

Investigating the relationship between magnetisation and oil geochemistry

Stacey Anne Emmerton

**Imperial College London
Department of Earth Science and Engineering
PhD Thesis**

I declare that this thesis ‘Investigating the relationship between magnetisation and oil geochemistry’ is entirely my own work and that where any material could be construed as the work of others, it is fully cited and referenced, and/or with appropriate acknowledgement given.

A handwritten signature in black ink, appearing to read 'S. A. Emmerton', with a large, stylized initial 'S' and 'E'.

Stacey Anne Emmerton

Supervisors: Dr. Adrian Muxworthy, Prof. Mark Sephton & Prof. Wyn Williams

Abstract

A relationship between hydrocarbons and their magnetic signatures has previously been alluded to but this is the first study to combine extensive geochemical and magnetic data of hydrocarbon-associated samples. A detailed study is reported that identifies a definitive connection between magnetic mineralogy and oil biodegradation within samples from Colombia, Canada, Indonesia and the UK.

Geochemical data revealed that all the oil samples were derived from mature type-II kerogen deposited in oxygen-poor environments allowing for an investigation into biodegradation. Biodegradation is the decrease of oil quality through the conversion of aliphatic hydrocarbons to polar constituents through the activity of bacteria. The percentage of oil components and the biodegradation state of the samples were compared to the magnetic susceptibility and magnetic mineralogy. A distinct decrease in magnetic susceptibility was correlated to decreasing oil quality as well as extractable organic matter percentages, which cannot be rejected at 99% confidence. Further magnetic characterisation revealed that the high quality oils were dominated by pseudo-single domain grains of magnetite and the lower quality oils by larger pseudo-single domain to multi domain grains of magnetite and hematite; with decreasing oil quality there is a progressive dominance of multi domain magnetite as well as the appearance of hematite. It is concluded that biodegradation is a dual process, firstly, removing aliphatic hydrocarbons reducing oil quality and secondly, both creating and destroying magnetic signatures. This complex relationship may explain why controversy existed in the past when studying hydrocarbon associated anomalies.

Remagnetisation due to hydrocarbon infiltration is also reported within the Wessex Basin, UK. Palaeodirectional data from Mupe Bay revealed oil migration was initiated in the Early Cretaceous and a two-phase staining model is correct. These findings reinforce the importance of bacteria within petroleum systems as well as providing a platform for the use of magnetisation as a hydrocarbon proxy.

Extended Abstract

A relationship between hydrocarbons and their magnetic signatures has been alluded to for decades (e.g., Donovan et al., 1979; Elmore & Crawford, 1990; Aldana et al., 2003) but this is the first study to combine robust geochemical and magnetic data of hydrocarbon-associated samples. A very detailed study is reported that identifies a definitive connection between magnetic mineralogy and biodegradation within oil-bearing sedimentary rocks. Samples from Colombia, Canada, Indonesia and the UK were collected and geochemically and magnetically characterised.

Geochemical biomarker data revealed that all oil samples were derived from type-II kerogen, which were deposited in oxygen-poor environments. All the samples were also classed as mature, that is to say the oil window of hydrocarbon generation was reached. As the samples show the same source and maturity this allows for an investigation into biodegradation variations. Biodegradation is the decrease of oil quality through the conversion of aliphatic hydrocarbons to polar constituents mainly through the activity of bacteria. The magnetic characterisation involved low temperature and high temperature magnetic experimentation as well as scanning electron microscopy (SEM) with electron dispersion x-ray (EDX) analysis to help identify magnetic mineralogy and grain size distributions.

A negative linear regression in log space between magnetic susceptibility (χ) and the percentage of extractable organic matter (EOM%) was observed for normalized samples. The correlation cannot be rejected at a 95% confidence level and has a nonparametric Spearman's rank correlation coefficient (R_s) of -0.9. This observation is the opposite to that determined in the past, which revealed a positive relationship, suggesting the formation of magnetite as a result of hydrocarbon impregnation. In contrast this study, which includes a large number of different oils, suggests the opposite, that hydrocarbon infiltration into a sedimentary unit decreases the magnetic susceptibility. To determine if this relationship was due to the activity of bacteria or migration of the oil, the percentage of oil components; aliphatic, aromatics, polars and asphaltenes and the biodegradation state of the samples were compared to the magnetic susceptibility and magnetic mineralogy.

A distinct decrease in magnetic susceptibility was correlated to decreasing oil quality (loss of aliphatic hydrocarbons, more biodegraded), which cannot be rejected at 99% confidence. The strongest correlation existed with the polar and asphaltene components $R_s=-0.9$ as well as the aliphatic hydrocarbons $R_s=0.9$. The aromatic hydrocarbons also showed a negative relationship to χ of $R_s=-0.6$, but no correlation was identified in the asphaltene $R_s=0.4$ which agrees with the literature.

Further magnetic characterisation revealed that the high quality, low biodegradation oils from Colombia have a higher magnetic susceptibility and are dominated by pseudo-single domain grains of magnetite. The lower quality oils i.e., the UK, Canadian and Indonesian samples, displayed decreased magnetic susceptibility and pseudo-single domain to multi domain grains of magnetite and hematite. Magnetite and pyrrhotite framboidal material were found in all but the Canadian samples. Therefore, with decreasing oil quality there is a progressive dominance of multi domain magnetite as well as the appearance of hematite. The presence of hematite only within heavily biodegraded samples suggests a possible later stage of biodegradation at the surface due to oxidation of magnetite. In conclusion, biodegradation is a dual process; firstly, it removes aliphatic hydrocarbons decreasing the oil quality and secondly, it both destroys single domain grains and possibly creates multi domain grains of magnetite through bacteria present in the oil. This realisation could account for why magnetic anomalies associated with hydrocarbons have been controversial in the past.

The introduction of hydrocarbons or indeed any fluid into a sedimentary rock can cause a chemical remanent magnetization (CRM) to be acquired by altered or newly formed magnetic minerals in the direction of the ambient field. Applying this theory, this study attempted to answer a long-standing question about the timing of oil generation within the Wessex Basin, Dorset, UK. A unique outcrop at Mupe Bay consists of a conglomerate where both the clasts and matrix are oil impregnated. Some studies have suggested this indicates a two phase staining model resulting in oil generation in the Early Cretaceous due to the clasts being oil saturated before transportation, however, a single staining model also exists where the oil impregnated the whole unit in situ and any differences in appearance are due to grain size variations in the clasts and matrix. The previous geochemical results were inconclusive because differences in maturity biomarkers, which would have to be present for two-phase staining can also be explained by biodegradation. Therefore a new method of analysis was needed and CRM remagnetisation was investigated. Orientated samples were taken from both the clasts and matrix of the Mupe Bay conglomerate and magnetically investigated. The mineralogy and domain characteristics of the magnetic minerals present suggested relatively higher concentrations of multi domain authigenic magnetite within the matrix resulting in softer coercivity than in the clasts. The matrix is known to be more biodegraded than the clasts and it may be possible that this biodegradation has resulted in this variation. These differences between the clasts and matrix also support the theory of continued oil migration into the matrix. Hematite was also identified within the clasts and is usually oxidized from magnetite. This suggests there was early incorporation of hydrocarbons into the clasts, which became oil cemented and subsequently isolated soon after oil migration. The early oil migration into the clasts could have insured early formation

of magnetite and subsequent oxidation to hematite due to the isolation of the clasts from the matrix. The lack of hematite within the matrix supports this theory because biodegraded hydrocarbons are still actively seeping into the matrix allowing the formation of larger multi domain grains of magnetite but limiting the opportunity for oxidation.

Palaeodirectional data revealed that the matrix and clasts had different magnetic field orientations implying that the matrix and the clasts were stained by two separate oil migration events. This interpretation is supported by statistical analysis, which suggests the independence of the matrix and the clasts magnetisation cannot be rejected at a 95% confidence level. A conglomerate test was performed on the clasts and revealed the same orientations and therefore must have had their remanence recorded after incorporation into the sand matrix. This interpretation requires limited opportunity for biodegradation and magnetite formation before clast erosion, transport and deposition. Sedimentological data supports this assertion and clasts are believed to have been transported only a small distance from Lulworth Cove and are considered to have been deposited into the matrix whilst soft due to their deformation. Comparison of the palaeodirectional data with polar wandering paths for Northern Eurasia during the Cretaceous yields a mean age for the CRM, and therefore staining, transport and incorporation of the clasts, as Early Cretaceous, however, it should be noted that the palaeopoles for the Cretaceous especially are sporadic. In addition to this, the magnetic data for the matrix showed the same magnetisation as the present day magnetic field at this location (-6° Declination, 65° Inclination) at 95% confidence, suggesting it is an active oil seep. This data clearly supports the classic two-stage oil-staining event, which involves the onset of oil migration in the Wessex Basin in the Early Cretaceous. The matrix was stained at a later date and the Mupe Bay matrix continues to seep oil at the present day.

A combination of magnetic experimentation and SEM/EDX analysis has allowed a full rock magnetic characterisation of samples from both hydrocarbon bearing and dry well cores from the North Sea, UK. A detailed comparison was made on anomalously high magnetic susceptibility samples with background samples for each well and comparisons on the hydrocarbon producing and dry well cores.

The well cores in this study showed varying numbers of anomalous magnetic susceptibility peaks and to differing magnitudes (1.8×10^{-5} - $8.4 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$). Magnetic characterisation of these samples showed variation across all well cores as well as within each well core. There appears to be a strong abundance of siderite within some of the well cores identified through the Néel transition in low-temperature magnetic experiments as well as through Mössbauer spectroscopy. Iron oxides were also identified in all the samples and are thought to be mainly multi domain magnetite with small

abundances of hematite present. Across all the well cores there appears to be a wide range of magnetic minerals including, siderite, magnetite and hematite that are most probably due to their original geological facies. The data reveals a distinct lack of a specific magnetic mineral in association to hydrocarbons. The abundant siderite in the samples is most probably due to siderite nodules, which are common within sedimentary units.

Comparing the anomalous magnetic susceptibility samples and the background samples, there was not a significant difference within each well core. Both sets of samples for each well core shared similar behavioural characteristics in low and high temperature magnetic experimentation and within SEM and EDX analysis. This revealed a lack of specific magnetic characterisation within anomalous magnetic susceptibility levels to try to use to characterise well cores associated with hydrocarbons. Comparing the non-hydrocarbon (dry) well cores and the hydrocarbon bearing well cores revealed similar magnetic mineralogies but did reveal significant differences. The dry well cores had a signal dominated by siderite with a small abundance of magnetite, the opposite of what was found in some of the hydrocarbon producing well cores. Statistical analysis determined whether the magnetic susceptibility profiles of the well cores correlated to well log data. A nonparametric Spearman's rank correlation coefficient (R_s) was used and the results showed correlations between magnetic susceptibility and nearly all of the properties investigated through all the well logs at a 99% confidence level.

Magnetic susceptibility peaks, which would be more important for an identification tool, showed no correlation with the well log data for any of the cores. Specific anomalous characteristics described in previous studies, were therefore not identified within this study suggesting that at this stage, there are no universal characteristics that could be used to identify hydrocarbons through routine magnetisation logging tools. There are many geological factors which affect any/all of the well logs and there may be a relationship between magnetic susceptibility and some well log data, however, at present it is masked by many contributing factors and no easy solution is apparent. Due to the relationships determined within this study, it would suggest that any hydrocarbons, which leak through lower hydrocarbon carrier beds, should leave a magnetic trace and therefore be identifiable as a hydrocarbon migration pathway. Unfortunately at this stage, the lack of suitable samples/data does not allow for this theory to be investigated further within this study.

This study has identified a relationship between magnetisation and the relative abundance of aliphatic organic compounds in oil. Biodegradation appears to remove both aliphatic hydrocarbons and magnetic susceptibility owing to the influence of bacterial metabolic activity that uses ferric iron minerals as electron acceptors reducing the overall magnetic signature. This study also

demonstrates the utility of magnetic data to constrain the timing of migration in petroleum basins. These findings reinforce the importance of bacteria within petroleum systems as well as providing a platform for the use of magnetisation as a hydrocarbon migration proxy and as an inexpensive and simple method to determine oil quality.

Acknowledgements

I would firstly like to thank NERC for funding this PhD and my main supervisors, Dr. Adrian Muxworthy and Prof. Mark Sephton who not only helped tailor this PhD but also provided constant help and advice throughout the project. My appreciation also goes to Prof. Wyn Williams, Milagrosa Aldana and Vincenzo Costanzo-Alvarez for working closely with me throughout the PhD and their help in publications.

Samples were donated to this study and I am very grateful to German Bayona, Andres Fajardo-Hocol S.A. (Bogotá, Colombia) and Vadim Kravchinsky for their contributions. Moreover, I thank Shell, BP, Statoil and CNR international for providing data from well cores of operational hydrocarbon fields. For the experimental work, I would like to thank the Institute of Rock magnetism (IRM) at the University of Minnesota, USA for awarding me two visiting fellowship positions, which allowed me to conduct the majority of the magnetic experimentation. Especially I am indebted to Mike Jackson and Pete Solheid for their time and patience during my visits. I would also like to show my gratitude to Conall Mac Niocaill for access to the facilities at Oxford University, UK and Paul Southern for his help and collaboration in using the SQUID VSM at the Royal institute, London, UK. I am appreciative of Scott Renshaw, Richard Sutherland and the staff at the BGS core stores at Gilmerton, Edinburgh and Keyworth, England for allowing me access to cores from the North Sea UK. In addition, I would to thank Dr. Mahmoud Ardakani within the department of Materials at Imperial College London who trained and guided me on the SEM equipment. Moreover, I am grateful to Georgi Lalev at the Cardiff Nanocenter who provided me with access to SEM equipment supported by the Engineering and Physical Sciences Research Council (EP/F056745/1). I am also very thankful to the technical staff within the Department of Earth Sciences and Engineering at Imperial College, specifically Graham Nash, Alexander Toth and Martin Gill in helping with building new equipment and laboratory experimentation. Multiple fieldwork trips were conducted in the Wessex Basin and I am thankful for field assistance from friends and colleagues, Hayley Allen and Annabel Dale.

Most importantly, I would like to show my appreciation to my family for their constant support during my PhD and especially during the last 6 months. Moreover, I thank my boyfriend Luke Buskie and my friends who kept me sane throughout the project and spent hours proof reading my thesis.

Publication List

Emmerton, S., Muxworthy A. R., Hezel, D. C. & Bland, P. A., 2011. Magnetic characteristics of CV chondrules with paleointensity implications, *Journal of Geophysical Research*, 116, E12007, doi:10.1029/2011JE003856.

Emmerton, S., Muxworthy, A. R. & Sephton, M. A., 2012. Magnetic characterisation of oil sands at Osmington Mills and Mupe Bay, Wessex Basin, UK. In: Elmore, R. D., Muxworthy, A. R., Aldana, M. M. & Mena, M. eds. *Remagnetization and Chemical Alteration of Sedimentary Rocks*. London: Geological Society London Special Publications. 371, doi: 10.1144/SP371.6.

Emmerton, S., Muxworthy, A. R. & Sephton, M., 2013. A magnetic solution to the Mupe Bay mystery. *Marine and Petroleum Geology*. In revision.

Emmerton, S., Sephton, M. A., Muxworthy, A. R., Bayona, G. & Mora, A., 2013. Investigating controls on the oil chemistry of oil families through the Saltarín 1A well, Llanos Foreland Basin, Colombia. *Journal of South American Earth Sciences*. Submitted.

Emmerton, S., Muxworthy, A. R., Sephton, M. A., Aldana, M., Costanzo-Alvarez, V., Bayona, G. & Williams, W., 2013. Correlating biodegradation to magnetization in oil bearing sedimentary rocks. *Geochimica et Cosmochimica Acta*. In revision.

Contents

Abstract	1
Extended Abstract	3
Acknowledgements	9
Publication List	11
Contents	13
Table of Figures	19
List of Tables	27
List of Acronyms	29
Chapter 1 - Introduction	31
1.1 Brief introduction to the thesis	32
1.2 Review of magnetisation	34
<i>1.2.1 Principles of magnetism</i>	<i>34</i>
<i>1.2.2 Domain theory</i>	<i>37</i>
<i>1.2.3 Remanence acquisition</i>	<i>38</i>
<i>1.2.4 Magnetic minerals</i>	<i>41</i>
<i>1.2.5 Magnetite formation</i>	<i>45</i>
1.3 Review of magnetisation and hydrocarbons	48
<i>1.3.1 Aeromagnetic surveys</i>	<i>48</i>
<i>1.3.2 Magnetic mineral formation and stability near hydrocarbon plumes</i>	<i>49</i>
<i>1.3.3 Remagnetisations</i>	<i>52</i>
<i>1.3.4 Hydrocarbon identification through magnetic investigation</i>	<i>54</i>
1.4 Review of organic geochemistry	57
<i>1.4.1 Organic matter and hydrocarbons</i>	<i>57</i>
<i>1.4.2 Oil composition</i>	<i>58</i>
<i>1.4.3 Source to reservoir</i>	<i>60</i>
<i>1.4.4 Primary processes in petroleum systems</i>	<i>63</i>
<i>1.4.5 Secondary processes in petroleum systems</i>	<i>64</i>
<i>1.4.6 Biodegradation</i>	<i>66</i>

1.4.7 Biomarkers	68
1.4.7.1 Source biomarkers	70
1.4.7.2 Maturity Biomarkers	72
1.4.7.3 Biodegradation biomarkers	73
Chapter 2 - Sampling and methodology	77
2.1 Sampling	78
2.1.1 <i>Oil impregnated sedimentary units</i>	78
2.1.1.1 UK	78
2.1.1.2 Colombia	84
2.1.1.3 Canada	87
2.1.1.4 Indonesia	88
2.1.2 <i>Well Cores</i>	91
2.1.2.1 North Sea, UK, geology	91
2.1.2.2 Hydrocarbon field cores, UK	94
2.2 Laboratory techniques	100
2.2.1 <i>Sample preparation</i>	100
2.2.2 <i>Geochemical experimentation</i>	102
2.2.3 <i>SEM & EDX</i>	102
2.2.4 <i>Magnetic experimentation</i>	103
2.2.5 <i>Well core sampling</i>	106
Chapter 3 - How do magnetic minerals correlate to the chemical signature of hydrocarbons?	109
3.1 Introduction	110
3.2 Samples	112
3.3 Chemical characterisation of hydrocarbons	112
3.3.1 <i>Bulk oil composition</i>	113
3.3.2 <i>Molecular composition of oils</i>	117
3.3.2.1 <i>n-Alkanes</i>	118
3.3.2.2 <i>Hopanes</i>	119
3.3.2.3 <i>Steranes</i>	121
3.3.3 <i>Molecular composition of asphaltenes</i>	122
3.3.4 <i>Source</i>	127
3.3.5 <i>Maturity</i>	129
3.3.6 <i>Biodegradation</i>	130

3.3.7 Geochemical summary	130
3.4 Magnetic characterisation of oil impregnated sedimentary units	131
3.4.1 Magnetic susceptibility	131
3.4.2 Magnetic mineralogy	132
3.4.2.1 Room temperature experimentation	132
3.4.2.2 Low temperature experimentation	135
3.4.2.3 High temperature experimentation	138
3.4.3 SEM and EDX	140
3.5 Oil impregnated versus oil free	142
3.6 Determining a relationship between magnetisation and biodegradation	144
3.6.1 Relationship between oil content and magnetic signature	144
3.6.2 Relationship between oil composition and magnetic signature	147
3.6.3 Diagenesis	150
3.6.4 Mechanisms	151
3.6.5 Implications	152
3.7 Conclusions	153
 Chapter 4 - Can magnetisation solve the Mupe Bay mystery?	 157
4.1 Introduction	158
4.2 Samples	160
4.3 Magnetic characterisation	160
4.3.1 Magnetic mineralogy and domain state	160
4.3.2 Palaeomagnetic directions	162
4.4 Discussion	167
4.5 Conclusions	171
 Chapter 5 - Investigating the dominant effect on oil chemistry and magnetic characterisation through the Saltarín 1A well, Llanos Foreland Basin, Colombia	 173
5.1 Introduction	174
5.2 Geological setting	175
5.3 Chemical characterisation	177
5.3.1 Extractable Organic Matter (EOM)	177
5.3.2 Bulk oil composition	177

5.3.3 <i>Fourier Transform-InfraRed spectroscopy</i>	178
5.3.4 <i>n-Alkanes and isoprenoidal hydrocarbons</i>	180
5.3.5 <i>Hopanes and steranes</i>	181
5.4. What is the dominant effect on oil chemistry in this region?	183
5.4.1 <i>Is more than one source rock contributing to the Colombian oils?</i>	183
5.4.2 <i>Is there evidence for varying maturities in the oils?</i>	185
5.4.3 <i>What post filling processes have occurred?</i>	185
5.4.4 <i>Is there evidence for compartmentalization?</i>	186
5.5 How do chemical variations relate to magnetisation through the well?	187
5.5.1 <i>Magnetic characterisation</i>	187
5.5.2 <i>How does the magnetic data relate to biodegradation?</i>	193
5.6 Magnetic data discussion	195
5.7 Conclusions	196
 Chapter 6 - Testing the universality of magnetic characterisations of hydrocarbon well cores in the North Sea, UK.	 199
6.1 Introduction	200
6.2 SEM imaging	201
6.3 Magnetic characterisation	203
6.3.1 <i>Room temperature experimentation</i>	203
6.3.1.1 <i>Hysteresis</i>	204
6.3.1.2 <i>Mössbauer spectroscopy</i>	205
6.3.2 <i>Low temperature experimentation</i>	206
6.3.2.1 <i>Hysteresis</i>	206
6.3.2.2 <i>ZFC, FC and RT magnetisation curves</i>	207
6.3.3 <i>High temperature experimentation</i>	210
6.3.3.1 <i>High temperature susceptibility</i>	210
6.3.3.2 <i>Hysteresis</i>	212
6.4 Is there a correlation between magnetic susceptibility and well log data?	214
6.5 Discussion	224
6.5.1 <i>Anomalous magnetic susceptibility</i>	224
6.5.2 <i>Hydrocarbon bearing wells versus dry wells</i>	225
6.6 Summary	227

Chapter 7 - Conclusions	229
7.1 Conclusions	230
<i>7.1.1 Magnetisation and biodegradation</i>	230
<i>7.1.2 Dating oil migration in the Wessex Basin</i>	234
<i>7.1.3 Well core magnetic characterisation</i>	236
7.2 Further work	239
 References	 241
 Appendix	 255
Appendix 1: Organic geochemistry	257
<i>Appendix 1.1 Aliphatic hydrocarbon chromatograms</i>	258
<i>Appendix 1.2 FTIR spectra and asphaltene chromatograms</i>	279
Appendix 2: Magnetic experimentation	297
<i>Appendix 2.1 Oil impregnated samples</i>	298
<i>Appendix 2.2 Well core samples</i>	319

Table of Figures

Figure 1.1. Classification of magnetic properties of materials.....	34
Figure 1.2. Schematic representation of a) Single domain structure (SD), b) two domain magnetic structure (PSD) and c) four domain structure (MD). The dashed lines represent domain walls and the arrows represent the direction of the saturation magnetisation (M_s) in each domain. Modified from Dunlop & Özdemir (1997).	37
Figure 1.3. Representative hysteresis loop for a ferromagnetic material, H_c is the coercive force, H_{cr} is the coercivity of remanence, M_s is the saturation magnetisation and M_{rs} is the saturation remanence. Modified from Dunlop & Özdemir (1997).	39
Figure 1.4. Ternary diagram of the main magnetic minerals including the key minerals and solid solution series. From Butler (1992).	41
Figure 1.5. The crystal structure of magnetite. White atoms = oxygen, black atoms = Site A: Tetrahedral Fe^{2+} and Site B: Octahedral $\text{Fe}^{2+}/\text{Fe}^{3+}$. From Banerjee & Moskowitz (1985).	42
Figure 1.6. Maghemitisation and surface cracking in a magnetite crystal $\sim 30 \mu\text{m}$ in size. From Gapeyev & Tsel'movich (1988).	43
Figure 1.7. TEM of nanoscale grains of magnetite (a) formed extracellularly through biologically induced mineralisation (BIM) during the reduction of ferric oxyhydroxide by the dissimilatory Fe(III)-reducing bacterium <i>Geobacter metallireducens</i> . (b) a negatively stained cell that biomineralises cube-octahedral grains of magnetite. Magnetite grains formed by biologically controlled mineralization (BCM) in cells of magnetotactic bacteria. From Bazylinski <i>et al.</i> (2007).	46
Figure 1.8. An example of an aeromagnetic survey conducted over the Cement field, Oklahoma. The magnetic profile along the flight line shows an elevated magnetic response above the location of the known oil field. Modified from Donovan <i>et al.</i> (1979).	49
Figure 1.9. Representative stability plot from Machel (1995). (a) $a_{\text{HS}} = 10^{-12}$ effectively a sulphur free zone and (b) pH constant at 7.8 to demonstrate the stabilities of iron oxide and carbonate minerals relative to iron sulphide minerals (a = activities). MAG=magnetite, SID=siderite, PY=pyrite, PYR=pyrrhotite and HEM=hematite.	50
Figure 1.10. SEM images of magnetite that replaced framboidal pyrite in Onondaga limestone. (a) Polished cross-section of pseudoframboid (bright cores are remnant pyrite (arrow)) and (b) pseudoframboid in crack of calcite. From Suk <i>et al.</i> (1990).	53
Figure 1.11. Magnetic susceptibility values plotted against sampling intervals for two producing wells from La Victoria ((a) LVT-4X and (b) LVT-1X) oil fields and a nonproducing well ((c) LVT-2X). After Aldana <i>et al.</i> (1999), Costanzo-Alvarez <i>et al.</i> (2000) and Diaz <i>et al.</i> (2000).	55
Figure 1.12. Research combining magnetic characterisation and hydrocarbons. (a) Plot of hysteresis properties, χ/M_{rs} and M_{rs}/M_s from wells M46 (•) and M36 (O). From Liu <i>et al.</i> (2006). (b) Magnetic susceptibility and density plot for different petroleum reservoir fluids including oil, formation waters and seawater. From Ivakhnenko and Potter (2004).	56
Figure 1.13. Diagram of oil and gas generation 'window' in relation to burial depth and temperature. Modified from Killops & Killops (2005).	57
Figure 1.14. Schematic of hydrocarbons origin. Kerogen is the polymeric organic matter from which hydrocarbons are generated. Bitumen is the solid or liquid hydrocarbon deposit that is soluble in an organic solvent or are fusible. Bitumen is composed of three fractions; hydrocarbons, asphaltenes and polars. Hydrocarbons can be separated into aliphatic and aromatic sub fractions.	58

Figure 1.15. Examples of the major hydrocarbons and simple heteroatomic compounds in crude oils: R = alkyl group. Modified from Peters <i>et al.</i> (2005c).	59
Figure 1.16. Schematic of potential oil and gas stratigraphic and structural traps. Gas (white) and oil (black).	62
Figure 1.17. Gas chromatograms showing the variations in biodegradation from a selection of crude oils from Africa. From Wenger & Isaksen (2002).	68
Figure 1.18. The general structure for (a) hopanes and (b) steranes. Elution orders of isomerization for identification purposes in chromatograms are also included. Modified from Peters <i>et al.</i> (2005c).	69
Figure 2.1. Map of the Wessex Basin, Dorset, UK. Exposure of several oil stained beds along the coast with sample locations marked on. Geological map modified from Stoneley & Selley (1986).	79
Figure 2.2. Generalised stratigraphic column modified from Underhill & Stoneley (1998) for the Wessex Basin.	80
Figure 2.3. Osmington Mills cliff face with stratigraphic units identified. Samples OS1-OS6.	82
Figure 2.4. Bran Point – active oil seep (Sample OS oil).	82
Figure 2.5. Mupe Bay, Wealden age sandstone conglomerate bed. Samples MBM and MBC.	83
Figure 2.6. Oil stained Wealden sandstones at Stair hole/Lulworth Cove. Sample LC.	84
Figure 2.7. Geological map for the Colombian Andes, Colombia. The location of the Saltarín 1A well in the Llanos Foreland Basin is highlighted. Modified from Copper <i>et al.</i> (1995b).	85
Figure 2.8. Generalised stratigraphic column for the Llanos Foreland Basin, Colombia. The samples are highlighted. Modified from Bayona <i>et al.</i> (2008b).	86
Figure 2.9. Geological map modified from Obermajer <i>et al.</i> (2004) and stratigraphic sequence modified from Mossop (1980).	87
Figure 2.10. Geological map of Buton, Indonesia, modified from Smith & Silver (1991). Stratigraphic sequence for Buton, Indonesia modified from Audley-Charles (1988).	89
Figure 2.11. Stratigraphic summary of the North Sea Graben Province split into northern, central and southern regions (Gautier, 2005). Geological units with oil and gas production are labelled.	92
Figure 2.12. Generalised stratigraphy within the North Sea from West to East between the Jurassic and the Tertiary. The different rifting stages and the stratigraphic position of the well cores investigated are marked on the diagram for reference.	94
Figure 2.13. Generalised map of the Northern North Sea with oil field locations marked.	95
Figure 2.14. Generalised sketch depicting how the stratigraphy in the Bressay area relates to the sedimentary fill in the neighbouring deep-water basin depocentre. Modified from Underhill (2001).	96
Figure 2.15. Structural cross section through central Brae. From Fletcher (2003).	97
Figure 2.16. Schematic geoseismic west-east section through the Tiffany Field. From Kerlogue <i>et al.</i> (1994).	98
Figure 2.17. Magnetic extractor at Imperial College London.	101
Figure 2.18. Automated core logger using an MS2C loop sensor controlled by a linear slide.	107
Figure 2.19. (a) Magnetic susceptibility readings over the entire 211/29-C4 well. (- - - noise limits). (b) High resolution magnetic susceptibility measurements over one piece of core from well 211/29-C4.	108
Figure 3.1. A ternary diagram representing the individual percentages of the compounds found within oil; aliphatic hydrocarbons, aromatic hydrocarbons and polar & asphaltenes. (a) Polar and asphaltene fractions and (b) polar fractions only. The samples are separated into their localities for reference.	114
Figure 3.2. FT-IR spectra for representative samples within this study with the characteristic absorption bands identified for interpretation. (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian samples.	115

Figure 3.3. FT-IR index graphs for all oil samples (a) aliphaticity vs. long chain indexes and (b) aromaticity vs. substitution indexes. Distinct groups of oils can be distinguished.	116
Figure 3.4. Representative TIC chromatograms of the aliphatic hydrocarbon fractions for the four sets of samples within this study. (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian samples.	118
Figure 3.5. Mass chromatograms (m/z 57) of the aliphatic hydrocarbon fractions in the Colombian samples to identify n -alkanes. C_{16} - C_{30} = C_{16} - C_{30} n -alkanes, Pr= Pristane, Ph= Phytane.	119
Figure 3.6. Representative mass chromatograms (m/z 191) of the aliphatic hydrocarbon fractions to identify hopanes for the four sets of samples, (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian samples. Compounds used for biomarkers are highlighted. Ts- C_{27} 18 α trisnorhopane, Tm- C_{27} 17 α trisnorhopane, C_{29} Ts-18 α -30-norneohopane, sequence of H_{29} - H_{35} = C_{29} - C_{35} hopanes.	120
Figure 3.7. Mass chromatograms (m/z 217) of the aliphatic hydrocarbon fractions to identify steranes for the four sets of samples, (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian. C_{27} - $C_{29}\beta\alpha$ (S+R) – C_{27} - C_{29} diasteranes. C_{27} - $C_{29}(\alpha\alpha\alpha$ (S+R) and $\alpha\beta\beta$ (S + R)) are elution orders for C_{27} - C_{29} steranes.	121
Figure 3.8. The aliphatic hydrocarbon fractions for C_{27} , C_{28} and C_{29} $\beta\beta$ steranes from m/z 217 for all the samples in this study.	122
Figure 3.9. Representative TIC stereograms of the asphaltene fractions for (a) UK, (b) Canadian and (c) Indonesian samples. The Colombian samples produced no asphaltenes.	123
Figure 3.10. Sterol distribution (relative abundance of C_{27} , C_{28} and C_{29} steranes) in relation to environment and source organisms after Huang & Meinschein (1979). All samples from this study are plotted.	127
Figure 3.11. Relation between n -alkanes and isoprenoids to determine possible depositional and source environments (Lijmbach, 1975). The Colombian ratios are taken from their aliphatic fractions, however, the asphaltene fraction was used for the UK, Canadian and Indonesian samples giving rise to the very low ratios representing no biodegradation.	128
Figure 3.12. Correlation of maturity parameters using C_{29} (S/(S+R)) and C_{29} ($\beta\beta/(\alpha\alpha+\beta\beta)$) steranes biomarkers.	129
Figure 3.13. Representative hysteresis loop showing the strong paramagnetic behaviour within all the oil sands. Sample OS4.	133
Figure 3.14. A “Day plot” (Day et al. 1977) of the ratios of the hysteresis parameters M_{rs}/M_s versus H_{cr}/H_c for the samples examined in this study. The regions commonly associated with SD, PSD and MD behaviour for magnetite are labelled for representative purposes. The oil-stained samples have been plotted and split into sample locations.	133
Figure 3.15. SIRM AF Demagnetisation curves for oil stained samples (squares) and cleaned samples (triangles) with MDF's (---). (a) UK, OS6 (b) UK, LC (c) Canada, A827.32 (d) Indonesia, KI (e) Colombia, C127.40 and (f) Colombia, C616.48.	134
Figure 3.16. MPMS measurements for zero field cooling (ZFC), field cooling (FC) curves and room temperature remanence curves (RT) for cooling ($\leftarrow$) and warming ($\rightarrow$) from 10 K – 300 K giving information on mineralogy and grain sizes. (a) UK, OS6 & LC (b) Canada, A1B & A827.75 (c) Colombia, C127.40 & C616.48 and (d) Indonesia, KI & LI. The inset is an expanded view of the RT curves to help identification of the Verwey and Morin transitions.	136
Figure 3.17. AC susceptibility as a function of frequency from 10 K to 300 K. (a) UK, OS3 & LC (b) Canada, A1B & A827.75 (c) Colombia, C127.40 & C616.48 and (d) Indonesia, KI & LI.	137
Figure 3.18. High temperature magnetic susceptibility measurements using 100 °C cycling steps from 50 °C to 700 °C. Oil free samples were used in an argon atmosphere to gain information on magnetic mineralogy through Curie	

temperatures. (a) UK, MBM & LC (b) Canada, A1B & A827.32 (c) Colombia, C127.40 & C616.48 and (d) Indonesia, KI & LI.	139
Figure 3.19. SEM images of magnetic particles within oil sands and corresponding EDX data (not calibrated). SEM images showing (a) UK, cubic magnetic minerals (iron oxides), (b) UK, iron oxide framboid ranging in size between 500 nm and 45 μm , (c) Canada, iron oxide minerals, (d) Colombia, iron sulphide framboids and (e) Indonesia, iron oxide framboid.	140
Figure 3.20. SEM image of a grain in the UK sample OS5. Microbe activity can be identified by the etched pattern on the surface.	141
Figure 3.21. A “Day plot” (Day et al., 1977) of the ratios of the hysteresis parameters M_{rs}/M_s versus H_{cr}/H_c for the samples examined in this study. The regions commonly associated with SD, PSD and MD behaviour for magnetite are labelled for representative purposes. The oil-stained (closed) and clean (open) samples have been plotted and split into sample locations.	142
Figure 3.22. Magnetic susceptibility for all the oil sands (black) and clean (grey) counterparts. Magnetic susceptibility is on a logarithmic scale (m^3kg^{-1}).	143
Figure 3.23. Plot of Log_{10} magnetic susceptibility versus EOM% for the UK, Osmington Mill samples. An exponential regression was determined to ascertain the best estimate for the ‘background’ χ (EOM%=0) with the same principle applied to the Canadian, Colombian and UK (MB & LC) samples. The trend line and 99% confidence limits are also plotted.	145
Figure 3.24. Log_{10} magnetic susceptibility versus percentage of extractable organic matter for all the samples tested. The samples have been split into their groups: UK (OS), UK (MB&LC), Canada, Colombia and Indonesia. The trend line and 95% confidence limits are also plotted.	146
Figure 3.25. Log_{10} change in magnetic susceptibility plot against the abundance of (a) polar and apshlatenes and (b) aliphatic hydrocarbons within each sample. The trendlines and 95% confidence limits are plotted. The samples are represented within their localities.	148
Figure 3.26. A “Day plot” (Day et al., 1977) of the ratios of the hysteresis parameters M_{rs}/M_s versus H_{cr}/H_c for the samples examined in this study. The regions commonly associated with SD, PSD and MD behaviour for magnetite are labelled for representative purposes. The oil-stained samples have been plotted and split into sample locations and corresponding biodegradation levels referred too: low and medium (open symbols) and high (closed symbols).	149
Figure 4.1. Generalised map of the Wessex Basin, Dorset, UK with Mupe Bay identified for reference. Fieldwork picture of the Wealden Group conglomerate with oil stained clasts and matrix.	158
Figure 4.2. MPMS measurements for zero field cooling (ZFC), field cooling (FC) curves and room temperature remanence curves (RT) for cooling ($\leftarrow$) and warming ($\rightarrow$) from 10 K – 300 K giving information on mineralogy and grain sizes. (a) Mupe Bay clast and (b) Mupe Bay matrix.	161
Figure 4.3. Cross section showing pre and post Cretaceous structuration. The context of oil impregnated matrix and clasts is described.	162
Figure 4.4. Representative Zijdeveld plots for (a) Clast 1, (b) Clast 2 (c) Clast 3 and (d) Matrix.	163
Figure 4.5. Sample directions in equal area projection from the most stable AF demagnetised samples. (a) All samples used for analysis (b) The mean matrix direction and the mean clast direction after combining clast 1 and clast 2 data. Today’s magnetic field (star) at the site location is also plotted. (c) Tilt correction for the clasts to calculate palaeo-coordinates.	165

Figure 4.6. A stereonet with the apparent polar wander curve for Northern Eurasia. The existing data between 291 Ma-30 Ma is represented in grey with associated errors. The mean data for the clasts from this study are represented with associated errors (black circles and lines). Modified from Irving and Irving, (1982) and Torsvik <i>et al.</i> (2001).	166
Figure 4.7. Palaeolatitudes through time (200-0 Ma) for Eurasia. Palaeolatitude data for the clasts are plotted (dashed lines) with the uncertainty (grey).	167
Figure 4.8. Three possible responses for magnetic directions in the Mupe Bay conglomeratic bed. (a) A single magnetic direction indicates a single-phase oil-staining event. The other two scenarios show different magnetic directions between the clasts and matrix indicating a two-phase oil-staining event, (b) random orientation in clasts. (c) consistent orientations in clasts. All scenarios have matrix magnetic direction correlating with present day magnetic field representing an active seep.	168
Figure 5.1. Cross section from NW to SE through the Eastern Cordillera, Llanos foothills and the Llanos Basin. The stratigraphic units found within the Saltarín 1A well at the Llanos Foreland basin are T80-T90 (Leon and Guayabo Formations) and T30-T70 (Carbonera Formation). Modified from Copper <i>et al.</i> (1995a).	175
Figure 5.2. Correlation of stratigraphic units K50 – T90 in the Llanos Basin based on seven representative wells. The location of the correlation section is shown on the map. In addition, the Saltarín 1A well from this study has been inserted where similar stratigraphic units can be found. Each well has a gamma ray log in API units; the gamma ray logs have been plotted twice by reversing the scale for the right curve. Wide separation of the two curves indicates a low gamma ray response (sands). Modified from Copper <i>et al.</i> (1995a).	176
Figure 5.3. Ternary diagram of oil constituents: aliphatic hydrocarbons, aromatic hydrocarbons and polars & asphaltenes. The samples are labelled for reference.	177
Figure 5.4. FT-IR spectra for representative samples within this study with characteristic absorption bands identified for interpretation.	178
Figure 5.5. FT-IR index graphs for all oil samples (a) aliphaticity vs. long chain indexes and (b) aromaticity vs. substitution indexes. Distinct groups of oils can be distinguished.	179
Figure 5.6. TIC chromatograms of the aliphatic fractions for samples from the Saltarín 1A well, Colombia. All even numbered <i>n</i> -alkanes are highlighted for reference as well as Pr (pristane) and Ph (phytane). <i>n</i> -C ₁₆ , hexadecane, -C ₁₈ , octadecane, -C ₂₀ , eicosane, -C ₂₂ , docosane, -C ₂₄ , tetracosane, -C ₂₆ , hexacosane, -C ₂₈ , octacosane, -C ₃₀ , triacontane, -C ₃₂ , docontane.	180
Figure 5.7. Mass chromatograms (<i>m/z</i> 191) of the aliphatic hydrocarbon fractions to identify hopanes for samples from the Saltarín 1A well, Colombia. Compounds used for biomarkers are highlighted. Ts-C ₂₇ 18 α trisnorhopane, Tm-C ₂₇ 17 α trisnorhopane, C ₂₉ TS-18 α -30-norneohopane, sequence of H ₂₉ -H ₃₅ = C ₂₉ -C ₃₅ hopanes, G-gammacerane.	181
Figure 5.8. Mass chromatograms (<i>m/z</i> 217) of the aliphatic hydrocarbon fractions to identify steranes for samples from the Saltarín 1A well, Colombia. C ₂₇ -C ₂₉ $\beta\alpha$ (S+R) – C ₂₇ -C ₂₉ diasteranes. C ₂₇ -C ₂₉ ($\alpha\alpha\alpha$ (S+R) and $\alpha\beta\beta$ (S + R)) are elution orders for C ₂₇ -C ₂₉ steranes.	182
Figure 5.9. The aliphatic hydrocarbon fractions for C ₂₇ , C ₂₈ and C ₂₉ $\beta\beta$ steranes from <i>m/z</i> 217.	183
Figure 5.10. Magnetic susceptibility warming and cooling curves as a function of temperature, increasing the peak temperature in 100 °C cycles from 50°C to 700 °C in argon. (a) C127.40, (b) C147.25, (c) C541.75, and (d) C616.48. --- 300 °C, — 400 °C, -- 500 °C, — 600 °C and ... 700 °C.	188

Figure 5.11. Zero field cooling (ZFC) and field cooling (FC) curves from 300 to 10 K in 10 K steps as well as room temperature remanence (RT) cooling and warming curves from 300-10 K in a zero field. (a) C127.40, (b) C147.25, (c) C541.75, and (d) C616.48. (FC ---, ZFC ----, RT warming →, RT cooling ←).	189
Figure 5.12. Susceptibility measurements for AC susceptibility at 7 frequencies between 10-300 K in 10 K steps at seven frequencies (1.0, 32.2, 10.0, 31.6, 100.1, 316.7, 997.3 Hz). (a) C127.40, (b) C147.25, (c) C541.75 and (d) C616.48.	190
Figure 5.13. Mössbauer spectroscopy results with fitting curves for (a) C147.25 and (b) C616.48. Magnetic hyperfine parameters are quoted in Table 5.5.	191
Figure 5.14. SEM images of samples; a) C127.40, b) C147.25, c) C541.68 and d) C616.48. Framboids were identified within samples C127.40 and C147.25.	192
Figure 5.15. Plot of the four samples in this study versus EOM% and parameters used for assessing the degree of biodegradation in the oil (Pr/n-C ₁₇ , Ph/n-C ₁₈ and UCM/C ₂₉) and magnetic susceptibility (χ).....	194
Figure 5.16. Magnetic susceptibility related to EOM% and biodegradation state for the Colombian samples using the Wenger scale of biodegradation (Wenger <i>et al.</i> 2001).	194
Figure 6.1. SEM images taken of well cores; (a) 9/09B-3 (Bruce), (b) 16/07A-A8 (Brae), (c) 16/17-13 (Tiffany), (d) 3/28A-4, (Bressay) (e) 211/29-C4 (Brent), (f) 3/03-11 (dry) and (g) 211/29-8A (dry).	202
Figure 6.2. Day plot used to interpret grain sizes (SD, PSD and MD) for all well core samples at room temperature. Anomalous χ samples (closed symbols) and background samples (open symbols). The dry well cores are represented by grey symbols.	204
Figure 6.3. Mössbauer spectroscopy results with fitting for (a) Well core 211/29-C4 sample 4 and (b) Well core 9B/9-3 sample 1.	205
Figure 6.4. Hysteresis loops for well core 211/29-C4 sample 2. (a) Hysteresis loops at increasing temperatures of 10 K (black) and 300 K (red) in a 1TFC and (b) hysteresis loops at 10 K after ZFC (black) and 1TFC (red).	206
Figure 6.5. Zero field cooling (ZFC ----), Field Cooling (FC - -) curves and room temperature remanence curves (RT —) for well cores (a) 9/09B-3 (b) 16/07A-A8 (c) 16/17-13 (d) 3/28A-4 and (e) 211/29-C4. The inset is the magnified behaviour of the RT SIRM cooling curves.	208
Figure 6.6. Zero field cooling (ZFC ----), Field Cooling (FC - -) curves and room temperature remanence curves (RT —) for well cores (a) 3/03-11 (b) 211/29-C4. The inset is the magnified behaviour of the RT curves.	209
Figure 6.7. AC susceptibility curve as a function of temperature for well core 211/29-C4 sample 3. The graph shows both the magnetic susceptibility (χ) (•) and the inverse of magnetic susceptibility ($1/\chi$) (◊). The dotted line is a fit to the $1/\chi$ curve between 40-300 K.	209
Figure 6.8. Magnetic susceptibility measurements as a function of temperature (up to 700 °C). The representative plots characterise the anomalously high magnetic samples (left) and the background samples (right). (a) 9/09B-3 (b) 16/07A-A8 (c) 16/17-13 (d) 3/28A-4 and (e) 211/29-C4.	211
Figure 6.9. Magnetic susceptibility measurements as a function of temperature (up to 700 °C). The representative plots characterise the anomalously high magnetic samples for the dry well cores within this study, (a) 3/03-11 (b) 211/29-8A.	212
Figure 6.10. High temperature hysteresis measurements between 200-600 °C on well core 9/09B-3 (a) Hysteresis loops at 200 °C, 400 °C and 600 °C for 9B-1 and (b) a Day plot of hysteresis parameters for 9B-1 (anomalous χ) and 9B-3 (background). The size of the symbols increases with increasing temperature.	213

Figure 6.11. Bi plots of (a) Gamma Ray well logs (GR) versus magnetic susceptibility and (b) Sonic well logs (DT) versus magnetic susceptibility. The plots show that there is no strong correlation between these properties and that any significance in a low correlation is due to the number of data points.....	216
Figure 6.12. Well log data for well core 16/07A-A8. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron (m^3m^{-3}), RES =resistivity (ohm.m) and SUSC=magnetic susceptibility (arbitrary units).....	217
Figure 6.13. Well log data for well core 16/17-13. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron (m^3m^{-3}), RES= resistivity (ohm.m) and SUSC=magnetic susceptibility (arbitrary units).....	218
Figure 6.14. Well log data for well core 3/28A-4. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron (m^3m^{-3}), RES= resistivity (ohm.m) and SUSC=magnetic susceptibility (arbitrary units).....	219
Figure 6.15. Well log data for well core 211/29-C4. DT=sonic (usft^{-1}), GR=gamma ray (gAPI), RES= resistivity (ohm.m) and SUSC=magnetic susceptibility (arbitrary units).	220
Figure 6.16. Well log data for well core 3/03-11. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron (m^3m^{-3}) and SUSC=magnetic susceptibility (arbitrary units).	221
Figure 6.17. Well log data for well core 211/29-8A. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron (m^3m^{-3}) and SUSC=magnetic susceptibility (arbitrary units).	222
Figure 6.18. A plot representing normalised magnetic susceptibility versus the Spearman's correlation coefficient of well log data (GR, DT and RES) for the Brent well core, 211/29-C4.....	223
Figure 6.19. Schematic of variations in magnetic characterisation within well cores due to the vicinity and migration pathway of a hydrocarbon reservoir.	226
Figure 7.1. Schematic sketch showing the difference in magnetic mineralogy in an oil-rich and oil-poor zone.	233

List of Tables

Table 1.1 Magnetic properties of some common magnetic minerals. Modified from Dunlop and Özdemir (1997).	45
Table 1.2 Summary of mineral changes from the surface to deep and from association with hydrocarbons to a hydrocarbon free zone. A-D represents increasing depth, temperature and pressure. LTS, MTS and HTS denote total sulphur levels. The magnetic contrasts are shown relative to background levels, an increase (+) or a decrease (-). Modified from Burton <i>et al.</i> (1993).	51
Table 1.3 Biomarker biodegradation numerical scale from Wenger <i>et al.</i> (2001).	67
Table 1.4 Summary of biomarkers commonly used to identify maturity and source characteristics of oils.	75
Table 2.1 Summary of samples collected at the Wessex Basin with descriptions.	81
Table 2.2 Summary table of oil sands and oil samples used within this study.	90
Table 2.3 Summary of well cores and corresponding fields from which samples have been taken.	95
Table 3.1 Summary of the samples used in this study with details about formation and sample type.	112
Table 3.2 Oil extraction and fractionation percentages for all the samples used in this study determined by GC-MS data (Appendix 1.1).	113
Table 3.3 Summary of analytical results of <i>n</i> -alkane retention for the samples from this study taken from the ion specific chromatogram <i>m/z</i> 57.	125
Table 3.4 Summary of analytical results of hopanes and steranes for the samples from this study taken from ion specific chromatograms, <i>m/z</i> 191 and 217 respectively.	126
Table 3.5 The magnetic parameters measured for the oil impregnated samples within this study and the cleaned counterparts. Results for susceptibility, hysteresis parameters and SIRM curves.	132
Table 3.6 A summary table of SEM and EDX observations for magnetic mineralogies for each set of samples including whether framboidal material was identified.	141
Table 4.1 Summarized hysteresis data, magnetic susceptibility and extractable organic matter content.	161
Table 4.2 Palaeomagnetic orientation data with applied tilt correction.	164
Table 4.3 Mean palaeomagnetic orientation data with applied tilt correction, statistical parameters and palaeo-coordinates.	165
Table 5.1 Oil extraction and fractionation percentages for each sample within this study.	177
Table 5.2 Summary of analytical results of <i>n</i> -alkanes for the samples from this study.	181
Table 5.3 Summary of analytical results of hopanes and steranes for the samples from this study.	183
Table 5.4 Magnetic parameter summary for all the Colombian samples. The data is given for the oil stained samples.	187
Table 5.5 Mössbauer spectroscopy for two sample; C147.25 and C616.48. Magnetic hyperfine parameters determined at room temperature.	192
Table 6.1 A list of well cores and depths analysed in this study.	201
Table 6.2 Summary of magnetic parameters measured from magnetic susceptibility and hysteresis data.	203
Table 6.3 Mössbauer parameters for two samples; well core 9/9B-3-1 and well core 211/29-C4-15 at room temperature.	206
Table 6.4 Results for Spearman's rank correlation coefficient (R_s) for the magnetic susceptibility and other well log data for the entire well core.	215

List of Acronyms

Magnetic terminology

Demagnetisation energy (E_d)
Anisotropy energy (E_{anis})
Exchange energy (E_{ex})
External field energy (E_h)
Total magnetic energy (E_{tot})
Curie temperature (T_c)
Critical size (d_0)
Saturation magnetisation (M_s)
Saturation remanence (M_{rs})
Coercive force (H_c)
Coercivity of remanence (H_{cr})
Single-domain (SD)
Pseudo-single domain (PSD)
Multi domain (MD)
Isothermal remanent magnetisation (IRM)
Saturation isothermal remanence magnetization (SIRM)
Thermoremanent magnetisation (TRM)
Anhysteretic remanence (ARM)
Chemical remanent magnetisation (CRM)
Detrital remanent magnetisation (DRM)
Viscous remanent magnetisation (VRM)
Median destructive field (MDF)
Magnetic susceptibility (χ)
Background magnetic susceptibility (χ_B)

Methodology terminology

Scanning Electron Microscope (SEM)
Energy Dispersive X-ray (EDX)
Gas Chromatography – Mass Spectroscopy (GC-MS)
Fourier Transform-Infra Red (FT-IR) Spectroscopy
Total Ion Current (TIC)
Field cooling curves at 2.5 T (FC)
Zero-field cooling curves (ZFC)
Room-temperature curves (RT)
Oil-stained samples (O)
Cleaned oil-free samples (C)
Extractable organic matter (EOM)
Unmixed Complex Mixture (UCM)

Analytical terminology

Spearman's rank correlation coefficient (R_s)
Correlation Coefficient (R^2)
Quadruple splitting (QS)
Isomer shift (IS)
Hyperfine field (B_{hf})
Magnetic susceptibility well log (SUSC)
Sonic well log (DT)
Gamma ray well log (GR)
Density well log (DEN)
Neutron well log (NEU)
Resistivity well log (RES)

Chapter 1

Introduction

1.1 Brief introduction to the thesis

Direct hydrocarbon identification has been an area of active research for decades and although links between magnetism and hydrocarbons have been elusive through both large and small spatial scale research (e.g., Donovan et al., 1979; Benthien & Elmore, 1987; McCabe et al., 1987; Elmore & Crawford, 1990; Díaz et al., 2000; Aldana et al., 2003; Ivakhnenko & Potter, 2004; Guzman et al., 2011; Venkatachalapathy et al., 2011) no unambiguous relationship has been found alongside a possible mechanism. Aeromagnetic studies for alternative exploration and assessment of hydrocarbons were examined based on the theory that magnetic anomalies at shallow depths could be associated with chemical alteration of magnetic minerals within a reducing environment in underlying hydrocarbon reservoirs. It has been suggested that chemical alteration of iron oxides to authigenic magnetite and/or iron sulphides could cause relative increases or decreases in the magnetic signal in a given area (Donovan et al., 1979; Elmore & Leach, 1990; Reynolds et al., 1990a; Reynolds et al., 1990b; Reynolds et al., 1991; Saunders et al., 1991; Foote, 1996; Leblanc & Morris, 1999), resulting in variable magnetic anomalies in these studies. One study by Elmore *et al.* (1993) recorded an increase in total magnetisation through the diagenetic formation of magnetite in the host rocks with little/no magnetisation before hydrocarbon infilling. A reduction in total magnetisation was also recorded however, in units where the formation of magnetite caused the destruction of relatively larger proportions of hematite. Several studies have also shown how environmental differences can result in variable magnetic anomalies (Machel & Burton, 1991; Gay, 1992; Machel, 1995; Machel, 1996). Magnetic anomalies do exist within hydrocarbon environments; however, the associated contrasts appear complex and cannot be used as a quick and direct tool for hydrocarbon identification.

These studies have identified a number of relationships between magnetic properties and hydrocarbons such as high magnetic susceptibility (χ) anomalies only associated with the presence of hydrocarbons relative to background readings, and magnetic susceptibility correlations to physical and chemical properties of oils, e.g., density, viscosity, sulphur content and diagenetic settings, however, very few mechanisms for the correlations have been suggested.

Hydrocarbons themselves have unique signatures owing to their source, maturity and biodegradation variations between different sets of oils. The host rock into which hydrocarbons migrate could also be affected by the chemical signature of the oil. Few studies have been conducted on the reservoir rocks themselves in terms of magnetic investigations and this PhD aims to characterise fully the magnetic signature and geochemical signature of oil impregnated sedimentary units and to provide plausible interpretations and insights.

Planned Research

This PhD thesis will try to achieve a full understanding of the magnetic mineralogy of hydrocarbon bearing sedimentary units and their associated environments, conducting a number of experiments through geochemical and geophysical analysis. This research has two main routes of investigation: 1) the magnetic and geochemical characterisation of oil impregnated sedimentary units and 2) an investigation into the 'bigger picture' in terms of well cores from above hydrocarbon reservoirs to identify whether migration pathways can be traced by magnetic variations for hydrocarbon exploration. This research uses magnetic investigations such as magnetic susceptibility, zero field and field cooling curves, hysteresis, high temperature experimentation and Mössbauer spectroscopy as well as chemical analysis such as oil extraction and column chromatography. Imaging and grain composition analysis through scanning electron microscopy and energy-dispersive x-rays are also used to try to answer the following questions:

1. What is the origin of the magnetic minerals in association with hydrocarbons?
2. What is the relationship between biodegradation state of oil and the magnetic signature?
3. Do magnetic minerals migrate and can migration pathways be determined through magnetic investigation?
4. Can remagnetisation be used to date hydrocarbon migration?
5. Could magnetic minerals be used in hydrocarbon exploration?

1.2 Review of magnetisation

1.2.1 Principles of magnetism

All materials are assigned to one of three magnetic categories; diamagnetic, paramagnetic or ferromagnetic. All materials are to some extent diamagnetic, and those that do not possess permanent magnetic moments are classified as diamagnetic (Fig. 1.1) (Kittel, 1967a). For materials, which also possess another form of magnetism, the diamagnetic contribution becomes negligible and are classed as either paramagnetic or ferromagnetic. Paramagnetic materials are those that contain atoms or ions with permanent magnetic moments with no long-range order and ferromagnetic (*sensu latu*) materials are those that contain atoms or ions with permanent magnetic moments, which possess long-range order (Fig. 1.1).

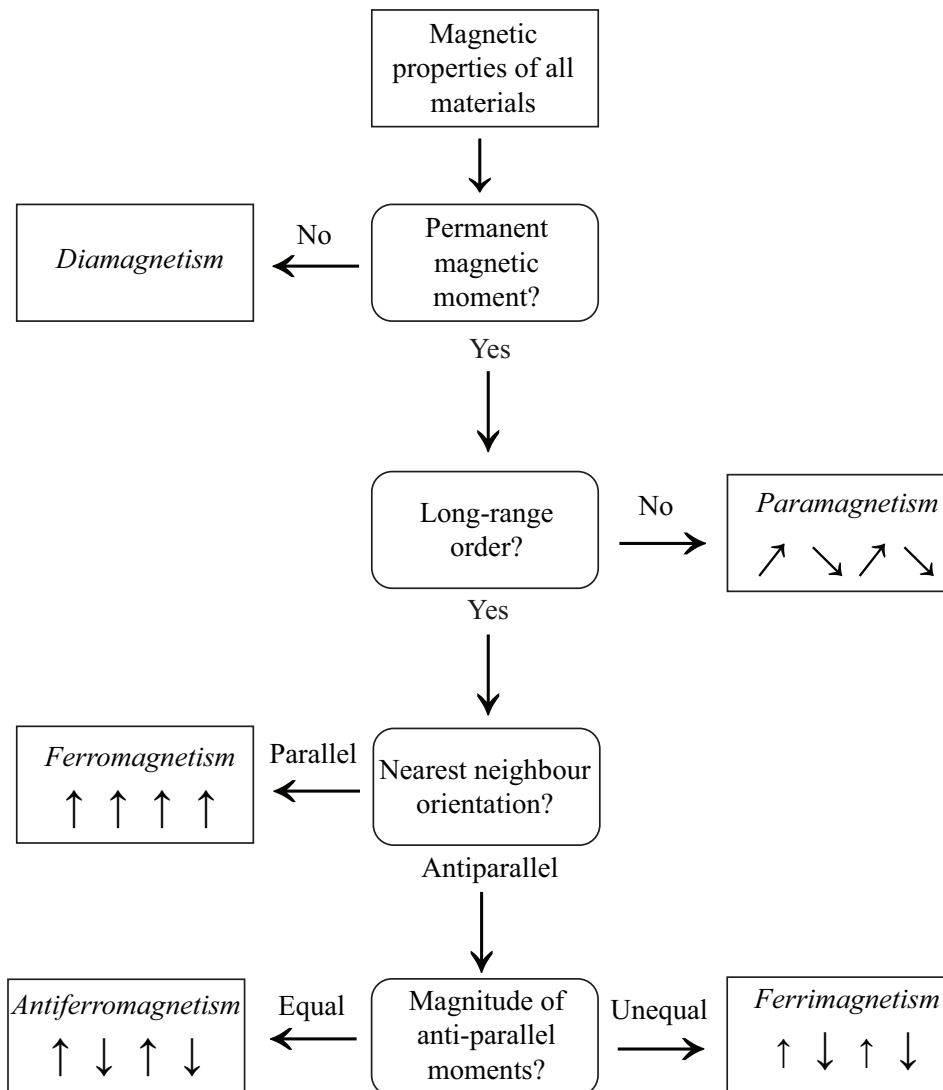


Figure 1.1. Classification of magnetic properties of materials.

The magnetic moment (**m**) of a material is the sum of all the orbital and spin magnetic moments of its electrons. It has dimensions Am^2 .

The net macroscopic magnetisation (**M**) of a material is due to the vector sum of the magnetic moments from the atoms (**m**) and is volume dependant (v), i.e.

$$\mathbf{M} = \sum \mathbf{m}/v \quad (1)$$

The magnetic behaviour of a material can be described as:

$$\mathbf{M} = \mathbf{M}_0 + \chi \mathbf{H} \quad (2)$$

Where $\mathbf{M}_0$ is the net magnetisation in the absence of a magnetic field, $\mathbf{H}$ is an applied field and χ is the magnetic susceptibility (Butler, 1992), i.e., $\chi \mathbf{H}$ is the induced magnetisation. Susceptibility is dimensionless and is strictly speaking the volume susceptibility (Bleaney & Bleaney, 1957; Dunlop & Özdemir, 1997).

To obtain the mass susceptibility (κ) it must be divided by the density (ρ) (Eq. 3). The mass susceptibility has dimensions of m^3kg^{-1} (Dunlop & Özdemir, 1997):

$$\kappa = \chi / \rho \quad (3)$$

Below is a detailed description of the individual types of magnetic properties of materials.

Diamagnetic

Diamagnetism is a property of all materials but is very weak. If a material is said to be diamagnetic then the induced magnetisation will be directly opposed to the magnetic field applied to the material. The diamagnetic response to an external magnetic field is due to the electron's orbit about the nucleus which gives rise to an electro-motive force in the current loop (Lenz's law) (Bleaney & Bleaney, 1957; Kittel, 1967a). The electron's angular velocity either decelerates or accelerates depending on the relative orientation of the field with the current loop orientation, in such a way as to generate an internal magnetic field in opposition to the external magnetic field. The diamagnetic contribution to the total magnetic susceptibility is negative (Butler, 1992). An example of a diamagnetic material is quartz (SiO_2).

