ratio of X-rays through the sample ranged from 0.07 to 0.25. Voxel resolution was 1.1 μm. The synchrotron facility at Diamond provided monochromatic X-rays that were unavailable with the bench top Versa. The data will be referred to as monochromatic scans to differentiate them from the polychromatic scans.
Figure 4.2: Schematic of the column where the sample is quartz powder. Caesium solutions were injected from the bottom port and effluent collected from the top port.
4.2.2 Data processing of quartz powder experiment

The Cs adsorbed to the quartz was inferred by the difference in the concentration of Cs during the batch adsorption experiments. The concentration (mol Cs/g qtz) was normalised to surface area (mol Cs/m² qtz) using the BET surface area 0.0307 ± 0.0011 m²/g.

Each of the batch adsorption and BET measurements were repeated three times. Therefore the uncertainty of the adsorbate concentration (mol/m²) was calculated by

\[
\Delta c_a = \left( \frac{\Delta c}{c} + \frac{\Delta a_B}{a_B} \right) c_a,
\]

where \( c \), \( a_B \), and \( c_a \) are the Cs adsorbed per gram of quartz (mol/g), quartz BET surface area (m²/g), and Cs adsorbed per m² of quartz (mol/m²) respectively. \( \Delta c \) and \( \Delta a_B \) are the standard deviations of \( c \) and \( a_B \) respectively, which are derived from repeated measurements.

In order to compare the scans of different concentrations of CsCl, all the scans except the reference scan were rescaled to match the reference scan. The scans were taken such that a portion of the material that housed the column of quartz was in frame. Each scan was reconstructed with the adaptive global scaling using Zeiss software. This is the convention when an unknown sample is scanned. Subsequent to the reconstruction, linear transforms were applied for each scan such that the average CT number of both the quartz and the polyetheretherketone (PEEK) material that housed the column were rescaled to those of the reference scan; these were approximately 14,000 and 25,000 CT units respectively within the 16 bit image taken when the column was dry.

Within the PEEK material, there were glass particles around 10 µm that had an average CT number of approximately 28,000 in the reference scan. Since PEEK was far more abundant by volume, the average CT number of the PEEK was easily identified by the mode of the distribution of CT numbers.

It was important that the rescaling was performed with higher precision than the original 16
4.2. Materials and Methods

bit unsigned integer format. Since the average CT number of PEEK was higher than that of water, and very similar to the 0.01M CsCl solution, information from these phases may be lost during rescaling otherwise. Therefore 64-bit floating-point format was used. The distributions of CT numbers of water and 0.01M CsCl phases were plotted to verify that the information was preserved.

Each scan was cropped to extract the volumes of PEEK and quartz and obtain their mode and mean respectively. Then, the CT number of each voxel, \( y \), in each scan was rescaled to \( z \) according to

\[
z = \overline{y}_{p,r} + (y - \overline{y}_p) \left( \frac{\overline{y}_{q,r} - \overline{y}_{p,r}}{\overline{y}_q - \overline{y}_p} \right),
\]

where \( z \) is the CT number after rescaling, \( \overline{y}_{p,r} \) is the average CT number of PEEK in the reference scan, \( y \) is the CT number before rescaling, and \( \overline{y}_p \) is average CT number of PEEK before rescaling. \( \overline{y}_{q,r} - \overline{y}_{p,r} \) and \( y_q - y_p \) are the difference in the average CT numbers of quartz and PEEK in the reference scan and before rescaling respectively.

4.2.3 Berea sandstone experiment

The monochromatic scans were reconstructed using proprietary scripts at Diamond Light Source (Didcot, UK). Pre-processing was applied to suppress ring artefacts to output images with approximately 2500 x 2400 x 2700 voxels. Each monochromatic scan was scaled uniformly to the same bit range. The method described in Equation 4.2 was not possible because the scans did not include the PEEK material. Instead, the data was scaled using ImageJ such that distribution of CT numbers had a minimum and maximum of -0.039 and 0.030 in 32-bit float format. The images with 0.2M and 0.5M CsCl solutions injected were aligned well. However, the image with water injected was offset from the other two. So it was translated -38 pixels in the Y direction, and +98 pixels in the X direction.
4.2.4 CT model of quartz column experiment

A model was made to estimate the impact of adsorption on the CT images of the quartz powder column experiment. The expected contribution to the average CT value of the CT image by adsorption was calculated. The extent of contribution by adsorption was calculated based on the batch adsorption experiment without pH buffering and 3 hours equilibration. The model is comprised of two parts: expected mass of the fluid, solid and adsorbate per cubic centimetre (g/cm$^3$), and the corresponding linear attenuation coefficient according to the fluid, solid and adsorbate components, $\mu$(cm$^{-1}$). A cubic centimetre was chosen as the control volume for ease of calculation and as a comparable volume to each CT scan of the quartz column.

A best fit of the adsorption isotherm provided the amount of caesium adsorbed per gram of quartz. Based on the adsorption isotherm and the amount of quartz observed in the CT image, the expected mass of Cs adsorbed per cubic centimetre was calculated. The expected mass of quartz per cubic centimetre was also calculated according to the porosity that measured from the CT images and the density of quartz.

