ADSORPTION OF FATTY ACIDS ON MINERAL SURFACES, THE EXPERIMENTAL IMPLICATION OF SORPTION-PROTECTION THEORY FOR FATTY ACIDS DIAGENESIS AND THE USE OF FLASH PYROLYSIS TO COMPREHEND THE FATTY ACID-MINERAL INTERACTIONS

A THESIS
IN ORGANIC GEOCHEMISTRY

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BY

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Abstract

A theoretical concept of adsorption as a substantial step during diagenesis has been experimentally verified for long chain fatty acids on calcite and clay minerals. The primary focus of this research is to establish an empirical method via experimental work to test the major hypothesis developed for the preservation of organic matter via minerals related to the formation of geomacromolecules or kerogen.

Addressing diagenesis, this research project is focused on the two major components of the sedimentary system i.e. fatty acids and minerals. The fatty acid is one of the most reactive organic compounds in the sedimentary system and is considered as an important precursor for petroleum hydrocarbons. Considering the importance of fatty acids in petroleum system, its adsorption on different minerals is challenging as well as equally important. Clay and calcite minerals have unique properties of adsorption, and catalysis and hence their affinity toward organic compounds has many implications in the petroleum industry and sedimentary system. A novel experimental method is developed to quantify the adsorption of fatty acids on mineral surfaces. Adsorption work coupled with flash pyrolysis is used to gain insight into fatty acids bonding with the mineral surfaces. Besides that flash pyrolysis work is used to apprehend the adsorption levels by benchmarking the difference in fatty acids adsorption on mineral surfaces. Like adsorption, a novel method is developed on Pyrolysis-GC-MS to recognise the breakdown products of three phases of fatty acids; pure fatty acids, fatty acids adsorbed on minerals and fatty acid salts.

This is the first study of its kind when a comprehensive experimental work is executed at laboratory scale to mimic the adsorption of fatty acids during diagenesis. Findings from each experimental result are conclusive and interpreted in a close relation to natural settings. Project conclusions are used to understand the sorption and protection of fatty acids in the context of diagenesis and thus have major implications for the generation of hydrocarbons in marine sediments. Also, flash pyrolysis being a major part of the project is used for first time to address the diagenetic change linked with the industrial problem and then the solution is reported.
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Acknowledgments

I truly believe that all events in this space-time boundary and beyond happen due to the will of ALMIGHTY ALLAH and so this project would not have been possible without his blessings and I am deeply grateful for that.

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I still remember when Prof Mark Sephton took me to the lab B109. It was 14\textsuperscript{th} March 2013, 11:00 am. He was briefly explaining me about the lab protocols and as we reached the B109 entrance, he said, Rabia “I don’t like failure”. Onward from that point, I took every effort to make this project a success and I should not be ashamed of saying that B109 has been my home during last 4 years. I am extremely gratified to him for providing me opportunity to pursue my research in his lab. I have had a thorough discussion with him for all my designed experiments and their data interpretation and his encouragement was a true motivation for me during my Ph.D.

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We learn from books, travelling, and experiences and then we affect people in our surrounding. We do not aim to change people but we meet them for reasons without knowing it and so, in the end, we see a change in ourselves and a change in them because change is inevitable.

Last, but not least, I would like to express my thanks to all those who expressed their love and care for me during my stay in London. I would also apologise to those people for not fulfilling their expectations for one reason or another.
Declaration

I certify that the research work presented in this thesis was performed by me during the last four years at Imperial College London and the literature cited has been appropriately referenced and/or acknowledged. No fraction of this thesis has been submitted in support of any other degree at Imperial College London, or anywhere else.

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Chapter 1

Organic compounds degradation and preservation in marine sediments

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1.1 Introduction

The carbon is ranked as the fourth most abundant element in the universe and its intrinsic property of compound formation with elements such as oxygen, hydrogen, and nitrogen played a great role in the creation and maintenance of life on planet Earth. Understanding the interaction of carbon with organic and inorganic components is challenging as well as a necessity to comprehend some of the complex natural processes including origin and evolution of life, climate change, and petroleum formation.

1.1.1 Carbon and the Earth

Carbon cycle involves various biochemical and geochemical transformations which can be used in organic geochemistry to answer the question of origin and evolution of life. It is believed that approx. $6.4 \times 10^{15}$ t C of organic carbon is preserved in sediments and soils (geological sub-cycle) on the time scale of tens of millions of years. This preserved organic carbon then returned to the earth surface either by anthropogenic action or by natural processes to participate again in the biological system (biochemical sub-cycle; carbon reservoir, $3 \times 10^{12}$ t C) (Tissot and Welte 1984). Between these two carbon sub-cycles, sediments and soils represent largest and most dynamic reservoirs of organic matter on earth and have gained much attention in the field of geochemistry (Siegenthaler and Sarmiento 1993). Despite the similarities and differences in the geochemistry of both reservoirs, yet both embody organic matter degradation and its interaction with minerals, water and living organisms (Hedges and Oades 1997). The work presented here focuses on specific organic compound-mineral interaction in the context of organic matter preservation mainly in marine sediments and to some extent in soils. The following sections review the background and the importance for this topic.
1.2 Production, preservation and degradation of organic matter in sedimentary settings

Marine sediments are generally envisaged as a homogenous large carbon reservoir (Hedges and Oades 1997) and are composed of organic and inorganic matter of biogenic origin along with particulate minerals (Wetzel 2001). Sedimentary organic matter is mainly divided into two categories i.e. dissolved organic matter (DOM; particle size ≤ 0.45 µm diameter) and particulate organic matter (POM) (Lee and Wakeham 1992). Water extractable organic matter and organic matter in pore water are also referred to as dissolved organic matter (Chen and Hur 2015). Both POM and DOM are further categorised into labile and refractory organic matter (Zonneveld et al. 2010). Although the accuracy of measurement of dissolved organic carbon (DOC) in dissolved organic matter has been questioned (Suzuki 1993), it is still considered as the largest carbon pool 96% (c.700 × 10^15 g) in marine settings contrary to the particulate organic carbon (POC) which only contains 5% (~30 × 10^15 g C) of total marine organic carbon in the oceans (Hedges 1992). More importantly dissolved organic carbon has input from both allochthonous (higher plants) and autochthonous (derived from algae, bacteria, and macrophyte) sources of organic carbon in a marine environment (Chen and Hur 2015) which reflects the diversity of organic compounds available for accumulation and preservation. The next section will review the production, degradation, and preservation of sedimentary organic matter.

1.2.1 Production of sedimentary organic matter

Today marine and terrestrial primary production are of the same size, contrary to the earlier Earth’s history when marine production was dominant (Hedges 1992). A major consensus exists for single-celled phytoplankton responsible for marine photosynthesis act as a major contributor to marine and lacustrine sedimentary organic matter. Due to high transfer efficiency (ratio of the net production at the higher level to that at the lower level), zooplankton is only second to phytoplankton for their sedimentary organic matter contribution along with the heterotroph bacteria who contribute to marine organic sediments with their own remains. Further higher plants contribute to sedimentary organic matter via coastal areas and lakes. Fungi have a less significant contribution to the marine sedimentary organic matter than in the terrestrial environments (Hedges and Oades 1997, Killops and Killops 2009).
1.2.2 Organic matter degradation

The contribution of terrestrial and marine source inputs to the marine sediments has been discussed in the previous section. Generally, the marine environment is considered as homogeneous in comparison to the terrestrial environment, yet it offers various physical, chemical and geological factors that control the production as well as the deposition of organic matter. Once organic matter produced it also starts degrading as it passes through the water column. The degradation reduces the bulk organic matter into a small fraction (<1 %) of primary production (Middelburg et al. 1993, Hedges and Keil 1995) that ultimately reaches the sediment for preservation and it mainly depends on its residence time in water and the amount of primary production in the euphotic zone (Wakeham et al. 1997, Wakeham et al. 2002). Fig 1.1 shows the simplified illustration of organic matter degradation and transformation in marine sediments (Zonneveld et al. 2010). Typically, degradation of organic matter is faster in an oxic portion of sediment column from where the degraded organic matter further transferred into an anoxic zone. Organisms such as bacteria, archaea, unicellular and, multicellular organisms are mainly responsible for degradation. Importantly the characteristic types of organic matter are consumed and produced due to the presence of redox-zones and associated microbial groups (Canfield and Thamdrup 2009) within the upper most layer of anoxic zone of sediments. Biotransformation rates slow down as the OM passes through these redox zones and ultimately is no longer available due to the transfer of OM from labile to the refractory OM pool which can then subsequently accumulate in the underlying sediments (Zonneveld et al. 2010).

Another important aspect of degradation is that it not only reduces the size of organic matter but also change the composition of most compound classes, therefore, the amount that ultimately reaches the seafloor is a product of significant regional variability (Lutz et al. 2002). Contrary to that a few studies also suggest a little change in the overall composition of organic matter. For instance, Hedges et al. (2001) reported the same composition of amino acids throughout the water column from $^{13}$C nuclear magnetic resonance (NMR) studies. However, it seems difficult to draw a conclusion from this study except that a least compositional change in such cases can only show a possibility for the protection of organic compounds in mineral matrices. Furthermore the use of certain analytical techniques is not considered useful in the molecular characterisation of accumulated organic matter in sediments and therefore it is reported that the detrital organic matter found in sediments still
contains similar proportions of identifiable compounds such as 10–20% carbohydrates, 10% nitrogenous compounds (mostly amino acids) and 5–15% lipids (Hedges and Oades 1997, Burdige 2007).

Abiotic recondensation occurs between degradation products and forms complex structures resistant to biodegradation and subsequently form complex compounds known as humic substances (Schnitzer 1991) which are ubiquitous in soil, marine and natural waters. Humic substances are a product of decomposition, oxidation, and polymerisation of organic substances and represent an extremely complex structure (Schulten and Schnitzer 1993, Raposo et al. 2016). Nevertheless, they are considered as the largest component of sedimentary organic matter while lacustrine sediments also contain 60-90 % of humic substances (Aiken et al. 1985, Hedges et al. 2000, McDonald et al. 2004). DOC contain almost 50 to 75% of humic acid in water (Hertkorn et al. 2002).

Fig 1.1 Simplified illustration of degradation and transformation of organic matter in sediments. Three processes are shown: chemical transformation processes, organic matter pools, and biotic processes (Zonneveld et al. 2010).
1.2.3 Organic matter preservation

Another major step during carbon cycle is the re-mineralization of the major component of organic matter ~ 55-80% along the continental margins which eventually leave the remaining organic matter fraction for preservation and burial for the longer-term components of the sedimentary cycle (Burdige 2005). Organic matter preservation in the natural environment is a complex phenomenon and its understanding is of great importance as it links all three global cycles of carbon, oxygen, and nitrogen over geologic time. Further to that, it has been an active field of research in the field of organic geochemistry due to its pivotal role as a progenitor of fossil fuels (Berner and Canfield 1989, Hunt 1996a, Engel and Macko 2013).

According to an estimate sediment depositing on deltas, continental shelves, and upper continental slopes carry almost 90% of total organic carbon $130 \times 10^{12}$ g C (Berner 1989) even though the continental margins share only ~10% of total ocean area and 20% of total ocean primary production (Killops and Killops 1993, Hedges et al. 1999). Nevertheless the process of organic matter preservation is complex and depends on variable factors (Henrichs 1992, Hedges and Keil 1995) which are interdependent and vary in complex patterns that usually shifts nonlinearly over time and space (Middelburg et al. 1993, Jahnke 1996).

Here I will only see the list of those factors as the detailed discussion of them is beyond the context of this introductory chapter. Factors affecting organic matter preservation in marine sediments include primary production rate (Calvert and Pedersen 1992), water column depth (Suess 1980), organic matter sources (Schubert and Stein 1996), sediment transport processes (Luckge et al. 1996), sediment accumulation rate (Henrichs 1992), bottom water oxygen concentration (Betts and Holland 1991), availability of O$_2$ and other electron receptors (Brandes and Devol 1995, Cai and Reimers 1995), microbial dynamics (Smith et al. 1992), mixing and irrigation by macrobenthos (Aller 1982), redox fluctuations (Aller et al. 1996), and sorption of organic matter on mineral surfaces (Keil et al. 1994b, Mayer 1994 a, 1994 b, Ransom et al. 1998). As a geochemist, my focus on these factors is based on my interest in organic-rich petroleum source rock and for this particular context, certain factors are more important than the others. For instance, organic matter preservation is enhanced due to factors such as higher primary productivity, oxygen minimum layer (region beneath euphotic zone where oxygen consumption is greater than supply), high sinking rate of detrital particles and rapid burial (Curiale and Curtis 2016 and references therein).
1.3 Sorption and protection of organic matter in marine sediments and its relationship with diagenesis

Preservation of organic matter in marine sediments depends on various factors as mentioned in section 1.2.3; nevertheless, organic matter preservation via sorption on mineral surfaces has gained much more importance in the field of geochemistry. This is largely due to the intimate relationship between organic matter and clay minerals in petroleum source rocks and recent sediments in upwelling zones (Salmon et al. 2000, Pichevin et al. 2004). The specific organic-mineral interaction has been hotly debated in early marine sediment studies which exclusively showed an increase in % organic carbon with the decrease in mean particle size (Tanoue and Handa 1979, Mayer et al. 1985, Nath et al. 2012, Arndt et al. 2013). Later on, it was further reported that direct relationship exists between % organic carbon and specific surface area for whole sediments (Mayer 1994 a, 1994 b, Keil and Cowie 1999, Kennedy and Wagner 2011, Lohr and Kennedy 2014) as well as for sediment size fractions (Keil et al. 1994d, Bergamaschi et al. 1997, Drouin et al. 2010b, Yu et al. 2012, Zhu et al. 2014) collected from different depositional environments.

The key finding of organic-mineral interaction studies was the organic matter coating which was preliminarily considered as continuous and more precisely described as a monolayer coating on the mineral surfaces (c.0.5 to 1.0 mg organic C m$^{-2}$ (Mayer 1994 b, Schmidt et al. 2010, Blair and Aller 2012, Cheng et al. 2012). However later on based on specific surface area (SSA) and microscopic analysis few other studies predicted the discontinuous or patchwise distribution of adsorbed organic matter on mineral surfaces (Mayer 1999, Wang and Xing 2005, Kaiser and Guggenberger 2007, Mikutta and Kaiser 2011, Saidy et al. 2013).

Considering a strong evidence for the association of sedimentary organic carbon in minerals (Salmon et al. 2000, Pichevin et al. 2004), the next intriguing question was how different organic compounds associate with mineral surfaces in marine sediments. In this context, sorption of organic compounds on mineral surfaces rather than occlusion between mineral particles (Hedges and Oades 1997) is considered important in sedimentary settings. The most enchanting features of the sorption model are that it offers a strong chemical bond between organic molecules and mineral surfaces (Kaiser and Guggenberger 2007, Mikutta and Kaiser 2011) and the protection of organic molecules into molecular-sized mineral pores from microbes and enzymes (Kaiser and Guggenberger 2003, Zimmerman et al. 2004, Mödl et al.
Further strong bonding between sorbed organic molecules and minerals surface not only lessen the chances of desorption (Kaiser and Guggenberger 2007) but also reduces biological mineralization (Keil et al. 1994b, Jones and Edwards 1998, Watanabe et al. 2005).

1.3.1 Diagenesis and kerogen formation

The contextual importance of adsorption of organic compounds during diagenesis was only appreciated when Henrichs (1992) first hypothesised that adsorption can be considered as a substantial step during diagenesis where it helps promotes condensation reactions required for the incorporation of labile monomers into geo-macromolecules. A conventional diagenetic model only includes biodegradation and polycondensation steps for the formation of geopolymers. Contrary to that diagenetic model with partitioning is comprised of biodegradation along with the partitioning of organic matter on mineral surfaces emphasising the importance of organic matter protection for preservation. Fig 1.2 shows both diagenetic models for comparison (Hedges et al. 1999, Zonneveld et al. 2010). The term diagenesis is a broad term and is applied to the processes affecting the products of primary production that take place prior to deposition and during the early stages of burial under the conditions of relatively low temperature and pressure (Vandenbroucke and Largeau 2007 and references therein, Killops and Killops 2009).
Fig 1.2 Conventional biodegradation/repolymerisation model and alternative biodegradation/sorption model for organic matter diagenesis and preservation (Hedges et al. 1999, Zonneveld et al. 2010)

Diagenesis results in polycondensed organic residue or geopolymer called kerogen in lacustrine or marine sediments, coal in coal mires and humin in soils. Kerogen is a peculiar term used for major organic form in petroleum geochemistry and represents a main organic carbon form in continental rocks (Vandenbroucke and Largeau 2007 and references therein). According to one definition, it is an insoluble macromolecular material derived from the biochemical remains of marine and terrestrial organisms and its average concentration in shales and limestones is approximated at ~ 0.1 weight % (Durand 1980, Tissot and Welte 1984, Behar et al. 1992, Vandenbroucke 2003). The formation pathway of kerogen has been hotly debated due to its complexity and therefore a number of theories have been put forward to explain it. The primitive one is the degradation-recondensation which states that the biodegradation products from biopolymers escaped from mineralization can recondense and
form an insoluble product of geopolymers which then subsequently form kerogen (Tissot and Welte 1984). Contrary to that the other theory emphasizes the formation of kerogen via selective preservation of resistant biomolecules (Largeau et al. 1984, Tegelaar et al. 1989, Boussafir and Lallier-Vergès 1997). As both theories are supported by findings in the literature, therefore, the most likely understanding is that both theories are operational in natural settings.

During diagenesis, the two pivotal controlling factors for the formation of kerogen/macromolecules are products of primary production such as amino acids, hexose and pentose and fatty acids and the interacting minerals involved during the early stages of burial. The products of primary production reflect diagenetic variation (microbial and chemical) in degradation of major organic compound classes such as the complete degradation of proteins into amino acids and the less rapid degradation of carbohydrates to hexose and pentose and the least degradation of lipids into fatty acids which are more resistant towards degradation than proteins and carbohydrates (Huc 1980, Vandenbroucke 1980, Vandenbroucke and Largeau 2007, Killops and Killops 2009). The major role appointed to the minerals during diagenesis is due to their heterogeneous catalytic properties required for condensation reactions (Bishop and Philp 1994, Consulchi et al. 2004, Wu et al. 2012 and references therein).

More recently the role of sorption protection of organic matter has been identified in the humification process by assembling small sorbed organic molecules through multiple hydrogen bonding and hydrophobic forces (Piccolo 2001, Sutton and Sposito 2005). Variations in the reactivity of humic substances towards the mineral surface (Benedetti et al. 1995, McKnight et al. 2002) depends on disparities in molecular size and the type of functional groups (Chin et al. 1994, Cabaniss et al. 2000, McKnight et al. 2002). It is generally suggested that the compounds having high molecular weight, more aromatic, carboxyl-rich and hydrophobic fractions of dissolved organic matter preferentially adsorb on mineral surfaces (McKnight et al. 1992, Day et al. 1994, Chorover and Amistadi 2001).

Considering the variety of organic compounds and minerals in marine settings, understanding the sorption mechanisms relevant to diagenesis is still remains the challenging questions in the field of geochemistry. The next section of this introduction will focus on the minerals in marine sediments and their role in catalysis of organic compounds.
1.4 Minerals in marine sediments

Sedimentary organic matter distribution is not uniform and therefore marine sediments show two extreme patterns from organic-rich sediments in anoxic basins and upper continental slopes to the organic poor (0.1 – 0.2 % organic carbon) pelagic sediments along with desert sands and loess beds (Curry et al. 1994, Hedges and Oades 1997, Burdige 2007). Besides these two extremes the intermediate sedimentary organic carbon concentration of 0.5 – 3 % were also reported within deltas and upper continental margins (Hedges and Oades 1997, Burdige 2007). As mentioned in section (1.2.3), various factors control the organic matter preservation, the disparity in deep sea sediments composition due to the presence of different principle sedimentary components i.e. lithic, and biogenic is obvious (Riley and Chester 1971, Chester 2009) which might control the preservation of organic matter.

Lithic components such as clay minerals and quartz are derived from land erosion, from submarine volcanoes or from underwater weathering (Goldberg 1954, Chester 2009, Strakhov 2014). Clays are fine-grained solids, hydrous silicates with layered structures, belong to the large group of phyllosilicates and are ubiquitous on earth (Brown 1984, Nadeau 1999, Stixrude and Peacor 2002). The layer silicates or phyllosilicates are composed of layers formed by the condensation of sheets of linked Si (O, OH)₄ tetrahedra with those of linked M₂-3(OH)₆ octahedra (M is either a divalent or trivalent cation). Condensation of layer sheets in different proportions such as 1:1 (kaolinite) or 2:1 (montmorillonite) give rise to dimorphic (1:1), trimorphic (2:1) or tetramorphic mineral types (2:1:1) (Theng 1974, Bergaya and Lagaly 2006, Ruiz-Hitzky and Van Meerbeek 2006). These clay minerals are extensively found in sediments and form almost <2 µm land-derived (carbonate free) fraction of the deep sea sediments (Chester 2009). Naturally existing clay minerals are mostly nano- to micro-sized particles with a high capacity for adsorption, ion exchange capability, and acid sites. They are solid acids having both Bronsted and Lewis acid sites (Xiao et al. 1997, Wu et al. 2012 and references therein). Catalytic activity of Bronsted acid sites in clay minerals depends on hydrated cations in the interlayer space, -OH and active broken-edge M-O-H²⁺ bonds on the layered clay minerals (Johns 1979, Geatches et al. 2010) while Lewis acidity of clay minerals is due to the electron pair accepting ability of phyllosilicate cations such a Al³⁺, Fe³⁺ in octahedral coordination at the edges of crystallite from OH groups (Beran et al. 1981, Stackhouse et al. 2001, Reddy et al. 2009, Liu et al. 2013a).
The biogenic component includes both organic and inorganic shell materials and the major sediment-forming biogenic components are carbonate and opaline silica shell material (Goldberg 1954, Chester 2009, Strakhov 2014). Calcite and aragonite are the most common and familiar carbonate minerals in sedimentary rocks while carbonates of different minerals such as dolomite (magnesium-calcium carbonate) and siderite (iron carbonate) are also commonly found in sedimentary rocks (Nichols 2009, Tucker 2009). Calcite is mainly biogenic and exists in two forms in nature due to the substitution of magnesium ions for calcium in the crystal lattice; low-magnesium calcite (<4% Mg) and high-magnesium calcite (>11% Mg) (Nichols 2009, Tucker 2009).

1.5 Mechanism of organic mineral association

Sorption of organic matter on minerals mainly depends on the nature of mineral surfaces with respect to chemical and molecular size fractionation (Chorover and Amistadi 2001, Feng et al. 2005). Clay minerals are ubiquitous in Earth’s crust and play a significant role in a sedimentary system during petroleum formation, migration, accumulation, and storage (Weaver 1960, Tannenbaum et al. 1986, Pollastro 1993, Wu et al. 2012). Their interactions with organic matter are most commonly observed in the natural system which is used to define the stability of organic matter. Thus the stability of organic matter also necessitates to understand the sorption-desorption patterns of organic-mineral interactions (Henrichs 1995, Mikutta et al. 2007).

A number of mechanisms reported for organic matter bound to mineral surfaces such as coulombic interactions which include anion and cation exchange, ligand exchange, cation bridges and hydrogen bonding while non-coulombic interaction mainly includes van der Waals interaction (Schlautman and Morgan 1994, Arnarson and Keil 2000, Feng et al. 2005). Out of bulk of these mechanisms for organic-mineral interactions, some of them are more commonly observed in a natural environment (Mikutta et al. 2007). For instance, ligand exchange mechanism is responsible for the displacement of surface hydroxyl/water groups of minerals by organic functional groups. By the same token, cation bridging is involved in the association of organic matter to negatively charged siloxane surfaces or to hydroxyls of phyllosilicates and oxides. In addition to that water bridging also plays a significant role in bridging anionic or polar organic ions with mineral surfaces (Schlautman and Morgan 1994, Sutton and Sposito 2006). Besides these main mechanisms, multivalent cations also play a
significant role by enhancing inter- or intramolecular linkages among organic molecules on mineral surfaces (Romkens and Dolfing 1998).

Carbonate rocks make up 20% of the volume of strata in sedimentary basins and serve both as source beds and as reservoir rocks for numerous major oil and gas fields (Palacas 1983, McCarthy et al. 2011, Burchette 2012). Organic-rich carbonate source rock also depends on how organic matter incorporates into CaCO$_3$ crystal structure (Ingalls et al. 2004, Burdige 2007) and therefore it has been categorized into two forms in biogenic CaCO$_3$ crystals. First is intracrystalline form in which organic matter retained within the crystal for longer duration due to the inaccessibility of strong oxidants (Gaffey and Bronnimann 1993) and retained within the crystal until the mineral dissolves (King and Hare 1972, Collins et al. 1991, Collins et al. 1992), and the second is intercrystalline form in which organic matter might come from sediments, pore water or be produced by the organism that precipitated the CaCO$_3$ (Endo et al. 1995, Sykes et al. 1995b, Blyth et al. 2008). The associated organic matter with carbonate minerals mainly exists in the form of adsorbed compounds due to the large surface area to volume ratio (Carter and Mitterer 1978, Ingalls et al. 2004, Gupta et al. 2006). Further to that marine humic and fulvic acids in carbonate mud-mounds also indicate the organic matter interactions with the carbonate minerals (Neuweiler et al. 1999, Neuweiler et al. 2000).