Paramagnetic

By the Pauli Exclusion Principle (Bleaney & Bleaney, 1957), the contribution from closed electron shells to the total orbit + intrinsic angular moment is zero. Therefore, only atoms with incomplete

shells have permanent magnetic moments. The contribution of diamagnetic material is usually insignificant in materials containing permanent magnetic moments. Paramagnetism occurs in atoms with partially filled electron shells (for example the 3d (iron group) and the 4d (palladium group)). Paramagnetic materials have no long-range order to their permanent magnetic moments (Fig. 1.1) and are unable to retain a remanent magnetisation i.e. the net magnetisation is zero. An example of a paramagnetic mineral is pyrite (FeS_2).

Ferromagnetism

The crystal lattices of ferromagnetic materials have adjacent atoms sufficiently close together that some electron orbits overlap and a strong interaction arises, called exchange coupling. This exchange coupling causes the magnetic moments of the atoms in the lattice to align instead of being randomly orientated (Fig. 1.1) (Jiles, 1991; Butler, 1992). This alignment remains when the field is zero, a measureable remanent or permanent magnetisation remains. These materials retain a 'memory' of the magnetic field history and show this 'memory' in hysteresis loops (Fig. 1.3) (See Section 1.2.3), which is a plot of $\mathbf{M}$ vs. $\mathbf{H}$.

Ferromagnetism is associated with the transition metals and can also occur naturally in many iron oxides. The Curie temperature (T_c) is the temperature at which thermal energy overcomes the exchange coupling and the material becomes paramagnetic (Kittel, 1967a).

Antiferromagnetic

Antiferromagnetism arises when all the atomic moments have the same strength but neighbouring atoms magnetic moments have opposing directions, e.g., antiparallel (Fig. 1.1) causing a zero net magnetization even though a strong exchange coupling exists. This spontaneous antiparallel coupling can be disrupted by heating and disappears entirely at the Néel temperature, an ordering temperature point characteristic of each antiferromagnetic material. Examples of antiferromagnetic minerals are goethite (αFeOOH) or hematite ($\alpha\text{Fe}_2\text{O}_3$) however, a weak remanent magnetisation can be present if there are lattice vacancies or defects (Kittel, 1967b) i.e. slightly ferromagnetic.

Ferrimagnetic

In ferrimagnetism the crystal lattice consists of two or more sites with cations in two different coordination states referring to two different atomic moments. As in antiferromagnetism the atomic moments are opposed, but a magnetisation can arise if the two types are sufficiently unequal (Fig.

1.1) (Kittel, 1967b), acting like a ferromagnetic material. An example of a ferrimagnetic mineral is magnetite (Fe_3O_4).

1.2.2 Domain theory

The magnetic behaviour of a material is affected by the controlling magnetic energies. The main magnetic energies are; 1) the demagnetisation energy (E_d) which is due to the long range effect of dipole-dipole interactions between atomic moments, 2) the anisotropy energy (E_{anis}), which depends on the orientation of the magnetisation relative to the crystallographic axes of the material, 3) the exchange energy (E_{ex}), which is simply the difference between two interacting spins and 4) the external field energy (E_h), which is the resultant energy due to the interaction of an external magnetic field and the magnetisation vector field. The total magnetic energy (E_{tot}) is given as:

$$E_{tot} = E_d + E_{anis} + E_{ex} + E_h \quad (4)$$

In ferromagnets, it is energetically favourable for the magnetic structure at a temperature below the Curie temperature (T_c) and above a critical size (d_0) to break up into patterns called domains. Domain structures are determined by the minimisation of E_{tot} (Eq. 4). Domain theory states that the moments are aligned parallel to one another within each domain, but change direction at the relatively thin domain walls (Fig. 1.2) (Kittel, 1949).

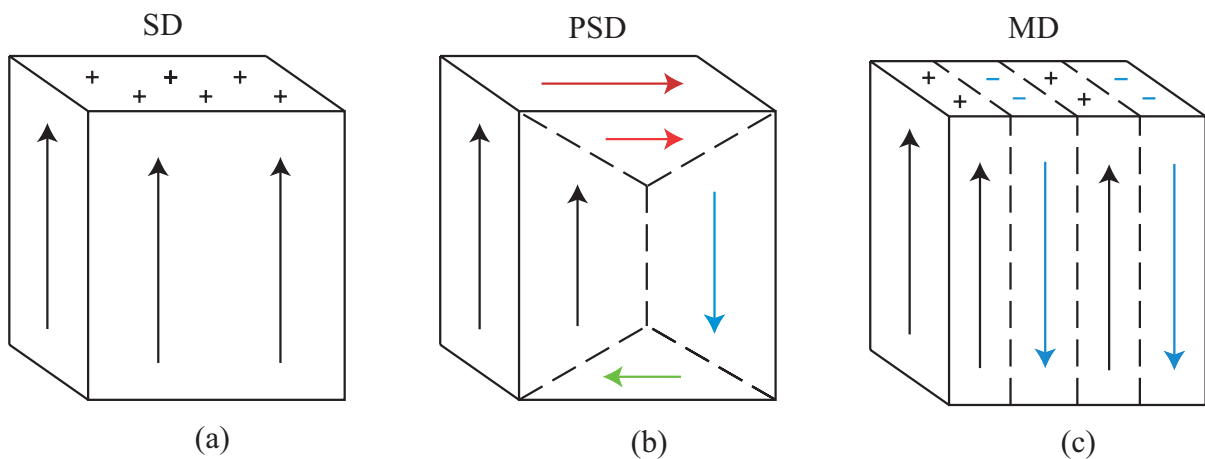


Figure 1.2. Schematic representation of a) Single domain structure (SD), b) two domain magnetic structure (PSD) and c) four domain structure (MD). The dashed lines represent domain walls and the arrows represent the direction of the saturation magnetisation (M_s) in each domain. Modified from Dunlop & Özdemir (1997).

Figure 1.2 depicts examples of domain states that can be achieved. A single domain structure (SD) is one in which all the magnetic moments are aligned (Fig 1.2a) (Kittel, 1967b). A SD grain exists below d_0 where a domain wall cannot be accommodated and therefore is uniformly magnetised at its saturation magnetisation. SD grains are magnetically hard and have high coercivities and remanence.

When the demagnetising energy becomes too large for a SD structure to be stable, the domain state can split into two, reducing the demagnetising energy (E_d) and causing the structure to act in a pseudo-single domain fashion (PSD) (Fig. 1.2b). The grains often exhibit a mixture of multi domain (MD)-like behaviour (low coercivity) and SD-like behaviour (high remanence).

A domain state with two or more domains is said to be multi domain (MD) and are magnetically soft with low coercivities and low remanences. The formation of closure domains can also occur (Özdemir et al., 1995) (Fig. 1.2c), which reduces the demagnetising energy (E_d) even further (Butler, 1992). MD grains are indicative of larger grains relative to SD grains.

1.2.3 Remanence acquisition

When a field is applied to a ferromagnetic material, the total energy (E_{tot}) increases, the magnetic domain structure changes to accommodate the E_{tot} difference and the sample is said to be magnetised. The magnetisation intensity is dependent on the domain structures ability to resist change in temperature and the inducing field. The response of a ferromagnetic mineral to an induced field at a certain temperature is termed a hysteresis loop (Fig. 1.3) (Dunlop & Özdemir, 1997). Key parameters found on a hysteresis loop are depicted in Figure 1.3. When a ferromagnetic sample is exposed to a high field it acquires a saturation magnetisation (M_s), removal of this field leaves the sample with its saturation remanence (M_{rs}) (Collinson, 1983; Dunlop & Özdemir, 1997). On removal of the field, the net moments of single-domain (SD) grains will be aligned in the same direction as the induced field and is said to have a remanence. Multi domain (MD) grains can have their domain walls “pinned” on removal of the field and the irreversible movement of the walls creates a remanence (M_{rs}) (Fig. 1.3) (Evans & Heller, 2003). The net moment is also in the direction of the applied field. The reverse field necessary to get the overall magnetisation, $\mathbf{M}$, to equal zero is termed the coercive force (H_c) and to get the sample to have zero remanence after the removal of the field, a stronger negative field is required, called the coercivity of remanence (H_{cr}) (Dunlop & Özdemir, 1997).

Domain theory states the domain will remain unaffected by the external field until the field applied is equal to the H_c . These are the most common parameters from hysteresis data and are commonly used to construct a “Day” plot (M_{rs}/M_s vs. H_{cr}/H_c) to help determine domain state and infer grain sizes (Day et al., 1977).

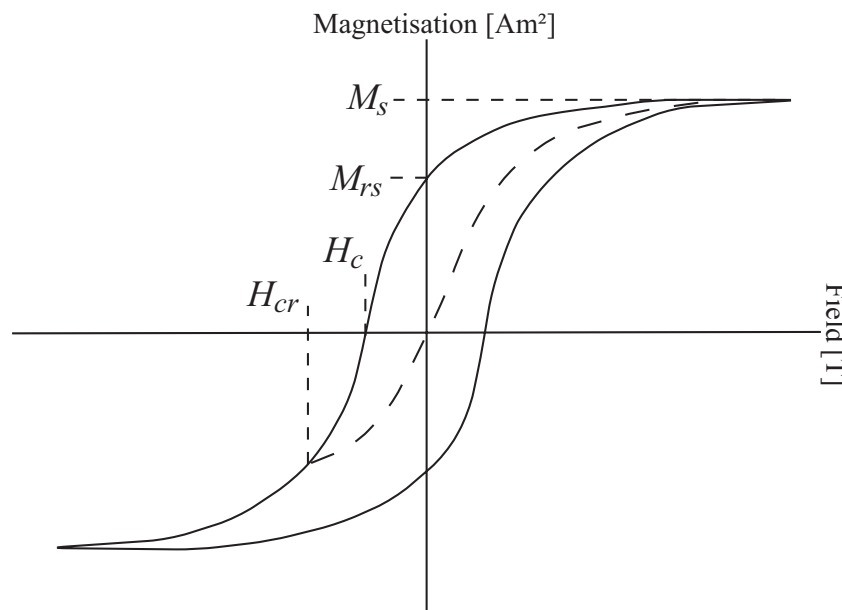


Figure 1.3. Representative hysteresis loop for a ferromagnetic material, H_c is the coercive force, H_{cr} is the coercivity of remanence, M_s is the saturation magnetisation and M_{rs} is the saturation remanence. Modified from Dunlop & Özdemir (1997).

There are several different types of remanence, most of which are summarised below:

Isothermal remanent magnetisation (IRM)

An IRM can be induced by applying a field for a temporary time at a given temperature. When saturated, it is described as an SIRM ($\equiv M_{rs}$ (Fig. 1.3)), which tends to be large and unstable (Collinson, 1983). IRM can be induced naturally by lightning strikes.

Thermoremanent magnetisation (TRM)

A TRM can be acquired by cooling a sample in a small field from its Curie temperature (T_c) and is common in igneous and metamorphic rocks. A TRM can be stable over geological time periods and is also much more intense than an IRM acquired in the same field. The reason for its stability and intensity is that it is acquired at high temperatures, where energy barriers are low compared to the

applied field, and stabilized by cooling to lower temperatures where the coercivities and energy barriers are high. If a TRM is acquired between temperatures other than room temperature and T_c , it is termed a partial TRM (pTRM) (Néel, 1949; Néel, 1955).

Anhyseretic remanence (ARM)

Anhyseretic remanence is induced using a combination of two fields; a DC biasing field, which induces a small remanence and a large AC field that activates the magnetic moments of ferromagnetic grains with coercivities less than the peak alternating field. ARM is an artificial remanence and is sometimes used as an analogue for TRM in palaeointensity experiments, avoiding heating which can cause chemical alterations (Bailey & Dunlop, 1977). ARMs have a greater intensity than IRMs for the same DC field.

Chemical remanent magnetisation (CRM)

A CRM is produced by the formation of a new magnetic mineral in the presence of a magnetic field (Heider & Dunlop, 1987). The new magnetic mineral can be formed by chemical alteration from one mineral/phase to another or by growth of a new mineral. This is typical of diagenetic sediments.

Detrital remanent magnetisation (DRM)

Detrital remanence magnetisation (DRM) is acquired when sediments are deposited and consolidated but is no more than a reconstitution of the TRM, CRM etc., of detrital magnetic grains from the source rock (Collinson, 1965).

Viscous remanent magnetisation (VRM)

Viscous remanent magnetisation (VRM) is acquired by a sample lying in a small magnetic field for a long period of time at a given temperature (Walton, 1983). All rocks can have altered natural remanent magnetisations (NRMs) due to acquisition of a VRM. The VRM component can be removed by stepwise demagnetisation before the ChRM component can be investigated.

Other remanences include piezoremanent magnetisation (PRM) due to stress and gyromagnetic remanent magnetisation (GRM) artificially induced in rotating fields in a laboratory.

1.2.4 Magnetic minerals

The most common magnetic minerals on Earth are oxides and oxyhydroxides of iron (sometimes containing titanium) and iron sulphides.

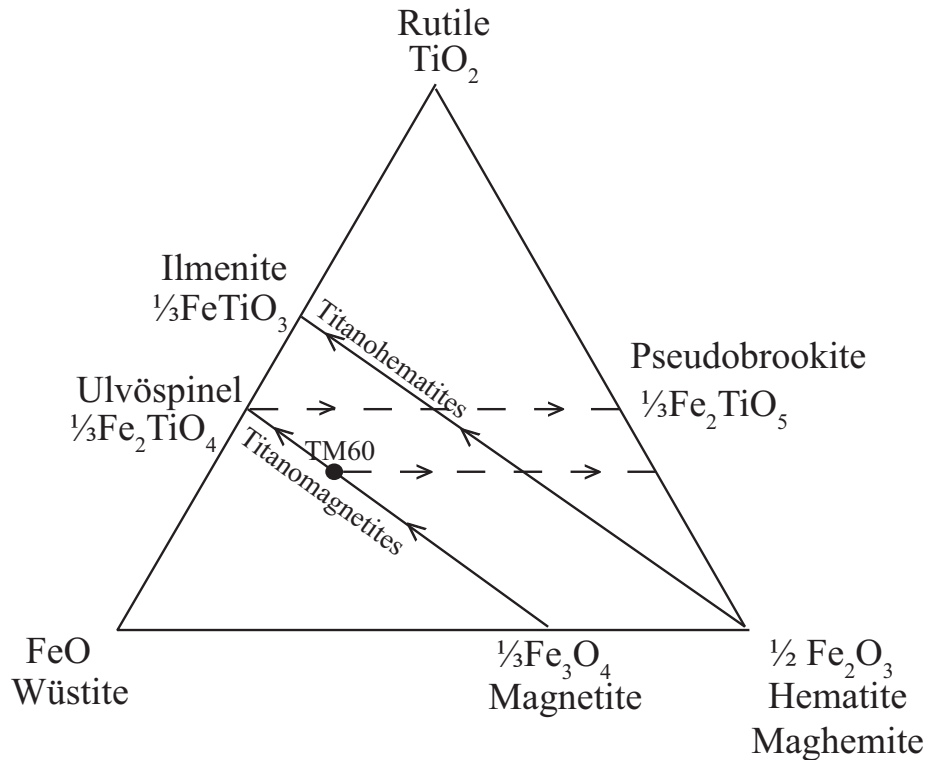


Figure 1.4. Ternary diagram of the main magnetic minerals including the key minerals and solid solution series. From Butler (1992).

Ternary diagrams can be used to describe solid series solutions, for example, titanium iron oxides can be represented by the FeO - TiO₂ - Fe₂O₃ diagram (Fig. 1.4): many common magnetic minerals fall within the system. This ternary system can be divided into two structural groups, 1) titanomagnetites and titanomaghemites; strongly magnetic cubic oxides and 2) solid solution titanohematites and hematite; weakly magnetic rhombohedral minerals (Butler, 1992; Evans & Heller, 2003).

Magnetite

Magnetite (Fe₃O₄ or Fe²⁺Fe₂³⁺O₄) is one of the most important magnetic minerals naturally occurring on Earth because it is abundant and magnetically strong. It is an iron oxide, which forms the dominant magnetic signature in most rocks (igneous, sedimentary and metamorphic) and understanding it is crucial to palaeomagnetic studies. It was first discovered in its natural form lodestone, and used to make the first magnetic compass.

Magnetite has a cubic, inverse spinel structure (Fig. 1.5). The oxygen anions form a face-centred cubic crystal structure with Fe^{3+} and Fe^{2+} cations in interstitial sites. There are two interstitial sites A and B. Site A have a lattice constant of $a=8.369 \text{ \AA}$ and are tetrahedrally coordinated with one Fe^{3+} ion. Site B are octahedrally coordinated with the remaining Fe^{2+} and Fe^{3+} cations (Evans & Heller, 2003).

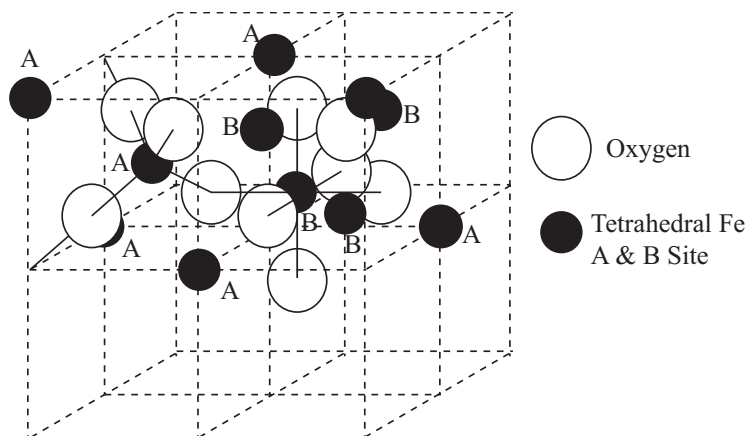


Figure 1.5. The crystal structure of magnetite. White atoms = oxygen, black atoms = Site A: Tetrahedral Fe^{2+} and Site B: Octahedral $\text{Fe}^{2+}/\text{Fe}^{3+}$. From Banerjee & Moskowitz (1985).

Magnetite is a ferrimagnetic mineral because the magnetic moments of the cations on the two sub lattices are antiparallel. The magnetic moments of the two Fe^{3+} cations cancel out and the net magnetic moment is due to the Fe^{2+} ion. Magnetite has two distinct characterising temperatures, the Curie temperature ($580 \text{ }^{\circ}\text{C}$) and the Verwey transition (Walz, 2002). The Verwey transition occurs about 100-125 K depending on the stoichiometry of the magnetite and is marked by a large drop in conductivity as well as a big increase in magnetocrystalline anisotropy (Muxworthy & McClelland, 2000). The mobility and distribution of the cations also vary such that the crystal structure is distorted from cubic to monoclinic symmetry.

Chemically, magnetite is unstable in the ambient environment gradually oxidising to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Fig. 1.6). This process is called maghemitisation (Fig. 1.6) and occurs on the surface of the crystals. The centres of the crystals can become oxidised by the diffusion of Fe^{2+} from the crystal interior to a free surface, where it is converted to Fe^{3+} . Oxidation is slow, controlled by Fe^{2+} diffusion rates and distance to the surface (Dunlop & Özdemir, 1997). Cracks appear due to the difference in crystal size between magnetite and the newly formed maghemite inducing stress. Magnetite has several variations due to replacement of iron with titanium giving rise to a solid-solution-series known as the titanomagnetites (Fig. 1.4) (See titanomagnetites and titanomaghemites).

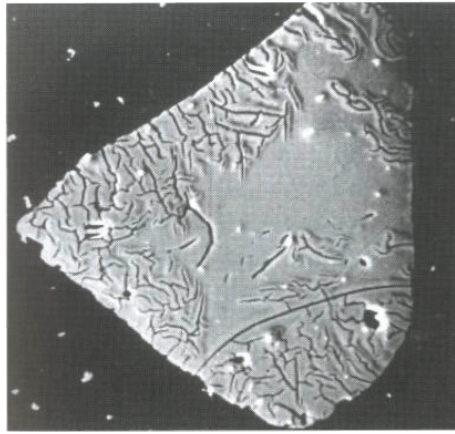


Figure 1.6. Maghemitisation and surface cracking in a magnetite crystal $\sim 30\ \mu\text{m}$ in size. From Gapeyev & Tsel'movich (1988).

Magnetite is formed initially in a variety of basaltic rocks, e.g. widespread basaltic lavas, and due to weathering and erosion they are also found in sedimentary and metamorphic environments. Magnetite is also found in huge deposits within banded iron formations (BIF) (e.g. Hamersley Basin in Western Australia), which is an important source of iron ore. Magnetite crystals have also been found within some bacteria (magnetotactium, magnetospirillum) as well as other animals for navigational purposes (e.g., Kirschvink & Gould, 1981; Lovley et al., 1987).

Hematite

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has a rhombohedral structure, which is antiferromagnetic between the Néel transition ($675\ ^\circ\text{C}$) and Morin transition ($-10\ ^\circ\text{C}$) (Morin, 1950; Vandenberghe et al., 2001). Within hematite there is a small canting in the A and B sub lattice spontaneous magnetisations, M_a and M_b , giving rise to a net spontaneous magnetisation perpendicular to M_a and M_b (Dunlop & Özdemir, 1997). At room temperature, hematite has a very high coercivity compared to similarly sized grains of magnetite. It is normally SD and has a significant contribution from impurities and crystal defects (Dunlop & Özdemir, 1997).

Maghemite

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is the oxidised equivalent of magnetite and is a body-centred-cubic structure and magnetically similar to magnetite; the magnetocrystalline and magnetostrictive constants are roughly one third of that for magnetite. At room temperature maghemite is metastable and when heated, inverts to weakly magnetic hematite between $300 - 600\ ^\circ\text{C}$ (Dunlop & Özdemir, 1997). An

accurate determination of Curie temperature is very difficult for maghemite because of this inversion.

Titanomagnetites and titanomaghemites

Titanomagnetites are also abundant in basalts, specifically TM60 ($\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$) within marine basaltic lavas whose magnetic anomalies are crucial for plate tectonics. Single-phase titanomagnetites $\text{Fe}_3\text{-Ti}_x\text{O}_4$ ($0 \leq x \leq 1$) are inverse spinels but represent increased substitution of titanium weakening the exchange coupling and decreasing the Curie temperature almost linearly with increasing x . Titanomaghemite is a partially oxidised titanomagnetite, with reduced magnetic properties (Wechsler et al., 1984) (Fig. 1.4).

Iron sulphides

Two common ferrimagnetic iron sulphides are pyrrhotite (Fe_7S_8) and greigite (Fe_3S_4) (Table 1.1). Pyrrhotite is weakly magnetic and is mainly found within igneous rocks. Greigite is commonly mistaken as magnetite because of its similar magnetic properties (Roberts, 1995) and spinel structure. It is commonly found in lacustrine sediments such as silts and clays.

Iron carbonate

Siderite (FeCO_3) is an iron bearing carbonate of authigenic origin and is common in sedimentary settings, specifically in marine and lacustrine environments and is typical of anoxic environments. It is paramagnetic at room temperature but can be identified with low-temperature experiments (<40 K) due to its Néel transition at 37-38 K (Jacobs, 1963; Frederichs et al., 2003). Siderite is well known to oxidise to magnetite, maghemite and hematite at high temperatures (from 490°C).

Other magnetic minerals

Two common hydrous iron oxides are lepidocrocite ($\gamma\text{-FeO(OH)}$) and goethite ($\alpha\text{-FeO(OH)}$). When warming to $100\text{-}300^\circ\text{C}$ these minerals dehydrate to oxides to give maghemite and hematite respectively (Dunlop & Özdemir, 1997; Evans & Heller, 2003). Basic magnetic parameters for all the minerals discussed are summarised in Table 1.1.

Table 1.1 Magnetic properties of some common magnetic minerals. Modified from Dunlop and Özdemir (1997).

Mineral	Composition	Magnetic order	T _c (°C)	M _s (Am ² kg ⁻¹)
Oxides				
Magnetite	Fe ₃ O ₄	Ferrimagnetic	~580	90
Hematite	αFe ₂ O ₃	Canted antiferromagnetic	675	0.4
Maghemite	γFe ₂ O ₃	Ferrimagnetic	~600-650	~80
Ilmenite	FeTiO ₂	Antiferromagnetic	-233	...
Ulvaspinel	Fe ₂ TiO ₂	Antiferromagnetic	-153	...
Sulphides				
Pyrrhotite	Fe ₇ S ₈	Ferrimagnetic	320	~20
Greigite	Fe ₃ S ₄	Ferrimagnetic	~330	~25
Oxyhydroxides				
Goethite	αFeOOH	Antiferromagnetic/weak	~120	<1
Lepidocrocite	γFeOOH	Antiferromagnetic	-196	<1
Metal				
Iron	αFe	Ferromagnetic	770	~270

T_c: Curie temperature

M_s: saturation magnetisation

1.2.5 Magnetite formation

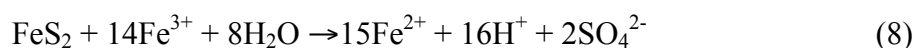
Magnetite can be formed through the dissolution of hematite in certain environmental conditions but an increasing number of studies demonstrate how microbial formation and destruction of other magnetic minerals is an important mechanism for magnetite formation.

It is well known that hematite can be reduced to magnetite at high temperatures (350-570°C) and pressures (1-2 Kbar) in the presence of water by equation (5) or the presence of iron metal, equation (6) (Matthews, 1976).



A series of laboratory experiments have demonstrated how pyrite (FeS₂) can be replaced by magnetite at the late stages of diagenesis (Brothers et al., 1996). Suk *et al.* (1990) gave similar conclusions when analysing pyrite framboids. The geochemistry is applicable to both near surface and deep reactions for pyrite dissolution and magnetite precipitation involving organically complexed ferric iron. Reactions at the surface could lead to the alteration of magnetite to hematite (continuing supply of oxygen molecules) but at greater depths the redox graduation would be halted at magnetite. The formation of magnetite needs 1.6 times more iron per unit volume than pyrite. Pyrite to magnetite formation can occur via reaction (7) in re-precipitation stage and (8) in the

dissolution stage. Equation 8 has been shown to work in acidic reactions as well as up to pH 7 (references within Brothers et al., 1996).



Microbial formation

There has been a lot of research into magnetite formation by microbes and it is now evident that magnetite can be formed by anaerobic and aerobic bacteria. The most studied group is the magnetotactic bacteria, which form intracellular chains of small (nm) single-domain chains ('magnetosomes') (e.g., Frankel & Blakemore, 1980; Faivre & Schuler, 2008).

Iron can be biomineralised through two different modes: 1) Iron biomineralisation by biologically induced mineralisation (BIM) (Fig. 1.7a), which involves bacteria creating a suitable chemical environment to help facilitate precipitation of magnetite (e.g., Bell et al., 1987; Sparks et al., 1990; Zhang et al., 1998). Anaerobic and microaerophilic bacteria form magnetite intracellularly within preformed vesicles (Bazylinski et al., 2007). Some microbes may allow the transport of dissolved Fe^{3+} into the cell whereas others express reductive enzymes and cause the reduction of Fe^{3+} external to the cell. 2) Biologically controlled mineralisation (BCM) (Fig. 1.7b) where bacteria control the mineralisation process genetically (Zhang et al., 1998). Bazylinski *et al.* (2007) demonstrates how magnetite can be generated extracellularly by various Fe^{3+} reducing bacteria within the bulk pore waters of sediments under anaerobic conditions. There may be several different methods for precipitation of magnetite such as, indirectly through the oxidation of Fe^{2+} followed by the reaction of dissolved Fe^{2+} with hydrolysed Fe^{3+} .

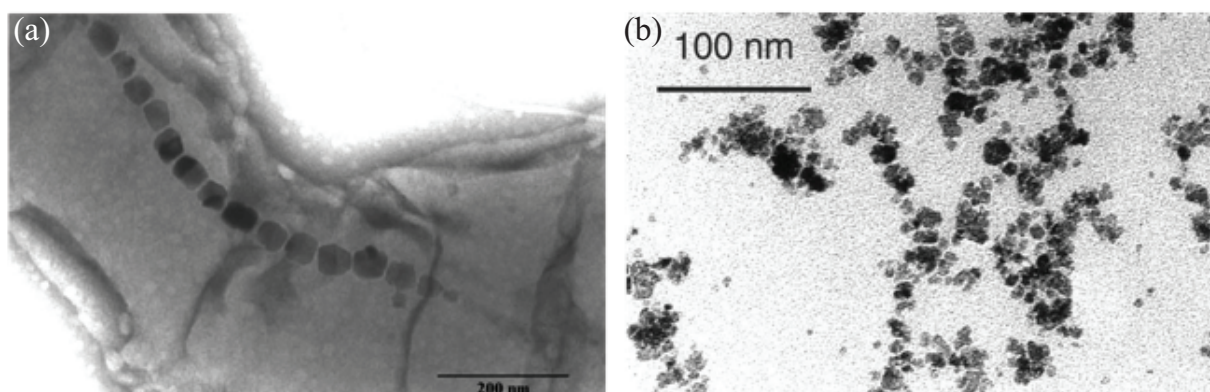
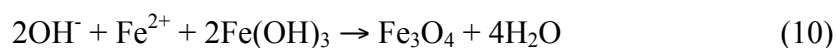


Figure 1.7. TEM of nanoscale grains of magnetite (a) formed extracellularly through biologically induced mineralisation (BIM) during the reduction of ferric oxyhydroxide by the dissimilatory Fe(III)-reducing bacterium *Geobacter metallireducens*. (b) a negatively stained cell that biomineralises cube-octahedral grains of magnetite. Magnetite grains formed by biologically controlled mineralization (BCM) in cells of magnetotactic bacteria. From Bazylinski *et al.* (2007).

Bell *et al.* (1987) demonstrated the importance of pH in magnetite formation by bacteria. Anaerobic bacteria from sediments of an iron-rich environment in Contrary Creek, Virginia were isolated and iron reduction was identified when the organisms were cultured in combinations of synthetic iron oxyhydroxide media but not when cultured individually. Magnetite was also formed with a concurrent increase in pH levels when yeast extract and acetate were introduced as carbon sources. Magnetite was identified as the dominant mineral in an iron-carbonate-water system at high pH and low Eh as predicted by Eh-Ph diagrams (Bell *et al.*, 1987). The formation of magnetite deposits appears to be an indirect product of microbial metabolism and not a direct product of enzymatic action. The organisms produce Fe^{2+} and change the Eh and pH conditions in the area, which in turn shift the mineral solubility equilibria. Bell *et al.* (1987) suggests the results indicate the generation of magnetite as the biogeochemical outcome of bacterial alteration of the environment, in turn influencing local solubility equilibria, a BIM process (Fig. 1.7b) (Karlin *et al.*, 1987; Zhang *et al.*, 1998; Bazylinski *et al.*, 2007).

Although the role of Fe^{3+} reducing bacteria in natural environments still remains unresolved, the inorganic reaction of Fe^{2+} produced by Fe^{3+} reduction with the remaining ferric hydroxide should be sufficient to precipitate magnetite. Hansel *et al.* (2003) showed that magnetite could be abiotically formed through the reduction of Fe^{2+} with ferrihydrite at circum-neutral pH. Bazylinski *et al.* (2007) suggests that high pH may favour magnetite formation, a condition needed during Fe^{3+} reduction (Eq. 9). The Fe^{2+} formed is then absorbed onto other ferric hydroxide grains where it is transformed into magnetite (Eq. 10). An appropriate combination of high pH and high Fe^{2+} concentration at the contact of the Fe^{3+} solid provides an ideal interface for secondary magnetite formation.



In modern freshwater and marine sediments, most magnetite formation occurs in the suboxic layers where Fe^{3+} reduction takes place (Hansel *et al.*, 2003). It has also been associated with solid bitumen and gas seeps where its formation seems to be linked to the reduction of ferric oxyhydroxides and microbial hydrocarbon biodegradation (e.g., McCabe *et al.*, 1987) with supporting experimental evidence conducted by Lovley (1990).

Several research projects have focused on the morphology and structure of the magnetite produced by bacteria (Sparks *et al.*, 1990; Zhang *et al.*, 1998; Bazylinski *et al.*, 2007). Bazylinski *et al.* (2007)

looked at proteobacteria such as *Shewanella* and *Geobacter metallireducens* (Fig. 1.7b), the most studied dissimilatory Fe^{3+} reducing bacterial species that produce magnetite crystals as a by-product of their metabolism when grown in cultures (Cooper et al., 2000; Hansel et al., 2003). The grain size, shape and concentration of magnetite produced by bacteria can vary significantly. For example, on a per cell basis, *Geobacter* can generate up to 5000 times more magnetite than magnetotactic bacteria and *MV-1* bacteria produce single chains of hexagonal magnetite grains whereas *GS-15* bacteria produce irregular rounded crystals (Sparks et al., 1990). Although different bacterium appear to form different magnetite grains there are some similarities e.g. size restrictions appear to be in the nano-scale.

1.3 Review of magnetisation and hydrocarbons

Magnetic research spans a variety of topics including palaeomagnetism, navigation and archeology to name a few. There are two main streams of research relevant to this study, first; remagnetisation studies in which magnetite and magnetic minerals appear to hold a secondary magnetisation but has not always been investigated based on its relation to hydrocarbons and, second; hydrocarbon and magnetic studies for a possible method for hydrocarbon identification. The magnetic minerals identified in both sets of studies is usually a secondary mineral mostly authigenic in origin.

1.3.1 Aeromagnetic surveys

Aeromagnetic studies for alternative exploration of hydrocarbons were assessed based on the theory that short wavelength magnetic anomalies could be associated with chemical alteration of magnetic minerals within a reducing environment in underlying hydrocarbon reservoirs (Fig. 1.8) (Donovan et al., 1979; Elmore & Leach, 1990; Reynolds et al., 1990a; Reynolds et al., 1990b; Reynolds et al., 1991; Saunders et al., 1991; Foote, 1996; Leblanc & Morris, 1999). The recorded resultant magnetic anomalies in these studies show variable responses.

One study by Elmore *et al.* (1993) recorded an increase in total magnetisation through the diagenetic formation of magnetite in the host rocks with little/no magnetisation before hydrocarbon infilling, however, a reduction in total magnetisation was also recorded in units where the formation of magnetite caused the destruction of relatively larger proportions of hematite. Suitable chemical conditions appear to be key in the formation of magnetic anomalies (Machel & Burton, 1991; Gay, 1992; Machel, 1995; Machel, 1996).

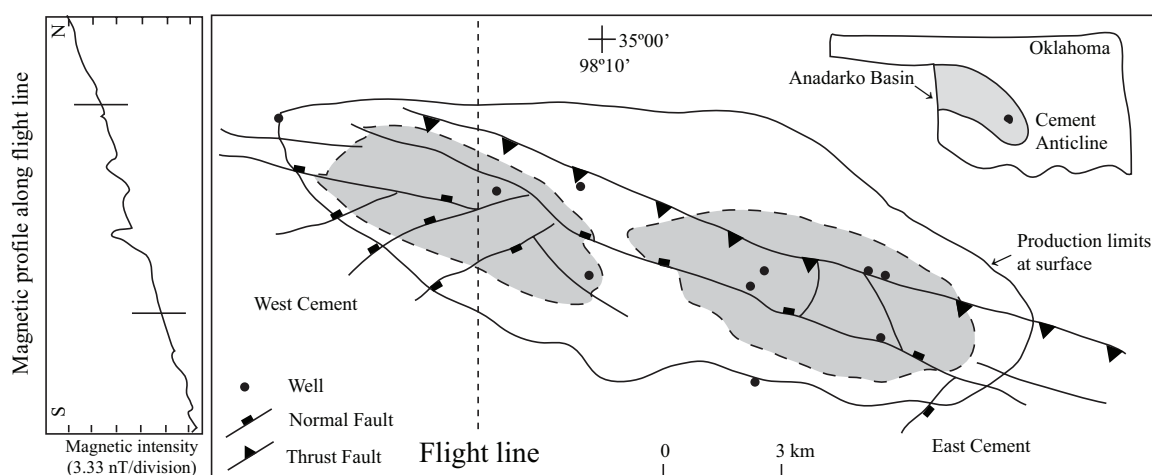


Figure 1.8. An example of an aeromagnetic survey conducted over the Cement field, Oklahoma. The magnetic profile along the flight line shows an elevated magnetic response above the location of the known oil field. Modified from Donovan *et al.* (1979).

Figure 1.8 demonstrates the use of an aeromagnetic flight across a known producing oil field in Oklahoma. The study conducted by Donovan *et al.* (1979) showed an increase in magnetisation restricted within the oil reservoir suggesting a new hydrocarbon exploration tool had been identified. The anomalous magnetisation in this study was later linked to contamination from the wells within the oil field (Reynolds *et al.*, 1990) and was dismissed as a useful petroleum technique. Magnetic anomalies do exist within hydrocarbon environments; however, the associated contrasts have been found to be complex and cannot be used as a quick and direct tool for hydrocarbon identification. Controversy also exists in some of these studies due to the realisation that the anomalous magnetisation produced by authigenic magnetite was actually due to contamination from the wells (e.g., Reynolds *et al.*, 1990a; Reynolds *et al.*, 1991).

1.3.2 Magnetic mineral formation and stability near hydrocarbon plumes

Machel (1995) studied the diagenetic setting of magnetite, hematite, siderite, pyrite, pyrrhotite and Fe^{2+} in association with hydrocarbons by simulating different environments in the laboratory. Machel (1995) stated mineral stability was dependent on seven major fluid geochemical parameters: temperature, pressure, dissolved inorganic carbon, dissolved iron, dissolved sulphur, pH and Eh. Ranges for such parameters were measured and calculated from ground (formation) waters of near surface to deep burial diagenetic settings by a number of sources (e.g., references within Machel, 1995). To look at relative stability of main magnetic minerals, a thermodynamic

stability diagram can be constructed showing the combinations of major geochemical parameters mentioned above at which these minerals are stable relative to other, non-magnetic iron phases, i.e. pyrite, Fe^{2+} and siderite. Several thermodynamic stability diagrams for geological environments ranging from near surface to deep burial diagenetic settings were calculated in Machel & Burton (1991) and Machel, (1995). Machel (1995) looked firstly at near surface diagenetic settings to identify the principal minerals (Figs. 1.9) and then extended the study to deeper diagenetic settings (summarised in Table 1.2).

Near surface setting

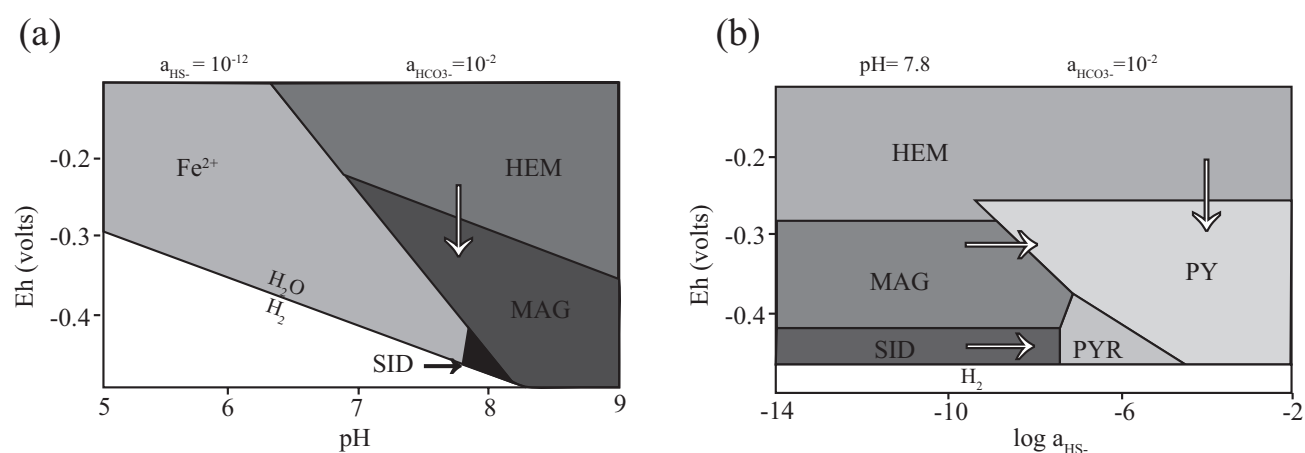


Figure 1.9. Representative stability plot from Machel (1995). (a) $a_{\text{HS}^-} = 10^{-12}$ effectively a sulphur free zone and (b) pH constant at 7.8 to demonstrate the stabilities of iron oxide and carbonate minerals relative to iron sulphide minerals (a = activities). MAG=magnetite, SID=siderite, PY=pyrite, PYR=pyrrhotite and HEM=hematite.

Two example stability plots are given in Figure 1.9 and all parameter ranges; e.g., a_{HS^-} , $a_{\text{HCO}_3^-}$, pH and Eh reflect measurements taken from ground waters of near surface to deep burial diagenetic environments. These plots were picked as representative examples of magnetic mineral stability in different environmental settings. Figure 1.9a represents an environment with extremely low total dissolved sulphur concentrations (activity of hydrogen sulphide, $a_{\text{HS}^-} = 10^{-12}$ effectively a sulphur free zone) and reveals Fe^{2+} ions in solution appear to be favourable over most Eh and pH conditions. Hematite precipitates at $\text{pH} \geq 6.5$ and the upper Eh values but as the conditions become more reducing, magnetite and then siderite become more stable. At $\text{pH} \geq 7$, a decrease in Eh will result in hematite dissolution and/or magnetite replacement (vertical arrow). Figure 1.9b holds pH constant at 7.8 to demonstrate the stability of iron oxides and carbonate minerals relative to iron sulphides. Significant increases in sulphide activity would result in dissolution of magnetite and siderite and/or replacement by pyrite and pyrrhotite (horizontal and vertical arrows). Machel (1995) concluded in near surface settings, that Eh in diagenetic settings commonly decrease markedly with depth or via hydrocarbon invasion.

Deep diagenetic setting

For deeper diagenetic settings Machel and Burton (1991) used the same ranges of pH, Eh, $a_{\text{HS-}}$ and $a_{\text{HCO}_3^-}$ as in the first set of diagrams (Fig. 1.9) but temperatures and pressures at: 50 °C, 150 bar; 100 °C, 300 bar and 200 °C, 600 bar, representing approximate conditions occurring downward in most mature sedimentary basins, i.e. with a normal geothermal gradient ($\sim 30 \text{ }^\circ\text{C km}^{-1}$). The additional 12 phase diagrams for deep burial settings can be found in Burton *et al.* (1993).

A summary of all the phase diagrams in Table 1.2 (Burton *et al.*, 1993) shows the fate of important magnetic minerals (hematite, magnetite and pyrrhotite) with increasing burial (A-D) and their proximity to hydrocarbons (zero, low and high concentrations). The stability of the minerals is defined as stable (S) or unstable (U). If the unstable alteration is known the new mineralogy is defined as well as the resultant magnetization change (positive or negative) (Table 1.2).

Several important results, firstly, compared to mineral dissolution, there appears to be a higher possibility of mineral replacement under high pH settings than under lower pH settings. Secondly, compared to original biogenic or detrital magnetisation of the sediments, remagnetisation is likely to increase with increasing depth and thirdly, in the vicinity of hydrocarbon traps, remagnetisation at shallow depths is likely to be a negative contrast and increasingly positive contrasts at depth with the pattern becoming more pronounced with greater proximity to the hydrocarbon accumulations (Table 1.2).

Table 1.2 Summary of mineral changes from the surface to depth and from association with hydrocarbons to a hydrocarbon free zone. A-D represents increasing depth, temperature and pressure. LTS, MTS and HTS denote total sulphur levels. The magnetic contrasts are shown relative to background levels, an increase (+) or a decrease (-). Modified from Burton *et al.* (1993).

		NO HYDROCARBONS			LOW CONCENTRATION OF HYDROCARBONS				HIGH CONCENTRATION OF HYDROCARBONS			
		HEM	MAG	PYR	HEM	MAG	PYR	(+/-)	HEM	MAG	PYR	(+/-)
A	LTS	S	U	U	MAG/	S/SID	U	(+/-)	U	U	U	(-)
	MTS				PY	U	U	(-)	U	U	U	(-)
	HTS				PY	U	PY	(-)	U/PY	U	U	(-)
B	LTS	S	U	U	MAG/	S/SID	U	(+/-)	U	U	U	(-)
	MTS				PY	S/SID	U	(-)	U/PY	U	U	(-)
	HTS				PY	U	S	(+)	PY	U	S	(+/-)
C	LTS	S	U	U	MAG	S/SID	U	(+/-)	U	U/SID	U	(-)
	MTS				MAG	S/SID	U	(+/-)	PY	U/SID	U	(-)
	HTS				PY	S/PY	S	(+)	PY	U	S	(+/-)
D	LTS	S	U	U	MAG	S/SID	U	(+/-)	MAG	S/SID	U	(+/-)
	MTS				MAG	S/SID	U	(+/-)	MAG	S/SID	U	(+/-)
	HTS				MAG	S/PY	S	(+)	MAG/P	S/PYR	S	(+)
		high Eh/pH low S, var Fe^{2+}			pH>7.5, med/low Eh, var Fe^{2+}				pH<7.5, med/low Eh, var Fe^{2+}			

U=unstable, S=Stable; or replaced by MAG=magnetite, SID=siderite, PY=pyrite, PYR=pyrrhotite and HEM=hematite.

Complications arise when considering microbial processes (Karlin et al., 1987; Lovley et al., 1987; Sakaguchi et al., 1993). Machel and Burton (1991) demonstrate how microbial metabolism can produce or promote the formation and/or dissolution of minerals which are thermodynamically unstable and stable respectively. Machel (1995) revealed aerobic magnetotactic bacteria live in conditions where magnetite is thermodynamically unstable (Bell et al., 1987; Karlin et al., 1987; Sakaguchi et al., 1993). Therefore these bacteria could generate, perhaps temporarily a disequilibrium assemblage.

1.3.3 Remagnetisations

Remagnetisation of minerals causes the magnetic history to be reset or overprinted. This so-called secondary magnetisation can occur by two methods: (1) Thermoviscous remanent magnetisation (TVRM) acquired by heat produced during burial or (2) Chemical remanent magnetisation (CRM) acquired during the formation of new minerals (See Section 1.2.3). Using geological and theoretical considerations it is possible to distinguish between CRM and TVRM origins (Dunlop & Özdemir, 1997; Evans & Heller, 2003); the mechanism behind remagnetisation has important implications to the magnetic mineralogy. For example, if the remagnetisation is a CRM then it is likely that the mineral was formed after burial and is diagenetic (i.e., post-depositional) in origin. Likewise the use of palaeotemperature information, carbon/oxygen isotopes and theoretical curves relating blocking temperatures and relaxation can be used to determine whether deep burial has occurred inferring a TVRM origins (Dunlop & Özdemir, 1997).

There is an extensive number of studies which have investigated remagnetisation of sedimentary units (e.g., Scotese et al., 1982; McCabe et al., 1983; Wisniowiecki et al., 1983; McCabe et al., 1984; McCabe et al., 1985; Benthien & Elmore, 1987; Elmore et al., 1987; McCabe & Elmore, 1989; McCabe et al., 1989; Elmore & Crawford, 1990; Saffer & McCabe, 1992; Belkaaloul & Aissaoui, 1997; Katz et al., 1998; Garner & Cioppa, 2006; O'Brien et al., 2007; Aubourg et al., 2008; Aubourg et al., 2012). Using palaeomagnetic poles, these studies discovered that magnetisation was not acquired during sediment burial but significantly later revealing the magnetic remanence was not primary and had been remagnetised (e.g., Scotese et al., 1982; Wisniowiecki et al., 1983). All these remagnetisation studies allude to the idea of migrating fluids being responsible for the authigenic magnetite (e.g., hydrocarbon fluids) (e.g., Oliver, 1986; Evans & Elmore, 2006), and identification of the magnetite by Scanning Electron Microscopy (SEM) was performed in most

of the studies (McCabe et al., 1987; Kilgore & Elmore, 1989) to identify the structure/texture of the magnetite.

Spherule, spherical aggregates or framboids (Fig. 1.10) were found in several different geological units e.g. carbonates and sandstones as well as within speleotherms (Elmore et al., 1987; Elmore & Crawford, 1990) and solid bitumen (McCabe et al., 1987). SEM images of the magnetic extracts reveal that abundant magnetite occurs as spherical crystal aggregates (Fig. 1.10), some with hollow cores (Wisniowiecki et al., 1983) with diameters ranging between 3-156 μm (McCabe et al., 1983; Wisniowiecki et al., 1983; Elmore et al., 1987).

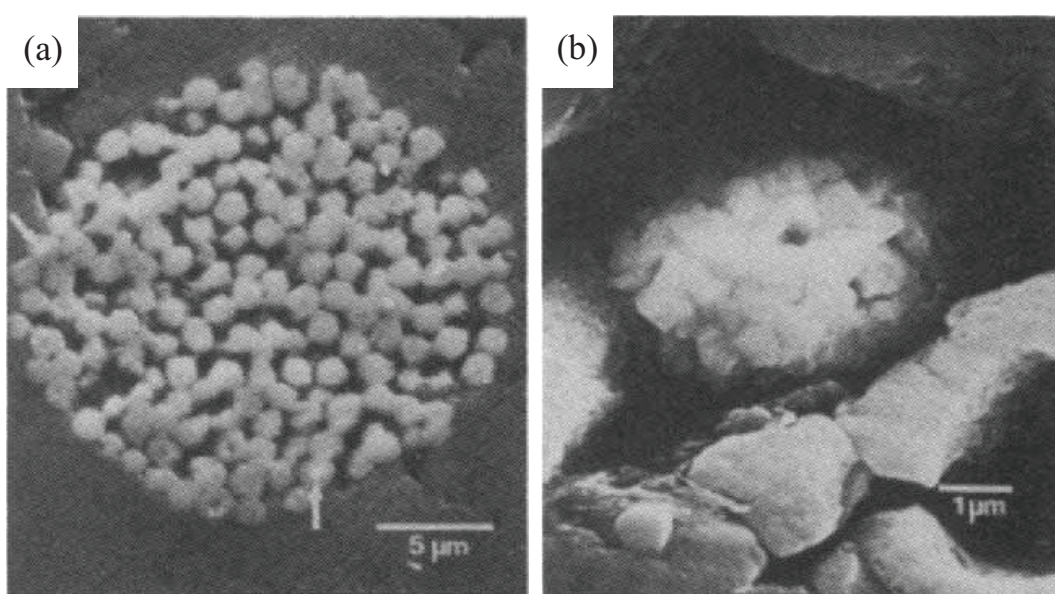


Figure 1.10. SEM images of magnetite that replaced framboidal pyrite in Onondaga limestone. (a) Polished cross-section of pseudoframboid (bright cores are remnant pyrite (arrow)) and (b) pseudoframboid in crack of calcite. From Suk *et al.* (1990).

The only cation present in the spheres, as a major or minor element is iron determined by qualitative Energy-Dispersive X-ray (EDX) analysis (Benthien & Elmore, 1987; McCabe et al., 1987; Kilgore & Elmore, 1989; Elmore & Crawford, 1990; Suk et al., 1990; Aldana et al., 2003). The formation of these magnetic framboids is not completely understood but Canfield and Berner (1987) have shown pyritisation of magnetite in unconsolidated sediments can form pyrite framboids and it is claimed the reverse can occur at later stages of diagenesis in limestones (Suk et al., 1990). It is thought that understanding how pyrite framboids develop could help us to understand magnetite framboids (Sawlowicz, 1993). Another suggested mechanism of magnetite framboid formation was introduced by McCabe *et al.* (1987) after they identified spherical crystal aggregates in solid bitumen, which appeared to be identical to magnetite spherules found in other studies

(McCabe et al., 1983; McCabe et al., 1984; Benthien & Elmore, 1987; Suk et al., 1990). These secondary magnetite framboids were strongly magnetic and formed naturally within solid bitumen. Solid bitumen can be formed by the thermal destruction of crude oil at relatively high temperature or as a result of crude oil biodegradation at relatively low temperatures (Sassen et al., 1989). Analysis indicated the composition of solid bitumen in this study was a result of biodegradation at shallow depths on what was once liquid crude oil. The occurrence of secondary magnetite within solid bitumen could be used as evidence for a link between crude oil and deposition of magnetite however magnetic framboids are found in many sedimentary units not all of which have associations with hydrocarbons.

1.3.4 Hydrocarbon identification through magnetic investigation

Research into the use of magnetics for hydrocarbon identification has been of interest for decades but the development of these ideas has proven difficult in the past. New research using both oil producing and non-producing wells has led to characterisation of magnetic anomalies above oil reservoirs with specific identification of the magnetic mineralogy of such anomalies.

Costanzo-Alvarez *et al.* (2000) and Aldana *et al.* (2003) have researched 13 wells in Venezuela and Colombia, three from the La Victoria field (two producing wells LVT-1X and 4X, one non-producing well 2X) and 10 wells from Guafita field (five producing wells but only two extensively studied GF-1X, 2X, and five non-producing wells but only two extensively studied GF-8X, 13X) to identify magnetic anomalies above oil reservoirs. Costanzo-Alvarez *et al.* (2006) analysed drill cuttings between 100 and 1500 m in intervals of roughly 15 m and conducted rock magnetic and Electron Paramagnetic Resonance (EPR) studies on all of the wells, including bulk magnetic susceptibility (χ) measurements (Fig. 1.11). Within the two sets of wells, anomalous values of χ were detected at certain depth intervals. For example, producer well LVT-1X (Fig. 11b) shows background values below $100 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, with an anomalous peak identified at depth 750-810 m at a χ value greater than $1250 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ (Aldana *et al.*, 1999). These anomalies were categorised into two types A and B.

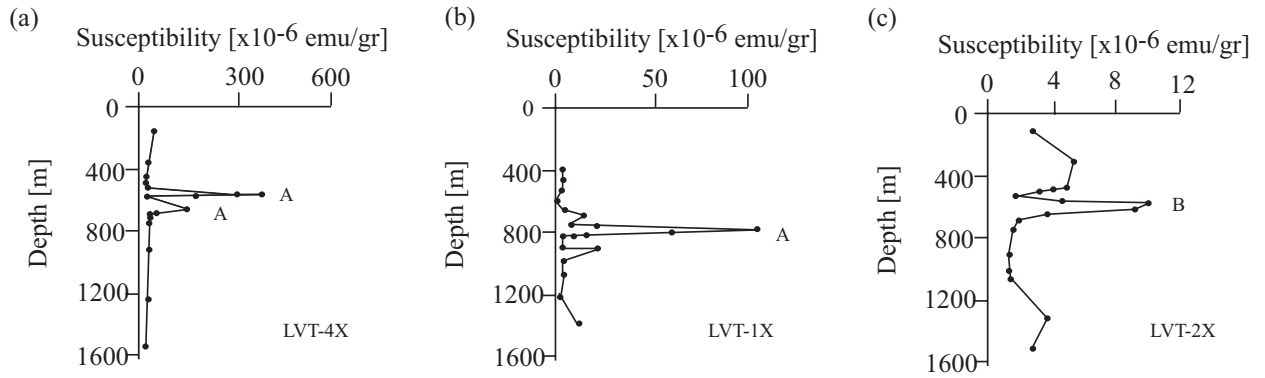


Figure 1.11. Magnetic susceptibility values plotted against sampling intervals for two producing wells from La Victoria ((a) LVT-4X and (b) LVT-1X) oil fields and a nonproducing well ((c) LVT-2X). After Aldana *et al.* (1999), Costanzo-Alvarez *et al.* (2000) and Diaz *et al.* (2000).

Anomaly A was characterised by Fe-rich spherical aggregates (as discussed in the previous section) of claimed authigenic origin as seen by SEM analysis and was found only in producing wells (LVT-1X (Fig. 11a), LVT-4X (Fig. 11b), GF-1X and GF-2X) (Costanzo-Alvarez *et al.*, 2000; Aldana *et al.*, 2003). The authors suggested that the dominant magnetic mineralogy in these anomalous depths was a low coercivity magnetic mineral, probably magnetite as seen in the IRM at low saturation fields (<200 mT), thermal demagnetisation of composite IRMs and χ studies. Anomaly B had no association with spherical aggregates and appeared in both non-producing and producing wells (Costanzo-Alvarez *et al.*, 2000; Aldana *et al.*, 2003). X-ray diffraction analysis revealed these anomalies were characterised by quartz, magnetite and hematite.

A similar study by Liu *et al.* (2006) looked at two wells from the Mawangmiao Oil Field in Hubei Providence of China, one dry well (M46) and one oil well (M36). Liu *et al.* (2006) conducted low-field magnetic susceptibility (χ) and standard hysteresis measurements (M_{rs} , M_s , H_c , H_{cr}). The results showed oil well M36 had χ , M_s and M_{rs} values between 24 and 36 times higher than corresponding values obtained from the dry well (M46). Liu *et al.* (2006) produced a plot of χ/M_{rs} and M_{rs}/M_s (Fig. 12a) showing the background samples from both wells plot separately to the data from the producing layer in well M36. M36 shows anomalously high ratios ~ 0.30 for the grain size proxy M_{rs}/M_s only within the oil-rich formation (Fig. 12a). Liu *et al.* (2006) concluded the major magnetic mineral contributing to these anomalies were maghemite with only minor contributions from magnetite, but did find magnetite spherules in other studies (Liu *et al.*, 1998a). Liu *et al.* (2006) claimed the siderite identified could have been produced during drilling, caused by the release of CO_2 , reacting with iron clay minerals but concluded the maghemite found was most probably the alteration product of siderite.

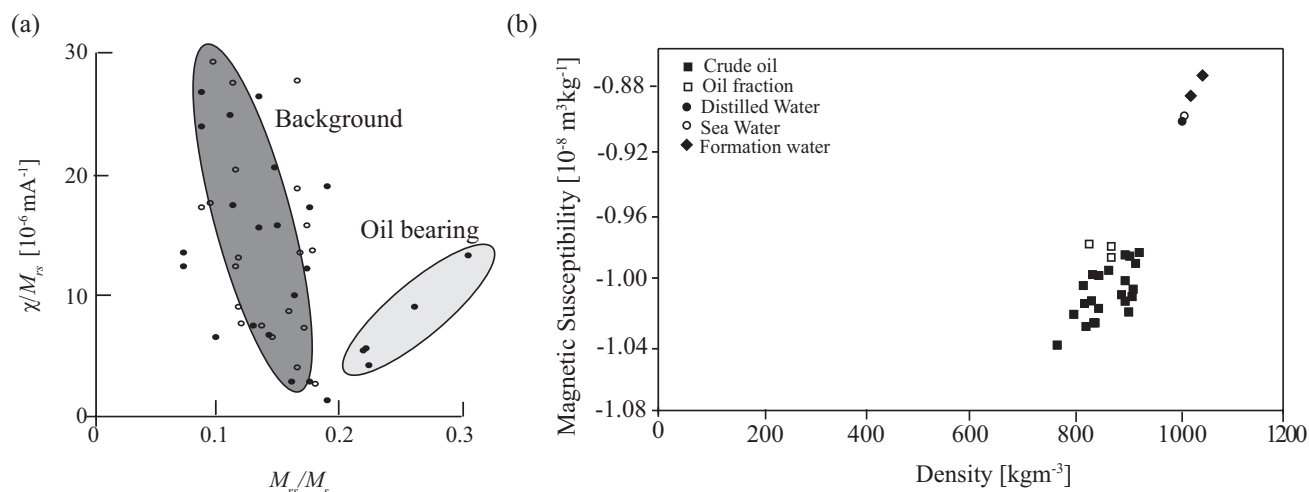


Figure 1.12. Research combining magnetic characterisation and hydrocarbons. (a) Plot of hysteresis properties, χ/M_{rs} and M_{rs}/M_s from wells M46 (●) and M36 (○). From Liu *et al.* (2006). (b) Magnetic susceptibility and density plot for different petroleum reservoir fluids including oil, formation waters and seawater. From Ivakhnenko and Potter (2004).

Ivakhnenko and Potter (2004) investigated the magnetic susceptibility of crude oils, refined oil fractions and formation waters from worldwide sites (Fig. 12b). All fluids measured were diamagnetic but had distinct differences in magnetic susceptibility, e.g. the crude oil was more negative than formation waters from the same location (Fig. 12b). The oils physical and chemical properties appeared to correlate with the magnetic susceptibility such as gravity, metal concentration, viscosity, sulphur content and density.

Several studies (e.g., Díaz *et al.*, 2000; Díaz *et al.*, 2006; Guzman *et al.*, 2011) identified positive correlations between extractable organic matter (EOM), organic matter free radical concentration (OMFRC) and χ values along oil producing wells, proposing that the areas of anomalous behaviour represent broad reducing bands with the presence of asphaltene suggesting a bacterial reducing process forming secondary minerals. Díaz *et al.* (2000) suggested these anomalies are a result of hydrocarbon gas leakage from below, causing alteration of organic matter resulting in a net transfer of electrons from altered organic matter to Fe (III). Other studies investigating hydrocarbon contamination in sediments (Rijal *et al.*, 2010; Venkatachalapathy *et al.*, 2010; Venkatachalapathy *et al.*, 2011; Rijal *et al.*, 2012) have shown similar positive correlations suggesting the resultant magnetic mineralogy must be due to the hydrocarbon contamination.

The above studies have potentially identified a link between hydrocarbons and magnetisation. However, very few mechanisms for such a relationship have been suggested and the studies often leave several unanswered questions due to the complex nature of the problem. The studies also appear to be specific to the environment investigated and few attempts have been made to see if they apply to a large range of situations.

1.4 Review of organic geochemistry

1.4.1 Organic matter and hydrocarbons

Petroleum generation is produced by the thermal alteration of kerogen during the continuous burial of sediments and organic matter (Killops & Killops, 2005). Many hydrocarbons undergo significant changes in their chemical structure as originally biological compounds adapt to geological conditions with higher temperatures and pressures. As temperature increases, kerogens progress through catagenesis and metagenesis to produce oil and gas (Fig. 1.13). The chemical structure of hydrocarbons and related compounds reflect the constitution of the kerogen structure (Fig. 1.13) (Killops & Killops, 2005).