In the pore space, the mass of the aqueous caesium chloride was calculated from the porosity of the CT images, and density of the solution. The density of the solution was interpolated from published data of aqueous CsCl density (Lidin et al. 1996) based on the effluent from the column experiment. The mass of CsCl and H$_2$O were calculated according to the molarity of the solution. Thus, the mass per cubic centimetre of Cs, CsCl, H$_2$O, and SiO$_2$ for each column experiment conditions were determined. The data used in the model and their definitions are shown in Table 4.1.
Table 4.1: Expected effect of adsorption on CT attenuation based on adsorption isotherm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source/Definition</th>
<th>0M</th>
<th>0.01M</th>
<th>0.1M</th>
<th>0.5M</th>
<th>1.0M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>ICP-MS</td>
<td>0</td>
<td>$8.36 \times 10^{-3}$</td>
<td>$8.35 \times 10^{-2}$</td>
<td>$4.26 \times 10^{-1}$</td>
<td>$7.55 \times 10^{-1}$</td>
</tr>
<tr>
<td>Cs adsorbed in batch experiment</td>
<td>ICP-MS</td>
<td>0</td>
<td>$3.70 \times 10^{-4}$</td>
<td>$1.70 \times 10^{-4}$</td>
<td>$1.52 \times 10^{-2}$</td>
<td>$2.14 \times 10^{-2}$</td>
</tr>
<tr>
<td>Qtz (g/L)</td>
<td>Balance</td>
<td>-</td>
<td>$7.3$</td>
<td>$7.7$</td>
<td>$7.6$</td>
<td>$7.0$</td>
</tr>
<tr>
<td>Qtz BET surface area, $a_B$ (m$^2$/g)</td>
<td>BET</td>
<td>-</td>
<td></td>
<td>$3.07 \times 10^{-2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs adsorbed, $c_a$ (mol/m$^2$ Qtz)</td>
<td>$\simeq \frac{a_p}{a_C}$</td>
<td>0</td>
<td>$1.65 \times 10^{-3}$</td>
<td>$7.18 \times 10^{-4}$</td>
<td>$6.52 \times 10^{-2}$</td>
<td>$9.95 \times 10^{-2}$</td>
</tr>
<tr>
<td>Porosity, $\phi$</td>
<td>CT</td>
<td>0.506</td>
<td>0.476</td>
<td>0.414</td>
<td>0.419</td>
<td>0.419</td>
</tr>
<tr>
<td>Qtz CT area, $a_C$ (cm$^2$/cm$^3$)</td>
<td>CT</td>
<td>$2.32 \times 10^2$</td>
<td>$2.43 \times 10^2$</td>
<td>$2.95 \times 10^2$</td>
<td>$2.98 \times 10^2$</td>
<td>$2.98 \times 10^2$</td>
</tr>
<tr>
<td>Corrected Qtz area, $a_C \left(\frac{a_B}{a_C}\right)$</td>
<td></td>
<td>$6.91 \times 10^2$</td>
<td>$7.24 \times 10^2$</td>
<td>$8.79 \times 10^2$</td>
<td>$8.88 \times 10^2$</td>
<td>$8.88 \times 10^2$</td>
</tr>
<tr>
<td>Cs molar mass, $M_{Cs}$ (g/mol)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>132.9</td>
</tr>
<tr>
<td>CsCl molar mass, $M_{CsCl}$ (g/mol)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>168.36</td>
</tr>
<tr>
<td>H$<em>2$O molar mass, $M</em>{H_2O}$ (g/mol)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18.02</td>
</tr>
<tr>
<td>Qtz density, $\rho_{qtz}$ (g/cm$^3$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.65</td>
</tr>
<tr>
<td>aq CsCl density, $\rho_{aqCsCl}$ (g/cm$^3$)</td>
<td>Lidin 2000</td>
<td>0.998</td>
<td>0.999</td>
<td>1.01</td>
<td>1.05</td>
<td>1.09</td>
</tr>
<tr>
<td>Mass of Cs adsorbed, $m_a$ (g/cm$^3$)</td>
<td>$(c_a \cdot 10^{-4})aM_{Cs}$</td>
<td>0</td>
<td>0</td>
<td>0.102</td>
<td>0.672</td>
<td>1.22</td>
</tr>
<tr>
<td>Mass of Qtz, $m_q$ (g/cm$^3$)</td>
<td>$(1 - \phi)\rho_{qtz}$</td>
<td>1.31</td>
<td>1.39</td>
<td>1.55</td>
<td>1.54</td>
<td>1.54</td>
</tr>
<tr>
<td>Mass of H$_2$O in pore, $m_w$ (g/cm$^3$)</td>
<td>$\phi(\rho_{sol} - [M_{CsCl}c_{sol} \cdot 10^{-3}])$</td>
<td>0.505</td>
<td>0.475</td>
<td>0.412</td>
<td>0.411</td>
<td>0.406</td>
</tr>
<tr>
<td>Mass of CsCl in pore, $m_s$ (g/cm$^3$)</td>
<td>$\phi M_{CsCl}c_{sol} \cdot 10^{-3}$</td>
<td>0</td>
<td>0.0007</td>
<td>0.0058</td>
<td>0.0300</td>
<td>0.0532</td>
</tr>
<tr>
<td>Total mass w/o ads, $\rho_1$ (g/cm$^3$)</td>
<td>$m_q + m_w + m_s$</td>
<td>1.81</td>
<td>1.86</td>
<td>1.97</td>
<td>1.98</td>
<td>2.00</td>
</tr>
<tr>
<td>Total mass with ads, $\rho_2$ (g/cm$^2$)</td>
<td>$m_q + m_w + m_s$</td>
<td>1.81</td>
<td>1.86</td>
<td>2.07</td>
<td>2.65</td>
<td>3.22</td>
</tr>
<tr>
<td>Mass attenuation coefficient w/o ads, $\mu_1/\rho_2$ (cm$^2$/g)</td>
<td>NIST$^3$</td>
<td>1.141</td>
<td>1.167</td>
<td>1.237</td>
<td>1.381</td>
<td>1.518</td>
</tr>
<tr>
<td>Mass attenuation coefficient w/ads, $\mu_2/\rho_2$ (cm$^2$/g)</td>
<td>NIST$^3$</td>
<td>1.141</td>
<td>1.167</td>
<td>1.934</td>
<td>4.949</td>
<td>6.802</td>
</tr>
<tr>
<td>Linear attenuation coefficient w/o ads, $\mu_1\rho_1$ (cm$^{-1}$)</td>
<td></td>
<td>2.07</td>
<td>2.18</td>
<td>2.44</td>
<td>2.74</td>
<td>3.03</td>
</tr>
<tr>
<td>Linear attenuation coefficient w/ads, $\mu_2\rho_2$ (cm$^{-1}$)</td>
<td></td>
<td>2.07</td>
<td>2.18</td>
<td>4.01</td>
<td>13.1</td>
<td>21.9</td>
</tr>
</tbody>
</table>

1 Cs concentration remaining in solution - from batch adsorption experiment.
2 Cs concentration adsorbed on solid - from batch adsorption experiment.
3 Taken from Xcom (2010) at 25keV.
Chapter 4. Visualisation of aqueous adsorption using X-ray CT

4.3 Results and Discussion

4.3.1 Quartz powder column experiment

Figure 4.3 shows typical 2D sections of the scans of the quartz powder column after rescaling. The images include scans of the column when dry, and saturated with solutions of CsCl at 0M, 0.01M, 0.1M, 0.5M, and 1M. 0M refers to deionised water.

The scans were cropped to exclude the PEEK material, Viton sleeve and confining fluid, and include 24.5 million voxels of the pore space and quartz powder. 24.5 million voxels is a volume equivalent to a cube 0.87mm in side, or similar in scale to those shown in Figure 4.3. The distribution of CT numbers in the images of the column for each concentration of CsCl are shown in Figure 4.4.

The rescaled scans were binarised to measure porosity. Morphological operations - erosion and opening - were applied to the binarised image to segment out regions of pore space and quartz that were well away from the interfaces where adsorption might have taken place. Figure 4.5 shows an example of the binary, pore space, and quartz phase outputs for the images of the column saturated with 0.1M CsCl. Figure 4.4 shows the resulting distribution of CT numbers for the pore space, and quartz separately.