1.5.1 Mineral geo-catalysis of organic compounds

Diagenesis is mainly mediated by biological agents along with the chemical transformation which involves the role of mineral catalysis. The characteristic properties of clay minerals such as sorption and catalysis are essential in the formation of chemical bonds between minerals and organic compounds (Kaiser and Guggenberger 2007) and subsequent catalytic recondensation reactions between degraded products of proteins, carbohydrates, and lipids to form kerogen (Wu et al. 2012). For instance, Maillard reactions (melanoidin; a mixture of fulvic acids-, humic acids-, humin-, and kerogen-like polymers) (Evershed et al. 1997, Hedges et al. 2000) and polyphenol theory of humic substance formation is proposed for humification and then kerogen formation involving clay mineral catalysis (Filley et al. 2002, Wu et al. 2012 and references therein). Also, their role in the catalytic decarboxylation of fatty acids into hydrocarbons has been well documented (Tong et al. 2010a). Importantly, geochemical reactions involving clay-humic acid complex have been emphasized as they
facilitate the condensation reaction for the adsorbed humic acid which is substantially required for kerogen formation (Wang and Xing 2005, Ghosh et al. 2009). Recently, Bosetto et al. (2002) reported the formation of humic-like compounds from the interaction between clay minerals (K\(^+\), Ca\(^{2+}\) and Al\(^{3+}\) saturated montmorillonite and kaolinite and quartz systems in the presence of the same cations), glucose (D-glucose) and amino acid (glycine). Furthermore, Gonzalez and Laird (2004) also reported humic-like polymeric compounds from the reaction between arginine and glucose with smectites and goethite. Formation of clay-humic complexes after adsorption of humic acid on clay minerals have been studied by using modern techniques such as scanning electron microscopy (SEM), solid state \(^{13}\text{C}\) nuclear magnetic resonance spectroscopy (\(^{13}\text{C}\) NMR) and energy dispersive X-ray analysis (Taguchi and Sampei 1986, Laird 2001). More recently it has been shown that aliphatic fraction in humic acids can preferentially adsorb on clay surface in comparison to aromatic fractions (Laird 2001). Another effective role of clay minerals is their significance for selective aggregation of recalcitrant biomacromolecules in kerogen formation (Kovac et al. 2004). Clay minerals also partly affect the generation of crude oil. For instance, clay mineral and organic matter ratio affect the conversion of kerogen into crude oil (Dembicki 1992). The low ratio of smectite minerals is more effective in organic matter catalysis. Later on Faure et al. (2006a) also showed that in the presence of high content of smectite clay minerals high molecular weight alkanes disappear and low molecular weight alkanes increase.

Like for clay minerals, a few studies also show the significant catalytic effect of CaCO\(_3\) minerals for hydrocarbon formation (Shimoyam.A and Johns 1972, Jiyang et al. 2001, Meredith et al. 2006, Luo et al. 2007, Liu et al. 2008, Helgeson et al. 2009) and this finding also alluded to the observation that the hydrocarbon contents of carbonate rocks are similar to those of shales (Hunt 1961, Cordell 1992, Li et al. 2003). Therefore one can speculate that the calcite minerals might play the same role of catalysis as clay minerals in shale during the formation of kerogen and its conversion into oil in carbonate source rocks.

### 1.6 Fatty acids in the natural environment

Lipids are considered as an important class of macromolecules and fatty acids embody a key fraction of the lipid pool in living and dead organic material (Venturini et al. 2012). Due to their source specificity with respect to individual compounds they have been used to identify the sources, transformations and organic matter fate in the water column and marine
sediments (Carrie et al. 1998, Niggemann and Schubert 2006). Fatty acids are present in each genus and species of marine organisms and their quantitative and qualitative composition varies depending on the environment (Rezanka and Sigler 2009). About seven fatty acids (12:0, 14:0, 16:0, 18:0, cis-18:1w9, cis,cis-18 : 2w6 and cis,cis,cis-18 : 3w3) constitute 95% of the total in combined leaf tissues and seed oil in higher plants (Harwood 2012). Palmitic and stearic acids are most commonly found in both microorganisms and higher plant material (Oldenburg et al. 2000) while saturated and unsaturated fatty acids with carbon chains shorter than 12 and longer than 22 atoms are less common. In addition, terrestrial OM mainly includes long carbon chain (≥ n-C20) fatty acids sourced from plant waxes (Yamamoto et al. 2008) and short chain fatty acids (≤ n-C20) mainly derived from algae (Shameel 1990). Branched fatty acids of iso- or anteiso- configuration with carbon numbers from 14 to 18 are most commonly found in bacteria (Tissot and Welte 1984, da Costa et al. 2011). Algae mainly contain saturated or unsaturated monocarboxylic acids with straight even-numbered carbon chains (C12 to C20) (Erwin 1973, Reuss and Poulsen 2002, Dalsgaard et al. 2003, Strandberg et al. 2015). Importantly, fatty acids of multicellular algae are mostly similar to those of higher plants (Johns et al. 1979, Reuss and Poulsen 2002) and contain a minor component of iso- or anteiso- configuration fatty acids.

1.6.1 Fatty acids in petroleum geochemistry

Fatty acids and esters are the two reactive classes of organic lipid compounds found in sedimentary organic matter (Vandenbroucke and Largeau 2007, Petersen et al. 2008) and their presence in crude oil and sediments has already been reported (Strandberg et al. 2015). Fatty acids can potentially contribute to the formation of macromolecular organic matter and form a considerable fraction of kerogen (Vandenbroucke and Largeau 2007, Glombitza et al. 2016). Lipids, particularly aliphatic chains and carboxylic acids are the major constituent of all three types of kerogen (Tissot and Welte 1984, Vandenbroucke 2003, Vandenbroucke and Largeau 2007). For instance, type 1 kerogen is mainly composed of lipid materials particularly aliphatic chains (Kamga et al. 2014) and the type 2 and 3 kerogens are also mainly comprised of carboxylic groups along with the heteratomic ketone and polyaromatic nuclei (Vandenbroucke 2003). In addition, fatty acids are significantly found in oil shales (Platonov et al. 2002, Vandenbroucke and Largeau 2007, Petersen et al. 2008). Further, it is speculated that the high concentration of aliphatic structures in marine humic acids is thought
to be due to fatty acids derived from microbial or higher plant sources, and also bonded by ester linkages to the macromolecular structures (Sun et al. 1997, McDonald et al. 2004).

More recently fatty acid interactions with minerals and macromolecules have been subject of a few studies elaborating the importance of fatty acids in petroleum geochemistry. Structurally fatty acids are critical in kerogen formation due to their hydrophobic aliphatic chain which is equivalent to hydrocarbons and, secondly the more polar carboxyl group which is involved in bonding with cations and other functional groups. For instance, fatty acids are bound to the alcohol and phenolic surface groups on the kerogen matrix via ester bond or as salt or complex with clay minerals in sediments (Dai et al. 2000, Derenne et al. 2000, Abbott et al. 2001, Blokker et al. 2001, Petersen et al. 2008). Besides that, they also act as potential bridging compounds between the mineral surface and bitumen-kerogen matrix (Sener and Senguler 1998, Dyni 2003, Pearson et al. 2005). Further to that the bitumen-carrying fatty acids might also react with the organic macromolecules or be adsorbed to the mineral surfaces (Valkova et al. 2009).

1.6.2 Diagenesis of fatty acids and its industrial applications

Interestingly fatty acids have gained much importance in the field of biofuel. In the context of growing population and concerns about climate change, biofuels are considered as an alternative to fossil fuels and have many environmental benefits (Fortes and Baugh 1994, Demirbaş 2003, Lappi and Alen 2009). Vegetable oils comprising triglycerides are certainly an important source of biofuels having a high heating value and being low in sulphur and nitrogen content (Maher and Bressler 2007, Lappi and Alen 2009). Fatty acids such as stearic, palmitic, oleic, lenolic and linolenic acids are ubiquitous in vegetable oils and studies of cracking on vegetable oil also showed the presence of heavy fraction in pyrolysate due to the presence of fatty acids (Fortes and Baugh 1994, Dandik and Aksoy 1999, Demirbaş 2003).

Most importantly aromatic carboxylic acids play a pivotal role in the diagenesis of coal (McDonald et al. 2004, Killops and Killops 2009) and further its subsequent role in the coal liquefaction process. Although both humic and fulvic acids are comprised of a single aromatic system, terrestrial humic acid is highly aromatic than the marine one (McDonald et al. 2004, Killops and Killops 2009). Similarly terrestrial fulvic acid is composed of lignin-derived polycarboxyl-phenol components (Hessen and Tranvik 2013). To date, many studies
reported the role of oxygen-containing groups such as carboxylic acids in structural models of lignin and coal kerogen (Hatcher et al. 1992, Vandenbroucke and Largeau 2007, Petersen et al. 2008). Most importantly one of the aromatic acids, a shikmic acid found in plants, is an intermediate in the formation of building blocks of lignin i.e. coumaryl, coniferyl and sinapyl alcohols (Haslam 1993, Killops and Killops 2009). Besides that humic substance of either terrestrial or marine nature have an interesting interaction with the metal cations. Metal cations not only dictate the organic-mineral interaction but are also trapped into the macromolecular structure of humic substances and enhance inter- and intramolecular linkages within the organic matter and cause precipitation of organic substances (Romkens and Dolfing 1998, Kerr and Eimers 2012, Schaumann et al. 2013). The occlusion of these metal cations during diagenesis might have a substantial effect on the properties of oxygen-containing functional groups such as the carboxyl group or phenol group in humic or fulvic acids and subsequently on kerogen and coal.

1.7 Rationale

The main thrust related to study sedimentary organic matter was to identify the origin of petroleum including characterising the marine depositional conditions under which the precursors formed (Trask 1932). Given the current state of knowledge, the mechanism of organic accumulation and preservation in marine sediments for the formation of source rocks is still an active research in the field of petroleum geochemistry. Interestingly, almost 99.9 % of organic carbon is stored in sedimentary rocks (Berner 1989, Blair and Aller 2012) and the potential fossil fuels only account for ~ 0.05 % of total sedimentary organic carbon (Hunt 1996a, Kvenvolden 2006, Chandra and Sinha 2008, Bennett et al. 2009).

Based on the literature review I suspect adsorption describing mineral-organic interactions has a direct influence on kerogen or fossil fuel formation. Despite the presence of kerogen formation theories such as the classical degradation-recondensation model (Tissot and Welte 1984) and selective preservation model (Largeau et al. 1984, Tegelaar et al. 1989, Boussafir and Lallier-Vergès 1997), yet there is a need to test the sorption-protection model by determining the adsorption of particular organic compounds on mineral surfaces.

Hitherto techniques such as thermal degradation or pyrolysis have been used for the structural elucidation of macromolecules such as kerogen (Ellis et al. 1999, Larter and Horsfield 2013).
I consider this approach as a bottom-up approach to understand the formation of kerogen or fossil fuels. Pyrolysis of kerogen generates characteristic hydrocarbons which to an extent provide an understanding of the structure of the parent kerogen. For instance, hydrocarbons generated from Type I and II kerogens mainly include alkane/alkene pairs, substituted benzenes, naphthalenes, phenanthrenes, and phenols while type III kerogen pyrolysates are more aromatic mainly due to ligneous debris than the Type I and II kerogens (Ellis et al. 1999). Besides these compounds, homologous series of alky cyclohexane and alkyl benzene hydrocarbons are also reported from pyrolysis of kerogen (Derenne et al. 1990, Gelin et al. 1994). The formation of above-mentioned classes of hydrocarbons from pyrolysis of kerogen is thought to be due to cyclisation and aromatisation of linear functional units from lipid precursors such as fatty acids and fatty alcohols (Derenne et al. 1990, Douglas et al. 1991).

In contrast to the bottom-up approach mentioned above, use of the top-down approach for understanding the dynamics of organic compounds interactions with minerals surfaces during diagenesis might be interesting. By and large, this approach will substantially focus on diagenesis and then the synthesis derived from this focus can then be used to understand the hydrocarbons that might plausibly be present in kerogen or fossil fuels. Fig. 1 shows the two approaches and the focus of this study.

Objectives of the present study are discussed in the next section along with the chapter-wise breakdown.
Fig 1.3 Left shows top-down approach for the formation of kerogen/fossil fuel, concentrating on early diagenesis and diagenesis in which low molecular weight compounds (LMW) such as fatty acid interactions with mineral surface is the focus of the present study. Flow sheet of the oil and gas formation from kerogen was modified from (Durand 1980, Tissot and Welte 1984, Vandenbroucke et al. 1993, Durand 2003). Right shows bottom-up approach for characterising the kerogen structure that involves pyrolysis or thermal degradation techniques. Pyrolysates from kerogen heating alone and kerogen heating with minerals include alkanes/alkenes, benzenes, phenantharenes, naphthalenes, phenols, alkylbenzene hydrocarbons and alkylcyclohexane (Ellis et al. 1999, Pan et al. 2009).

1.8 Objectives

The aim of this study is two-fold firstly to quantify the adsorption of long chain fatty acids on carbonate and clay minerals to envisage the importance of the adsorption process during diagenesis, and secondly to comprehend the fatty acid-mineral interaction for the formation of different classes of hydrocarbons via flash pyrolysis. The project also aims to understand the industrial implication of diagenetic occlusion of divalent cations on macromolecules by pyrolysing the aromatic compounds. Fig 1.4 shows the scheme followed as objectives in this research project.
1.9 Structure of this thesis

The four investigative chapters of this thesis will address the objectives in details.

Chapter 2 presents the novel adsorption and pyrolysis methods developed for this study along with the sample preparation steps and analytical techniques used in this study.

Chapter 3 investigates the adsorption of tetradecanoic acid in aqueous NaCl solution (35 %) on one of the carbonate minerals i.e. calcite. The adsorbed tetradecanoic acid-calcite minerals were then flash pyrolysed by using pyrolysis-gas chromatography-mass spectrometry. Tetradecanoic acids salts of sodium, calcium, and magnesium were flash pyrolysed to compare the pyrolysis products with the pyrolysates from tetradecanoic acid-calcite to understand the transformation of fatty acid to different classes of hydrocarbons in the presence of calcite minerals.

Chapter 4 attempts to determine the adsorption of tetradecanoic acid in aqueous NaCl solution (35 %) on 1:1 phyllosilicate minerals i.e. kaolinite. The adsorbed tetradecanoic acid-kaolinite minerals were then flash pyrolysed to understand the formation of different classes of hydrocarbons. Further adsorption and pyrolysis experiments were performed on alumina and silica to understand the interaction of two functionalities i.e. one siloxane (tetrahedral face) and one hydroxyl surface (octahedral face) of kaolinite with tetradecanoic acid.

Chapter 5 examines the adsorption of tetradecanoic acid in aqueous NaCl solution (35 %) on phyllosilicate mineral i.e. 2:1 montmorillonite. The adsorbed tetradecanoic acid-montmorillonite minerals were then flash pyrolysed to determine the transformation of tetradecanoic acid on montmorillonite. Further, the adsorption of tetradecanoic acid on montmorillonite and their pyrolysis products were compared with the fatty acid adsorption on kaolinite and its pyrolysis products.

Chapter 6 probes the use of mono and di-aromatic acids and their calcium salts for flash pyrolysis. The products were compared and an intrinsic approach was given to improve the liquid hydrocarbon yield from macromolecules such as coal.

Chapter 7 summarises the conclusions and discusses the application of this study by focusing on adsorption, diagenesis, fatty acid and minerals contribution to the classes of hydrocarbons.
formed. The chapter also outlines the future work required as a forward step from the present work.

Fig 1.4 Research project objectives scheme
1.10 Publication

Following work has been published in a journal


Most of the work included in publication (Zafar et al 2016) (See Appendix A) has been taken from Chapter 3. This was the first study as a part of this research project and it focuses on understanding the adsorption of fatty acids on calcite minerals in the context of diagenesis and the use of flash pyrolysis on adsorbed fatty acids mineral samples to gain insight into the transformation of fatty acids into different classes of organic compounds.

Work is in progress to submit Chapters 4, 5 and 6 as publications. Thesis chapters are written in a comprehensive style including introduction, literature review, experimental and discussion sections. Work on adsorption of aromatic acids on minerals was part of this research project, however, only flash pyrolysis of aromatic salts (Chapter 6) is included as part of this thesis.
Chapter 2

Experimental workflow

*Imperial college London, Lab B109: Photo taken during pyrolysis tube preparation*
2.1 Introduction

Adsorption of organic compounds on mineral surfaces is a natural phenomenon and to mimic this process at the laboratory scale requires a specifically designed analytical method. Besides the choice of minerals and organic compounds, adsorption experiments extensively rely on the way the experiments are performed. Quantitative analysis in adsorption experiments heavily depends on sample preparation. The next critical step after deciding upon materials and methods is the choice of analytical techniques for the quantitation and interpretation of results. Use of specifically designed analytical instruments helps to optimise the methods of analysis which ensures that the data obtained are of high quality and the interpretation of data is precise and up to the mark.

The two theoretical approaches used as part of this research work are adsorption and flash pyrolysis and the two key analytical techniques used are gas chromatography-flame ionisation detector (GC-FID) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), with supplementary data provided by Fourier transform infrared spectroscopy (FTIR). In subsequent sections, first theories of adsorption and pyrolysis are discussed then sample preparations along with the general overview of the equipment are given. In the method development section, a comprehensive discussion shows how the method is employed for each instrument based on the requirement of the experiment. The schematic representation is shown in Fig 2.1.
Fig 2.1 Schematic view of experimental plan
2.2 Adsorption & adsorption isotherms

Generally, adsorption is considered as a concentration of a substance at the surface or it can be defined as an equilibrium between adsorbed and dissolved phases of target adsorbate (James Cleaves Ii et al. 2012).

Adsorption is mainly expressed in the form of isotherms which can be termed as sorption or adsorption isotherm commonly used to determine the concentration of retained solute or solid particle on the mineral surface. The adsorption isotherm is expressed via $Q = f(C)$ relationship in which $C$ (mol L$^{-1}$ or kg L$^{-1}$), is the remaining solute concentration of a compound and $Q$ (mol kg$^{-1}$ or kg kg$^{-1}$) is the concentration of the same compound adsorbed on the mineral surface (Limousin et al. 2007). Different authors use different terms to express isotherms such as retention isotherm, adsorption isotherm (Sposito 1984) or the curve of the disappearance of the solute (Schweich and Sardin 1981), however, in this study, I will use adsorption isotherm as a unanimous term for the adsorption of fatty acids on minerals. Fig 2.2 shows the simple illustration of adsorption of an organic compound on the solid surface.
Adsorption isotherm is mainly classified into four classes i.e. C-isotherm, S-isotherm, L-isotherm and H-isotherm (Giles et al. 1974). The four classes of isotherms are also divided into subgroups and subclasses based on the plateaus, points of inflection and maxima (Fig 2.3).

Here I will briefly discuss the four main classes of adsorption isotherm. The C-isotherm shows that the ratio called the distribution coefficient or partition coefficient between the concentrations of the compound remaining in solution and adsorbed on the solid is the same at any concentration (Giles et al. 1974, Limousin et al. 2007). In contrast to the C-isotherm, the L-isotherm shows a decrease in ratio between the concentration of the compound retained in solution and adsorbed when the solute concentration increases and the isotherm is often expressed as a curve that reaches a strict asymptotic plateau or that does not reach any plateau (Giles et al. 1974, Limousin et al. 2007). The H-isotherm is a slightly modified form...
of the L-isotherm in which an initial high slope shows the great affinity for solid (Toth 1994). The curve in the S-isotherm is sigmoidal and shows the point of inflection which indicates the cooperative adsorption between the adsorbed molecules on the mineral surface (Giles et al. 1974, Hinz 2001).

<table>
<thead>
<tr>
<th>Class</th>
<th>Subgroup</th>
<th>vs. c</th>
<th>vs. ( K_d )</th>
<th>vs. log ( K_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>convex</td>
<td>positive slope</td>
<td>positive slope</td>
</tr>
<tr>
<td>L</td>
<td>1</td>
<td>convex</td>
<td>negative slope, curve</td>
<td>negative slope</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>curve</td>
<td>negative slope, curve</td>
<td>negative slope</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>line</td>
<td>zero slope</td>
<td>zero slope</td>
</tr>
<tr>
<td>SLH</td>
<td>2</td>
<td>plateau, inflection</td>
<td>seg. slope, line or curve</td>
<td>( c_m ) or low ( K_d )</td>
</tr>
<tr>
<td>SLH</td>
<td>3</td>
<td>plateau, inflection</td>
<td>minimum</td>
<td>minimum</td>
</tr>
<tr>
<td>SLH</td>
<td>4</td>
<td>plateau, rise, plateau</td>
<td>maximum</td>
<td>maximum</td>
</tr>
</tbody>
</table>

Fig 2.3 Four classes of isotherms are also divided into subgroups and subclasses based on the plateaus, points of inflection and maxima.
2.2.1 Isotherms modelling

Various isotherm equations have been used to mathematically interpret the adsorption isotherms (Limousin et al. 2007). Simple Freundlich and Langmuir isotherm equations are most frequently used to explain the adsorption isotherm. The Freundlich isotherm is mathematically expressed as $Q_e = K_f C_e^{(1/n)}$, where $Q_e$ is the adsorbed quantity and $C_e$ is the remaining solute concentration, $K_f$ (L kg$^{-1}$) is the adsorption capacity and $1/n$ is the adsorption intensity (dimensionless) evaluated by linearizing the equation (Freundlich 1909). Both $K_f$ and $1/n$ are empirical constants and depends on various factors. The value of $n$ is greater than 1 and if $1/n$ is equal to 1, this shows the equation is linear. The value of $1/n$ usually lies within the range of 0.1 and 1.0 and is indicative of favourable adsorption of chemical species on adsorbent (Marco Aurelio et al. 2005). The logarithmic form of equation, $\log q_e = \frac{1}{n} \log C_e + \log k_f$ is a straight line with the slope of $1/n$ and intercept of $\log k_f$ are used to determine the values of $k_f$ and $1/n$ (Limousin et al. 2007).

The main assumption of simple Freundlich isotherm is that the isotherm does not achieve a plateau as the remaining solute concentration increases and its most frequently use to explain L and H adsorption isotherms (Limousin et al. 2007). In some cases, the Freundlich isotherm is also used to explain S-isotherm (Parbhakar et al. 2007).

Simple Langmuir isotherm is the most frequently used isotherm to explain monolayer adsorption. The Langmuir isotherm first shows a steady rise in adsorption with an increase in solute concentration, and finally approaches an asymptotic maximum point which reflects monolayer adsorption of a particular solute (James Cleaves II et al. 2012). The mathematical expression of the Langmuir model is given by $q_e = \frac{Q_{max} b C_e}{1 + b C_e}$, where $C_e$ is the equilibrium concentration of analyte in solution (µM of tetradecanoic acid / L), $q_e$ is the equilibrium sorption capacity (µmol/g sorbent), $Q_{max}$ is the maximum adsorption capacity (µmol/g sorbent), $b$ is constant (L/g) (Langmuir 1918). The linearised form of Langmuir model ($C_e/q_e = 1/Q_{max} b + C_e/Q_{max}$) can be used to obtain the parameters $Q_{max}$ and $b$ from experimental data on equilibrium concentration and adsorbent loading.

Further to that the Langmuir isotherm mainly follows two assumptions, firstly all the adsorption sites are equal and retain only a single molecule of the adsorbed compound, secondly the adsorption sites are energetically and sterically independent of the amount of adsorbed compound (Langmuir 1918). Due to the complexity of the natural environment, however, the Langmuir isotherm of adsorption is sometimes considered as a grossly oversimplified model.
2.3 Sample preparation

2.3.1 Mineral preparation

Pure calcite mineral was purchased from Sigma-Aldrich while montmorillonite, SWy-2 (Na-rich) and kaolinite, KGa-1b was obtained from the Source Clay Repository of the Clay Mineral Society.

Both calcite and clay minerals were extensively cleaned to avoid any contamination. Calcite mineral was stirred with 10 % H$_2$O$_2$ (Sigma-Aldrich) at 80 °C and then rinsed with deionized water (18.2 MΩ cm$^{-1}$) to remove any organic impurity.

Both clay minerals were first stirred with 1.0 M HCl (Fischer Scientific) for 1 hour to remove any calcite and then rinsed with deionized water until a neutral pH was observed (Fig 2.4). The dissolution of calcite left some Ca$^{2+}$ ions in the interlayer of clay minerals that were removed by exchanging them with (0.01 M) NaCl (Fischer Scientific). Clay samples were then subsequently washed with deionized water until the chloride ions could not be detected using the AgNO$_3$ method (Fig 2.5). In the last step, clay samples were stirred with H$_2$O$_2$ at 80 °C to remove any organic impurity.
˚C for 1 hour and then rinsed with deionised water for 5 times to remove any organic impurity.

Fig 2.5 Montmorillonite mineral in 50 mL centrifuge tubes for washing with deionised water

2.3.2 Adsorbate preparation (Fatty acid solution)

Tetradecanoic acid (Sigma-Aldrich) was used in all adsorption experiments. The main obstacle in adsorption experiments was the low solubility of tetradecanoic acid in water (0.0024 g/100 mL water). The solubility limitations in adsorption experiments were overcome by taking two steps; first was the use of a minimum concentration of fatty acids in adsorption experiments and second was the use of solvents such as methanol in small amounts to aid dissolution of tetradecanoic acid. For the adsorption experiments, a stock solution (219 µM) was first prepared by dissolving 0.002 g of tetradecanoic acid in 2 ml of methanol and then this mixture was added to 98 ml of deionised water containing 3.5 gm of NaCl. The resulting solution was then heated at 27 °C. Dilute concentrations in the range of 22-175 µM were subsequently prepared from the stock solution for adsorption experiments.
Experimental work also includes sub-analysis of aliphatic carboxylate salts of calcium, magnesium and sodium cations and aromatic carboxylate salts of calcium were synthesised from laboratory grade reagents according to the methods available in the literature (for full details see Chapter 3 & 4 method section).

2.3.3 Organic solvent extraction

Extraction of unadsorbed fatty acids in supernatant solution after 24 hours of equilibration was performed by using dichloromethane (DCM) (Fig 2.6 a & b). The DCM extraction step was repeated 3 times (x 5 ml) for each sample and the extracts were combined in a round bottom flask and then concentrated using a rotary evaporator. Anhydrous sodium sulphate was used as a dehydrating agent to remove any residual water from the DCM extracts (Fig 2.7 a, b & c).
Fig 2.6 a, b. Sample preparation for GC-FID; After equilibration for 24 hours, supernatant solutions were separated from glass tubes for liquid-liquid extraction.
Fig 2.7 a, b, c. GC-FID sample preparation: a) After 24 hours of equilibration, supernatant solution containing unadsorbed tetradecanoic acid was separated from minerals and the extracted in DCM using separatory funnel and round bottom flask, b) DCM extract containing unadsorbed tetradecanoic acid was concentrated in a rotary evaporator and then collected in an insert vial for GC-FID analysis. c) Insert vial rack containing samples and blanks in insert vials for GC-FID analysis.
2.3.4 Internal standard

Saturated fatty acids with odd carbon number (CN) are most commonly used as an internal standard due to their low abundance in natural samples. In this study, heptadecanoic acid (C\textsubscript{17}) was used as an internal standard in adsorption experiments. Calibration standards with the same concentrations of tetradecanoic acid were also prepared in DCM for the quantitative analysis by GC-FID.