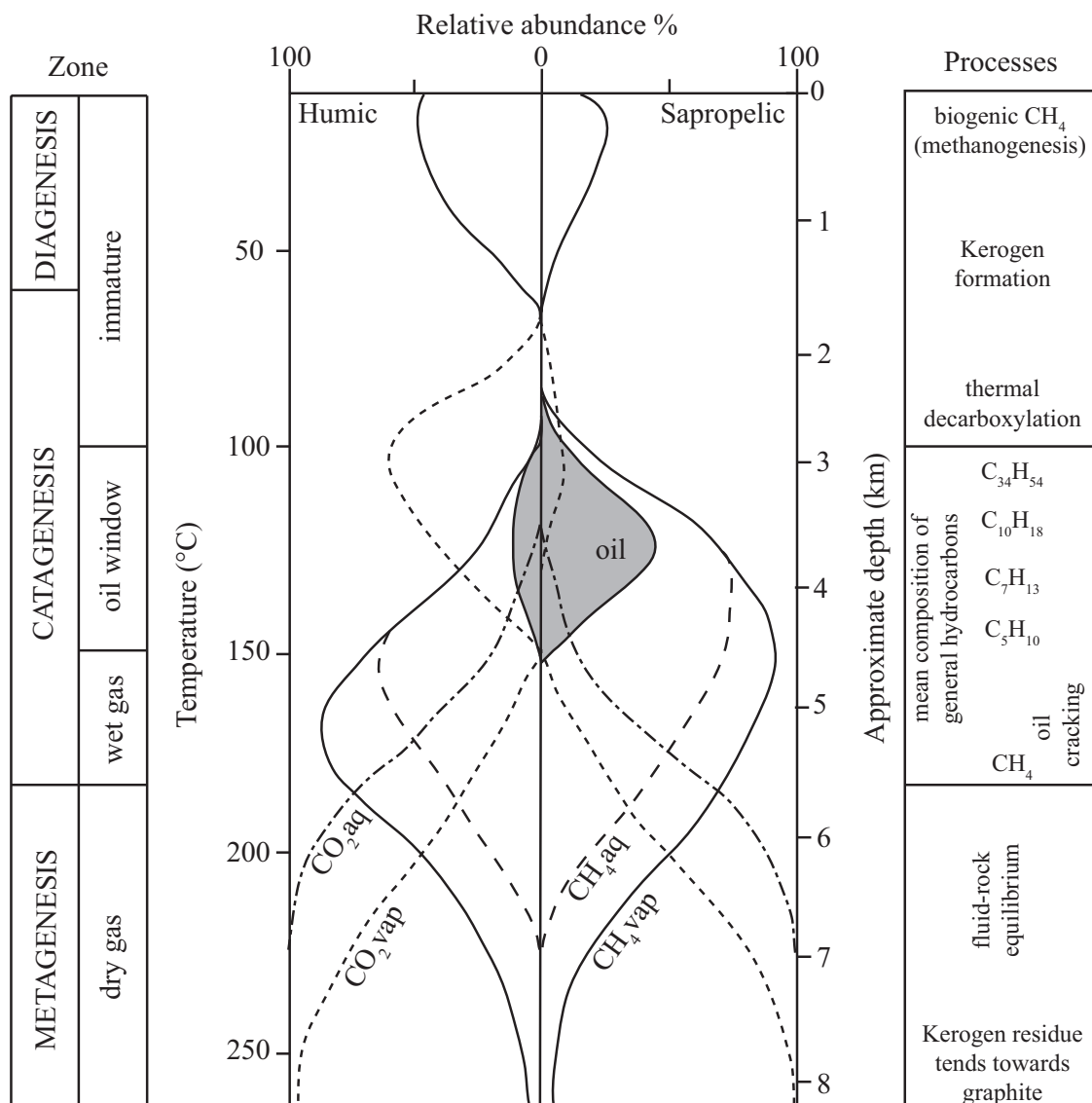


Figure 1.13. Diagram of oil and gas generation 'window' in relation to burial depth and temperature. Modified from Killops & Killops (2005).

Kerogen is the polymeric organic matter (Fig. 1.14) from which hydrocarbons are generated. Bitumen is a term for solid or liquid hydrocarbon deposits that are soluble in common organic solvents (Fig. 1.14) and is itself made up of four main constituents: asphaltenes, polars, aromatic compounds and aliphatic compounds. Asphaltenes have molecular weights of 1000-2000 atomic units and can be removed from the remaining bitumen (the maltenes) by precipitation following the addition of excess non-polar organic solvent (Fig. 1.14) (Berkowitz, 1997). Polars, aromatic and aliphatic compounds can be separated based on their relative polarity using column chromatography.

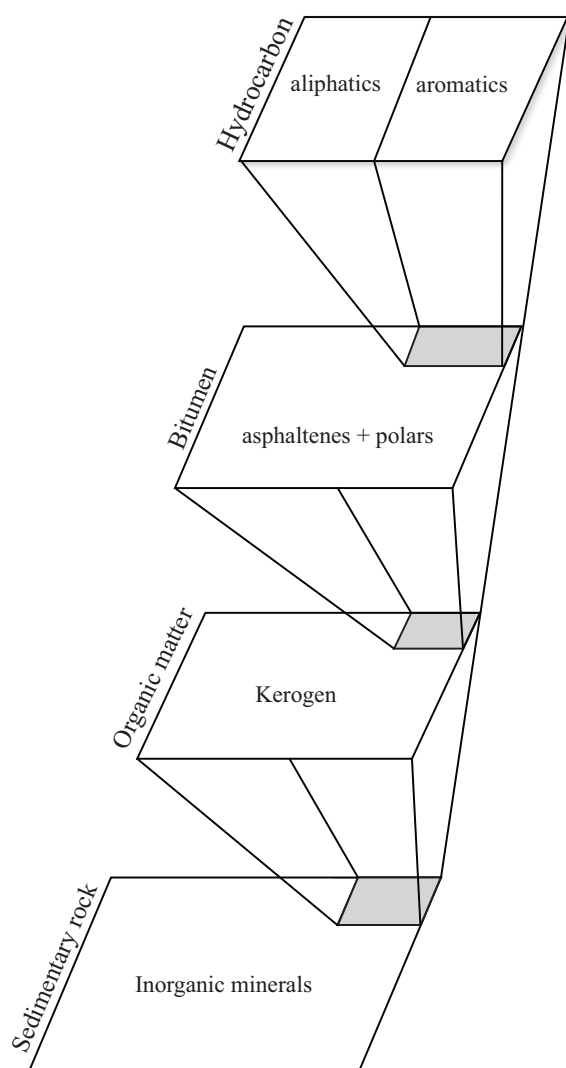


Figure 1.14. Schematic of hydrocarbons origin. Kerogen is the polymeric organic matter from which hydrocarbons are generated. Bitumen is the solid or liquid hydrocarbon deposit that is soluble in an organic solvent or are fusible. Bitumen is composed of three fractions; hydrocarbons, asphaltenes and polars. Hydrocarbons can be separated into aliphatic and aromatic sub fractions.

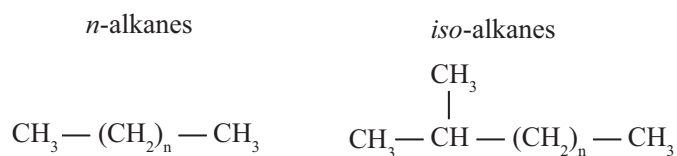
1.4.2 Oil composition

The average composition of crude oil is 57% aliphatic hydrocarbons, 29% aromatic hydrocarbons and 14% polars and asphaltenes, but there are a wide range of oil compositions giving rise to ‘light’

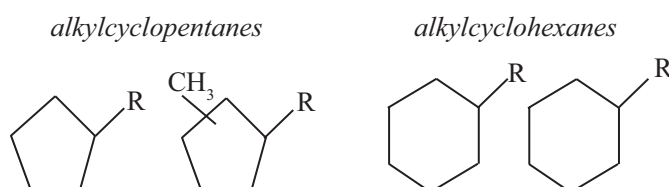
and ‘heavy’ oils (Killops & Killops, 2005). The primary differences in oil composition are due to the chemical composition of the source rock and the thermal maturity of the oil (described in detail in Section 1.4.4).

Aliphatic hydrocarbons (saturate hydrocarbons) are divided into cycloalkanes (naphthenes) and acyclic alkanes (normal and branched) (Fig. 1.15). In oils, the straight-chained (normal) alkanes dominate with modes around C₆-C₈ but alkanes up to C₁₂₀ can be present. Surface conditions distinguish the acyclic alkanes <C₅ as gases where as >C₅ are liquids with >C₁₅ tending towards viscous liquids into solid waxes (Killops & Killops, 2005; Peters et al., 2005c). Cycloalkanes are liquids, but grade into solids with increasing alkyl chain length.

(a) acyclic alkanes



(b) cycloalkanes



(c) aromatic hydrocarbons

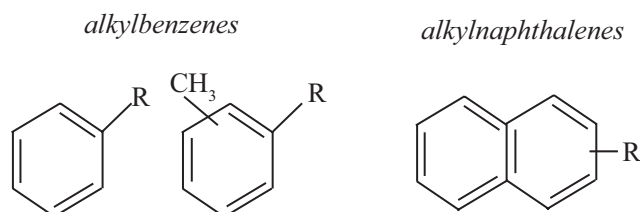


Figure 1.15. Examples of the major hydrocarbons and simple heteroatomic compounds in crude oils: R = alkyl group. Modified from Peters *et al.* (2005c).

Aromatic hydrocarbons (Fig. 1.15) with alkyl groups are common with low molecular weight alkyl benzenes being the most abundant. Under Earth surface conditions, alkylbenzenes of short chain

length are liquids whereas longer chains and polycyclic aromatic hydrocarbons are solids (Peters et al., 2005c).

Polars (polars are used throughout the text but it should be noted that polars and resins are synonymous) and asphaltenes are light molecular weight heteroatomic molecules that are not well defined. When a large quantity of a low molecular weight alkane is added to the bitumen (e.g., *n*-pentane) the polars are soluble whereas asphaltenes are insoluble and precipitate out (Peters et al., 2005c). Therefore the fundamental difference between polars and asphaltenes are the relative solubility and relative sizes.

Elemental composition of crude oils typically consist of; 82.2-87.1% carbon, 11.8-14.7% hydrogen, 0.1-5.5% sulphur, 0.1-4.5% oxygen, 0.1-1.5% nitrogen and <0.1% others (Berkowitz, 1997). The polars and asphaltenes from crude oil contain most of the nitrogen, sulphur and oxygen and are collectively named the polar NSO compounds. Other elements typically found within oil include metals such as nickel and vanadium (Barwise, 1990). The composition of an oil can vary through many processes, these changes are described in detail in Sections 1.4.4 (primary processes) and 1.4.5 (secondary processes).

1.4.3 Source to reservoir

Source:

There are three classifications of kerogen categorized by the source input (Tissot et al., 1974). Type I kerogens are primarily made up of liptinite and are similar to sapropelic coals consisting of algae and alginites. Type III kerogen is primarily terrestrial plant matter and is similar to humic coals consisting of vascular plants and plant debris. Type II is therefore an intermediate between types I and III and can be formed in any environment. In marine conditions, it is predominantly made up of a mixture of phytoplankton and authochthonous organic matter. Type I kerogen is not very common whereas Type II and III kerogen are widespread. A type IV kerogen exists but it has no hydrocarbon potential and is therefore sometimes not considered a real kerogen (Killops & Killops, 2005). It is comprised of extremely oxidised plant matter. As the burial of the source rock continues, compaction and expulsion of water creates an overall dense rock with low porosity and permeability, this is the stage of main petroleum generation.

Generation:

When a rock containing kerogen is subjected to continued burial, the kerogen experiences thermal alteration. The resultant hydrocarbon rich fluids and gases are all termed petroleum (Killops & Killops, 2005). The generation of petroleum is simply the result of the kerogen structure attempting to achieve thermodynamic equilibrium as temperatures and pressures increase with continued burial. However, if a rock unit containing kerogen is uplifted, exposed and eroded, the kerogen is weathered away to carbon dioxide and water and has no petroleum prospectivity.

Primary Migration:

As petroleum travels from the source rock to the reservoir rock, pressure, compaction and temperature all play key roles (Tissot & Welte, 1984; England et al., 1987; Braun & Burnham, 1992). It is generally believed that hydrocarbons move through microfractures via capillary fracture under the influence of over pressure, compaction and buoyancy. Continued pressure and fracturing processes could be cyclic and may help to drive hydrocarbon expulsion. The insolubility of hydrocarbons in water and the lack of un-bound water in such compacted rocks suggest that one phase of pressure-driven hydrocarbon expulsion would occur. An alternative mechanism involves the thermally activated diffusion of hydrocarbons through the source rock (Stainforth & Reinders, 1990). The rate of diffusion of the hydrocarbons from their origin in the source rock has been estimated to equal the magnitude of rate of thermal generation. This would result in the loss of low molecular hydrocarbons at least during the early phase of expulsion. Both mechanisms allow hydrocarbons to migrate from both the top and bottom of a source rock (Mackenzie et al., 1988). The expulsion of hydrocarbons is also dependent on sufficient levels of hydrocarbon generation in the source rock and the amount of hydrocarbons expelled is due to the type and amount of kerogen to begin with.

Secondary Migration:

Secondary migration from the source rock into hydrocarbon traps is controlled by vertical buoyancy forces due to the density difference of petroleum and formation waters (Schowalter, 1979). Hydrocarbons migrate as immiscible and separate phases through the water saturated rock within 'carrier beds'. The capillary pressure difference between water and oil acts in opposition to the buoyancy forces and therefore causes the hydrocarbons to migrate along coarser (more porous) routes through a carrier bed (England, 1994). These pathways are often convoluted with a combination of vertical and lateral migration due to the presence of heterogeneities within the subsurface rock. When hydrocarbons begin to fill into a trap, the tortuous migration pathway will tend to fill from one side. Compositional changes within the oil can occur during filling as the

source rock becomes more mature (England, 1994). Faults can be either sealing faults (part of the trap) or open faults in which hydrocarbons can also migrate through.

Reservoir:

Reservoir rocks are termed so because of the large amount of hydrocarbons they are able to accumulate within them. Reservoir rocks must have suitable permeability (1-1000mD) and porosity (10-25%) to allow the migration of petroleum into the unit. The reservoir rocks have to be in place before the migration of the hydrocarbons and are mainly within clastic rocks (sandstones ~ 60%) and carbonate rocks (~30%). Examples of reservoir units are channel sands, submarine fans, barrier sand bars and islands as well as carbonate reefs (Selley, 1997). As well as a suitable reservoir rock, to have an accumulation of hydrocarbons there must be a trap, e.g., a 3-D geological feature preventing hydrocarbons escaping. Traps typically form in two ways; 1) structural and 2) stratigraphic (Selley, 1997) (Fig. 1.16). Structural traps are caused by tectonic processes such as folding (anticlines) and faulting as well as salt tectonics. Most of these structures form due to outward flow requiring movement opposite to the buoyancy forces as well as flow being opposed by large capillary forces in the lower porosity/permeability units at any fault intersection. Salt tectonics can cause domes and other 3-D structures similar to standard folding formations. Secondary migration can occur through faulting as well.

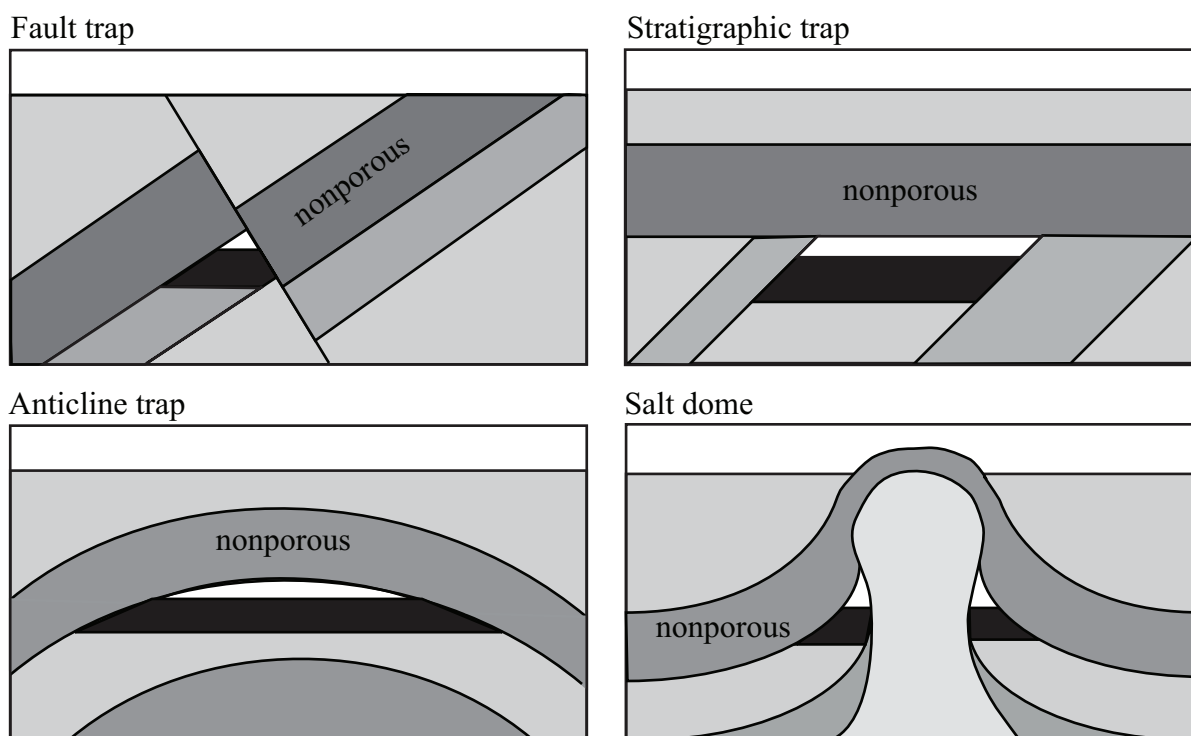


Figure 1.16. Schematic of potential oil and gas stratigraphic and structural traps. Gas (white) and oil (black).

Stratigraphic traps are a result of depositional features. These are typically formed by the reservoir being surrounded by impermeable units such as shales or limestones, which have reduced porosities and low permeability relative to the reservoir rock acting as a seal. Often reservoir traps are a combination of these types of traps (Fig. 1.16). Hydrocarbons can escape an accumulation trap by exceeding the spill point at which hydrocarbons will simply spill out of the trap and continue to migrate. Also, the buoyancy forces of the hydrocarbons can exceed the resistant force of the displacement pressure causing the hydrocarbons to migrate through the cap rock and form a hydrocarbon plume above (Schowalter, 1979). Gases can often escape through seals due to their smaller molecules and can be termed 'leaky'.

1.4.4 Primary processes in petroleum systems

Source

As described in the previous section, there are three different types of kerogen, which has a fundamental effect on the source of hydrocarbons and ultimately the oil composition in terms of the type of organic matter, marine or terrestrial (Section 1.4.3).

Maturity

Diagenesis

With increasing burial during diagenesis, the only hydrocarbons are those formed directly from living organisms in addition to the methane produced through methanogens (Killops & Killops, 2005). Due to the continued burial and consequently the reduced permeability, increased overburden and water expulsion, the end products of anaerobic degradation can no longer escape (immature) (Fig. 1.13).

Catagenesis

Catagenesis is when the thermal energy is sufficient enough to break apart the kerogen and cause certain hydrocarbon fragments to be expelled, this occurs as temperature increases with burial depth. With increasing temperature (and therefore maturity) the size of hydrocarbons evolved during catagenesis decreases (Fig. 1.13) (Killops & Killops, 2005), separating hydrocarbon formation into two zones; 1) oil window, and 2) wet gas zone (Fig. 1.13). The main phase of the oil window

(mature) is thought to be limited to ~ 2.5-4.5 km depth and ~100-150 °C (Mackenzie & Quigley, 1988) and is characterised by large productions of low to medium molecular weight liquid hydrocarbons. Gas production occurs down to ~ 230 °C and changes from methane production near the surface to methane plus hydrocarbon gases at depth. The thermal alteration of the kerogen forms hydrocarbon liquids typically $> C_6$ and gaseous hydrocarbons of C_1 - C_4 (C_5 can be both liquid or gas at the surface). Hydrocarbon gases also contain dissolved hydrocarbons, which would normally be liquids and vice versa. Condensate is the term used to describe the expulsion of liquid hydrocarbons from gases at the surface. As catagenesis continues, the production of gases increases to form the wet gas zone (Killops & Killops, 2005).

Metagenesis

At the end of catagenesis the production of methane increases dramatically with increased temperatures until methane is the only hydrocarbon produced (metagenesis). This dry gas zone is called such due to the lack of condensates.

1.4.5 Secondary processes in petroleum systems

There are several processes that occur after petroleum generation which cause the alteration of the hydrocarbons relative to its original bitumen in the source rock. This alteration changes the proportions of aromatic, aliphatic and polar compounds. The major secondary processes that occur are described below;

Migration

As the hydrocarbons migrate through different rock units, a polar surface to the compounds is created by the bound pore water and minerals of the pore walls. The polar constituents as well as the asphaltenes and to a lesser degree the aromatic hydrocarbons are attracted to this polar surface and therefore become concentrated within the interfacial layer and are much harder to expel from the source rock (e.g., Killops & Killops, 2005). This process continues within secondary migration and results in the reservoir oil being depleted in polar and asphaltene components as well as slightly less aromatic hydrocarbons relative to aliphatic hydrocarbons compared to the source rock.

De-asphalting

Asphaltenes are insoluble in light hydrocarbons (C_1 - C_8) which means if a light oil or gas is introduced into the fluid either in the reservoir through multiple charging episodes, oil mixing and/or during migration it can cause the precipitation of the asphaltenes.

Water-washing

Water washing can cause the loss of light hydrocarbons, e.g. toluene, benzene and other aromatics (Palmer, 1993) by removing the more water-soluble polar constituents. Water washing can also be present with biodegradation because active water recharging can provide aerobic bacteria with the oxygen needed. Water washing, however, has a lower effect overall on the chemical and physical properties of oil relative to biodegradation.

Thermal alteration

Depending on the burial depth of the reservoir and the geothermal history, the oil can continue to undergo thermal alteration. At temperatures above 160-200 °C thermal cracking can occur. Thermal cracking is when the thermal energy is sufficient to cause hydrocarbon fragments to break off and be expelled from the kerogen (Killops & Killops, 2005). Continued thermal alteration creates lower molecular weight organic matter and relatively larger aliphatic fractions by transforming non-polar fragments (Killops & Killops, 2005).

Biodegradation

Petroleum biodegradation is primarily an oxidation process resulting in the alteration of crude oil, decreasing the oil quality. Biodegradation is caused by living organisms, mainly aerobic and anaerobic bacteria that can degrade large volumes of oil in a short time relative to geochemical and geological timescales (Connan, 1984; Palmer, 1993; Blanc & Connan, 1994). Increasing biodegradation results in a decrease in gravity, quality, net volume and consequently an increase in viscosity, NSO (nitrogen, sulphur and oxygen) compounds, non-hydrocarbon gases and trace metals. Biodegradation causes aliphatic material to be preferentially metabolized and the biodegradation state of an oil can be determined by the degree of alkane preservation.

1.4.6 Biodegradation

Controls on petroleum biodegradation

For biodegradation to occur, conditions must be suitable for microbial life to thrive. The following conditions must be met;

- 1) Correct microorganisms for degrading oil must be present. It was originally suggested that living organisms could only survive a few meters below the sediment-water interface but now microbe activity has been identified at large depths, below 1000 m (e.g., Parkes & Maxwell, 1993).
- 2) There must be sufficient porosity and permeability within the rock fabric to allow the mobility of the bacteria and the diffusion of nutrients. It has been shown that open fabrics, e.g. coarse grained lithologies show greater biodegradation than closed, fine grained rock fabrics (e.g., Fredrickson et al., 1997; Krumholz, 2000).
- 3) Water must be present to allow access to petroleum, inorganic nutrients and electron acceptors. Hydrocarbons are ideal electron donors but are mostly insoluble in water, the microorganisms have therefore evolved several different mechanisms to access hydrocarbons. Some bacteria utilize hydrocarbons directly at the oil-water contact whilst others, for example, excrete biosurfactants that emulsify hydrocarbons, which can then be diffused across cellular membranes (Peters et al., 2005a).
- 4) Salinity of the formation water must be less than ~100-150 parts per thousand, reservoirs with higher salinity are typically non-biodegraded. The exact effect of salinity on biodegradation is uncertain but limited microorganisms can survive at higher salinities e.g. halophilic microorganisms within carbonate and evaporate source/reservoir rocks (Kirkland & Evans, 1981; Peters et al., 2005a).
- 5) Reservoir temperatures generally less than ~ 80 °C are needed to support life, these temperatures typically correspond to depths < 2000 m using typical geothermal gradients. Microbial degradation is optimal at the surface and near-surface temperatures. Thermophilic bacteria can grow at significantly higher temperatures (up to ~100 °C), however, the lower limit of 60-80 °C is suitable for the growth and survival of many mesophilic bacteria

(references within Peters et al., 2005a). Subsided reservoirs can be at much greater depths than when oil was originally charged at < 80 °C where it may be possible for biodegradation to occur before reservoir sterilization at greater depths.

- 6) H₂S is a by-product of bacterial sulphate reduction and for anaerobic sulphate reducers the H₂S level must be less than ~ 5% (a few can be > 5%) and non-existent for aerobic microbes (Peters et al., 2005a). Other toxic chemicals mostly inhibit microbe activity.

The removal of certain compounds within hydrocarbons due to differential resistance can be indicative of the level of biodegradation. Wenger *et al.* (2001) (Table 1.3) produced a table of biomarkers and compounds to assign a numerical value to the biodegradation state. Specific compounds are systematically removed starting with *n*-alkanes and others are formed e.g. 25-norhopanes (Fig. 1.17). Of the aromatic species, the light aromatic compounds are the first to be removed (e.g., Palmer, 1993). With the use of chromatograms from GC-MS analysis (described in Section 2.2) biodegradation can be distinguished because as the major compounds are diminished, the baseline of the chromatograms reflect a more prominent unresolved complex mixture (UCM) (Fig. 1.17) made up of bioresistant compounds. Biomarkers also allow the identification of biodegradation (Section 1.4.7.3).

Table 1.3 Biomarker biodegradation numerical scale from Wenger *et al.* (2001).

Biomarker Biodegradation Scale	L M H			Severe							
	0	1	2	3	4	5	6	7	8	9	10
<i>n</i> -alkanes		→									
Alkylcyclohexanes			→								
Isoprenoids				→							
C ₁₄ -C ₁₆ bicyclic terpanes					→ ?						
Hopanes (25-norhopanes formed)						→					
Steranes						→					
25-norhopanes or hopanes							→				
Diasteranes								→			
C ₂₆ -C ₂₉ aromatic steroids									→		
Porphyrins										→	

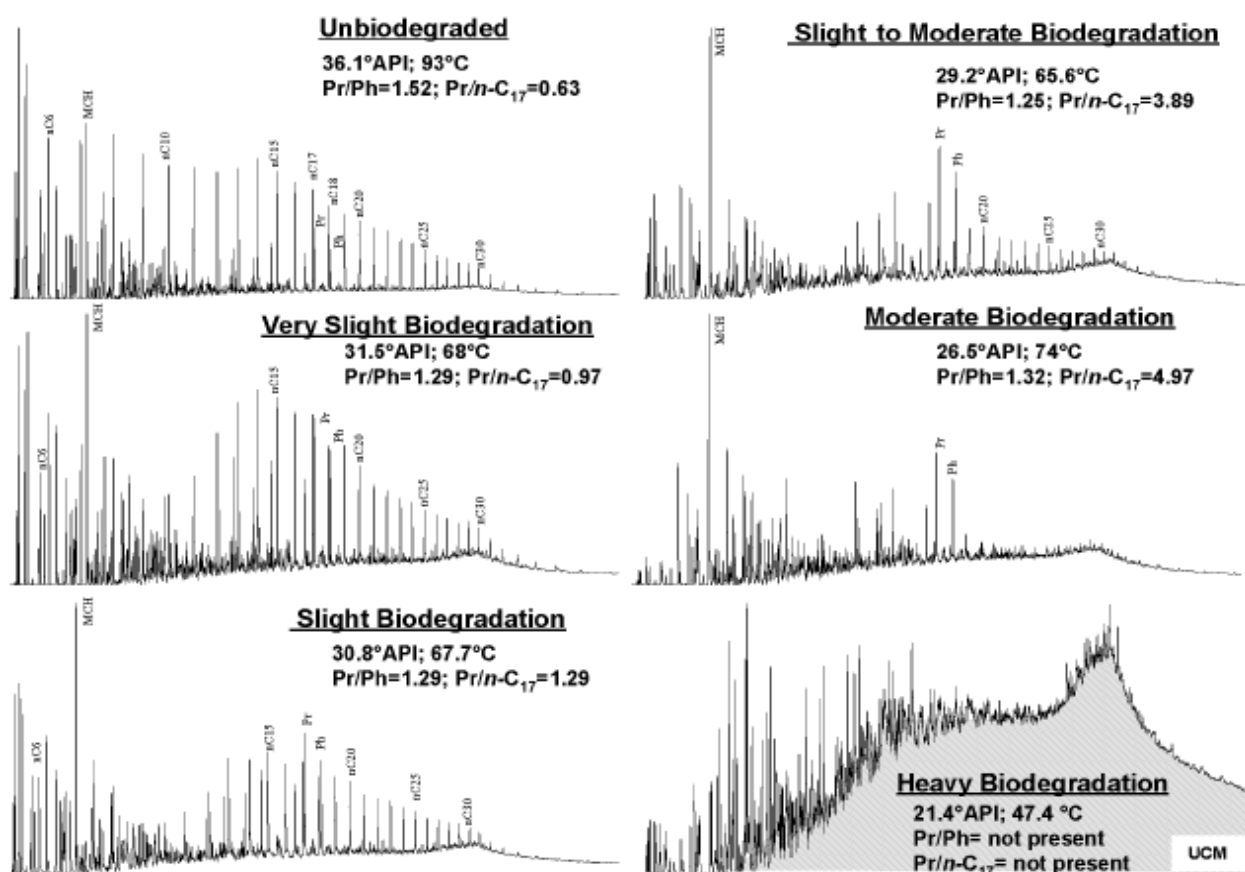


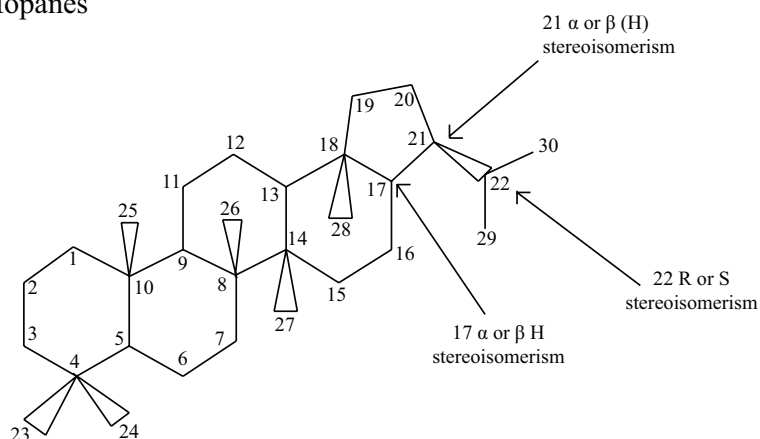
Figure 1.17. Gas chromatograms showing the variations in biodegradation from a selection of crude oils from Africa. From Wenger & Isaksen (2002).

1.4.7 Biomarkers

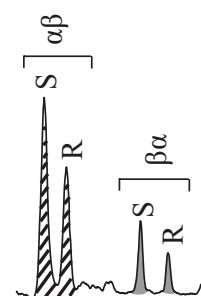
Certain organic compounds can be related to the parent organism and are termed biological markers or “biomarkers”. The biomarkers can help rapidly distinguish between source, maturity and biodegradation differences in oils. Common biomarkers are typically split into three groups; 1) *n*-alkanes, 2) hopanes and 3) steranes. A description of these compounds and the major biomarkers are described below;

Acyclic alkanes are split into *n*-alkanes (normal alkanes) which are compounds with linear carbon atoms and secondly isoalkanes (branched alkanes) which are non-linear (Peters et al., 2005c). Both sets of compounds are part of a series of saturated hydrocarbons with the formula C_nH_{2n+2} .

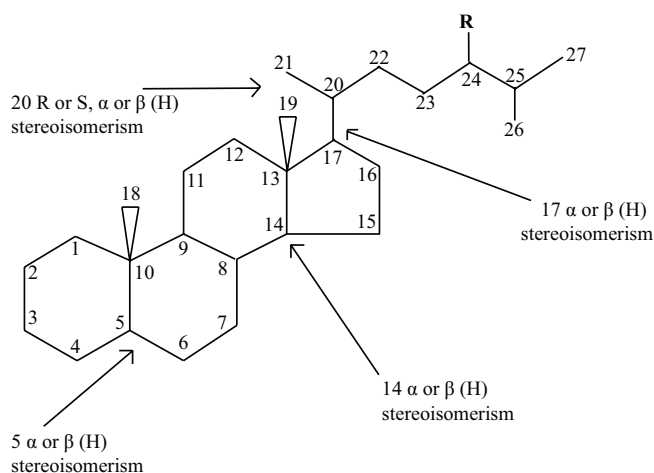
(a) Hopanes



Elution order for m/z 191



(b) Steranes



Elution order for m/z 217

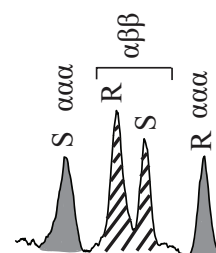


Figure 1.18. The general structure for (a) hopanes and (b) steranes. Elution orders of isomerization for identification purposes in chromatograms are also included. Modified from Peters *et al.* (2005c).

Hopanes originate mainly from compounds within the cell membrane of bacteria and can be used as indicators of source rocks in petroleum environments. Hopanes are characterised by three stereoisomeric series, $17\alpha, 21\beta(H)$, $17\beta, 21\beta(H)$ and $17\beta, 21\alpha(H)$ (Fig. 1.18). R, S, α and β are simply used to describe asymmetrical configurations at ring carbons and are used to determine elution order and compound identification within chromatograms. The $\alpha\beta$ series within C_{27} - C_{35} are indicative of petroleum because they are more thermodynamically stable than the $\beta\beta$ and $\beta\alpha$ series (Peters *et al.*, 2005c). The $\beta\beta$ series is thermally unstable during early catagenesis and therefore is not found within petroleum but is transformed into the $\alpha\beta$ and $\beta\alpha$ during diagenesis and catagenesis (Peters *et al.*, 2005c). The $\beta\alpha$ series are referred to as moretanes. The $22R$ natural configuration found in bacteriohopaneterol converts to a mixture of $22R$ and $22S$ (Fig. 1.18). Common hopanes to

identify are C₂₇ 17 α -trisnorhopane (Tm or 17 α -22,29,30-trisnorhopane), C₂₇ 18 α -trisnorhopane (Ts or 18 α -22,29,30-trisnorhopane) and the hopane series between C₂₉-C₃₅ (See the following sections).

Steranes are derived from steroid molecules that reside in both algae and higher plants and specifically sterols in eukaryotic organisms (Peters et al., 2005c). Isomerisation of the 5 α ,14 α ,17 α (H) 20R configuration ($\alpha\alpha\alpha$ R) results in an increase in the other stereoisomers ($\alpha\alpha\alpha$ R, $\alpha\alpha\alpha$ S, $\alpha\beta\beta$ R, $\alpha\beta\beta$ S) until the equilibrium ratio of 1:1:3:3 is achieved (Peters et al., 2005c) (Fig. 1.18). Steranes are useful for biomarker interpretation because regular steranes can be used to determine source material and diasteranes can be used to infer lithology and maturity variations (Waples & Machihara, 1990).

To identify these compounds, chromatograms produced by GC-MS analysis (Chapter 2) are used. Total Ion Current (TIC) chromatograms show the whole range of compounds selected from a given sample and hold a lot of information. To identify specific compounds, particular m/z (mass-to-charge ratio) ions can be selected which isolate given compounds. Hopanes are easily identifiable on m/z 191, steranes on m/z 217 and n -alkanes on m/z 57.

1.4.7.1 Source biomarkers

Source biomarkers are chemical biomarkers used to determine the type of kerogen the hydrocarbons are derived from. Environment can also be investigated in terms of terrestrial vs. marine and anoxic vs. oxic conditions.

n-Alkanes and n-alkane ratios

The n -alkane distribution can also be used to infer source material and therefore kerogen type, because lower molecular weight (<C₂₁) n -alkanes are derived from bacteria and algae (Wakeham, 1990), but high molecular weight (>C₂₂) n -alkanes generally originate from higher plants (Huang et al., 1999). Evidence of a great odd preference (odd numbered carbons) for n -C₂₉, n -C₃₁ and n -C₃₃ alkanes is also associated with higher plant components in immature organic assemblages. In addition, the ratio of certain n -alkanes can be used as a very crude indicator of source input. The terrigenous/aquatic ratio (TAR= $(nC_{27}+nC_{29}+nC_{31})/(nC_{15}+nC_{17}+nC_{19})$) (Peters et al., 2005d) must be used with caution, because it is also sensitive to secondary processes such as thermal maturation and biodegradation as well as an inherent bias due to land plant organic matter containing more n -alkanes than aquatic organic matter.

Pristane/phytane

Pristane (C₁₉ Pr) and phytane (C₂₀ Ph) are mainly found within the phytol side chain of chlorophyll and can be indicative of redox conditions of the source rock but must be used with caution due to other contributing factors such as thermal maturity and source input. Depending on the conditions experienced, the phytol side chain can cleave producing phytane (suboxic-anoxic) or the complete conversion of phytol to pristane can occur (oxic) (Peters et al., 2005d). The ratio of pristane: phytane can help infer the oxygenation of the environment with higher ratios indicative of oxic conditions (>1). Low ratios (<1) are thought to represent source material deposited in an anoxic environment (Didyk et al., 1978; Ten Haven et al., 1987). Pristane and phytane ratios can be complicated however by contributions other than chlorophyll (Ten Haven et al., 1987).

Ts/Ts+Tm

Dependent on both source and maturity (Moldowan et al., 1986), the ratio of Ts and Tm can be a useful source indicator (Table 1.4). This biomarker is based on the relative stability of C₂₇ hopanes; C₂₇ 17 α -trisnorhopane (Tm) is less stable compared to C₂₇ 18 α -trisnorhopane (Ts) during catagenesis. Additionally the Ts/Ts+Tm is sensitive to clay-catalysed reactions e.g. very low ratios within carbonate source rocks compared to shales (e.g., McKirdy et al., 1983; McKirdy et al., 1984; Price et al., 1987). Inaccurate Ts/Ts+Tm ratios are common due to the co-elution of Tm and Ts with the presence of tricyclic or tetracyclic terpanes on a *m/z* 191. Ts/Ts+Tm ratios are low within carbonate rocks and high in clays (McKirdy et al., 1983), however, the ratio is also indicative of anoxic environments when high (Fan et al., 1987; Mello et al., 1987; Farrimond et al., 1989).

C₃₀ sterane index

The C₃₀ sterane index (C₃₀/(C₂₇-C₃₀)) is very specific to marine organic matter input. The presence of C₃₀ 4-desmethylsteranes within crude oil is one of the most powerful tools for distinguishing between marine and terrestrial organic matter. The identification of C₃₀ steranes relative to C₂₇-C₃₀ steranes can give ratios of > 4 (marine) or < 4 (terrestrial) (Table 1.4) (Moldowan et al., 1985).

C₂₇-C₂₈-C₂₉ steranes

A ternary plot of the C₂₇, C₂₈ and C₂₉ sterol homologs are interpreted to show variations in ecosystems. Studies (e.g., Mackenzie et al., 1983; Moldowan et al., 1985) have shown there is

extensive overlap in known source rock and crude oils resulting in caution when used. However, the sterane ternary plot is useful to identify differences between oils and/or source rocks distinguishing groups of oils from different organic facies of the same source rock or oils from different source rocks (Peters et al., 2005d). Ratios of these steranes are also used to infer source input and therefore environment. $C_{27}/(C_{27}+C_{28}+C_{29})$ sterane ratio is > 0.7 for planktonic, open marine sources whereas $C_{29}/(C_{27}+C_{28}+C_{29})$ sterane ratio is > 0.7 for land plant, terrestrial sources (Huang & Meinschein, 1979) (Table 1.4).

1.4.7.2 Maturity Biomarkers

Some biomarkers are affected by thermal maturity of the oils and therefore can reveal the level of thermal maturity attained. Some of the biomarkers work up to the oil window (i.e. in immature rocks) whereas others work into the oil window (i.e. in mature rocks). Immature rocks have a fraction of solvent soluble compounds that are inherited from the biological source organisms rather than generated from kerogen which respond to heat in predictable ways. In the oil window kerogen degradation products, i.e. oil, flood the natural solvent soluble compounds.

$22S/(22S+22R)$

Homohopane isomerization at C-22 (See section 1.4.7) in the C_{31} - C_{35} range is used to identify immature to early oil generation. The proportions of 22R and 22S can be calculated from any or all of these compounds. The ratio varies between 0 to ~ 0.6 (Table 1.4), but for ratios between 0.50-0.54 the oil has just entered the oil window compared to ratios of 0.57-0.62, which means the oil generation has been reached (Ensminger et al., 1977; Seifert & Moldowan, 1980).

Moretanes ($\beta\alpha$)/*hopanes* ($\alpha\beta$)

The $\beta\alpha/\alpha\beta$ ratios are used to identify immature to early oil generation maturities and are based on the thermally less stable $17\beta,21\alpha(H)$ moretanes relative to the more stable $17\alpha,21\beta(H)$ hopanes. The C_{29} and C_{30} moretanes decrease in abundance relative to their corresponding hopanes with thermal maturity from ~ 0.8 (immature) to < 0.15 (mature) (Table 1.4) (Mackenzie et al., 1980; Seifert & Moldowan, 1980). Additional studies suggest that this ratio can also depend on environment deposition or source input (e.g., Isaksen & Bohacs, 1995).

$Ts/Ts+Tm$

Dependent on both source (described above) and maturity (Moldowan et al., 1986), it can be a useful maturity indicator but only when evaluating oils from a common source of consistent organic facies. This ratio can help identify maturity differences because ratios between 0-1 represent immature to end of oil window respectively (Table 1.4) (Seifert & Moldowan, 1980).

$20S/(20S+20R)$

The C_{29} $5\alpha,14\alpha,17\alpha(H)$ sterane shows isomerization at C-20, which causes the ratio of $20S/(20S+20R)$ to increase from 0 to ~ 0.55 with increasing thermal maturity. The isomerization ratios can be used for C_{27} , C_{28} , C_{29} but are mostly identified in C_{29} due to easier identification using m/z 217 (Seifert & Moldowan, 1980) (Table 1.4). Caution must be taken using this ratio due to coelution as well as other factors such as biodegradation, weathering and facies which can affect sterane isomerization (e.g., McKirdy et al., 1983; Moldowan et al., 1986).

$C_{29}Ts/(C_{29} \text{ hopane} + C_{29}Ts)$

The 18α -30-Norneohopane ($C_{29}Ts$) abundance relative to the 17α -hopane has been reported to be related to thermal maturity. $C_{29}Ts$ elutes immediately after C_{29} 17α -hopane using m/z 191 and is correspondingly more stable than the 17α -30-norhopane to an extent which is comparable with Ts/Tm ratios. Therefore a mature oil will have a higher $C_{29}Ts/(C_{29} \text{ hopane} + C_{29}Ts)$ ratio (Peters et al., 2005b).

1.4.7.3 Biodegradation biomarkers

Certain biomarker ratios are altered by the effect of biodegradation on the oil. The preferential removal of certain compounds relative to others can allow for the biodegradation state of the oil to be determined. Biodegradation research (Wenger et al., 2001; Wenger & Isaksen, 2002) shows aliphatic hydrocarbons are preferentially biodegraded and lighter components such as the aromatic hydrocarbons can be lost through water washing. Therefore differences in bulk composition in terms of aliphatic and polar components are most likely to be the result of these two processes. The absence of *n*-alkanes also suggests high levels of biodegradation (Table 1.3).

Pr/n-C₁₇ and Ph/n-C₁₈

Ratios of pristane: normal C₁₇-alkane (Pr/n-C₁₇) and phytane: normal C₁₈-alkane (Ph/n-C₁₈) can also be used as an indicator of biodegradation as well as source environment (Lijmbach, 1975). The isoprenoidal hydrocarbons pristane and phytane are more resistant to degradation than normal alkanes (*n*-C₁₇ and *n*-C₁₈) resulting in an increase in the relative ratios (Pr/n-C₁₇ and Ph/n-C₁₈) when the oils are biodegraded.

Sterane/diasteranes

Sterane biomarkers also display variable responses to biodegradation with regular steranes being more susceptible to degradation compared to diasteranes. The ratio of steranes/diasteranes therefore decreases with increasing levels of biodegradation (Peters et al., 2005a). This biomarker should be used with caution however, because discriminating between source effects and subsequent biodegradation processes is difficult.

UCM/C₂₉

Biodegradation accounts for the enhancement of Unresolved Complex Mixtures (UCM) by the preferential removal of *n*-alkanes over branched and cyclic forms (Wenger et al., 2001) (See Section 1.4.6). An unconventional biodegradational parameter to use is the ratio of UCM height and the *n*-alkane (C₂₉) height (above the UCM) (Ross et al., 2010). Increased biodegradation causes higher ratios due to the increasing UCM and decreasing *n*-alkane content.

Table 1.4 Summary of biomarkers commonly used to identify maturity and source characteristics of oils.

Biomarker	<i>m/z</i>	Interpretation	Reference
<i>Hopane source ratios</i>			
Ts/Tm	191	Low in carbonate rocks. High in clay rocks.	McKirdy <i>et al.</i> (1983)
Ts/Tm	191	High in hypersaline environments	Fan Pu <i>et al.</i> (1987)
<i>Hopane maturity ratios</i>			
C ₂₇ hopanes Ts/(Ts+Tm)	191	0 (immature) 1 (end of oil generation, start of dry gas window)	Seifert & Moldowan (1980)
Moretane/hopane	191	Immature (0.8), mature <0.15 to a min. of 0.05	Seifert & Moldowan (1980)
C ₃₁ or C ₃₂ 22S/(22S+22R)	191	Immature (0) to oil window (0.6)	Ensminger <i>et al.</i> (1977)
<i>Sterane source ratios</i>			
C ₃₀ /(C ₂₇ -C ₃₀)	217	<4 = terrestrial, >4 = marine	Moldowan <i>et al.</i> (1985)
C ₂₇ /(C ₂₇ +C ₂₈ +C ₂₉) steranes	217	Plankton, open marine (>0.7)	Huang & Meinshein (1979)
C ₂₉ /(C ₂₇ +C ₂₈ +C ₂₉) steranes	217	Land plants, terrestrial (>0.7)	Huang & Meinshein (1979)
<i>Sterane maturity ratios</i>			
20S/(20S+20R)	217	Immature (0), oil window (0.40), start of wet gas window (0.55)	Seifert & Moldowan (1980)

Chapter 2

Sampling and methodology

Introduction

This PhD concentrates on two subsets of samples, firstly; oil impregnated sedimentary units have been investigated from four locations worldwide, (1) UK, (2) Canada, (3) Colombia and (4) Indonesia (Section 2.1.1). These samples were either collected during fieldwork or donated to the study. Secondly; well cores from the North Sea, UK were examined (Section 2.1.2). The cores originated from above the reservoirs of both dry and oil producing wells. A full description of the samples and geological settings is given below. The multidisciplinary experimentation conducted on all of the samples, geochemical and magnetic investigations are discussed in Section 2.2.

2.1 Sampling

2.1.1 Oil impregnated sedimentary units

Oil saturated sedimentary samples were collected worldwide for this study and are described in detail below. The UK samples were collected during three fieldwork trips in 2010, 2011 and 2012. All the other samples were donated to the study through the University of Alberta, Canada, the Universidad Simon Bolivar, Venezuela and the Buton Asphalt Indonesia Company.

2.1.1.1 UK

Samples were hand selected at the Wessex Basin, Dorset, UK, where some of Europe's best examples of oil stained reservoirs have been uplifted along the coast and are easily accessible.

Wessex Basin, UK

Fieldwork was conducted at the Wessex Basin, Dorset, UK; (Fig. 2.1, Table 2.1) (Selley, 1992) where samples were collected from oil stained beds exposed at Osmington Mills, Lulworth Cove and Mupe Bay (Fig. 2.1). The Wessex Basin is characterised by the presence of an anticlinal feature at the surface and is part of a system of linked Mesozoic basins trending across Southern England and Northern France (Underhill & Stoneley, 1998). The Variscan orogeny is responsible for the east-west structural trend reflecting the basement structure (Lake & Karner, 1987) and inversion of the basin depocentres during the Late Tertiary resulted in significant uplift and complex structuring (Chadwick, 1993; Underhill & Paterson, 1998). Improved technologies allowed the exploration of inverted anticlines and extensional structures to the north to be targeted leading to the discovery of

the Wytch Farm, Kimmeridge and Wareham oil fields. The exposed oil beds at the coast occur in northerly dipping beds, directly south of structural faults and have variable biodegradation levels (see Chapter 3). An active oil seep was also collected at Bran Point, at the end of the sandstone exposure at Osmington Mills.

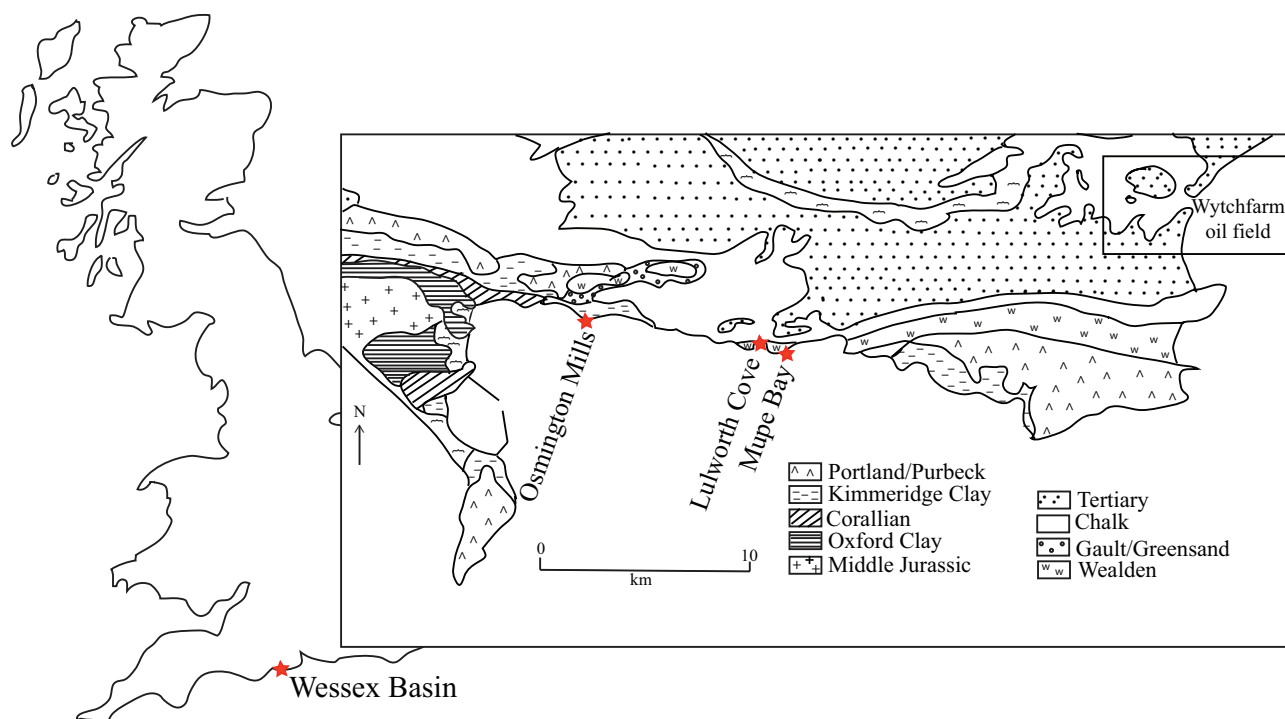
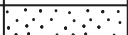
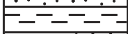
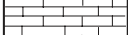
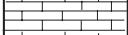
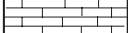
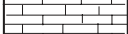
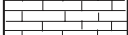
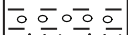
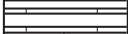
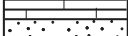
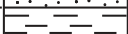
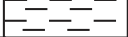
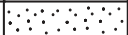
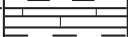
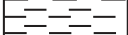
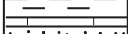
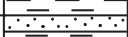
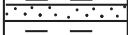
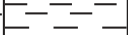
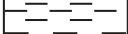
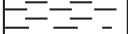
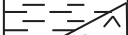
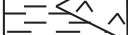
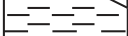


Figure 2.1. Map of the Wessex Basin, Dorset, UK. Exposure of several oil stained beds along the coast with sample locations marked on. Geological map modified from Stoneley & Selley (1986).

The Wessex Basin is characterised by three potential source rocks, organic rich black shales of the Jurassic; the Liassic shales (Blue Lias), Oxford Clay (Callovian-Oxfordian) and the Kimmeridge Clay (Fig. 2.2) (Stoneley & Selley, 1986). All three sources have organic matter dominated by algal input and minor woody material, and are slightly immature where these beds outcrop (Watson et al., 2000). The principal source kitchen is thought to be to the South in the Portland-Wight Basin (Buchanan, 1998) and formed prior to inversion during the Late Cretaceous and Oligocene-Miocene when the area was at great burial depths.

The main reservoirs are Triassic and Jurassic in age, resulting from vertical and lateral migration. There are several potential sandstone reservoirs in the Wessex Basin; e.g. the Sherwood sandstone (Triassic); Bencliff Grit (Jurassic), Portland sandstone (Jurassic) and Wealden (Cretaceous) (Fig. 2.2) (Stoneley & Selley, 1986). In most cases, the traps are structural due to faulting, but the Kimmeridge Clay has also been shown to act as a seal as well as a source rock (See Section 2.1.2).

		AGE	LITHOLOGY	FORMATION			
TERTIARY	EOCENE	LOWER	  	Bagshot Beds London Clay Reading Beds			
CRETACEOUS	UPPER	Senonian		Chalk			
		Turonian					
		Cenomanian		Upper Greensand			
		Albian		Gault			
	LOWER	Aptian		Lower Greensand			
		Neocomian		Wealden			
JURASSIC	UPPER	Portlandian	  	Purbeck Portland Limestone Portland Sand			
		Kimmeridgian		Kimmeridge Clay			
		Oxfordian		Corallian			
		MIDDLE	Callovian		Oxford Clay		
	Bathonian			Forest Marble			
	Bajocian			Fuller's Earth			
	Aalenian			Inferior Oolite			
	LOWER (LIASSIC)	Toarcian	  	Bridport Sand Down Cliff Clay Thorncombe Sands			
		Pliensbachian		Down Cliff Sands			
		Sinemurian		Lias			
		Hettangian					
	TRIASSIC			  	Rhaetic Mercia Mudstone (local evaporites)		
				Sherwood sandstone			
				Budleigh Salterton			
  				Red Marls Exmouth Beds Dawlish Sands			
PERMIAN				Exeter Traps			
DEVONIAN-CARBONIFEROUS			 	Hercynian basement Dartmoor Granite			
	Sandstone		Conglomerate		Limestone		Mudstone/Clay

 Sandstone
  Conglomerate
  Limestone
  Mudstone/Clay

Figure 2.2. Generalised stratigraphic column modified from Underhill & Stoneley (1998) for the Wessex Basin.

A summary of all the samples collected at the Wessex Basin, UK are shown in Table 2.1 and discussed in detail below.

Table 2.1 Summary of samples collected at the Wessex Basin with descriptions.

Sample	Age	Geological unit	Field observations	Description	Grid Reference
OS1	Jurassic	Bencliff Grit, Corallian Group	Not discoloured	Unstained	SY 741915
OS2	Jurassic	Bencliff Grit, Corallian Group	Youngest (top) – unit 1	Lightly stained	SY 739826
OS3	Jurassic	Bencliff Grit, Corallian Group	Oldest (bottom) – unit 1	Heavily stained	SY 739826
OS4	Jurassic	Bencliff Grit, Corallian Group	High oil content patch – unit 1	Very heavily stained	SY 739241
OS5	Jurassic	Bencliff Grit, Corallian Group	Oldest (top) – unit 2	Lightly stained	SY 740165
OS6	Jurassic	Bencliff Grit, Corallian Group	Oldest (bottom) – unit 2	Heavily stained	SY 740165
MBC	Cretaceous	Wealden Group	Heavily biodegraded clast	Very heavily stained	SY 843798
MBM	Cretaceous	Wealden Group	Heavily biodegraded matrix	Heavily stained	SY 843798
LC	Cretaceous	Wealden Group	Large oil stained area	Heavily stained	SY 824799
OS oil	Jurassic	Bencliff Grit, Corallian Group	Low tide- sheen on water	Free flowing oil	SY 743814

Osmington Mills

Six samples were collected from Osmington Mills (OS1-OS6) (Fig. 2.1, Table 2.1). Osmington Mills was selected because of its variable degree of oil-stained sands within the two main cross-bedded sandstones separated by a shale bed within the Bencliff Grit of the Corallian Group (Oxfordian) (Fig. 2.2) (Selley, 1992; Bigge & Farrimond, 1998; Watson et al., 2000). At Osmington Mills there is a 60 m exposure of the Corallian Group (Oxfordian-Jurassic), which consists of a variable series of sandstones, limestones and shales (Bigge & Farrimond, 1998; Watson et al., 2000). The Bencliff Grit, a member of the Redcliff Formation is a 5-6 m exposure (Fig. 2.3) comprising of 80-90 % cross-bedded oil stained sandstones. These units represent well-sorted and transported deposits.

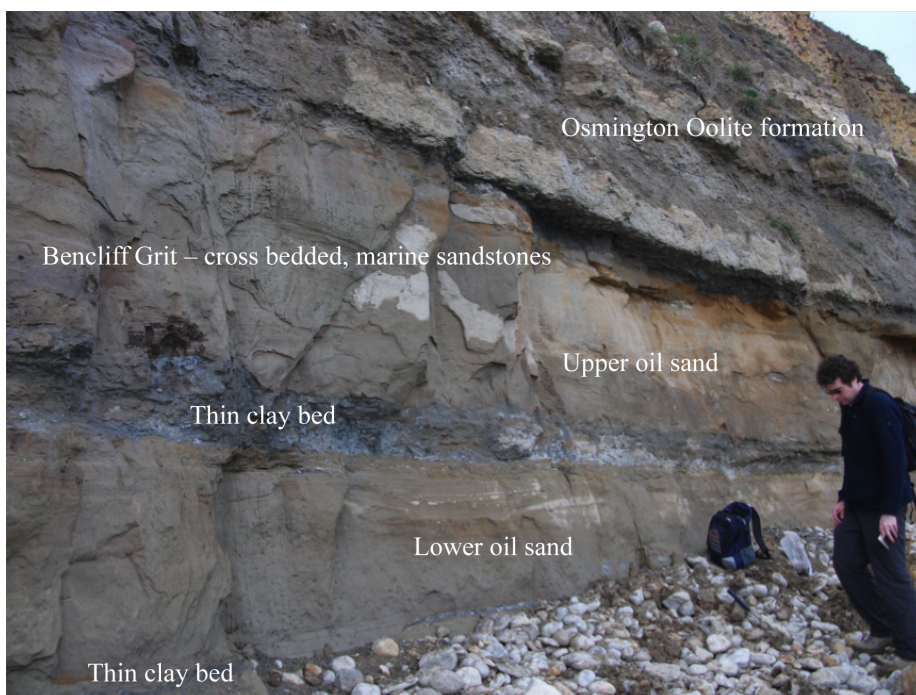


Figure 2.3. Osmington Mills cliff face with stratigraphic units identified. Samples OS1-OS6.

An active oil seep was also sampled at low tide from Bran point (Fig. 2.4) at the edge of the Osmington Mills exposure (Watson et al., 2000). The seep is also from the Bencliff Grit at the point it hits the seal. The exposure can only be identified at low tide (Lees & Cox, 1937).



Figure 2.4. Bran Point – active oil seep (Sample OS oil).

Mupe Bay

Two sets of samples were also collected from the Wealden Group at Mupe Bay (Neocomian) (Table 2.1) (Selley & Stoneley, 1987; Cornford et al., 1988). The oil stained sandstone unit at Mupe Bay is rather unique because it exposes a moderately oil stained sandstone matrix (MBM) with heavily oil stained sandstone clasts (MBC) (Fig. 2.5) with some authors proposing that this represents two phases of oil staining (Bigge & Farrimond, 1998; Watson et al., 2000).



Figure 2.5. Mupe Bay, Wealden age sandstone conglomerate bed. Samples MBM and MBC.

It is suggested that the original sandstone was deposited in the Early Wealden and redeposited as oil-cemented clasts in a fluvial Wealden sandstone which itself was later stained (Wimbledon et al., 1996; Hesselbo, 1998). The Wealden unit is a heavily oil stained fluvial deposit and not well sorted. The theory has been backed up by identified maturity differences (Cornford et al., 1988), however, these results are controversial because Miles *et al.* (1993) and Parfitt and Farrimond (1998) attributed the difference to differential biodegradation. This intriguing mystery is explained and investigated in Chapter 4. Both the matrix and the clasts were sampled multiple times (Fig. 2.5). Mupe Bay oils are already known to be more heavily biodegraded and have a lower maturity (extent of hydrocarbon generation) than Osmington Mills (Bigge & Farrimond, 1998).

Lulworth Cove/Stair Hole

One sample was collected from a slope at Stair Hole where a large outcrop of oil stained sandstone from the Wealden Group sits (Sephton, 1992) (Fig. 2.6, Table 2.1).



Figure 2.6. Oil stained Wealden sandstones at Stair hole/Lulworth Cove. Sample LC.

This sandstone in principle is the same as exposed at Mupe Bay with differences attributed to biodegradation contrasts. The source rock for this area is proposed as the organic rich black shales in the Lower Lias (Jurassic) (Fig. 2.2). The other potential source rocks, the Oxford Clay and Kimmeridge Clay are very immature in this area.