Karacan & Okandan (2001) describes a method of quantifying adsorbed gas in coal samples using X-ray CT. The authors determine the mass change before and after gas injection and attribute that to free gas stored in the pore space and adsorbed gas. We use the same method here, with the difference in the method of determining the density or mass of the free solutes i.e. free Caesium cations. Karacan & Okandan (2001) uses a calibrated pressure-density relationship for the gas to establish the density or mass of free gas in each voxel. Here we use the average CT number of the pore space away from the solid-fluid interface to work out the density or CT number contribution of the free solutes. Figure 4.7 shows the expected distribution of CT numbers for a column experiment with a column of quartz powder with the pore space filled with a solution of caesium chloride. The voxels corresponding to the pore space and solid have
Figure 4.3: Quartz powder column experiment: Images show a column of quartz powder with various concentrations of CsCl solution injected: a. dry; b. wet; c. 0.01M; d. 0.1M; e. 0.5M; f. 1M. Images were taken using X-ray CT at 50kV with voxel resolution of 3\(\mu\)m.
Figure 4.4: Quartz powder column experiment: Plot shows probability distributions of CT numbers for scans of a quartz column saturated with various concentrations of CsCl solution. The horizontal bars do not indicate error but the mean and standard deviation of each distribution. Off chart values are added and indicated by the star. The CT images were taken at 50kV with voxel resolution of 3µm.
Figure 4.5: Quartz powder column experiment: Images show the typical segmentation routine, shown here for the quartz saturated in 0.1M CsCl. a. Raw CT image; b. pore space; c. solid phase; d. binarised CT image. The pore and solid segmentation are used to measure the average CT number of the pore and solid phase respectively. The binarised image is used to calculate porosity.
Figure 4.6: Quartz powder column experiment: Plot shows probability distributions of CT numbers for the solid and pore phases obtained from segmentation of scans of a quartz column saturated with various concentrations of CsCl solution. The horizontal bars do not indicate error but the mean and standard deviation of each distribution. Off chart values are added and indicated by the star. The CT images were taken at 50kV with voxel resolution of 3µm.
some mean CT numbers, shown here with arbitrary means of 10,000 and 20,000. The voxels corresponding to the fluid-solid interface where adsorption is expected are shown to have an arbitrary mean of 30,000. It is expected that none of the mean values should be zero.

The images of the pore space and quartz phase provided the average CT number of the fluid in the pore space and the quartz. Subtracting the contribution of the pore space and quartz phases from the average CT number of the whole image allowed the global contribution of any adsorption occurring at the surfaces to be inferred. The mean contribution by adsorption was calculated according to

$$\bar{x}_a = \bar{x} - \bar{x}_s (1 - \phi) - \bar{x}_p \phi,$$

where $\bar{x}$ is mean CT number and $\phi$ is porosity. The subscripts $s$, $p$, and $a$ refer to the solid,
pore, and adsorbed components respectively. The uncertainty associated with the adsorption contribution is composed of those from the calculation of the average CT number of the overall image, pore space, and solid quartz phase. The uncertainty of the adsorption contribution was calculated according to

\[
\Delta x_a = \left( \frac{\Delta x}{\overline{x}} + \frac{\Delta x_s(1 - \phi)}{\overline{x}_s} + \frac{\Delta x_p \phi}{\overline{x}_p} \right) \overline{x}_a, \tag{4.4}
\]

where:

- $\Delta x$ = uncertainty of $x$. It is the larger of $\Delta x_s$ and $\Delta x_p$.
- $\overline{x}$ = mean CT number of the whole image: pore, quartz and adsorption.
- $\Delta x_s$ = standard deviation of quartz CT numbers.
- $\phi$ = porosity from binarised CT image.
- $\overline{x}_s$ = mean CT number of the quartz phase.
- $\Delta x_p$ = standard deviation of pore space CT numbers.
- $\overline{x}_p$ = mean CT number of the pore space.
- $\overline{x}_a$ = mean CT number of adsorption contribution.

In a similar manner to Lai et al. (2015), the surface area of the quartz powder was measured from the CT images and a comparison made to the measurement from nitrogen BET. The measurement was carried out based on the binarised images. Based on the 5 images of the column when it was saturated with fluid and the density of quartz, 2.65g/cm$^3$, the average surface area was 0.0103 ± 0.0012m$^2$/g. The surface area derived from CT is compared to the BET measurement of 0.0307 ± 0.0011m$^2$/g to derive a quartz roughness factor of 3. The roughness factor of 3 for the quartz powder is reasonable in comparison with the first order estimate of sandstone quartz roughness factor of 13 (Lai et al. 2015). The roughness factor for the sandstone quartz was based on images at a comparable voxel resolution of 1 µm.
4.3. Results and Discussion

Figure 4.8: Quartz powder column experiment: Plot shows concentration of effluent samples collected during injection of fluid between scans. The legend entries indicate concentration of CsCl of the injected fluid. Injection proceeds in the following order: 0M, 0.01M, 0.1M, 0.5M, and 1M. 0M refers to deionised water.

Between each scan, as fluid was injected into the column, effluent samples were collected over 24 minutes. Figure 4.8 shows the concentration of the effluent samples. The effluent analysis showed that the Cs concentration in the column experiments reached within 9%, at the lowest Cs concentration, and 0.5% at the highest Cs concentration, of the final concentrations measured in the batch adsorption experiments. Hence, the concentration of caesium measured in the batch adsorption experiment and column experiments are within the same range. Therefore it was accurate to use and interpolate from the batch adsorption measurements to estimate the amount of adsorption that was expected to take place within the column experiments as described in Section 4.3.3.

If a non-adsorbing tracer was used in the column experiment, it would have been possible to verify that adsorption occurred. From the breakthrough curves, a non-adsorbing tracer arriving earlier than the adsorbing Caesium solution would indicate adsorption has occurred.
Figure 4.9: Quartz powder column experiment: Plot shows on the left vertical axis, measured metric of adsorption, $x_a$, and on the right measured porosity, $\phi$. The measurements were made on CT images taken at 50kV with voxel resolution of 3µm. $x = x_s(1 - \phi) + x_p\phi + x_a$, where $x$ is mean CT number and $\phi$ is porosity. The subscripts $s$, $p$, and $a$ refer to the solid, pore, and adsorbed components respectively.

The average contribution by Cs adsorption to the mean CT number of the column, according to Equation 4.3, is shown in Figure 4.9. Porosity was observed to change between experiments at each concentration, and in particular between the 0M and 0.01M experiments. This is explained by the shift in the packing of the quartz powder in the column. The CT image was collected near the top of the column away from the injection port. This minimised the magnitude of disturbance to the packing but some change were still observed. The porosities are quantified from the images and accounted for by Equation 4.3. The adsorption values have been plotted at the effluent concentration measurements. The values are 2 to 3 orders of magnitude smaller than those of the quartz and fluid in the pore space. There is no significant indication of any adsorption.
4.3. Results and Discussion

4.3.2 Berea sandstone experiment

The monochromatic scans of the Berea sandstone were examined to identify quartz, clay, carbonate, pyrite and pore space. Figure 4.10 shows an example of a region of clay and quartz for the sandstone injected with 0M, 0.2M and 0.5M of CsCl. Six samples of regions for each type were identified and their mean and standard deviation calculated. Figure 4.11 shows the trend of the average CT numbers of the five regions.