2.4 Instrumentation

2.4.1 Gas chromatography-flame ionisation detector (GC-FID)

GC has been used for half a century in a number of research areas for fatty acids (Seppanen-Laakso et al. 2002). The instrument had undergone a number of improvements to achieve higher sensitivity, accuracy, and precision over a period of time. Accessories such as support materials for packed columns, liquid phases of different polarities and detector systems, thermal conductivity (Craig and Murty 1959) and flame ionisation detectors (Horning et al. 1964) have become common to GC analytical work. The improvement in accuracy and reproducibility, along with the new methods such as cold on-column injection (Schomburg et al. 1981) and the programmed temperature vaporisation technique (Schomburg et al. 1983) are some of the major improvements that have led to GC use for various kind of analyses (Seppanen-Laakso et al. 2002 and references therein).
2.4.2 Equipment overview

GC-FID is a sensitive, simple technique and has long been used for analysis and identification of fatty acid isomers in natural and synthetic samples. GC-FID analyses were performed on a PerkinElmer Auto System XL gas GC-FID fitted with a FID detector (Fig 2.8 a & b). The column used was a 30 m J & W Scientific DB-FFAP column, 0.25 mm internal diameter and 0.25 µm film thickness. Splitless and split liners were used for solvent injection. Totalchrom Navigator software was used for data analysis and quantification (Fig 2.9 a, b & c).

2.4.3 Method development

Instrument optimisation is an essential step in any analytical procedure and affects data quality. The nature of analyte and the choice of solvent are some of the factors that influence the response of the instrument to samples. Instrument optimisation includes changes in instrument parameters to obtain quality data.

Previously, different methods were used for the quantitation of unadsorbed fatty acids. Meyers and Quinn (1971b) used multiple analytical steps such as saponification and esterification for the quantitation of acids during which loss of sample might have occurred. Similarly, Suess (1973) measured the unadsorbed fatty acid in his experiment but he used the 14C-labelled stearic acid and the concentrations were measured by liquid scintillation counting. Liquid scintillation counting is a sensitive technique, however and the procedure involved in this technique required first cooling and then filtering unadsorbed fatty acid. Cooling of unadsorbed fatty acid causes precipitation at room temperature and likewise filtering might also cause loss of sample. Therefore for the current study, I developed a novel method by using a direct quantitation approach which involves fewer analytical steps and therefore the data obtained is of high precision.

Initially, adsorption experiments were performed on different fatty acids such as C_6, C_{10} and C_{12} and the amount of unadsorbed fatty acid was quantified in water with the split injection method. Quantification of unadsorbed fatty acids in water did not indicate any peak from GC-FID and suggested that the unadsorbed analyte is present in a trace amount and cannot be quantified using the split injection method. The unadsorbed fatty acid was then analysed in splitless injection mode after extraction in DCM. Sample volumes used were in microliters.
due to the low concentration of unadsorbed fatty acid and high sensitivity of GC-FID for fatty acids. The main steps for GC-FID set up are shown in Table 2.1. The automatic sampler was used to obtain a high degree of reproducibility in a sequence of runs. Insert vials were used for sample quantitation in GC-FID to minimise the chance of DCM evaporation while queued on the autosampler.

Table 2.1. GC-FID operating parameters. Split and splitless injection methods were used to optimise the quantification of unadsorbed tetradecanoic acid in adsorption experiment. Splitless method with DCM was then used to quantify the unadsorbed tetradecanoic acid in all adsorption experiments.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Setting</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection method</td>
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<td>Splitless</td>
</tr>
<tr>
<td>Solvent</td>
<td>Water</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>Start temperature (°C)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Hold time (minutes)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ramp (°C min⁻¹)</td>
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<td>10</td>
</tr>
<tr>
<td>Final temperature (°C)</td>
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<td>240</td>
</tr>
<tr>
<td>Hold time (minutes)</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Injector temperature (°C)</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>Flow rate (ml min⁻¹)</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Split ratio</td>
<td>10:1</td>
<td>--</td>
</tr>
</tbody>
</table>
Fig 2.8 Data acquisition in GC-FID: a) Front screen of GC-FID b) Autosampler containing samples in insert vials for analysis
2.4.4 Quantification

Quantitation in the capillary GC-FID is an accurate technique and the advantage of this technique is that the quantitative response of the FID is approximately the same for equal weights of any hydrocarbons. Therefore quantitation of fatty acid is based on the comparison of their peak areas and the peak area of a suitable internal standard (Johansen et al. 1983).

Relative response factor (RRF) was used to quantify the unadsorbed acid after the adsorption experiment (Matisova 1998). Firstly the individual response factors were calculated. Response factor A (calibration standard analyte; tetradecanoic acid, C$_{14}$) and response factor B (internal standard; heptadecanoic acid, C$_{17}$) were calculated first to determine the RRF. The pre-determined RRF between calibration standard analyte and internal standard were then used to quantify an unknown concentration of tetradecanoic acid (unadsorbed acid) in the presence of a known concentration of internal standard, C$_{17}$. Response factor for each concentration analyte i.e. (C$_{14}$) and internal standard (C$_{17}$) acid is determined by using equation (1).

\[
Response \ Factor = \frac{\text{Peak area}}{\text{Concentration}} \quad (1)
\]

Then the relative response factor is determined by using the equation (2).

\[
\text{Relative Response Factor (RRF)} = \frac{\text{Response Factor A}}{\text{Response Factor B}} \quad (2)
\]

The amount of unadsorbed fatty acid for each concentration is then measured by using equation (3). In this equation, peak area A is the area of unknown concentration of unabsorbed tetradecanoic acid and peak area B is the area of internal standard used, RRF is the relative response factor calculated from response factors of standard analyte concentration and internal standard while concentration B is the concentration of internal standard which is 300 µg/1000 µl.

\[
\text{Concentration A (unadsorbed tetradecanoic acid)} = \frac{\text{Peak area A}}{\text{Peak area B}} \times 1 \times \frac{1}{\text{RRF}} \times \text{Concentration B} \quad (3)
\]
Finally the amount of adsorbed fatty acid is then measured by subtracting the concentration $A$ of tetradecanoic acid from the initial concentration.

### 2.4.5 Interpreting data

Data acquisition in GC-FID results in a chromatogram (See Chapters 3, 4, 5, & 6). Detector response (mV) is on the vertical axis, and the time runs along the bottom of the chart. The overall detector response is shown in a basic plot called a total ion chromatogram (TIC). The peak area was identified based on the specific retention time of analyte (tetradecanoic acid; 18.265 min) and internal standard (heptadecanoic acid; 20.945 min). The peak area was calculated by using the manual integration tool in Totalchrom Navigator analysis software. The peak areas were acquired from the display peak report section in the software and were used to calculate RRF as shown above.
Fig 2.9 a, b. GC-FID analysis: Totalchrom Navigator software showing analysis of samples in GC-FID to quantify unadsorbed fatty acid
2.5 Pyrolysis GC-MS

2.5.1 Pyrolysis of organic-mineral compounds

Artificial maturation is an important aspect of petroleum exploration. Thermal degradation techniques such as pyrolysis have been used for the characterisation of organic molecules and to simulate maturation process. Pyrolysis is almost 20-30 years old analytical technique used to degrade large molecules into smaller volatile molecules on heating (Sobeih et al. 2008). Although significant difference exists in the heating rate between laboratory pyrolysis (heating rate; \(~ 10^{-1} \) K/min) and geological maturation (heating rate; \(10^{-10} \) to \(10^{-12} \) K/min) (Saxby and Riley 1984), pyrolysis experiments have been used for the analysis of petroleum related compounds such as humic acid or fulvic acid (Faure et al. 2006a, Faure et al. 2006f), kerogen (Tannenbaum and Kaplan 1985a, Pan et al. 2008), and synthetic organic compounds (Liu et al. 2013h, Yuan et al. 2013). Pyrolysis, combined with gas chromatography and/or mass spectrometry is an easy to use and effective technique for the structural elucidation of macromolecules and organic compounds. More importantly, the technique has been used to define kerogen classes (Douglas and Maxwell 1980, Philp and Mansuy 1997). Py-GC-MS has been used by various studies for the analysis of pure organic compounds as well as macromolecules (Meier and Faix 1992). The chromatographic information obtained from pyrolysis of compounds is used to determine the composition or structure of compounds (Sobeih et al. 2008).

The use of pyrolysis experiments is particularly advantageous to understand the importance of organic-mineral interactions during petroleum formation. Owing to the high surface area (Sing et al. 1985), clay minerals tend to adsorb heavy compounds generated during pyrolysis which influence the pyrolysis maturity indicator, composition, and quantity of the pyrolysate and kinetics of the reaction (Horsfield et al. 1983, Dąbrowski 2001, Yang and Horsfield 2016). Furthermore, clay minerals also affect the gas oil ratio, aromaticity, oxygen index of the pyrolysis products due to their catalytic properties (Dembicki Jr 1990, Wu et al. 2012).

Generally, three main classes of pyrolysis are used in maturation studies; open pyrolysis, closed pyrolysis which includes hydrous and anhydrous pyrolysis and flash pyrolysis. Each of this pyrolysis class has specific properties. For example, hydrous pyrolysis is part of a closed pyrolysis system which generates a larger amount of oil than any other pyrolysis

Recently, online or flash pyrolysis has been used for carboxylic acids and carboxylate salts (Lappi and Alen 2009) reporting reaction mechanisms such as decarboxylation, decarbonylation, and dehydration for the formation of different organic compounds. For instance, hydrocarbons have been reported by decarboxylation of a fatty acids-bentonite mixture in the presence and absence of water (Jurg and Eisma 1964) and fatty acids-montmorillonite mixture (Shimoyama and Johns 1971). Likewise, Shimoyama and Johns (1972) also reported hydrocarbon formation with two carbon atoms less than the parent fatty acids in the presence of calcium carbonate.

### 2.5.2 GC-MS overview

GC-MS analyses were performed on a 7890 gas chromatograph coupled to a 5975 mass selective detector (both Agilent Technologies). The column used was a 30 m J&W Scientific DB-5MS ultra inert column of 0.25 mm internal diameter and 0.250 µm film thickness. Single taper deactivated liners were used for solvent injection. ChemStation control & data analysis software was used.

### 2.5.3 Sample preparation for pyrolysis GC-MS

Wet mineral samples from adsorption experiments were frozen in liquid nitrogen and then dried in a vacuum freeze dryer for 5 hours. The samples were dried in the same glass tubes in which adsorption experiments were performed (Fig 2.10 a, b). The dried mineral samples were then homogenised prior to using in pyrolysis GC-MS (Fig 2.11 a, b & c). Carboxylic salts were synthesised in the laboratory and washed with water and chloroform to control any contamination. Carboxylic acids salts were dried at 110 °C in an oven to remove any moisture prior to using them in pyrolysis GC-MS (See Chapter 3).
Fig 2.10 a, b. Pyrolysis-GC-MS sample preparation: a) Mineral samples obtained from adsorption experiments were freeze dried in liquid nitrogen in an open Dewar. b) After freeze drying, mineral samples were capped with aluminium foil with a small hole in it and placed them in vacuum drier flasks.
Fig 2.11 a, b, & c. Sample preparation for pyrolysis-GC-MS: a) Vacuum freeze dryer containing acids adsorbed mineral samples for drying. b) Flask connected to the freeze dryer containing acid adsorbed mineral samples. c) Glass tubes containing acid adsorbed mineral samples after drying in vacuum freeze dryer.
2.5.4 Pyrolysis-GC-MS method development

Two Py-GC-MS methods were used to pyrolyse the three types of samples i.e. pure carboxylic acids, fatty acid adsorbed minerals, and carboxylic acid salts.

Pure fatty acids were analysed on a 5200 Pyroprobe (CDS Analytical) coupled via a heated transfer line (320 °C) to GC-MS (See section 3.2.1). A minimum quantity of pure acids (~ 0.5 mg) was employed in a quartz pyrolysis tube, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms⁻¹ the sample was held at this temperature for 15 s in a flow of helium, and upon pyrolysis the interface was heated from 40 to 350 °C at 100 °C s⁻¹ where it was held for 15 min to prevent volatilisation of the samples prior to pyrolysis.

Carboxylic acid adsorbed minerals and carboxylic acid salts were analysed on a 2000 Pyroprobe (CDS Analytical) unit fitted via a 1500 valve interface and coupled to GC-MS (See Chapters 3, 4, 5 and 6). Dried carboxylic acid adsorbed samples from adsorption experiments and carboxylic acid salts were loaded in quartz pyrolysis tubes, with quartz wool at each end. Approximately 20 mg of calcite samples and 10 mg of each kaolinite, montmorillonite and calcite-clay mineral mixture were used for pyrolysis experiments (Fig 2.12). Due to high purity, carboxylate salts were used in minimum quantities (~ 5 mg). Following heating to 650 °C at a rate of 20 °C ms⁻¹ the sample was held at this temperature for 15 s in a flow of helium. The interface was held at 200 °C until pyrolysis when it was ramped to 350 °C at 60 °C s⁻¹. The pyrolysis interface temperature has a major effect on the pyrolysates of particularly fatty acid adsorbed minerals. Preliminarily when interface temperature was kept at 200 °C the high molecular weight compounds were not observed, however as the temperature was ramped from 200 to 350 °C a full range of compounds were observed in the pyrolysates (Fig 2.13). In addition, the pyrolysate of carboxylate salts does not show much difference from those of Lappi and Alen (2009) who have used high interface temperature for the pyrolysis of sodium salts. The main steps of GC-MS set up are shown in Table 2.2.

For pure samples such as carboxylic acids and salts, the split mode is operated with a high split ratio. The higher split ratio is beneficial as it is associated with a greater efficiency of sample transfer (Blokker et al. 2005). However, the low split ratio is suitable for low analyte samples such as carboxylic acid adsorbed minerals so that a lesser amount of sample will be...
swept out of the split vent. Blanks were run before running samples and also between samples to minimise the cross-contamination from compounds remaining in transfer lines. Pyrolysis of adsorbed carboxylic acid mineral samples required extreme care as any irregularity in sampling and then in pyrolysis can change the quantity and quality of pyrolysates.

![Pyrolysis-GC-MS samples](image)

Fig 2.12 Pyrolysis-GC-MS samples: Dried mineral mixture of montmorillonite (10 mg), kaolinite (10 mg) and calcite (20 mg) for pyrolysis experiment
Table 2.2. GC-MS operating parameters for pyrolysis of pure carboxylic acids, carboxylate salts and carboxylic acids adsorbed minerals. Split ratios for carboxylic acid adsorbed minerals are less than the split ratio of pure carboxylic acids and salts.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start temperature (°C)</td>
<td>35</td>
</tr>
<tr>
<td>Hold time (minutes)</td>
<td>2</td>
</tr>
<tr>
<td>Ramp (°C min⁻¹)</td>
<td>5</td>
</tr>
<tr>
<td>Final temperature (°C)</td>
<td>300</td>
</tr>
<tr>
<td>Hold time (minutes)</td>
<td>20</td>
</tr>
<tr>
<td>Injector temperature (°C)</td>
<td>270</td>
</tr>
<tr>
<td>Flow rate (ml min⁻¹)</td>
<td>1.1</td>
</tr>
<tr>
<td>Scan range (amu)</td>
<td>50-500</td>
</tr>
<tr>
<td>Split ratio for pure carboxylic acids</td>
<td>50:1</td>
</tr>
<tr>
<td>Split ratio for carboxylic salts</td>
<td>50:1</td>
</tr>
<tr>
<td>Split ratio for carboxylic acid adsorbed minerals</td>
<td>10:1</td>
</tr>
</tbody>
</table>

2.5.5 Interpreting data and Quantification

Data acquisition result into total ion current (TIC). TIC represents the overall detector response. The total ion current plot shows time on the x-axis and detector response is shown as abundance on a vertical axis. Peaks were identified by using software and also confirmed by extracting a particular mass/charge value from the total signal, called an extracted ion chromatogram.

Semi-quantification was performed on total ion chromatograms of carboxylic acids adsorbed mineral samples. Manual integration tool in ChemStation control & data analysis software was used to quantify the peak area. The quantified peak areas were then used to calculate the ratios of hydrocarbons to ketones and aldehydes (See Chapters 3).
Fig 2.13 Comparison of TIC obtained from flash pyrolysis of tetradecanoic acid adsorbed on calcite. At low interface temperature (200 °C) high molecular weight products are not observed when the temperature is ramped from 200 to 350 °C, a full range of high molecular weight products are observed.
### 2.5.6 Contamination control

Contamination control was a major part of sample preparation in adsorption experiments and also later on running samples on analytical instruments. Adsorption experiments are quantitative and any contamination might seriously affect the end results. To control organic or inorganic contamination, glassware was extensively cleaned in multiple steps (Fig 2.14). First, the glassware was soaked overnight in a Decon bath and then thoroughly rinsed with tap water. After drying them at room temperature they were first rinsed with DCM, methanol, and then with deionised water. After washing, glassware was dried in an oven at 110 °C.

![Fig 2.14 Glass tubes cleaning for adsorption experiments](image)

Pyrolysis tubes were also extensively washed prior to analysis. Following the dry cleaning step, pyrolysis tubes were first rinsed with deionised water and rinsed with a dilute HCl solution (0.0001 M). Afterward, pyrolysis tubes were then extensively washed with deionised water making sure that no HCl residue was left over and then dried in an oven at 110 °C. Pyrolysis tubes were then sterilised with a butane torch as the last step of cleaning.
Quartz wool used in pyrolysis experiments was cleaned by heating at a temperature of 500 °C for 5 hours in the furnace. Cleaning quartz wool at a high temperature was not only meant to remove contamination but also to control any moisture which could affect the pyrolysis products.

Besides the above-mentioned cleaning procedures, every attempt was made to minimize exposure to typical contaminants. Use of a rotary evaporator to reduce the DCM extract was a critical step and the sample analysis in GC-FID confirmed the quality of samples obtained from the rotary evaporator. Therefore the rotary evaporator was cleaned thoroughly during the sample preparation. Rotary evaporator condenser and adapter were rinsed with DCM at the start of sampling and then rinsed again after every 3 samples.

The analytical instruments can also carry contamination such as residues from previously analysed samples, therefore to avoid residual contaminations blanks were run at intervals between samples.

2.5.7 Fourier Transform – Infrared Spectroscopy

Data acquisition by FTIR is based on the excitation of vibrational motions of ionic lattices and covalently bonded molecules by infrared radiations (IR). Commonly FTIR spectra are collected by transmission modes (KBr pellets, Nujol mulls, disposable cards, liquid cells, and gas cells), reflection modes attenuated total reflection (ATR), diffuse reflectance, and specular reflectance (Tao 2012).

ATR with FTIR is a fast analytical technique in comparison to traditional IR transmission spectroscopy as it requires less sample preparation, gives better reproducibility and precise verification and identification to collect spectra from different media such as solids, liquids, semisolids, and thin films (Rodriguez-Saona and Allendorf 2011). IR beam travelling inside the crystal create an evanescent wave (standing wave of radiation) which interact with the sample in contact with the crystal. The sample then absorbs IR radiation and the energy difference between incident radiation and transmitted radiation is detected and measured in wavenumber cm$^{-1}$. The technique is named ATR, due to the attenuation of evanescent wave by the sample’s absorbance. Typically, the crystal used in ATR-FTIR is made of diamond, zinc selenide, KRS-5 (thallium iodide/thallium bromide), or germanium. Depending on the
length and thickness of the crystal and the angle of incidence, the number of reflections at the surface of the crystal varies (Rodriguez-Saona and Allendorf 2011).

The purity of carboxylic acids and carboxylate salts were assessed by ATR-FTIR (Nicolet™ 5700 spectrometer) (See Chapters 3 & 7). Background spectra were collected before each sample in order to compensate for the signal of the crystal. Background and sample spectra were acquired at 4 cm\(^{-1}\) as a typical resolution, and the spectra were acquired in the region of 400 to 4000 cm\(^{-1}\).
Chapter 3

Organic compound-mineral interactions: using flash pyrolysis to monitor the adsorption of fatty acids on calcite

Calcite crystal (Source: geologycafe.com)

Transparent calcite, Iceland spar, Mexico (Source: Geology.com)
3.1 Introduction

3.1.1 Diagenesis of organic compounds

Diagenesis represents a major link between Earth’s surficial carbon reservoirs and their counterparts in the geosphere (Berner 1982, Hunt 1996c). During diagenesis the juxtaposition of organic matter and minerals provides the opportunity for organic-inorganic interactions. There is a strong relationship between organic matter and clay minerals in petroleum source rocks and continental shelf sediments that has been explained on the basis of sorption of organic matter onto minerals (Salmon et al. 2000, Pichevin et al. 2004). The adsorption of organic molecules onto mineral surfaces has been proposed as a key mechanism for the enhancement of organic matter accumulation and preservation (Keil et al. 1994d, Mayer 1994a, Papadimitriou et al. 2002).

3.1.2 Organic compounds interaction on carbonate minerals

Adsorption protects organic compounds from microbial degradation in sediments (Henrichs and Sugai 1993, Wang and Lee 1993, Hedges and Keil 1995) and is controlled by various mechanisms such as ligand exchange, cation bridging, van der Waals interactions and hydrophobic effects (Theng 1979, Lü et al. 2010). The nature of adsorption is inevitably related to the organic compound being adsorbed and depends on various factors such as size and functional group content (Henrichs and Sugai 1993, Liu and Lee 2006, 2007). Adsorption to carbonate minerals is particularly important owing to the fact that carbonate minerals preferentially attract acidic organic compounds at their surface (Muller and Suess 1977, Carter and Mitterer 1978), besides incorporating organic compounds in intra- and inter-crystalline locations (Endo et al. 1995, Sykes et al. 1995a). Owing to the large surface area to volume ratio of fine grained calcium carbonate found in marine sediments, the potential for organic compound adsorption on to their surfaces is relatively high (Suess 1973, Carter and Mitterer 1978).

3.1.3 Adsorption of fatty acids on carbonate minerals

Previously, a few studies have investigated the adsorption of different classes of organic compounds such as sugars (Hedges 1977), amino acids (Jackson and Bischoff 1971, Hedges 1977) and fatty acids (Suess 1970, Meyers and Quinn 1971b, Lahann and Campbell 1980) on carbonate minerals in water. Fatty acids are a particularly important class of organic
compounds owing to their widespread occurrence in the biosphere and their role as sedimentary organic matter precursors (Killops and Killops 2009). Furthermore the number and scope of fatty acids adsorption studies on carbonate minerals are limited, possibly because of the relative insolubility of fatty acid compounds in water. Hence most of the fatty acids adsorption studies so far used organic solvents to achieve the solubility of fatty acids. Nonetheless it should be noticed that the use of organic solvents in adsorption experiments does not mimic the natural marine environment.

### 3.1.4 Flash pyrolysis as a thermal degradation technique

A common method for visualising the presence of organic compounds in mineral matrices is on-line or “flash” pyrolysis. The rapid thermal evaporation or dissociation of organic matter effectively liberates the compounds from their associated minerals. The pyrolysis of fatty acids has been used to investigate the production of hydrocarbon fuels (Lima et al. 2004, Maher and Bressler 2007, Prado and Antoniosi Filho 2009) but the technique has not been used previously to monitor the interactions of fatty acids and carbonate minerals.

### 3.1.5 Objectives

The primary purpose of this study was to investigate the behaviour of calcite towards the adsorption of tetradecanoic acid in a saline aqueous solution. Calcite-fatty acids interaction is then further used to explore the transformation of fatty acids into different classes of organic compounds via flash pyrolysis (on-line pyrolysis). The flash pyrolysis products obtained from pure tetradecanoic acid and calcite-tetradecanoic acid were then used to understand the process of fatty acids pathway into the geosphere by adsorption onto calcite mineral surfaces during diagenesis.

### 3.2 Experimental

#### 3.2.1 Preparation of calcite mineral

Approximately 10 g of calcite (Sigma-Aldrich) was placed into 250 ml conical flask and stirred with 10% H₂O₂ at 80 °C for 3 hours and then rinsed with deionized water (Type I, 18.2 MΩ cm⁻¹) 7 times before drying at 110 °C. The dried calcite was powdered in a pestle and mortar. The specific surface area of calcite was determined by micromeritics-Brunauer, Emmett and Teller (BET) gas (nitrogen) adsorption method analysis.
3.2.2 Preparation of fatty acid solution

The method for tetradecanoic acid stock solution preparation is given in Chapter 2, section 2.3.2. The NaCl (0.1 M) solution and tetradecanoic acid stock solution were used to prepare different fatty acid concentrations (22, 44, 88, 110 and 131 µM). An internal standard solution was prepared of heptadecanoic acid (3 mM) in DCM.

3.2.3 Preparation of calcium, magnesium and sodium salts of tetradecanoic acid

Calcium salt of tetradecanoic acid was prepared by adding calcium hydroxide solution (0.2 M; 0.9 g in 50 ml water) to the dissolved acid solution (0.2 M; 5 g in 100 ml water) at 50 °C, while stirring.

Magnesium tetradecanoate was prepared by adding sodium hydroxide solution (2.5 mM; 0.1 g in 20 ml of water) to tetradecanoic acid solution (2.5 mM; 0.5 g in 50 ml of water). Subsequently, magnesium chloride solution (1.2 mM; 0.25 g in 5.0 ml water) was added to the tetradecanoic acid/sodium hydroxide solution under vigorous agitation.

Sodium tetradecanoate was prepared by first adding sodium hydroxide solution 2.5 M (5 g in 50 ml water) to 5 ml ethanol (95%) solution. Tetradecanoic acid (5 g) was then added to the sodium hydroxide/ethanol solution and then heated at 40 °C on a hot plate for about 20 minutes. During heating a small amount of the 95% ethanol/water mixture was added to stop foaming in the reaction mixture. The mixture was then quickly combined with sodium chloride solution (0.8 M; 2.5 g in 50 ml water). In all cases, the resulting insoluble precipitates were filtered, washed with water and dried in air at room temperature. The dried powders were washed 3 times in chloroform and dried again at room temperature. The purity of tetradecanoic acid and tetradecanoate salts were assessed by ATR-FTIR (Nicolet™ 5700 spectrometer). Spectra were collected for 128 scans at a resolution of 4 cm⁻¹ in the scanning range of 400 to 4000 cm⁻¹ range (Fig 3.1).
Fig 3.1 ATR-FTIR spectra of tetradecanoic acid (black line), calcium tetradecanoate (red line), magnesium tetradecanoate (green line), and sodium tetradecanoate (blue line). C=O stretching absorption of 1700 cm\(^{-1}\) moves to the lower wave number for salts

### 3.3 Adsorption experiments

The tetradecanoic acid (219 µM) and NaCl (0.1 M) stock solutions were used to prepare five different concentrations (22, 44, 88, 110 and 131 µM) of tetradecanoic acid in 10 ml borosilicate test-tubes with 50 mg of calcite. The glass test-tubes were sealed with screw caps (PTFE liner) and placed in a rotator at a constant temperature of 23 ± 2 °C. The samples were equilibrated for 24 hours, after which the glass tubes were centrifuged 3 times for 5 minutes at 380 RCF and the supernatant was transferred into 20 ml glass tubes. Each glass test tube was rinsed with 5ml of water and centrifuged again for 5 minutes at 380 RCF to remove the excess acid attached to the walls of the tubes.
3.3.1 Quantification of unadsorbed tetradecanoic acid in adsorption experiment

The supernatants were acidified with 3 ml of 0.1 M HCl and then 300 µl of internal standard stock solution (C\textsubscript{17:0}) (3 mM) was added to each glass tube. The unadsorbed fatty acid in the supernatant fluid after the adsorption experiment was extracted by liquid-liquid extraction with DCM in a separating funnel. The DCM extraction step was repeated 3 times for each sample and the extracts were combined in a round bottom flask and then concentrated using a rotary evaporator.