2.1.1.2 Colombia

The Colombian Andes are characterised by three major orogenic belts: the Western Cordillera, the Central Cordillera and the Eastern Cordillera, formed as a result of interaction between the South American, Caribbean and Nazca plates since the Late Cretaceous (Bayona et al., 2008b). The Eastern Cordillera is interpreted as a Cretaceous extensional basin, which has experienced a complex tectonic history including two phases of stretching, inversion during the Cenozoic and polyphase tectonics since Precambrian time (Dengo & Coy, 1993; Cooper et al., 1995a; Cooper et al., 1995b; Roeder & Chamberlain, 1995; Mora et al., 2006; Bayona et al., 2008a). The Eastern Cordillera and its surroundings have been extensively geochemically studied (Palmer & Russel, 1988; Ramón & Dzou, 1999; Ramón et al., 2001; Gonçalves et al., 2002; Sarmiento & Rangel, 2004; Sánchez & Permanyer, 2006) due to the presence of Upper Cretaceous source rocks in the

region. This study concentrates on the little deformed eastern flank of the Eastern Cordillera called the Llanos Foreland Basin (Fig. 2.7). The Llanos Basin is located mainly within Colombia spanning approximately 200,000 km² into Venezuela. Stratigraphically, the Llanos Basin consists of a crystalline basement with Ordovician to Holocene sediments, predominantly siliclastics, however the Foreland Basin is characterised by numerous lithological contrasts due to the broad complex geological system (Fig. 2.8).

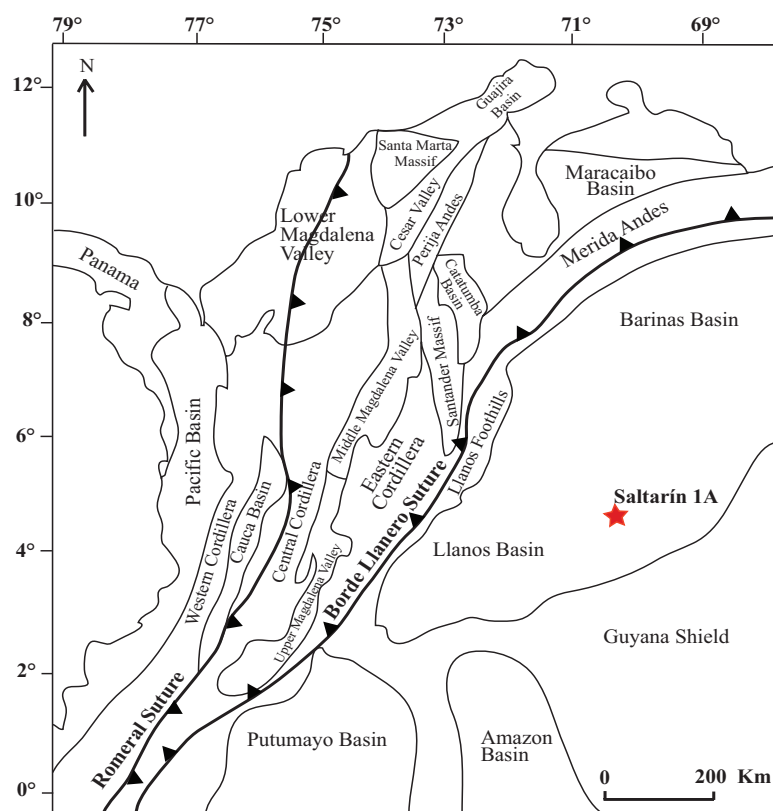
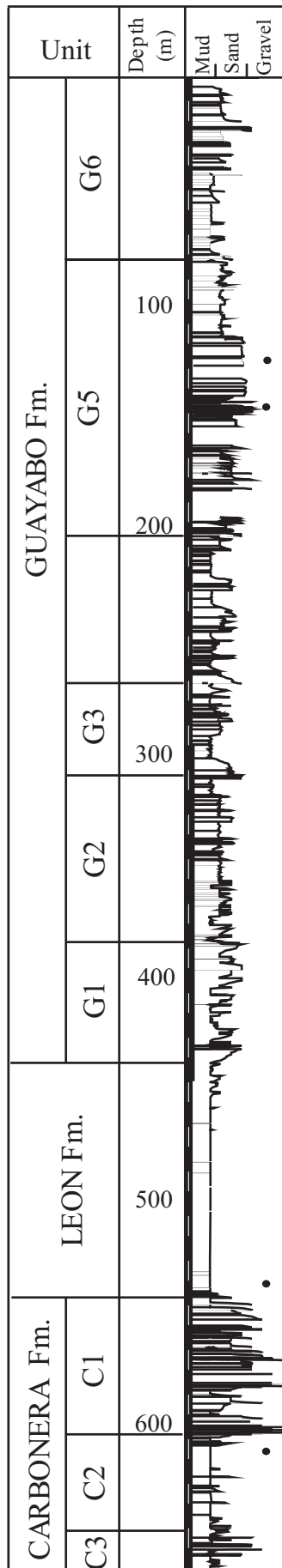


Figure 2.7. Geological map for the Colombian Andes, Colombia. The location of the Saltarín 1A well in the Llanos Foreland Basin is highlighted. Modified from Copper *et al.* (1995b).

Samples were taken from the vertical Saltarín 1A well (Fig. 2.7). The major lithologies and interpretation of their corresponding sedimentary conditions within the well have been determined (Bayona *et al.*, 2008b) (Fig. 2.8). Samples were taken down to 620 m covering the Carbonera, León and the Guayabo Formations (Table 2.2, Fig. 2.8). The Carbonera Formation (Oligocene-Early Miocene) is the lowermost section of the cored well and consists of eight units dominated by sandstones and mudstones, which represent fluvial to lacustrine systems. Sample C616.48 is from the C2 interval (Fig. 2.8), which is a mudstone interval. Hydrocarbon impregnations have been confirmed within the sand dominated units in the Carbonera. Sample C541.75 was taken from the base of the León Formation (Early-Middle Miocene), which is a predominantly muddy lacustrine sequence topped by the Guayabo Formation (Late Miocene-Pliocene), which consists of relatively uniform units of mudstone and sandstone (samples C127.40 and C147.25) (Fig. 2.8).



The organic-rich sediments of the La Luna Formation (Upper Cretaceous) and its lateral equivalents have been allocated as the major source rock for many oil plays within Colombia and neighbouring regions (Villamil, 2003). The La Luna Formation is an algal, marine carbonate rich source (Zumberge, 1984). Further source rocks have been proposed as the Upper Cretaceous Gachetá and Une Formations due to the identification of different oil families within the area (Palmer & Russel, 1988; Rangel et al., 1996). Hydrocarbons within this region have also shown the possible contribution of a Tertiary source (Dzou et al., 1999; Cortes et al., 2010).

The Llanos Foreland Basin appears to be a complex hydrocarbon region with large amounts of mixing of different oils in an intricate geological setting owing to complicated basin and trap tectonics. Reservoir oil is subdivided into a number of different oil families corresponding to different sources, mixing or levels of biodegradation (Palmer & Russel, 1988; Rangel et al., 1996; Cortes et al., 2010). Chemical variation brought about by long distance lateral migration has been discounted as an important mechanism (Ramón & Dzou, 1999).

Figure 2.8. Generalised stratigraphic column for the Llanos Foreland Basin, Colombia. The samples are highlighted. Modified from Bayona *et al.* (2008b).

2.1.1.3 Canada

The large oil sands deposited over central Canada are described as unconventional oil sands because of the large quantity of these exposures as well as API differences (8-10° in oil sands, 25-40° in conventional crudes). The area of interest in this study extends from the large Athabasca oil field in northeast Alberta down to Plover Lake in the Southwest of Saskatchewan (Fig. 2.9). The general geological history for the area consists of large regional unconformities separating the Lower Cretaceous from the underlying Devonian-Mississippian and overlying Upper Cretaceous units.

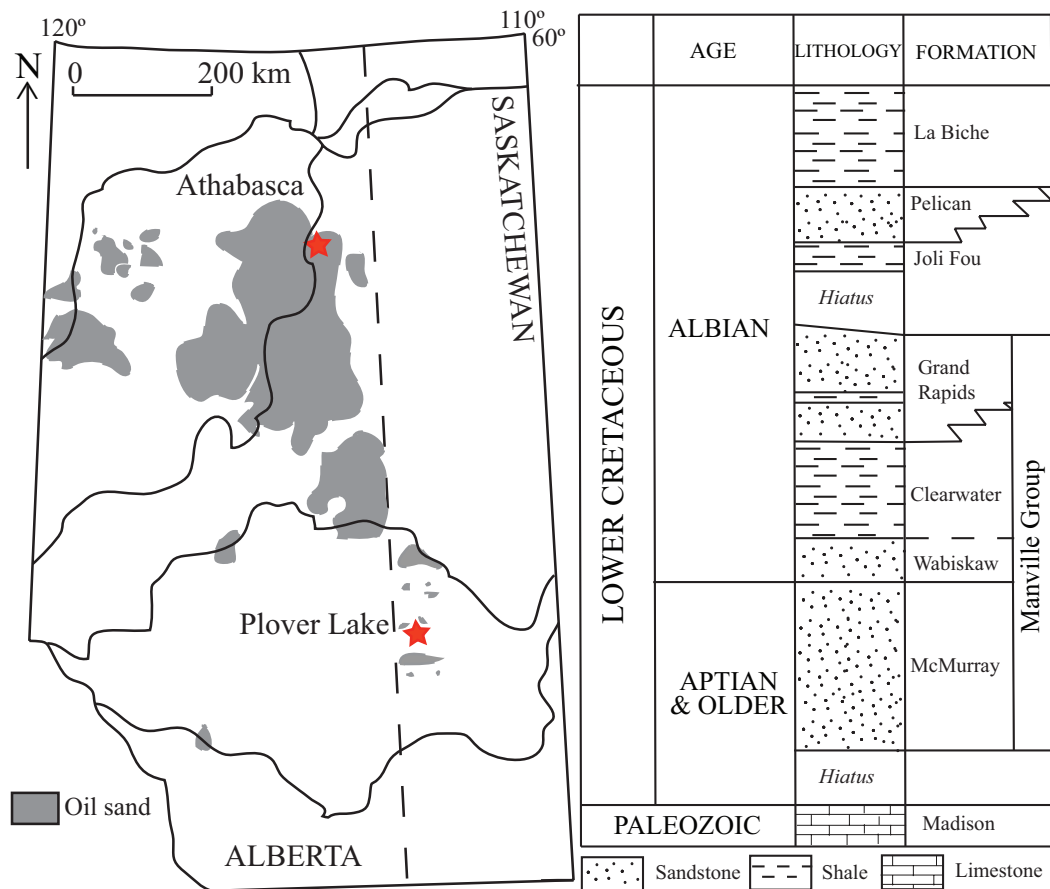


Figure 2.9. Geological map modified from Obermajer *et al.* (2004) and stratigraphic sequence modified from Mossop (1980).

The oil sands mainly reside in the Cretaceous Mannville reservoirs but some are found in the Mississippian Bakken reservoir (underlying the Madison Formation) to the South (Fig. 2.9). The Mannville succession comprises of clastic, deltaic and fluvial deposits and the petroleum accumulation is primarily controlled by facies variations (Hetzel, 1936; Wiryosujono & Hainim, 1975).

The source rock over the whole area is controversial, however, it is proposed that the source rocks are the Exshaw Formation and/or the Bakken Formation (Obermajer et al., 2004). Whether these units are the source rocks or not, it is generally agreed that the oils are mature marine oils which have been biodegraded and most probably charged from pre-Cretaceous source rocks (Brooks et al., 1988; Riediger et al., 1999). The oil sands are suggested to have originated from conventional crude oils which have been biodegraded (Rubinstein & Strausz, 1977).

There are two sets of samples; two samples from the Athabasca oil sands (A1B and A3B) which are consolidated outcrops from the Lower Cretaceous McMurray Formation (Ranger & Pemberton, 1997) and two samples from Plover lake, Western Saskatchewan (A827.32 and A827.75) (Table 2.2). These samples are unconsolidated Cretaceous oil sands from drilling cores (Obermajer et al., 2004).

2.1.1.4 Indonesia

Buton Island is in the Province of South East Sulawesi, Indonesia and is part of a Neogene collision zone which encompasses most of the eastern margin of Sulawesi. Sulawesi is split into three regions; an eastern belt of ophiolite complex imbricated with sedimentary rocks and melange; a central belt of highly deformed sedimentary rocks and schists and a western arc of volcanic deposits, Cretaceous and Tertiary in age (Smith & Silver, 1991). Buton's geological history is dominated by the Miocene collision of micro-continents placing the Tukang Besi platform (TBP) against Buton through a west-dipping subduction zone and is discussed as a detached part of the Australian-New Guinea continent (Hamilton, 1979; Pigram & Panggabean, 1984; Zumberge, 1984; Audley-Charles, 1988; Villamil, 2003). This collision resulted in the Wolio complex, dominated by deep-water limestones from the Late Triassic to the Oligocene (Winto, Ogena, Ranu, Tobelo Formations).

The oil shales and/or asphalt/tar sands are found within the sandstone layer of the Tondo Formation and the sandy limestone of the Sampolakosa Formation running from the North to the South of Buton through a central belt (Fig. 2.10). The Tondo Formation (Miocene) is a sequence at least 1,300 m thick consisting of mudstone, conglomerate and sandstones with large lateral and vertical facies variations (Hamilton, 1979; Pigram & Panggabean, 1984; Audley-Charles, 1988; Smith & Silver, 1991). These sediments represent a mixture of turbidite fan, fan-delta and slope facies at bathyal to neritic depths as well as minor contributions from shallow marine and fluvial facies. The overlying Sampolakosa Formation (Miocene – Pliocene) is a fine grained pelagic chalk as thick as 1200 m (Hetzl, 1936; Wiryosujono & Hainim, 1975) with lenses of sandstone deposits.

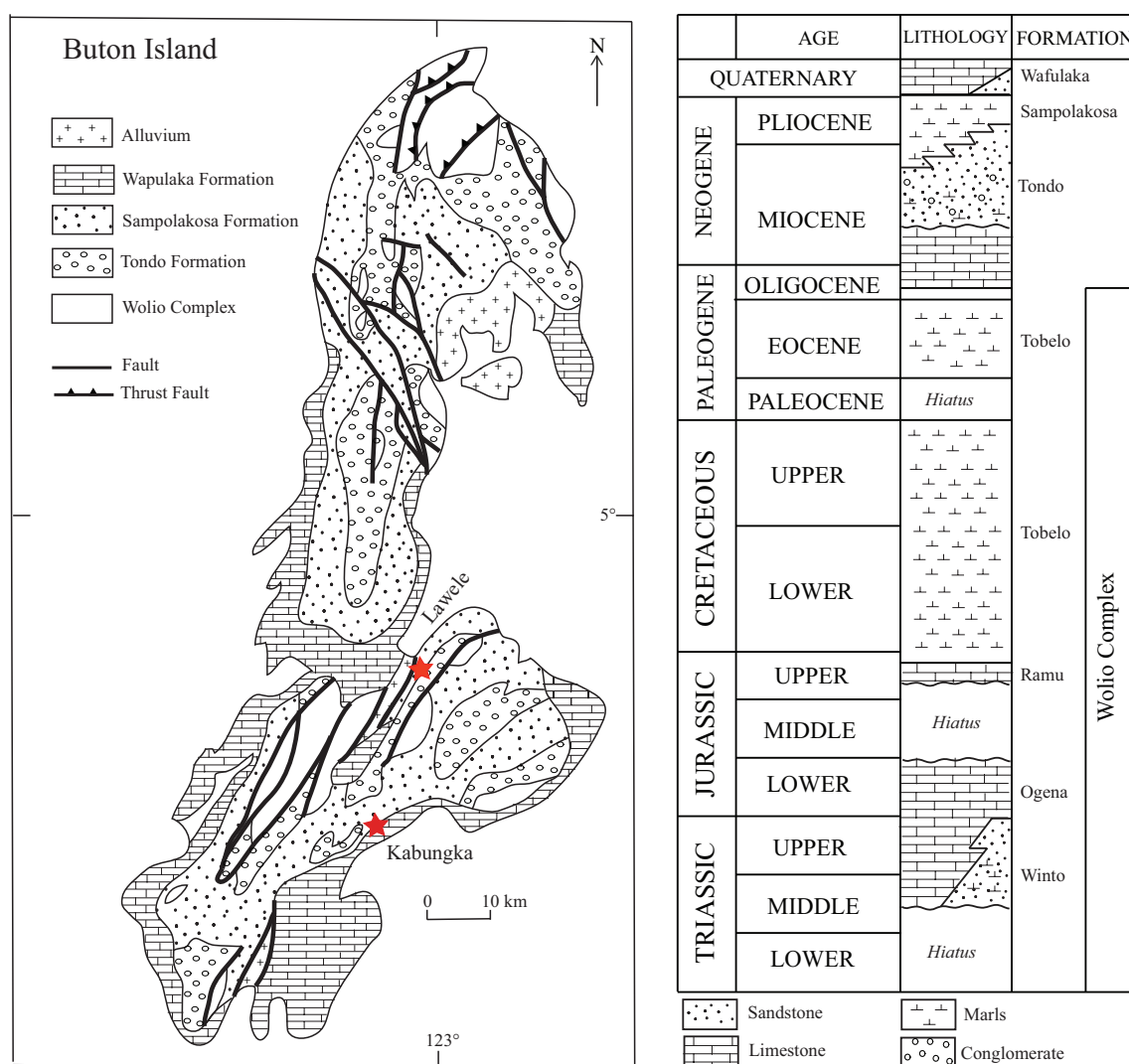


Figure 2.10. Geological map of Buton, Indonesia, modified from Smith & Silver (1991). Stratigraphic sequence for Buton, Indonesia modified from Audley-Charles (1988).

The source rocks and geochemistry of the oils throughout SE Asia have been well documented (e.g., Schiefelbein & Cameron, 1997; Todd et al., 1997). The primary source rocks over this area are thought to be marine mudstones and marls with type II/III kerogen deposited under anoxic environments (Peters et al., 1999; Doust & Noble, 2008) most probably the Upper Miocene Klasafet Formation (Peters et al., 1999) and/or the Triassic bituminous limestones and shales (Davidson, 1991).

Two samples from Kabungka (KI) and Lawele (LI), Buton Island (Fig. 2.10) were collected by the Buton Asphalt Indonesia Company from the Tondo and Sampolakosa Formations and are heavily oil saturated (Table 2.2).

Table 2.2 Summary table of oil sands and oil samples used within this study.

Country	Location	Sample name	Age	Geological unit	Type
UK	Osmington Mills	OS1	Jurassic	Bencliff Grit, Corallian Group	Sandstone
UK	Osmington Mills	OS2	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS3	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS4	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS5	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS6	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Mupe Bay	MBC	Cretaceous	Wealden Group	Oil sandstone (clast)
UK	Mupe Bay	MBM	Cretaceous	Wealden Group	Oil sandstone (matrix)
UK	Lulworth Cove	LC	Cretaceous	Wealden Group	Oil sandstone
UK	Bran point	OS oil	Jurassic	Bencliff Grit, Corallian Group	Oil
Canada	Athabasca	A1B	Cretaceous	McMurray Fm, Mannville Group	Oil sandstone
Canada	Athabasca	A3B	Cretaceous	McMurray Fm, Mannville Group	Oil sandstone
Canada	Plover Lake	A827.32	Cretaceous	Mannville Group	Oil sandstone
Canada	Plover Lake	A827.75	Cretaceous	Mannville Group	Oil sandstone
Colombia	Saltarín 1A well	C127.40	Pliocene	Guayabo - G5	Oil sandstone
Colombia	Saltarín 1A well	C147.25	Pliocene	Guayabo - G5	Oil sandstone
Colombia	Saltarín 1A well	C541.75	Miocene	León	Oil mudstone
Colombia	Saltarín 1A well	C616.48	Miocene	Carbonera – C2	Oil mudstone
Indonesia	Kabungka	KI	Miocene	Tondo & Sampolakosa	Oil sandstone
Indonesia	Lawele	LI	Miocene	Tondo & Sampolakosa	Oil sandstone

2.1.2 Well Cores

Well cores from the North Sea, UK and Wytch Farm, UK were used in this study because of the large number of cores available at the British Geological Survey (BGS) core stores at Gilmerton, Edinburgh, Scotland and Keyworth, England. These cores were investigated to try to identify if magnetic characterisation could be used to identify hydrocarbons by looking at a selection of dry and oil-bearing cores. A brief overview of the North Sea geology is given below followed by a description of the well cores and their corresponding fields (Section 2.1.2.2). The well cores are analysed and discussed in Chapter 6.

2.1.2.1 North Sea, UK, geology

The North Sea, UK, is a hydrocarbon rich area with hundreds of oil and gas fields. Hydrocarbon production and retention is due to the geological rifting during the Jurassic creating reservoir traps and suitable source rocks (Balson et al., 2002; Gautier, 2005). The geological history of the North Sea is characterised by extensional tectonics and failed rifting during the Late Jurassic to Early Cretaceous. The history is typically split into the pre-rift, syn-rift and post-rift events.

Pre-rifting consists of Caledonian crystalline and metamorphic basement rock of Early Palaeozoic age unconformably overlain by Devonian sediments (Fig. 2.11). During the Devonian, red-bed molasses and lacustrine sedimentation was widespread during extensional collapse of the Caledonian mountains and as the mountain ranges were eroded. During the Early Carboniferous, shallow marine and fluvio-deltaic sediments as well as some local volcanics accumulated in parts of the Central North Sea during regional crustal extension. Clastic sediments, however, dominated the Northern North Sea. During the Late Permian, aeolian red beds were widespread and followed by a marine transgression resulting in cyclical evaporitic successions. In the Triassic, sandstone- and mudstone-dominated red bed successions were laid down due to a return to arid, continental conditions. Following the Permo-Triassic rifting, a phase of thermal subsidence allowed a period of marine deposits to accumulate in the Early Jurassic covering the majority of North West Europe including the North Sea.

As a precursor to the main Late Jurassic phase of North Sea rifting, a Middle Jurassic thermal dome formed in the North Sea and represented an extensional uplift covering $\sim 700,000 \text{ km}^2$ centred around the triple-junction of the Viking Graben, Central Graben and Moray Firth/Witch Ground (Underhill & Partington, 1993). The resulting uplift and erosion/onlap onto the rift dome is classed as the mid-Cimmerian unconformity (Figs. 2.11 and 2.12) and is represented by a large stratigraphic separation near the triple junction, although the separation decreases progressively away from the

triple junction until it becomes a correlatable conformity marked by a basinward shift in facies (Underhill & Partington, 1993). The dome caused sediment to be deflected into adjacent rift basins and regressive paralic sediments accumulated.

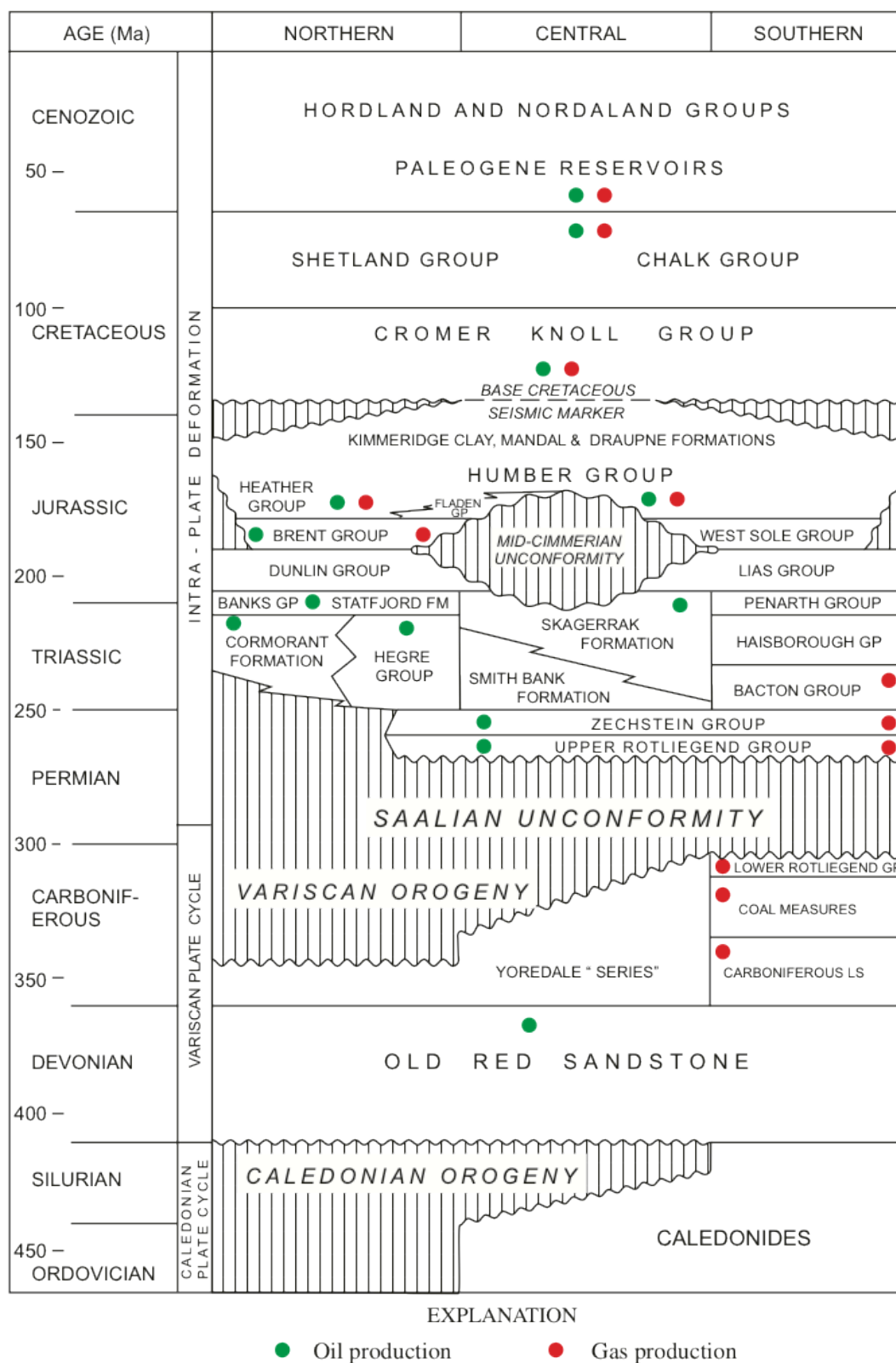


Figure 2.11. Stratigraphic summary of the North Sea Graben Province split into northern, central and southern regions (Gautier, 2005). Geological units with oil and gas production are labelled.

Middle Jurassic sedimentary sequences hold the majority of oil and gas reservoirs such as the Brent Group which make up ~ 50% of the North Sea reservoirs. Relative sea level changes caused a marine regression within the Early-Middle Jurassic followed by a marine transgression in the Late Jurassic (Fig. 2.12). The Late Jurassic is defined by major extensional faulting which initiated at the edges of the Graben system and propagated towards the center of the dome (Rattee & Hayward, 1993). Marine sediments continued to accumulate within the deepening basins and show onlap onto the mid-Cimmerian unconformity demonstrating that progressive marine flooding occurred (Underhill & Partington, 1993). To the East of the North Sea, turbidites were a mix of syn-rift fan delta deposits and post-rift basin floor fan sediments, which are shown to interdigitate with the Kimmeridge Clay Formation. The Kimmeridge Clay plays a key role in the North Sea petroleum system as the major source rock throughout the North Sea. A series of long, interconnected and narrow basins formed by the Late Jurassic causing rapid sedimentation near the major fault system boundaries.

Rifting ended within the North Sea by the Early Cretaceous due to the switch of extension to the west of the British Isles on faults such as the More and 'End of the World' fault. Large amounts of post-rift sediments accumulated, especially near the abandoned axis of the rift. By Late Cretaceous large deposits (>1000 m) of chalk were accumulating in depocentres (Figs. 2.11 and 2.12). The Cenozoic was dominated by thermal subsidence in response to Late Jurassic rifting and more importantly by uplift and basinward tilting of the Scottish mainland as a result of the incipient Iceland hot spot. This resulted in the accumulation of most turbidite sands and muds through out the Tertiary.

The oil and gas accumulations in the area are due to a petroleum system called the Kimmeridgian Total Petroleum System (TPS) (Gautier, 2005). The source rocks were deposited in the Late Jurassic-Early Cretaceous. Oil and gas generation started in the North Sea Graben Province by the Cretaceous and reservoirs have been identified in strata ranging in age from Devonian to Eocene. Examples of the North Sea geology can be seen in Figures 2.11 and 2.12.

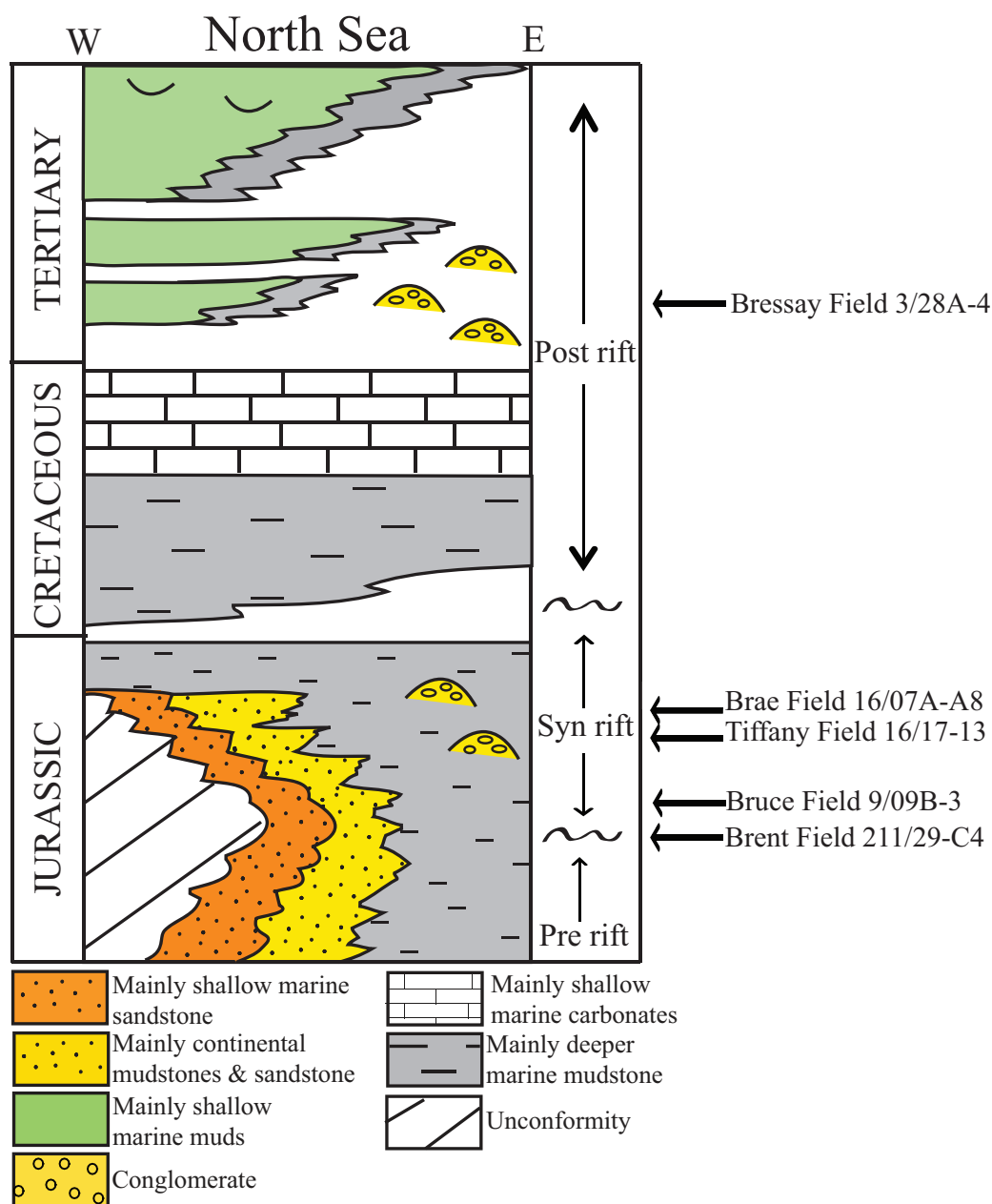


Figure 2.12. Generalised stratigraphy within the North Sea from West to East between the Jurassic and the Tertiary. The different rifting stages and the stratigraphic position of the well cores investigated are marked on the diagram for reference.

2.1.2.2 Hydrocarbon field cores, UK

A list of cores viewed at the BGS Core stores, Gilmerton, Edinburgh and Keyworth, Nottingham are summarised in Table 2.3. Cores were selected based on their accessibility and recovery percentage. The fields/well cores investigated are shown on Figures 2.12 and 2.13.

Table 2.3 Summary of well cores and corresponding fields from which samples have been taken.

Well	Sample name	Field	Reservoir Age	H/C type	Drill Date	Depths (m)	# of Cores
3/28A-4	3/28A-	Bressay	Tertiary	Oil	1981	1051-1153	25
211/29-C4	2/11-	Brent	Jurassic	Oil	1971	3422-3801	26
16/07A-A8	16/A8-	Brae	Jurassic	Oil/Condensate	1976	4645-4670	26
16/17-13	16/13-	Tiffany	Jurassic	Oil	1979	3942-4300	28
9/09B-3	9B-	Bruce	Cretaceous/Jurassic	Condensate	1974	3540-4004	23
211/29-8A	211/8A-	...	...	...	1982	3330-3607	8
3/03-11	3/11-	...	...	...	1989	1335-3535	5

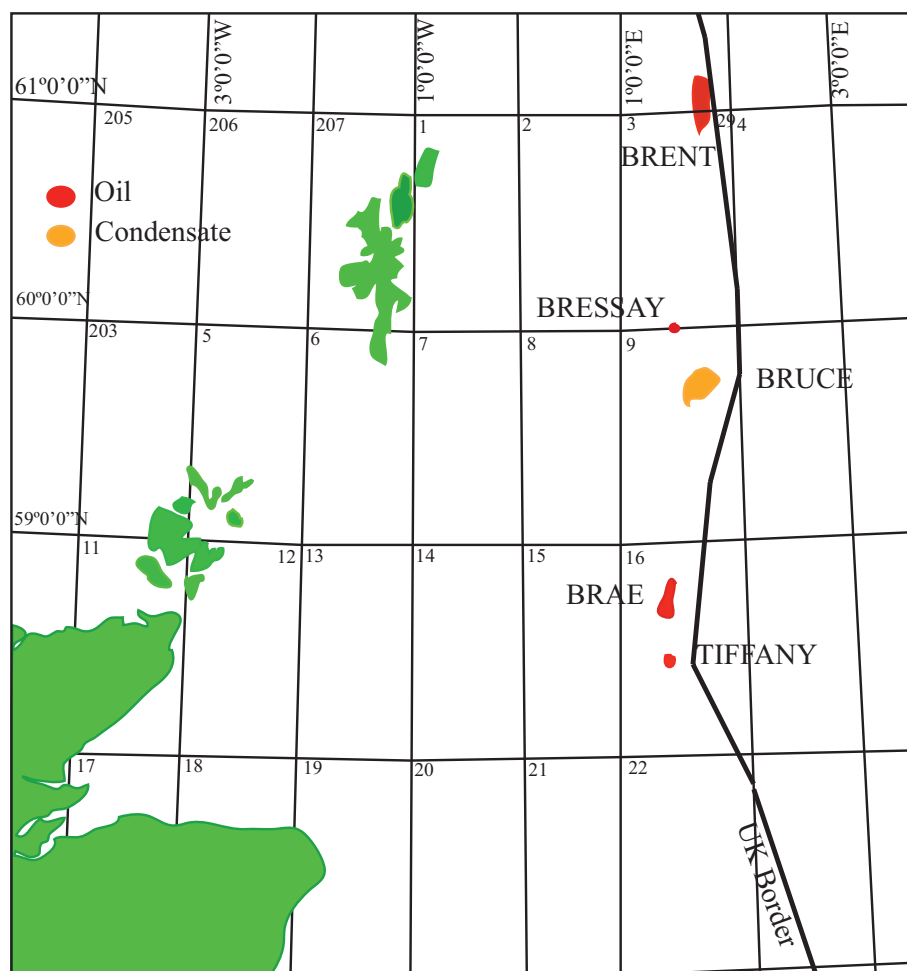


Figure 2.13. Generalised map of the Northern North Sea with oil field locations marked.

Bressay Field (3/28A-4)

The Bressay field (Fig. 2.13) was discovered in 1981 on the East Shetland platform. The reservoir is a structural closure within the Upper Palaeocene (Teal Member) and Lower Eocene (Upper Dornoch Formation) and is part of a larger 10 km elongated feature involving the sand rich Dornoch delta (Fig. 2.14). The reservoirs are post rift Tertiary sediments residing roughly 1000 m below the seabed. The reservoir is up to 230 m thick and is at a relatively low temperature, 37 °C. Well core 3/28A-4 penetrates the centre of the Bressay Field through the Bressay Sandstone Formation (Figs. 2.12 and 2.14)

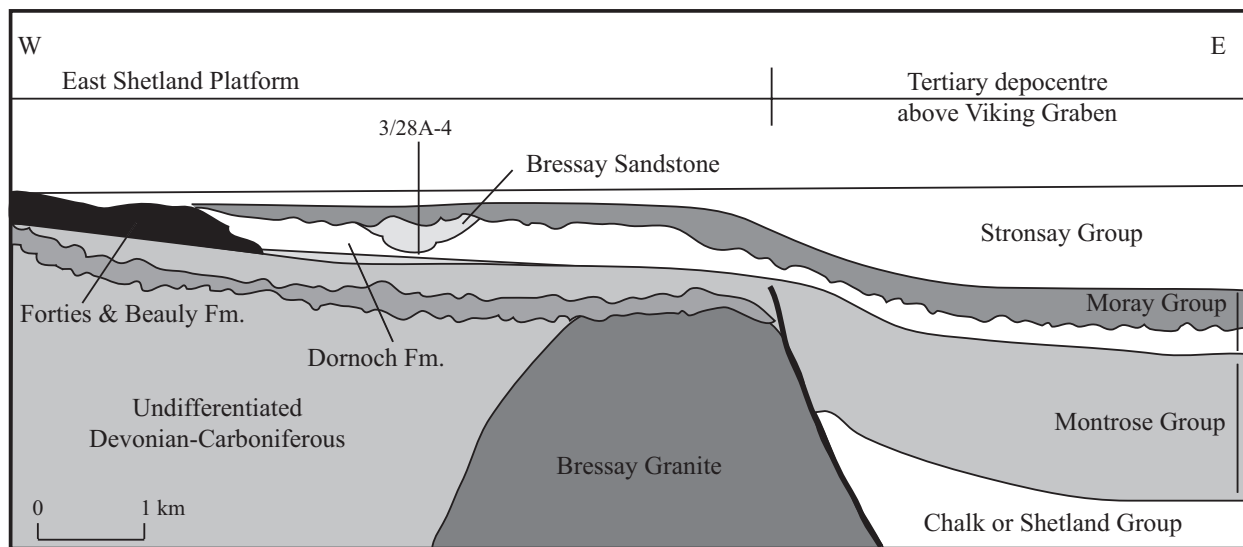


Figure 2.14. Generalised sketch depicting how the stratigraphy in the Bressay area relates to the sedimentary fill in the neighbouring deep-water basin depocentre. Modified from Underhill (2001).

Brent Field (211/29-C4)

The Brent Field (Fig. 2.13) was discovered in 1971 and is located ~ 100 miles northeast of the Shetland Islands (Struijk & Green, 1991). The field has two main reservoirs, the Brent Group (Middle Jurassic) and the Startjford Formation (Lower Jurassic), which accumulated during the major Jurassic rifting event (Fig. 2.12). The Brent Group is subdivided into at least five formations but all are fine to coarse-grained sandstones. The Startjford Formation is more complex with marine sands, carbonate cemented sands as well as the presence of shales, which act as vertical permeability barriers. The field is within a fault controlled unconformity trap within a westerly dipping tilted fault block (Struijk & Green, 1991) and is a relatively simple dip closure structure. The Brent Group reservoir is at a depth of ~ 2500 m below the seabed and is ~300 m thick with a temperature of ~ 80 °C. The source rock is the Kimmeridge Clay Formation over both the Viking

Graben and the East Shetland Basin. The Kimmeridge Clay is younger than the Brent Group, however, due to faulting in the area, the older Brent Group sediments have overridden the Kimmeridge Clay and also allowed migration of hydrocarbons through the steep faulted scarp and up the shallower dip slope of the block (Struijk & Green, 1991). Well core 211/29-C4 penetrates the crest of the Brent field.

Two dry (no detected hydrocarbons) wells were also analysed from outside the Brent field for comparison with oil producing wells. Both the 211/29-8A (East of the major field) and 3/03-11 (West of the major field) well cores are characterised by the same geological units found at the Brent area. It has been assumed for this study that migrating hydrocarbons may have travelled through well core 211/29-8A but not through 3/03-11 well core. These wells were selected because the Brent field core (211/29-C4) showed the most magnetic anomalies and provided an opportunity to make comparisons to potentially non-hydrocarbon bearing cores nearby and to identify any differences in their magnetic signal (Chapter 6).

Brae Field (16/07A-A8)

The Brae field (Fig. 2.13) is within the Viking Graben and was discovered in 1976 (Fletcher, 2003).

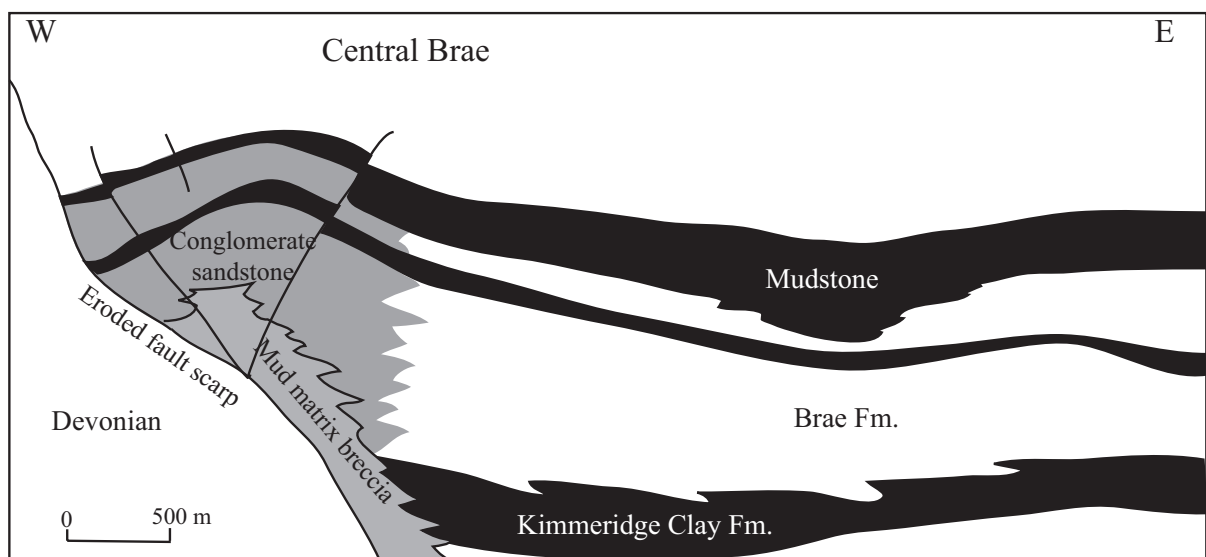


Figure 2.15. Structural cross section through central Brae. From Fletcher (2003).

The reservoir is a proximal submarine fan sequence deposited as a steep sedimentary cone at the margin of the South Viking Graben (Fig. 2.15) formed during Jurassic rifting (Fig. 2.12). The units are dominated by sand matrix conglomerates and sandstones with minor mudstone contributions. A mudstone facies creates a stratigraphic seal to the North and South. The Kimmeridge Clay

Formation acts as an overlying seal as well as the source rock. Hydrocarbon generation and migration from the Kimmeridge Clay which interdigitates with the Brae member (Fig. 2.15) started in the Late Cretaceous. The reservoir itself is a faulted anticline with a dip closure to the East and a fault seal to the West (Fletcher, 2003). The field is at a depth of ~ 3580 m below the seabed with a reservoir thickness of between ~ 30 – 510 m and a temperature of 120 °C. The well core 16/07A-A8 is in the crest of the structure.

Tiffany Field (16/17-13)

The Tiffany field (Fig. 2.13) was discovered in 1979 on the Western margin of the South Viking Graben ~ 160 km northeast of Aberdeen (Kerlogue et al., 1994). The reservoir is at a depth of ~3770 m below the seabed and resides within the ~ 400 m of Brae Formation (Upper Jurassic) (Figs. 2.12 and 2.16) composed primarily of massive conglomerates and pebbly sandstones but a secondary reservoir also exists within the Upper Aptian to Lower Albian turbidites. The trap is both structural and stratigraphic formed by the inversion of the basin boundary fault to the West as well as lateral pinchout of the reservoir facies along strike during the Jurassic rifting. The source rock is the Kimmeridge Clay Formation which overlays and interdigitates the reservoir, which is at a temperature of ~ 135 °C (Kerlogue et al., 1994), due to the turbidite nature of the field. The well core 16/17-13 resides within the crest of the Tiffany field.

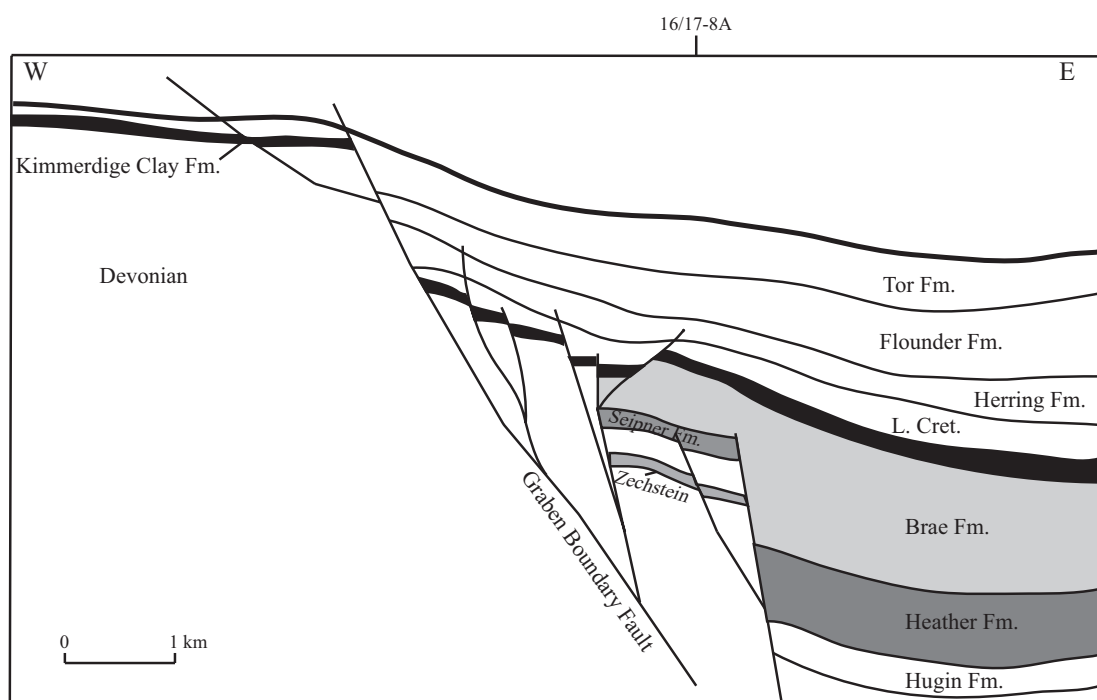


Figure 2.16. Schematic geoseismic west-east section through the Tiffany Field. From Kerlogue *et al.* (1994).

Bruce Field (9/09B-3)

The Bruce field (Fig. 2.13) was first discovered in 1974 and is located ~ 340 km northeast of Aberdeen. The field lies at the Northern edge of the Beryl Embayment, which is a complex area of fault blocks between the Viking Graben and the East Shetland Platform. It is characterised by three reservoirs; the Turonian (Upper Cretaceous) limestone (gas condensate), Bruce (Middle Jurassic) sandstone (oil and gas condensate) (Fig. 2.12) and the Statfjord (Lower Jurassic) sandstone (oil and gas condensate). Condensate is a light crude, which exists as a gas under reservoir conditions. The reservoir is 4000 m below sea level, has a maximum thickness of 250 m and is at a temperature of ~ 99 °C. The field is a structural trap but is complicated by separate accumulations as well as separate structural areas, the Western Flank, the Central Panel and the Eastern High. The well core 9/09B-3 resides in the Central Panel of the Bruce field.

2.2 Laboratory techniques

Three types of experiments have been undertaken: 1) chemical analysis; 2) Analytical Scanning Electron Microscopy (SEM) imaging and Energy Dispersive X-ray (EDX) analysis; and 3) magnetic mineral analysis. The combination of all these techniques enables a thorough analysis, which combines the magnetic and chemical nature of the samples.

2.2.1 Sample preparation

To remove oil from the samples for magnetic analysis and SEM analysis the following procedure was used. Further chemical steps were performed for chemical analysis.

Chemical extraction of oil

Powdered oil sand was weighed (typically between 2-11 g) and placed into a 15 ml test tube and a solvent mixture of dichloromethane (DCM) and methanol (MeOH) in a 93:7 ratio was added to approximately half full and put into a ultrasonic bath at room temperature for 10 minutes. The sample was placed into a centrifuge at 1600 rpm for 5 minutes and the supernatant solvent was pipetted off into a round-bottomed flask. The process was repeated until the supernatant solvent was clear (> 3 times). A rotary evaporator was used at 50 °C to reduce the supernatant fraction to < 1 ml. The fraction was transferred into a clean vial using a pipette and a small amount of DCM to wash the flask. The fraction was left to dry and the organic matter extract weighed. The extracted rock powder was also dried and weighed as 'clean' (oil free) sands.

Column chromatography

Column chromatography allows the separation of the aliphatic, aromatic and polar constituents of the bitumen for Gas Chromatography – Mass Spectroscopy (GC-MS) analysis.

The asphaltenes were first removed from the extracted organic matter by placing the oil into a flask with a minimal amount of DCM. A non-polar solvent (pentane) was slowly added (10-fold quantity) and the asphaltenes were left to settle out over night. The clear supernatant (maltenes) was pipetted off and the sample centrifuged for 2 minutes at 3000 rpm, collecting the remaining supernatant and the whole process repeated three times. The asphaltenes were collected, washed with cold pentane and allowed to dry. The supernatant collected was used in column chromatography.

Column chromatography is a method at which progressively stronger solvents are added to a sample and the components elute at different speeds, resulting in collection of different fractionations. Firstly the pre-extracted alumina was activated in an oven for 1 hr at 150 °C and then the column was prepared by plugging a small pipette with quartz wool. The activated alumina was added into the column and a small amount of pre-extracted alumina was also added into the weighed sample and stirred with a spatula. When the sample was dry, it was added into the column and the sample eluted with the first fraction, hexane. The aliphatic fraction was collected in a test tube and labelled. The procedure was repeated with two other solvents, DCM for the aromatic fraction and methanol for the polar fraction. The final step was to reduce each fraction to <1 ml under a stream of nitrogen. Clean vials were weighed and the final fractions added into individual vials and allowed to dry completely.

Magnetic extractions

A magnetic extractor was built using a large iron finger attached to a powerful magnet with a plastic sleeve (Fig. 2.17). Water with rock powder in suspension was circulated through the system via a pump resulting in many magnetic particles attaching themselves to the iron finger. The thin plastic cover was removed and the extract collected. The extracts were weighed and used in further experimentation.

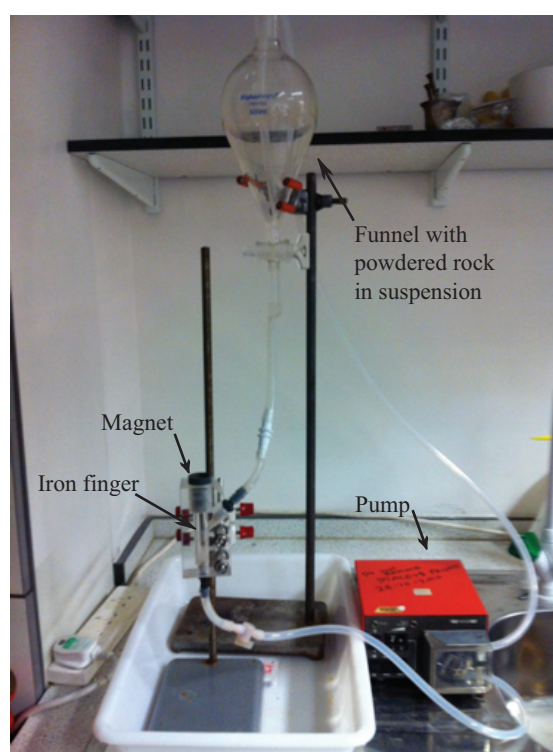


Figure 2.17. Magnetic extractor at Imperial College London.

2.2.2 Geochemical experimentation

Gas Chromatography – Mass Spectroscopy (GC-MS)

GC-MS allows for the identification of individual compounds within complex organic mixtures. GC of the aliphatic fractions was performed on an Agilent 6890N GC fitted with a 30 m DB-5 MS column and using He as a carrier gas. The GC oven temperature was initially held at 50 °C for 1 min before a ramp of 4 °C/min to 310 °C. The samples were injected in splitless mode with an injector temperature of 250 °C. Compound detection and identification was performed by mass spectrometry (MS) using an Agilent 5973 inert Mass Selective Detector operating with a scan range of m/z 50-550. Pyrolysis-GC-MS of the asphaltene fractions was performed on an Agilent 6890N GC fitted with a pyroprobe 5200 using the same parameters as above except for a split of 10:1. The GC oven temperature was initially held at 50 °C before a ramp of 4 °C/min to 310 °C for 82 min. *n*-Alkane, hopane and sterane distribution analysis was determined based on elution order and mass spectrometric fragmentation patterns. The relative response of individual compounds was calculated by integration of the peaks using Chemstation software.

Fourier Transform-Infra Red (FT-IR) Spectroscopy

Fourier Transform-Infra Red (FT-IR) Spectroscopy allows identification of chemical bonds within organic mixtures. Attenuated Total Reflectance (ATR) FT-IR of the bulk bitumen samples was performed on a Nicolet 5700 FT-IR-Spectrometer. A small amount of the bitumen (< 0.05 g) was placed onto the diamond crystal plate of a Smart Orbit accessory with a pressure tower. FT-IR data were collected at wavenumbers between 0-4000 cm^{-1} and analysed using OMNIC software.

2.2.3 SEM & EDX

Visitor access was awarded to the Nanocentre at Cardiff University through the EPSRC program “Access to Nanoscience and Nanotechnology equipment”. This access allowed the imaging of the cleaned sand samples using SEM and compositional analysis using EDX and TEM analysis. All samples were imaged using an SEM/FIB (Focused Ion Beam) system, Zeiss XB1540 combining a Gemini Field Emission Scanning Electron Microscope (FESEM) with a Focused Ion Beam (FIB) with SEM resolution of 1.1 nm at 20 kV and FIB resolution of 7 nm at 30 kV. SEM work was also conducted at the Department of Materials at Imperial College using a JEOL6400 SEM. The oil sands had all oil removed before preparation (organic matter extraction), and the sand grains and

well-core chips were powdered and adhered to an SEM holder by carbon tape. To increase conductivity and reduce the effect of scatter, the samples were coated with gold for 2 minutes during sample preparation. The SEM images were taken between 200 μm to 10 nm and several areas were observed from each sample.

EDX analysis was then performed to determine composition of particular grains, all elements were analysed and 3-4 iterations were conducted. FIB milling was attempted at the Nanocentre, Cardiff University, however, due to the uneven surfaces of the samples (chips and grains) it was extremely difficult and only two samples were completed, but showed insufficient data.

2.2.4 Magnetic experimentation

Magnetic susceptibility measurements were initially conducted along well cores (Section 2.2.5) to select samples for the well core study. Subsequently, most of the experiments were completed at the Institute of Rock Magnetism (IRM) at the University of Minnesota after the award of two 10-day IRM visiting fellowships. Experiments were also conducted at Oxford University, the Royal Institution of Great Britain and Imperial College London. The samples in this study display very weak magnetic signals and noise to signal ratios were a problem with most experimentation.

Magnetic susceptibility

Magnetic susceptibility at room temperature was measured using a Bartington MS2B dual frequency sensor (low frequency = 0.47 kHz, high frequency = 4.7 kHz). The measurement was repeated three times and an average taken. Both the oil stained and ‘cleaned’ samples were measured at Imperial College London.

Samples were measured on an AGICO KLY-2 KappaBridge AC Susceptibility Bridge with a CS-2 furnace to record susceptibility as a function of temperature and to determine (pseudo) Curie temperatures. The system has a temperature range of 300-975 K and a sensitivity limit of 4×10^{-8} SI. Sample preparation involved powdering the sample and weighing it into a test tube (no more than 1 cm in height) and placing it into the holder with a thermoconductor. The ‘cleaned’ oil sands were heated from room temperature to 700 °C in multiple cycles increasing by 100 °C for every heating loop (e.g., heated 25 °C - 100 °C and cooled, heated 25 °C – 200 °C and cooled etc.) except for the Osmington Mills samples, which had both the oil stained and the clean counterparts heated in one cycle (heated 25 °C – 700 °C and cooled). Early on, the oil-impregnated samples were found to carbon combust at ~ 300 °C, which had the potential to break the thermocouple and was not

repeated for further oil sands. Well core samples were heated from room temperature to 700 °C in one cycle. All samples were measured in an argon atmosphere to minimize chemical alteration. The original oil stained samples could not be run due to the high organic content.

Magnetic Property Measurement System (MPMS)

At the IRM, University of Minnesota, two Quantum Designs MPMS2 cryogenic susceptometers were used, both with the same capabilities. The MPMSs have a temperature range of 2.1-400 K, can produce magnetic fields between 0-5 T and have a dynamic range between 10^{-10} to 10^{-3} Am². A Quantum Design SQUID VSM at the Royal Institution, London was also used with the same temperature, magnetic field and sensitivity ($\sim 5 \times 10^{-11}$ Am²) capabilities as the MPMSs. Lower temperature experiments on the MPM can allow magnetic mineralogy and grain size to be determined through low temperature transitions.

Samples were ground into a powder using a pestle and mortar and weighed. For the MPMS, the samples were then placed into a gelatin capsule with a capacity of about 500 mg and sealed using non-magnetic cello tape and inserted into a plastic straw and labelled. The straw was attached to a metal holder to which it was cello taped, the gelatin capsule pushed up into position, air holes created and the bottom sealed. Each sample was inserted into the MPMS and centred automatically or manually. Two types of measurements were taken: 1) Warming curves of saturation isothermal remanence magnetization (SIRM) induced in a field of 2.5T at 10 K after field cooling (FC) (2.5 T) and zero-field cooling (ZFC) from 300 K in 10 K steps as well as cooling and warming curves of room-temperature (RT) induced SIRM to identify low-temperature crystallographic transitions and 2) the measurement of AC magnetic susceptibility as a function of temperature (from 300 to 10 K in 10 K steps) and frequency (1.0, 32.2, 10.0, 31.6, 100.1, 316.7, 997.3 Hz). By measuring several different heating and cooling curves in this manner, a full spectrum of different types of transitions can be identified. For the SQUID VSM, < 10 mg of the powdered samples were placed into holders, labelled and attached to the metal holder. The same FC, ZFC and RT curves were measured, however, the system does not have the capability to perform AC susceptibility measurements.

Vibrating Sample Magnetometer (VSM)

Two Princeton Measurements Vibrating Sample Magnetometers (VSMs) at the IRM were used for high and low temperature measurements for the well core samples. The low temperature VSM can produce magnetic fields between 0-1.8 T in a temperature range of 10-473 K by the addition of a liquid helium cryostat. Its sensitivity limit is 5×10^{-9} Am². The low temperature VSM sample preparation involved filling a polycarbonate gel cap three quarters full and attaching it to a sample

probe, which screwed onto a glass rod. The samples were firstly cooled to 10 K in zero field, measured and then repeated but cooled to 10 K in a 1 T field. Hysteresis and backfield curves were measured at 20 K intervals up to 290 K. FORC diagrams were attempted but these were unsuccessful due to high noise to signal ratios. Room temperature measurements were made on the low temperature VSM before fitting the helium cryostat and these samples were full gelatin capsules prepared in the same way as the MPMS.

The high-temperature VSM has temperature capabilities between room temperature and 1025 K and magnetic fields between 0-1.8 T. The sensitivity limit is $5 \times 10^{-9} \text{ Am}^2$ and has a flowing helium gas furnace. Preparation for the high temperature VSM involved the cementing of the sample (no bigger than a few 10s of milligrams) onto a sample probe and dried over night. The samples were then screwed onto a glass rod and suspended in the middle of the VSM. Cyclic warming and cooling curves were measured between 200-650 °C in steps of 50 °C except for samples with a high carbon content, which were heated to a maximum of 300 °C. Hysteresis, back field and FORC diagrams were measured at the end of each step. Some of the samples were strong enough for hysteresis loops, however, overall the samples were still too weak and were later re-measured at room temperature using an AGM, which is more sensitive.

Alternating Gradient Magnetometer (AGM)

Hysteresis and backfield curves were measured at room temperature on a Princeton Alternating Gradient Magnetometer (AGM) due to its high sensitivity ($1 \times 10^{-11} \text{ Am}^2$) at the IRM and at Imperial College London. The loose material (<0.5 mg) was weighed and packaged within non magnetic tape and attached to the holder using silica gel. High temperature experimentation could not be performed due to the hydrocarbons present within the samples. Although the instrument is more sensitive than the VSM there is a trade off due to the smaller amount of sample that can be used on the AGM relative to the VSM. Nearly all the samples, both the oil sands and well cores produced good hysteresis curves but were typically dominated by paramagnetic behaviour, which can have limitations when analysing.

Superconducting Quantum Interference Device (SQUID)

To determine the samples AF demagnetisation spectra, samples were placed in 10 cm^3 cubes and weighed accordingly. Non-orientated samples were alternating field (AF) demagnetized using an automated 2-G SQUID magnetometer, with a sensitivity of $\sim 1 \times 10^{-11} \text{ Am}^2$ at the University of

Minnesota. The samples were induced with a saturating isothermal remanence (SIRM) and demagnetized in 40 steps from 0 - 170 mT.