If the adsorption of Cs was significant in the regions where clay is likely to be present, then the average CT number of those clay regions would be expected to rise considerably more with caesium concentration in solution than the regions of quartz, carbonate or pyrite. In other words, the gradient of average CT number with caesium concentration in solution is expected to be greater for the clay regions than regions of other types of rock minerals.
Figure 4.11: Monochromatic scans of Berea sandstone experiment: The graph shows the analysis of six regions of quartz, clay, carbonate, pyrite and pore space in a Berea sandstone. The mean and standard deviation are indicated for the regions when 0, 0.2, and 0.5 M CsCl solutions were injected into the rock. The data was measured from CT images taken at Diamond Light Source at 25keV using a double-crystal monochromator. Voxel resolution is 1.1µm. The changes in CT number are small. Figure 4.12 shows the rate of change in CT number as a function of concentration based on the best fit lines.

As caesium concentration in solution increases, the average CT number of the pore space is expected to increase as well. If the change in average CT number of the clay regions rises further than the fluid, then it is evidence of higher concentrations of Cs in the clay regions than in the fluid. That may suggest that CT imagery is useful observing adsorption. However the increase in average CT number of the clay regions did not surpass that of the fluid. Figure 4.11 shows the change in average CT number as a function of concentration of CsCl in the solution injected.

The change in average CT number in Figure 4.12 were relatively small compared to their absolute values. Hence, lines of best fit were constructed for each region, and the rate of change of the average CT number with caesium concentration in solution calculated. The gradient and goodness of fit of the best fit lines, $R^2$ are shown in Figure 4.12.
4.3. Results and Discussion

It is clear that the quartz, carbonate and pyrite regions had a gradient in the negative when they were expected to be zero. The negative trend suggests that the scaling of CT images were not perfect and the constant materials such as quartz had a decreasing CT number as a function of the Cs concentration. Imperfect CT scaling is a likely explanation because only six regions were sampled for each material type (quartz, clay, pore space etc). A finite degree of uncertainty in the gradient measurements are to be expected. A possible alternative explanation is material is being lost from the regions, such as pyrite, therefore exhibiting a negative change in average CT number. However this is judged unlikely.

It was observed that only the pyrite region shows a significant negative gradient. If the trend from pyrite is excluded, the remaining quartz and carbonate trend of near zero suggests the scaling is reasonably good. So with that in mind, it was observed that the pore space had a clear positive trend as the X-ray CT is picking up on the increasing concentration of Cs in the fluid. The clay regions had a markedly lower magnitude in its positive trend.

The apparent positive trend of the clay regions can be explained partly by Figure 4.10. It shows that the regions selected where clay is thought to be present includes some pore space. Consequently, the increasing CT number with Cs concentration was likely to have derived from the fluid mixed in the clay regions. Equally however, it would be difficult to observe adsorption in the clays without pore space with CT imagery. It is a difficult problem to contend with. A simpler experiment may offer a better chance of disentangling the two factors.

It is proposed that the same aqueous CsCl is used. The adsorbent would be the vial containing the aqueous solution instead of the clay within a rock specimen. Vials of two different material can be used. The materials will be chosen such that one has a net negative and the other a net positive surface charge. The solution in the vial would be scanned in the same way. The vial with the net negative surface charge will cause the adsorption of caesium and the vial with the net positive surface charge will attract the chloride ions. Since chlorine is four times less attenuating than caesium, CT images of the two experiments should provide the better opportunity to assess if CT imagery can be used to observe adsorption of caesium.

Since the effect of the increasing caesium concentration in the pore fluid could not be dis-
entangled from the possible effects of caesium adsorbing in the clay regions, the experiments performed with Berea sandstone does not suggest that the detection of caesium adsorption can be made. Overall, the results of the analysis of the monochromatic X-ray CT scans are similar to those of the polychromatic X-ray CT images of the quartz powder column experiment.

### 4.3.3 CT model of quartz column experiment

Figure 4.13 shows the expected mass of quartz, pore fluid and adsorbed Cs per cubic centimetre volume. The mass of quartz is changing because after each injection of aqueous CsCl at increasing concentrations, the quartz powder shifts in the column and each CT image has a different porosity. The mass attenuation coefficients for each component were extracted from published data (Xcom 2010) according to the component mass fractions. The relative linear attenuation coefficients were calculated based on the mass attenuation coefficients and component densities.
Figure 4.13: CT model of quartz powder column experiment: The plot shows expected mass of quartz, pore fluid and adsorbed Cs components. The y-axis indicates component mass (of quartz, adsorbed Cs or fluid) per cm$^3$ of the quartz powder column. The mass of adsorbed Cs was based on the batch adsorption experiment. The 3 hours equilibration and unbuffered conditions are comparable to the column experiment where CT imagery was collected. The mass of quartz and fluid components are based on porosity measured from CT imagery, and densities of quartz and the solutions.
Figure 4.14 are the results of the model. At the low concentration of 0.01M, the adsorbed Cs was expected to contribute nothing to the mean CT number of the overall image. However, starting from 0.1M to 1M, the amount of adsorbate reported by the batch adsorption experiments suggest that the adsorbed Cs should make-up 39% up to 86% of the mean CT number. This is in stark contrast to the observations shown in Figure 4.9. In the following are presented hypotheses as for why the observations do not match the modelled expectation.

The first hypothesis is that the adsorption isotherm was incorrect. It was difficult to find published adsorption isotherm data at the same concentrations, buffer condition and for the same adsorbent as used in the experiments. Miah et al. (2010) reports on unbuffered adsorption of caesium using caesium chloride and porous ceiling tiles containing minerals such as gypsum. Miah et al. (2010) measured the highest amount of adsorption of 3.69 μmole of Cs per gram of
ceiling tile with 0.151 mmol Cs/L remaining in solution. In the batch adsorption experiments measured in this study, the closest condition was 50.7 µmole of caesium adsorbed per gram of quartz and the concentration of caesium remaining in solution was 8.36 mmol/L. If a proportional relationship was assumed between concentration in solution and concentration adsorbed, then there is not such a significant difference between the two measurements. Bergaoui et al. (2005) reports on adsorption of caesium using caesium chloride and sodium chloride, at constant ionic strength and sodium clay. Bergaoui et al. (2005) measured the highest amount of adsorption of 0.28 mmol Cs per gram of sodium clay with 0.56 mmol Cs/L remaining in solution. If the same proportional relationship was assumed, then there is an order of magnitude difference in this comparison. There is weak evidence to either support and reject the hypothesis that the adsorption isotherm was incorrect. An independent adsorption isotherm at exactly the same conditions is needed to fully test this hypothesis.