Following evaporation the extract containing unadsorbed fatty acids and internal standard was transferred into glass insert vials (300 µl) for analysis. Five standard samples of tetradecanoic acid (22, 44, 88, 110 and 131 µM) were also prepared in DCM as described above containing the internal standard.

All samples were quantified using a Perkin Elmer Auto System XL GC-FID fitted with a DB-FFAP column (30 m length × 0.25 mm internal diameter and 0.25 µm film thickness; J & W). Hydrogen was used as the carrier gas at a column flow rate of 1.1 ml/min. Injection was splitless (0.5 µl) and the inlet temperature was 240 °C. The oven was held at 60 °C min\textsuperscript{-1} followed by a temperature ramp of 10 °C min\textsuperscript{-1} to 240 °C, where the temperature was held for 9 min and the FID was maintained at 270 °C. The peak areas were measured for quantification using Totalchrom Navigator software and corrected for their RRF. Details of the quantification method for unadsorbed fatty acids have been discussed in Chapter 2, section 2.4.4. The samples of calcite with adsorbed fatty acids were dried in a freeze dryer for subsequent analysis by on-line Py-GC-MS.
3.4 Pyrolysis-GC-MS of tetradecanoic acid

Py-GC-MS was performed using a 5200 Pyroprobe (CDS Analytical) coupled via a heated transfer line (320 °C) to a 7890 GC and a 5975 MS (both Agilent Technologies). Tetradecanoic acid (0.5 mg) was placed in a quartz pyrolysis tube, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms⁻¹ the sample was held at this temperature for 15 s in a flow of helium, and upon pyrolysis the interface was heated from 40 to 350 °C at 100 °C s⁻¹ where it was held for 15 min to prevent volatilisation of the samples prior to pyrolysis. The GC injector was held at 270 °C and operated at a 50:1 split with a helium column flow rate of 1.1 mL min⁻¹. Separation was performed on a DB-5MS ultra inert column (J&W; 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness). The GC oven temperature was held for 2 min at 35 °C and subsequently ramped to 300 °C at a rate of 5 °C min⁻¹ and held at this temperature for 9 min. Mass spectra were acquired in electron impact mode (70 eV) from 50 to 500 amu.

3.5 Pyrolysis-GC-MS of tetradecanoic acid adsorbed on calcite and salts of tetradecanoic acid

Py-GC-MS was performed using a 2000 Pyroprobe (CDS Analytical) fitted via a 1500 valve interface and coupled to 6890 GC and a 5973 MS (both Agilent Technologies). Dried acid adsorbed calcite samples from adsorption experiment were homogenised and approximately 20 mg were placed in quartz pyrolysis tubes, with quartz wool at each end. Similarly, dried salt samples (5 mg) were prepared in quartz pyrolysis tubes with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms⁻¹ the sample was held at this temperature for 15 s in a flow of helium. The interface was held at 200 °C until pyrolysis when it was ramped to 350 °C at 60 °C s⁻¹. The pyrolysis method for adsorbed fatty acids on minerals is discussed in Chapter 2, section 2.5.4. The GC injector was held at 270 °C and operated at a 10:1 spilt for adsorbed samples and 50:1 split for salt samples with a helium constant column flow rate of 1.1 ml min⁻¹. All other conditions were the same as for the pyrolysis of fatty acids described above.
3.6 Results

3.6.1 Adsorption isotherm

The adsorption of fatty acids on carbonate mineral surfaces could be monitored by the production of isotherms. BET analysis (Table 3.1) shows that the surface area is small and the initial concentration of acid used for the adsorption experiment is well below 0.01M at which maximum adsorption (plateau) of fatty acids is reached on calcite (Lagerge et al. 1993, Madsen et al. 1996). The shape of the isotherm produced in our adsorption experiment (Fig 3.2, Table 3.2) could be described as an s-isotherm according to published classifications (Giles et al. 1974). The s-isotherm describes cooperative adsorption which is indicative of multilayer adsorption (Hinz 2001). The adsorption data was further analysed by using the linear form of the Langmuir and Freundlich adsorption isotherms (Limousin et al. 2007). Both isotherm equations and linear plots are discussed in detail in Chapter 2, section 2.2.1. Correlation coefficients ($R^2$) for Langmuir ($R^2 = 0.607$; Fig. 3.2) and Freundlich ($R^2 = 0.947$; Fig 3.3) models for tetradecanoic acid adsorption on calcite showed a better fit with the Freundlich model.

Table 3.1. Micromeritics Tristar-BET (Brunauer–Emmett–Teller) surface area for the calcite used. Analysis adsorptive gas was nitrogen (N$_2$) and bath temperature was 77.35 K.

<table>
<thead>
<tr>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.219</td>
<td>10.74</td>
</tr>
<tr>
<td>0.201</td>
<td>11.25</td>
</tr>
<tr>
<td>0.206</td>
<td>11.26</td>
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</table>
Fig 3.2 The adsorption isotherm obtained for tetradecanoic acid adsorbed on calcite in 35‰ NaCl saline solution; $q_e$ (µM/g) is the concentration of tetradecanoic acid adsorbed on calcite while $C_e$ (µM/L) is the equilibrium concentration of tetradecanoic in supernatant.

Fig 3.3 Langmuir isotherm plot: The slope is equal to $1/Q_{max} = -0.0004$ where $Q_{max} = -2500$ (µM/g) is the maximum adsorption capacity. The y-axis intercept is equal to $1/Q_{max}b$, where $b$ is a constant (L/g).
Fig 3.4 Freundlich isotherm plot: Logarithmic plot of adsorption data. The y-intercept is equivalent to log $K_f$ and the slope is equal to $1/n$. log $K_f = 2.1622$, $1/n = 1.4081$ and $R^2 = 0.947$

Table 3.2. Adsorption of tetradecanoic acid on calcite in 35‰ NaCl solution. Equilibrium concentration of tetradecanoic acid $C_e$ (µM/L) represents the amount retained in the glass tubes after 24 hours equilibration at 21 ± 2 °C and is calculated as a relative response factor.

<table>
<thead>
<tr>
<th>Calcite (g)</th>
<th>Tetradecanoic acid initial concentration (µM/L)</th>
<th>$C_e$, equilibrium concentration of tetradecanoic acid (µM/L)</th>
<th>Adsorbed concentration of tetradecanoic acid (µM/L)</th>
<th>$q_e$, concentration of adsorbed tetradecanoic acid per gram (µM/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
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<td>2</td>
<td>20</td>
<td>390</td>
</tr>
<tr>
<td>0.05</td>
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<td>40</td>
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<tr>
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<td>8</td>
<td>123</td>
<td>2462</td>
</tr>
</tbody>
</table>
3.6.2 Pyrolysis products of tetradecanoic acid

Pyrolysis of tetradecanoic acid produced tridecane, alkenes (C₄ to C₁₄), a series of saturated (C₈ to C₁₀ & C₁₄) and mono-unsaturated low molecular weight fatty acids (C₆ to C₁₂), and toluene (Fig 3.5a, See Appendix B for full list of compounds).

3.6.3 Pyrolysis products of calcium, magnesium and sodium salts of tetradecanoic acid

Pyrolysis of the calcium salt of tetradecanoic acid produced a series of alkanes (C₈ to C₁₃), a range of alkenes (C₆ to C₁₄), tetradecanoic acid, toluene, tetradecanal and a series of ketones (C₁₅ to C₂₇). The main product was a symmetrical mid-chain ketone, 14-heptacosanone (C₂₇) (Fig 3.5b, See Appendix B for full list of compounds). There were only minor differences between the different salts, even between the monovalent and divalent metals (Fig 3.6, See Appendix B for full list of compounds). Only subtle differences in molecular weight ranges for the products were evident.
Fig 3.5 Total ion chromatograms showing products from flash pyrolysis at 650 °C. (a) tetradecanoic acid, retention time between 1.606 to 60.00 min. (b) calcium tetradecanoate, retention time between 0.450 to 60.00 min. C_{12:1} shows the dominant peak dodocene, K refers to the dominant ketones with the number in the subscript indicating the total number of carbon atoms. See Appendix B for full list of compounds identified.
Fig 3.6 Total ion chromatograms showing products from flash pyrolysis at 650 °C. (a) sodium tetradecanoate (b) magnesium tetradecanoate (c) calcium tetradecanoate. C_{12:1} shows the dominant peak of dodocene, K refers to the dominant ketones with the number in the subscript indicating the total number of carbon atoms. See Appendix B for full list of compounds identified.
3.6.4 Pyrolysis of tetradecanoic acid adsorbed on calcite

The pyrolysis products of the tetradecanoic acid adsorbed on calcite selected from the different parts of the isotherm were distinct from the free tetradecanoic acid results but similar to those from the calcium and other salts of tetradecanoic acid (Fig 3.7 See Appendix B for full list of compounds).

The relative abundance of hydrocarbons and ketones in the flash pyrolysates of varying amounts of tetradecanoic acid adsorbed on calcium carbonate (Fig 3.8, Table 3.4) revealed that when the amount of tetradecanoic acid adsorbed on calcite increases the ratio of hydrocarbons/ketones in the pyrolysate decreases. Expressed statistically, there was a linear negative correlation ($R^2 = 0.877$) of hydrocarbons relative to proportion of the tetradecanoic acid adsorbed.
Fig 3.7 Total ion chromatograms showing products from flash pyrolysis of tetradecanoic acid adsorbed on calcite at 650 °C. $C_{12:1}$ shows the dominant peak of dodocene, K refers to the dominant ketones with the number in the subscript indicating the total number of carbon atoms. See Appendix B for full list of compounds identified.
Fig 3.8 Peak areas ratio obtained after manual integration of total ion chromatograms of flash pyrolysis of calcite samples with adsorbed tetradecanoic acid at 650 °C plotted against the amount of tetradecanoic acid adsorbed on calcite (µM/g).

Table 3.3. Peak areas obtained after manual integration of total ion chromatograms of flash pyrolysis at 650 °C. \( \frac{\sum \text{area of hydrocarbons}}{\sum \text{area of hydrocarbons} + \sum \text{area of ketones including aldehydes}} \) shows the ratio of hydrocarbons to ketones including aldehyde. \( q_e \), tetradecanoic acid adsorbed on calcite (µM/g) in 35‰ NaCl solution.

<table>
<thead>
<tr>
<th>( q_e ), tetradecanoic acid adsorbed on calcite (µM/g) in 35 % NaCl solution</th>
<th>( \sum \text{Area} ) (hydrocarbons)</th>
<th>( \sum \text{Area} ) (ketones including aldehydes)</th>
<th>( \frac{\sum \text{area of hydrocarbons}}{\sum \text{area of hydrocarbons} + \sum \text{area of ketones including aldehydes}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>( 8.13 \times 10^8 )</td>
<td>( 5.07 \times 10^8 )</td>
<td>0.62</td>
</tr>
<tr>
<td>796</td>
<td>( 1.69 \times 10^9 )</td>
<td>( 1.15 \times 10^9 )</td>
<td>0.60</td>
</tr>
<tr>
<td>1656</td>
<td>( 2.51 \times 10^9 )</td>
<td>( 3.76 \times 10^9 )</td>
<td>0.40</td>
</tr>
<tr>
<td>2064</td>
<td>( 1.55 \times 10^9 )</td>
<td>( 4.06 \times 10^9 )</td>
<td>0.28</td>
</tr>
<tr>
<td>2462</td>
<td>( 3.16 \times 10^9 )</td>
<td>( 5.94 \times 10^9 )</td>
<td>0.35</td>
</tr>
</tbody>
</table>

\[ y = -0.0002x + 0.6918 \]

\( R^2 = 0.8777 \)
3.7 Discussion

3.7.1 Pyrolysis mechanisms of pure tetradecanoic acid

Typically, pyrolysis of pure fatty acids follows the radical mechanism for the formation of $n$-alkanes and $n$-alkenes. The pyrolysis products of tetradecanoic acid (Fig 3.5a) include tridecane, which indicates the decarboxylation of tetradecanoic acid. The alkenes are the products of alkyl chain scission, where random delocalisation of the radical along the alkyl chain occurs to eventually break the chain at different sites. The saturated and unsaturated low molecular weight fatty acids are also the products of alkyl chain scission and reveal that chain scission is preferred over decarboxylation for the free acid. The formation of a series of short chain saturated and unsaturated carboxylic acids is consistent with the results obtained in a previous study (Maher et al. 2008). Homolysis commonly produces one saturated and one unsaturated compound and the relative lack of alkanes suggest that chain scission and intramolecular and intermolecular hydrogen transfer affecting the alkenes must involve the alkanoic moiety. Toluene is a common aromatic hydrocarbon often seen in pyrolysis products owing to the stability of the tropyllium ion which cools to produce toluene.

3.7.2 Pyrolysis mechanisms of calcium, magnesium and sodium salts of tetradecanoic acid

Following flash pyrolysis of calcium, magnesium and sodium salts of tetradecanoic acid (Fig 3.6), the absence of unsaturated fatty acids indicates that the transformation of fatty acid salts proceeds readily to alternative products. The symmetrical aliphatic ketones also known as fatty ketones i.e. 14-heptacosanone are formed by ketonic decarboxylation (Raven et al. 1997).

From this data (Fig 3.6) radical mechanism is proposed for the formation of a homologous series of ketones and associated alkenes/alkanes from 14-heptacosanone. The pyrolysis of fatty acid salts shows a series of saturated and unsaturated homologous ketones with a base peak $m/z$ 211 $[\text{CH}_3\text{(CH}_2)_{12}\text{CO}]^+$ in the spectra, therefore based on the assumption of Hites and Biemann (1972), it can be speculated that this series of ketones and alkene/alkanes are formed from the radical decomposition of the primary product, 14-heptacosanone. In contrast to Hites and Biemann (1972) who only reported a saturated homologous series of ketones, our pyrolysis products also showed the formation of a homologous series of unsaturated
ketones which can only be produced by the radical based pyrolytic degradation of the symmetric mid chain ketone, 14-heptacosanone.

The formation of 2-pentadecanone and 1-dodecene proceeds by a γ-hydrogen transfer mechanism (Leung et al. 1995, Raven et al. 1997). As can be seen in Fig 3.9, 14-heptacosanone, a symmetric mid chain ketone after γ-H transfer and six centre rearrangement to form dominant 1-dodecene and enol product, 2-hydroxy-1-pentadecene, which by keto-enol tautomerism, form 2-pentadecanone (Leung et al. 1995, Raven et al. 1997). The resulting ketone, 2-pentadecanone then undergoes the same mechanism to produce 1-dodecene. The formation of dominant 1-dodecene and 2-pentadecanone show that γ-H transfer is the most likely mechanism for the formation of these compounds.

The aldehyde is the plausible product of homolysis and loss of an inorganic radical comprising the metal cation and an oxygen atom (e.g. CaO) to leave a tetradecanoyl radical which can receive hydrogen from another molecule to produce tetradecanal (Hartgers et al. 1995).

From the above discussion it seems reasonable to infer that the ketonic decarboxylation results in the formation of symmetric mid chain ketones, 14-heptacosanone which via radical mechanism form alkenes/alkanes and a series of unsaturated/saturated ketones. 2-pentadecanone and 1-dodecene are also possibly formed from 14-heptacosanone which experiences six member ring arrangement (γ-H transfer mechanism). Significant to this insight is that the 14-heptacosanone is a precursor for the formation of alkenes/alkanes and saturated/unsaturated ketones which suggest that the fatty acids are degraded to its subsequent pyrolysis products via ketone formation.
3.7.3 Adsorption and relative abundance of flash pyrolysate hydrocarbons and ketones

Data obtained in previous studies (Suess 1970, Meyers and Quinn 1971b, Lahann and Campbell 1980) indicated that the adsorption of fatty acid by carbonate minerals can be shown as a linear or s-isotherm. According to Meyers and Quinn (1971b), the adsorption of heptadecanoic acid on calcite in 35% saline water was linearly related to the concentration of acid levels reported for natural seawater. In contrast to that, Suess (1973) obtained an s-isotherm for his data expressed as adsorption vs final concentration. Formation of an s-isotherm in this experiment is indicative of a cooperative adsorption mechanism (Hinz 2001), which reflects the formation of multilayers, following the formation of a monolayer of adsorbent (Karimi-Lotfabad et al. 1996). An s-isotherm is typical for non-polar organic compounds (Limousin et al. 2007) and is commonly reported for surfactants (Smith et al. 1990, Groisman et al. 2004).
The adsorption isotherm obtained in this study is significantly different from the previous studies which may be due to several factors including difference in method. Detailed discussion of previous methods employed for adsorption isotherm is given in Chapter 2, section 2.4.3.

As the adsorption of tetradecanoic acid on calcite mineral increases, the overall yield of hydrocarbons and ketones increases, however the abundance of hydrocarbons decreases relative to ketones (Fig 3.7 & 3.8, Table 3.3). Apparently, the increase in ketones can be attributed to the high yield of the primary product 14-heptacosanone from which other homologous ketones are formed (Fig 3.7). The apparent reason for the high yield of ketones is a possible reaction between the fatty acid and short chain carboxylate salts (Raven et al. 1997). The minor fatty acid peaks at the adsorption maximum (Fig 3.7 d and e) indicate the excess layers of acids that can react with the carboxylate salt to form ketones.

The flash pyrolysis of tetradecanoic acid produces hydrocarbons and a series of low molecular weight fatty acids while flash pyrolysis of tetradecanoic acid salt produces hydrocarbons and a series of ketones. Thus the formation of salt and then subsequent ketonisation are the major outcome of fatty acids adsorption on calcite mineral.

On an industrial scale, ketonisation is considered as an efficient process for the removal of highly reactive carboxylic functional group (Pham et al. 2013) and also increases the size of the carbon chain. Further, ketone products can easily react with other bio-oil products to form longer chain molecules that resemble fuel products (Nie and Resasco 2012, Zapata et al. 2012). The reduction in the ratio of hydrocarbons/ketones in the pyrolysis products following an increase in the amount of fatty acid adsorbed onto calcite (Fig 3.7, Table 3.3) provides an opportunity to monitor the progress of fatty acid adsorption in natural settings.

3.7.4 Implications for monitoring fatty acid diagenesis

The mechanisms of organic matter accumulation and preservation in marine sediments are important for understanding the formation of source rocks. Organic-mineral interactions are critical either during transit in water, or during early burial or later stages of diagenesis (Berthonneau et al. 2016).
When organic matter reaches the base of the water column in marine environments it is juxtaposed to minerals. The nature of the interaction between the organic compound and the mineral surface has a significant control on the fate of the organic matter. Besides that various factors as discussed in Chapter 1 Section 1.2.3 control the degradation and preservation of organic matter. There are a number of theories that rely on the adsorption of certain organic structures to mineral surfaces (Keil et al. 1994d, Mayer 1994 b, Papadimitriou et al. 2002). For instance, Bishop and Philp (1994) proposed a hypothesis for kerogen formation via clay mineral adsorption. Nevertheless the substantial role of adsorption for the formation of different classes of organic compounds has never been reported. The key question in this context is how the surface processes such as adsorption play a role in organic-mineral interaction during diagenesis. The ability to monitor the interaction of quantitatively important and relatively universal organic compounds such as fatty acids with calcite mineral surfaces provides a means to obtain insights into early diagenetic process particular to carbonate rocks.

This study has revealed that distinct flash pyrolysis responses occur for those acids which are free and those which are adsorbed onto calcite mineral surfaces. Calcite minerals are unique, and have a distinctive hexagonal trigonal crystal system which differs from that of clay minerals. The formation of salt after the adsorption of fatty acids on calcite is the highlight of this study. The formation of salts after the adsorption of fatty acids on calcite minerals unequivocally supports the finding of carboxylate salts along with the organic acids in marine strata (Andresen et al. 1994, Dias et al. 2002). Carboxylate salts in marine carbonate strata are a source of gas at high temperature due to their higher thermal stability (Liu et al. 2009). The presence of calcium salt of carboxylic acids in marine carbonate strata also explain the inadequate measurement of TOC and hence underestimation of the hydrocarbon capacity of marine source rocks (Liu et al. 2013). This evidence indicates that in marine source rocks, calcium carbonate mineral will form salts of carboxylic acids; however, it is important to mention that the natural system is more competitive, where the presence of other minerals might bring complexity in the formation of intermediates such as salts and hence, the generation of hydrocarbons depends on many other factors. Therefore this study represents a simple model where hydrocarbons and ketones are formed after adsorption.

The newly recognised diagnostic information offers the use of flash pyrolysis to reflect the state of fatty acids in the presence of minerals as they pass into the geosphere. The
unadsorbed acid recently released from its role in biological organisms is indicated by the presence of alkenes and a characteristic series of unsaturated and saturated low molecular weight fatty acids. Once the fatty acid is adsorbed onto the surface of carbonate minerals its flash pyrolysis products become saturated hydrocarbons, unsaturated hydrocarbons and a characteristic homologous series of relatively high molecular weight saturated and unsaturated ketones. The on-line pyrolysis data can, therefore, track fatty acid-mineral interactions during diagenesis.

### 3.8 Conclusions

This study has successively shown the fatty acid-calcite mineral interactions via adsorption which results into the formation of an intermediate such as salt. The formation of salt which then subsequently undergoes ketonisation reactions is a major finding of this work as it might suggest the role of salts for the formation of hydrocarbons in carbonate source rocks. Online “flash” pyrolysates of tetradecanoic acid adsorbed as a multilayer on calcite and tetradecanoic acid salts contain saturated hydrocarbons, unsaturated hydrocarbons, and a homologous series of saturated and unsaturated ketones. On-line pyrolysates of the pure tetradecanoic acid include alkenes, an alkane and a series of unsaturated and saturated low molecular weight fatty acids. Our data indicate that on-line pyrolysis can be used to diagnose interactions between fatty acids and calcite mineral surfaces. Progressive adsorption can be recognised by the increase in ketones relative to hydrocarbons in the pyrolysates. On-line pyrolysis, therefore, is an effective method for monitoring the fate of these near ubiquitous lipids as they undergo diagenesis. In particular, theories that invoke the adsorption of organic compounds such as fatty acids to mineral surfaces can be tested in the natural environment.
Chapter 4

Flash pyrolysis of adsorbed tetradecanoic acid on kaolinite minerals: A method for characterising the catalytic efficiency of clay minerals for adsorbed fatty acids

Kaolinite mineral: source Encyclopedia Britannica

Fig 4.1 Kaolinite structure: modified from Grim. (1968).
4.1 Introduction

4.1.1 Clay minerals and sedimentary organic matter
Various complex physical and chemical complex processes control the distribution of organic compounds on mineral surface in sediments. Organic matter-clay interactions play an important role in many geochemical settings such as petroleum formation, maturation (Hunt 1979) and the global carbon cycle (Mayer 1994 b, Hedges and Keil 1995). The petroleum industry provides many examples such as clay minerals being involved in cracking kerogen (Fan et al. 2004) and their diagenetic transformation during the burial process favouring crude oil migration (Zhang et al. 2010, Cai et al. 2012). Moreover, acidic sites on clay minerals catalyse biomarkers such as diasteranes via rearrangement reactions which involve a series of carbocation-alkene interconversions (Rubinstein et al. 1975, Peakman and Maxwell 1988, van Kaam-Peters et al. 1998).

4.1.2 Adsorption and preservation of organic matter
Adsorption of organic compounds is of key consideration in explaining the organic matter-clay interactions particularly, for the preservation and accumulation of organic molecules onto the surface of minerals (Keil et al. 1994d, Mayer 1994 a, Papadimitriou et al. 2002). The adsorption process is generally advocated as a shielding mechanism for organic compounds from microbial degradation in sediments (Henrichs and Sugai 1993, Wang and Lee 1993, Hedges and Keil 1995). Besides many other factors, adsorption mainly depends on the type of organic compound, nature of clay particles and the underlying mechanism of adsorption (Henrichs and Sugai 1993, Liu and Lee 2006, 2007). The relationship between organic carbon content and the surface area of minerals in sediments can be described in terms of a monolayer coating of organic matter equivalent of 0.5-1.0 mg Organic C m\(^{-2}\) (Mayer 1994 a, 1999) or a patchy distribution of organic compounds on mineral surfaces (Arnarson and Keil 2001).

4.1.3 Adsorption of carboxylic acids on clay minerals
Clay minerals such as kaolinite, 1:1 aluminosilicate formed by superposition of silicon tetrahedral sheets and aluminium octahedral sheets (Auerbach et al. 2004) (Fig 4.1), display a strong affinity for organic compounds due to the presence of the external basal face and the broken bonds at particle edges, including their cation exchange capacity from isomorphous
substitution near the surfaces (Lebedeva and Fogden 2011). Owing to the characteristic surface properties and a strong affinity for organic compounds, kaolinite plays a key role from petroleum accumulation in sedimentary rocks to wettability alteration in oil reservoirs (Bantignies et al. 1997, van Duin and Larter 2001, Lebedeva and Fogden 2011).

Understanding adsorption of carboxylic acids on clay minerals is important as these compounds act as a bridge between the mineral surfaces and the bitumen-kerogen matrix (Sener and Senguler 1998, Dyni 2003, Pearson et al. 2005) and their presence in crude oil might alter the solid surface wettability (Tabrizy et al. 2011). Previously, a few studies demonstrated the adsorption of fatty acids on clay minerals (Meyers and Quinn 1971a, Meyers and Quinn 1973, Balistrieri and Murray 1987, Bayrak 2006, Gautier et al. 2009, Drouin et al. 2010b) and a few simulation studies were conducted by mixing of clay minerals and fatty acids (Faure et al. 2006a, Faure et al. 2006f). The number of these studies is limited especially in aqueous solution due to the solubility limitations of carboxylic acids in water. Most adsorption studies have been conducted on minerals, such as calcite (Suess 1970, Meyers and Quinn 1971b, Lahann and Campbell 1980) and montmorillonite (Meyers and Quinn 1971a), however, the adsorption of fatty acids on kaolinite is relatively unexplored.