Orientated samples were alternating field (AF) demagnetized using an automated 2-G SQUID magnetometer, with a sensitivity of $\sim 1 \times 10^{-11} \text{ Am}^2$ at the University of Oxford. The samples were demagnetized in 17 steps from 0 - 100 mT. A tilt correction for the steeply dipping beds was also applied where appropriate and Fisher statistics (Fisher, 1953) were used to determine means (Chapter 4).

Mössbauer Spectrometry

A Ranger Scientific Mössbauer Spectrometer with a radioactive ^{57}Co source was used at the IRM. The source creates gamma rays, which are absorbed by ^{57}Fe as a function of the Fe minerals lattice distinguishing between Fe sulphides and oxides. It has the capability to cool to 77 K and up to room temperature within a zero field.

The samples were ground into a powder using a pestle and mortar and weighed. The powder was spread into a small Delron disk with a 12.7 mm diameter and 1 mm deep well and was held into place by non-magnetic tape. Samples took between 3-4 days to run and its success was dependent on the iron content. Most samples proved unsuccessful with too little iron present, only a few samples had enough magnetic material to proceed and these measurements were made at room temperature only.

2.2.5 Well core sampling

For sample selection along well cores, an in-house core-logging sensor (Fig. 2.18) was built using a Bartington susceptibility loop connected to a linear slide. A loop sensor of 112 mm was used to provide high-resolution volume susceptibility measurements on whole cores. The equipment was modified to become automated with the use of a linear slide with precision down to nanometer scale although we only needed it at the 1 cm scale. Software was also written to run the experiment and record the values along with drift and background corrections. The MS2C has a very low drift with measurement accuracy within 5-10 mm core clearance. The samples were measured every 10 mm along an approximate 1 m core (Fig. 2.19b). The measurements were also repeated at high resolution and sometimes at low spacing (5 mm) at every sample location. Due to the time consuming nature of retrieving and analysing the cores, roughly every other core was measured and

specifically over areas where lithological changes occurred. Samples were taken at elevated susceptibility values and further characterised by SEM imaging and magnetic analysis.

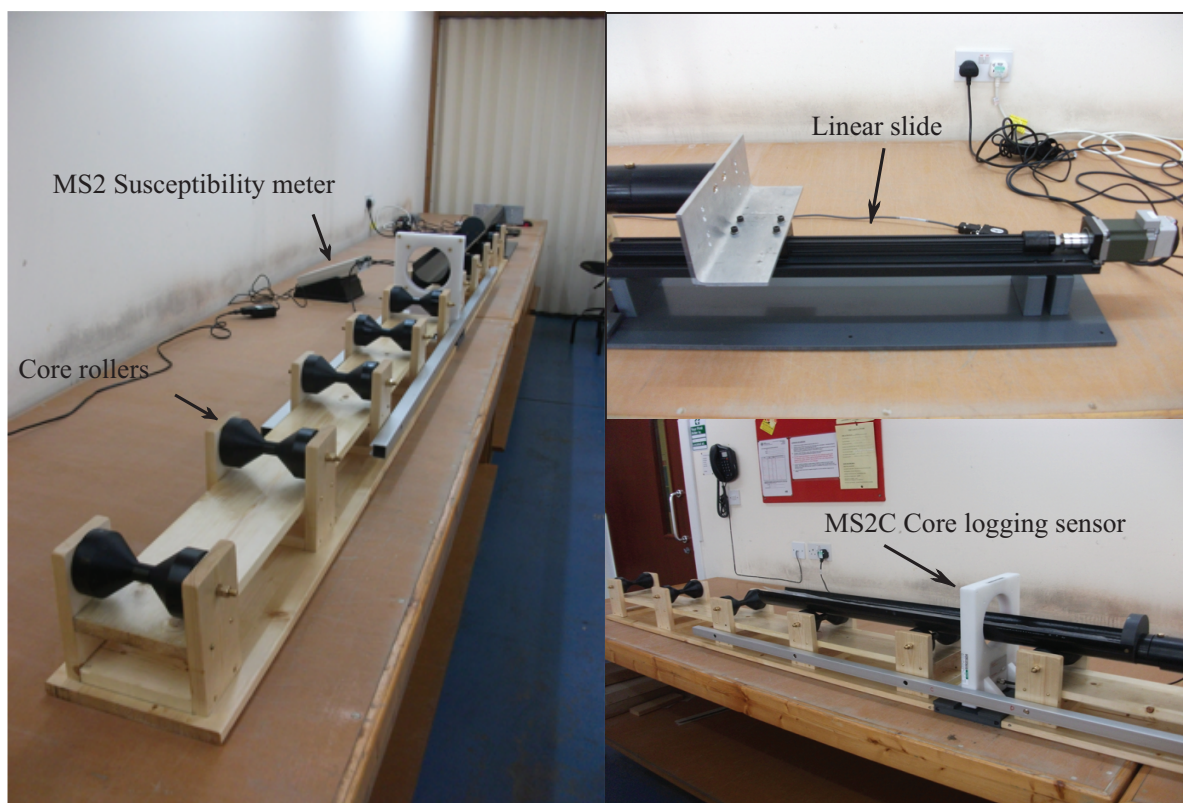


Figure 2.18. Automated core logger using an MS2C loop sensor controlled by a linear slide.

Figure 2.19 shows an example of the susceptibility profiles produced by these cores (well core: 211/29-C4). The full magnetic susceptibility profiles, samples and well log data for the well cores are discussed in detail in Chapter 6. The well log data for this study were retrieved from various oil companies but could not be obtained for all the well cores.

To select background samples, the average magnetic susceptibility reading was recorded and sub sampled (e.g., Fig. 2.19, background magnetic susceptibility at 1 (arbitrary units)). There were often too many magnetic susceptibility peaks to sample and therefore a subsample of these were selected based on geological formations and magnitude to try and get a full suite of data.

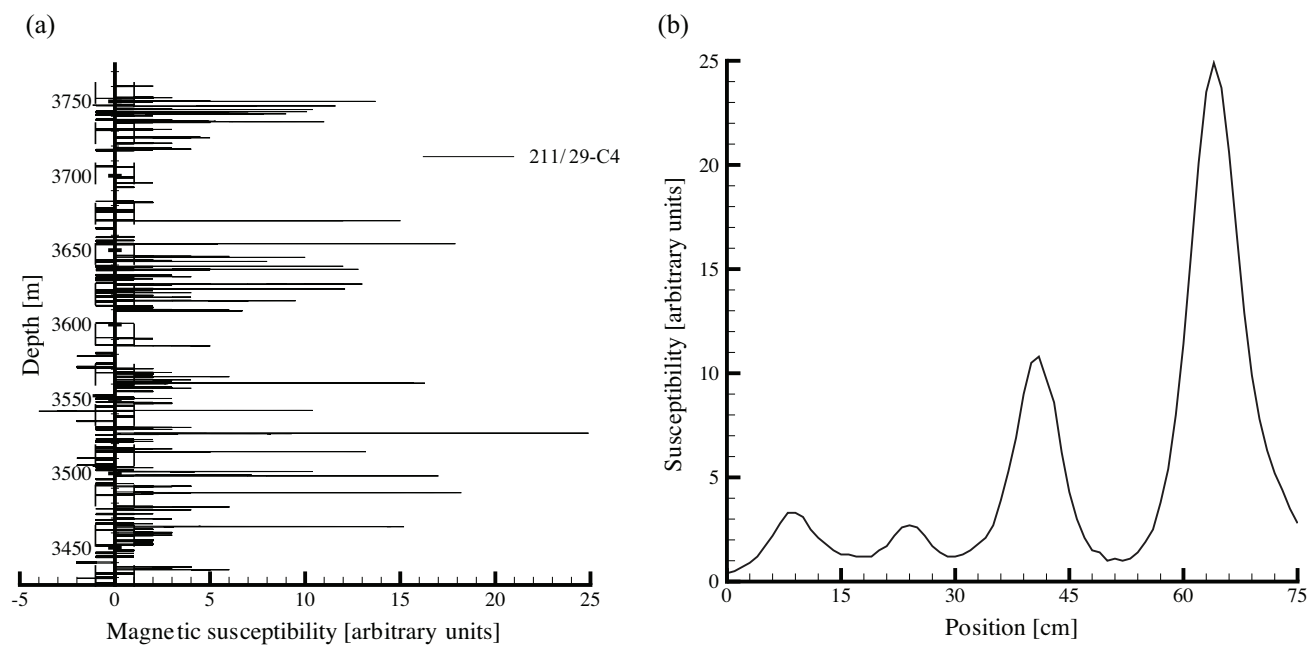


Figure 2.19. (a) Magnetic susceptibility readings over the entire 211/29-C4 well. (- - - noise limits). (b) High resolution magnetic susceptibility measurements over one piece of core from well 211/29-C4.

Chapter 3

**How do magnetic minerals
correlate to the chemical signature
of hydrocarbons?**

3.1 Introduction

Direct hydrocarbon identification has been an area of active research for decades. Currently the main method for hydrocarbon identification is the indirect interpretation of seismic data. This method mainly relies on the processing and interpretation of the data to identify structural features where hydrocarbons may accumulate. Seismic methods are valuable tools in hydrocarbon exploration, but are expensive and can carry large uncertainties in both the processing and the interpretation (e.g., Rankey & Mitchell, 2003; Osypov et al., 2011). The search for other hydrocarbon identification methods has lead to amongst others, magnetic research at both large and small spatial scales (Donovan et al., 1979; Benthien & Elmore, 1987; Elmore & Crawford, 1990; Aldana et al., 2003; Liu et al., 2004; Venkatachalapathy et al., 2011). Links between magnetic signals and hydrocarbons have only been alluded to in these instances and no unambiguous relationship has been established.

Well core, soil and oil fluid studies associated with hydrocarbons have also been a topic of growing research, especially with magnetic mineral characterisation (e.g., Díaz et al., 2000; Gonzalez et al., 2002; Aldana et al., 2003; Ivakhnenko & Potter, 2004; Costanzo-Alvarez et al., 2006; Liu et al., 2006; Rijal et al., 2010; Aldana et al., 2011; Venkatachalapathy et al., 2011; Rijal et al., 2012). These studies have identified a number of characteristics between magnetic properties and hydrocarbons, such as high magnetic susceptibility (χ) anomalies which are only associated with the presence of hydrocarbons relative to background readings and magnetic susceptibility correlations to physical and chemical properties of oils, e.g., density, viscosity and sulphur content. Several studies (e.g., Díaz et al., 2000; Díaz et al., 2006; Guzman et al., 2011) identified positive correlations between extractable organic matter (EOM), organic matter free radical concentration (OMFRC) and magnetic susceptibility values along oil producing wells, proposing that the areas of anomalous behaviour represent broad reducing bands with the presence of asphaltenes, suggesting a bacterial reducing process forming secondary minerals. Díaz *et al.* (2000) suggested these anomalies are a result of hydrocarbon gas leakage from below, causing alteration of organic matter resulting in a net transfer of electrons from altered organic matter to Fe (III). Previous studies (e.g., Díaz et al., 2000; Díaz et al., 2006; Guzman et al., 2011) found anomalous magnetic susceptibility peaks correspond to anomalously high EOM values through producing wells. These studies typically looked at well cores above oil reservoirs, identifying magnetic differences within samples spanning several geological formations.

Machel (1995) created a detailed report on magnetic mineral assemblages in diagenetic environments in association with high concentrations of hydrocarbons. Magnetite and pyrrhotite are the more stable minerals under anaerobic/reducing conditions compared to higher stability for goethite and hematite under aerobic/oxidizing conditions (Machel & Burton, 1991; Machel, 1995). The introduction of fluids such as hydrocarbons are already known to result in diagenetic remagnetisation e.g., Elmore *et al.* (2001). The results suggest that on a large spatial scale, anomalous magnetic susceptibility can form as a result of EOM accumulations around reservoirs due to the formation of secondary magnetic materials. However, there are still many unknowns about the magnetic signature of reservoirs themselves.

Hydrocarbons themselves have unique signatures owing to their source, maturity and biodegradation variations between different sets of oils. These differences such as the presence of bacteria biodegrading the oil could also have an effect on the host rock in which they migrate.

This study investigates the effect of biodegradation on the magnetic signature of oil-impregnated units. Biodegradation causes a reduction in the quality of the oil and is primarily an oxidation process, which is controlled by conditions needed to support microbial life (Connan, 1984). Biodegradation therefore needs a number of conditions to occur: 1) host rock that provides sufficient porosity and permeability for water mobility, 2) temperatures that are $<80^{\circ}\text{C}$ to support the microbes, and 3) salinity and H_2S levels that are suitable for either aerobic or anaerobic bacteria (Connan, 1984; Palmer, 1993; Blanc & Connan, 1994). Due to these conditions, it can be assumed that biodegradation typically increases towards the surface, however, it can also increase towards an oil-water contact (Head *et al.*, 2003; Larter *et al.*, 2003), therefore, potentially increasing with depth. A basic interpretation of biodegradation can be taken from the relative proportions of oil constituents (aliphatic hydrocarbons, aromatic hydrocarbons, polar and asphaltenes) because biodegradation causes the reduction of aliphatic hydrocarbons and the corresponding increase in polar and asphaltene proportions. More sophisticated means of assessing biodegradation involves the Wenger scale (Wenger *et al.*, 2001), which uses biomarkers to identify the intensity of biodegradation from low (0) to severe (10).

In this chapter, the constitutions of several oils have been assessed and compared to their magnetisation to identify any correlation within the variety of samples (Chapter 2). This research is a multidisciplinary study utilising geochemistry and magnetisation to robustly test if a relationship exists between hydrocarbons and magnetisation. The possible mechanisms for such a relationship

are also explored. These findings have direct relevance to studies of magnetic susceptibility in particular, its use in hydrocarbon exploration.

3.2 Samples

Samples were collected from four sources worldwide: (1) Llanos Foreland Basin, Colombia (2). Kabungkan and Lawele, Buton Island, Indonesia (3) Athabasca, Alberta and Plover Lake, Saskatchewan, Canada and (4) Wessex Basin, Dorset, UK as described in Chapter 2 (Table 3.1).

Table 3.1 Summary of the samples used in this study with details about formation and sample type.

Country	Location	Sample	Age	Geological unit	Type
UK	Osmington Mills	OS1	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS2	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS3	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS4	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS5	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Osmington Mills	OS6	Jurassic	Bencliff Grit, Corallian Group	Oil sandstone
UK	Mupe Bay	MBM	Cretaceous	Wealden Group	Oil sand matrix
UK	Mupe Bay	MBC	Cretaceous	Wealden Group	Oil sand clast
UK	Lulworth Cove	LC	Cretaceous	Wealden Group	Oil sandstone
UK	Bran point	OS oil	Jurassic	Bencliff Grit, Corallian Group	Oil
Canada	Athabasca	A1B	Cretaceous	McMurray Fm, Mannville Group	Oil sandstone
Canada	Athabasca	A3B	Cretaceous	McMurray Fm, Mannville Group	Oil sandstone
Canada	Plover Lake	A827.32	Cretaceous	Mannville Group	Oil sandstone
Canada	Plover Lake	A827.75	Cretaceous	Mannville Group	Oil sandstone
Colombia	Saltarín 1A well	C127.40	Pliocene	Guayabo - G5	Oil sandstone
Colombia	Saltarín 1A well	C147.25	Pliocene	Guayabo - G5	Oil sandstone
Colombia	Saltarín 1A well	C541.75	Miocene	León	Oil mudstone
Colombia	Saltarín 1A well	C616.48	Miocene	Carbonera – C2	Oil mudstone
Indonesia	Kabungka	KI	Miocene	Tondo & Sampolakosa	Oil sandstone
Indonesia	Lawele	LI	Miocene	Tondo & Sampolakosa	Oil sandstone

3.3 Chemical characterisation of hydrocarbons

All samples were geochemically analysed using the techniques described in Chapter 2 and the results are discussed in detail below.

3.3.1 Bulk oil composition

The percentage of extractable organic matter (EOM) (Table 3.2) was determined as described in Section 2.2.1. The UK samples presented EOM percentages between 0-12 % compared to 0-8 % for Canadian samples and 1-7 % for Colombian samples. The Indonesian oil sands were very heavily oil saturated at 31-33 % (Table 3.2).

Table 3.2 Oil extraction and fractionation percentages for all the samples used in this study determined by GC-MS data (Appendix 1.1).

Sample	EOM %	Asphaltene %	Aliphatic %	Aromatic %	Polar %
OS1	0	...	...	...	...
OS2	0.5	23.9	47.9	13.0	15.2
OS3	4.8	20.0	40.0	20.0	20.0
OS4	11.8	23.5	40.2	17.7	18.6
OS5	2.9	43.5	39.1	10.9	6.5
OS6	10.3	36.9	40.0	9.2	13.9
OS oil	...	0	66.7	22.9	10.4
MBM	2.6	15.2	13.0	15.3	56.5
MBC	5.8	21.7	13.0	21.7	43.6
LC	6.1	27.8	16.7	16.7	38.8
A1B	8.1	40.0	20.0	20.0	20.0
A3B	0.2	28.6	28.5	14.3	28.6
A827.32	5.4	25.0	25.0	12.5	37.5
A827.75	5.9	28.6	28.6	14.3	28.5
C127.40	1.1	0	73.5	11.8	14.7
C142.25	1.9	0	74.1	9.3	16.7
C541.75	6.6	0	92.2	3.9	3.9
C616.48	6.9	0	94.2	2.9	2.9
KI	31.2	41.7	25.0	16.6	16.7
LI	32.8	25.0	18.8	18.7	37.5

The bulk compositions of the extracted bitumen are represented in Table 3.2 and in ternary diagrams (Fig. 3.1), which compare their chromatographically separated fractions. The asphaltene content ranged between 15-44 %, 25-40 % and 25-42 % in the UK, Canadian and Indonesian samples respectively. The Colombian samples had no asphaltenes and displayed much higher abundances of aliphatic hydrocarbons between 74-94 % compared to the UK 13-48 %, Canadian 20-29 %, and Indonesian 19-25 % samples. The active oil seep sample from the UK (OS oil) showed no asphaltenes and a high proportion of aliphatic hydrocarbons, 67%. All the samples show variable aromatic hydrocarbon percentages that remain below 23% (Table 3.1, Fig. 3.1).

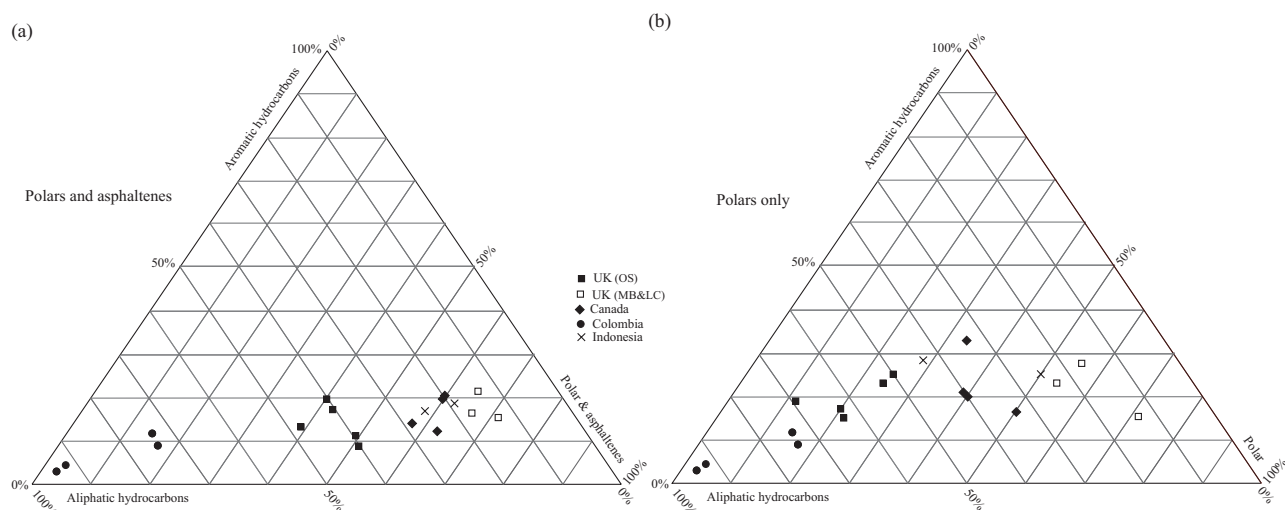


Figure 3.1. A ternary diagram representing the individual percentages of the compounds found within oil; aliphatic hydrocarbons, aromatic hydrocarbons and polar & asphaltenes. (a) Polar and asphaltene fractions and (b) polar fractions only. The samples are separated into their localities for reference.

Figure 3.1 reveals the importance of asphaltenes on the oil composition with Figure 3.1a representing polar and asphaltene percentages combined compared to Figure 3.1b, which only includes polar components. In the later, the data becomes far more variable and it can be seen that the asphaltene abundance makes a significant difference to the chemical composition of the UK (OS), Canadian and to some degree the Indonesian samples. On the other hand, the inclusion of asphaltenes on oil composition has little effect on the UK (MB & LC) samples and no effect on the Colombian samples because the samples have a very high percentage of polar components and no asphaltenes present respectively.

The relative abundances of oil components are confirmed by Fourier Transform-InfraRed Spectroscopy (FT-IR) analysis, which also allows the identification of the nature of the functional groups present in the oils (Fig. 3.2). Overall, the spectra are relatively complex with a number of main characteristic absorption bands representing organic molecular bonds. The FT-IR spectra for all the samples can be found in Appendix 1.2.

The results reveal well-defined absorptions between $3200\text{--}2700\text{ cm}^{-1}$ (Fig. 3.2) characteristic of carbon and hydrocarbon containing species with variations due to C-H stretching (Coates, 2000). In all four sample sets, the main absorptions are below 3000 cm^{-1} , which are indicative of saturated hydrocarbons. Specifically, the strong absorptions between $2960\text{--}2860\text{ cm}^{-1}$, the strong methylene/methyl band ($\sim 1470\text{ cm}^{-1}$) relative to a weaker methyl band ($\sim 1380\text{ cm}^{-1}$) (Fig. 3.2) and small absorptions at 720 cm^{-1} most probably represent a long linear aliphatic chain (Coates, 2000). These responses appear to be greater in the Colombian samples relative to the other samples. In

contrast, the lack of absorptions above 3000 cm^{-1} and specifically between $3150\text{--}3000\text{ cm}^{-1}$ which are almost exclusively indicative of unsaturated and aromatic compounds (Coates, 2000), reveals the relatively low percentage of aromatics within all four sets of samples. However, C=C-C and C-H aromatic ring related vibrations can be identified at $\sim 1510\text{ cm}^{-1}$ and $900\text{--}670\text{ cm}^{-1}$ respectively (Fig. 3.2). Other common absorption bands were also categorized (Fig. 3.2) such as C=O ($\sim 1700\text{ cm}^{-1}$), aliphatic N-O ($\sim 1540\text{ cm}^{-1}$) C-O ($1150\text{--}1200\text{ cm}^{-1}$) and C-N ($1090\text{--}1020\text{ cm}^{-1}$). These observations are consistent with the fractionation data and ternary plot (Fig. 3.1, Table 3.2), which reveals dominant aliphatic contributions with relatively small quantities of aromatic fractions in all sets of samples.

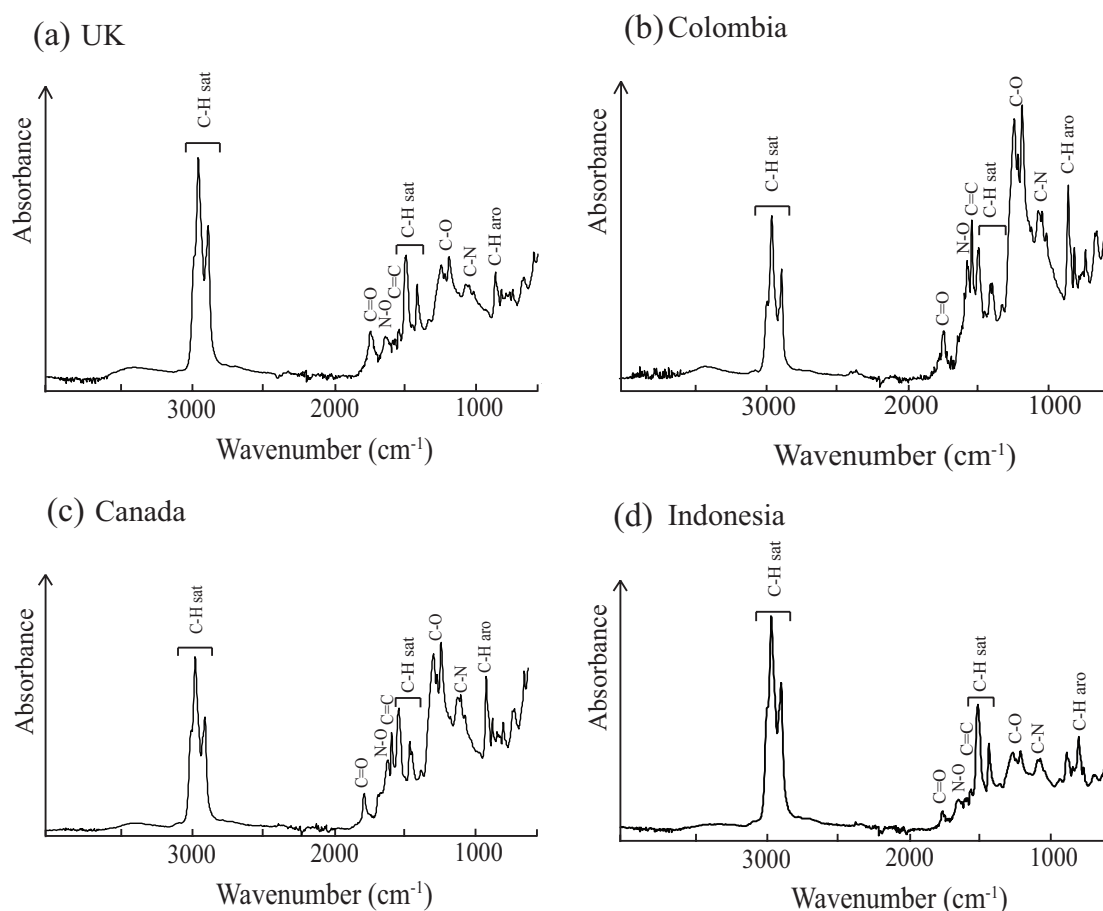


Figure 3.2. FT-IR spectra for representative samples within this study with the characteristic absorption bands identified for interpretation. (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian samples.

FT-IR spectroscopy can also be a complimentary tool for oil assessment (Permanyer et al., 2002; Permanyer et al., 2007) by using main IR band indexes. The use of index ratios allows small variations in oil composition to be identified and the results shown in Figure 3.3 help to

differentiate between oils from different localities as well as variation within each oil set. The following indexes and plots were calculated using the procedure outlined in Permanyer *et al.* (2002):

Long chain index: $A_{724}/(A_{1460}+A_{1376})$

Aliphatic index: $(A_{1460}+A_{1370})/\Sigma A_{ali}$

Aromatic index: $A_{1600}/\Sigma A_{aro}$

Substitution: $A_{864}/A_{864}+A_{814}+A_{743}$

ΣA_{ali} : $A_{1700}+A_{1600}+A_{1460}+A_{1376}+A_{1030}+A_{864}+A_{814}+A_{743}+A_{724}+A_{(2953,2923,2862)}$

ΣA_{aro} : $A_{814}+A_{743}+A_{724}$

Figure 3.3 shows the index graphs for these FTIR indexes. The aliphatic and long chain indexes (Fig. 3.3a) give information on the quantity of long chain aliphatics and aliphatic rate. The aromatic and substitution indexes (Fig. 3.3b) reveal information on the condensation degree of the aromatic compounds.

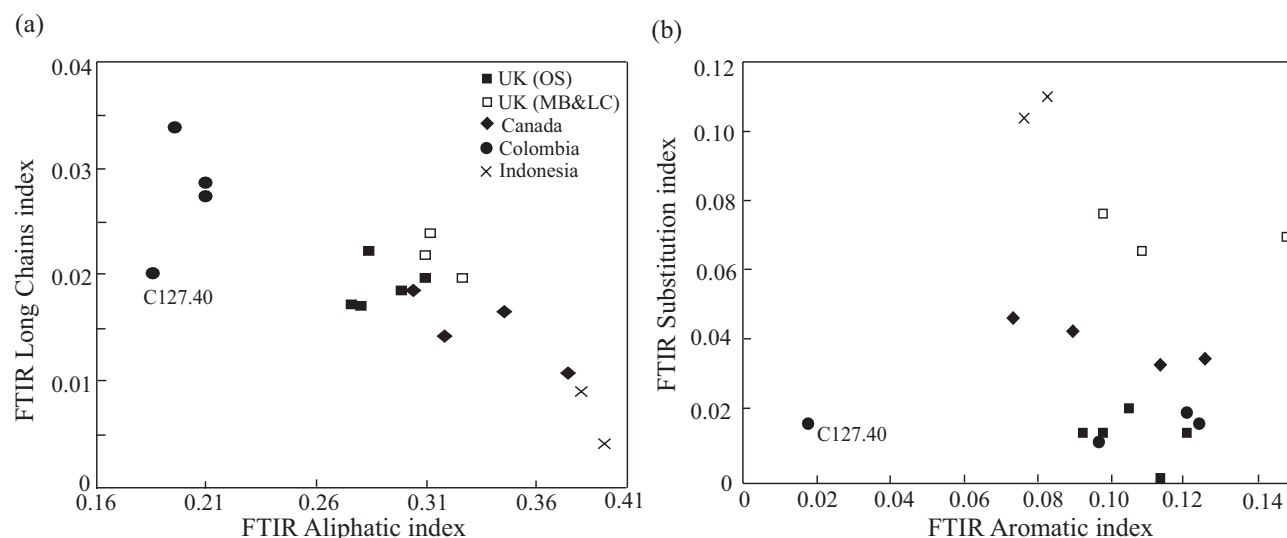


Figure 3.3. FT-IR index graphs for all oil samples (a) aliphaticity vs. long chain indexes and (b) aromaticity vs. substitution indexes. Distinct groups of oils can be distinguished.

The Colombian samples clearly have a larger quantity of long chain aliphatics compared to the UK, Canadian and especially the Indonesian samples (Fig. 3.3a) due to the lower aliphatic index as well as a higher long chain index. The aromatic ratios give information on the condensation degree of the aromatic compounds and Figure 3.3b suggests the aromatic character varies from high to low for Indonesian, UK (MB & LC), Canadian, UK (OS) and Colombian samples, respectively but all

samples show strong condensed structures except for sample C127.40. Within each sample set, there is no substantial variation except for sample C127.40, which displays a lesser aliphatic and aromatic character than all other Colombian samples (Fig. 3.3). The Colombian samples are separately investigated in Chapter 5 to try to identify the differences within this set of samples. The aromatic and substitution indexes (Fig. 3.3b) reveal a gradational change between the sets of the samples with distinct compositional variations.

For compositional changes to be identified more precisely further Gas Chromatography-Mass Spectroscopy (GC-MS) fingerprinting is needed. GC-MS analysis was conducted as described in Section 2.2.2. The GC-MS total ion current (TIC) chromatograms allow the direct identification of compounds within the oil. Specific ions can also be extracted from the chromatogram to make it easier to identify specific compounds. The TIC chromatogram for the aliphatic extract (Fig. 3.4) and the mass chromatograms of m/z 57 (Fig. 3.5), 191 (Fig. 3.6) and 217 (Fig. 3.7) are shown. The only aliphatic fractions to retain a series of n -alkanes were the Colombian samples (Fig. 3.4b) therefore, pyrolysis of the asphaltene fractions was also performed to retrieve information on n -alkanes lost in the aliphatic fractions due to biodegradation. The pyrolysis-GC-MS data for the asphaltene fractions from the four sets of samples are presented in Figure 3.9. Selected molecular parameters are outlined in Table 3.3 and 3.4 to enable the characterisation of source maturity and biodegradation of the oils. All aliphatic hydrocarbon chromatograms (TIC, m/z 57, m/z 191, m/z 217) can be found in Appendix 1.1 and the asphaltene TIC and m/z 57 can be found in Appendix 1.2 for each sample in this study.

3.3.2 Molecular composition of oils

Representative GC-MS total ion current chromatograms for the aliphatic fractions from the four sets of samples are presented in Figure 3.4. The whole chromatogram for the saturate hydrocarbons (aliphatics) can give information about what compounds have been retained/lost within the sample. The most notable components in the aliphatic fractions are the series of n -alkanes retained within the set of Colombian samples and their absence in all other samples. All sets of samples display an unresolved complex mixture (UCM) to differing degrees (small UCM in Colombian samples and no UCM in sample C127.4). In the UK, Canadian and Indonesian samples the UCM is very prominent and is comprised of many aromatic and polar compounds as identified by the clear correlation of increased relative weights of aromatic and polar elutes with the presence of a UCM (Table 3.2, Figs. 3.1 and 3.2). The Colombian samples have a much smaller UCM of mainly branched and cyclic aliphatic material (due to the low abundance of polar components and absence of asphaltenes in the samples (Table 3.2)). The UK, Canadian and Indonesian samples show no n -

alkane retention but larger abundances of hopanes and steranes indicating altered/biodegraded oils. The identification of specific biomarkers (Section 1.4.6) can allow the degree of biodegradation to be obtained as well as identifying the maturity and source of the oils. The following section records the characterisation of these oils.

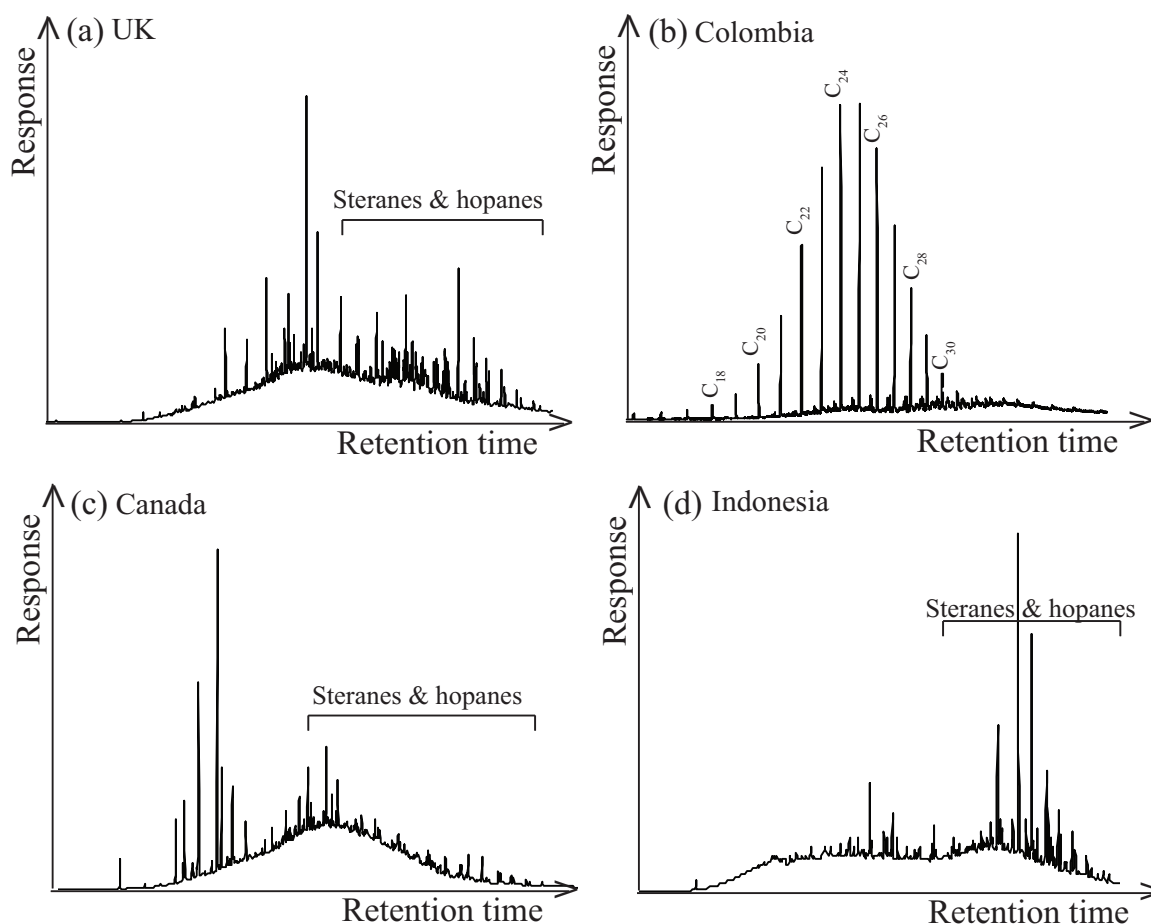


Figure 3.4. Representative TIC chromatograms of the aliphatic hydrocarbon fractions for the four sets of samples within this study. (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian samples.

3.3.2.1 *n*-Alkanes

The series of *n*-alkanes retained within the set of Colombian samples are easily identifiable within Figure 3.5. The absence of similar systematic peaks throughout the aliphatic fractions for all the other samples reveals the absence of *n*-alkanes within the samples (other than low levels of contamination). Individual chromatograms for *m/z* 57 which are used to identify *n*-alkanes are in Appendix 1.1 (aliphatics) and 1.2 (asphaltenes). The prominent *n*-alkanes in the Colombian samples range from *n*-C₁₅ to *n*-C₃₃ (Fig. 3.5, Table 3.3) and exhibit a unimodal distribution and have no

overwhelming odd-dominance. The Colombian samples are the only sample set to retain *n*-alkanes suggesting low alteration of the samples in comparison to the UK, Canadian and Indonesian samples, which must have experienced biodegradation to remove these compounds.

m/z 57

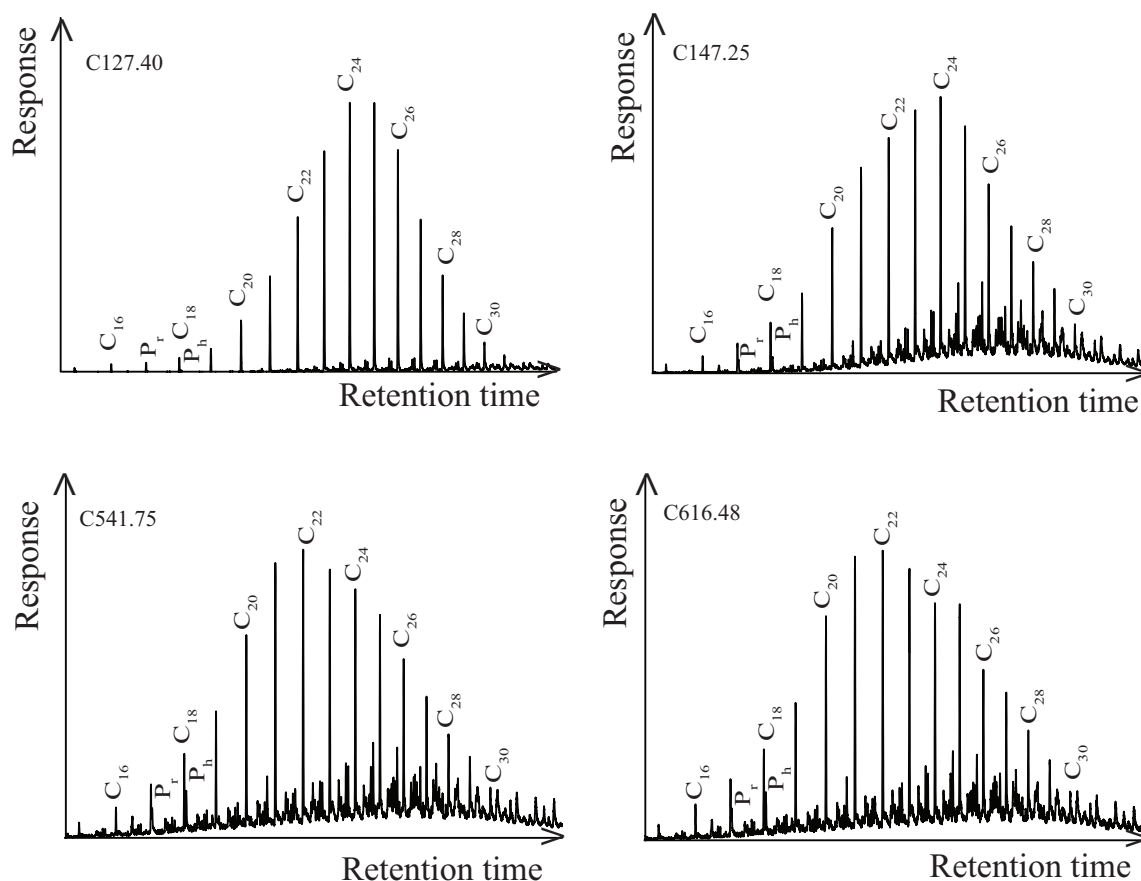


Figure 3.5. Mass chromatograms (*m/z* 57) of the aliphatic hydrocarbon fractions in the Colombian samples to identify *n*-alkanes. C₁₆-C₃₀ = C₁₆-C₃₀ *n*-alkanes, Pr= Pristane, Ph= Phytane.

Isoprenoidal hydrocarbons are also present in the Colombian samples with pristane and phytane the most notable representatives of this compound class. Pristane/phytane ratios vary between 0.53-0.65 and the ratios of pristane: normal C₁₇-alkane (Pr/*n*-C₁₇) and phytane: normal C₁₈-alkane (Ph/*n*-C₁₈) (Table 3.3) which are used as indicators of source environment, kerogen type and oil biodegradation are between 0.33-0.79 and 0.26-0.87 for ratios of Pr/*n*-C₁₇ and Ph/*n*-C₁₈ respectively (Table 3.3).

3.3.2.2 Hopanes

Ion selection can allow the separation and identification of hopanes (*m/z* 191) (Fig. 3.6) without the interference of other compounds.

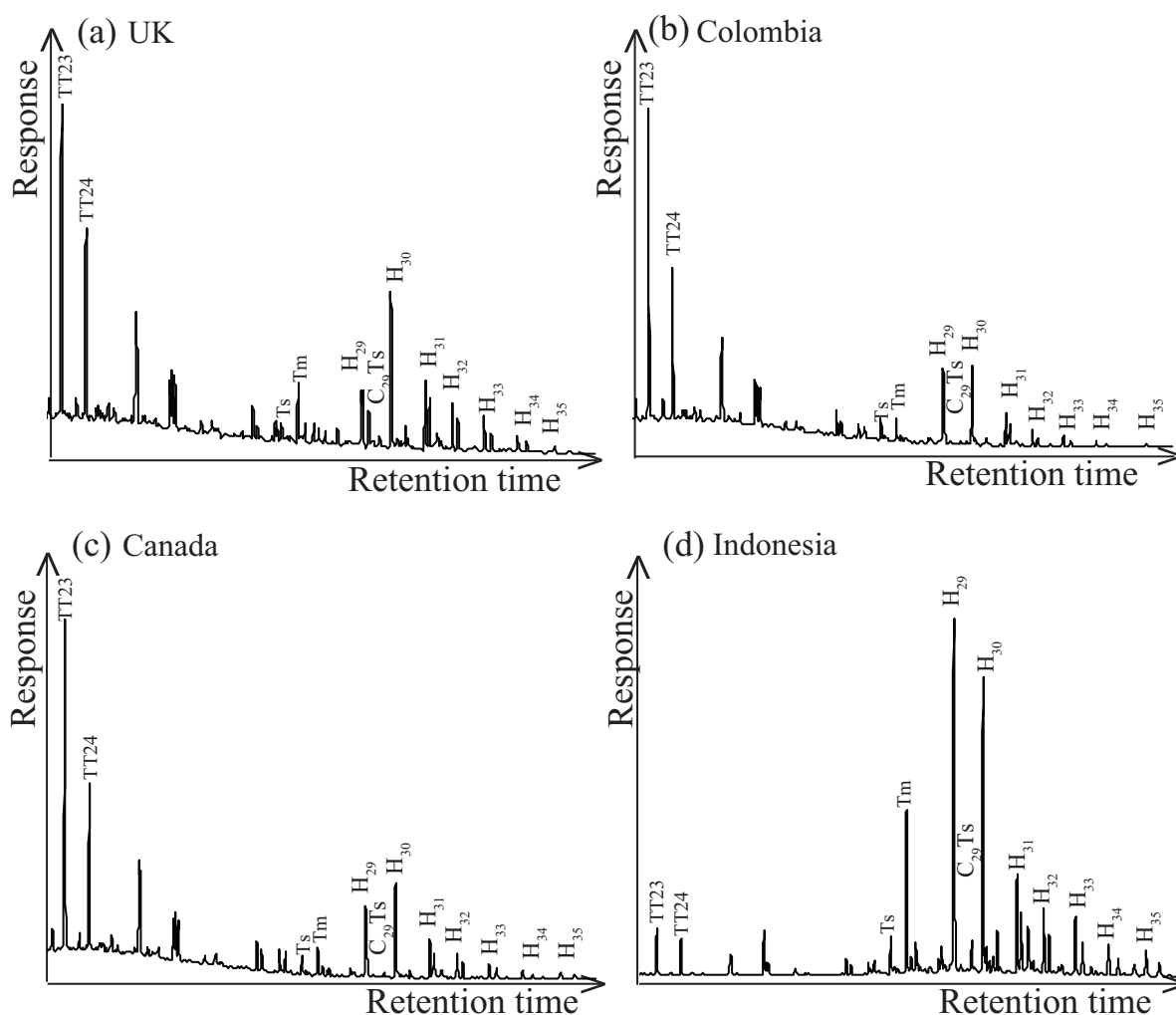


Figure 3.6. Representative mass chromatograms (m/z 191) of the aliphatic hydrocarbon fractions to identify hopanes for the four sets of samples, (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian samples. Compounds used for biomarkers are highlighted. Ts–C₂₇ 18 α trisnorhopane, Tm–C₂₇ 17 α trisnorhopane, C₂₉Ts–18 α -30-norneohopane, sequence of H₂₉–H₃₅ = C₂₉–C₃₅ hopanes.

In the m/z 191 mass chromatograms, the homohopanes extend to C₃₅ with a steady decrease in response with carbon number for every set of samples from C₃₀. The UK samples show a much lower abundance of C₂₉ compared to C₃₀ (Fig. 3.6a) with the Canadian samples revealing the same behaviour but to a lesser degree (Fig. 3.6c). The Colombian samples, however, have approximately the same abundance of C₂₉ and C₃₀ (Fig. 3.6b) whereas the Indonesian samples show much higher abundances of C₂₉ than C₃₀ (Fig. 3.6d). Responses from Ts and Tm are identified in all the samples with ratios between 0.50-0.61, 0.52-0.56, 0.52-0.59, and 0.50-0.63 for the UK, Canadian, Colombian and Indonesian samples respectively (Fig. 3.6, Table 3.4). All sets of hopanes show the

normal elution order as described in Section 1.4.7 and biomarker ratios were obtained from the chromatogram and are represented in Table 3.4, e.g., $C_{29}Ts/C_{30}\alpha\beta$ and $C_{30}(\beta\alpha/\alpha\beta)$.

3.3.2.3 Steranes

Ion selection at m/z 217 allows the identification of steranes and diasteranes (Fig. 3.7) for biomarker investigations.

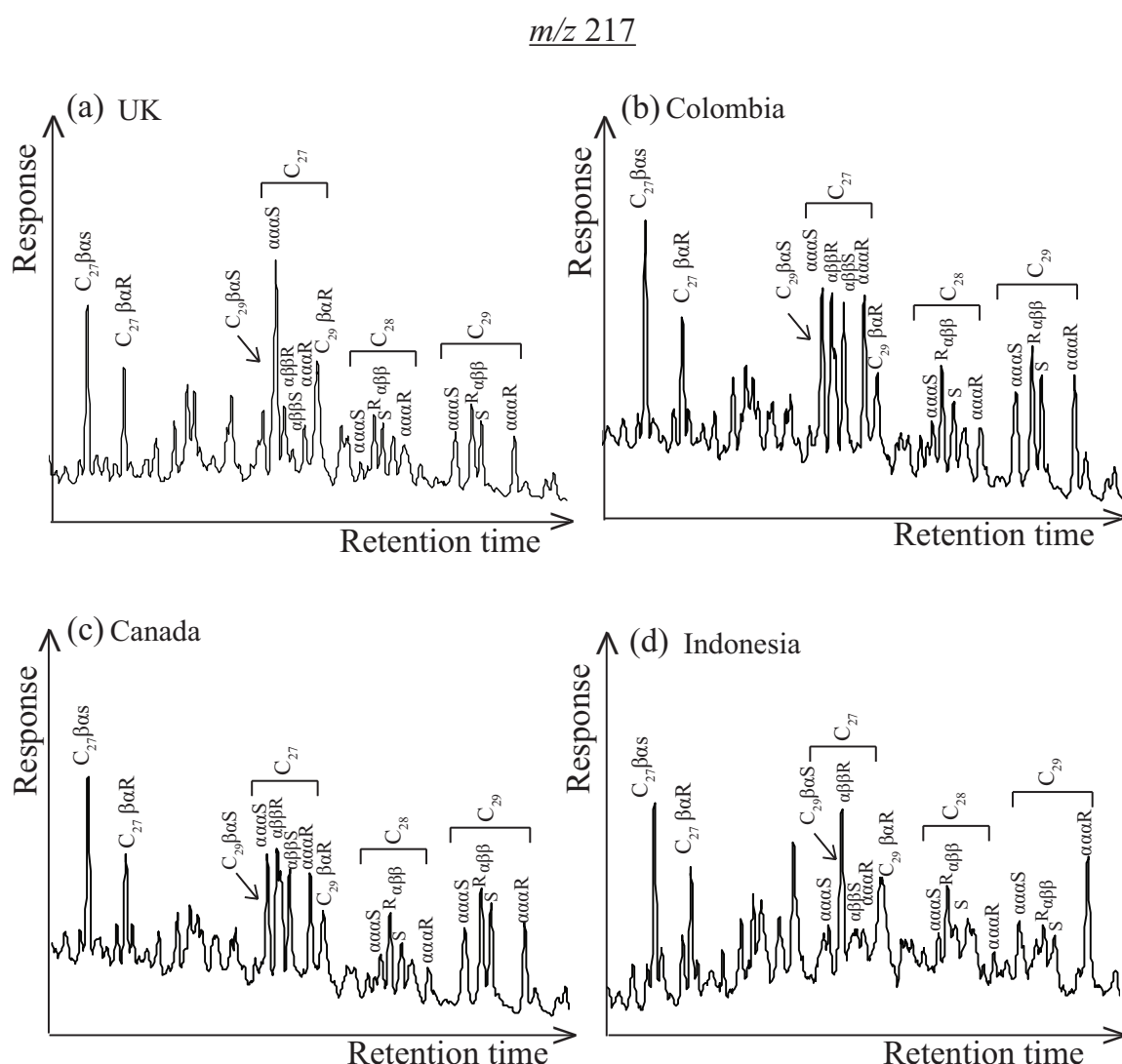


Figure 3.7. Mass chromatograms (m/z 217) of the aliphatic hydrocarbon fractions to identify steranes for the four sets of samples, (a) UK, (b) Colombian, (c) Canadian and (d) Indonesian. C_{27} – $C_{29}\beta\alpha(S+R)$ – C_{27} – C_{29} diasteranes. C_{27} – $C_{29}(\alpha\alpha\alpha(S+R)$ and $\alpha\beta\beta(S+R)$ are elution orders for C_{27} – C_{29} steranes.

In the m/z 217 mass chromatograms, all four sets of samples contain strong responses from C_{27} regular steranes ($\alpha\alpha\alpha S$, $\alpha\beta\beta R$, $\alpha\beta\beta S$ and $\alpha\alpha\alpha R$) with less dominant responses from their C_{28} and C_{29}

counterparts. Diasteranes ($\beta\alpha S$ and $\beta\alpha R$) are also noticeable in all the m/z 217 mass chromatograms between C_{27} - C_{29} . All sets of steranes and diasteranes show the normal elution order as described in Section 1.4.7 and biomarker ratios have been recorded from the chromatograms and are represented in Table 3.4, e.g., C_{29} $\alpha\alpha\alpha$ (S/S+R), C_{29} (diasterane/diasterane+steranes) and C_{27}/C_{29} ($\beta\alpha$ diasterane).

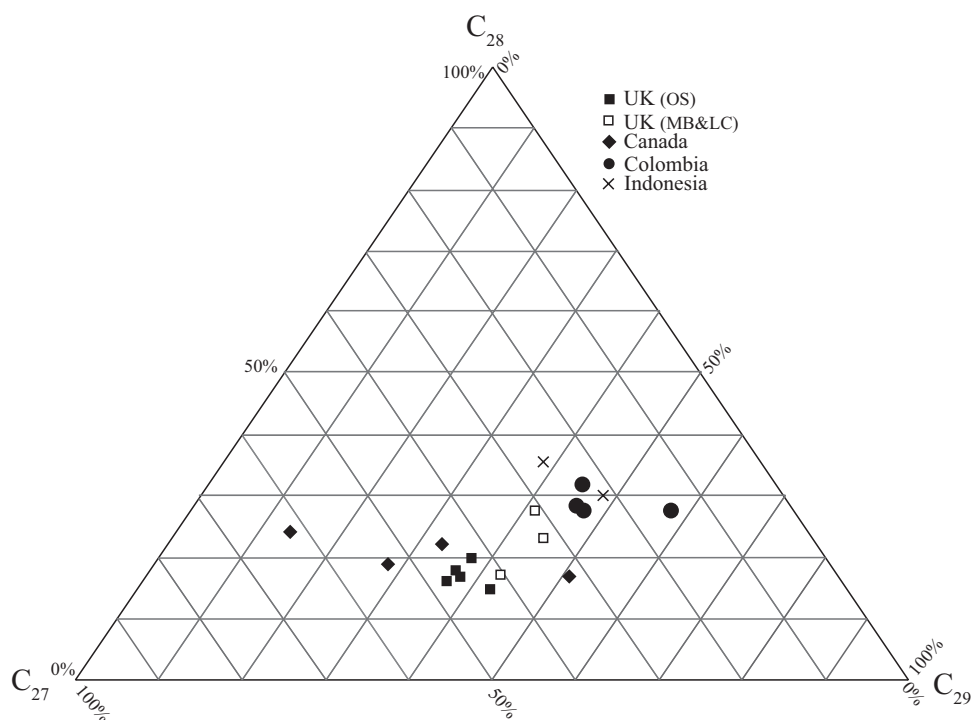


Figure 3.8. The aliphatic hydrocarbon fractions for C_{27} , C_{28} and C_{29} $\beta\beta$ steranes from m/z 217 for all the samples in this study.

The percentage of C_{27} , C_{28} and C_{29} $\beta\beta$ ratios are represented in Figure 3.8. The relative abundance of C_{27} , C_{28} and C_{29} $\beta\beta$ steranes can be used to help determine source material and environment and clearly shows separation of the sample sets. The Colombian samples have much higher C_{29} abundances compared to the Canadian and UK samples, which show higher percentages of C_{27} steranes. The Indonesian samples have the highest proportions of C_{28} of all the samples.

3.3.3 Molecular composition of asphaltenes

Asphaltenes can retain information about the source material, as they are less susceptible to alteration than the aliphatic fractions, because they are more resilient to microbial attack.

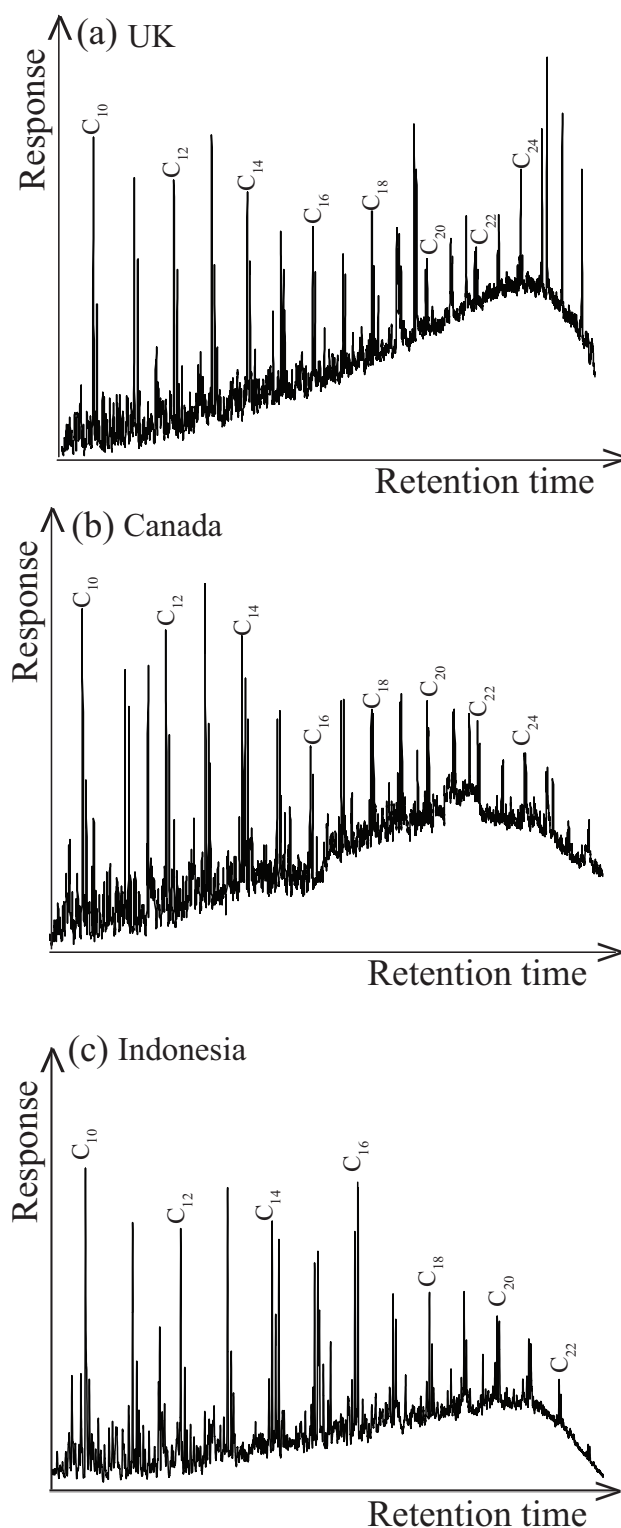


Figure 3.9. Representative TIC stereograms of the asphaltene fractions for (a) UK, (b) Canadian and (c) Indonesian samples. The Colombian samples produced no asphaltenes.

The Colombian samples had no asphaltene fractions but retained their *n*-alkanes within their aliphatic fraction, therefore, a comparison is made between the asphaltene *n*-alkanes within the UK, Canadian and Indonesian and the *n*-alkanes retained in the Colombian aliphatic fractions (Table

3.3). Representative GC-MS total ion current chromatograms for the asphaltene fractions from the three sets of samples are presented in Figure 3.9.

The prominent *n*-alkanes in the Canadian samples range from *n*-C₉ to *n*-C₃₀ (Fig. 3.9, Table 3.3) and exhibit a unimodal distribution with a mode at *n*-C₁₂ in all but one sample (A3B), which displays a bimodal distribution with corresponding modes of *n*-C₁₀ and *n*-C₂₆. The UK samples all displayed *n*-alkanes between *n*-C₉ to *n*-C₃₁. They have bimodal distributions with modes typically at *n*-C₁₀₋₁₁ and *n*-C₂₄₋₂₆. The prominent *n*-alkanes in the Indonesian samples range from *n*-C₁₁ to *n*-C₃₁ and exhibit a unimodal distribution with a mode at *n*-C₁₀₋₁₁ (Fig. 3.9, Table 3.3).

There is no overwhelming odd-dominance in the *n*-alkanes in any of the samples suggesting little/no contribution from higher plant matter and they all have a noticeable UCM. The UCM is most likely comprised of aromatic and polar compounds. Pristane and phytane can also be identified with pristane/phytane ratios approaching 0.5 for most of the UK samples (Table 3.3), but are higher within the Canadian samples (0.67-0.90) and the Indonesian samples (0.76-0.83). The ratios of pristane: normal C₁₇-alkane (Pr/*n*-C₁₇) and phytane: normal C₁₈-alkane (Ph/*n*-C₁₈) (Table 3.3) for the UK, Canadian and Indonesian samples have been taken from the asphaltene fractions which retain information lost in the aliphatic fractions through biodegradation, therefore information on biodegradation cannot be inferred, however, the ratios can be used to deduce source environment (Section 3.2.4). The Colombian samples show relatively higher ratios of Ph/*n*-C₁₈ and Pr/*n*-C₁₇ compared to the other samples because the ratios were determined from *n*-alkanes in their saturate hydrocarbons.

Table 3.3 Summary of analytical results of *n*-alkane retention for the samples from this study taken from the ion specific chromatogram *m/z* 57.

Sample	<i>n</i> -Alkanes			Isoprenoids			Maturity
	Range	Distribution	Peak	Pr/Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈	Odd/Even
OS2	C ₉ -C ₃₁	Bimodal	C ₁₁ , C ₂₆	0.55	0.10	0.19	1.00
OS3	C ₉ -C ₃₁	Bimodal	C ₁₁ , C ₂₅	0.54	0.13	0.24	0.97
OS4	C ₉ -C ₃₁	Bimodal	C ₁₁ , C ₂₄	0.62	0.11	0.18	0.95
OS5	C ₉ -C ₃₁	Bimodal	C ₁₁ , C ₂₆	0.49	0.11	0.23	0.92
OS6	C ₉ -C ₃₁	Bimodal	C ₁₀ , C ₂₆	0.49	0.10	0.23	0.81
MBM	C ₉ -C ₃₁	Bimodal	C ₁₁ , C ₂₆	0.54	0.11	0.25	0.94
MBC	C ₉ -C ₃₁	Bimodal	C ₁₁ , C ₂₆	0.70	0.15	0.24	1.00
LC	C ₉ -C ₃₁	Bimodal	C ₁₃ , C ₂₅	0.57	0.13	0.26	0.87
A1B	C ₉ -C ₃₀	Unimodal	C ₁₂	0.74	0.13	0.19	0.95
A3B	C ₉ -C ₃₀	Bimodal	C ₁₀ C ₂₆	0.86	0.14	0.19	1.16
A827.32	C ₉ -C ₃₀	Unimodal	C ₁₂	0.90	0.12	0.15	1.02
A827.75	C ₉ -C ₃₀	Unimodal	C ₁₂	0.67	0.12	0.19	1.01
C127.40*	C ₁₅ -C ₃₃	Unimodal	C ₂₄	0.65	0.33	0.26	0.96
C147.25*	C ₁₅ -C ₃₃	Unimodal	C ₂₄	0.54	0.61	0.49	1.02
C541.75*	C ₁₅ -C ₃₁	Unimodal	C ₂₂	0.56	0.79	0.87	0.98
C616.48*	C ₁₅ -C ₃₁	Unimodal	C ₂₂	0.53	0.68	0.81	0.97
KI	C ₉ -C ₃₁	Unimodal	C ₁₀	0.83	0.09	0.19	0.98
LI	C ₉ -C ₃₁	Unimodal	C ₁₁	0.76	0.10	0.17	0.95

Pr/Ph: Pristane/phytane

Pr/*n*-C₁₇: pristane: normal C₁₇-alkane

Ph/*n*-C₁₈: phytane: normal C₁₈-alkane

Odd/Even: C₂₁+6C₂₃+C₂₅/4C₂₂+4C₂₄

*Data taken from saturate hydrocarbon

Table 3.4 Summary of analytical results of hopanes and steranes for the samples from this study taken from ion specific chromatograms, m/z 191 and 217 respectively.