The second hypothesis is that there is some optical phenomenon occurring at the surface of the quartz grains that is not understood. The diffraction of X-rays from the source occurs at the edge of the quartz grains forming bright and dark fringes on either side of the edge where adsorption takes place. Such fringes may overwhelm and blur the effect adsorption may have on the attenuation of the X-rays. Figure 4.15 shows the edge of a quartz grain in two X-ray CT images. In both images, the quartz powder was in a column filled with 0.5 M aqueous caesium chloride. The images was taken at similar conditions: 55kV and 50kV on a Versa-500 with a 3.5 µm and 3 µm voxel resolution. Prominent fringes were observed in the scan shown in Figure 4.15(a), where the source and detector were positioned at a distance of 46.5 mm from the centre of the column. In Figure 4.15(b), diffraction fringes were not obvious and minimal. In this scan, the source and detector were positioned distances of 13.6 and 17.3 mm from the centre of the column respectively. In both cases, a minimal amount of the average attenuation of the image could be attributed to adsorption. So there is weak evidence to reject this hypothesis. Cosslett & Nixon (2014) describes the calculation of the width of such fringes for monochromatic X-rays based on the distance of the source, detector and wavelength of the X-rays. It would be difficult to correctly estimate this for X-rays of multiple wavelengths as those produced in the Versa-500. The impact of this phenomenon can be tested if the refractive index of the fluid injected into
the column is matched to the solid. Dimethyl sulfoxide is a solvent that has a refractive index very close to that of quartz. It dissolves both polar and non-polar compounds and could be adjusted to match quartz exactly. This would allow aqueous adsorption to take place without the impact of diffraction fringes.

4.4 Conclusions

Batch adsorption experiments of Cs on quartz were carried out. The measurements provide an estimate of the amount of Cs expected to be adsorbed onto quartz within a range of concentration of Cs in the fluid. Based on the mass of the Cs expected to adsorbed, a model of the expected enhancement of CT attenuation was made. The model suggested that the average CT number of the CT image should at least triple. In other words, adsorption should comprise up to 86% of the CT attenuation on average in the image.

Two column experiments were carried out. In the first, quartz powder were packed in the column and CsCl of various concentrations injected. The column was scanned using polychromatic X-ray CT after each injection to produce 3D images. In the second experiment, Berea sandstone was used instead of quartz powder. Monochromatic X-ray CT was used to scan the sample in this experiment.
In both experiments, the results did not provide clear and convincing evidence that the adsorption of caesium was detected using X-ray CT imaging. In the quartz powder column experiment, the CT data did not corroborate the expected effect of Cs adsorption on average CT attenuation of the column that was predicted by the batch experiments and modelling. In the sandstone experiment, the CT data suggests no clear evidence that adsorption has been observed as well.

In order to establish a more definite conclusion on whether micro X-ray CT can be used to visualise adsorption, the adsorption isotherm describing the expected amount of adsorption should be independently verified. If instead, adsorption is being masked by an optical distortion to the X-rays at the solid-fluid interface, then this will be a useful area to investigate in future work. Future work is discussed further in Section 5.2.
Chapter 5

Conclusions and future work

5.1 Conclusions

In the first part of this thesis, the use of X-ray CT to characterise reactive surface area for multi-mineralogic systems was developed. This enabled a statistical characterisation of pore-scale heterogeneity in the reactive surface area of minerals within permeable rocks based on direct observation of the pore morphology and mineral distribution in three dimensions.

Combined use of BET measurements and X-ray CT imagery provided measurements of the roughness factor, $\beta$. Roughness factors was measured to range from $10 < \beta < 200$. Higher roughness factors were associated with higher total surface area in the rock, the presence of clay, and microporosity. Comparative BSE images and EDS data suggested that X-ray CT imagery can characterise mineral volume fractions well. In the Berea sandstone, clays preferentially coated quartz grains and resulted in no correlation between the modal mineral composition of the rock and the fraction of surface area made up by the mineral. In situations like this, using the mineral composition of the rock as a proxy for surface area would lead to significant error in reaction modelling. On the other hand, the volumetric composition and surface area fraction in the Edwards carbonate were strongly correlated. In cases like this, the assumption is reasonable.
5.1. Conclusions

The information produced can be used directly in statistically-based models of reactive transport including the emerging group of pore network models focused on characterising reactive processes. Statistical analysis of fifteen images suggest that at the length scale of 600 µm, the observations do not yet form a representative elementary volume. In pore network models it will be important to put physically based constraints on combinations of properties for individual pores. In this work it was found combinations of pore volume and surface area for a specific pore were constrained to values ranging between five times those that would be obtained for clay lined spheres and those that would be obtained for quartz lined spheres. This work extends the work of Peters (2009), Landrot et al. (2012), Golab et al. (2013) and Hezel et al. (2013) by characterising mineralogy and surface area directly allowing mineral specific surface area to be spatially correlated to distribution of flow velocities within the rock. The impact of spatial heterogeneity can be quantified in a similar way to Salehikhoo & Li (2015).

The dual-energy X-ray CT method improved phase identification. Scans of several specimens of known minerals revealed that albite may be difficult to separate from quartz, and plagioclase from orthoclase. The mineral pairs biotite-orthoclase and hematite-magnetite posed a similar difficulty. It was possible to uniquely identify pairs of the remaining combinations of minerals investigated: quartz, kaolinite, orthoclase, plagioclase, albite, biotite, calcite, dolomite, pyrite, magnetite, and hematite. This conclusion is specific to the X-ray CT setup. However no special modifications were made to a commercial system in order to achieve this. The dual-energy method was able to identify the same groups of minerals as single-energy X-ray CT despite operating at less favourable X-ray energies. The dual-energy method may yield better contrast, specimen size capacity or both.

In an exploratory study, batch adsorption experiments of caesium on quartz were carried out. The measurements provided an estimate of the amount of Cs expected to adsorbed onto quartz. Based on the mass of the caesium expected to adsorbed, a model was made to calculate the expected increase CT attenuation. The model suggested that adsorption should make up to 86% of the average attenuation in the CT image. Two column experiments were carried out. In the first, quartz powder were packed in the column and CsCl of various concentrations injected. The column was scanned using polychromatic X-ray CT after each injection to produce 3D images.
In the second experiment, Berea sandstone was used instead of quartz powder. Monochromatic X-ray CT was used to scan the sample in this experiment.

In both experiments, the results did not provide clear and convincing evidence that the adsorption of caesium was detected using X-ray CT imaging. From the polychromatic scans, less than 1% of the average attenuation in the CT image could be attributed to adsorption. From the monochromatic scans, the increase in CT attenuation was not sufficiently significant to be disentangled from the contribution from the increased concentration of caesium in the fluid in the pore space. Thus the study did not successfully establish that adsorption could be observed at the pore-scale in 3D using X-ray CT. We cannot conclude that CT scanning is not suitable for visualising pore-scale adsorption. X-ray CT has been used to observe adsorption albeit not at a pore-structure resolved scale and for gas adsorption (Karacan & Okandan 2001).