4.1.4 Flash pyrolysis and organic-mineral interactions

Pyrolysis experiments have been in use for a long time to comprehend the importance of organic-inorganic interactions during petroleum formation (Yang and Horsfield 2016). For example, a few studies reported hydrocarbon generation by decarboxylation of carboxylic acid mixed with bentonite and montmorillonite (Jurg and Eisma 1964, Shimoyama and Johns 1971). More recently online or “flash” pyrolysis has been used for fatty compounds to study the formation of potential fuels and chemicals (Lima et al. 2004, Maher and Bressler 2007, Prado and Antoniosi Filho 2009). Previously, studies reported the flash pyrolysis of fatty compounds such as fatty acid sodium salts (Lappi and Alen 2009) and carboxylic acids (Maher et al. 2008) suggested mechanisms such as decarboxylation, decarbonylation, and dehydration for the formation of different organic compounds (Lappi and Alen 2009, Frety et al. 2014). Yet, despite much work done on flash pyrolysis of fatty molecules, the compounds evolved after the adsorption of carboxylic acids on clay minerals remains poorly understood.
4.1.5 Objective

The present work focuses on the adsorption of tetradecanoic acid (C\textsubscript{14}) on kaolinite in 35‰ aqueous NaCl solution. The adsorbed acid samples were subjected to online pyrolysis and the products formed were compared with the pyrolysate of tetradecanoic acid alone. Adsorption and online pyrolysis results are used to gain insight into adsorbed fatty acids-kaolinite interaction. As part of this study, the adsorption and pyrolysis experiments were also performed on silica and alumina to reveal the role of alumina and silica surfaces on kaolinite in the formation of pyrolysis products.

4.2 Experimental

4.2.1 Preparation of kaolinite

Approximately 10 g of kaolinite, (KGa-1b; Source Clay Repository of the Clay Mineral Society, CEC; 2.0 meq/100 g, Surface area; 10.05 ± 0.02 m\textsuperscript{2}/g) was stirred with 1.0 M HCl for 1 hour in a 250 ml conical flask and then rinsed with deionized water (Type I, 18.2 MΩ cm\textsuperscript{-1}) until neutral pH was reached. Subsequently, NaCl (0.01 M) solution was added to the clay, the mixture stirred for 1 hour and then rinsed with deionized water 15 times. In the last step, 10% H\textsubscript{2}O\textsubscript{2} was added to the clay and heated at 80 °C for 1 hour to remove any organic matter present. The resulting clay mixture was then rinsed with deionized water 5 times before drying at 110 °C for 24 hours. The dried kaolinite sample was then ground in a pestle and mortar. Alumina (Aluminium oxide, basic, Brokmann I, 50 - 200 µm, 60Å, surface area, 135 to 165 m\textsuperscript{2}/g ) and silica (silica gel, 60 - 200 µm, 60Å; surface area, 460 to 510 m\textsuperscript{2}/g) both from Acros organics, were heated at 500 °C for 5 hours to remove any moisture before using for adsorption experiments.

4.2.2 Preparation of fatty acid solution

The method for tetradecanoic acid stock solution preparation is given in chapter 2, section 2.3.2. The NaCl (0.1 M) solution and tetradecanoic acid stock solution were then used to prepare different fatty acid concentrations (22, 44, 88, 131, and 175 µM). An internal standard solution was prepared of heptadecanoic acid (3 mM) in DCM.
4.2.3 Adsorption experiments

The tetradecanoic acid and NaCl stock solutions were used to prepare five different concentrations (22, 44, 88, 131, 175 µM) of tetradecanoic acid in 10 ml borosilicate test-tubes that each contained 28 mg of kaolinite. A high concentration (219 µM) of tetradecanoic acid was also prepared for the adsorption on silica and alumina (50 mg each). The glass test-tubes were sealed with screw caps and placed in a rotator at a constant temperature of 23 ± 2 °C for 24 hrs, after which the glass tubes were centrifuged for 5 minutes (x 3) at 380 RCF and the supernatant was transferred into 20 ml glass tubes. Each glass test-tube was rinsed with 5 ml of water and centrifuged to remove the excess acid attached to the walls of the tubes.

The supernatants were acidified with 3 ml of 0.1 M HCl and then 300 µl of internal standard stock solution (C₁₇:₀) (3 mM) was added to each glass tube. The unadsorbed fatty acid in the supernatant fluid after the adsorption experiment was extracted by liquid-liquid extraction with DCM in a separating funnel. The DCM extraction step was repeated 3 times for each sample and the extracts were combined in a round bottom flask and then concentrated using a rotary evaporator. Following evaporation the extract containing unadsorbed fatty acids and internal standard was transferred into glass insert vials (300 µl) for analysis. Five calibration standard samples of tetradecanoic acid (22, 44, 88, 131, 175 and 219 µM) were also prepared in DCM as described above containing the internal standard.

4.2.4 Quantification of unadsorbed fatty acid in adsorption experiment

All samples were quantified using a Perkin Elmer Auto System XL GC-FID fitted with a DB-FFAP column (30 m length × 0.25 mm internal diameter and 0.25 µm film thickness; J & W). Hydrogen was used as the carrier gas at a column flow rate of 1.1 ml/min. Injection was splitless (0.5 µl) and the inlet temperature was 240 °C. The oven was held at 60 °C min⁻¹ followed by a temperature ramp of 10 °C min⁻¹ to 240 °C, where the temperature was held for 9 min and the FID was maintained at 270 °C. The peak areas were measured for quantification using Totalchrom Navigator software and corrected for their RRF. For details of the quantification of unadsorbed fatty acids please see Chapter 2, section 2.4.4. The samples of kaolinite with adsorbed fatty acids were dried in a freeze drier for subsequent analysis by on-line Py-GC-MS.
4.3 Pyrolysis-GC-MS of tetradecanoic acid

Py-GC-MS was performed using a 5200 Pyroprobe (CDS Analytical) coupled via a heated transfer line (320 °C) to a 7890 GC and a 5975 MS (both Agilent Technologies). Tetradecanoic acid (0.5 mg) was placed in a quartz pyrolysis tube, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms\(^{-1}\) the sample was held at this temperature for 15 s in a flow of helium, upon pyrolysis the interface was heated from 40 to 350 °C at 100 °C s\(^{-1}\) where it was held for 15 min to prevent volatilisation of the samples prior to pyrolysis. The GC injector was held at 270 °C and operated at a 50:1 split with a helium column flow rate of 1.1 mL min\(^{-1}\). Separation was performed on a DB-5MS ultra inert column (J&W; 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness). The GC oven temperature was held for 2 min at 35 °C and subsequently ramped to 300 °C at a rate of 5 °C min\(^{-1}\) and held at this temperature for 9 min. Mass spectra were acquired in electron impact mode (70 eV) with a scan range from 50 to 500 amu.

4.4 Pyrolysis-GC-MS of tetradecanoic acid adsorbed on kaolinite

Py-GC-MS was performed using a 2000 Pyroprobe (CDS Analytical) fitted via a 1500 valve interface and coupled to 6890 GC and a 5973 MS (both Agilent Technologies). Dried tetradecanoic acid adsorbed kaolinite samples from adsorption experiment were homogenised and approximately 10 mg were placed in quartz pyrolysis tubes, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms\(^{-1}\) the sample was held at this temperature for 15 s in a flow of helium. The interface was held at 200 °C until pyrolysis when it was ramped to 350 °C at 60 °C s\(^{-1}\). The pyrolysis method for adsorbed fatty acids on minerals is discussed in Chapter 2, section 2.5.4. The GC injector was held at 270 °C and operated at a 10:1 split for adsorbed samples with a helium constant column flow rate of 1.1 ml min\(^{-1}\). All other conditions were the same as for the pyrolysis of tetradecanoic acids as described above. Similarly adsorbed fatty acid alumina and silica samples were pyrolysed under the same conditions.
4.5 Results

4.5.1 Adsorption isotherm

The shape of the isotherm produced from adsorption of tetracanoic acid on kaolinite (Fig 4.2, Table 4.1) can be described as an s-isotherm according to published classifications (Giles et al. 1974). Alumina and silica adsorption responses are shown in Table 4.2.

Fig 4.2 The adsorption isotherm obtained for tetracanoic acid adsorbed on kaolinite in 35‰ NaCl saline solution; $q_e$ (µM/g) is the concentration of tetracanoic acid adsorbed on kaolinite while $C_e$ (µM/L) is the equilibrium concentration of tetracanoic in supernatant.
Table 4.1. Adsorption of tetradecanoic acid on kaolinite in 35‰ aqueous NaCl solution. Equilibrium concentration of tetradecanoic acid \( C_e \) (µM/L) represents the amount retained in the glass tubes after 24 hours equilibration at 21 ± 2 °C and is calculated as a relative response factor.

<table>
<thead>
<tr>
<th>Kaolinite (g)</th>
<th>Tetradecanoic acid initial concentration (µM/L)</th>
<th>( C_e ), equilibrium concentration of tetradecanoic acid (µM/L)</th>
<th>Adsorbed concentration of tetradecanoic acid (µM/L)</th>
<th>( q_e ) concentration of adsorbed tetradecanoic acid per gram (µM/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.028</td>
<td>22</td>
<td>0.56</td>
<td>21</td>
<td>766</td>
</tr>
<tr>
<td>0.028</td>
<td>44</td>
<td>1.04</td>
<td>43</td>
<td>1534</td>
</tr>
<tr>
<td>0.028</td>
<td>88</td>
<td>1.17</td>
<td>87</td>
<td>3101</td>
</tr>
<tr>
<td>0.028</td>
<td>131</td>
<td>1.37</td>
<td>130</td>
<td>4630</td>
</tr>
<tr>
<td>0.028</td>
<td>175</td>
<td>1.96</td>
<td>173</td>
<td>6180</td>
</tr>
</tbody>
</table>

Table 4.2. Adsorption of tetradecanoic acid on alumina (Aluminium oxide, basic, Brokmann I, 50-200 µm, 60Å, surface area; 135 to 165 m\(^2\)/g) and silica (silica gel, 60 - 200 µm, 60Å; surface area; 460 to 510 m\(^2\)/g) in 35‰ NaCl solution. Equilibrium concentration of tetradecanoic acid \( C_e \) (µM/L) represents the amount retained in the glass tubes after 24 hours equilibration at 21 ± 2 °C and is calculated as a relative response factor.

<table>
<thead>
<tr>
<th>Sample (g)</th>
<th>Tetradecanoic acid initial concentration (µM/L)</th>
<th>( C_e ), equilibrium concentration of tetradecanoic acid (µM/L)</th>
<th>( q_e ), concentration of tetradecanoic acid adsorbed (µM/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>219</td>
<td>9.44</td>
<td>210</td>
</tr>
<tr>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>219</td>
<td>3.49</td>
<td>216</td>
</tr>
<tr>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The adsorption data was further analysed by using the linear form of the Langmuir and Freundlich adsorption isotherms (Limousin et al. 2007). Both isotherm equation and linear plots are discussed in detail in Chapter 2, section 2.2.1. Correlation coefficients ($R^2$) Freundlich ($R^2 = 0.967$; Fig. 4.3) and Langmuir ($R^2 = 0.63$; Fig. 4.4) models for tetradecanoic acid adsorption on kaolinite showed a better fit with the Freundlich model.

Fig 4.3 Freundlich isotherm plot: Logarithmic plot of adsorption data. The $y$-intercept is equivalent to $\log K_f$ and the slope is equal to $1/n$. $\log K_f = 0.2302$, $1/n = 2.712$ and $R^2 = 0.967$
Fig 4.4 Langmuir isotherm plot: The slope is equal to $1/Q_{\text{max}} = -0.0002$ where $Q_{\text{max}} = -5000$ ($\mu$M/g) is the maximum adsorption capacity. The y-axis intercept is equal to $1/Q_{\text{max}}b$, where $b$ is a constant (L/g).

4.5.2 Pyrolysis products of pure tetradecanoic acid

Pyrolysis of free tetradecanoic acid produces tridecane, alkenes ($C_4$ to $C_{14}$), a series of saturated and mono-unsaturated low molecular weight fatty acids ($C_6$ to $C_{11}$), and toluene (Fig 4.5, See Appendix C for full list of compounds).
4.5.3 Pyrolysis of tetradecanoic acid adsorbed on kaolinite

Products obtained from the pyrolysis of tetradecanoic acid adsorbed on kaolinite (Fig 4.6, See Appendix C for full list of compounds) are different from the pyrolysis products of free tetradecanoic acid (Fig 4.5). The main classes of organic compounds identified; a range of dominant alkenes (C_4 to C_{14}), alkanes (C_{11}, C_{13} & C_{14}), aromatic compounds, a peak of aldehyde, tetradecanal, a dominant peak of tetradecanoic acid and a dominant asymmetric ketone, 2-pentadecanone (Fig 4.6). The difference in the pyrolysis products between different adsorbed acid samples is apparent as the adsorption of acid increases (Fig 4.6). At high levels of adsorption the number of oxygenated products increases and a homologous series of ketones along with the dominant symmetric ketone 14-heptacosanone is observed.
Fig 4.6 Pyrolysis-GC-MS total ion chromatogram of tetradecanoic acid adsorbed on kaolinite at 650 °C. Symbols represent following classes of compounds, See Appendix C for full list of compounds identified.
4.5.4 Pyrolysis of tetradecanoic acid adsorbed on silica and alumina

The pyrolysis products of tetradecanoic acid adsorbed on alumina $C_{14}$-Al$_2$O$_3$, silica $C_{14}$-SiO$_2$ and kaolinite are shown in Fig 4.7 (See Appendix C for full list of compounds). A significant difference in the pyrolysis products is observed between $C_{14}$-SiO$_2$ and $C_{14}$-Al$_2$O$_3$. The pyrolysis of tetradecanoic acid adsorbed alumina, $C_{14}$-Al$_2$O$_3$ produces alkanes ($C_8$ to $C_{14}$), alkenes, ($C_4$ to $C_{14}$), and ketones ($K_{15}$ and $K_{16}$). Other than these compounds, aromatic compounds such as benzene and its derivative along with the indane and its derivatives are also observed. The chromatogram of tetradecanoic acid adsorbed silica, $C_{14}$-SiO$_2$ is relatively simple and shows terminal alkenes ($C_4$ to $C_{14}$), alkanes ($C_{11}$ and $C_{13}$), tetradecanal and abundant tetradecanoic acid. Along with these major compounds, two minor peaks of benzene and toluene are also observed.
Fig 4.7 Pyrolysis-GC-MS total ion chromatogram of the pyrolysis products of tetradecanoic acid adsorbed on alumina, silica and kaolinite at 650 °C. See Appendix C for full list of compounds identified.
The difference in the pyrolysis products from C_{14}-Al_{2}O_{3} and C_{14}-SiO_{2} showed the difference in the adsorption efficiency due to different reactivity of alumina and silica. The pyrolysis chromatogram of C_{14}-Al_{2}O_{3} shows no untransformed tetradecanoic acid which suggests alumina is more efficient in the full conversion of adsorbed tetradecanoic acid to different compounds. Another difference is of unsaturation and aromatisation of the pyrolysis products of C_{14}-Al_{2}O_{3}. The formation of these compounds can be attributed to the higher acidity of alumina, due to the higher acidity of its hydroxyl groups than that of the silica surface (Hair 1967, Busca 1999). The aluminol group on alumina stimulates hydrogen transfer reactions which help in the formation of saturated compounds (C_{8} to C_{14}) and unsaturated compounds with isomerisation (C_{4} to C_{14}). Although both C_{14}-Al_{2}O_{3} and C_{14}-SiO_{2} show the formation of a dominant C_{12} alkene, the area percentage of the last two alkenes i.e. dodecene and tridecene is higher in the chromatogram of C_{14}-SiO_{2} than that of C_{14}-Al_{2}O_{3} (Table 4.3).

Table 4.3. Peak area percentage of 1-alkenes of from acid adsorbed silica and alumina pyrolysis chromatogram.

<table>
<thead>
<tr>
<th>Pyrolysis products from fatty acid adsorbed silica</th>
<th>Area percentage of 1-alkenes from fatty acid adsorbed silica</th>
<th>Area percentage of 1-alkenes from fatty acid adsorbed alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>4.4</td>
<td>7.8</td>
</tr>
<tr>
<td>1-heptene</td>
<td>7.9</td>
<td>11.7</td>
</tr>
<tr>
<td>1-octene</td>
<td>10.8</td>
<td>11.5</td>
</tr>
<tr>
<td>1-nonene</td>
<td>11.7</td>
<td>12.3</td>
</tr>
<tr>
<td>1-decane</td>
<td>14.4</td>
<td>12.2</td>
</tr>
<tr>
<td>1-undecene</td>
<td>11.6</td>
<td>13.4</td>
</tr>
<tr>
<td>1-dodecane</td>
<td>29.9</td>
<td>26.7</td>
</tr>
<tr>
<td>1-tridecane</td>
<td>9.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>
4.5.5 Pyrolysis of mixture of symmetric ketone, 14-heptacosanone and kaolinite.

To test whether 14-heptacosanone formed in acid adsorbed kaolinite can further degrade to form products similar to the fatty acid adsorbed kaolinite, the mixture of 14-heptacosanone (0.15 mg) and kaolinite (50 mg) was pyrolysed (15 mg) (Fig 4.8). Pyrolysis of the mixture of 14-heptacosanone and kaolinite showed a dominant peak of 14-heptacosanone and 2-pentadecanone, a peak of tetradecanal and saturated/unsaturated hydrocarbons with four phenyl derivatives and an indene derivative (Fig 4.8).

Fig 4.8 Pyrolysis-GC-MS total ion chromatogram of a) tetradecanoic acid adsorbed on kaolinite, b) mixture of 14-heptacosanone (0.15 mg) and kaolinite (50 mg) at 650 °C. See Appendix C for full list of compounds identified.
4.6 Discussion

4.6.1 Adsorption of tetradecanoic acid to kaolinite

Two characteristic properties of kaolinite make it an interesting case to apprehend its interaction as a common sedimentary mineral with a hydrophobic organic compound. First is its two functionalities i.e. one siloxane (tetrahedral face) and one hydroxyl surface (octahedral face) having different affinities for organic and water phases (Murgich and Rodríguez M 1998, Teppen et al. 1998, van Duin and Larter 2001) and second is its heterogeneous wettability due to heterogeneous surface charge. The major implication of heterogeneous wettability is its purported effect in making the kaolinite particles oil wet after the adsorption of the negatively charged carboxylate ions from bitumen (Takamura and Chow 1985, Tombácz and Szekeres 2006).

Aluminosilicate sediments have less than 15 % of their surface coated with the organic material and that organic material is clustered in small patches on mineral surfaces (Arnarson and Keil 2001). The formation of an s-isotherm from the adsorption of tetradecanoic acid on kaolinite (Fig 4.2) can be used to explain the hypothesis of layered architecture of organic matter patches on the mineral surface. The interpretation of results as the formation of a multilayer of fatty acids on the kaolinite surface (Fig 4.2) can be correlated with the hypothesis of multilayer organic matter accumulation on the mineral surface in the natural settings (Gougeon et al. 2003, Wang and Xing 2005).

The chemical reactivity of amphoteric site bonds including inorganic surface hydroxyl groups (ISOH) such as silanol and aluminol on the broken edges of kaolinite has been reported (Johnston and Tombacz 2002). The OHs of the hydroxyl basal surface of kaolinite might interact with solute molecules via H-bonding; however, they are chemically less reactive than the amphoteric bonds on edge surfaces (Brady et al. 1996, Avena et al. 2003). The pH of the highest concentration of the tetradecanoic acid solution used for adsorption is 6.8, which is moderately acidic and lies in the range of 5 to 8 where the heterogeneous charges might develop on the different parts of kaolinite. Therefore, it is suspected that both edge surfaces and hydroxyl-terminated planes of kaolinite minerals are involved in bonding with carboxylate ions.
Likewise, the interaction of alumina with tetradecanoic acid can be explained via outer sphere bonding through electrostatic interactions and H-bonding with $\text{Al}_2\text{OH}^0$ or $\text{Al-OH}^{0.5}$ sites of acidic character (Yoon et al. 2004, Yoon et al. 2005) as the pH is neither very acidic nor basic (Tong et al. 2010b, Rubasinghege et al. 2013).

Siloxane surfaces normally adsorb water and cations while hydrophobic interaction between the siloxane surface of aluminosilicates and long chain paraffinic moieties of organic molecule has been reported (Laird and Fleming 1999, Namjesnik-Dejanovic et al. 2000, Sheng et al. 2001). Nevertheless the mechanism of interaction of organic molecules with the siloxane surface also depends on the presence of cations. For instance due to the presence of Na$^+$ metal ions in this study, the hydrophobic interaction is probably less expected than the electrostatic interaction between carboxylic acid ions and basal surface via Na$^+$ metal cation bridging. The presence of Na$^+$ ions might enhance the adsorption of carboxylic acids on kaolinite as the Na$^+$ metal ions compensate negative surface charge of the basal planes on kaolinite and involve in interaction with the carboxylic acid anions. This synthesis is consistent with those of Nevskaiia et al. (1998) who have shown an increase in adsorption of anionic surfactant on quartz and kaolin in the presence of NaCl.

4.6.2 Characterisation of pyrolysis products obtained from adsorbed tetradecanoic acid samples on kaolinite, alumina and silica

The catalytic efficiency of clay minerals is due to their large specific surface area and their inherent property as a strong acid, both Bronsted and Lewis (Nasser and Mingelgrin 2012 and references therein). Acidic catalysts, in particularly, enhance the formation of aromatics and polyaromatics (Santos et al. 1998) while non-acidic catalysts favour the formation of linear saturated and unsaturated hydrocarbons (Dosanjos et al. 1983, Santos et al. 1998).

Our pyrolysis experiment on tetradecanoic acid adsorbed kaolinite showed both straight chain hydrocarbons and aromatic hydrocarbons (Fig 4.6). Most notably, this is the first study to my knowledge to report a range of organic compounds from the adsorption of tetradecanoic acid on kaolinite and most interestingly there is a reasonable change in pyrolysis products as the adsorption increases. These results provide compelling evidence for the catalytic effect of kaolinite on the adsorbed fatty acid. Pyrolysis of tetradecanoic acid shows distinct products (Fig 4.5), including alkenes which are the products of alkyl chain scission, and alkanes such as tridecane, which is the decarboxylation product of tetradecanoic acid (Zafar et al. 2017).
Along with that saturated and unsaturated low molecular weight fatty acids are also produced as a result of alkyl chain scission and showed that chain scission is preferred over decarboxylation for the free acid.

To comprehend the role of the two surfaces in kaolinite for the formation of different products, adsorption and pyrolysis experiments were also conducted on alumina and silica under the same conditions (Fig 4.7). A striking difference is obtained in the pyrolysis products of acid adsorbed alumina and silica. Further to that, results reported in this study provide compelling evidence for the interaction of both surfaces of kaolinite in bonding with carboxylic acids (Fig 4.7).

A characteristic tetradecanoic acid peak is dominant in the chromatogram of adsorbed tetradecanoic acid on silica and kaolinite, however, such a peak is not observed in the chromatogram of alumina (Fig 4.7). The appearance of a tetradecanoic acid peak in the chromatogram of silica and kaolinite (Fig 4.7) shows that the silanol groups on both minerals are involved in bonding with the tetradecanoic acid ions. In addition, a tetradecanal is also commonly observed in both tetradecanoic acid adsorbed kaolinite and silica chromatograms. Previously, Nierop and van Bergen (2002) reported the formation of C\textsubscript{18} alkanal from the mixture of stearic acid and kaolinite due to alpha cleavage next to the carbonyl group of pentatricontan-18-one. Contrary to that, tetradecanal in this study is also observed from the low concentration of adsorbed tetradecanoic acid-kaolinite samples which does not form symmetric ketones i.e. 14-heptacosanone. Although the presence of tetradecanoic acid and tetradecanal peaks show that silanol groups are reactive on kaolinite and involved in bonding with the fatty acid after adsorption, the rest of the pyrolysates from tetradecanoic acid adsorbed kaolinite are similar to the fatty acid adsorbed alumina chromatogram. For instance, alkene isomerization is dominant in the pyrolysis products of fatty acid adsorbed kaolinite and alumina, while no alkene isomerization is observed in the fatty acid adsorbed silica. Although alkene isomerization is common between fatty acid adsorbed alumina and kaolinite chromatograms, one difference is the formation of alkanes (C\textsubscript{8} to C\textsubscript{14}) in the chromatogram of the alumina, and the later only showed two saturated hydrocarbons (C\textsubscript{11} & C\textsubscript{13}). This difference in saturated hydrocarbons might be linked to the difference in acidity of kaolinite and alumina.
Previous studies suggest that the end peak area hydrocarbon ratio in the pyrolysis products allow an estimate of the relative importance of hydrodeoxygenation (HDO) over decarboxylation-decarbonylation (DCO) decomposition routes (Kubička and Kaluža 2010, Kubička et al. 2014). The \((C_{14}/C_{13})\) hydrocarbon area ratio of tetradecanoic acid adsorbed on kaolinite and silica is in the range of 0.05 to 0.09; however, the ratio is slightly higher (0.19) for fatty acid adsorbed alumina (Table 4.4). The low peak area ratio of hydrocarbon suggests that under the present experimental conditions of pyrolysis, DCO is the main reaction pathway.

Table 4.4. Peak area ratio of hydrocarbons (saturated/unsaturated) obtained after manual integration of total ion chromatograms of fatty acid adsorbed kaolinite, silica and alumina.

<table>
<thead>
<tr>
<th>Clay</th>
<th>(q_e) adsorbed tetradecanoic acid (\mu\text{M/g})</th>
<th>Ratio of hydrocarbons ((C_{14}/C_{13}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetradecanoic acid adsorbed on kaolinite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.028</td>
<td>1529</td>
<td>0.054</td>
</tr>
<tr>
<td>0.028</td>
<td>3086</td>
<td>0.070</td>
</tr>
<tr>
<td>0.028</td>
<td>4643</td>
<td>0.072</td>
</tr>
<tr>
<td>0.028</td>
<td>6179</td>
<td>0.088</td>
</tr>
<tr>
<td>Tetradecanoic acid adsorbed on alumina</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>4191</td>
<td>0.191</td>
</tr>
<tr>
<td>Tetradecanoic acid adsorbed on silica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>4310</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Interestingly, both silica and alumina show dominant dodecan-1-ene in contrast to the kaolinite which shows dominant tridecan-1-ene with a mid-chain double bond in its pyrolysis products. Previously, I have shown that fatty acid adsorbed calcite minerals show dominant dodecan-1-ene which shows the difference in the catalysis of calcite and clay mineral (Zafar et al. 2017). Further, high selectivity is observed for terminal alkenes, 1-alkenes are dominant in fatty acid adsorbed silica and alumina in comparison to the kaolinite pyrolysis products. However by comparing peak areas of 1-alkenes from alumina and silica chromatogram, the latter shows the high area percentage only for \(C_{12}\) and \(C_{13}\) alkenes (Table 4.3) indicating that
the absence of acidic sites on silica might affect the formation of higher 1-alkenes from the adsorbed tetracanoic acid.