Sample	C_{27}/C_{29} ($\alpha\alpha\alpha R$)	C_{27}/C_{29} ($\beta\alpha$ dia)	$C_{29}Ts/C_{29}$ $\alpha\beta$	$C_{29} Tri/ C_{30}$ $\alpha\beta$	Ts/Ts+Tm	$C_{29} \alpha\alpha\alpha$ (S/S+R)	$C_{30} (\beta\alpha/\alpha\beta)$	$C_{29} Dia/dia+ste$	$C_{29} \beta\beta/(\alpha\alpha+\beta\beta)$
OS2	0.47	0.39	0.97	0.19	0.53	0.56	0.15	0.50	0.55
OS3	0.29	0.29	0.81	0.15	0.50	0.56	0.18	0.37	0.56
OS4	0.63	0.47	0.87	0.26	0.51	0.69	0.16	0.48	0.60
OS5	0.48	0.39	1.06	0.25	0.53	0.59	0.17	0.51	0.54
OS6	0.46	0.47	1.08	0.22	0.54	0.55	0.15	0.46	0.56
MBM	0.50	0.40	0.66	0.23	0.61	0.49	0.13	0.47	0.53
MBC	0.49	0.38	0.69	0.21	0.52	0.57	0.16	0.44	0.51
LC	0.35	0.47	0.60	0.17	0.52	0.44	0.16	0.27	0.53
A1B	0.81	0.66	0.20	0.36	0.56	0.62	0.08	0.55	0.60
A3B	0.84	0.63	0.16	0.68	0.55	0.44	0.09	0.71	0.44
A827.32	0.74	0.72	0.30	0.70	0.52	0.57	0.08	0.38	0.52
A827.75	0.51	0.58	0.21	0.41	0.53	0.55	0.07	0.28	0.53
C127.40	0.43	0.52	0.46	0.17	0.52	0.53	0.12	0.23	0.53
C142.25	0.50	0.62	0.21	0.18	0.59	0.52	0.09	0.22	0.51
C541.75	0.09	0.54	0.24	0.16	0.54	0.57	0.12	0.25	0.53
C616.48	0.54	0.55	0.30	0.23	0.59	0.52	0.12	0.25	0.56
KI	0.32	0.33	0.75	0.10	0.50	0.56	0.20	0.24	0.40
LI	0.34	0.43	0.79	0.10	0.63	0.45	0.11	0.48	0.42

C_{27}/C_{29} ($\alpha\alpha\alpha R$): $C_{27}\alpha\alpha\alpha R/ C_{29}\alpha\alpha\alpha R$ steranes

C_{27}/C_{29} ($\beta\alpha$ dia): $C_{27}\beta\alpha(S+R)/ C_{29}\beta\alpha(S+R)$

$C_{29} Ts/ C_{29} \alpha\beta$: $C_{29} 18\alpha$ norneohopane/ $C_{29}\alpha\beta$ hopane

$C_{29} Tri/ C_{30} \alpha\beta$: C_{29} tricyclic terpane/ $C_{30}\alpha\beta$ hopane

Ts/Ts+Tm: $C_{27} 18\alpha$ trisnorhopane/ ($C_{27} 18\alpha$ trisnorhopane + $C_{27} 17\alpha$ trisnorhopane)

$C_{29} \alpha\alpha\alpha$ (S/S+R): $C_{29}\alpha\alpha\alpha S/ (C_{29}\alpha\alpha\alpha S + C_{29}\alpha\alpha\alpha R)$ steranes

$C_{30} (\beta\alpha/\alpha\beta)$: $C_{30}\beta\alpha$ moretane/ $C_{30}\alpha\beta$ hopane

Dia/dia+steranes: C_{29} diasterane/ (C_{29} diasterane + C_{29} sterane)

$C_{29} \beta\beta/(\alpha\alpha+\beta\beta)$: $C_{29} \alpha\beta\beta(S+R)/ (C_{29} \alpha\alpha\alpha(S+R) + C_{29} \alpha\beta\beta(S+R))$

3.3.4 Source

The *n*-alkane distributions (Figs. 3.5, 3.9, Table 3.3) can be used to infer source material because generally lower molecular weight ($<C_{21}$) *n*-alkanes are derived from bacteria and algae (Wakeham, 1990) but high molecular weight ($>C_{22}$) *n*-alkanes generally originate from higher plants (Huang et al., 1999). All the samples show *n*-alkanes between *n*-C₉ to *n*-C₃₀ with modes between *n*-C₁₀ to *n*-C₁₂ suggesting they are derived from marine algae. There is no evidence for a great odd preference (odd numbered carbons) for *n*-C₂₉, *n*-C₃₁ and *n*-C₃₃ alkanes associated with higher plant components in immature organic assemblages in any of the samples. The predominance of C₂₇ regular steranes (Fig. 3.10) in all samples also implies a marine, algal organic matter dominated source rock (Huang & Meinschein, 1979). Any variation within the sample sets, e.g. Canadian sands, could be the result of facies changes over the large sampling area. The Colombian sample C127.40 is the only sample to show possible contributions from higher plant matter, this is discussed in detail in Chapter 5. The presence of diasteranes in the oils (Table 3.4) may indicate that the source rock from which the oils were derived had significant amounts of clay minerals in its matrix (Rubinstein et al., 1975; Van Kaam-Peters et al., 1998) although biodegradation is another mechanism by which these organic compounds can be enhanced (Wenger et al., 2001).

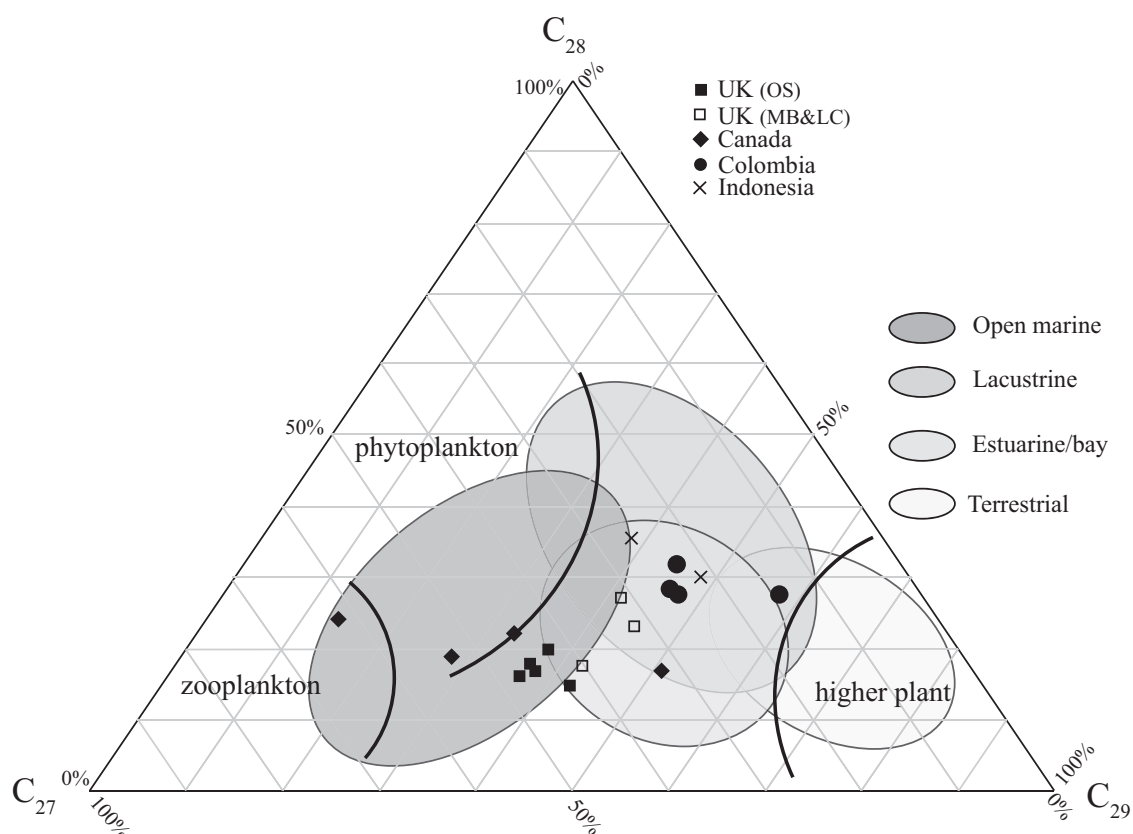


Figure 3.10. Sterol distribution (relative abundance of C₂₇, C₂₈ and C₂₉ steranes) in relation to environment and source organisms after Huang & Meinschein (1979). All samples from this study are plotted.

The ratio of pristane: phytane can help infer the oxygenation of the environment with higher ratios indicative of oxic conditions (>1) and very low ratios for hypersaline conditions (<0.5) (Didyk et al., 1978). The pristane/phytane concentrations for all the samples vary between 0.49-0.83 (Table 3.3) suggesting the organic matter was deposited in an anoxic environment (Didyk et al., 1978; Ten Haven et al., 1987). This interpretation is consistent with the responses from the trisnorhopanes Ts and Tm, which at a ratio of >0.4 are also indicative of anoxic environments (Mello et al., 1987; Farrimond et al., 1989) (Table 3.4). Ratios of pristane: normal C₁₇-alkane (Pr/*n*-C₁₇) and phytane: normal C₁₈-alkane (Ph/*n*-C₁₈) (Table 3.3) can also be used as indicators of source environment as well as biodegradation (Lijmbach, 1975). In terms of source, the relative abundances of the two ratios can help differentiate between terrestrial and marine environments (Fig. 3.11) as well as the oxygenation state of the environment. The Pr/*n*-C₁₇ and Ph/*n*-C₁₈ ratios for all the samples show a reducing, marine source with slightly more terrestrial input in the Colombian samples (Fig. 3.11), which is in agreement with all other source biomarkers. The Colombian samples reveal higher overall ratios because the data were taken from the aliphatic compounds whereas all the other samples could only have these ratios determined using the asphaltenes.

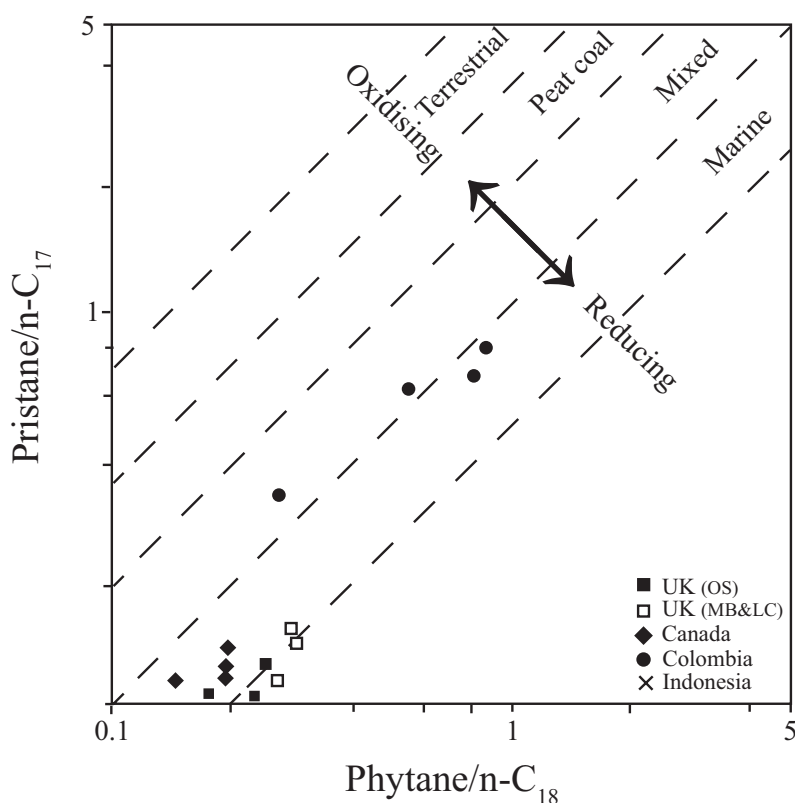


Figure 3.11. Relation between *n*-alkanes and isoprenoids to determine possible depositional and source environments (Lijmbach, 1975). The Colombian ratios are taken from their aliphatic fractions, however, the asphaltene fraction was used for the UK, Canadian and Indonesian samples giving rise to the very low ratios representing no biodegradation.

3.3.5 Maturity

Certain hopane and sterane biomarkers are responsive to thermal maturation and can allow estimation of the relative maturity of oils. Various biomarker maturity parameters (Tables 3.3 and 3.4) indicate that the organic matter in all the samples are mature. For example, no overwhelming odd preference in *n*-alkanes (~ 1) implies the oils are not immature (Table 3.3) and Figure 3.12 shows the percentage ratios of the $C_{29}(S/(S+R))$ and $C_{29}(\beta\beta/(\alpha\alpha+\beta\beta))$ steranes which can help deduce maturity levels due to their relative increase with increasing maturity. Although the Indonesian samples and one Canadian sample (A827.32) show relatively lower ratios than the other samples, the data suggest a maturity that corresponds with the oil being generated just after the rock has entered the oil window. All oils show a similar level of maturity.

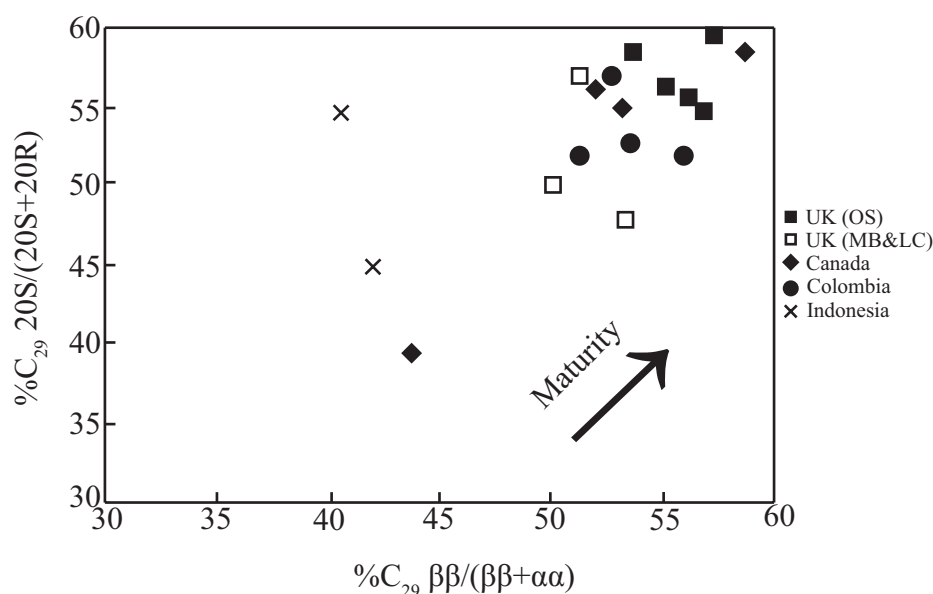


Figure 3.12. Correlation of maturity parameters using $C_{29}(S/(S+R))$ and $C_{29}(\beta\beta/(\alpha\alpha+\beta\beta))$ steranes biomarkers.

The maturity biomarkers presented in Table 3.4 include $C_{30}\beta\alpha/\alpha\beta$ ratios between 0.07-0.18 (oil window <0.15) as well as $C_{29}\alpha\alpha\alpha$ sterane ratios ($S/S+R$) between 0.44-0.69 (oil window >0.4) and T_s/T_s+T_m between 0.50-0.63 (oil window >0.4) (Fig. 3.12, Table 3.3 and 3.4) which all agree that the samples have been heated to temperatures consistent with the oil window.

3.3.6 Biodegradation

Biodegradation research (Wenger et al., 2001; Wenger & Isaksen, 2002) shows that aliphatic hydrocarbons are preferentially biodegraded and lighter components such as the aromatic hydrocarbons can be lost through water washing. Therefore, differences in bulk composition in terms of aliphatic and polar components (Fig. 3.1) are most likely the result of these two processes.

The aliphatic abundance is greatest in the Colombian samples and decreases in the UK (OS), Canadian, Indonesian and UK (MB & LC) samples respectively. This suggests that the biodegradation state also increases in this order within the samples (Fig. 3.1).

Ratios of $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ (Table 3.3) can also be used as an indicator for biodegradation because the isoprenoidal hydrocarbons (pristane and phytane) are more resistant to degradation than normal alkanes ($n\text{-C}_{17}$ and $n\text{-C}_{18}$), an increase in the relative ratios ($\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$) occur when the oils are biodegraded (Fig. 3.11) (Lijmbach, 1975). Only the Colombian samples had these compounds present within their aliphatic fractions and displayed ratios between 0.32-0.79 and 0.26-0.87 for $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ respectively (Fig. 3.11), which are considered low biodegradation levels. The ratios of $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ in Table 3.3 for the UK, Canadian and Indonesian samples cannot be used to infer biodegradation because they were analysed from the asphaltene fraction not the aliphatic hydrocarbons, however, the absence of these compounds from the aliphatic fractions suggests high levels of biodegradation relative to the Colombian samples (Wenger et al., 2001).

Sterane biomarkers (Table 3.4) also display variable responses to biodegradation with regular steranes being more susceptible than diasteranes. The UK, Canadian and Indonesian samples contain abundant diasteranes, but discriminating between source effects and subsequent biodegradation processes is difficult. Overall, the GC-MS data suggest that the Colombian, UK, Canadian and Indonesian oils are all biodegraded and increase in biodegradation respectively.

3.3.7 Geochemical summary

All the oils within the study are derived from type II kerogens deposited in oxygen poor environments (Tables 3.2-3.4 and Figs. 3.1-3.12). The samples are from a marine source except for sample C127.40, which might have a small contribution from higher plant matter as well. The data

suggest a maturity that corresponds with the oil being generated just after the rock has entered the oil window. The samples have a similar source and maturity but have significant differences in the level of biodegradation experienced. The intensity of biodegradation increases from the Colombian, UK (OS), Canadian, UK (MB & LC) and Indonesian oils allowing an examination of the relationship between biodegradation and magnetisation.

3.4 Magnetic characterisation of oil impregnated sedimentary units

All results from the magnetisation investigation can be found in Appendix 2.1. Representative samples have been chosen to demonstrate the different behaviour within the sample sets. Where possible, both the oil stained and clean counterpart samples were magnetically investigated.

3.4.1 Magnetic susceptibility

Magnetic susceptibility at room temperature was measured at least three times for each oil-stained and cleaned sample and averaged. The magnitude of mass normalized magnetic susceptibility varied between $10^{-4} \text{ m}^3\text{kg}^{-1}$ for the Colombian samples, 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for UK, 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for Canadian and 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for the Indonesian samples (Table 3.5). The majority of the samples displayed increased susceptibilities after cleaning, however, most of the UK samples (OS2, OS3, OS6, MBM, MBC, LC) and one Canadian sample (A827.75) showed the opposite trend. This variation in magnetic signature from oil extraction is investigated in Section 3.5.

Table 3.5 The magnetic parameters measured for the oil impregnated samples within this study and the cleaned counterparts. Results for susceptibility, hysteresis parameters and SIRM curves.

Sample	χ ($10^{-5} \text{ m}^3 \text{ kg}^{-1}$)		H_{cr} (mT)		H_c (mT)		M_s ($10^{-3} \text{ Am}^2 \text{ kg}^{-1}$)		M_{rs}/M_s		MDF (mT)	
	O	C	O	C	O	C	O	C	O	C	O	C
OS1	7.70	...	30.4	...	10.0	...	0.44	...	0.11	...	28	...
OS2	6.19	5.08	46.0	41.0	11.1	15.8	1.79	0.78	0.13	0.09	34	36
OS3	1.49	1.30	35.4	37.1	10.7	10.5	0.81	0.73	0.13	0.13	32	30
OS4	1.15	1.43	37.7	36.6	11.2	11.3	1.24	0.56	0.14	0.14	30	29
OS5	1.60	1.76	38.0	38.0	11.5	11.5	1.69	1.69	0.11	0.11	32	31
OS6	1.30	1.22	34.8	30.8	12.8	14.8	0.78	0.72	0.15	0.16	31	30
MBC	0.46	0.43	33.7	35.5	10.7	8.74	0.71	0.55	0.11	0.10	25	21
MBM	0.55	0.49	40.7	31.8	8.34	8.88	0.39	0.43	0.12	0.13	27	22
LC	0.38	0.47	38.1	38.9	10.6	8.18	0.55	0.92	0.12	0.11	25	22
A1B	0.50	0.64	40.5	34.7	11.8	8.92	1.05	0.79	0.12	0.10	28	24
A3B	4.11	5.19	54.2	38.5	13.3	7.85	1.04	0.76	0.11	0.07	46	37
A827.32	0.17	0.22	23.1	21.9	5.38	5.35	1.48	1.11	0.07	0.10	20	13
A827.75	1.51	1.82	26.2	31.2	6.79	9.08	2.41	1.71	0.07	0.08	20	19
C127.40	90.6	95.9	19.9	27.1	6.84	4.78	23.9	37.1	0.08	0.05	11	12
C147.25	34.2	43.4	28.2	25.4	5.02	4.24	31.3	79.8	0.05	0.04	14	14
C541.75	19.6	23.6	34.1	15.0	13.1	3.32	0.75	0.98	0.13	0.08	22	22
C616.48	10.0	12.3	57.9	60.4	23.8	30.3	2.03	1.59	0.28	0.34	48	47
KI	4.37	5.64	29.9	25.7	6.73	7.85	0.57	0.57	0.13	0.13	27	22
LI	0.82	0.98	41.1	22.2	9.71	12.3	0.61	0.40	0.12	0.26	36	25

EOM% = percentage of extractable organic matter, χ = magnetic susceptibility, H_{cr} = remanent coercivity, H_c = coercivity, M_{rs}/M_s = ratio of saturation remanence to saturation magnetization and M_s = saturation magnetism. MDF = Median destructive field. The samples are in two forms; O = oil-stained and C = cleaned (oil-free).

3.4.2 Magnetic mineralogy

To determine the magnetic mineralogy of the sample a combination of low temperature, room temperature and high temperature experiments were conducted and are discussed below,

3.4.2.1 Room temperature experimentation

Room-temperature hysteresis data are represented in Table 3.5. The samples were all dominated by strong paramagnetic behaviour (Fig. 3.13).

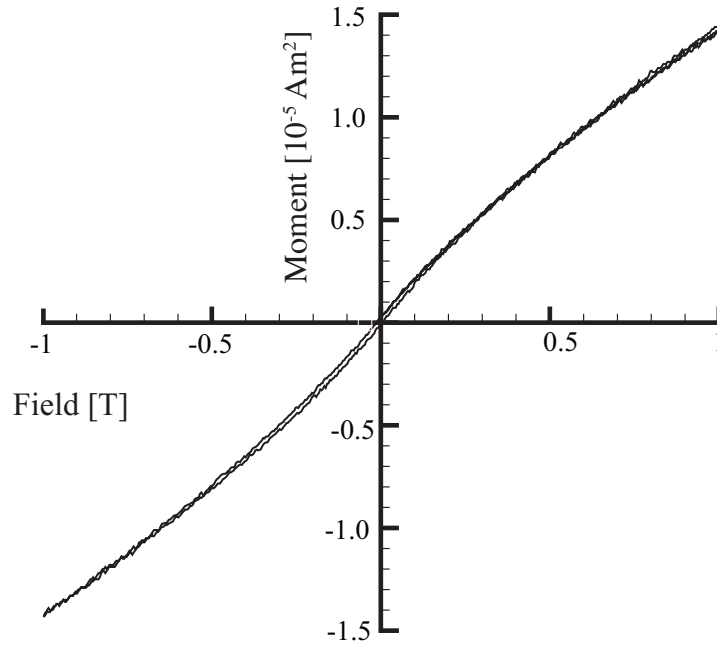


Figure 3.13. Representative hysteresis loop showing the strong paramagnetic behaviour within all the oil sands. Sample OS4.

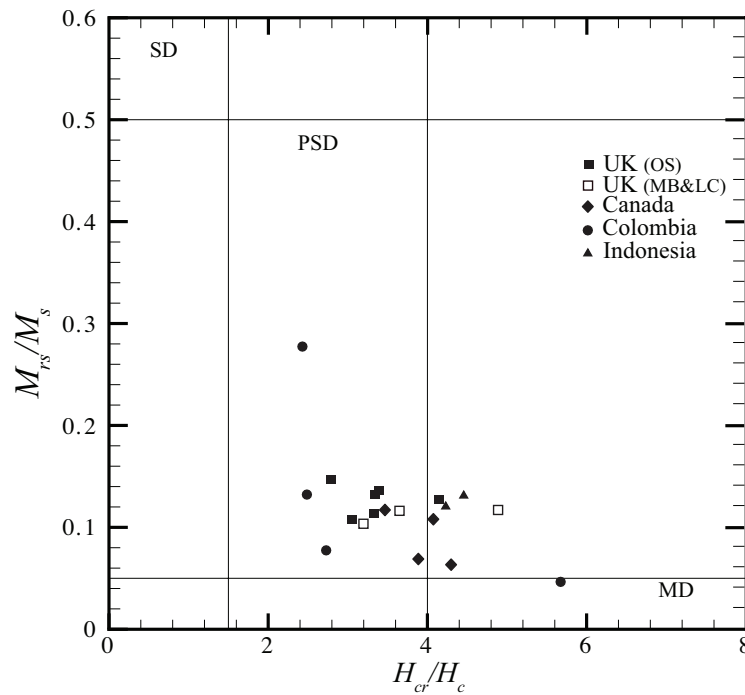


Figure 3.14. A “Day plot” (Day et al. 1977) of the ratios of the hysteresis parameters M_{rs}/M_s versus H_{cr}/H_c for the samples examined in this study. The regions commonly associated with SD, PSD and MD behaviour for magnetite are labelled for representative purposes. The oil-stained samples have been plotted and split into sample locations.

In Figure 3.14, hysteresis parameters are represented on a “Day plot” (Day et al., 1977): a plot of ratios of saturation remanence magnetisation to saturation magnetisation (M_{rs}/M_s) and remanence

coercivity to coercivity (H_{cr}/H_c). Day plots are used for distinguishing between domain-state: single domain (SD), pseudo-single domain (PSD) and multi domain (MD), which can be utilized to infer grain sizes for a given mineralogy. Details of these parameters and domain states are given in Section 1.2. All samples generally showed variations within site locations (Fig. 3.14) but all the UK samples show PSD towards MD behaviour similar to the Indonesian samples. The Canadian samples show slightly more MD behaviour whereas the Colombian samples show more PSD to SD behaviour with the exception of one sample, C127.40.

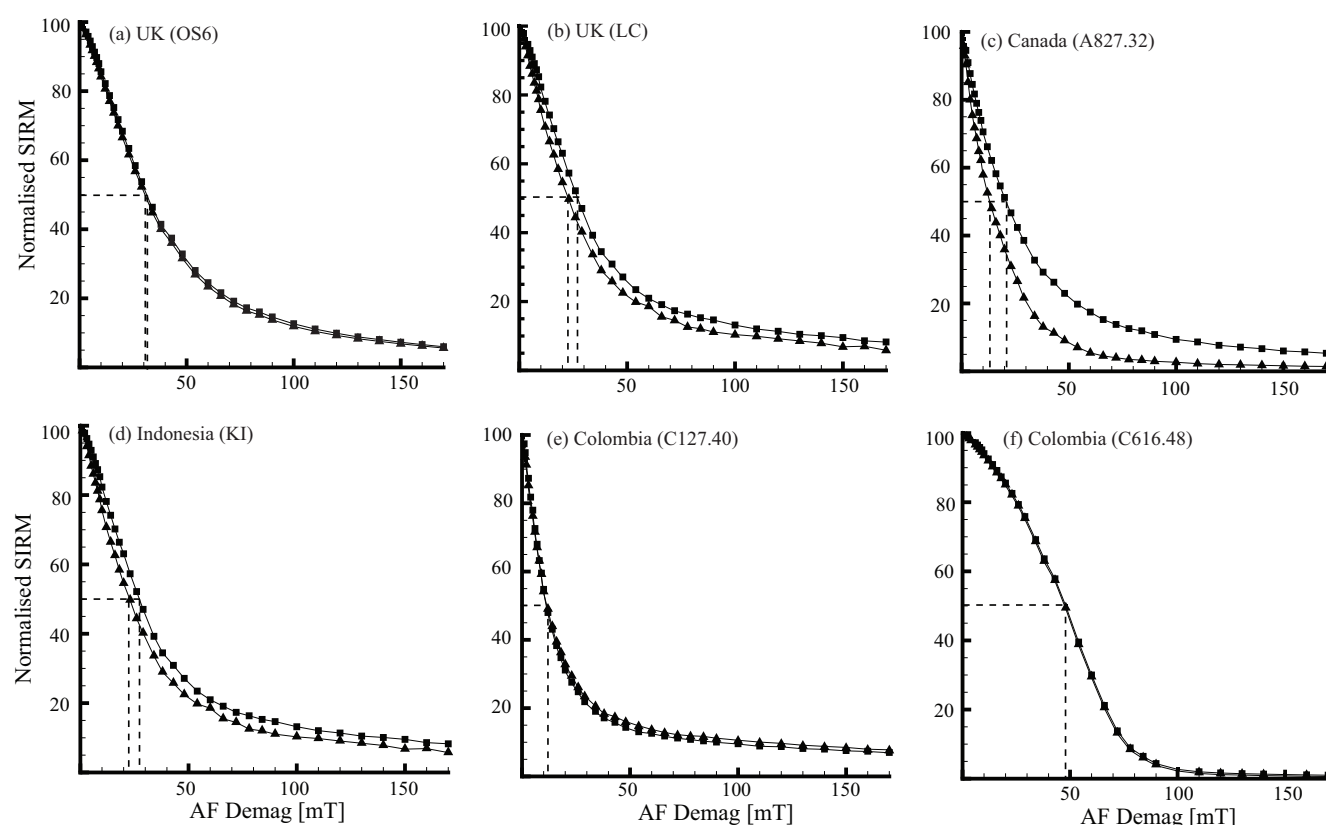


Figure 3.15. SIRM AF Demagnetisation curves for oil stained samples (squares) and cleaned samples (triangles) with MDF's (- - -). (a) UK, OS6 (b) UK, LC (c) Canada, A827.32 (d) Indonesia, KI (e) Colombia, C127.40 and (f) Colombia, C616.48.

SIRM AF demagnetisation curves (Fig. 3.15) also revealed differences in terms of median destructive fields (MDFs) between the samples (Table 3.5). The MDFs varied and were much lower for the shallow Colombian samples (C127.40 – C147.25) 11 mT and 14 mT (Fig. 3.15e) compared to all other samples. The UK (OS) samples have MDFs between 28-34 mT in comparison to 25-27 mT for UK (MB & LC), 20-28 mT for Canadian samples, 27-36 mT for the Indonesian sands and 22-48 mT (Fig. 3.15) for the deeper Colombian samples (Table 3.5) (Fig. 3.15f).

3.4.2.2 Low temperature experimentation

Warming and cooling curves of SIRM induced in different fields are displayed in Figure 3.16 including the warming curves of SIRM induced in a field of 2.5 T at 10 K after field cooling (FC) (field = 2.5 T) and zero-field cooling (ZFC). A number of different magnetic transitions can be identified by this set of experiments and these are outlined below and within Figure 3.16. The FC curves are typically at higher magnetisations than the ZFC for a given temperature except for samples OS6, C127.40 and C147.25. Sample OS6 shows a stronger remanence in the ZFC curve apposed to FC, FC remanences are usually larger than ZFC but the presence of multi domain magnetite can counter this (Carter-Stiglitz *et al.*, 2006) (Fig. 3.16a). At 10 K the FC SIRM intensity has been observed to be significantly greater than the ZFC SIRM intensity at 10 K in some of the samples (e.g., OS2 at 10 K is was $0.014 \text{ Am}^2\text{kg}^{-1}$ for FC curve and $0.003 \text{ Am}^2\text{kg}^{-1}$ for the ZFC curve). Frederichs *et al.* (2003) attributed this difference to the acquisition of thermoremanence on cooling through the Néel temperature. Both the ZFC and FC curves mostly display a steady decay to $\sim 120 \text{ K}$ at the Verwey transition for magnetite (Walz, 2002). This behaviour was observed in all but one of the Canadian samples, two (from four) Colombian samples (C127.40 and C147.25) and one (from two) Indonesian sample (KI). However the majority of UK samples and two Colombian samples (C541.75 and C616.48) display steep decays in remanence at 35-40 K on warming (Fig. 3.16c) which is indicative of the Néel transition of siderite at 37-38 K (Jacobs, 1963). Canadian sample A3B also displayed similar behaviour.

Room temperature (RT) warming and cooling SIRM curves show a divergence between 90-100 K in all the Canadian, Indonesian and Colombian samples and a significant increase at $\sim 120 \text{ K}$ indicating the presence of multi domain magnetite within all the samples (Fig. 3.16). The Colombian samples show no sign of hematite, however, sample C541.75 has a large decrease from 50 K down to 10 K. Hematite was identified within all other samples to differing degrees and was identified by the Morin transition $\sim 250 \text{ K}$ (Morin, 1950).

AC susceptibility curves as a function of frequency (Fig. 3.17) were also analysed to determine magnetic mineralogy. The curves clearly show the presence of magnetite within the two Colombian samples (C127.40 and C147.25) as well as a large frequency dependency below 100 K. The other two Colombian samples show a large frequency dependency below 50 K (Fig. 3.17c). All Canadian samples displayed similar behaviour below 50 K as well as an inflection at 120 K for magnetite comparable to the UK and Indonesian samples (to a lesser degree in OS3 and KI). The Indonesian samples also show increased frequency dependency with increasing temperature from 50 K. Low temperature frequency dependency can be due to the presence of siderite or pyrrhotite.

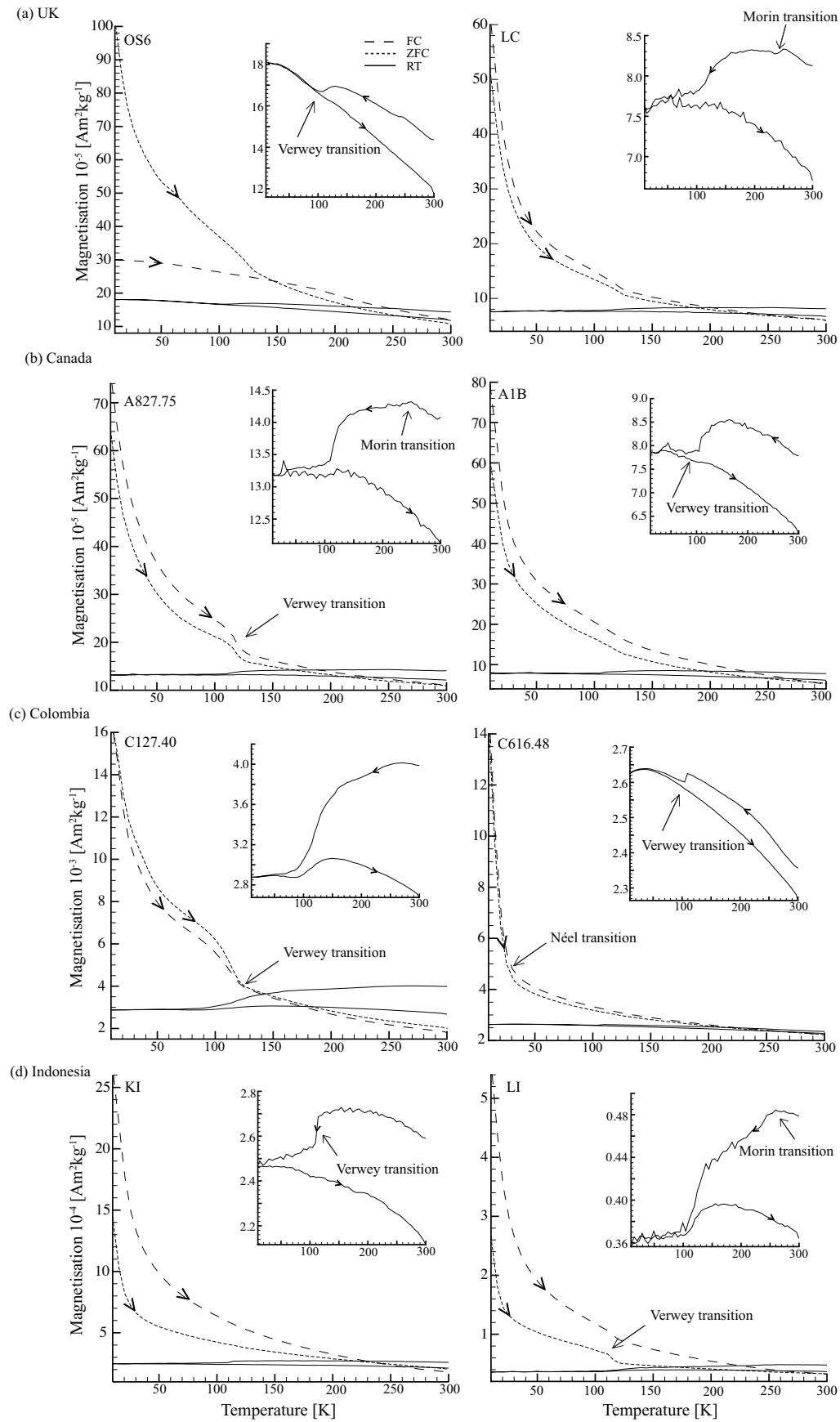


Figure 3.16. MPMS measurements for zero field cooling (ZFC), field cooling (FC) curves and room temperature remanence curves (RT) for cooling ($\leftarrow$) and warming ($\rightarrow$) from 10 K – 300 K giving information on mineralogy and grain sizes. (a) UK, OS6 & LC (b) Canada, A1B & A827.75 (c) Colombia, C127.40 & C616.48 and (d) Indonesia, KI & LI. The inset is an expanded view of the RT curves to help identification of the Verwey and Morin transitions.

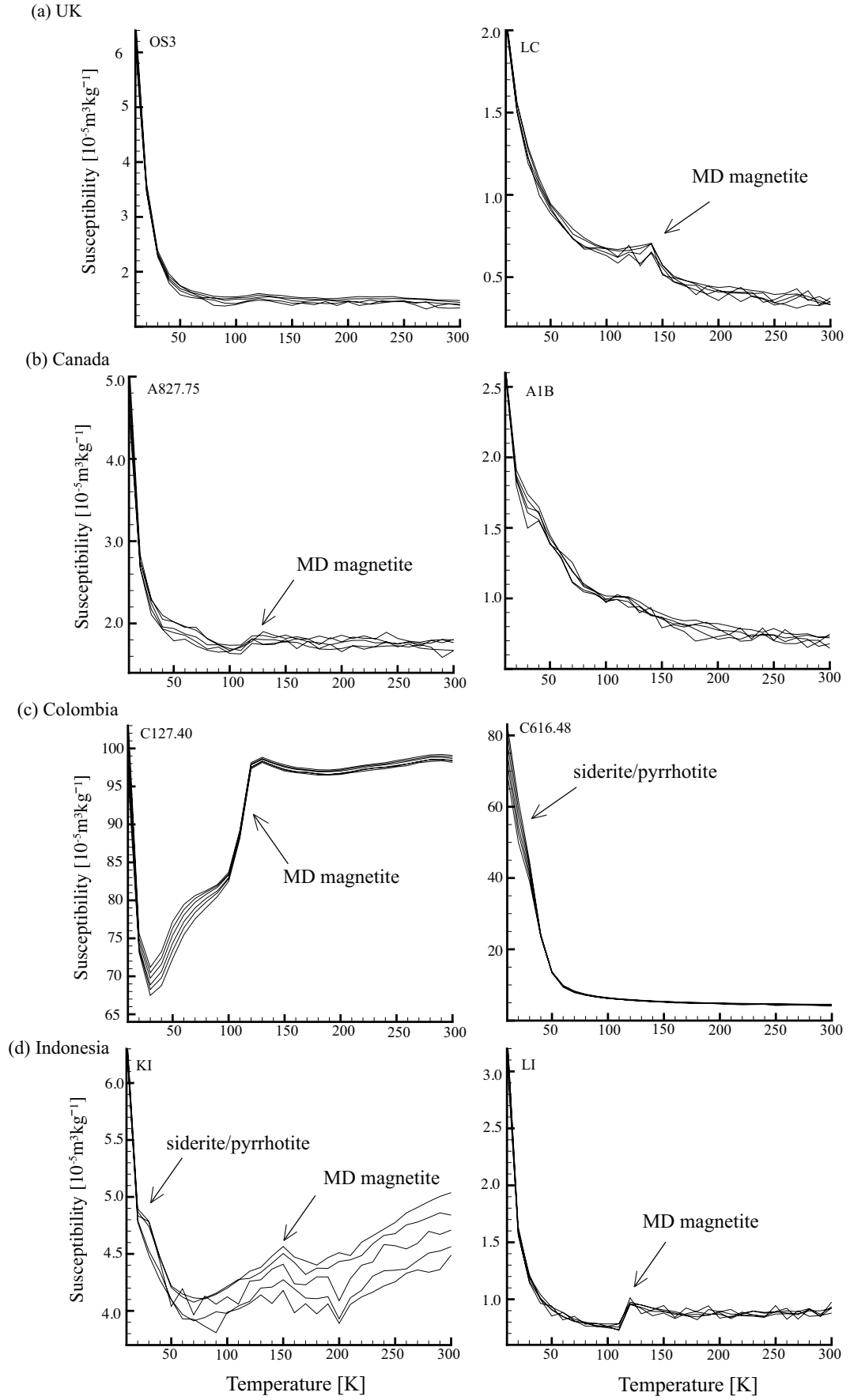


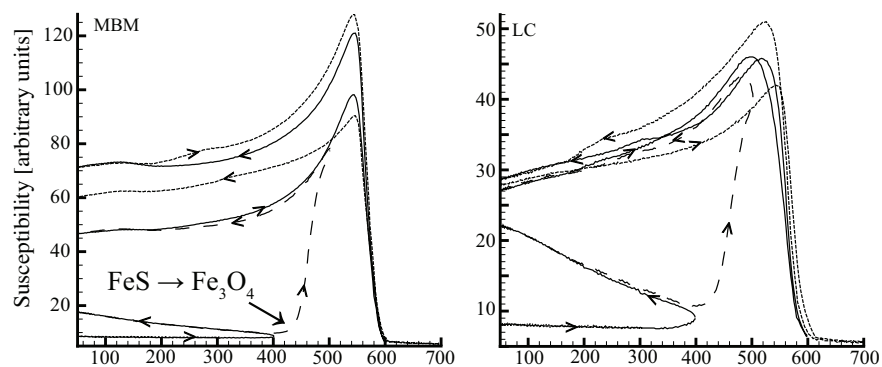
Figure 3.17. AC susceptibility as a function of frequency from 10 K to 300 K. (a) UK, OS3 & LC (b) Canada, A1B & A827.75 (c) Colombia, C127.40 & C616.48 and (d) Indonesia, KI & LI.

3.4.2.3 High temperature experimentation

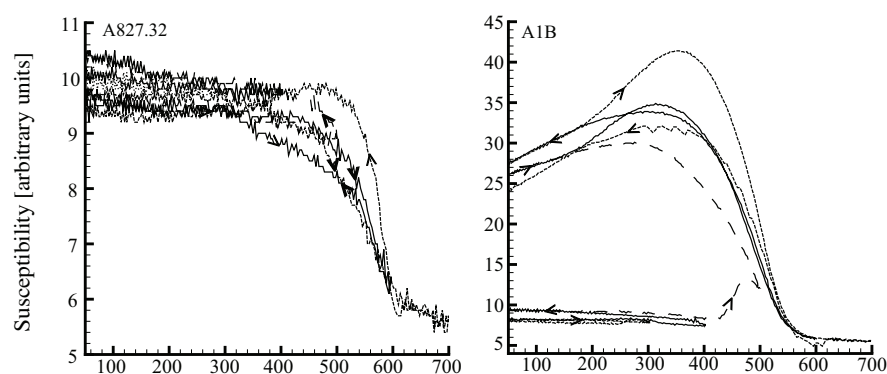
High temperature experiments were limited due to the inevitable combustion of carbon $\sim 300\text{ }^{\circ}\text{C}$ and potential damage to equipment. Therefore, oil free ‘cleaned’ samples were used in high temperature susceptibility measurements.

High-temperature mass susceptibility measurements from $100\text{--}700\text{ }^{\circ}\text{C}$ are shown in Figure 3.18. Sample behaviour was classified into 3 types: A) reversible Curie curves (Fig. 3.18b), B) the formation of a stronger ferromagnetic mineral on heating typically at $400\text{--}550\text{ }^{\circ}\text{C}$ represented by sharp increases in susceptibilities (Fig. 3.18a) and C) similar behaviour to type B but with the formation of a new magnetic mineral from $250\text{--}300\text{ }^{\circ}\text{C}$ (Fig. 3.18c). Behaviour A (Fig. 3.18c, C127.40) typically produced reversible heating and cooling magnetite Curie temperatures $\sim 560\text{ }^{\circ}\text{C}$ determined through taking the second derivative. Some samples increased susceptibility as heating increased, suggesting magnetite formation. Samples with type A behaviour are the Canadian Plover Lake samples (A827.32, A827.75), the Indonesian samples (KI, LI), the shallowest Colombian samples (C127.40, C147.25) and OS4. On the Day plot these samples show the most multi domain behaviour and are typically the most biodegraded samples except for the Colombian samples, which are the least biodegraded. Behaviour B (Fig. 3.18a) was the most common and was represented by the formation of a more ferromagnetic mineral between $400\text{--}500\text{ }^{\circ}\text{C}$ with continued increased susceptibilities. On heating to $700\text{ }^{\circ}\text{C}$ and subsequent cooling, the slope was representative of magnetite in all samples. This behaviour was identified within samples A1B, OS1, OS5, A3B, C541.75 and LC, the latter three showed Hopkinson peaks. A Hopkinson peak occurs when blocked stable SD grains become superparamagnetic unblocked grains at temperatures near the Curie temperature. Superparamagnetic grains have relatively higher susceptibilities and therefore produce a peak in high temperature susceptibility measurements. All these samples plot within the PSD/MD area of the Day plot and represent the medium biodegraded samples. A few samples showed behaviour C (Fig. 3.18c, C616.48), which also displayed the formation of a more ferromagnetic mineral on heating but from a lower temperature of $250\text{--}300\text{ }^{\circ}\text{C}$. The samples OS3 OS6 and C616.48 also revealed Curie temperatures indicative of magnetite after cooling from $700\text{ }^{\circ}\text{C}$ and represent the SD/PSD samples in the Day plot and are also the least biodegraded samples.

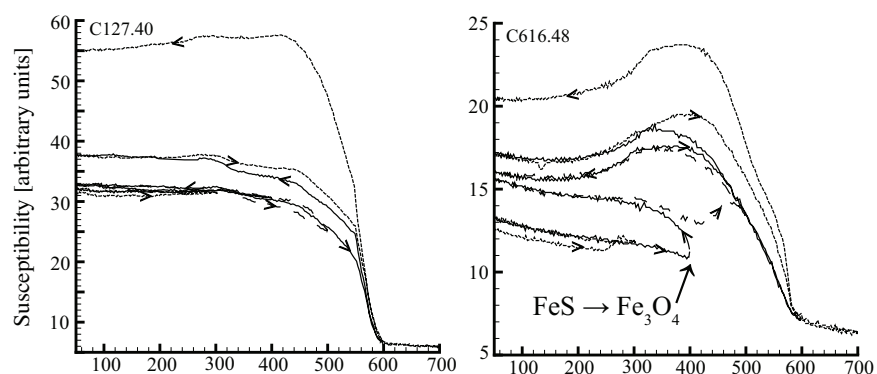
(a) UK



(b) Canada



(c) Colombia



(d) Indonesia

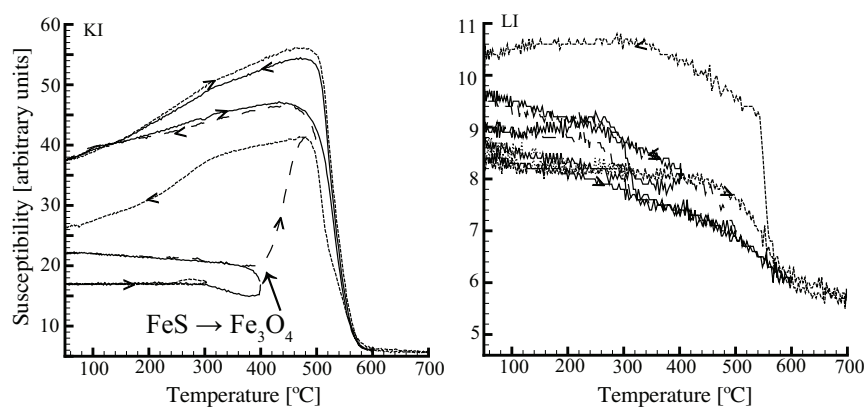
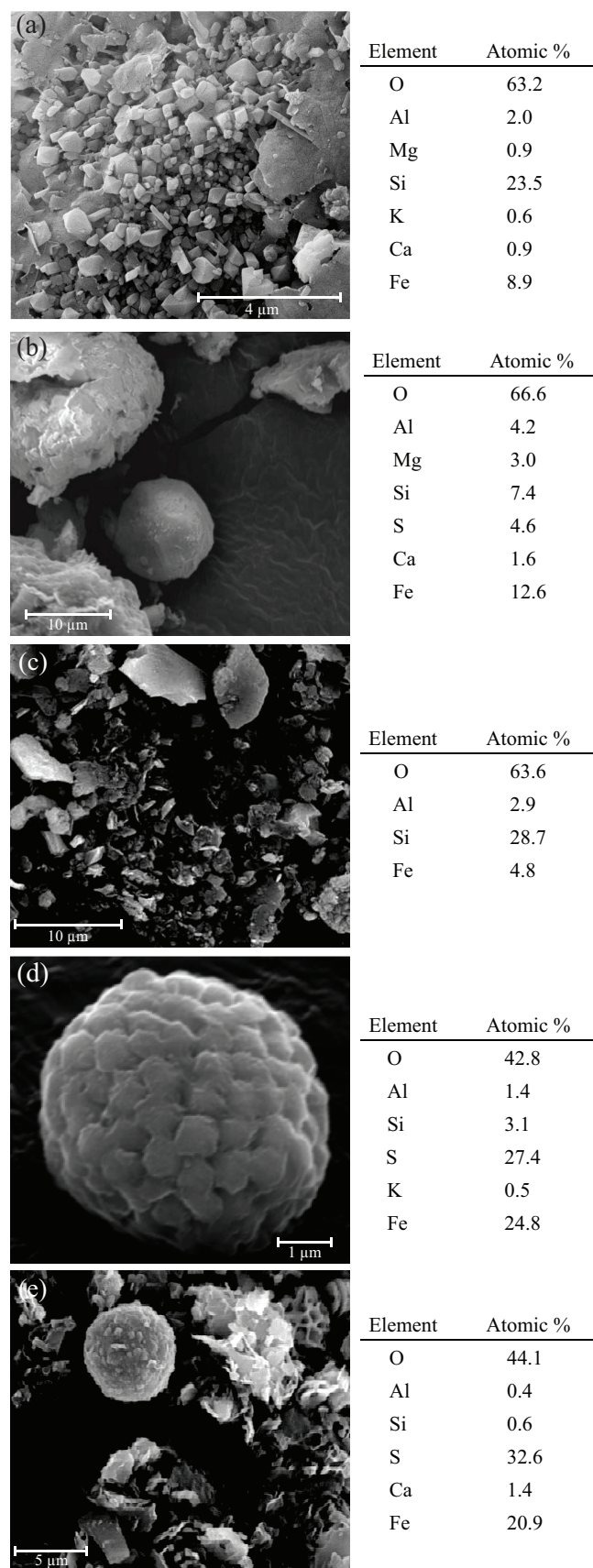


Figure 3.18. High temperature magnetic susceptibility measurements using 100 °C cycling steps from 50 °C to 700 °C. Oil free samples were used in an argon atmosphere to gain information on magnetic mineralogy through Curie temperatures. (a) UK, MBM & LC (b) Canada, A1B & A827.32 (c) Colombia, C127.40 & C616.48 and (d) Indonesia, KI & LI.

3.4.3 SEM and EDX



Examples of SEM images from each set of samples are shown in Figure 3.19. The magnetic minerals are mainly characterised by iron-oxide grains from 200 nm to 60 μm (Fig. 3.19) identified by EDX and their characteristic cubic morphology (Fig. 3.19a) (Table 3.6). The spherical clusters or framboids ranged in size between 500 nm to 45 μm within the UK (Fig. 3.19b), Colombian (Fig. 3.19d) and Indonesian samples (Fig. 3.19e) (Table 3.6). The UK samples revealed framboids dominated by an iron oxide which is consistent with the findings of Aldana *et al.* (1999) and Costanzo-Alvarez *et al.* (2006). No framboids were identified within the Canadian oil sands, which were characterised by the presence of iron oxides only (Fig. 3.19c). Colombian samples C127.40 and C147.25 showed framboids within magnetic extracts dominated by Fe and S (Fig. 3.19e) compared to C541.75 and C616.48, which revealed no framboids but were also dominated by S and Fe. The Indonesian oil sands revealed the presence of both iron sulphides and iron oxides (Fig. 3.19e).

Figure 3.19. SEM images of magnetic particles within oil sands and corresponding EDX data (not calibrated). SEM images showing (a) UK, cubic magnetic minerals (iron oxides), (b) UK, iron oxide framboid ranging in size between 500 nm and 45 μm , (c) Canada, iron oxide minerals, (d) Colombia, iron sulphide framboids and (e) Indonesia, iron oxide framboid.

Table 3.6 A summary table of SEM and EDX observations for magnetic mineralogies for each set of samples including whether framboidal material was identified.

Samples	EDX composition	Framboids
UK	Iron oxides	Iron oxides
Canada	Iron oxides	...
Colombia	Iron sulphides & Iron oxides	Iron sulphides & iron oxides
Indonesia	Iron oxides	Iron sulphides & iron oxides

Signs of microbe activity were also identified within some of the grains (Fig. 3.20). The microbe activity can be identified by the etching pattern on the surface of the grains. This confirms that bacteria are present within the samples and therefore biodegradation would have occurred in these samples.

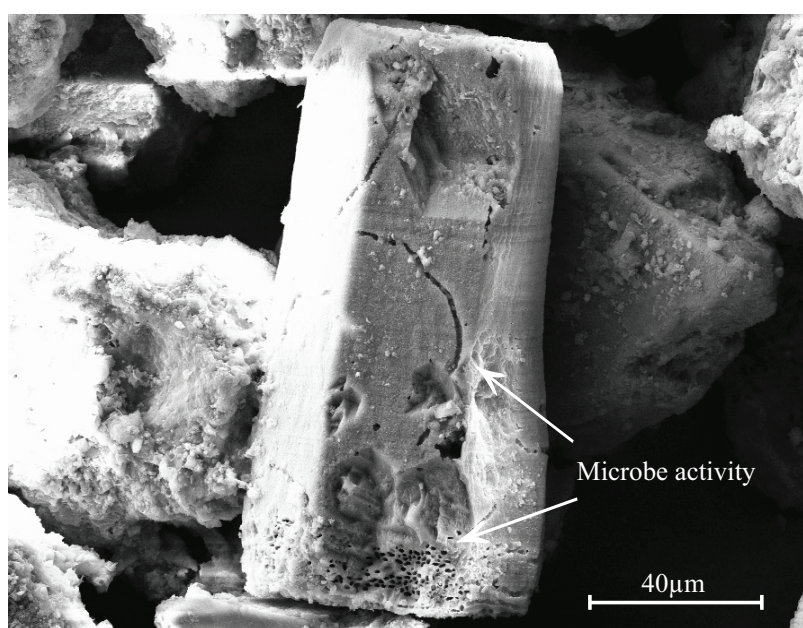


Figure 3.20. SEM image of a grain in the UK sample OS5. Microbe activity can be identified by the etched pattern on the surface.

3.5 Oil impregnated versus oil free

Both oil-stained and cleaned samples were investigated to try to determine if the oil extraction had an effect on the magnetic minerals present. The oil and ‘cleaned’ magnetic properties are shown in Table 3.5.

Figure 3.21 is a Day plot with both oil stained and clean counterparts exhibited to try to identify any variations within the sample sets. There are variable effects on M_{rs}/M_s and H_{cr}/H_c after removal of the oil. All but the shallowest Colombia sample (C616.48) showed increased H_{cr}/H_c but the same or reduced M_{rs}/M_s ratios (Fig. 3.21). The UK (OS) samples typically had no change in M_{rs}/M_s values after oil removal compared to the UK (MB & LC) samples, which had decreased M_{rs}/M_s but all UK samples show reduced H_{cr}/H_c ratios. The Indonesian samples had increased M_{rs}/M_s and decreased H_{cr}/H_c compared to the Canadian samples, which typically revealed small decreases in M_{rs}/M_s and variable H_{cr}/H_c behaviour.

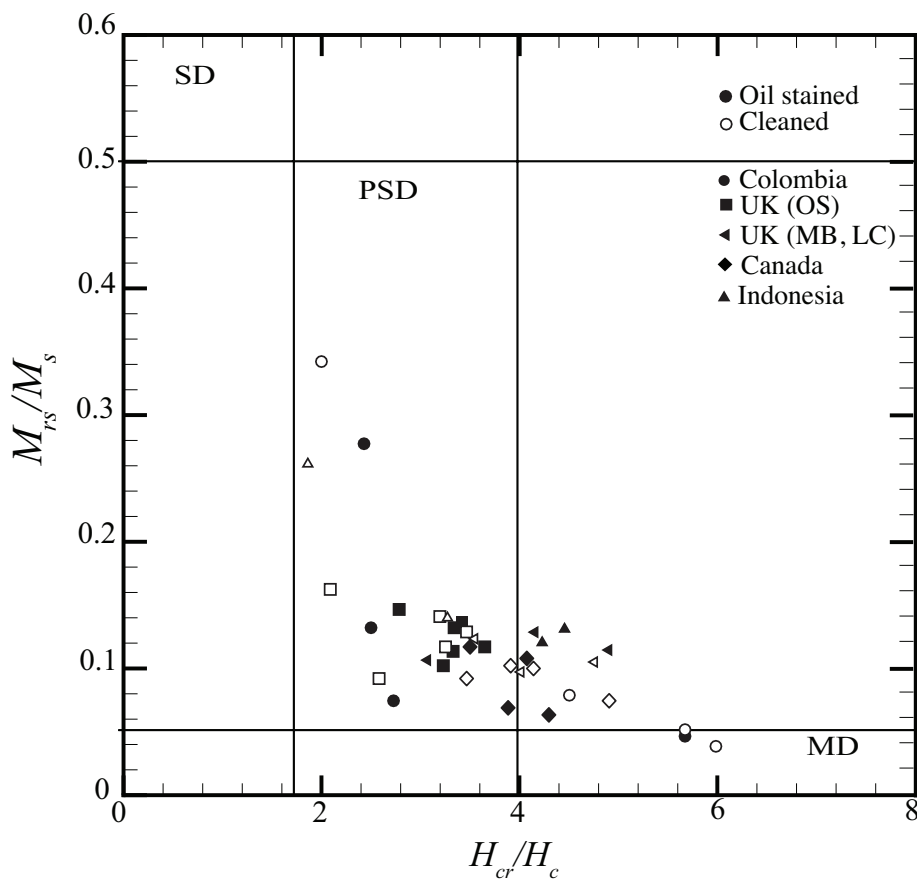


Figure 3.21. A “Day plot” (Day et al., 1977) of the ratios of the hysteresis parameters M_{rs}/M_s versus H_{cr}/H_c for the samples examined in this study. The regions commonly associated with SD, PSD and MD behaviour for magnetite are labelled for representative purposes. The oil-stained (closed) and clean (open) samples have been plotted and split into sample locations.

Figure 3.22 shows the variation in magnetic susceptibility before and after oil extraction. The majority of the samples displayed increased susceptibilities after cleaning, however, most of the UK samples (OS2, OS3, OS6, MBM, MBC) showed the opposite trend. The samples generally show larger variations between oil stained and clean sands with increasing oil content. The magnetic susceptibility values for each sample had standard deviations up to 16%, which means the variation between oil stained and cleaned magnetic susceptibility is within error.

Organic matter is diamagnetic (Ivakhnenko & Potter, 2004), therefore by removing the oil from the samples you would expect a small increase in magnetic susceptibility, however, it can be seen that the variations can be negative in some cases (Fig. 3.22). It may be possible that in several cases some of the ferrimagnetic minerals responsible for the samples' susceptibility were washed out with the extraction. The formation of new Fe minerals should be minimal due to the oxygen free solvents used and the change in mass by cleaning and removing the oil could be responsible for increasing magnetic susceptibility due to the increase in the density of magnetic minerals left within the cleaned samples.