The results of this work in this PhD has been to develop and advance three dimensional and multi-mineral characterisation of rock samples at the pore-scale using X-ray CT. This significantly adds to the body of work already completed by other projects within the Qatar Carbonates and Carbon Storage Research Centre programme. The ability to characterise multi-mineralogic and complex carbonate reservoirs will be greatly enhanced. In addition, the impact of pore-scale mineral and surface area heterogeneity was investigated. This combined with dissolution rate measurements of CO$_2$ and brine in contact with carbonate rocks, and our new ability to observe transport heterogeneity and multiphase flow will open up new avenues of investigation and allow current reactive transport models to be tested and developed. This will in turn support improvements to our understanding and development of upscaling techniques for accurate and efficient modelling of chemical processes. Ultimately, this will improve our understanding of how these rocks trap gas and fluids for the application of CO$_2$ storage in carbonates.
5.2 Future work

Future work is needed to draw a definitive conclusion on the experiments to visualise aqueous adsorption. The batch adsorption measurements and the expected level of change to CT images by aqueous adsorption of caesium should be verified independently. If they are accurate, then experiments are needed to determine how X-ray attenuation at the solid-fluid interface are being affected by diffraction. The experiments should investigate how diffraction may be influencing the impact adsorption has on CT number at the finer pore-scale resolution.

There is also scope in creating a workflow to optimise the parameters of a CT scan for specific mineralogy. This will involved determining the most challenging pairs of minerals to be distinguished. The optimum energy settings depending on the size of the specimen and selected pair of minerals to be distinguished. With these information, the expected difference in CT number between the minerals can be modelled based on the Beer-Lambert law. If the equipment’s source spectrum and detector response are known or can be measured, the accuracy of the model will improve considerably. The lack of information on the source spectrum and detector response was one of the challenges and drawbacks in the practical optimisation for mineral identification.

Characterising the distribution of surface area was one of the first steps in this work. For future work, it will be valuable to correlate the mineral-specific surface area to the distribution of flow velocities. This information is available from CT imaging such as those by Menke et al. (2016) and Andrew et al. (2015). It will be of great interest to incorporate this information into our reactive transport models. There are still questions about how representative a statistical characterisation would be. Differences in the surface area distributions collected in this work was analysed for statistical significance, and it was concluded that at the scale of the images collected in a single scan of less than a mm of Berea sandstone, it was not representative yet of the rock. So there is scope for future work to determine the requirements in obtaining a representative characterisation. It is not yet clear if time and effort may be an onerous factor. This length scale for even a relatively homogeneous rock such as Berea sandstone would be even larger when mineral-specific characterisation is considered. In summary, characterising
and correlating surface area and flow velocity distributions at a representative scale would be of great value to the community.
Appendix A

Appendix: Mineral surface area and heterogeneity

A.1 Procedure for estimating the mineral mass fraction from chemical composition obtained from XRF measurements

Estimates of the mineral mass fractions from XRF observations were obtained by solving Equation A.1 for each mineral fraction, where \( e_i \) is the element concentration (g/g), \( m_j \) is mineral concentration (g/g), \( s_i \) is element mole fraction from mineral stoichiometry for element \( i \) in mineral \( j \), and \( A_i \) is relative atomic mass for element, \( i \).

\[
e_i = \sum_{j=1}^{12} m_j s_i A_i \frac{s_i A_i}{\sum_{i=1}^{12} s_i A_i}
\]  

(A.1)

The relationship between mineral composition, \( m_j \) and element concentrations, \( e_i \) was posed as a minimisation problem to solve for the mineralogical makeup of the rock that produced element
concentrations with the least difference to the XRF data. For all specimens, seven elements were considered in the minimisation problem, comprising those present in the XRF measurements. Similarly, twelve minerals were considered including those identified from XRD in addition to albite, anorthite, chamosite, clinochlore, illite and smectite, which were present in analyses using SEM-EDS discussed below. This analysis also showed minor amounts of muscovite, magnesite, hematite, siderite, pyrite, titanite, rutile, ilmenite and zircon but these were not considered. The mineral stoichiometries \( s_i \) are shown in Table A.1. Mineral abbreviations are according to Whitney & Evans (2009).

The minimum was determined with Matlab R2012b using an interior-point nonlinear minimisation algorithm named “GlobalSearch” which was found to produce similar results to a number of other available solvers. The mineral fractions were constrained to sum to 1 and individual mineral fractions were bound in the range 0-1.

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Table A.1: Element mole ratios from mineral stoichiometries

Tables A.2 and A.3 show the match between the algorithm results and XRF data. For the
Berea sandstone the estimated composition was 70 and 73% quartz, 15 and 16% feldspar group minerals, 3-4% clay, and 3 to 6% relatively high density minerals including carbonates and chlorite. The composition estimates for the limestone were a mixture consisting of primarily dolomite and calcite, with poor match of certain elements such as iron because minerals such as pyrite were not included in the solver. The absence of pyrite in the sandstone cases forces the bulk of the carbonates to be identified as ankerite.

<table>
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Table A.2: Best fit element concentrations produced from fitting XRF data to mineral compositions of the Berea sandstone. The units are weight percent.
Edwards Estaillades Guelph Indiana Ketton

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Table A.3: Best fit element concentrations produced from fitting XRF data to carbonate mineral compositions. The units are weight percent.

A.2 Process for segmenting electron images

The electron microscope was operated at 20kV acceleration voltage, 0.1nA probe current, 15 mm working distance, and 100 µs per pixel dwell time to collect 2048x1920 pixel images.

Each specimen was cut to 1 cm² blocks, placed in a 38 mm diameter mould where Struers EpoFix epoxy was allowed to vacuum impregnate the specimen, and cure at ambient pressure for 12 hours. Once cured, the specimens were ground until the rock surface was exposed, and their surfaces finished, using a Buehler EcoMet AutoMet 300. The specimens were examined in BSE mode at 20kV acceleration voltage, 0.6nA probe current, 15 mm working distance, and 100 µs per pixel dwell time to collect 2048x1920 pixel images. Microanalytical X-ray (Energy Dispersive Spectroscopy or EDS) make chemical compositional determination possible.

The electron gun was operated at 15kV acceleration voltage, 1nA probe current, 15 mm working distance, 100 µs per pixel dwell time to collect a 2048x1920 pixel image which was subsequently processed with Oxford Instruments INCA to produce elemental maps. The EDS map resolution at accelerating voltage, $E_0 = 15keV$ and density, $\rho = 2.1 \text{g cm}^{-3}$ is 2.1 µm, according to Potts
(1987), where lateral resolution, \( y(\mu m) = \frac{0.077E^{1.5}}{\rho} \). The map was collected over 60 minutes and covered 0.873 mm\(^2\).