The most exceptional difference among the pyrolysis products of alumina, silica and kaolinite is the formation of oxygenated hydrocarbons i.e. ketones. The chromatogram of pyrolysis products of fatty acid adsorbed kaolinite (adsorbed acid, 6180 µM/g; initial concentration 175 µM/L) has a homologous series of saturated ketones (K\textsubscript{15-24}) and a symmetric ketone i.e. 14-heptacosanone (K\textsubscript{27}) (Fig 4.6 d). In contrast, the pyrolysis products of fatty acid adsorbed on silica (adsorbed acid, 4310 µM/g; initial concentration 219 µM/L) do not show any ketones, while pyrolysis of fatty acid adsorbed alumina (adsorbed acid, 4191 µM/g; initial concentration 219 µM/L) shows only 2-pentadecanone and 3-hexadecanone (Fig 4.7). This anomaly can be explained on the basis of adsorption results. At low adsorption, kaolinite behaves in exactly the same manner as fatty acid adsorbed alumina and shows only two ketones, i.e. 2-pentadecanone and 3-hexadecanone (Fig 4.6 a, b & Fig 4.7a). With the increase in the level of acid adsorption, ketones also increase in the pyrolysis products (Fig 4.6 c & d). Although Leung et al. (1995) previously reported the formation of symmetric ketones after pyrolysing the C\textsubscript{4} to C\textsubscript{12} carboxylic acids over activated alumina at 450 °C and atmospheric pressure, this study does not show symmetric ketone formation at low adsorption levels (Fig 4.6 a & b). Therefore, the apparent difference in the ketone formation between kaolinite and alumina may be due to the difference in the amount of adsorbed tetracanoic acid.

A key question here is why the formation of symmetric ketones is enhanced at high adsorption levels of acid on kaolinite. One possible reason for the formation of symmetric ketones might be due to the involvement of the basal surface via Na\textsuperscript{+} metal ions in adsorption, however, this factor remains constant at all concentrations in adsorption.

Previously, my work showed that the symmetric ketone, 14-heptacosanone, formed from calcium tetracanoate, further degraded to produce a homologous series of ketones and hydrocarbons (Zafar et al. 2017). Pyrolysis products of a ketone-kaolinite mixture are significantly different from the chromatograms of fatty acid adsorbed kaolinite (Fig 4.7 & 4.8). Hydrocarbons (unsaturated/saturated) are substantially scattered in the ketone-kaolinite mixture and also the number of aromatic compounds is less than in the fatty acid adsorbed kaolinite. It appears from mixture chromatogram (Fig 4.8) that 14-heptacosanone formed
from fatty acid adsorbed kaolinite might further degrade to form hydrocarbons and aromatics. Nevertheless, hydrocarbons, aromatics, aldehyde, and 2-pentadecanone are formed even in the absence of 14-heptacosanone (Fig 4.6 a & b) which means that the 14-heptacosanone cannot be considered as a stand-alone compound for the formation of all classes of organic compounds from fatty acid adsorbed kaolinite. One prominent difference in the pyrolysis products of fatty acid adsorbed calcite (Zafar et al. 2017) and kaolinite is that the latter show the formation of a homologous series of ketones and symmetric ketone only at high adsorption. This difference gives me clue that the excess fatty acid after the monolayer formation might be involved in the formation of symmetric ketones in the fatty acid adsorbed kaolinite. Therefore ketonisation at high adsorption in kaolinite might be due to the dimerization of fatty acid molecules at high concentration. As mentioned early the adsorption curve is an s-isotherm which reflects multilayer adsorption, and the adsorption of carboxylate ions renders the kaolinite surface oil wet or hydrophobic, such that further adsorption of carboxylate ions is promoted via hydrophobic interaction which makes the surface layer hydrophilic. The surface hydrophilic ends are available for dimerization which on pyrolysis might be able to generate ketones.

Thus until now most studies focused on the acidic catalytic effect of kaolinite minerals, however, this is the first study of its kind in which carboxylic adsorption is linked with the formation of various classes of organic compounds. Importantly, the study features an explanation for the generation of different organic compounds as the adsorption changes from the monolayer to multilayer.

4.7 Conclusion

This study shows that the adsorption of fatty acid on kaolinite is not limited to a monolayer, but a multilayer is also possible due to the hydrophobic interaction between adsorbed acid components which can mimic the layered organic matter distribution on mineral surface in natural settings. Adsorption on the kaolinite mineral is linked with the pyrolysis products. As mentioned earlier this is the first study of my knowledge in which the pyrolysis products of fatty acid adsorbed kaolinite are explained analogously to the pyrolysis products obtained from the adsorption of tetradecanoic acid on alumina and silica. The most remarkable finding of this study is that on adsorption both functionalities of kaolinite are involved in bonding with the carboxylic acids, as indicated from pyrolysis results. The work has remarkable
implications in investigating the role of kaolinite minerals in fixation and preservation of fatty acids in marine sediments leading to the formation of source rocks.
Chapter 5

Formation of aromatic hydrocarbons from adsorbed carboxylic acids on montmorillonite: A method characterising the catalytic efficiency of montmorillonite at high temperature pyrolysis.

Montmorillonite (Source: mindat.org)

Fig 5.1 Montmorillonite structure: modified from Grim. (1968)
5.1 Introduction

5.1.1 Diagenesis and the role of clay minerals in hydrocarbon formation

Diagenetic changes in clay minerals are responses to burial and thermal maturation in sedimentary basins (Weaver 1960, Pollastro 1993). Humic substances, resistant biomacromolecules /geomacromolecules (Largeau et al. 1984, Tegelaar et al. 1989, Boussafir and Lallier-Vergès 1997), sulphur-rich macromolecules (Sinninghe Damste and De Leeuw 1990, Boussafir et al. 1995), and low molecular weight biomolecules are considered as sources of kerogen formation (Killops and Killops 2009 and references therein). The adsorption of organic molecules on clay surfaces is one of the main mechanisms for the accumulation and preservation of organic matter in the geosphere (Keil et al. 1994d, Mayer 1994 b). Organic compounds that adsorb on fine grained mineral matrix in clay mineral-rich sedimentary rocks exist either as a monolayer (Mayer 1999) or patchwise distribution (Arnarson and Keil 2001), are protected and encapsulated against the diagenetic degradation (Bock and Mayer 2000, Salmon et al. 2000, Vandenbroucke and Largeau 2007). The protected labile organic carbon can then contribute to kerogen (Vandenbroucke and Largeau 2007). Therefore understanding the adsorption of organic molecules on clay mineral surfaces is of critical importance in monitoring the fate of organic compounds during diagenesis.

5.1.2 Clay minerals in sedimentary settings

Owing to their inherent property of natural catalysts (Johns 1979, Occelli 1983, Zhou 2011), clay minerals have attracted great interest in studies of petroleum formation, migration, accumulation, and storage (Wu et al. 2012 and references therein). Moreover organic enrichment and preservation mechanisms involving clay minerals for the formation of source rocks are active research fields in petroleum geochemistry (Berthonneau et al. 2016). A most striking feature of clay minerals is their association with OM and the direct proportionality between the concentration of OM and the sediment surface area (Keil et al. 1994d, Mayer 1994 b). Association between OM and clay minerals in sediments has led many studies to focus on the so-called clay-organic complex, particularly because of the potential role of clay minerals in hydrocarbon formation (Li et al. 1998, Wei et al. 2006, Pan et al. 2008, Yuan et al. 2013). Previously, few studies reported the irregular coating of organic carbon on mineral surfaces (Ransom et al. 1997, Ransom et al. 1998). Recently, Curry et al. (2007) reported the
protection of sorbed polysaccharides on nano- and microfabrics of clay-rich sediments from microbial degradation.

5.1.3 Clay geo-catalysis of organic compounds

Smectite clays, such as montmorillonite, type 2:1 clay mineral, with one octahedral sheet of alumina sandwiched between two tetrahedral sheets of silica (Fig 5.1) are particularly important because of their abundance in low-maturity organic-rich rocks and their potential catalytic activities. Due to the reduction of activation energies and Arrhenius coefficients in the presence of clay minerals (Goldstein 1983), many studies have demonstrated the catalytic effectiveness of smectite clays in hydrocarbon generation from natural organic compounds (kerogen and bitumen) (Tannenbaum and Kaplan 1985a, c, Huizinga et al. 1987a, b, Li et al. 1998, Pan et al. 2008). Besides natural organic compounds, clay geo-catalysis is studied on structurally simple synthetic organic compounds, such as amino acids (Liu et al. 2013b, Yuan et al. 2013) and fatty acids (Jurg and Eisma 1964, Shimoyama and Johns 1971, Aizenshtat et al. 1984, Hellerkallai et al. 1984). In a natural setting, the presence of naturally occurring interlayer clay-organic complexes has been reported (Theng 1974, Theng et al. 1986, Schulten et al. 1996), and therefore a few studies have also reported the interlayer clay-organic complexes of simple organic compounds.

5.1.4 Carboxylic acids in natural environment

Carboxylic acids are one of the most abundant dissolved organic compounds in natural sea water (Thurman 1985) and pure clays have been shown to adsorb high proportions of linear saturated and unsaturated fatty acids under saline conditions (Meyers and Quinn 1971a, Meyers and Quinn 1973, Sansone et al. 1987, Drouin et al. 2010a). From a geochemical point of view, carboxylic acids have been considered as hypothetical intermediates in oil generation processes from lipids or other precursor constituents (Cooper 1962, Shimoyama and Johns 1971). Free fatty acids in the range of $C_{14}$-$C_{26}$ have been reported in immature crude oil samples sourced either from source rocks or from the biodegradation of oil or biosynthesized by organisms (Mackenzie et al. 1983, Meredith et al. 2000). Moreover, laboratory simulation experiments on carboxylic acids reported the decarboxylation of fatty acids into long-chain alkanes which are then subsequently cracked into other hydrocarbons (Jurg and Eisma 1964, Shimoyama and Johns 1971, Johns and Shimoyama 1972, Aizenshtat et al. 1984).
5.1.5 Clay minerals acidity and high temperature pyrolysis

Flash Py-GC-MS is a technique that has been used to characterise OM in soil and sediments (Faure et al. 2006a and references therein). Pyrolysis has also been shown to be useful in the synthesis of petroleum related deoxygenated compounds such as alkanes, alkenes, and aromatic compounds (Maher and Bressler 2007 and references therein, Frety et al. 2014). The nature of organic compounds (Dosanjos et al. 1983) and the surface properties of minerals (Purnell 1990, Ishiwatari et al. 1995, Brown and Rhodes 1997, Nierop and van Bergen 2002) affect the composition of pyrolysis products. High-temperature pyrolysis in the presence of a catalyst produces light products such as gases and compounds with limited heteroatom contents (Lima et al. 2004, Prado and Antoniosi Filho 2009). Moreover, acidic catalysts (Bronsted sites) enhance the formation of aromatic and polycyclic aromatic compounds (Santos et al. 1998, Faure et al. 2006f) while non-acidic catalysts favour the formation of linear saturated and unsaturated hydrocarbons (Dosanjos et al. 1983, Santos et al. 1998).

5.2 Objective

The purpose of this study is to quantify the adsorption of tetradecanoic acid (C_{14}) on montmorillonite in aqueous NaCl (35 ‰) solution. The approach used in this study aims to gain insight of the mechanism by which tetradecanoic acid adsorbed onto montmorillonite minerals transform during flash heating into different classes of organic compounds. More specifically, the study attempts to explain pyrolysis products in the context of organo-mineral surface complexion formed after adsorption. Adsorption and pyrolysis experiments were conducted under identical conditions to those of kaolinite minerals (Chapter 4) so that the adsorption and pyrolysis products could be compared.
5.3 Experimental

5.3.1 Preparation of montmorillonite

Approximately 50 g of Na-rich montmorillonite, (SWy-2; Source Clay Repository of the Clay Mineral Society; CEC, 76.4 meq/100g; Surface area, 31.82 ± 0.22 m²/g) was stirred with 1.0 M HCl for 1 hour in a 500 ml conical flask and then rinsed with deionized water (Type I, 18.2 MΩ cm⁻¹) until neutral pH. Subsequently, NaCl (0.01 M) solution was added to the clay, stirred for 3 hours and then rinsed with deionized water until chloride ions could not be detected using AgNO₃ solution. In the last step, 10% H₂O₂ was added to the clay and heated at 80 °C for 1 hour to remove any organic matter present. The resulting clay mixture was then rinsed with deionized water 10 times before drying at 110 °C for 48 hours. The dried montmorillonite sample was then ground in a pestle and mortar.

5.3.2 Preparation of fatty acid solution

The method for tetradecanoic acid stock solution preparation is given in Chapter 2, section 2.3.2. Fatty acid concentrations of (22, 44, 88, 110, and 131 µM) were then prepared for the adsorption of tetradecanoic acid on montmorillonite. An internal standard solution was prepared of heptadecanoic acid (3 mM) in DCM.

5.3.3 Adsorption experiments

Adsorption experiments were performed by using concentrations (22, 44, 88, 110, 131 µM) of tetradecanoic acid in 10 ml borosilicate test-tubes that each contained 50 mg of montmorillonite. The glass test-tubes were sealed with PTFE lined screw caps and placed in a rotator at a constant temperature of 23 ± 2 °C. The samples were equilibrated for 24 hours, and following equilibration the glass tubes were centrifuged 3 times for 5 minutes at 380 RCF and the supernatant was transferred into 20 ml glass tubes. Each glass test-tube was rinsed with 5 ml of water and centrifuged again for 5 minutes at 380 RCF to remove the excess acid attached to the walls of the tubes.

The supernatants were acidified with 3 ml of 0.1 M HCl and then 300 µl of internal standard stock solution (C₁₇₀) (3 mM) was added to each glass tube. The unadsorbed fatty acid in the supernatant fluid after the adsorption experiment was extracted by liquid-liquid extraction with DCM in a separating funnel. The DCM extraction step was repeated 3 times for each
sample and the extracts were combined in a round bottom flask and then concentrated using a rotary evaporator. Following evaporation the extract containing unadsorbed fatty acids and internal standard was transferred into glass insert vials (300 µl) for analysis. Five standard samples of tetradecanoic acid (22, 44, 88, 110, and 131 µM) were also prepared in DCM as described above.

5.3.4 Quantification of unadsorbed fatty acid in adsorption experiment

All samples were quantified using a Perkin Elmer Auto System XL GC-FID fitted with a DB-FFAP column (30 m length x 0.25 mm internal diameter and 0.25 µm film thickness; J & W). Hydrogen was used as the carrier gas at a column flow rate of 1.1 ml/min. Injection was splitless (0.5 µl) and the inlet temperature was 240 °C. The oven was held at 60 °C min⁻¹ followed by a temperature ramp of 10 °C min⁻¹ to 240 °C, where the temperature was held for 9 min and the FID was maintained at 270 °C. The peak areas were measured for quantification using TotalChrom Navigator software and corrected for their RRF. For details of quantification of unadsorbed fatty acids please see Chapter 2, section 2.4.4. The samples of montmorillonite with adsorbed fatty acids were dried in a freeze drier for subsequent analysis by on-line Py-GC-MS.

5.4 Pyrolysis-GC-MS of tetradecanoic acid

Py-GC-MS was performed using a 5200 Pyroprobe (CDS Analytical) coupled via a heated transfer line (320 °C) to a 7890 GC and a 5975 MS (both Agilent Technologies). Tetradecanoic acid (0.5 mg) was placed in a quartz pyrolysis tube, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C s⁻¹ the sample was held at this temperature for 15 s in a flow of helium, and upon pyrolysis the interface was heated from 40 to 350 °C at 100 °C s⁻¹ where it was held for 15 min to prevent volatilisation of the samples prior to pyrolysis. The GC injector was held at 270 °C and operated at a 50:1 split with a helium column flow rate of 1.1 mL min⁻¹. Separation was performed on a DB-5MS ultra inert column (J&W; 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness). The GC oven temperature was held for 2 min at 35 °C and subsequently ramped to 300 °C at a rate of 5 °C min⁻¹ and held at this temperature for 9 min. Mass spectra were acquired in electron impact mode (70 eV) with a scan range from 50 to 500 amu.
5.5 Pyrolysis-GC-MS of tetradecanoic acid adsorbed on montmorillonite

Py-GC-MS was performed using a 2000 Pyroprobe (CDS Analytical) via a 1500 valve interface and coupled to 6890 GC and a 5973 MS (both Agilent Technologies). Dried adsorbed fatty acid montmorillonite samples were homogenised and approximately 10 mg were placed in quartz pyrolysis tubes, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms\(^{-1}\) the sample was held at this temperature for 15 s in a flow of helium. The interface was held at 200 °C upon pyrolysis when it was ramped to 350 °C at 60 °C s\(^{-1}\). The pyrolysis method for adsorbed fatty acids on minerals is discussed in Chapter 2, section 2.5.4. The GC injector was held at 270 °C and operated at a 10:1 split for adsorbed samples with a helium constant column flow rate of 1.1 ml min\(^{-1}\). All other conditions were the same as for the pyrolysis of tetradecanoic acids as described above.

5.6 Results

5.6.1 Adsorption isotherm

The shape of the isotherm produced in this adsorption experiment (Fig 5.2, Tab.1) can be described as an s-isotherm according to published classifications (Giles et al. 1974). Previously, a linear adsorption isotherm was reported for heptadecanoic acid adsorption on montmorillonite in 35‰ NaCl solution (Meyers and Quinn 1971a). However more recently an s-isotherm was reported for the adsorption of l-lysine on montmorillonite (Parbhakar et al. 2007).
The adsorption isotherm obtained for tetradecanoic acid adsorbed on montmorillonite in 35‰ NaCl saline solution, $q_e$ (µM/g) is the concentration of tetradecanoic acid adsorbed on montmorillonite while $C_e$ (µM/L) is the final tetradecanoic concentration.

Table 5.1. Adsorption of tetradecanoic acid on montmorillonite in 35‰ NaCl solution. Equilibrium concentration of tetradecanoic acid $C_e$ (µM/L) represents the amount retained in the glass tubes after 24 hours equilibration at 21 ± 2 °C and is calculated as a relative response factor.

<table>
<thead>
<tr>
<th>Montmorillonite (g)</th>
<th>Tetradecanoic acid initial concentration (µM/L)</th>
<th>$C_e$, equilibrium concentration of tetradecanoic acid (µM/L)</th>
<th>Adsorbed concentration of tetradecanoic acid (µM/L)</th>
<th>$q_e$, concentration of adsorbed tetradecanoic acid per gram (µM/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>22</td>
<td>0.394</td>
<td>21.6</td>
<td>432</td>
</tr>
<tr>
<td>0.05</td>
<td>44</td>
<td>0.773</td>
<td>43.2</td>
<td>865</td>
</tr>
<tr>
<td>0.05</td>
<td>88</td>
<td>0.931</td>
<td>87.1</td>
<td>1741</td>
</tr>
<tr>
<td>0.05</td>
<td>110</td>
<td>1.192</td>
<td>108.8</td>
<td>2176</td>
</tr>
<tr>
<td>0.05</td>
<td>131</td>
<td>1.424</td>
<td>129.6</td>
<td>2592</td>
</tr>
</tbody>
</table>

The adsorption data were further analysed by using the linear form of the Langmuir and Freundlich adsorption isotherms (Limousin et al. 2007). Details of both Langmuir and Freundlich adsorption isotherms were discussed in Chapter 2, section 2.2.1.
Correlation coefficients ($R^2$) obtained from adsorption of tetradecanoic acid on montmorillonite for Freundlich model is $R^2 = 0.920$ (Fig 5.3) and Langmuir model is $R^2 = 0.687$ (Fig. 5.4) models showed a better fit with the Freundlich model.

![Freundlich isotherm plot](image1.png)

**Fig 5.3** Freundlich isotherm plot: Logarithmic plot of adsorption data. The y-intercept is equivalent to $\log K_f$ and the slope is equal to $1/n$. $\log K_f = 2.525$, $1/n = 0.195$ and $R^2 = 0.920$

$$y = 0.1957x + 2.5259$$

$$R^2 = 0.9202$$

-0.40 -0.11 -0.03 0.08 0.15

0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00

Log $q_e$, concentration of tetradecanoic acid adsorbed on Montmorillonite ($\mu$M/g)

Log $C_e$, final concentration of tetradecanoic acid ($\mu$M/L)

![Langmuir isotherm plot](image2.png)

**Fig 5.4** Langmuir isotherm plot: The slope is equal to $1/Q_{\text{max}} = -0.0004$ where $Q_{\text{max}} = -2500$ ($\mu$M/g) is the maximum adsorption capacity. The y-axis intercept is equal to $1/Q_{\text{max}}b$, where $b$ is a constant (L/g).

$$y = -0.00041x + 0.0011$$

$$R^2 = 0.68$$

0 0.5 1 1.5

$C_e$, final concentration of tetradecanoic acid ($\mu$M/L)

$C_{\text{eq}}$, equilibrium concentration of tetradecanoic acid ($\mu$M/L)
5.6.2 Pyrolysis products of pure tetradecanoic acid

Pyrolysis of free tetradecanoic acid produces tridecane, alkenes (C$_4$ to C$_{14}$), a series of saturated and mono-unsaturated low molecular weight fatty acids (C$_6$ to C$_{11}$), and toluene (Fig 5.5, See Appendix D for full list of compounds).

![Pyrolysis-GC-MS total ion chromatogram of tetradecanoic acid at 650 °C. See Appendix D for full list of compounds identified.](image)

5.6.3 Pyrolysis of tetradecanoic acid adsorbed on montmorillonite

Pyrolysis products of tetradecanoic acid adsorbed on montmorillonite (Fig 5.6, See Appendix D for list of compounds) are significantly different from the pyrolysis products of free tetradecanoic acid (Fig 5.5). The classes of organic compounds identified are alkenes (C$_4$ to C$_{14}$), alkanes (C$_{10}$ to C$_{14}$), benzene and its derivatives, indane and its derivatives, alicyclic compounds, naphthalene and its derivatives, a dominant peak of tetradecanoic acid, tetradecanal, and a homologous series of ketones (K$_{15}$ to K$_{19}$) along with the symmetric ketone, K$_{27}$. 
Fig 5.6 Pyrolysis-GC-MS total ion chromatogram of tetradecanoic acid adsorbed on montmorillonite at 650 °C. Symbols represent following classes of compounds, See Appendix D for full list of compounds identified.
5.7 Discussion

5.7.1 Adsorption of tetradecanoic acid to montmorillonite

Adsorption of OM is reported on both mesopores (Zimmerman et al. 2004) and clay edge particles of minerals (Mayer et al. 2004). Different mechanisms such as cation exchange, cation bridge, ligand exchange, van der Waals bonding and hydrophobic effects have been proposed for the sorption of organic matter on clay minerals (Arnarson and Keil 2000). Understanding the underlying mechanism of adsorption between an organic molecule and clay minerals which depends solely on clay mineral structure and the nature of the organic molecule might be helpful in monitoring the fate of adsorbed organic molecules during diagenesis.

The two important processes that have been discussed in the context of organo-mineral interactions, particularly for smectite minerals, are intercalation and adsorption. Intercalation is the penetration of organic molecules into the interlayer space of clay minerals and is an effective way of constructing ordered inorganic-organic and inorganic-inorganic assemblies resulting in an organo-clay nanocomposite (Theng et al. 1986, Sposito et al. 1999, Kennedy et al. 2002, Kennedy and Wagner 2011, Lohr and Kennedy 2014). Contrary to intercalation, adsorption is the concentration of a substance at the surface and results in an organo-mineral surface complex (Keil et al. 1994a, Mayer 1994 b). This work aims to answer the significance of adsorption of one of the naturally found long chain fatty acids, tetradecanoic acid onto montmorillonite and its transformation into different classes of organic compounds upon flash pyrolysis.

Clay lamella have polar sites of Al-OH (octahedral) and Si-OH (tetrahedral) at the broken edge surfaces along with the exposed hydroxyl-terminated planes (Johnston and Tombacz 2002). These edge surfaces and the exposed hydroxyl-terminated planes of clays are thought to be involved in the adsorption of organic molecules (Kubicki et al. 1997, Nordin et al. 1997). In contrast to kaolinite, montmorillonite has a single type of basal surface i.e. siloxane which can normally adsorb water and cations (Liu and Lu 2006, Vasconcelos et al. 2007, Anderson et al. 2010). Chorover and Amistadi (2001) reported that cation bridging, entropy-driven processes and hydrophobic interactions are more important than the ligand exchange mechanisms for the sorption of organic matter on expanding 2:1 layer clays such as montmorillonite. Hydrophobic interaction between siloxane surface of aluminosilicates and
long chain alkane moieties has been reported (Laird and Fleming 1999, Namjesnik-Dejanovic et al. 2000, Sheng et al. 2001), however due to the presence of Na$^+$ metal ions in this study, the hydrophobic interaction is probably less expected than the electrostatic interaction between carboxylic acid ions and basal surface via Na$^+$ metal cation bridging. This synthesis is consistent with the work of Nevgskaia et al. (1998) who reported an increase in adsorption of anionic surfactant on quartz and kaolin due to the presence of Na$^+$ metal cations.

Besides its basal surface, the edge surfaces of kaolinite were also thought to be involved in bonding with tetradecanoic acid in an aqueous solution containing NaCl (See chapter 4). Therefore it is hypothesised that under the same experimental conditions, the adsorption of tetradecanoic acid on montmorillonite might also be accompanied at broken edge surfaces via electrostatic interactions.

Moreover, in my previous work on kaolinite (See chapter 4), I explained the correlation of fatty acids adsorption on kaolinite with the adsorption on its two surfaces i.e. tetrahedral (siloxane) and octahedral (hydroxyl). Based on the pyrolysis products obtained from adsorbed fatty acid on kaolinite, silica and alumina, it was predicted that the aluminol/silanol groups and basal planes are involved in bonding with the fatty acid. Interestingly in this study, I can see the exceptional similarities among the pyrolysis products of fatty acid adsorbed on montmorillonite and kaolinite, and therefore it can be hypothesised that both the edge surfaces and basal planes of montmorillonite are involved in forming a fatty acid-mineral complex on mineral surface.