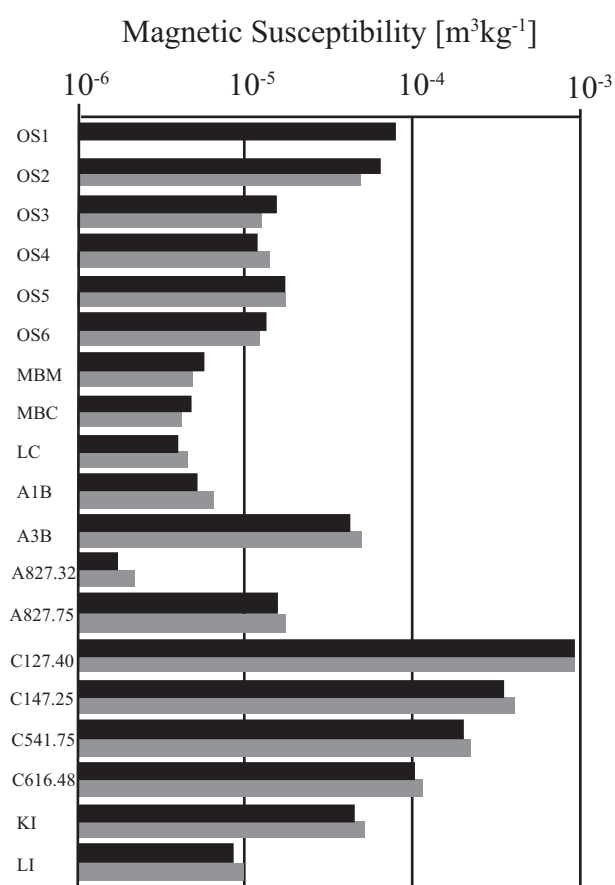


Figure 3.22. Magnetic susceptibility for all the oil sands (black) and clean (grey) counterparts. Magnetic susceptibility is on a logarithmic scale (m^3kg^{-1}).

Although there is variability in behaviour between the samples, it is proposed the removal of the oil from the host rock causes the magnetic properties in the sample to become enhanced due to an increase in the density of magnetic minerals. The difference in magnetic susceptibility before and after oil extraction is within the standard deviation of the samples (<16 %). Care should still be taken when comparing experiments conducted on oil stained and cleaned sands (SEM imaging and high temperature experimentation).

3.6 Determining a relationship between magnetisation and biodegradation

From the extensive geochemical analysis of the oils and the magnetic characterisation of the oil impregnated units in the previous sections, a comparison can now be made between magnetisation and oil composition. The following section investigates possible relationships and mechanisms.

3.6.1 Relationship between oil content and magnetic signature

The magnitude of mass normalized magnetic susceptibility varied between 10^{-4} , 10^{-5} , 10^{-5} - 10^{-6} , 10^{-5} - 10^{-6} and 10^{-6} m³kg⁻¹ for the Colombian, UK (OS), Canadian, Indonesian and UK (MB & LC) samples respectively (Table 3.5). There is natural variability in magnetic susceptibility for each geological formation and therefore, where possible, multiple (3 or 4) sub samples were measured for each sample and an average used for analysis.

Combining magnetic susceptibility and the percentage of extractable organic matter (EOM%), each set of samples, representing a different reservoir, reveal negative regressions i.e., there is an inverse relationship between magnetic susceptibility (χ) and EOM% ($R^2=0.5-0.8$). The number of samples within each data set varies between 2-6, which limits suitable statistical analysis. The Indonesian samples have not been used for statistical analysis due to the low number of samples (two samples).

The UK, Osmington Mills samples (OS1-OS6) include an oil free sample described as a background sample as well as enough samples within a subset suitable for statistical analysis. It is difficult to ascertain oil saturated and background samples from the same geological

formations/facies and was not possible for the other samples within this study. Based on the UK Osmington Mills data set, an exponential regression was shown to estimate the background sample (χ_B) (Fig. 3.23): the assumption was made that all the data sets act in the same way and regressions were taken to zero EOM% to represent ‘oil free samples’ within each data set.

The variation in each samples magnetic susceptibility was no more than 20%, the average data and the associated errors are shown in Figure 3.23. The figure also shows the linear regression in log space with 99% confidence limits. The results show that although variation in magnetic susceptibility exists in all samples, the regression still satisfies the normalisation of the samples. To normalize the different data sets, all the subsets were individually normalized removing any differences in χ (assumed to be from original facies variations). It should be noted that the regression appears to underestimate χ_B . Ideally, multiple samples would be obtained for oil free background samples and the variation in original magnetic susceptibility due to small facies changes could be investigated, however, in this study, samples were limited and the variation was determined by subsampling available samples.

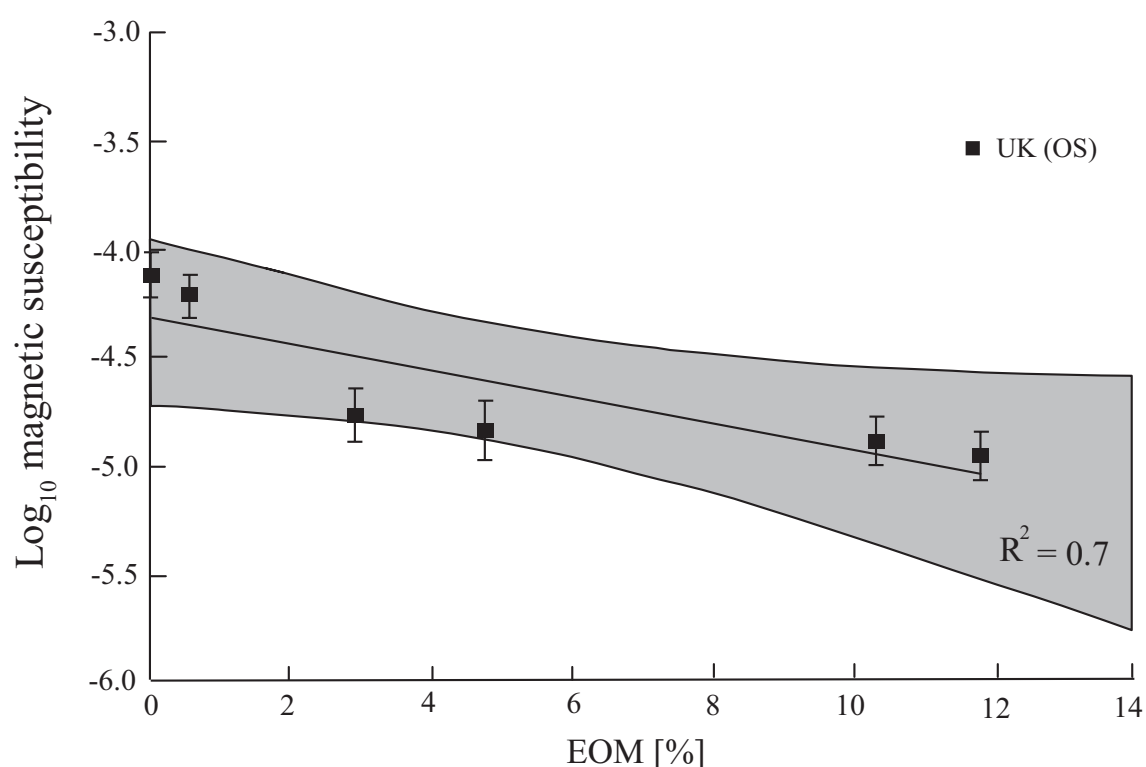


Figure 3.23. Plot of Log_{10} magnetic susceptibility versus EOM% for the UK, Osmington Mill samples. An exponential regression was determined to ascertain the best estimate for the ‘background’ χ (EOM%=0) with the same principle applied to the Canadian, Colombian and UK (MB & LC) samples. The trend line and 99% confidence limits are also plotted.

Figure 3.24 represents all the normalized samples (17 samples) against EOM% and shows a clear negative regression in log space. The confidence in the regression limits is also shown for 95%

confidence levels. The t-distribution confirms the correlation cannot be rejected at a 99% confidence level and the Spearman's Rank correlation coefficient ($R_s = -0.8$) confirms that an association between EOM% and χ does exist.

The magnitude of magnetisation appears to be dependent on not just the magnetic mineralogy of the original host rock but also to the amount of hydrocarbon migration and accumulation within the rock. Previous studies (e.g., Díaz et al., 2000; Díaz et al., 2006; Guzman et al., 2011) found anomalous magnetic susceptibility peaks correspond to anomalously high EOM values through producing wells. These studies looked at well cores above oil reservoirs, identifying magnetic differences within samples spanning several geological formations. Previously it was assumed that newly generated magnetite would strengthen magnetic signals in biodegraded samples. The results within this study find that the opposite effect occurs and that it is the removal of magnetite and reduction in magnetic signal that leads to variation in oils.

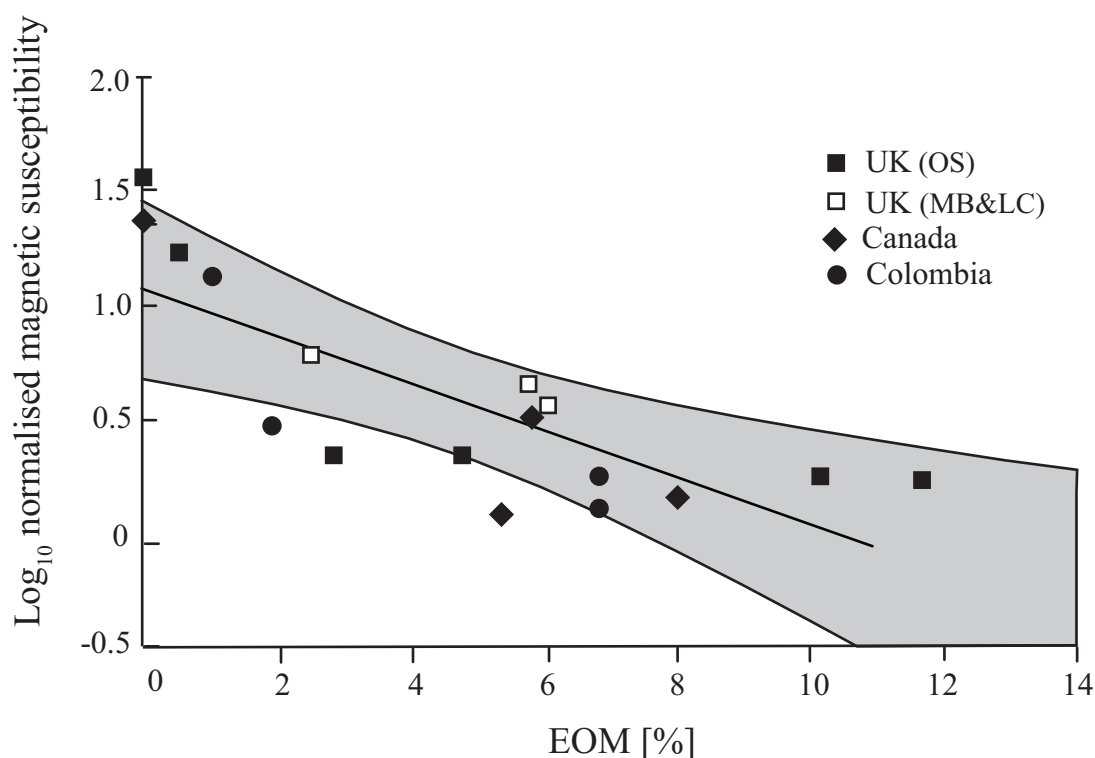


Figure 3.24. Log₁₀ magnetic susceptibility versus percentage of extractable organic matter for all the samples tested. The samples have been split into their groups: UK (OS), UK (MB & LC), Canada, Colombia and Indonesia. The trend line and 95% confidence limits are also plotted.

This study however, concentrates on magnetic characterisation of oil-impregnated samples from the reservoir itself. The samples are from the same geological formations or its equivalent within each

dataset. The exception to this are the Colombian samples, which have one sample from each individual geological unit and are therefore all plotted together. Combining all these studies, the results suggest that on a large scale, anomalous magnetic susceptibility and EOM accumulations can form above reservoirs due to the formation of secondary magnetic material through the net transport of electrons from altered organic matter possibly through leaking hydrocarbons. Within the reservoir and oil impregnated units themselves, the host rock can hold its own anomalous magnetic susceptibility, the amount of oil saturation appears to decrease the magnetic signal. This complicated relationship may go some way as to explain why both high and low anomalies have been associated within hydrocarbon accumulations in the past (e.g., Donovan et al., 1979; Elmore et al., 1993; Reynolds & Goldkaber, 1993).

To try to distinguish whether the magnetic response is due to the oil itself e.g., porosity/migration or due to bacteria, the magnetic susceptibility was also compared to individual oil components in the following section. If the magnetisation is not linked to variations within oil composition, which is due to bacterial action, then the dominant response would not be due to bacteria but migration. The effect of biodegradation was also investigated because it is a fundamental consequence of bacterial action in oil.

3.6.2 Relationship between oil composition and magnetic signature

All samples in this study originate from marine kerogen type II source rocks and have oil maturities corresponding with the oil being generated just after the rock has entered the oil window. All oils show a similar source rock and level of maturity and therefore the magnetic mineralogy cannot be contrasted in terms of source environment. As the samples have the same source environments it allows for the investigation between magnetic mineralogy and biodegradation.

The relative percentages of the three components within oil: 1) aliphatic hydrocarbons 2) aromatic hydrocarbons and 3) polar and asphaltenes are commonly used to identify general biodegradation levels. Using the Wegner biodegradation scale (Wenger et al., 2001) (Section 1.4.6) the results show variable degrees of biodegradation for the samples within this study with increasing biodegradation from Colombia, UK (OS), Canada, UK (MB & LC) and Indonesian samples.

Using statistical analysis (SPSS software), individual oil constituents were compared to magnetic susceptibility to determine the strength of the relationship. It was originally assumed that the

difference between the original recorded magnetic susceptibility (χ) and the normalised magnetic susceptibility (χ/χ_B) was due to the geological facies of the individual samples. To test whether this was the only cause of this variation and to remove the effect the amount of EOM% has on the magnetic susceptibility as seen in Figure 3.45, the difference between the original magnetic susceptibility and the normalised magnetic susceptibility was investigated ($\log_{10}\chi - \log_{10}\chi/\log_{10}\chi_B$) (χ_B =background magnetic susceptibility). The variation found between the samples was used to identify whether a correlation existed between magnetic susceptibility and oil components (Fig. 3.25). The nonparametric Spearman's rank correlation coefficient (R_s) was used to investigate the statistical significance of any correlations.

The strongest negative correlation exists between magnetic susceptibility and the combined polar and asphaltene fractions which represents increasing biodegradation (Fig. 3.25a). This relationship has a correlation of $R_s=-0.9$ and cannot be rejected at 99% confidence. Due to the nature of biodegrading oils, which involves the removal of aliphatic components to create polar and asphaltene compounds there is a corresponding strong positive correlation between magnetic susceptibility and the aliphatic abundances ($R_s=0.9$) (Fig. 3.25b) as well as a negative correlation between χ and aromatic components ($R_s=-0.7$). All these correlations cannot be rejected at a 95% confidence level. There appears to be no correlation between χ and asphaltene abundances ($R_s=-0.4$), which agrees with the literature (Elmore et al., 1993).

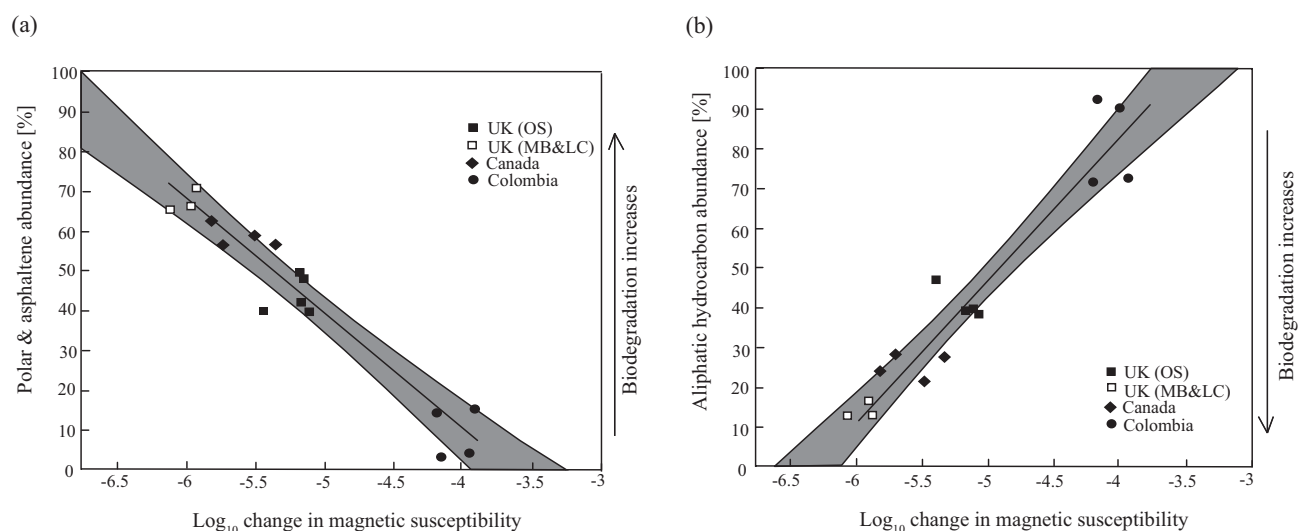


Figure 3.25. $\log_{10}$ change in magnetic susceptibility plot against the abundance of (a) polar and asphaltene and (b) aliphatic hydrocarbons within each sample. The trendlines and 95% confidence limits are plotted. The samples are represented within their localities.

The samples clearly show a stronger magnetic susceptibility towards the non-biodegraded samples with decreasing magnetisation with increasing levels of biodegradation (Fig. 3.25). These

correlations confirm that bacteria (therefore biodegradation) must play a key role in the alteration of the magnetic signature of an oil-bearing rock. Migration or maturity cannot be completely ruled out as a contributing factor but the magnitude variability in magnetic susceptibility shown by biodegradation and oil abundances confirms that the resultant changes in oil chemistry due to biodegradation dominate the magnetic signature of the host rock.

To try to identify further the connection between magnetic mineralogy and biodegradation a Day plot with samples split into different biodegradation levels is shown in Figure 3.26. The results show distinct grouping for biodegradation levels. Samples with high levels of biodegradation show higher ratios of H_{cr}/H_c and varying ratios of M_{rs}/M_s (Table 3.5, Fig. 3.26) corresponding to multi domain grains in Canadian Indonesian and UK (MB & LC) samples compared to UK (OS) samples, which show stronger PSD behaviour. The Colombian samples show more PSD to SD-like behaviour with the exception of one sample (C147.25) (Fig. 3.26). The M_s values also show an overall decrease (Table 3.5) with increasing biodegradation suggesting preferential removal of SD particles.

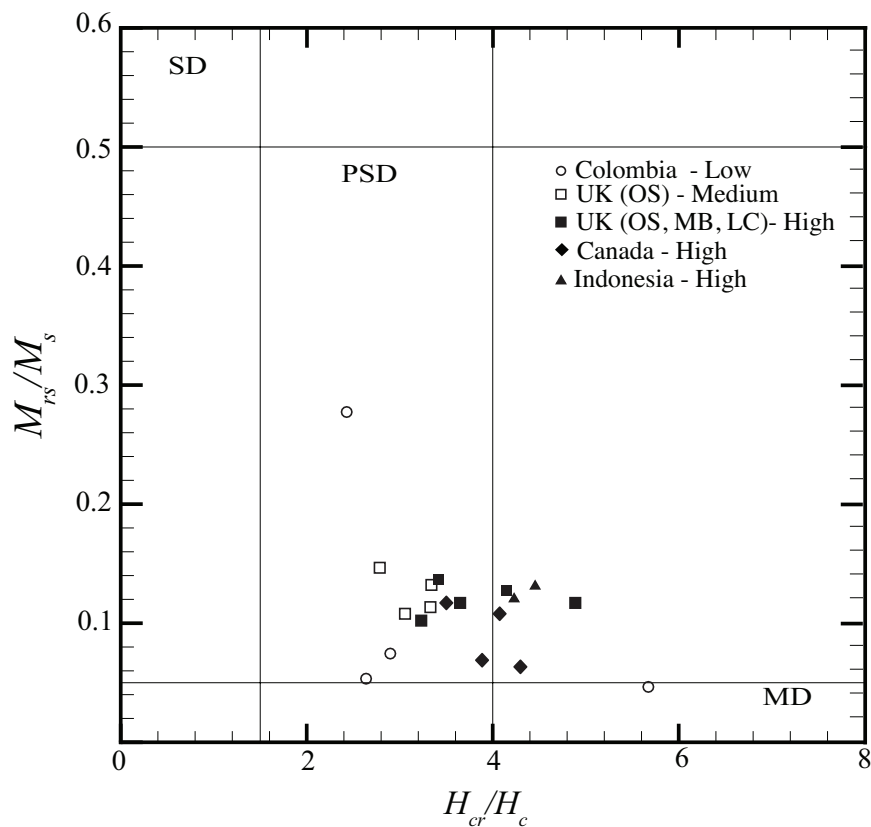


Figure 3.26. A “Day plot” (Day et al., 1977) of the ratios of the hysteresis parameters M_{rs}/M_s versus H_{cr}/H_c for the samples examined in this study. The regions commonly associated with SD, PSD and MD behaviour for magnetite are labelled for representative purposes. The oil-stained samples have been plotted and split into sample locations and corresponding biodegradation levels referred too: low and medium (open symbols) and high (closed symbols).

The magnetic signature appears to become more MD-like with increased biodegradation, i.e., the signal of the rock is being dominated by larger magnetic particles. There are two possible mechanisms: 1) due to their higher surface/volume ratios smaller SD grains are preferentially removed during biodegradation, or 2) in addition to the removal of SD grains, during the processes of biodegradation and change in environment, sulphide-rich framboids (like pyrite) and other magnetic minerals are oxidized to oxide-rich minerals, including magnetite framboids. The overall magnetisation is reduced, as is seen by the reduction in M_s (Table 3.5), suggesting that more SD particles are being removed.

3.6.3 Diagenesis

Machel (1995) created a detailed report on magnetic mineral assemblages in diagenetic environments in association with hydrocarbon plumes. Magnetite and pyrrhotite are the more stable minerals under anaerobic/reducing conditions compared to higher stability for goethite and hematite under aerobic/oxidizing conditions (Machel & Burton, 1991; Machel, 1995). The introduction of fluids such as hydrocarbons is already known to result in diagenetic remagnetisation e.g., Elmore *et al.* (2001). The results in this study clarify that there can be a change in magnetisation due to the formation or destruction of magnetic minerals; however, the quality of oil also seems to affect the magnetisation. All the samples showed the presence of multi domain magnetite sometimes as framboids as well as iron sulphide framboids (Fig. 3.19). The presence of these multi domain magnetite framboids does not seem to be a single characteristic of hydrocarbon invasion due to the lack of framboids within the Canadian samples, but could be a potential indicator within certain conditions. The formation and/or destruction of the original magnetic minerals within host rocks has also been documented to potentially hold a remagnetisation and therefore can be used as a tool for dating hydrocarbon migration (McCabe *et al.*, 1987; Elmore & Crawford, 1990; Elmore *et al.*, 2001) (Chapter 4). The presence of anaerobic bacteria (Lovley *et al.*, 1987) within the hydrocarbons is responsible for not only the biodegradation of the oil but also the overall reduction in magnetic susceptibility of the host rock and a shift in the magnetisation's signature from SD-like to more MD-like. The additional presence of hematite (Fig. 3.16) in the more severely biodegraded samples and the lack of it within non-biodegraded samples suggests a later stage of biodegradation occurred most probably at the surface due to oxidation of magnetite (Machel, 1995). Iron sulphides also exist within the UK, Colombian and Indonesian samples mainly as framboidal pyrite and/or pyrrhotite most probably formed as a result of the generation of reduced sulphur by anaerobic sulphate-reducing bacteria which have been shown to also cause biodegradation of oils (Rueter *et al.*, 1994).

3.6.4 Mechanisms

There are two possible mechanisms for the negative correlation between oil content and oil composition with magnetisation that we observe: (1) there are several well-known bacteria (Heider et al., 1998) that readily use Fe ions in anaerobic processes within oil biodegradation (Bigge & Farrimond, 1998) or (2) the correlation could reflect the nature of the oil itself, e.g. as the oil is transported from its source, the magnetic minerals are dispersed into the reservoir, implying the relationship could be due to porosity and/or migration.

The negative correlations found between magnetic signals and both the EOM% and biodegradation levels within this study (Figs. 3.24 and 3.25) suggests that iron reducing anaerobic bacterium within the oil consumes Fe ions from iron minerals within the host rock. The removal of these Fe ions reduces the magnetic signature with oil content (Fig. 3.24). The bacteria within the oil can further affect the host rock; the activity of bacteria responsible for biodegradation further reduces the magnetic signal by continued reduction of iron (Fig. 3.25). The magnetic mineralogy also appears to change in the presence of hydrocarbons by creating conditions suitable for the alteration and/or formation of multi domain magnetite (Fig. 3.16). The formation of these larger magnetic grains, often in the form of framboids can also cause a reduction in magnetic signal relative to the original single domain, smaller grained magnetic minerals within the host rock. The overall magnetic signature appears to become more MD-like with increased biodegradation, i.e., the signal of the rock is being dominated by larger magnetic particles. There are two possible mechanisms: 1) due to their higher surface/volume ratios smaller SD grains are preferentially removed during biodegradation, or 2) in addition to the removal of SD grains, during the processes of biodegradation and change in environment, sulphide-rich framboids (pyrrhotite and/or pyrite) and other magnetic minerals are oxidized to oxide-rich minerals, including magnetite framboids. The overall reduction in magnetisation, as is seen by the reduction in M_s (Table 3.5), suggests that more SD particles are being removed than MD particles formed.

Secondary migration of hydrocarbons from the source rock into hydrocarbon traps travel through carrier beds that have the least resistance (most porous). These pathways are often a combination of vertical and lateral migration due to the presence of heterogeneities within the subsurface rock. When hydrocarbons begin to fill into a trap, the tortuous migration pathway will tend to fill from one side. Compositional changes within the oil can occur during migration and filling such as de-asphalting and thermal alteration (Section 1.4.5). These alterations can change the relative abundances of the individual oil components (aliphatics, aromatics and polars), which have been shown to affect the magnetic signature (Fig. 3.25). Although biodegradation is the dominant effect

to change the abundance of these components causing a negative magnetic response, some of these processes have the opposite effect on oil composition and therefore could show a positive magnetic response.

Studies identifying similar relationships over large distances of core above reservoirs in terms of magnetic susceptibility and EOM content have shown the opposite correlation suggesting a very complex relationship must exist. Combining all these studies suggests, that on a large scale, anomalous magnetic susceptibility and EOM can form above a reservoir due to the formation of secondary magnetic material through the net transport of electrons from altered organic matter possibly through leaking hydrocarbon gases as suggested by Díaz *et al.* (2006) and/or by the processes experienced by migrating hydrocarbons which cause a change in the the oil composition resulting in a positive magnetic susceptibility. However, within the reservoir and oil impregnated units themselves, the host rock can hold its own anomalous magnetic susceptibility. This complicated relationship may go some way as to explain why both high and low anomalies have been associated with hydrocarbon accumulations in the past (e.g., Donovan et al., 1979; Elmore et al., 1993; Reynolds & Goldkaber, 1993).

Transportation of oil cannot be ruled out as another contributing factor but it is clear that bacteria plays a dominant role in the biodegradation and the resultant magnetic signal of hydrocarbon-bearing rocks.

3.6.5 Implications

This study confirms a detailed relationship between the magnetic mineralogy and signature of oil-impregnated units and the invasion of hydrocarbons into the system, specifically the biodegradation of the oil. There are three major implications of this work:

1) The prospect of a proxy for identifying hydrocarbon migration pathways by employing magnetic procedures. The different magnetic signatures left by migrating hydrocarbons (positive) as well as the accumulation of hydrocarbons (negative) can help distinguish migration pathways. This theory could not be rigorously tested within this study due to a lack of suitable samples; a number of core samples would be needed from a single reservoir (oil saturated rock) as well as a general understanding of where the reservoir must have filled from to test the hypothesis. More detail on this concept is discussed in Chapter 6.

2) Palaeomagnetism could be used to date the migration of hydrocarbons into rock formations. The alteration and/or formation of magnetic minerals through the introduction of fluids (in this case, hydrocarbons) into a host rock can lead to an imprint in magnetisation associated with the same event. For example, the formation of authigenic magnetite could hold a CRM (see Section 1.4) corresponding to the date of formation. This implication is investigated separately in Chapter 4, where it is shown that it is possible to date ancient migration events as well as identifying active oil seeps.

3) This study also offers a base for continued studies into other oil variations and corresponding magnetic signatures such as source, maturity, biotic vs. abiotic formation and bacteria, which could ultimately lead to a direct identification tool for hydrocarbon exploration. There are significant links between hydrocarbons and magnetic mineralogy; however, there are a great number of factors that could contribute to the general magnetic signature that we observe. All these variations would need to be investigated to ultimately discover whether magnetic properties could be used as a tool of hydrocarbon identification.

3.7 Conclusions

Combining the geochemical analysis with magnetic analysis for four sets of samples from the UK, Canada, Colombia and Indonesia, allowed for the first time, a unique relationship between hydrocarbons and magnetisation to be established.

Biomarker data revealed that all oil samples were derived from type-II kerogen, deposited in oxygen-poor environments. The data suggests a maturity level that corresponds with the oil being generated just after the rock has entered the oil window. All the oils show a similar level of maturity. The Colombian samples showed little biodegradation due to the retention of *n*-alkanes within their aliphatic fractions, compared to the UK, Canadian and Indonesian samples that displayed heavy to severe biodegradation with no *n*-alkanes retained. Pyrolysis data for the asphaltene fractions for these three sets of samples were consistent with a type II kerogen source. This study investigates the detailed magnetic characterisation of different oil bearing sediments with marine kerogen type II source rocks. The suite of samples available allows for the comparison of magnetic mineralogy with differing biodegradation levels within the oil. With increased biodegradation from low to high levels for Colombia, UK (OS), Canada, UK (MB & LC), Indonesia samples respectively.

Relationships between magnetic mineralogy and hydrocarbons have already been investigated (e.g., Elmore et al., 1987; McCabe et al., 1987; Kilgore & Elmore, 1989), but this more detailed magnetic study suggests this relationship is very complex, affected by a number of different factors especially biodegradation. Through these samples, a relationship has been identified between magnetisation, the EOM% and the relative abundance of aliphatic organic compounds in oil. The magnitude of mass normalised magnetic susceptibility varied between $10^{-4} \text{ m}^3\text{kg}^{-1}$ for the Colombian samples, 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for UK, 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for Canadian and 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for the Indonesian samples (Table 3.5). The magnetic susceptibility of hydrocarbon-bearing rocks can be seen to decrease with increasing oil content indicating that hydrocarbons do affect the magnetic mineralogy of the host rock. A negative correlation between magnetisation and EOM% for each given reservoir was identified with correlations between $R^2=0.5-0.8$ with a normalized relationship of $R_s=-0.78$ which cannot be rejected at a 99% confidence level (Fig. 3.24). The magnitude of magnetic susceptibility appears to be dependent on not just the magnetic mineralogy of the original host rock (background samples) but also to the amount of hydrocarbon migration, accumulation and biodegradation within the rock. To try to distinguish whether the magnetic response is due to bacteria and/or migration, magnetic susceptibility was compared to individual oil components.

This study has identified a relationship between magnetisation and the relative abundance of aliphatic organic compounds in oil (Fig. 3.25). Biodegradation appears to remove both aliphatic hydrocarbons and magnetic susceptibility owing to the influence of bacterial metabolic activity that uses ferric iron minerals as electron acceptors. Magnetically, the more biodegraded samples (increasing biodegradation from Colombian, UK (OS), Canadian, UK (MB & LC), Indonesian samples) display more multi domain characteristics, which can be inferred as larger magnetite grains (Fig. 3.27) as well as an increasing presence of hematite (Fig. 3.16). The percentage of aliphatic and polar components within the oil is also indicative of biodegradation as the original aliphatic compounds are destroyed and polar compounds as well as asphaltenes become relatively more abundant as a consequence of biodegradation. Figure 3.25 shows a negative correlation for magnetic susceptibility and polar and asphaltene compounds. These results conclude that magnetic susceptibility decreases with increasing effects of biodegradation, decreasing oil quality and cannot be rejected at a 99% confidence level.

Further magnetic characterisation revealed that the high quality, low biodegradation oils from Colombia have a higher magnetic susceptibility and are dominated by pseudo-single domain grains of magnetite. The lower quality oils i.e., the UK, Canadian and Indonesian samples, displayed decreased magnetic susceptibility and pseudo-single domain to multi domain grains of magnetite and hematite (Fig. 3.26). Therefore, with decreasing oil quality there is a progressive dominance of

multi domain magnetite as well as the appearance of hematite. The additional presence of hematite in the more severely biodegraded samples and the lack of it within non-biodegraded samples suggests a later stage of biodegradation occurred most probably at the surface due to hematite being more stable in aerobic/oxidizing environments. Magnetite and pyrite framboidal material were found in all but the Canadian samples.

Correlations observed within this study (Figs. 3.25 and 3.26) suggest that bacteria play a key role in changing the magnetic signature of the host rock through anaerobic and aerobic biodegradation of the oil. There are several well-known bacteria (Heider et al., 1998) that readily use Fe ions in anaerobic processes within oil biodegradation (Bigge & Farrimond, 1998). The magnetic signature appears to become more MD-like with increased biodegradation, i.e., the signal of the rock is being dominated by larger magnetic particles, through the preferential removal of small SD grains and possibly the transformation of sulphide-rich framboids to oxide-rich framboids. The overall magnetisation is reduced, as is seen by the reduction in M_s (Table 3.5), suggesting that more SD particles are being removed and MD particles formed. Iron sulphides also exist within all but the Canadian samples mainly as framboidal pyrrhotite most probably formed as a result of the generation of reduced sulphur by anaerobic sulphate-reducing bacteria, which have been shown to also cause biodegradation of oils (Rueter et al., 1994). Furthermore, the results suggest that the progression of biodegradation within the oil is related to both the formation of multi domain magnetite and the overall reduction in magnetic susceptibility.

Previous studies showed the opposite relationship between magnetic susceptibility and oil content. These studies were mainly based on very small quantities of non-biodegraded oils and therefore suggest that biodegradation within the oil have a very strong effect on magnetic susceptibility. Combining this study with previous research, it is suggested that on a large spatial scale, anomalous magnetic susceptibility can form above a reservoir. This may be due to the formation of secondary magnetic material through the net transport of electrons from altered organic matter possibly through leaking hydrocarbon gases and/or by the processes experienced by migrating hydrocarbons which cause a change in the the oil composition resulting in a positive magnetic susceptibility. However, within the reservoir and oil impregnated sedimentary units themselves, the host rock can hold its own anomalous magnetic susceptibility. The amount of oil saturation and biodegradation appears to decrease the magnetic signal. This complicated relationship may go some way as to explain why both high and low anomalies have been associated within hydrocarbon accumulations in the past (e.g., Donovan et al., 1979; Elmore et al., 1993; Reynolds & Goldkaber, 1993).

These findings reinforce the importance of bacteria within petroleum systems as well as providing a platform for the use of magnetisation as a hydrocarbon migration proxy and as an inexpensive and simple method to determine oil quality. A relationship between hydrocarbons and their magnetic signatures has been alluded to for decades but this is the first study to combine extensive geochemical and magnetic data. These results suggest a very complex relationship between magnetisation and hydrocarbons through not only the change in magnetic signature within the host rock as a result of oil impregnation but also as a result of bacterial action.

Chapter 4

**Can magnetisation solve the Mupe
Bay mystery?**

4.1 Introduction

The unusual outcrop at Mupe Bay (Wessex Basin, Dorset UK, SY843798) (Chapter 2) contains a conglomeratic bed of Early Cretaceous age comprising of clasts and matrix, both stained with oil (Fig. 4.1). It has been proposed that the clasts were stained and cemented by oil prior to transport by Wealden rivers and incorporation into the conglomerate (Cornford, et al., 1988; Kinghorn et al., 1994). In this scenario a second later phase of oil migration then stained the matrix. This interpretation constrains the onset of oil migration in the Wessex Basin to at least the Early Cretaceous. The timing of migration in the Wessex Basin is key to understanding how oil reservoirs, such as those in the Wytch Farm oilfield, were filled in the area (Selley & Stoneley, 1987). Yet controversy exists and a single phase, rather than a double-phase staining event has also been proposed where both the clasts and matrix were deposited and then stained in situ (Miles et al., 1993).

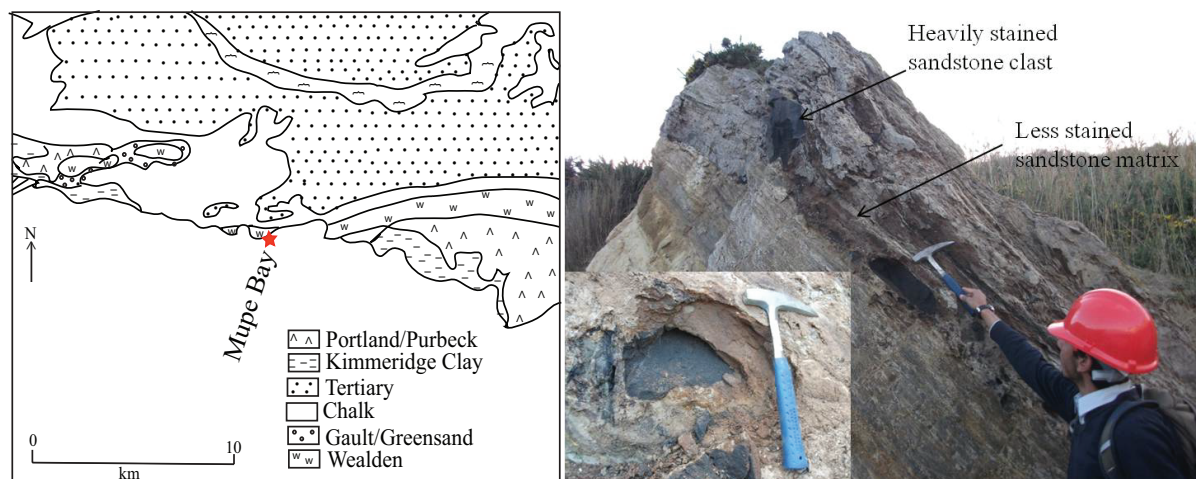


Figure 4.1. Generalised map of the Wessex Basin, Dorset, UK with Mupe Bay identified for reference. Fieldwork picture of the Wealden Group conglomerate with oil stained clasts and matrix.

Both the Mupe Bay clasts and matrix were geochemically analysed within this study and are described in detail in Chapter 3. Generally, the results are in agreement with the literature (Miles et al., 1993; Bigge & Farrimond, 1998; Parfitt & Farrimond, 1998), that the matrix is more biodegraded than the clasts but biomarkers used to distinguish between different sources/ages are unclear as they can also be explained by biodegradation as described by Bigge & Farrimond (1998). Organic geochemical data are somewhat ambiguous and have failed to settle the controversy. Studies originally stated that maturity differences between the oil in the matrix and the clasts reinforced a two-phase staining model (Cornford et al., 1988; Kinghorn et al., 1994). However,

these differences can also be attributed to variations in biodegradation between clasts and matrix (Bigge and Farrimond, 1998; Miles et al., 1993; Seifert and Moldowan, 1979). A rigorous study attempted to isolate the least biodegraded aliphatic biomarker maturity parameters through principal component analysis of 49 biomarker peaks (Parfitt and Farrimond, 1998) and the results revealed similar maturities between the matrix and clasts but could not rule out the two-phase staining scenario favoured by some previous authors (e.g. Wimbledon et al., 1996). Clearly new approaches are needed to solve the mystery of the Mupe Bay record of oil migration. This chapter investigates this problem by determining the age of remagnetisation of the clasts and matrix.

The use of remagnetisations to date hydrocarbon migrations is described in detail in Section 1.3.3. A brief description of the underlying theory follows; studies investigating remagnetisation by fluids (Reynolds et al., 1985; Benthien & Elmore, 1987; Elmore et al., 1987; McCabe et al., 1987; Elmore & Crawford, 1990; Cioppa & Symons, 2000; Garner & Cioppa, 2006) suggest that migration of fluids (e.g., hydrocarbons) into a host rock can cause chemical conditions suitable for formation of authigenic magnetite and acquisition of the related chemical remanence (Elmore & Crawford, 1990). When they are formed, the magnetite grains record the magnetic direction of the ambient Earth's magnetic field, which can potentially be preserved to the present day. The chemical remanent magnetisation (CRM) results from alteration of an existing magnetic phase or the formation of a new magnetic mineral in the presence of a magnetic field (McCabe et al., 1984; McCabe & Elmore, 1989; Suk et al., 1993; Evans et al., 2000). Crucially, the Earth's magnetic field changes with time allowing both relative and absolute dates to be assigned to the production of magnetite grains.

The utility of this approach has been demonstrated by a detailed study on speleotherms from southern Oklahoma (Elmore and Crawford 1990). A chemical remanent remagnetisation from authigenic magnetite within dark-hydrocarbon saturated bands was recognized but no such remagnetisation was evident within non-hydrocarbon bearing bands. The speleotherm study suggested that palaeomagnetic directions could be determined and potentially used to date the migration of hydrocarbons into the host rock.

The original remanence recorded in the host rock can be altered due to re-mobilization of the magnetic particles (Collinson, 1965) or due to thermal relaxation of the magnetisation (Dunlop, 1973). If the hydrocarbons are mobile and associated with active seepage then the magnetic orientation would give a present day magnetic field orientation at that given site. The recognition of active seepage in this way is an additional important piece of information for understanding the petroleum migration history of basins.

Therefore, using magnetic methods, it is possible to date fossil hydrocarbon impregnations and to recognize oil occurrences that are being actively recharged at the present day. We report the first use of magnetic data in the Wessex Basin to constrain the timing of hydrocarbon migration. This study argues that the data settles a long-standing argument over interpretations of the Mupe Bay conglomeratic bed and its record of oil migration in the Wessex Basin.

4.2 Samples

The oil-stained conglomerate outcrop at Mupe Bay is located to the north of the steps into Mupe Bay from the Lulworth Cove coastal path (Fig. 4.1). The outcrop consists of ~ 5 m of sandstones and shales with differing impregnations of hydrocarbons. The samples were collected from the conspicuous layer containing large sandstone boulders. The sandstone matrix is a light brown oil-stained sand with well sorted, medium to coarse grains, which are poorly cemented. The matrix is a bedded channel sandstone with some indication of flow from the south-west (Miles et al., 1993). The sandstone clasts however, are darker oil cemented fine-grained sands and range in size between 2-50 cm. The clasts are typically rounded and oval in shape but some are slightly angular. Forty orientated samples were collected from both the matrix (10 samples) and 3 large clasts (30 samples) using standard palaeomagnetic boxes. The clasts were sampled from the centre to the edge of the clasts. Larger clasts were sampled to gain as many subsamples as possible to help statistical analysis. Most clasts were inaccessible on the outcrop and orientated samples were increasingly difficult to acquire. Non-orientated samples were also taken from both the matrix and clasts to conduct rock magnetic characterisation. All samples were small and care was taken to avoid damage to the appearance of the outcrop where sampling is limited in this geological area.

4.3 Magnetic characterisation

4.3.1 Magnetic mineralogy and domain state

Low temperature warming and cooling curves of saturation isothermal remanence magnetization (SIRM), induced in different fields, are displayed in Figure 4.2 and help to identify magnetic mineralogy and grain sizes. The warming curves of SIRM were induced in a field of 2.5 T at 10 K

after field cooling (FC) (field = 2.5 T) and zero-field cooling (ZFC) whilst cooling from 300 K, display steep decays in remanence between 10-50 K in both the matrix and the clasts. The ZFC and FC curves within the clasts also show inflections at 100-120 K as well as significant divergence of the room temperature (RT) cooling and warming SIRM curves revealing the presence of multi domain magnetite through the Verwey transition (100-120 K) (Walz, 2002). There is also divergence between 50-100 K in addition to hematite identified by a slight kink in the curve associated with its Morin transition at ~250 K (Fig. 4.2a) (Morin, 1950). The matrix in contrast, shows only the presence of multi domain magnetite within the RT warming and cooling SIRM curves (Fig. 4.2b).

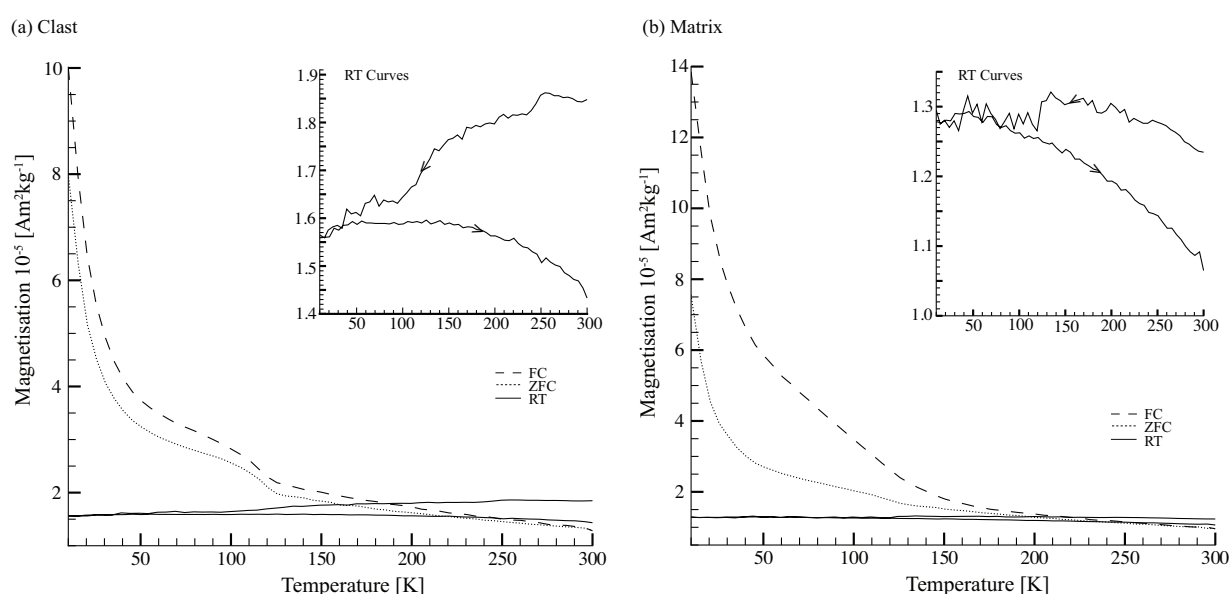


Figure 4.2. MPMS measurements for zero field cooling (ZFC), field cooling (FC) curves and room temperature remanence curves (RT) for cooling (←) and warming (→) from 10 K – 300 K giving information on mineralogy and grain sizes. (a) Mupe Bay clast and (b) Mupe Bay matrix.

The room temperature hysteresis data for the oil-stained and clean samples are represented in Table 4.1.

Table 4.1 Summarized hysteresis data, magnetic susceptibility and extractable organic matter content.

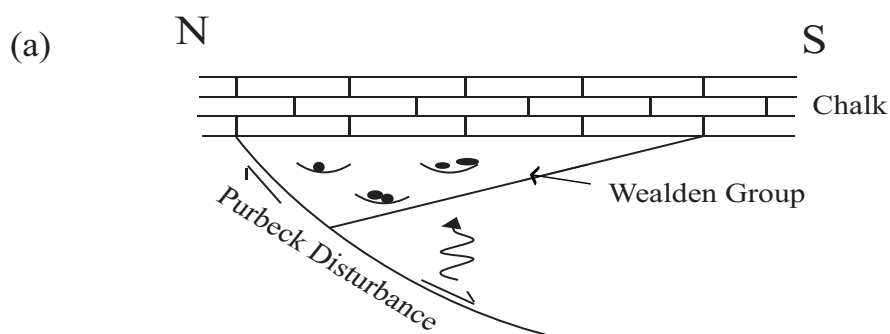
Sample	EOM %	χ ($10^{-5} \text{ m}^3 \text{ kg}^{-1}$)		H_{cr} (mT)		H_c (mT)		M_{rs}/M_s		H_{cr}/H_c	
		O	C	O	C	O	C	O	C	O	C
Clast	5.8	0.46	0.43	33.7	35.5	10.7	8.74	0.11	0.10	3.2	4.0
Matrix	2.6	0.55	0.49	40.7	31.8	7.81	8.88	0.12	0.13	5.2	3.6

EOM = extractable organic matter, χ = magnetic susceptibility, H_{cr} = remanent coercivity, H_c = coercivity, M_{rs}/M_s = ratio of saturation remanence to saturation magnetisation. The samples are in two forms; O = oil-stained and C = cleaned (oil-free).

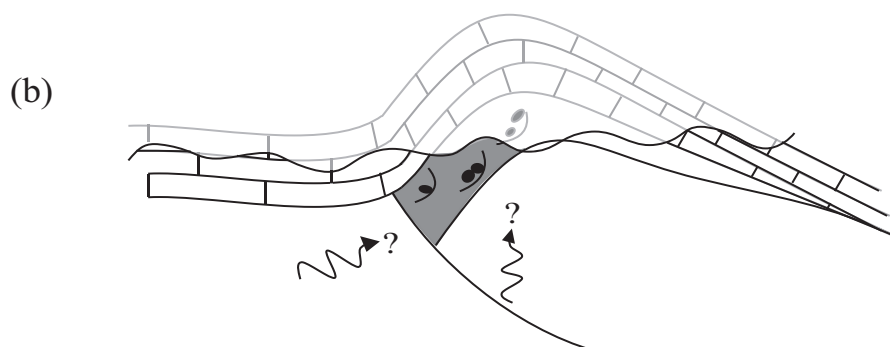
The matrix displays higher H_{cr}/H_c (5.2) and M_{rs}/M_s (0.12) ratios compared to the clasts which measured 3.2 and 0.11 respectively indicating the matrix displays multi domain behaviour, which can be inferred as larger grains than the clasts. The matrix also displays larger differences between oil stained and oil-free samples implying the oil is relatively mobile and affecting the oil stained magnetic properties greater within the matrix compared to the oil cemented clasts (Table 4.1).

4.3.2 Palaemagnetic directions

Figure 4.3 shows a schematic cross section showing pre- and post-Cretaceous structuring at Mupe Bay. This figure helps explain how a 2-phase staining model would predict different palaeomagnetic directions for the matrix and clasts but how if stained in 1-phase both sets of samples would retain the same palaeomagnetic direction.



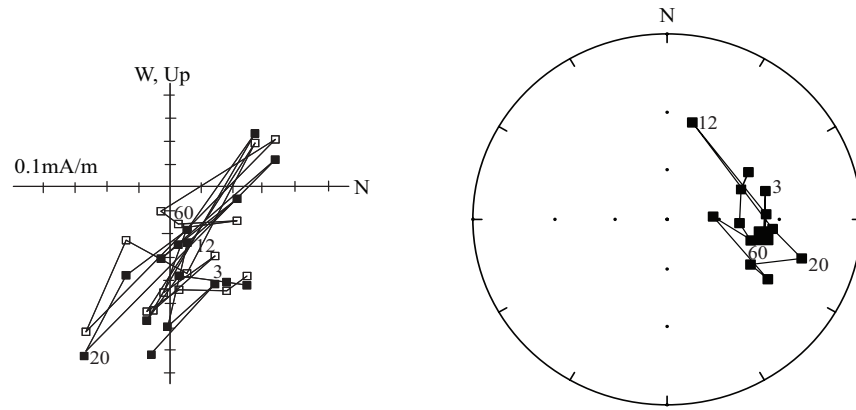
Sketch of original deposition of the Wealden Group (Cretaceous) at Mupe Bay. Possible oil migration into sandstone clasts (2 oil-staining phase model).



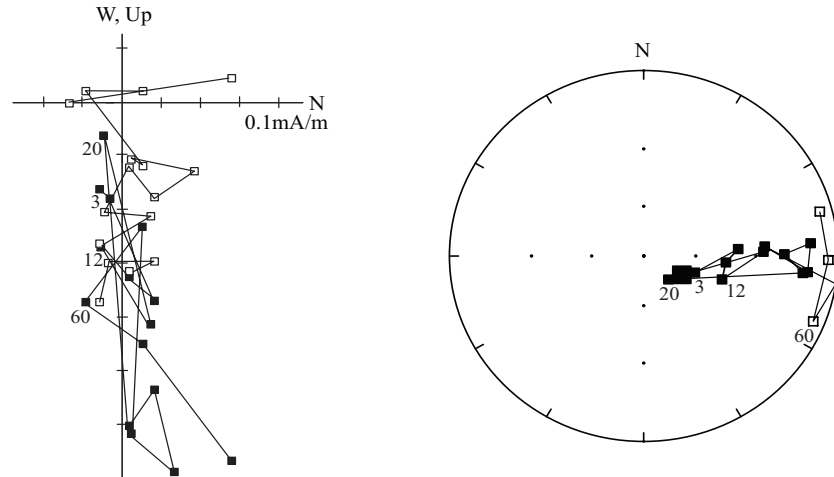
Present day cross section. The whole area has been folded, rotated and eroded to reveal the oil stained Wealden Group. Active oil seep (1 or 2 oil-staining phase model).

Figure 4.3. Cross section showing pre and post Cretaceous structuration. The context of oil impregnated matrix and clasts is described.

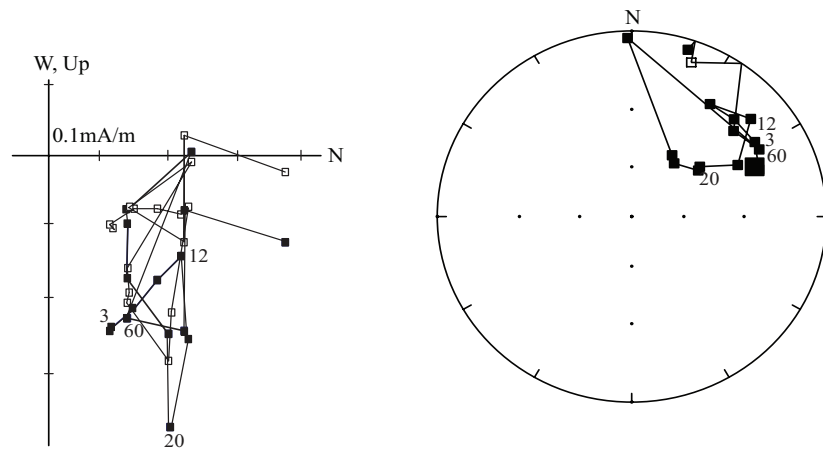
(a) Clast 1



(b) Clast 2



(c) Clast 3



(d) Matrix

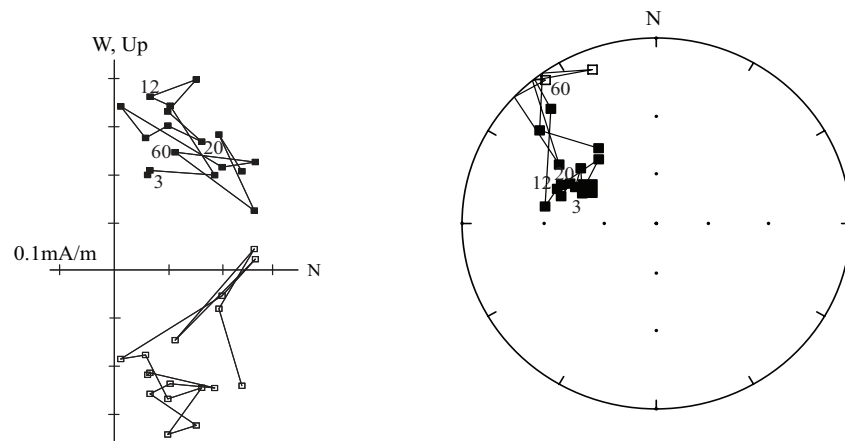


Figure 4.4. Representative Zijderveld plots for (a) Clast 1, (b) Clast 2 (c) Clast 3 and (d) Matrix.

Three clasts were originally sampled, however, the data for one of the clasts was too noisy to convincingly use for palaeomagnetic analysis. Although, it should be noted that the overall orientation and direction for all three clast were consistent (Fig. 4.4). The NRM intensities ranged between $0.51\text{-}3.1 \times 10^{-2} \text{ Am}^2\text{kg}^{-1}$, $1.1\text{-}4.2 \times 10^{-2} \text{ Am}^2\text{kg}^{-1}$ and $1.5\text{-}1.9 \times 10^{-2} \text{ Am}^2\text{kg}^{-1}$ for the matrix, clast 1 and clast 2 respectively. AF demagnetisation intensities were very close to the noise and sensitivity of the machine (2G SQUID located at the University of Oxford). In both sets of samples measurements over 80 mT become random as the sample demagnetised (Fig. 4.4). Due to the noise within the samples, directions were calculated using Fisher statistics which gave relatively large maximum angle of deviations (MADs) and α_{95} s (circle of 95% confidence) (Table 4.2). Due to the low NRM intensities and noisy behaviour, a smaller subset of samples was used for further analysis (Table 4.2).

Table 4.2 Palaeomagnetic orientation data with applied tilt correction.

	In Situ		α_{95}	Tilt corr	
	Dec °	Inc°		Dec °	Inc°
C1-2	98.2	52.2	10.9	10.4	60.3
C1-4	93.9	55.9	16.8	4.1	57.2
C1-6	102.4	48.6	11.3	17.3	63.4
C1-8	86.4	63.3	14.2	352.9	52.0
C2-1	116.5	62.8	17.1	340.3	63.8
C2-2	117.4	65.1	15.3	336.5	62.2
C2-6	99.7	43.6	13.3	28.	61.5
C2-8	104.2	44.2	12.6	27.3	64.7
M-3	319.0	41.0	9.8	-	-
M-4	358.6	58.5	14.5	-	-
M-6	355.1	29.7	9.6	-	-
M-9	353.2	51.8	13.5	-	-

α_{95} =circle of 95% confidence (Tauxe, 2010).

The inclination values for the matrix are positive and vary between $29.7^\circ\text{-}58.5^\circ$ with a mean of 46.4° (Fig. 4.5). The declination varies between $319^\circ\text{-}358.6^\circ$ with a mean of 345.8 (Tables 4.2, 4.3). This is in agreement with the present Earth's magnetic field (354° Dec, 62° Inc) at this site (50° N and 1° W) (Fig. 4.5b) at 95% confidence level. The α_{95} for the combined matrix samples (Table 4.3) is large, implying more samples are needed to provide a better defined mean direction, however, the proximity of the data to the present field direction allows the data to be interpreted as an active oil seep.

The clasts however do not show the same direction as the matrix, showing positive inclinations between $44.2^\circ\text{-}65.1^\circ$ and declinations between $86.4^\circ\text{-}117.4^\circ$ for both clasts (Fig. 4.4). Clast 1 and clast 2 have mean inclinations of 55.1° and 54.2° respectively and declinations of 96° and 107.6°

respectively (Tables 4.2, 4.3). The orientations of clast 1 and clast 2 overlap significantly and therefore were combined for statistical analysis (Table 4.3 and Fig. 4.5). Three clasts were originally sampled and although the third clast had data that was too noisy to include in the statistical analysis it also showed the same general direction and orientation as the other two clasts (Fig. 4.4).

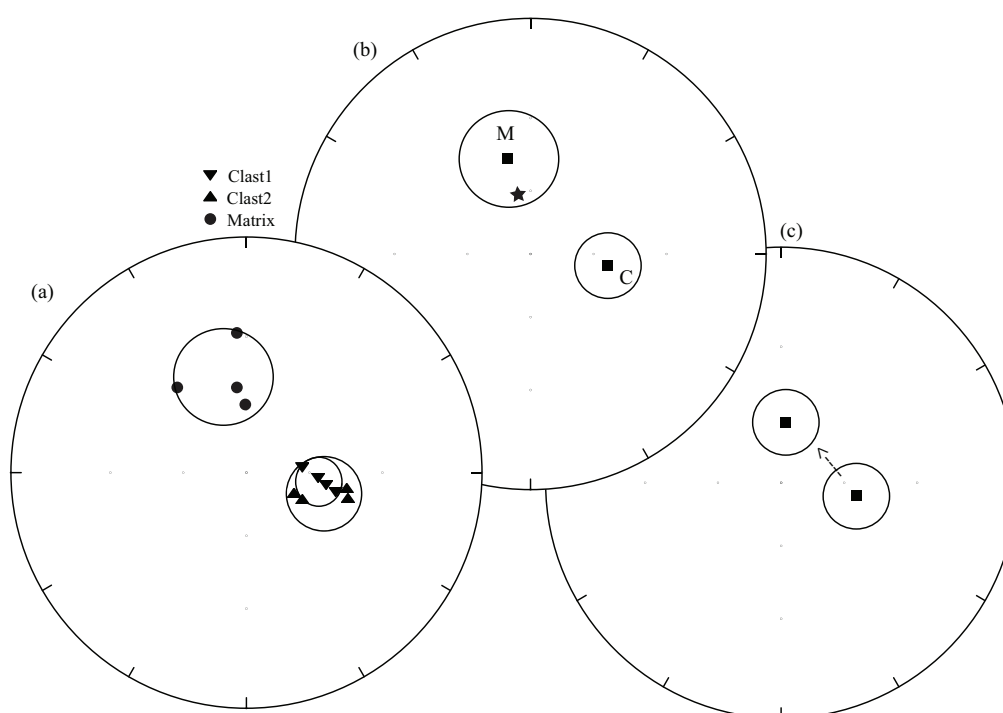


Figure 4.5. Sample directions in equal area projection from the most stable AF demagnetised samples. (a) All samples used for analysis (b) The mean matrix direction and the mean clast direction after combining clast 1 and clast 2 data. Today's magnetic field (star) at the site location is also plotted. (c) Tilt correction for the clasts to calculate palaeo-coordinates.