The false-colour BSE-EDS map was split into three channels, where each channel was an 8-bit greyscale of the red, green, and blue intensity of the false-colour map. The red spectrum corresponds to higher aluminium concentrations, which were linked to the clays in the BSE image, the green indicated regions of higher concentrations of potassium coinciding with feldspars, and the lavender areas showed elevated concentrations of Ca, Mg, and Fe, correlating to chlorites, carbonates and oxides. The 3D equivalent volume, surface area of the mineral groups from the 2D area and perimeter fractions were inferred from the segmented 2D BSE-EDS image. The 2D area fraction was calculated by counting the number of pixels, and the perimeter fraction using a marching squares and linear interpolation (Kroon, DJ 2011). The mineral-group-specific perimeter fraction calculation was the 2D equivalent of the surface area extraction using the marching cubes algorithm in 3D.

The BSE and 8 elemental maps, K, Ti, Fe, Mg, Al, Si, Na, and Ca were used. The 8-bit BSE image was thresholded into 3 phases at values 15 and 240, representing the pore space, every mineral group except ‘others’, and ‘others’. The elemental maps were thresholded into two phases to indicate significant concentration and background. Thresholding was applied using Otsu’s criterion (Otsu 1975), implemented in Matlab 8.0 with the functions “multithresh” and “imquantize”. The minor amounts of Mg, Na, and Ca uniformly distributed throughout the segmented images were removed by erosion and dilation, in Matlab 8.0 with the functions “strel, imerode” and “imdilate”, using a flat disk-shaped structuring element of radius one pixel. The grouping was then defined according to the following sequential criteria, implemented as a series of if and else if statements: Others identified in the BSE, Ti, Fe, and Ca maps, feldspar identified by positive indications in either the K or Na map, Clay identified by either positive Mg or Al signals, Quartz by any positive Si indications, pore space identified in the BSE image, or else unidentified. These assignments were then used as initial seeds for watershed segmentation.

Figure A.1 shows the results of the image processing of the BSE and EDS aluminium map for a Berea sandstone sample. The false-colour map shown in Figure A.1(b) assigns a colour to
X-ray photons based on their energy. Figure A.1c shows the mineral map with segmentation of the BSE image based on the overlay in Figure A.1b.

Figure A.1: (a) Backscattered electron (BSE) image of Berea sandstone sample measuring 0.873 mm$^2$. (b) Energy dispersive spectroscopy (EDS) overlaid on the BSE to create a false colour elemental map: lavender regions indicate greater concentrations of Ca, Mg, and Fe, red areas have more Al, and green sections reflect greater amount of K. (c) Mineral map based on BSE and EDS maps: light blue - pore space, royal blue - clay, red - quartz, green - feldspars and chlorites, and yellow - other phases of higher density, including calcite.

A.3 Procedure for obtaining the mineral-specific surface area from micro CT imagery

The surface area between the solid and pore space for each mineral group was calculated using the multi-segmented images. The images first needed to be reformed into two phases in order to mesh a surface. For an image with $n$ number of phases, there are $2^{n-1} - 1$ ways to binarise, and $\frac{n!}{2(n-2)!}$ pairs of phases involved. The combinations constitute a system of linear equations $Ax = B$, where $A$ are the pairings associated with the combination $C$, $x$ are the pairs, and $B$ is the surface area for combination $C$. For the five phase Berea sandstone images, there were 15 combinations, and 10 pairings (Table A.4). A marching cubes algorithm was implemented in Matlab 8.0 (Hammer, P 2013) to mesh the surfaces for each combination, and calculate the area, $B$ using Heron’s formula. Since the pore space was defined as group 1, the first 4 pairings, $x_1$ to $x_4$ represent the surface area for each mineral group; the groups 2-4 are clay, quartz, feldspar, and others respectively. An analogous procedure was performed for the Edwards carbonate.
### A.4. Surface area calculations from X-ray imagery and N$_2$ BET measurements

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Table A.4: Binary combinations, C for determining mineral-specific surface areas, x. A is the interfaces associated with the binary combination, and B is the surface area of the binary combination.
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Table A.5: BET CT Data
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Table A.6: BET CT Data
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A.5 Statistical descriptions of the surface area of the rock samples

Figure A.2: Mono-mineralogical surface area distribution for Berea sandstone 1 plug 2
Figure A.3: Mono-mineralogical surface area distribution for Berea sandstone 1 plug 3
Figure A.4: Mono-mineralogical surface area distribution for Berea sandstone 1 plug 4
Figure A.5: Mono-mineralogical surface area distribution for Edwards carbonate
A.5. Statistical descriptions of the surface area of the rock samples

Figure A.6: Mono-mineralogical surface area distribution for Guelph carbonate
Figure A.7: Mono-mineralogical surface area distribution for Estaillades carbonate
A.5. Statistical descriptions of the surface area of the rock samples

0
0.1
0.2
0.3
0.4
Surface area / pore volume [µm$^{-1}$]

Probability

75µm

Clay
µ: 0.0543. σ: 0.109
Quartz
µ: 0.298. σ: 0.687
Feldspar
µ: 0.0702. σ: 0.093
Others
µ: 0.0558. σ: 0.172

50µm

Clay
µ: 0.0527. σ: 0.0987
Quartz
µ: 0.382. σ: 0.73
Feldspar
µ: 0.076. σ: 0.131
Others
µ: 0.0456. σ: 0.169

100µm

Clay
µ: 0.0475. σ: 0.0585
Quartz
µ: 0.225. σ: 0.125
Feldspar
µ: 0.0703. σ: 0.0702
Others
µ: 0.0359. σ: 0.0675

200µm

Clay
µ: 0.0445. σ: 0.0295
Quartz
µ: 0.177. σ: 0.045
Feldspar
µ: 0.0586. σ: 0.0326
Others
µ: 0.0212. σ: 0.0309

Log (Surface area / pore volume) [µm$^{-1}$]

Clay
µ: −3.91. σ: 1.85
Sampling fraction:0.82
Quartz
µ: −1.42. σ: 0.95
Sampling fraction:0.99
Feldspar
µ: −3.25. σ: 1.58
Sampling fraction:0.85
Others
µ: −4.6. σ: 2.72
Sampling fraction:0.55

Clay
µ: −3.84. σ: 1.61
Sampling fraction:0.92
Quartz
µ: −1.57. σ: 0.763
Sampling fraction:1
Feldspar
µ: −3.19. σ: 1.37
Sampling fraction:0.93
Others
µ: −4.69. σ: 2.44
Sampling fraction:0.79

Clay
µ: −3.62. σ: 1.2
Sampling fraction:0.96
Quartz
µ: −1.64. σ: 0.66
Sampling fraction:1
Feldspar
µ: −3.08. σ: 1.07
Sampling fraction:0.98
Others
µ: −4.66. σ: 1.95
Sampling fraction:0.9

Clay
µ: −3.34. σ: 0.705
Sampling fraction:1
Quartz
µ: −1.76. σ: 0.236
Sampling fraction:1
Feldspar
µ: −3.02. σ: 0.663
Sampling fraction:1
Others
µ: −4.55. σ: 1.16
Sampling fraction:1

Figure A.8: Multi-mineralogical surface area distribution for Berea 1 plug 2
Figure A.9: Multi-mineralogical surface area distribution for Berea 1 plug 3
A.5. Statistical descriptions of the surface area of the rock samples