Despite similarities in pyrolysis products, differences in the sorption capacity of kaolinite and montmorillonite have also been observed. By comparing the adsorption isotherms of montmorillonite and kaolinite, it is observed that kaolinite has more sorption capacity than montmorillonite (Fig 5.7). Previously, Zhou et al. (1994) and Feng et al. (2005) reported the higher adsorption of humic acid on kaolinite than on montmorillonite. For humic acid, the higher adsorption on kaolinite might be due to the montmorillonite selective uptake of lower molecular weight compounds and kaolinite preferential adsorption of larger molecules (Chorover and Amistadi 2001). Another reason could be due to the high edge area of 20 to 30 \% to surface area of kaolinite while montmorillonite, although displaying a high surface area, has an edge area of only 1\% (Wan and Tokunaga 2002). Furthermore the relationship between surface area and the pore size is also very important as with the increase in surface
area, the average pore size decreases which can hinder the adsorbate to access the clay surface (Silva et al. 2013). In this study, montmorillonite (31.82 ± 1.02 m²/g) has although high surface area then kaolinite (10.5 ± 0.02 m²/g), must have less average pore size than in kaolinite thus hinder the carboxylate ions to access the mineral surface.

Fig 5.7 The adsorption isotherm obtained between tetradecanoic acid adsorbed on kaolinite and montmorillonite, y-axis; qₑ (µM/g) concentration of tetradecanoic acid adsorbed on kaolinite and montmorillonite, x-axis; initial concentration (µM/L) of tetradecanoic acid in 35‰ NaCl saline solution

In contrast to the aforementioned sorption capacity difference, montmorillonite has more solid acid sites than kaolinite (Liu et al. 2013b). This may be due to the fact that kaolinite does not contain interlayer cations or naturally intercalated water, and therefore has fewer acid sites than montmorillonite (Liu et al. 2013b). Despite the fact that montmorillonite is more acidic than kaolinite, it is, however, interesting to mention here that at high-temperature kaolinite dehydroxylates to transform into meta-kaolinite, and during this transformation Bronsted acid sites are formed due to the break off of hydroxyl groups and Lewis acid sites are formed due to the formation of four- or five-coordinate aluminium cations (Rong and
Xiao 2002). More recently Liu et al. (2013f), reported that heating increases the total acidity of montmorillonite until the temperature approaches to 600 °C. With the increase in temperature, Lewis acidity increase due to the exposure of some unsaturated Al\(^{3+}\) ions at the particle edges which were previously behaving as Bronsted acid sites due to the adsorbed water (Rupert et al. 1987). Furthermore these Lewis acid sites, unsaturated Al\(^{3+}\) ions are either formed from the rupture of Si-O-Al or dehydroxylation at high temperature are of high acid strength (Bhattacharyya and Sen Gupta 2008). In contrast to Lewis acidity, at high-temperature Bronsted acidity which is mainly due to interlayer water coordinated to exchangeable cations or H\(_3\)O\(^+\) ions associated with the negatively charged AlO\(_4\) tetrahedra (Rupert et al. 1987) decreases. Interlayer water decreases at 120 °C and around 200 °C it disappears reducing the source of protons which results into reduced weak Bronsted acid sites (Liu et al. 2013f). However at 600 °C Liu et al. (2011) reported Bronsted acidity due to the re-adsorbed water on the unsaturated Al\(^{3+}\) ions. Although I suspect that the freeze drying of fatty acid adsorbed montmorillonite might have reduced the interlayer water or H\(_3\)O\(^+\) ions associated with the negatively charged AlO\(_4\) tetrahedra eventually decrease the Bronsted acidity, it seems likely from the above discussion that the both Lewis and Bronsted acidity increased upon pyrolysis. The effect of both Lewis and Bronsted acidity is also evident from the pyrolysis products of adsorbed fatty acid on montmorillonite which showed both saturated/unsaturated hydrocarbons along with the aromatic hydrocarbons.

Importantly the number of clay acid sites is proportional to the catalytic effect (Liu et al. 2013b) which essentially means that montmorillonite has a more catalytic effect on organic compounds relative to kaolinite. Pyrolysis products of fatty acid adsorbed montmorillonite showed distinctly more polycyclic aromatic compounds (Fig 5.6) than the fatty acid adsorbed kaolinite (Fig 4.6) supporting the hypothesis that montmorillonite is more acidic than kaolinite. The higher amount of polycyclic aromatic and saturated compounds is attributed to the highly acidic character of clay, due to hydrogen transfer in catalytic reactions as described in a few studies (Corma et al. 1985, Frety et al. 2014).

As detailed by Johns (1979) in the absence of acid catalyst, a radical mechanism is responsible for carbon-carbon cleavage and the subsequent thermal cracking of hydrocarbons while the carbonium ion pathway is applicable when a clay mineral with Bronsted acid sites is present to initiate a carbocation mechanism (Johns 1979). A mineral acid catalyst with strong Bronsted sites favours the formation of aromatic and polycyclic aromatic...
hydrocarbons (Santos et al. 1998, Faure et al. 2006a). Fatty acid adsorbed montmorillonite showed significant aromatic and polycyclic aromatic compounds indicating the strong Bronsted acidity of montmorillonite clay minerals (Fig 5.6).

Further Bronsted acid sites are also active source of hydrogen, available for the conversion of n-alkenes to n-alkanes by hydrogenation (Wu et al. 2012). The formation of n-alkanes (C_{10} to C_{14}) from fatty acid adsorbed montmorillonite indicates the effect of the C-C cleavage after decarboxylation and the availability of active hydrogen Bronsted acid sites. The transformation of adsorbed fatty acids on montmorillonite to hydrocarbons is mainly due to Lewis acidity which is responsible for the decarboxylation of fatty acids (Almon and Johns 1977).

Previously, studies suggested that the end hydrocarbon ratio in the pyrolysis products allow an estimate of the relative importance of hydrodeoxygenation (HDO) over decarboxylation-decarbonylation (DCO) decomposition routes (Kubička and Kaluža 2010, Kubička et al. 2014). The hydrocarbon ratio (C_{14}/C_{13}) is used to estimate the relative importance of hydrodeoxygenation (HDO) over decarboxylation-decarbonylation (DCO) decomposition route for acid adsorbed montmorillonite (Table 5.2). The low hydrocarbon ratios obtained indicate that DCO is the main reaction pathway.
Table 5.2. Peak area ratio of hydrocarbons obtained after manual integration of total ion chromatograms of fatty acid adsorbed montmorillonite.

<table>
<thead>
<tr>
<th>Tetradecanoic acid adsorbed on montmorillonite, qe (µM/g)</th>
<th>Ratio of hydrocarbons (C₁₄/C₁₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1741</td>
<td>0.041</td>
</tr>
<tr>
<td>2176</td>
<td>0.043</td>
</tr>
<tr>
<td>2592</td>
<td>0.037</td>
</tr>
</tbody>
</table>

5.7.2 Geochemical implication for the formation of aromatic compounds from the adsorbed acid on montmorillonite.

Previously, the association of clays with fatty acids was simulated by simple mechanical grinding of pure fatty acid compounds with clay minerals (Jurg and Eisma 1964, Shimoyama and Johns 1971, Aizenshtat et al. 1984, Hellerkallai et al. 1984). In contrast to those studies this is the first report of the high-temperature pyrolysis of fatty acid adsorbed onto montmorillonite exclusively obtained from adsorption experiments. The pyrolysis products obtained in this study from the fatty acid adsorbed montmorillonite are significantly different from the high temperature-pressure pyrolysis products of intercalated 12-amino lauric acid on Montmorillonite (Yuan et al. 2013). Besides the difference in the nature of pyrolysed compound and the difference in temperature and pressure, the main difference exists in the classes of organic compounds obtained after pyrolysis. For instance, Yuan et al. (2013) reported C₁-5 hydrocarbons from intercalation of 12-amino lauric acid on montmorillonite, however, the authors do not discuss the formation of any other classes of organic compounds as reported in this study from the high temperature pyrolysis of adsorbed tetradecanoic acid on montmorillonite (Fig 5.6). Here a key question is whether the formation of various classes of organic compounds are specific to the organo-mineral surface complex formed after adsorption and the formation of low molecular weight hydrocarbons are only characteristic of organo-clay nanocomposite formed after interlayer reactions.

The most remarkable feature of this study is the formation of a variety of aromatic and polycyclic aromatic hydrocarbons from the pyrolysis of adsorbed tetradecanoic acid on montmorillonite (Fig 5.6). Clay minerals, particularly acidic minerals, play a critical role for the formation of aromatic compounds from n-alkane and isoprenoid chains in the petroleum distillate via a carbocationic mechanism and aromatization reactions (Kissin 1998). The formation of light aromatic compounds (phenyl derivatives) at high-temperature pyrolysis is
also the highlight of the flash pyrolysis experiment in this study. Typically, these light aromatic compounds are usually observed during catagenesis stage of petroleum formation (Albrecht et al. 1976, Vandenbroucke and Largeau 2007). In the absence of montmorillonite, pyrolysis of tetradecanoic acid at 650 °C yields toluene only (Fig 5.5) while in the presence of montmorillonite a range of light aromatic compounds is observed (Fig 5.6). Contrary to that, Kissin (1998) reported the formation of benzene, toluene, ethyl benzene and 1,3,5-tri methyl benzene at 300 °C for 24 hours heating. This essentially implies that at high temperature pyrolysis decarboxylation is dominant over aromatization for alkanoic acids, in contrast to mild temperature (300-350 °C) heating where both decarboxylation and aromatization are dominant.

With the increase in adsorption of tetradecanoic acid on montmorillonite, the yields of light aromatic compounds decrease relative to the combined yields of aliphatic products with similar boiling points (Table 5.3). One reason for this decrease in light aromatic compounds might be due to reduction in clay surface area relative to organic reactants; however the exact reason cannot be detailed here from the current work. At high fatty acid adsorption, ketonisation is observed which is similar to the ketonisation observed at high fatty acid adsorption in kaolinite (See Chapter 4) and therefore I suspect that this might be related to the dimerization reaction between fatty acid molecules at high adsorption.

Table 5.3. Relative yields of light aromatic compounds in high temperature pyrolysis of adsorbed tetradecanoic acid on montmorillonite. Aromatic compounds yields are relative to the combined yields of aliphatic products with similar boiling points. Bz; benzene, Tol; toluene, Et-Bz; ethyl benzene, Xyl; xylene, 1,3,5-Me3-Bz; 1,3,5 tri methyl benzene.

<table>
<thead>
<tr>
<th>q_e, adsorbed tetradecanoic acid on montmorillonite µM/g</th>
<th>([\text{Bz}]/[\sum (C_7)])</th>
<th>([\text{Tol}]/[\sum (C_8)])</th>
<th>([\text{Et-Bz}]/[\sum (C_9)])</th>
<th>([\text{Xyl}]/[\sum (C_9)])</th>
<th>([1,3,5-\text{Me}_3-\text{Bz}]/[\sum (C_9)])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1741</td>
<td>0.15</td>
<td>0.53</td>
<td>0.14</td>
<td>0.28</td>
<td>0.17</td>
</tr>
<tr>
<td>2176</td>
<td>0.13</td>
<td>0.49</td>
<td>0.12</td>
<td>0.26</td>
<td>0.16</td>
</tr>
<tr>
<td>2592</td>
<td>0.12</td>
<td>0.36</td>
<td>0.12</td>
<td>0.22</td>
<td>0.15</td>
</tr>
</tbody>
</table>
5.8 Conclusion

This work distinctly shows pyrolysis products including aromatic compounds and polycyclic aromatic hydrocarbons formed at high temperature from the adsorption of straight chain carboxylic acids on montmorillonite. The adsorption isotherm of montmorillonite is expressed as an s-isotherm which represents the multilayer adsorption of fatty acid molecules on mineral surface. Importantly, current experimental work showed a significant difference in adsorption and catalysis between montmorillonite and kaolinite minerals. Montmorillonite shows less adsorption and has a greater catalytic effect than kaolinite. Light aromatic compounds including benzene, toluene, ethyl benzene, xylene, and trimethyl benzene were observed; however, their ratio decreases relative to the hydrocarbons as adsorption increases.
Chapter 6

Co-pyrolysis of aromatic carboxylate and formate salts: A new method for addressing cross-linking in coal liquefaction

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6.1 Introduction

6.1.1 Occlusion of metal cations in macromolecular structure during diagenesis

Aromatic carboxylic acids are ubiquitous in natural environment and have a two-fold importance as a fraction of humic substances (Wood 1996 and references therein) and as a relatively abundant moiety in sub-bituminous coals and lignites (low rank) (Joseph and Forrai 1992, Sugano et al. 1999, Kaneko et al. 2000, Vasireddy et al. 2011) have been investigated in voluminous literature. Besides kerogen, the end product of diagenesis is brown coal in coal mires. Diagenesis is a diverse group of processes and during these processes inclusion of metal cations such as Fe$^{3+}$, Ca$^{2+}$ in coal has been reported. Moreover, these metal cations can also be present as a biogeneic material in coal and are retained in macromolecular stages during peatification and coalification (Killops and Killops 2009). Presumably, these cations cause precipitation and form salt in macromolecular structures.

6.1.2 Aromatic carboxylic acids in coal

Oxygen is the second most abundant element in the macromolecular structure of coals. In comparison to sub bituminous coal, bituminous coals contain a less significant proportion of carboxylic acids and the macromolecular structure is composed of highly substituted, cyclical carbon structures of condensed rings bounded by alkyl or ether bridges (Vasireddy et al. 2011). Based on inorganic content, bituminous coals are also different from sub bituminous coals as the latter contain minerals both in discrete and organic bound form (Joseph and Forrai 1992). Low-rank coal mainly contains organic-bound minerals as carboxylate salts of alkali and alkaline earth metals (AAEM) species. Moreover, due to their low cost and ability to produce low molecular weight products they have been used as feedstocks in the coal liquefaction process (Derbyshire and Hager 1994). During liquefaction, minerals can be beneficial as a catalyst or they can also be unfavourable due to the deposition of poisons catalyst on the liquefaction reactor (Gorbaty 1994). From coal, discrete minerals can be removed by the sink float technique and bound minerals can also be segregated by using aqueous SO$_2$ or pre-swelling techniques (Joseph and Forrai 1992), however, the presence of divalent cations such as Ca$^{2+}$ cations significantly decreases the liquid hydrocarbon yields in pyrolysis and liquefaction processes (Tyler and Schafer 1980, Franklin et al. 1983, Joseph and Forrai 1992). Besides that, the presence of divalent cations also enhances the moisture
sorption capacity of coal (Schafer 1972) and also improves catalysis for hydrogasification (Radovic et al. 1985) and steam gasification of char (Matsumoto and Walker 1986).

### 6.1.3 Coal liquefaction

Coal liquefaction is defined as the breakdown of macromolecules into smaller hydrocarbon molecules that can be distilled. During liquefaction, liquid phase formation is the first step in which small molecules of coal are fused at a temperature above 350 °C. First ether linkages cleave (Vernon 1980) and then methylene bridges break (Kuhlmann et al. 1981) during uncatalysed liquefaction pyrolysis at 400-450 °C. Free radicals are also generated during the liquefaction process via thermal scission or homolysis of bonds which are then capped by the H-atoms from the donor molecules (McMillen and Malhotra 2006, Vasireddy et al. 2011). In the absence of an H-atom source, the free radicals repolymerise in coupling reactions or can also form stable high molecular weight products via a complex series of reactions. These reactions and hydrogen termination of reactions that produce tetrahydrofuran insoluble fractions are called retrogressive or retrograde reactions (Vasireddy et al. 2011). The formation of benzyl-type radicals is also involved in retrogressive reactions (Song et al. 1992, Saini et al. 1993). Further, it is suggested that the presence of oxygen-containing functional groups in low-rank coals is a major contributor to retrograde products by cross-linking reactions, which inhibit the formation of liquid fuels (Serio et al. 1991, Mae et al. 1998).

### 6.1.4 Decarboxylation linked with cross-linking

Primarily the low-temperature decarboxylation reactions were linked to the cross-linked products formed from coal pyrolysis (Suuberg et al. 1985, Solomon et al. 1990, Ibarra et al. 1991). According to Manion et al. (1996) hydrogen-activated benzoic acids can undergo coupling reactions which can be inhibited by an H-donor, however, the electron transfer agent can enhance decarboxylation. Later on, it was suggested that in coal pyrolysis, both cross- linking reactions and decarboxylation can be minimised by reactions such as methylation, demineralization (Mochida et al. 1983), or ion exchange of the inorganic cations (Serio et al. 1993a). In contrast to that, demineralised coal having oxidised or cation exchanged (Na⁺, K⁺, Ca²⁺ etc) was reported to increase cross-linking with CO₂ evolution (Joseph and Forrai 1992, Serio et al. 1993b). Decarboxylation via an acid promoted cationic pathway was observed without cross-linking from pyrolysis of certain carboxylic compounds at the temperature range of 325 to 425 °C (Eskay et al. 1996). Nevertheless when pyrolysis is
performed in the presence of non-proton donor solvents, minor cross-linking indirectly associated with decarboxylation was observed (Eskay et al. 1997, Britt et al. 1998). Cross-linking in these studies was observed due to the formation of low-temperature reaction intermediates, such as anhydrides formed by the condensation of aromatic carboxylic acids, and these intermediates decompose via radical-induced decomposition pathway (Eskay et al. 1997, Britt et al. 1998).

6.2 Objective

Previously pyrolysis of aromatic carboxylate salts and acids at different temperatures have been reported to understand the cross-linking in coal (Eskay et al. 1996, 1997, Britt et al. 1998, Dabestani et al. 2003, Dabestani et al. 2005). The main focus of these studies was the decarboxylation linked with crosslinking, coal liquefaction temperature, light aromatic hydrocarbon formation or pyrolysis conditions such as a hydrogen or nitrogen atmosphere. Considering the fact that there are a number of factors such as coal pretreatment, coal rank, and solvent effects that affect the coal liquefaction (Vasireddy et al. 2011), designing small scale analytical experiments to address the problems related to liquefaction or to improve the efficiency of liquid hydrocarbons yield from coal is still a practical approach. As part of this study, I used a simple comparative approach of co-pyrolysis of divalent carboxylate salts at a certain temperature to address the plausible crosslinking observed in mono-aromatic and di-aromatic carboxylate salts.

6.3 Experimental section

Benzoic acid, ortho-, iso-, terephthalic acids and calcium formate were purchased from Sigma-Aldrich. Calcium benzoate, calcium ortho-, iso-, and terephthalate were synthesised in the laboratory (details below) by using analytical grade reagents and high purity water (18.2 MΩ cm\(^{-1}\)). The purity of all acids and salts were assessed by ATR-FTIR (NicoletTM 5700 spectrometer). All spectra were collected for 128 scans at a resolution of 4 cm\(^{-1}\) with a scanning range from 400 to 4000 cm\(^{-1}\) (Fig 6.1).

6.3.1 Preparation of calcium benzoate

Calcium benzoate was prepared by neutralizing benzoic acid solution (0.8 M; 5g in 50 ml methanol) with sodium hydroxide solution (0.8 M; 1.6g in 50 ml methanol) by heating at 30
°C under vigorous stirring. Subsequently, anhydrous calcium chloride (0.4 M; 2.2g in 50 ml water) was then added to the benzoic acid/sodium hydroxide solution. The white solid product was extensively washed with water and dried in an oven at 90 °C for 10 hours.

6.3.2 Preparation of calcium ortho-, iso- and terephthalate.

Calcium orthophthalate was synthesised by adding calcium hydroxide solution (0.1M; 2.5g in 250 ml water) to the dissolved phthalic anhydride solution (0.1M; 5g in 250 ml water). The mixture was stirred for 6 hours; the precipitated product was washed with water for 7 times and then dried at 110 °C for 12 hours.

Calcium isophthalate was prepared by first neutralizing isophthalic acid solution (0.3M; 5g in 100 ml water) with sodium hydroxide solution (2.5M; 5g in 50 ml water), and then calcium chloride solution (0.9M; 5g in 50 ml water) was added over one hour with constant stirring at 25 °C. After stirring for 3 hours, the product was filtered, extensively washed with water and then dried at 100 °C.

Calcium terephthalate was formulated by slowly adding terephthalic acid solution (0.3M; 5g in 100 ml water) to the calcium hydroxide solution (0.3M; 2.3g in 100 ml water) at 90 °C. The mixture was stirred for 1 hour and the pH was neutralised from 11 to 7 by adding a small quantity of terephthalic acid. The reaction mixture was then stirred for an additional hour at 90 °C, washed with water 7 times and dried in an oven at 110 °C.
Fig 6.1 ATR-FTIR spectra: All aromatic carboxylic acids show a characteristic carbonyl peak (1650-1700 cm$^{-1}$). In aromatic carboxylate salts, C=O stretching absorption of 1700 cm$^{-1}$ moves to the lower wave number and the formation of two features due to asymmetric and symmetric vibrations of COO$^-$ group coordinated to the metal centres are obvious.

6.4 Pyrolysis-GC-MS of benzoic acid, ortho-, iso- and terephthalic acids.

Py-GC-MS was performed using a 5200 Pyroprobe (CDS Analytical) coupled via a heated transfer line (320 °C) to a 7890 GC and a 5975 MS (both Agilent Technologies). About 0.01 mg of each acid sample was placed in a quartz pyrolysis tube, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms$^{-1}$ the sample was held at this temperature for 15 s in a flow of helium, and upon pyrolysis the interface was heated from 40 to 350 °C at 100 °C s$^{-1}$ where it was held for 15 min to prevent volatilisation of the samples prior to pyrolysis. The GC injector was held at 270 °C and operated at a 50:1 split with a helium
column flow rate of 1.1 mL min\(^{-1}\). Separation was performed on a DB-5MS ultra inert column (J&W; 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness). The GC oven temperature was held for 2 min at 35 °C and subsequently ramped to 300 °C at a rate of 5 °C min\(^{-1}\) and held at this temperature for 9 min. Mass spectra were acquired in electron impact mode (70 eV) with a scan range from 50 to 500 amu.

6.5 **Pyrolysis-GC-MS of calcium salt of benzoic acid, ortho, iso and terephthalic acids and salt mixtures.**

Py-GC-MS was performed using a 2000 Pyroprobe (CDS Analytical) fitted via a 1500 valve interface and coupled to 6890 GC and a 5973 MS (both Agilent Technologies). Dried salt samples of approx. 0.01 mg were placed in quartz pyrolysis tubes, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms\(^{-1}\) the sample was held at this temperature for 15 s in a flow of helium. The interface was held at 200 °C until pyrolysis when it was ramped to 350 °C at 60 °C s\(^{-1}\). The GC injector was held at 270 °C and operated at a 50:1 split for salt samples with a helium constant column flow rate of 1.1 ml min\(^{-1}\). All other conditions were the same as for the pyrolysis of aromatic acids, as described above.

6.6 **Results**

6.6.1 **Pyrolysis products of benzoic acid and calcium benzoate**

Pyrolysis of benzoic acid produced mainly carbon dioxide, benzene, benzoic acid and benzophenone (Fig 6.2). A range of aromatic hydrocarbons was observed from the pyrolysis of a calcium salt of benzoic acid (Fig 6.2, Table 6.1). Calcium benzoate pyrolysates include carbon dioxide, benzene, benzaldehyde, benzoic acid, 2-ethylnaphthalene, diphenylmethane, fluorene, benzophenone, 9H-Fluoren-9-one, 9,10-anthracenedione, triphenylmethane, 9-phenyl-9H-fluorene, Methanone, [1,1'-biphenyl]-4-ylphenyl-, o-dibenzoyl benzene, 1,3 dibenzoyl benzene, 9-phenylantharcene, and 9,10-diphenylanthracene (Fig 6.2, Table 6.1).
Fig 6.2 Pyrolysis-GC-MS total ion chromatogram of benzoic acid and calcium benzoate at 650 °C. See Table 6.1 for the list of compounds identified.
Table 6.1. Pyrolysis products from benzoic acid, calcium benzoate and from mixture of calcium benzoate and calcium formate

<table>
<thead>
<tr>
<th>Pyrolysis products from benzoic acid</th>
<th>Pyrolysis products from calcium benzoate</th>
<th>Co-pyrolysis of calcium benzoate and calcium formate</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>carbon dioxide</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>benzene</td>
<td>benzene</td>
<td>benzene</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>benzaldehyde</td>
<td>benzoic acid</td>
</tr>
<tr>
<td>benzophenone</td>
<td>benzoic acid</td>
<td>biphenyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>diphenylmethane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>benzophenone</td>
</tr>
<tr>
<td>Fluorene</td>
<td></td>
<td>Fluorene</td>
</tr>
<tr>
<td>9H-Fluoren-9-one</td>
<td></td>
<td>9H-Fluoren-9-one</td>
</tr>
<tr>
<td>9,10-anthracenedione</td>
<td></td>
<td>9,10-anthracenedione</td>
</tr>
<tr>
<td>triphenylmethane</td>
<td></td>
<td>triphenylmethane</td>
</tr>
<tr>
<td>9-phenyl-9H-Fluorene</td>
<td></td>
<td>9-phenyl-9H-Fluorene</td>
</tr>
<tr>
<td>methanone, [1,1,biphenyl]-4-ylphenyl-</td>
<td></td>
<td>methanone, [1,1,biphenyl]-4-ylphenyl-</td>
</tr>
<tr>
<td>9-phenylanthracene</td>
<td></td>
<td>9-phenylanthracene</td>
</tr>
<tr>
<td>o-dibenzoyl benzene</td>
<td></td>
<td>o-dibenzoyl benzene</td>
</tr>
<tr>
<td>1,3-dibenzoylbenzene</td>
<td></td>
<td>1,3-dibenzoylbenzene</td>
</tr>
<tr>
<td>9,10-diphenyl anthracene</td>
<td></td>
<td>9,10-diphenyl anthracene</td>
</tr>
</tbody>
</table>

6.6.2 Pyrolysis products of ortho-, iso- and terephthalic acids, their calcium salts and mixture of calcium salts.

Pyrolysis of ortho-, iso-, and terephthalic acids yielded two common compounds i.e. benzene, and benzoic acid (Fig 6.3). Compound such as phthalic anhydride are commonly found in the pyrolysis products of iso- and orthophthalic acids while biphenyl was only observed in iso- and orthophthalic acid pyrolysates (Fig 6.3, Table 6.2).
Fig 6.3 Pyrolysis-GC-MS total ion chromatogram of phthalic acid isomers (ortho-, iso- and tere-) at 650 °C. See Table 6.2 for the list of compounds identified.
Table 6.2. Pyrolysis products from phthalic acid isomers

<table>
<thead>
<tr>
<th>Pyrolysis products from orthophthalic acid</th>
<th>Pyrolysis products from isophthalic acid</th>
<th>Pyrolysis products from terephthalic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Benzene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Benzoic acid</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>Phthalic anhydride</td>
<td>Phthalic anhydride</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Biphenyl</td>
<td>Biphenyl</td>
</tr>
</tbody>
</table>

The commonly observed aromatic hydrocarbons in all three calcium phthalate isomers were carbon dioxide, benzene, benzophenone and 9H-fluoren-9-one (Fig 6.4). Calcium isophthalate yielded biphenyl, 9, 10 anthracenedione, triphenylmethane and 9-phenyl-9H-Fluoren. Benzaldehyde was observed in the pyrolysis products of both calcium ortho- and terephthalate. Like calcium isophthalate, calcium orthophthalate also showed 9, 10 anthracenedione and 9-phenyl-9H-Fluoren. In addition to that, calcium orthophthalate also showed phthalic anhydride, o-dibenzoyl benzene, and 9, 10-diphenyl anthracene. Calcium terephthalate predominantly showed 2-ethenynaphthalene, fluorene, diphenylmethane and triphenylmethane (Fig 6.4, Table 6.3).
Fig 6.4 Pyrolysis-GC-MS total ion chromatogram of calcium ortho-, iso-, terephthalate and their mixture at 650 °C. See Table 6.3 for the list of compounds identified.
Table 6.3. Pyrolysis products from calcium salts of all three phthalic acid isomers, mixture of salts and mixture of calcium ortho phthalate and calcium formate

<table>
<thead>
<tr>
<th>Pyrolysis products from calcium orthophthalate</th>
<th>Pyrolysis products from calcium isophthalate</th>
<th>Pyrolysis products from calcium terephthalate</th>
<th>Co-pyrolysis of calcium orthophthalate and calcium formate</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>carbon dioxide</td>
<td>carbon dioxide</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>benzene</td>
<td>benzene</td>
<td>benzene</td>
<td>benzene</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>2-ethenyl naphthalene</td>
<td>benzaldehyde</td>
<td>benzaldehyde</td>
</tr>
<tr>
<td>phthalic anhydride</td>
<td>benzophenone</td>
<td>biphenyl</td>
<td>biphenyl</td>
</tr>
<tr>
<td>benzophenone</td>
<td>9H-Fluoren-9-one</td>
<td>Diphenylmethane</td>
<td>benzophenone</td>
</tr>
<tr>
<td>9H-Fluoren-9-one</td>
<td>9,10-Anthracenedione</td>
<td>Fluorene</td>
<td>9H-Fluoren-9-one</td>
</tr>
<tr>
<td>9,10-Anthracenedione</td>
<td>Triphenylmethane</td>
<td>benzophenone</td>
<td>9,10-Anthracenedione</td>
</tr>
<tr>
<td>9-phenyl-9H-Fluoren</td>
<td>9-phenyl-9H-Fluoren</td>
<td>9H-Fluoren-9-one</td>
<td>o-dibenzoyl benzene</td>
</tr>
<tr>
<td>o-dibenzoyl benzene</td>
<td>Triphenylmethane</td>
<td>benzophenone</td>
<td>9,10-diphenyl anthracene-</td>
</tr>
<tr>
<td>9,10-diphenyl anthracene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.6.3 Co-pyrolysis products of salt mixtures: calcium benzoate and calcium formate, calcium ortho phthalate and calcium formate.

Co-pyrolysis of a mixture of calcium benzoate and formate produced only carbon dioxide, benzene, benzaldehyde and benzoic acid (Fig 6.5 Table 6.1). Co-pyrolysate of a mixture of calcium orthophthalate and formate also showed minimal products; carbon dioxide and benzaldehyde (Fig 6.6, Table 6.3).
Fig 6.5 Pyrolysis-GC-MS total ion chromatogram of a mixture of calcium benzoate and formate and calcium benzoate at 650 °C. See Table 6.1 for the list of compounds identified.
Fig 6.6 Pyrolysis-GC-MS total ion chromatogram of calcium orthophthalate and formate, and calcium orthophthalate at 650 °C. See Table 6.3 for the list of compounds identified.
6.7 Discussion.

6.7.1 Flash pyrolysis of mono- and di- aromatic carboxylic acids and salts

Flash Py-GC-MS has been used widely for the characterisation of macromolecular structures such as coal, humic acids, and kerogen (Hatcher and Clifford 1994). Reactive radical sites left after the loss of carboxyl groups during direct liquefaction of coal, if not capped with hydrogen, have potential to combine with each other to form newly resistant structures (Vernon 1980). The extent of formation of aromatic and hydroaromatic condensed rings system (coupling products) due to thermal degradation or pyrolysis is different in aromatic carboxylic acids than in their salts. The flash pyrolysis study reported as a part of this research project not only shows the difference in pyrolysates from mono and di aromatic acids and their calcium salts but also determines the effect of co-pyrolysis of formate salt on coupling products.

At 650 °C benzoic acid decomposes via decarboxylation to form benzene, benzoic acid, and benzophenone (Fig 6.2). Previously, Moldoveanu (2009) reported the same decomposition products from benzoic acid at 500 °C. Contrary to Artok and Schobert (2000a) who reported coupling products such as biphenyl, p-phenylbenzoic acid, 4,4'-dicarboxybiphenyl from benzoic acid at 450 °C at a high pressure under a nitrogen atmosphere conditions, the present work did not show such coupling products at 650 °C. Similarly, Artok and Schobert (2000d) also reported benzene and benzaldehyde from benzoic acid at 450 °C under a hydrogen atmosphere. According to Artok and Schobert (2000a, 2000d) the formation of benzene can be explained via decomposition of a benzoic anhydride intermediate via induced homolysis, this can also be true in the present work, except that, no benzaldehyde is observed in this study. This essentially indicates that the pyrolysis conditions, including temperature and hydrogen/nitrogen atmosphere, can significantly affect the pyrolysis products.

Furthermore at 650 °C benzene and benzoic acid are the two common products not only from the pyrolysis of benzoic acid but also from phthalic acid isomers (Fig 6.2 & 6.3). Apparently, there is not much difference in the pyrolysis products in the presence of either single carboxylic group or double carboxylic acids group on a benzene ring except that a single coupling product, i.e. biphenyl, is observed in the pyrolysates of ortho- and isophthalic acid isomers only. Benzoic acid offers a significant difference from all three phthalic acid isomers in the formation of cyclic ketone, i.e. benzophenone, via keto-enol tautomerization due to
stearic conditions. Decomposition temperatures of all three phthalic acid isomers are different, as previously reported (Moldoveanu 2009) and the isomers showed minor differences in the pyrolysates. For instance, it is reported that the orthophthalic acid mainly decomposes at 200 °C to form phthalic anhydride via liberation of a water molecule, whereas isophthalic acid decomposes at a higher temperature of 450 °C via decarboxylation and forms benzoic acid and benzene (Moldoveanu 2009). At 650 °C a large peak of phthalic anhydride is observed from orthophthalic acid, while isophthalic acid pyrolysate showed only a minor peak of phthalic anhydride and no anhydride is observed from terephthalic acid (Fig 6.3). Terephthalic acid is more stable than the other two isomers and only sublimes at a low temperature of 300 °C but behaves similarly to isophthalic acid at a higher temperature and on prolonged heating (Moldoveanu 2009). At a temperature of 650 °C, terephthalic acid decomposes into i.e. benzene, and benzoic acid suggesting that further fragmentation can only be achieved at a temperature higher than 650 °C (Fig 6.3).

Pyrolysis of calcium benzoate was first reported by Hites and Biemann (1972) at 500 °C via a radical mechanism and then by Dabestani et al. (2003), Dabestani et al. (2005) who have reported an anionic mechanism for the formation of benzene, benzophenone, biphenyl, diphenyl methane, triphenyl methane and 9-phenylfluorene. Pyrolysis products of calcium benzoate in this study (Fig 6.2) are quite close to the pyrolysis products reported by Dabestani et al. (2003), Dabestani et al. (2005) except that a few polycyclic aromatic compounds such as 2-ethenyl naphthalene, phenyl anthracene, diphenyl anthracene, methanone, [1,1,biphenyl]-4-ylphenyl- were also observed. Another noticeable difference in this study (Fig 6.2) from those of Dabestani et al. (2003), Dabestani et al. (2005) is the lower benzene yield than benzophenone which indicates the absence of water molecules in the pyrolysed sample of calcium benzoate.

Cyclic ketones, particularly benzophenone, are primarily observed from calcium benzoate, calcium phthalate isomers and calcium phthalate salt mixtures pyrolysis (Fig 6.2 and 6.4). Likewise, keto-group containing compounds such as 9H-Fluoren-9-one and 9,10-anthracenedione are observed in all calcium salts except that the calcium terephthalate pyrolysates do not show 9,10-anthracenedione. Recently, St Pierre et al. (2015) reported the formation of cyclic ketones from the calcium salt of muconic acid and further my own work also reported the ketonisation from the calcium salts of aliphatic carboxylic acids (Zafar et al. 2017). Ketonic decarboxylation or ketonisation is the oldest reported organic reaction in the
field of organic chemistry and has potentially many industrial applications (Renz 2005). Thus from pyrolysis work on aromatic acids and salts it seems likely that the ketonisation reactions are potentially responsible for coupling products in retrogressive reactions during direct coal liquefaction.

Pyrolysis of aromatic carboxylates (Fig 6.2 & 6.4) showed significantly more coupling products than the aromatic carboxylic acids (Fig 6.2 & 6.3). This specifies that at 650 °C condensation/polymerisation reactions or retrogressive reactions are more dominant from aromatic salts than from aromatic acids. This finding is to some extent parallel to those of Artok and Schobert (2000a) who have reported more condensation reactions from benzoic acid at a higher temperature of 450 °C under a nitrogen atmosphere.

6.7.2 Co-pyrolysis of mono- and di- aromatic carboxylate salt with calcium formate

The use of calcium formate as a co-pyrolysis salt has drastically changed the pyrolysis products from both calcium benzoate and calcium orthophthalate (Fig 6.5 & 6.6). Co-pyrolysis products of calcium benzoate-formate showed only carbon dioxide, benzene, benzaldehyde and benzoic acid contrary to the coupling products obtained from calcium benzoate. Similarly, co-pyrolysis of calcium orthophthalate-formate exhibited carbon dioxide and benzaldehyde without any coupling products. The presence of calcium formate in the pyrolysis salt mixture might acts as a source of reactive hydrogen (hydrogenating agent). The presence of reactive hydrogen helps in deoxygenating the products and in decreasing char formation which eventually results in high carbon liquid fuels (Case et al. 2012, Mikkamala et al. 2012, Case et al. 2014).

Carboxylic salts decomposition is also involved in the formation of carbonaceous residues besides carbonate, oxalate, oxide and metal (Gorski and Krasnicka 1987) as reaction products. The carbonaceous residues also reduce the amount of carbon available for the condensable volatile products. Carbonaceous residues from carboxylate salts are thought to be formed due to coupling products or condensation products. Recently, St Pierre et al. (2015) reported fewer carbonaceous residues due to the reduction in coupling products during sodium muconate-formate co-pyrolysis. Although the carbonaceous residue was not quantified in this study, the absence of coupling products from co-pyrolysis of calcium
formate with benzoate and phthalate salts showed the correlation between coupling products and carbonaceous residues.

Furthermore, Artok and Schobert (2000d) found no significant effect of gaseous hydrogen and nitrogen on the pyrolysis products of benzoic acid and suggested an additional active hydrogen catalyst in benzoic acid and its salts. On an industrial scale, hydrogen is directly added to coal-oil slurry in the presence of a hydrogenation catalyst or H-donor solvent, tetranaphthalene (tetralin) (Vasireddy et al. 2011). Apparently, hydrogen addition or H-donor solvent serves the purpose of suppressing the retrogressive reactions by capping radical moieties and further preventing repolymerisation reactions. Importantly, the present co-pyrolysis results showed no coupling products, due to the anticipated hydrogenation from calcium formate, and thus I propose that calcium formate can be used as an active hydrogen agent in the direct coal liquefaction process. Nevertheless, it is important to mention here that the use of calcium formate as an active hydrogen donor in liquefaction process should be tested further at slightly lower coal liquefaction temperatures (400-450 °C) than the one used in this experiment. Additionally, the effect of formate salt should also be tested on low-rank coal samples or on other model compounds exclusively representing coal to comprehend its importance as an active hydrogen donor during the coal liquefaction process.

**6.8 Conclusion**

Benzoic acid, phthalic acids isomers and their calcium salts were pyrolysed at 650 °C. The present work and its comparison to the previous work in literature showed that the choice of reaction conditions such as temperature affect the product formation. Both mono- and di-aromatic acids produce fewer coupling products than their salts which indicate the cross-linking induced by the divalent calcium ion. Further, this work explicitly showed that the coupling products formed due to induced cross-linking can be reduced by co-pyrolysis of calcium formate salt. Based on this simple experiment result, it is therefore speculated that the calcium formate salt can be used as an active hydrogen source in the coal liquefaction process after testing it on low-rank coal samples.
Chapter 7

Discussion, conclusion and future work

Imperial college London, Lab B109: Photo taken during pyrolysis tube preparation
7.1 Summary

The main intent of this thesis was to understand the adsorption of fatty acids* on minerals in the context of diagenesis and the use of flash pyrolysis technique was meant to understand the transformation of adsorbed fatty acids to different classes of organic compounds on mineral surfaces. Based on these objectives, fatty acid interactions with different minerals were explored and subsequently addressed in each chapter. Findings of relevant chapters are reiterated and discussed below.

7.2 S-isotherm and diagenesis

Adsorption isotherms obtained from the adsorption of tetradecanoic acids on calcite and clay minerals show the characteristic chemical properties of fatty acids as an adsorbate. Having a polar head available for binding with the mineral surface and a hydrophobic tail end exposed to water has affected the adsorption structure, which conclusively represents multilayer adsorption on the basis of this study. I suspect that this sort of multilayer adsorption is also representative of a zonal architecture or patch wise distribution of organic compounds in natural settings. Zonal architecture is reflected in the s-isotherms observed in this study, which shows the point of inflection representative of cooperative adsorption (Fig 7.1 & 7.2). The important consequence of cooperative adsorption is the hydrophobic interaction that bounds the outer hydrophilic layer to the inner hydrophobic layer. This sort of arrangement reduces the hydrocarbon exposure to water and maximises the entropy as previously reported (Kleber et al. 2007). Another dimension of multilayer adsorption is the formation of a constant molecular layer of fatty acids close to the mineral surface and as the degree of adsorption increases the thickness of fatty acids layer increases. The multilayer adsorption of fatty acids on different minerals gives substantial benefits to the condensation reactions which are considered as a critical step during diagenesis. The closely held adsorbed molecules of fatty acids interact with each other and can polymerise due to their vibrational and rotational movement.

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* fatty acids; tetradecanoic acid
Fig 7.1 Multilayer adsorption of fatty acids on calcite mineral showing hydrophobic interaction between adsorbed fatty acids molecule and also reflected from s-isotherm. The outer exposed layer is more accessible to microbial degradation than the inner protected layer.
Fig 7.2 Adsorption of fatty acids on kaolinite. The negatively charged siloxane basal surface is bonded with carboxylic acid group via cation bridging. Aluminol and silanol groups on edge sites of both octahedral and tetrahedral surfaces are bonded with carboxyl groups via ligand exchange mechanism. Hydrophobic interaction can be induced on both types of bonding as shown by s-isotherms in adsorption experiments.

7.3 Mechanism of fatty acids-mineral interaction and chemical nature of bonding

S-isotherms suggesting a multilayer architecture of fatty acids on all three types of minerals also address the chemical nature of bonding. S-isotherms exclusively suggest the multilayers which essentially mean that the first intimate layer to the mineral surface has a different chemical nature from the one above it.
7.3.1 Fatty acids-calcite mineral interaction

As I have shown in Chapter 3, fatty acids form salts after interacting with calcite minerals and as adsorption increases the growing layer of fatty acids tends to arrange itself via hydrophobic interaction on top of the first layer of salt. Contrary to that if the adsorption of fatty acids is accompanied by monolayer adsorption only, and then there is the possibility of formation of the salt layer on calcite mineral surfaces.

7.3.2 Fatty acids-clay mineral interaction

The pH of the fatty acid solution used in adsorption experiments is moderately acidic which means that heterogeneous charges might have developed on both kaolinite and montmorillonite clay minerals during adsorption process (See Chapter 4 & 5). Based on the literature review and on the structure of the clay minerals, I suspect that silanol and aluminol bonds at the edge surface of clay minerals are involved in bonding with fatty acids via a ligand exchange mechanism. Besides this mechanism, fatty acid molecules might also bond with the basal hydroxyl surface via H-bonding. In addition fatty acids are presumably bonded with the negatively charged siloxane surface of kaolinite and montmorillonite via sodium metal cations (cation bridging) in a saline solution. Again, in this case fatty acids bonded with the metal cations are likely to act like a salt, and as adsorption increases the next adsorbed acid layers start accumulating on top of the first layer. Further to that, intercalation (within the layer) or adsorption on the external surface is expected for montmorillonite interaction with fatty acids. It was observed that intercalation is not possible under the experimental conditions used and so the adsorption on an external surface is the main mechanism which can be recognised as the fatty acid-mineral surface complex.

Importantly an s-isotherm is observed in fatty acid adsorption on both calcite and clay minerals (See Chapters 3, 4, & 5) which means that adsorption is mainly dependent on the nature of the adsorbate (Fig 7.1 & 7.2). Nevertheless, the bonding mechanism for fatty acid adsorption is different between calcite and clay minerals, and this difference is subsequently reflected in the flash pyrolysis products.
7.4 Sorption-protection model for fatty acids and stability dynamics

The stability of organic matter on a mineral surface is the most challenging question raised for organic matter diagenesis in mineral sediments. Organic matter stability depends on its protection from degradation in a certain physical environment. In a free environment, organic matter is susceptible to biodegradation, while organic matter associated with minerals via adsorption provides protection against degradation.

A few possible mechanisms suggested so far for protection via sorption are the direct sorption of organic molecules on small pores, which can inhibit the hydrolytic enzymes, or organic molecules are strongly bonded to the mineral surface (chemisorption). Besides that the intercalation of organic matter within the clay interlayer also protects organic matter from degradation. In this regard, one important consideration is that microorganisms can still be able to use sorbed organic matter (Arndt et al. 2013 and references therein).

Multilayer fatty acid adsorption was observed on mineral surfaces, as can be seen in Chapters 3, 4, and 5. It is hypothesised that multilayer adsorption of fatty acids offers a difference to the previous view of sorption and protection of organic matter (Fig 7.1 & 7.2). From this finding, I propose that the outer most fatty acid layers adsorb via hydrophobic interaction are more susceptible to degradation than those found in close proximity to the mineral surface (Fig 7.1). In other words, the outer fatty acid layer protects the inner fatty acid layers from degradation. The surface sorbed fatty acid molecules behave differently due to their direct interaction with the mineral surface, such that they may tend to precipitate as salts on the surface of minerals. Previously, Mayer (1999) and Arnarson and Keil (2001) presented the idea of organic matter protection via formation of organo-clay aggregates instead of a continuous organic matter coating on the mineral surface. Further, these authors speculate that refractory organic matter at the surface of the aggregate or mineral matrix protects the organic matter from microbial attack. From this project finding, it can be envisaged that such organo-clay aggregate might initiate from multilayer adsorption of organic matter. For instance, aggregation requires chelation. In a natural setting, Ca$^{2+}$ ions chelation of marine dissolved organic matter leads to aggregation which then subsequently forms marine polymer gels that contain soluble humic substances and biopolymers. My experimental findings suggest that the formation of a salt layer on calcite mineral surfaces might act as a chelating agent and cause aggregation on a mineral surface.
7.5 Transformation of fatty acids to other classes of hydrocarbons: Implications of flash pyrolysis

The increase in fatty acid adsorption is well reflected from adsorption isotherms and the difference in the amount of fatty acid adsorbed on the mineral surface is also well emulated from the difference in total ion chromatograms (See chapters 3, 4 and 5). Therefore flash pyrolysis experiments not only indicate the formation of different classes of organic hydrocarbons (qualitative analysis) but also designate the amount of fatty acid adsorbed relative to the amount of mineral. Fig 7.3 shows a simple illustration for the formation of different classes of organic compounds from calcite and clay minerals.

7.5.1 Fatty acids-calcite interaction and their flash pyrolysis products

Fatty acids adsorbed on calcite predominantly form hydrocarbons and a series of ketones including high chain symmetric ketones (Fig 7.3). From my experimental data, I infer that a symmetric ketone, 14-heptacosanone, is formed via ketonic decarboxylation of calcium tetradecanoate which on further fragmentation forms hydrocarbons and ketones (See chapter 3). Identification of ketone intermediates for the formation of hydrocarbons from calcite minerals was the major finding of the experiment investigating fatty acid adsorption on calcite minerals. The formation of a high yield of ketones has been observed with an increase in adsorption on calcite minerals, which indicated that as adsorption increases, more carboxylate salts are formed, which eventually resulted into more ketones. Further, my work also showed that different cations such as calcium, magnesium, and sodium have no effect on flash pyrolysates (hydrocarbons and ketones).
7.5.2 Fatty acids-clay mineral interaction and their flash pyrolysis products

Selectivity of minerals towards the formation of different classes of organic compounds is very explicit from our flash pyrolysis work (See chapters 3, 4 & 5; Fig 7.3). Both straight chain and aromatic hydrocarbons are observed from both kaolinite and montmorillonite due to the catalytic efficiency and acidic properties of both minerals (Fig 7.3). The major finding for clay minerals comes from the empirical test which displayed that both siloxane (tetrahedral) and hydroxyl (octahedral) surfaces are involved in bonding with fatty acids, and therefore different classes of organic compounds are formed after fatty acid adsorption. Pyrolysis products of fatty acid adsorbed kaolinite, alumina, and silica indicate that the pyrolysates of kaolinite are more close to the pyrolysates from alumina. However, some similarity also exists between pyrolysates of silica and kaolinite, as both showed a dominant fatty acid peak comparable to the pyrolysates from alumina. Flash pyrolysis results from alumina, silica and kaolinite indicated that the aluminol bonds on both alumina and kaolinite are more reactive towards fatty acid adsorption; therefore there exists many similarities between their pyrolysates. Further, based on the finding of fatty acid adsorption on kaolinite, it is hypothesised that the (hydroxyl surface) octahedral face is more reactive towards fatty acid adsorption while siloxane (tetrahedral face) is less reactive and bonded with fatty acids via...
cation bridging. Cation bridged-fatty acids might act like salts and induce hydrophobic interaction for the other adsorbed fatty acid molecules or can also precipitate as salts on the surface of clay minerals.

Further pyrolysis products from kaolinite and montmorillonite are comprised of both straight chain hydrocarbons and aromatic hydrocarbons. Nevertheless, montmorillonite is more acidic and therefore produced more polycyclic aromatic compounds from adsorbed tetradecanoic acids. Light aromatic hydrocarbons were predominantly observed from fatty acid adsorbed montmorillonite, in contrast to the pure fatty acid pyrolysis which only produced toluene. The increase in adsorption decreased light aromatic products in comparison to the combined yield of aliphatic products of the same boiling points. The pyrolysis products obtained from fatty acids adsorbed on montmorillonite are a result of the organo-mineral complex, which can possibly be different from an organo-clay nanocomposite formed after intercalation within the montmorillonite layers.

### 7.6 Ketonisation in aliphatic carboxylic salts

Ketonisation observed from the fatty acid adsorbed calcite and from carboxylate salts is an important finding. This is the first kind of study to my knowledge in which ketonisation is reported from adsorption experiments that were mainly designed to understand diagenesis. In the biofuel industry, ketonisation has been considered useful, as it removes highly reactive carboxylic functional groups and forms stable high energy content products (Jackson 2013, Pham et al. 2013). Still much work is needed to understand the significance of ketonisation during diagenesis and its effect on hydrocarbon formation in marine settings.

### 7.7 Cross-linking in coals due to the diagenetic inclusion of metal cations.

Diagenesis is a dynamic process and involves many physical, chemical and biological reactions and transformations. During diagenesis, inclusion of metal cations, particularly divalent cations such as Ca$^{2+}$, has a substantial effect on the liquid hydrocarbon yields from coal. Pyrolysis of mono- and diaromatic carboxylic acids produced less cross-linking products than their counter carboxylic salts. Further to that, the major finding of co-pyrolysis was the use of the calcium formate as a hydrogenating agent for inhibiting the cross-linking products.
However, the study only depicted the laboratory scale results which require further tests prior to use on an industrial scale.

7.8 Conclusion

This multifaceted research project has focused on different aspects of diagenesis. The main aspect of diagenesis studied as part of this work was adsorption of fatty acids on different classes of minerals i.e. calcite, kaolinite, and montmorillonite. Fatty acid adsorption on different minerals resulted into multilayers which have provided a new dimension for the protection of fatty acids during diagenesis and also offers an exposition of the zonal or patches-wise architecture of organic matter and organo-mineral aggregation in natural marine settings. The present adsorption study emphasises the role of fatty acids, mineralogy, and cations. Fatty acid transformation into various classes of organic compounds upon pyrolysis depends on the catalysis of calcite and clay minerals. High-temperature pyrolysis showed that both calcite and clay minerals were substantially active catalytic minerals. Products formed from flash pyrolysis of adsorbed fatty acids on minerals were used to comprehend the bonding trends between minerals and fatty acids which provide useful information for fatty acid interaction with minerals in a natural environment. Ketonisation and hydrogenation of coupling products were the highlights of the flash pyrolysis work of this project which has enormous industrial applications.

7.9 Future work

Flash pyrolysis is a high-temperature thermal degradation technique, and cannot be equivalent to catagenesis. For future work, it is therefore suggested that a comprehensive thermal maturation study such as hydrous pyrolysis which is considered close to natural maturation should be designed for adsorbed fatty acids on minerals. The work done as a part of this research project will then possibly be used as a baseline study for such a future project which would help to understand the effect of adsorption during diagenesis on hydrocarbon formation under natural catagenesis conditions.
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Appendices

Appendix A. Publication

http://dx.doi.org/10.1016/j.jaap.2016.12.007

Appendix B. Classes of compounds identified from the flash pyrolysis of tetradecanoic acid, adsorbed tetradecanoic acid on calcite and salts of tetradecanoic acid (calcium, magnesium, sodium).

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| of saturated and   |              |              |              |              |
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Appendix C. Classes of compounds identified from the flash pyrolysis of tetradecanoic acid, adsorbed tetradecanoic acid on kaolinite, alumina and silica.

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Appendix D. Pyrolysis products obtained from tetradecanoic acid adsorbed on montmorillonite and from tetradecanoic acid.

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### Appendix D, continued

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