Probability

Surface area / pore volume [µm$^{-1}$]

50µm

Clay
µ: 0.0816. σ: 0.142
Quartz
µ: 0.346. σ: 0.363
Feldspar
µ: 0.0447. σ: 0.321
Others
µ: 0.00175. σ: 0.00983

Probability

Log (Surface area / pore volume) [µm$^{-1}$]

Clay
µ: −3.41. σ: 1.67
Quartz
µ: −1.36. σ: 0.778
Feldspar
µ: −3.67. σ: 1.98
Others
µ: −6.74. σ: 2.18

Sampling fraction: 0.96
Sampling fraction: 1
Sampling fraction: 0.5
Sampling fraction: 0.24

75µm

Clay
µ: 0.0665. σ: 0.0733
Quartz
µ: 0.254. σ: 0.15
Feldspar
µ: 0.0302. σ: 0.046
Others
µ: 0.00116. σ: 0.00368

Probability

Log (Surface area / pore volume) [µm$^{-1}$]

Clay
µ: −3.35. σ: 1.3
Quartz
µ: −1.52. σ: 0.554
Feldspar
µ: −4.14. σ: 2.02
Others
µ: −7.43. σ: 1.99

Sampling fraction: 0.99
Sampling fraction: 1
Sampling fraction: 0.69
Sampling fraction: 0.44

100µm

Clay
µ: 0.0657. σ: 0.0646
Quartz
µ: 0.224. σ: 0.0978
Feldspar
µ: 0.0295. σ: 0.0349
Others
µ: 0.0011. σ: 0.0026

Probability

Log (Surface area / pore volume) [µm$^{-1}$]

Clay
µ: −3.21. σ: 1.08
Quartz
µ: −1.59. σ: 0.443
Feldspar
µ: −4.01. σ: 1.55
Others
µ: −7.66. σ: 1.94

Sampling fraction: 1
Sampling fraction: 1
Sampling fraction: 0.81
Sampling fraction: 0.65

200µm

Clay
µ: 0.0603. σ: 0.0299
Quartz
µ: 0.193. σ: 0.0397
Feldspar
µ: 0.0305. σ: 0.0151
Others
µ: 0.001. σ: 0.00104

Probability

Log (Surface area / pore volume) [µm$^{-1}$]

Clay
µ: −2.93. σ: 0.501
Quartz
µ: −1.67. σ: 0.208
Feldspar
µ: −3.68. σ: 0.757
Others
µ: −7.44. σ: 1.55

Sampling fraction: 1
Sampling fraction: 1
Sampling fraction: 1
Sampling fraction: 0.85

Figure A.10: Multi-mineralogical surface area distribution for Berea 1 plug 4
Figure A.11: Multi-mineralogical surface area distribution for the Edwards carbonate
Figure A.12: Multi-mineralogical surface area boxplots for Berea 1 plug 1
Figure A.13: Multi-mineralogical surface area boxplots for Berea 1 plug 2
A.5. Statistical descriptions of the surface area of the rock samples

![Boxplots](image)

**Figure A.14:** Multi-mineralogical surface area boxplots for Berea 1 plug 3
Figure A.15: Multi-mineralogical surface area boxplots for Berea 1 plug 4
Figure A.16: Multi-mineralogical surface area boxplots for the Edwards carbonate
Table A.8: Summary statistics for mineral-specific surface area distributions.

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<th>Sample</th>
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<th>Mineral</th>
<th>Mean</th>
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<td>[µm⁻¹]</td>
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Plug 2 Quartz 0.382 0.73 -1.42 0.95 0.99
Feldspar 0.076 0.131 -3.25 1.58 0.85
Others 0.0456 0.169 -4.6 2.72 0.55
75 Clay 0.0543 0.109 -3.84 1.61 0.92

Continued on next page
A.5. Statistical descriptions of the surface area of the rock samples

Table A.8: Summary statistics for mineral-specific surface area distributions.

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A.5. Statistical descriptions of the surface area of the rock samples

Table A.8: Summary statistics for mineral-specific surface area distributions.

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<th>Sample</th>
<th>Scale [µm]</th>
<th>Mineral</th>
<th>Mean [µm]</th>
<th>SD [µm]</th>
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End of table
Figure A.17: Sub volume of Berea rock with 5 phase segmentation showing from top to bottom: least, typical, and greatest clay surface area per pore volume.
Figure A.18: Sub volume of Berea rock with 5 phase segmentation showing from top to bottom: least, typical, and greatest quartz surface area per pore volume.
Figure A.19: Sub volume of Berea rock with 5 phase segmentation showing from top to bottom: least, typical, and greatest surface area per pore volume of other minerals.
Figure A.20: Sub volume of Edwards rock with binary segmentation showing from top to bottom: least, typical, and greatest surface area per pore volume.
Figure A.21: Sub volume of Edwards rock with 4 phase segmentation showing from top to bottom: least, typical, and greatest quartz surface area per pore volume.
Figure A.22: Sub volume of Edwards rock with 4 phase segmentation showing from top to bottom: least, typical, and greatest dolomite surface area per pore volume.
Figure A.23: Sub volume of Edwards rock with 4 phase segmentation showing from top to bottom: least, typical, and greatest surface area per pore volume of other minerals.
**A.6 Bar plot of surface area fraction of each mineral**

The geometric surface area fraction of each mineral group is shown in a stacked bar plot in Figure A.24. The plot is sorted by the geometric surface area to pore volume ratio and there was no apparent correlation between this value and the surface area abundance of each mineral group, e.g., clay was not more or less abundant at the pore surfaces of those sub volumes with higher or lower surface area to pore volume ratios.

![Bar plot of surface area fraction of each mineral](image)

Figure A.24: A stacked bar plot of the geometric surface area fraction of each mineral grouping in the Berea sandstone subsampled by 100µm cubes. The bars are sorted by the surface area to pore volume ratio and geometric mineral surfaces show no clear correlation with this value.

**A.7 Cumulative distribution function of surface area to pore volume ratio**

Figure A.25 shows the observed distribution, as a cumulative distribution function, with and without the surface area - pore volume coupling, compared with the distribution from Li et al. (2007a). The uncorrelated distributions are much more similar at values of surface area to pore volume ratios less than 300 µm\(^{-1}\). The nature of the distributions used by Li et al. (2007a) limit the range, however, of the values of the ratio compared to the uncorrelated observations.
Figure A.25: This figure shows the cumulative distribution of the surface area to pore volume ratio for the values observed in this work, the values obtained when removing the correlation between the properties and the values assumed in the work of Li et al. (2007a).
Appendix B

Appendix: Copyright checks

Figure B.1: Reproduction permission for materials from published article: Lai, P., Moulton, K. & Krevor, S. (2015), Pore-scale heterogeneity in the mineral distribution and reactive surface area of porous rocks, Chemical Geology 411, 260-273.
Bibliography


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