Table 4.3 Mean palaeomagnetic orientation data with applied tilt correction, statistical parameters and palaeo-coordinates.

	n	In situ		K	α_{95}	Tilt corr		Palaeopole		Dp	Dm
		Dec °	Inc °			Dec °	Inc °	°N	°E		
M	4	345.8	46.4	20.3	21	-	-	-	-	-	-
C1	4	96.0	55.1	123	8.3	5.2	58.5	78.6	158.2	9.1	12.3
C2	4	107.6	54.2	40.9	15	2.9	65.2	86.7	142.9	19	23.5
C1&2	8	101.9	54.8	62.8	7.0	4.1	61.9	82.6	155.2	8.4	10.8

n= number of samples, K=precision parameter, α_{95} =circle of 95% confidence, Dp = semi axis parallel to lines of latitude and Dm = semi axis parallel to lines of longitude determined by $dm = \alpha_{95}(\cos \lambda / \cos I)$ and $dp = 0.5 \alpha_{95}(1 + 3 \sin^2 \lambda)$ (Tauxe, 2010).

It is possible to determine a palaeopole for the clasts after applying a tilt correction for the bed (48-51°) (Fig. 4.5c) and, with comparison to the Northern Eurasia apparent polar wandering (APW) path, (Irving & Irving, 1982; Van der Voo, 1993; Torsvik et al., 2001) an age estimate of formation (Fig. 4.6). The orientation of the tilt correction was 228° taken from field measurements. This orientation is in general agreement with a regional map interpretation as well. An alternative approach to minimise errors associated with uncertainties in the tilt correction is to calculate palaeolatitudes through time from the APWP and compare this to the palaeolatitude calculated from the results within this study (Fig. 4.7). Given the small sample set and high-noise levels in the data, it is not robust enough to make an exact quantitative estimate.

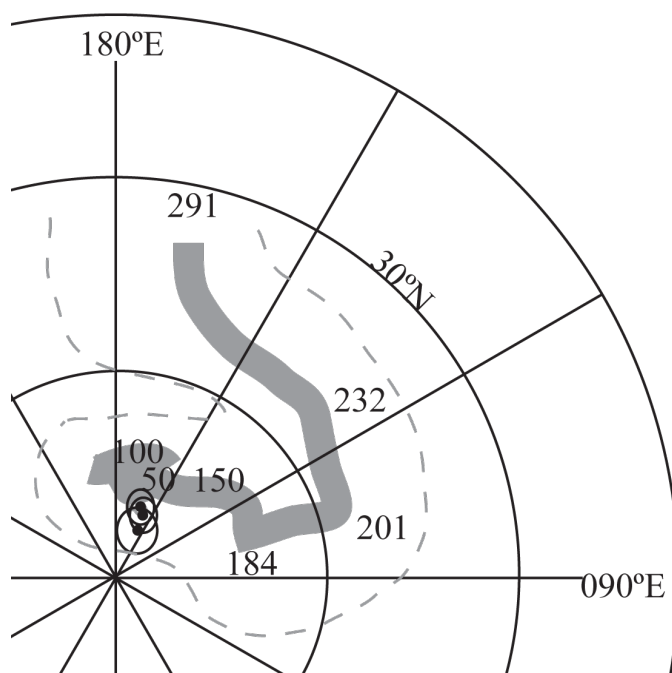


Figure 4.6. A stereonet with the apparent polar wander curve for Northern Eurasia. The existing data between 291 Ma-30 Ma is represented in grey with associated errors. The mean data for the clasts from this study are represented with associated errors (black circles and lines). Modified from Irving and Irving, (1982) and Torsvik *et al.* (2001).

However, the palaeomagnetic directions (Fig 4.6) and palaeolatitudes (Fig. 4.7) appear to intersect at the Early Cretaceous (~135 Ma). The APW does not change greatly over this time period resulting in relatively large age uncertainties (Fig. 4.6).

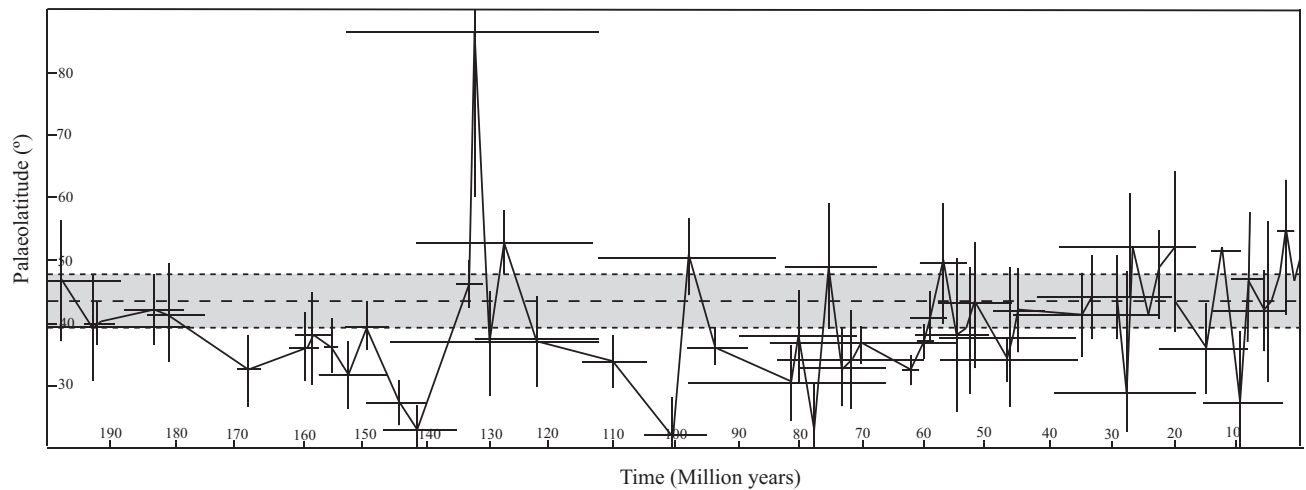


Figure 4.7. Palaeolatitudes through time (200-0 Ma) for Eurasia. Palaeolatitude data for the clasts are plotted (dashed lines) with the uncertainty (grey).

4.4 Discussion

The Mupe Bay intraformational conglomerate occupies an important position in the petroleum geology of the Wessex Basin because of its potential record of the timing of oil migration in the region. Yet two conflicting interpretations of the Mupe Bay outcrop are possible:

- i) The clasts represent previously oil stained and cemented boulders that were produced and transported in Wealden times before incorporation into a conglomeratic bed. The matrix of the conglomerate bed was then stained by later migrating oil, or
- ii) The clasts were transported unstained and both clasts and matrix were impregnated during a single oil-staining event at an undefined time, anytime after the bed was deposited in the Early Cretaceous.

Only the former scenario constrains the onset of oil migration in the Wessex Basin to the Early Cretaceous. Owing to the ambiguous nature of existing organic geochemical data, controversy exists over which interpretation is correct. Attempts have been made to use petroleum biomarker maturity parameters to reconstruct events. During a period of on-going subsidence in the Late Cretaceous a later second phase of oil staining would have been derived from a deeper and therefore more mature source rock. Yet for biodegraded oils such as those at Mupe Bay, interpretation of biomarker data can be complicated because within individual biological marker classes, compounds which are more thermally stable tend to be the most resistant to biodegradation and therefore differences can be explained by both maturity and biodegradation (Parfitt & Farrimond, 1998). There is a clear need for new methods and magnetic approaches have the potential to provide new insights.

Two key pieces of data are forthcoming. The first data set reflects the mineralogy and domain characteristics of the magnetite. The matrix is known to be more biodegraded than the clasts (Parfitt & Farrimond, 1998) and it may be possible that this biodegradation has resulted in relatively higher concentrations of multi domain authigenic magnetite within the matrix resulting in softer coercivity (Table 4.1). These differences between the clasts and matrix also support the theory of continued oil migration into the matrix.

Hematite was also identified within the clasts (Fig. 4.2) and is usually oxidized from magnetite. This suggests there was early incorporation of hydrocarbons into the clasts, which became oil cemented and subsequently isolated soon after oil migration. The early oil migration into the clasts could have insured early formation of magnetite and subsequent oxidation to hematite due to the isolation of the clasts from the matrix. The lack of hematite within the matrix supports this theory because biodegraded hydrocarbons are still actively seeping into the matrix allowing the formation of larger multi domain grains of magnetite but limiting the opportunity for oxidation.

Magnetic susceptibility and hysteresis parameters differ before and after oil extraction in both the clasts and matrix. However the magnitude of variation is larger within the matrix. The larger variations suggest the oil within the matrix is still mobile which can cause alteration in magnetic parameters. This is a result of unstable magnetic grains as well as their ability to realign in magnetic fields when 'mobile'. In contrast, the clasts show less variation because they are cemented oil sands allowing no movement of the magnetic grains and consequently are more stable.

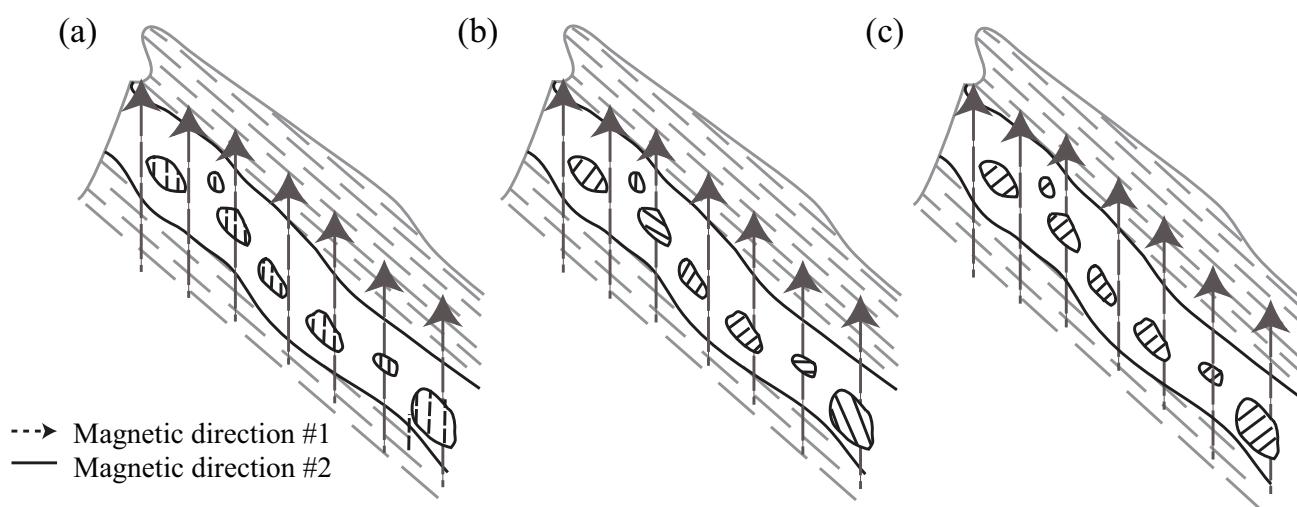


Figure 4.8. Three possible responses for magnetic directions in the Mupe Bay conglomeratic bed. (a) A single magnetic direction indicates a single-phase oil-staining event. The other two scenarios show different magnetic directions between the clasts and matrix indicating a two-phase oil-staining event, (b) random orientation in clasts. (c) consistent orientations in clasts. All scenarios have matrix magnetic direction correlating with present day magnetic field representing an active seep.

The second data set comprises palaeodirection information. One of three possible responses may be expected (Fig. 4.8).

- i) Magnetic directions are consistent in both Mupe Bay clasts and matrix indicating a single phase oil-staining event (Fig. 4.8a), or
- ii) Magnetic directions are different in Mupe Bay clasts and matrix indicating a double phase oil-staining event with sampled clasts having random directions reflecting magnetite formation prior to clast transport (which induced the random orientation) and incorporation into the conglomerate bed (Fig. 4.8b), or
- iii) Magnetic directions are different in Mupe Bay clasts and matrix indicating a double phase oil-staining event with all sampled clasts having consistent directions reflecting magnetite formation following clast incorporation into the conglomerate bed (Fig. 4.8c).

The data reveals that the matrix and clasts show different magnetic field orientations implying that the matrix and the clasts were stained by two separate oil migration events. This interpretation is supported by statistical analysis that indicates the independence of the matrix and the clasts magnetisation cannot be rejected at a 95% confidence level.

A conglomerate test is normally performed on clasts owing to their transportation and incorporation into another host rock to determine if they were magnetised before (random remanence directions) or after (same remanence directions) deposition into the conglomerate bed. In this study the clasts show the same remanence orientation and therefore must have had their remanence recorded after incorporation into the matrix, however, the direction of magnetisation does not match that of the matrix. Therefore the clasts must have been oil stained before transportation but not have been fully oil cemented and the magnetisation not 'locked in' until incorporated into the conglomerate bed (Fig. 4.8c).

This interpretation requires limited opportunity for biodegradation and magnetite formation before clast erosion, transport and deposition. Sedimentological data support this assertion and clasts are believed to have been transported only a small distance from Lulworth Cove (Wimbledon et al., 1996) and are considered to have been deposited into the matrix whilst soft due to their deformation (Miles et al., 1993; Wimbledon et al., 1996). Palaeomagnetic coordinates for the Cretaceous using the apparent polar wandering curve for Northern Eurasia are sporadic. Few very reliable constraints exist especially for the Early Cretaceous (Irving & Irving, 1982; Van der Voo, 1993; Torsvik et al.,

2001), however, estimated mean palaeopoles from 140-120 Ma are between 73°N, 138°E and 77°N, 170°E with associated errors (Fig 4.6). The data plotted on Figure 4.6 give a mean age for the CRM, and therefore staining, transport and incorporation of the clasts, as Early Cretaceous.

A final revelation is derived from the magnetic data from the matrix. Two possibilities exist for the matrix staining process:

- i) That the Mupe Bay matrix was stained some time after the Early Cretaceous but is now inactive.
- ii) That the Mupe Bay matrix represents a seep, which is active at the present day.

The magnetic data for the Mupe Bay matrix shows the same magnetisation as today (-6° Declination, 65° Inclination) at 95% confidence, suggesting it is an active oil seep. This interpretation is concordant with other seeps along the Dorset coast, some of which are active at the present day, e.g. Bran Point (Watson et al., 2000).

This study demonstrates the utility of magnetic data to constrain the timing of migration in petroleum basins. This data clearly supports the classic two-stage oil-staining event, which involves the onset of oil migration in the Wessex Basin in the Early Cretaceous. The matrix was stained at a later date and the Mupe Bay matrix continues to seep oil at the present day.

4.5 Conclusions

1. Magnetic data from Mupe Bay, Dorset, provide new insights into the controversial record of timing of oil migration in the Wessex Basin.
2. Biodegradation of the oil in both clasts and matrix of the Mupe Bay conglomeratic bed has produced micron-sized magnetite grains.
3. Magnetic directions are different in the clasts and matrix that make up the Mupe Bay conglomerate supporting interpretations that invoke a two-phase oil-staining event. One staining event pre inversion and the second post inversion.
4. Palaeomagnetic directions in the clasts are consistent with biodegradation processes operating on the oil in the Early Cretaceous.
5. Consistent directions in separate clasts imply that the biodegradation and magnetite formation took place following transportation of the oil-cemented clasts and their incorporation into the conglomerate bed.
6. Magnetic directions in the Mupe Bay matrix are in harmony with the Earth's current magnetic field indicating that seepage is active at the present day.

Chapter 5

Investigating the dominant effect on oil chemistry and magnetic characterisation through the Saltarín 1A well, Llanos Foreland Basin, Colombia

5.1 Introduction

The Eastern Cordillera and its surroundings are of great interest to petroleum geoscientists (Palmer & Russel, 1988; Roeder & Chamberlain, 1995; Ramón & Dzou, 1999; Ramón et al., 2001; Gonçalves et al., 2002; Sarmiento & Rangel, 2004; Sánchez & Permanyer, 2006) owing to the presence of organic-rich source rocks in the region. The Llanos Basin is on the eastern edge of the Andes Mountains and is one of the sub-Andean basins extending from Venezuela to Argentina and is known to include hydrocarbons (Chapter 2).

The organic-rich sediments of the La Luna Formation (Upper Cretaceous) and its lateral equivalents have been allocated as the major source rocks for many oil plays within Colombia and neighbouring regions (Villamil, 2003). The La Luna Formation is an algal, marine carbonate rich source (Zumberge, 1984). Further source rocks have been proposed, namely the Upper Cretaceous Gachetá and Une Formations (Palmer & Russel, 1988; Rangel et al., 1996). Hydrocarbons within this region have also indicated a possible contribution from a Tertiary source rock (Dzou et al., 1999; Cortes et al., 2010) through the detection of a relatively high abundance of oleanane - a Tertiary-age biomarker (Murray et al., 1994).

The Llanos Foreland Basin appears to be a complex hydrocarbon region in an intricate geological setting. Within the Llanos Basin the recognition of contributions from different source rocks within the region has been determined through the use of organic markers such as diamondoids (Springer et al., 2010) and diterpanes (Dzou et al., 1999). Reservoir oil is subdivided into a number of different oil families corresponding to different sources, mixing or levels of biodegradation (Palmer & Russel, 1988; Rangel et al., 1996; Cortes et al., 2010). Chemical variation brought about by long distance migration has been discounted as an important mechanism (Ramón & Dzou, 1999).

In response to the remaining uncertainty associated with variations in oil chemistries in the area, the geochemical signature of oil impregnations through a vertical profile within the Saltarín 1A well in the distal Llanos Foreland Basin (Chapter 2) has been characterised. Using a vertical succession, this study investigates the following hypotheses: is the primary control of oil chemistry in this region due to contributions from more than one source rock, oil generation at different maturities, post filling modification or distinct filling histories? Furthermore, using the chemical results, the magnetic characterisation is compared to chemical variations in an attempt to understand further the relationship between hydrocarbons and magnetisation.

5.2 Geological setting

The samples taken from the vertical Saltarín 1A well, Llanos Foreland Basin, Colombia (Fig. 5.1) are described in detail in Chapter 2, Section 2.1.1.2. Four samples were taken at depths of 127.40, 147.25, 541.75 and 616.48 m covering the Carbonera (1 sample), León (1 sample) and the Guayabo (2 samples) Formations.

Within the Llanos Basin there are two major hydrocarbon systems, the Gacheta/Mirador system and the Gacheta/Carbonera/Mirador system. These systems generated and expelled hydrocarbons during the Eocene-Oligocene and the Andean orogeny respectively (Cortes et al., 2010). The main reservoir rocks are thought to be the Une Formation (Early Cretaceous), Guadalupe/Barco Formation (Late Cretaceous/Palaeocene) and the Carbonera Formation (Units C1-C8) (Oligocene-Early Miocene) (Rangel et al., 1996). Samples in this study come from the Carbonera Formation (reservoir rock) the Leon Formation, which is considered a regional seal and the Guayabo Formation (Fig. 5.2). No significant hydrocarbon shows have been identified within the Leon or Guayabo Formations. It has been documented that there are both marine Cretaceous source rocks as well as a significant Tertiary source differentiated by high concentrations of plant markers in the later (Dzou et al., 1999; Ramón et al., 2001) within the Llanos Basin.

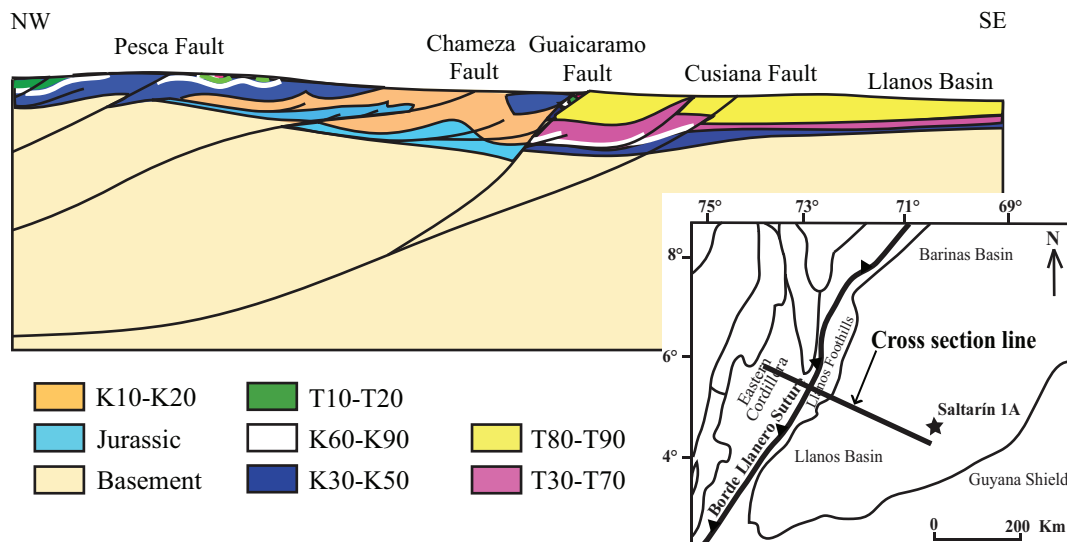


Figure 5.1. Cross section from NW to SE through the Eastern Cordillera, Llanos foothills and the Llanos Basin. The stratigraphic units found within the Saltarín 1A well at the Llanos Foreland basin are T80-T90 (Leon and Guayabo Formations) and T30-T70 (Carbonera Formation). Modified from Copper *et al.* (1995a).

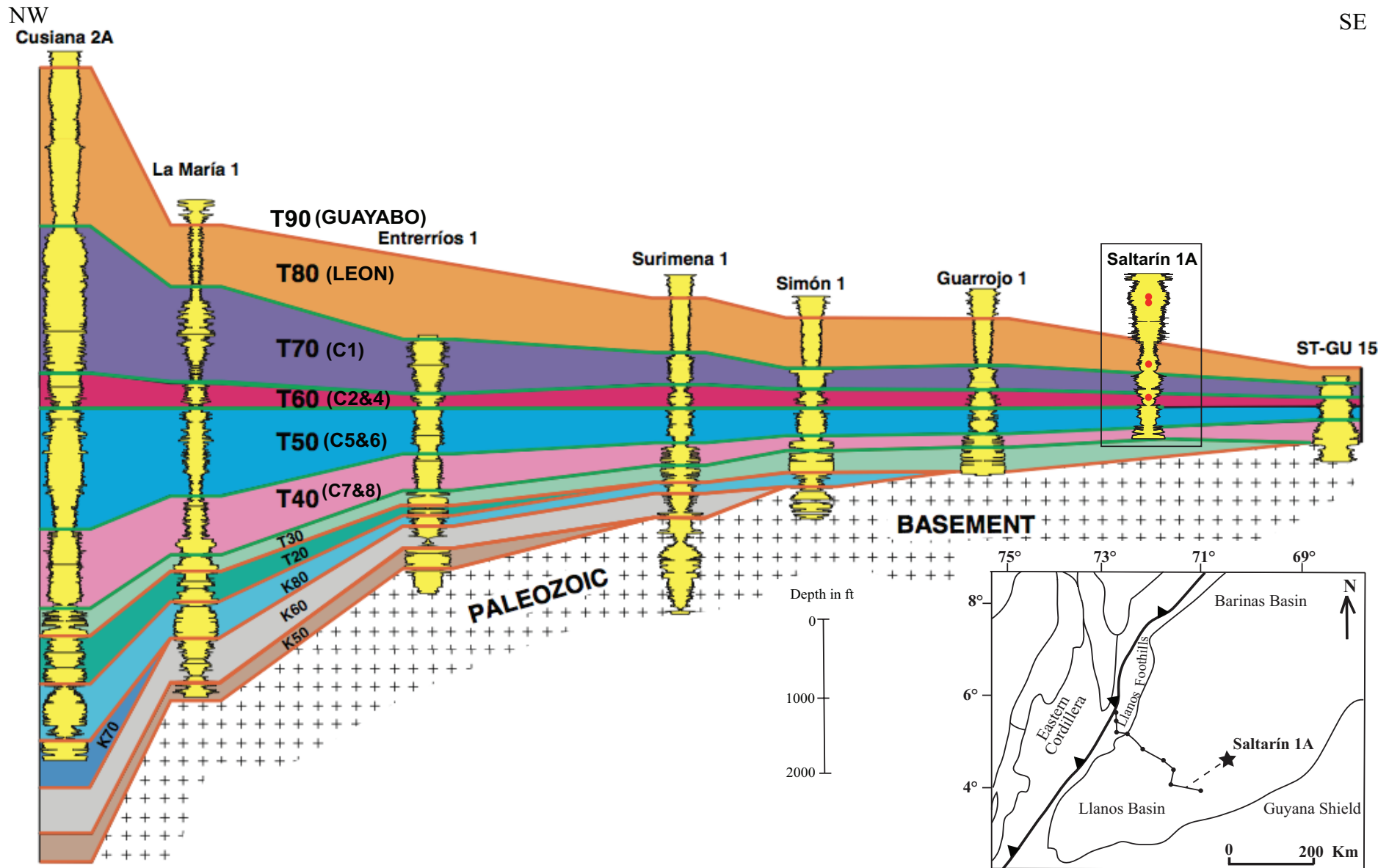


Figure 5.2. Correlation of stratigraphic units K50 – T90 in the Llanos Basin based on seven representative wells. The location of the correlation section is shown on the map. In addition, the Saltarín 1A well from this study has been inserted where similar stratigraphic units can be found. Each well has a gamma ray log in API units; the gamma ray logs have been plotted twice by reversing the scale for the right curve. Wide separation of the two curves indicates a low gamma ray response (sands). Modified from Copper *et al.*, (1995a).

5.3 Chemical characterisation

The oil extraction procedure and analysis was performed on these samples as described in Section 2.2. The chemical analysis of these samples is in addition to that shown in Chapter 3 with emphasis on variations between this set of samples.

5.3.1 Extractable Organic Matter (EOM)

The percentages of EOM for the four samples are shown in Table 5.1. The range of EOM% was between 1-6.9 % (Table 5.1) and appears to increase with sample depth.

Table 5.1 Oil extraction and fractionation percentages for each sample within this study.

Sample	EOM%	Asphaltene %	Aliphatic %	Aromatic %	Polar %
C127.40	1.1	0	73.5	11.8	14.7
C147.25	1.9	0	74.0	9.3	16.7
C541.75	6.6	0	92.2	3.9	3.9
C616.48	6.9	0	94.2	2.9	2.9

5.3.2 Bulk oil composition

The bulk compositions of the extracted bitumen in terms of their chromatographically separated fractions are given in Table 5.1.

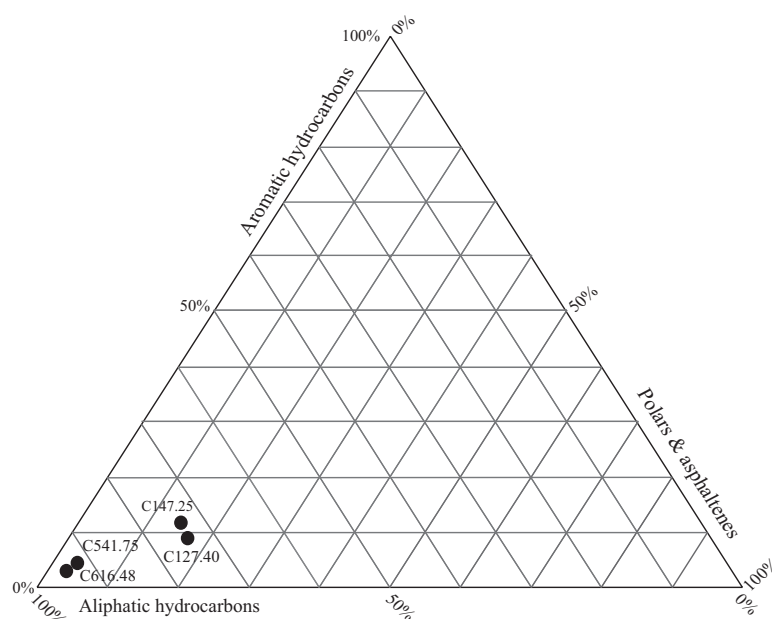


Figure 5.3. Ternary diagram of oil constituents: aliphatic hydrocarbons, aromatic hydrocarbons and polars & asphaltenes. The samples are labelled for reference.

The samples contained no asphaltenes; the bitumen comprised 74-94% aliphatic fraction (hexane elute), 3-12% aromatic fraction (dichloromethane elute) and 3-17% polar fraction (methanol elute). The relative abundances of the three fractions from this study are represented on a ternary diagram where the dominance of the aliphatic fractions is readily evident (Fig. 5.3).

5.3.3 Fourier Transform-InfraRed spectroscopy

FT-IR analysis was conducted to identify the nature of the functional groups present in the oils (Fig. 5.4). Overall, the spectra are relatively complex with a number of main characteristic absorption bands representing organic molecular bonds.

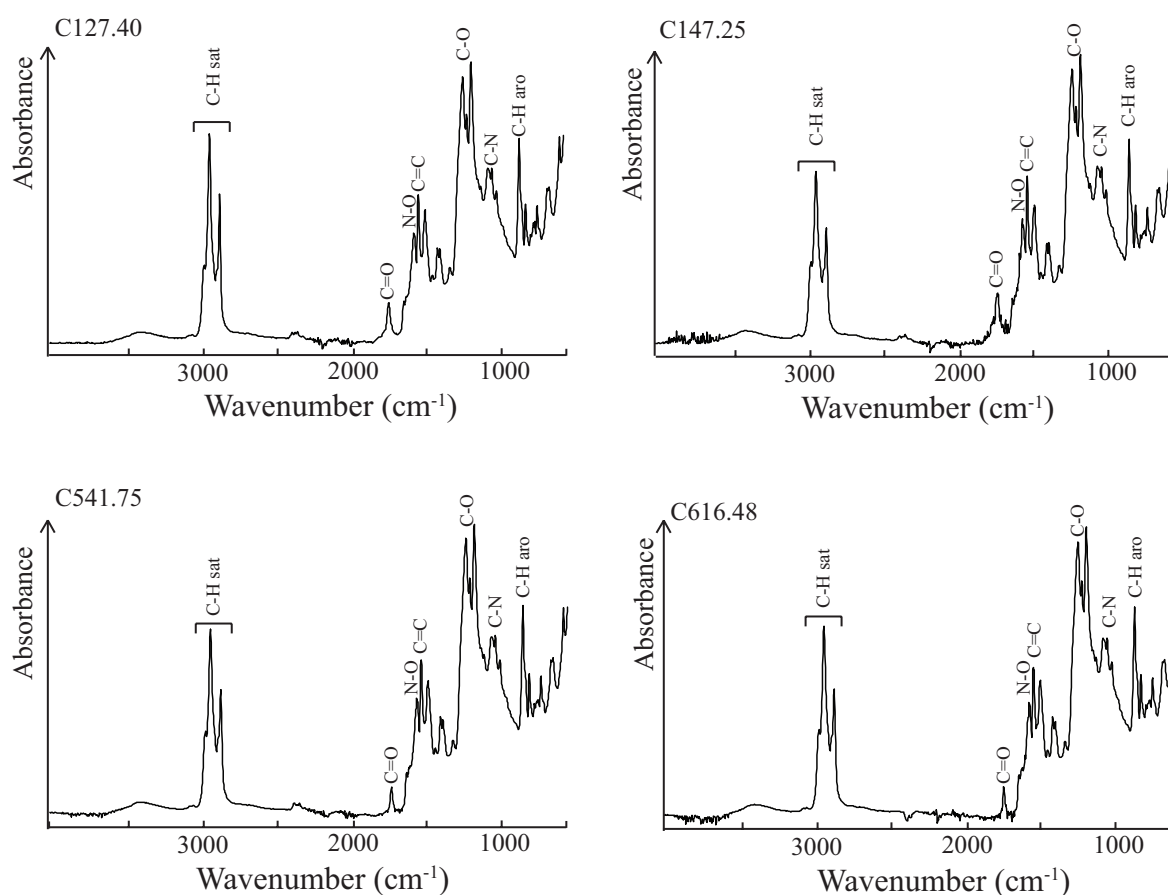


Figure 5.4. FT-IR spectra for representative samples within this study with characteristic absorption bands identified for interpretation.

The well-defined absorptions between 3200-2700 cm^{-1} (Fig. 5.4) are characteristic of carbon and hydrocarbon containing species with variations due to C-H stretching (Coates, 2000). In all four samples the main absorptions are below 3000 cm^{-1} , which are indicative of saturated hydrocarbons.

Specifically, the strong absorptions between 2960-2860 cm^{-1} , the strong methylene/methyl band ($\sim 1470 \text{ cm}^{-1}$) relative to a weaker methyl band ($\sim 1380 \text{ cm}^{-1}$) (Fig. 5.4) and small absorptions at 720 cm^{-1} most probably represent a long chain linear aliphatic chain (Coates, 2000). In contrast the lack of absorptions above 3000 cm^{-1} and specifically between 3150-3000 cm^{-1} which are almost exclusively indicative of unsaturated and aromatic compounds (Coates, 2000), reveals the relatively low percentage of aromatics within all four samples. However, C=C-C and C-H aromatic-ring related vibrations can be identified at $\sim 1510 \text{ cm}^{-1}$ and 900-670 cm^{-1} respectively (Fig. 5.4). Other common absorption bands were also categorized (Fig. 5.4) such as C=O ($\sim 1700 \text{ cm}^{-1}$), aliphatic N-O ($\sim 1540 \text{ cm}^{-1}$) C-O (1150-1200 cm^{-1}) and C-N (1090-1020 cm^{-1}). These observations are consistent with the fractionation data and ternary plot (Fig. 5.3, Table 5.1), which reveals dominant aliphatic contributions with relatively small quantities of aromatic fractions.

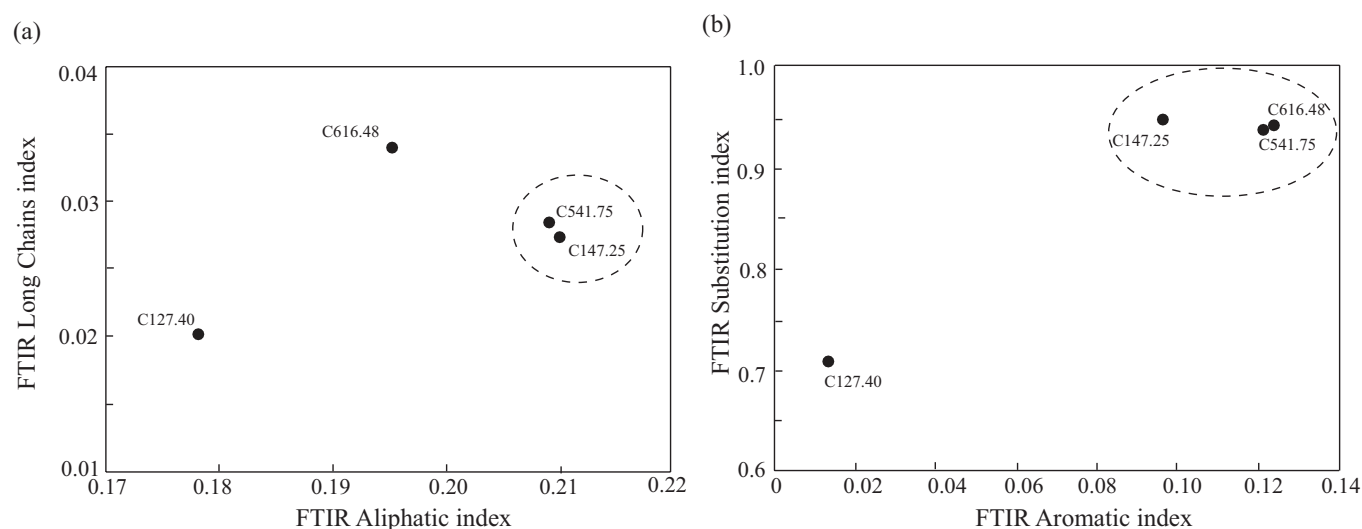


Figure 5.5. FT-IR index graphs for all oil samples (a) aliphaticity vs. long chain indexes and (b) aromaticity vs. substitution indexes. Distinct groups of oils can be distinguished.

FT-IR spectroscopy can also be a complimentary tool for reservoir compartmentalization assessment (Permanyer et al., 2002; Permanyer et al., 2007) by using main IR bands indexes. The results shown in Figure 5.5 help to differentiate between oils throughout the well. Sample C127.40 displays a lesser aliphatic character and a lower degree of condensation of aromatic compounds than all other samples (Fig. 5.5). The aromatic and substitution indexes (Fig. 5.5b) distinguish two groups with distinct compositional variation.

5.3.4 *n*-Alkanes and isoprenoidal hydrocarbons

The GC-MS total ion current chromatograms for the aliphatic fractions from the four samples are presented in Figure 5.6. The most notable components in the aliphatic fractions are a series of *n*-alkanes. The prominent *n*-alkanes in all samples range from *n*-C₁₅ to *n*-C₃₃ (Table 5.2) and exhibit a unimodal distribution. There is no overwhelming odd-dominance in the *n*-alkanes. The modes for the *n*-alkanes in the four samples are *n*-C₂₄ for the relatively shallow samples (C127.40 and C147.25) and *n*-C₂₂ for the two relatively deeper samples (C541.75 and C616.48).

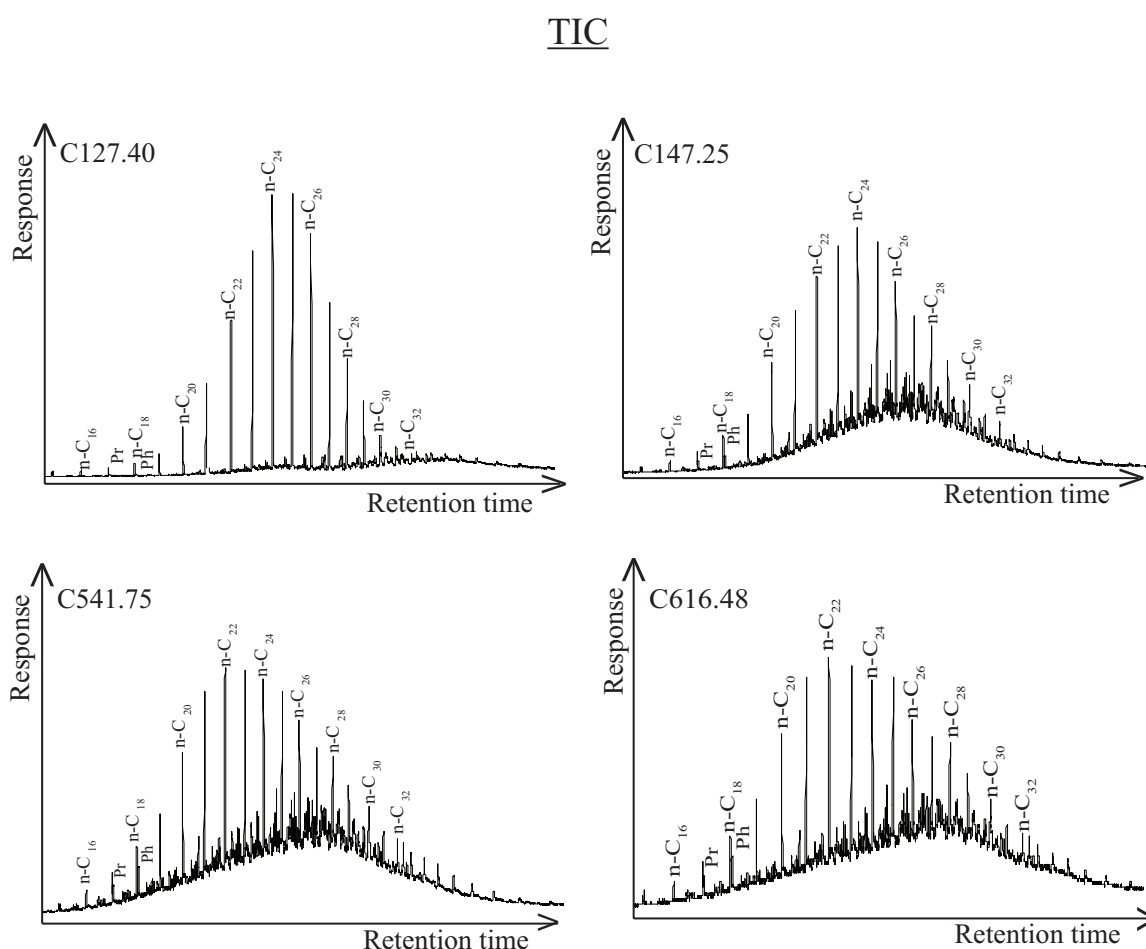


Figure 5.6. TIC chromatograms of the aliphatic fractions for samples from the Saltarín 1A well, Colombia. All even numbered *n*-alkanes are highlighted for reference as well as Pr (pristane) and Ph (phytane). *n*-C₁₆, hexadecane, -C₁₈, octadecane, -C₂₀, eicosane, -C₂₂, docosane, -C₂₄, tetracosane, -C₂₆, hexacosane, -C₂₈, octacosane, -C₃₀, triacontane, -C₃₂, docontane.

All but the shallowest sample have a small but noticeable unresolved complex mixture (UCM). The GC-MS data also reveal strong responses from $m/z = 55$ (mass-to-charge ratio) and isoprenoidal hydrocarbons are present in the aliphatic fractions with the most notable representatives of this compound class, pristane and phytane identified (Fig. 5.6). Phytane is consistently more abundant than pristane and pristane/phytane ratios approach 0.5 (Table 5.2).

Table 5.2 Summary of analytical results of *n*-alkanes for the samples from this study.

Sample	<i>n</i> -Alkanes	Isoprenoids			
	Range	Pr/Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈	Odd/Even
C127.40	C ₁₅ -C ₃₃	0.65	0.33	0.26	0.96
C147.25	C ₁₅ -C ₃₃	0.54	0.62	0.54	1.02
C541.75	C ₁₅ -C ₃₁	0.56	0.79	0.87	0.98
C616.48	C ₁₅ -C ₃₁	0.53	0.68	0.81	0.97

Pr/Ph: Pristane/phytane

Pr/*n*-C₁₇: pristane:normal C₁₇-alkane

Ph/*n*-C₁₈: phytane:normal C₁₈-alkane

Odd/Even: $C_{21}+6C_{23}+C_{25}/4C_{22}+4C_{24}$ (Scalan and Smith, 1970)

5.3.5 Hopanes and steranes

Ion selection allows the identification of hopanes (*m/z* 191) (Fig. 5.7) and steranes (*m/z* 217) (Fig. 5.8).

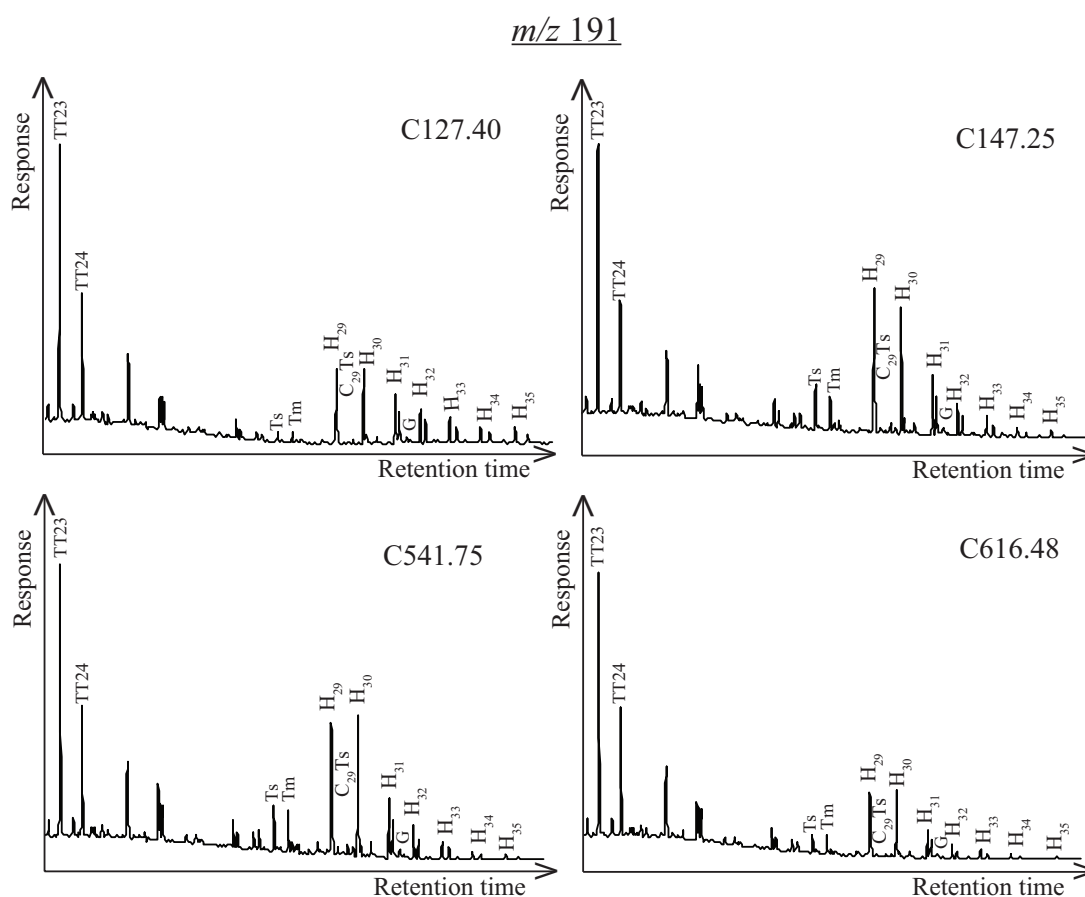


Figure 5.7. Mass chromatograms (*m/z* 191) of the aliphatic hydrocarbon fractions to identify hopanes for samples from the Saltarín 1A well, Colombia. Compounds used for biomarkers are highlighted. Ts-C₂₇ 18 α trisnorhopane, Tm-C₂₇ 17 α trisnorhopane, C₂₉TS-18 α -30-norneohopane, sequence of H₂₉-H₃₅ = C₂₉-C₃₅ hopanes, G-gammacerane.

In the m/z 191 mass chromatogram, all four samples contain responses from Ts and Tm. The Ts/Tm+Ts ratio ranges from 0.52 to 0.59. The homohopanes extend to C_{35} with a steady decrease in response with carbon number. The relative abundance of C_{29} and C_{30} are much higher in the C147.25 and C541.75 samples. C_{29} $\alpha\alpha\alpha$ (S/S+R) ratios approximate to 0.5 (Table 5.3). All samples contain gammacerane (Fig. 5.7) with the gammacerane/ C_{30} hopane ratio ranging from 0.21 to 0.99.

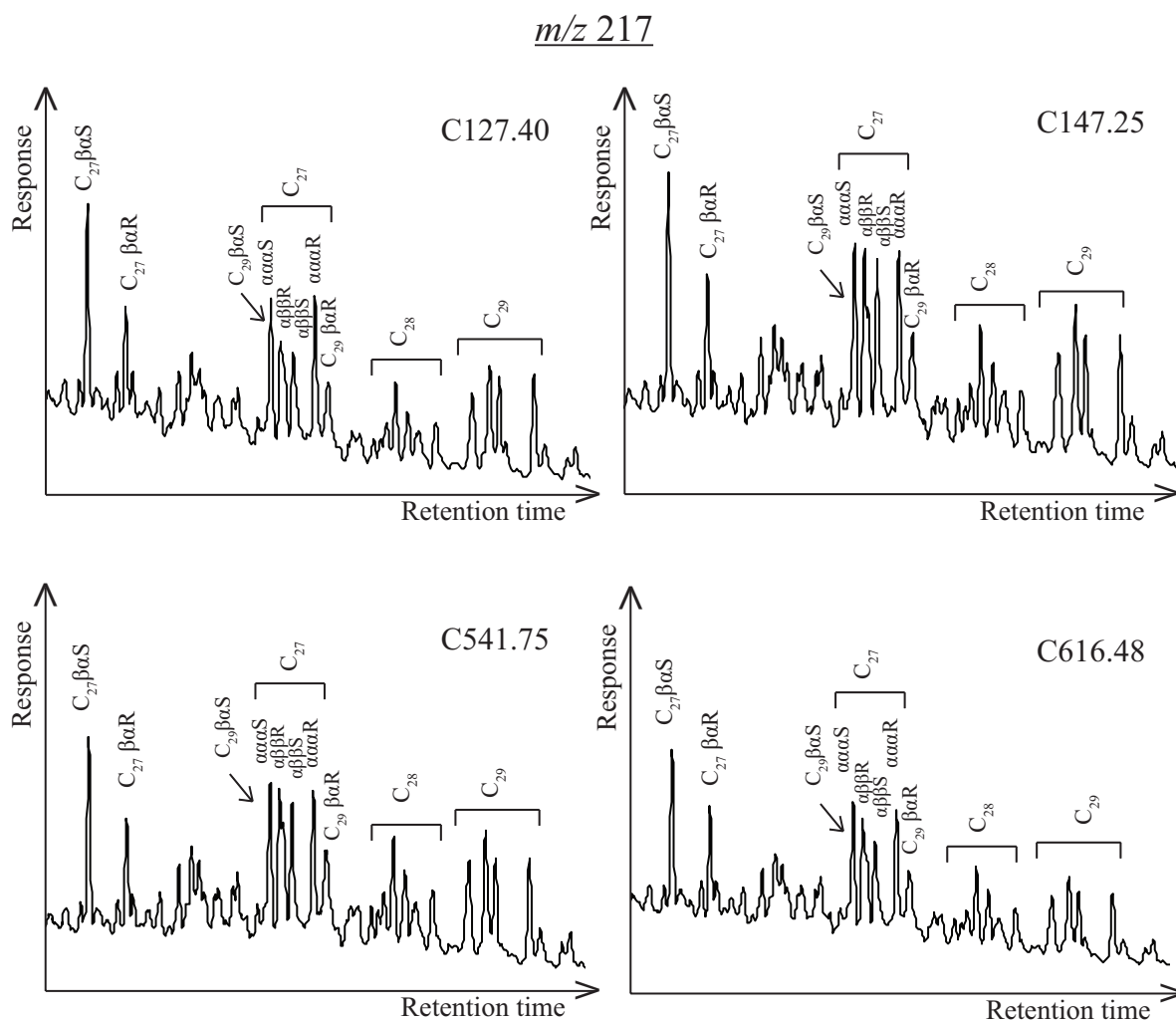


Figure 5.8. Mass chromatograms (m/z 217) of the aliphatic hydrocarbon fractions to identify steranes for samples from the Salarín 1A well, Colombia. C_{27} – $C_{29}\beta\alpha$ (S+R) – C_{27} – C_{29} diasteranes. C_{27} – $C_{29}(\alpha\alpha\alpha$ (S+R) and $\alpha\beta\beta$ (S + R)) are elution orders for C_{27} – C_{29} steranes.

In the m/z 217 mass chromatogram (Fig. 5.8), all four samples contain strong responses from C_{27} regular steranes ($\alpha\alpha\alpha S$, $\alpha\beta\beta R$, $\alpha\beta\beta S$ and $\alpha\alpha\alpha R$) with less dominant responses from their C_{28} and C_{29} counterparts (Fig. 5.9). Diasteranes ($\beta\alpha S$ and $\beta\alpha R$) are also noticeable in the m/z 217 mass chromatogram.

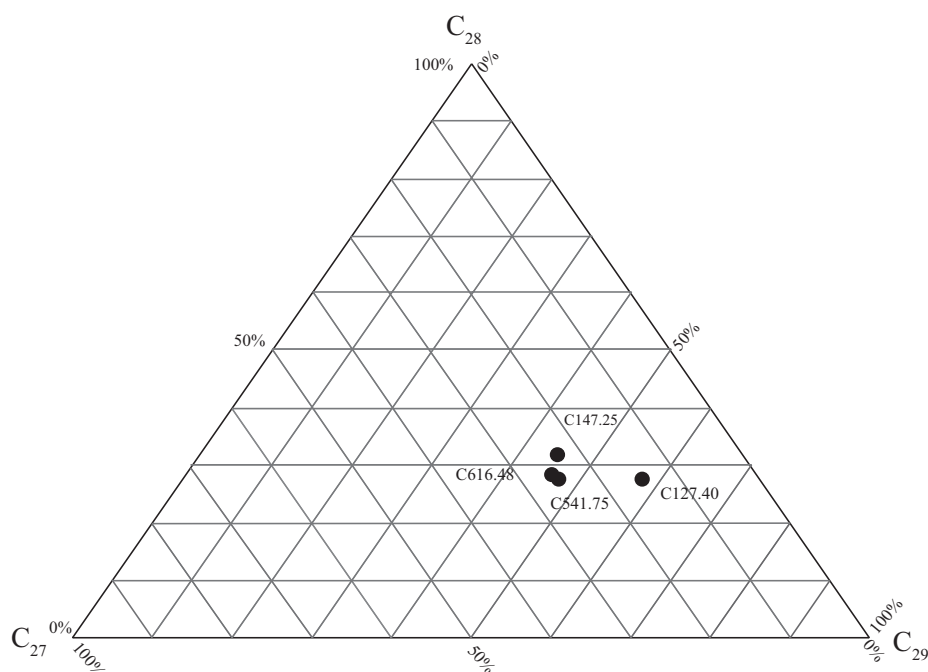


Figure 5.9. The aliphatic hydrocarbon fractions for C₂₇, C₂₈ and C₂₉ $\beta\beta$ steranes from m/z 217.

Table 5.3 Summary of analytical results of hopanes and steranes for the samples from this study.

Sample	Maturity/Source					Biodegradation		
	Ts/Ts+Tm	C ₂₉ $\alpha\alpha\alpha$ (S/S+R)	C ₃₀ ($\beta\alpha/\alpha\beta$)	ol/(ol+C ₃₀)	Dia/dia+steranes	C ₂₉ $\beta\beta/(\alpha\alpha+\beta\beta)$	Gam/C ₃₀ $\alpha\beta$	UCM/C ₂₉
C127.40	0.52	0.53	0.12	0.08	0.23	0.53	0.99	0.19
C147.25	0.59	0.52	0.09	0.05	0.22	0.51	0.80	0.79
C541.75	0.54	0.57	0.12	0.04	0.25	0.53	0.21	1.71
C616.48	0.51	0.52	0.12	0.05	0.25	0.56	0.28	1.07

Ts/Ts+Tm: C₂₇ 18 α trisnorhopane/ (C₂₇ 18 α trisnorhopane + C₂₇ 17 α trisnorhopane)

C₂₉ $\alpha\alpha\alpha$ (S/S+R): C₂₉ $\alpha\alpha\alpha$ S/ (C₂₉ $\alpha\alpha\alpha$ S+ C₂₉ $\alpha\alpha\alpha$ R) steranes

C₃₀ ($\beta\alpha/\alpha\beta$): C₃₀ $\beta\alpha$ moretane/ C₃₀ $\alpha\beta$ hopane

Dia/dia+steranes: C₂₉ diasterane/ (C₂₉ diasterane+ C₂₉ sterane)

C₂₉ $\beta\beta/(\alpha\alpha+\beta\beta)$: C₂₉ $\alpha\beta\beta$ (S+R)/ (C₂₉ $\alpha\alpha\alpha$ (S+R)+ C₂₉ $\alpha\beta\beta$ (S+R))

Ol/(ol+C₃₀): 18 α / β Oleanane/ (18 α / β Oleanane + C₃₀ hopane)

Gam/C₃₀ $\alpha\beta$: Gammacerane/ C₃₀ $\alpha\beta$ hopane

UCM/C₂₉: UCM height/ C₂₉ alkane

5.4. What is the dominant effect on oil chemistry in this region?

5.4.1 Is there more than one source rock?

The GC-MS total ion chromatograms for the aliphatic fractions from the four samples are presented in Figure 5.6. The most notable components in the aliphatic fractions are a series of n -alkanes. Selected molecular parameters are outlined in Table 5.2. The n -alkane distribution (Fig. 5.6) can be

used to infer source material because lower molecular weight ($<C_{21}$) *n*-alkanes are derived from bacteria and algae (Wakeham, 1990), but high molecular weight ($>C_{22}$) *n*-alkanes generally originate from higher plants (Huang et al., 1999). There is no evidence of a great odd preference for *n*- C_{29} , *n*- C_{31} and *n*- C_{33} alkanes associated with higher plant components in immature organic assemblages. The modes for the *n*-alkanes in the four samples are between *n*- C_{24} for the relatively shallow samples (C127.40 and C147.25) and *n*- C_{22} for the two relatively deeper samples (C541.75 and C616.48) (Table 5.2). The oil samples examined in this study are, therefore, most likely to be derived from marine algae although some contribution from higher plants may be present (Fig. 5.9).

The ratio of pristane: phytane can help infer the oxygenation of the environment with higher ratios indicative of oxic conditions (>1). The pristane/phytane concentrations are low (0.53-0.65) (Table 5.2) suggesting the organic matter was deposited in an anoxic environment (Didyk et al., 1978; Ten Haven et al., 1987). Such an interpretation would be consistent with the relatively strong responses from the trisnorhopanes Ts and Tm (Table 5.3), which are also indicative of anoxic environments (Mello et al., 1987; Farrimond et al., 1989).

All but the shallowest sample (C127.40) have very similar sterane distributions ($\beta\beta$ steranes) (Fig. 5.9, Table 5.3) suggesting a common source rock for the oils sampled. The predominance of C_{27} regular steranes in all samples implies a marine, algal organic matter dominated source rock for each (Huang & Meinschein, 1979). The shallowest sample is still dominated by C_{27} steranes but has a higher percentage of C_{29} steranes, which could specify a greater proportion of higher plant matter than in the samples from greater depths possibly indicating oil source differences or oil mixing. The presence of diasteranes in the oils may indicate that the source rock from which the oils were derived had significant amounts of clay minerals in its matrix (Rubinstein et al., 1975; Van Kaam-Peters et al., 1998) although biodegradation is another mechanism by which these organic compounds can be enhanced (Wenger et al., 2001).

The Llanos Basin data may also be explained by the mixing of oils from a number of sources. It is appropriate, therefore, to attempt to examine age-specific organic indicators of source. Oleanane is a possible Tertiary age-diagnostic biomarker, when present in the relevant amounts (Moldowan et al., 1994), however it can be difficult to determine oleanane abundances because firstly; it co-elutes with C_{30} 20S-25-norhomohopane (m/z 191) and, secondly; Late Cretaceous facies also contain oleanane (Moldowan et al., 1994). Oleanane was potentially identified within the samples (Table 5.3), but these ratios are very low (<0.2) resulting in inconclusive data on whether there is a substantial Tertiary source (Dzou et al., 1999).

5.4.2 Is there evidence for varying maturities in the oils?

The GC-MS total ion current chromatograms for the aliphatic fractions from the four samples are presented in Figure 5.6. There is no overwhelming odd-dominance in the *n*-alkanes (Table 5.2), which is consistent with relatively mature organic assemblages (Scalan & Smith, 1970). All samples exhibit relatively mature values (0.96-1.02) (Table 5.2) however the slightly lower molecular weight mode for the deeper samples would also be consistent with a greater maturity although greater levels of biodegradation could also account for this difference.

Certain biomarkers are responsive to thermal maturation and can allow estimation of the relative maturity of oils. Various biomarker maturity parameters indicate that the organic matter is mature and has been heated to temperatures consistent with the oil window. Examples are presented in Table 5.3 and include $C_{30}\beta\alpha/\alpha\beta$ between 0.09 and 0.12 (oil window <0.15), $C_{29}\alpha\alpha\alpha$ sterane ratios (S/S+R) between 0.52 - 0.57 (oil window >0.4) and $Ts/Ts+Tm$ between 0.52 - 0.59 (oil window > 0.4). No major maturity differences, therefore, are evident in the various Saltarín 1A well oils.

5.4.3 What post filling processes have occurred?

The modes for the *n*-alkanes in the four samples are *n*-C₂₄ for the relatively shallow samples (C127.40 and C147.25) and *n*-C₂₂ for the two relatively deep samples (C541.75 and C616.48). The lower molecular weight mode for the deeper samples would be consistent with a greater maturity or greater levels of biodegradation. Long chain *n*-alkanes are more susceptible to biodegradation than their shorter chain counterparts (Fritsche & Hofrichter, 2008). All but the shallowest sample have noticeable UCMs. Biodegradation would account for the enhancement of UCMs by the preferential removal of *n*-alkanes over branched and cyclic forms (Wenger et al., 2001). An unconventional biodegradational parameter to use is the ratio of UCM height and the *n*-alkane (C₂₉) height (above the UCM) (Table 5.3) (Ross et al., 2010). This data suggests that the most biodegraded samples are the deeper samples C541.75 (1.71) and C616.48 (1.07).

Ratios of pristane:normal C₁₇-alkane (Pr/*n*-C₁₇) and phytane:normal C₁₈-alkane (Ph/*n*-C₁₈) are given in Table 5.2 and can be used as indicators of oil biodegradation. The isoprenoidal hydrocarbons pristane and phytane are more resistant to degradation than normal alkanes (*n*-C₁₇ and *n*-C₁₈) giving an increase in the relative ratios (Pr/*n*-C₁₇ and Ph/*n*-C₁₈) when biodegraded (Lijmbach, 1975; Wenger et al., 2001; Ross et al., 2010). There is a substantial variation between 0.32-0.79 and 0.26-0.87 for Pr/*n*-C₁₇ and Ph/*n*-C₁₈ respectively (Table 5.2).

Sterane biomarkers also display variable responses to biodegradation with regular steranes being more susceptible than diasteranes. All samples contain abundant diasteranes (Fig. 5.8), but discriminating between source effects and subsequent biodegradation processes is difficult.

Several of the features observed in the oils from the Llanos Basin can be explained by varying levels of biodegradation. The overall level of biodegradation throughout the well is low to moderate. Biodegradation is primarily an oxidation process, which is controlled by conditions needed to support microbial life (Connan, 1984). Biodegradation therefore needs a number of conditions to occur: 1) water for mobility, 2) a host rock that provides sufficient porosity and permeability for mobility, 3) temperatures that are $<80^{\circ}\text{C}$ to support the microbes, and 4) salinity and H_2S levels that are suitable for either aerobic or anaerobic bacteria (Connan, 1984; Palmer, 1993; Blanc & Connan, 1994). Biodegradation is typically more intense in shallower settings, where microbes are more populous; and it decreases with depth (Whitman et al., 1998), however, biodegradation has also been shown to increase with vicinity towards an oil-water contact (Head et al., 2003; Larter et al., 2003). The latter explanation would appear to be the most satisfying interpretation for the observed increase in biodegradation with depth in the Saltarín 1A well.

5.4.4 Is there evidence for compartmentalization?

Where biodegradation displays unusual field relationships, compartmentalization of the reservoir, which isolates and maintains specific microbial environmental conditions, is a suggested explanation. Such a scenario is implied by the Llanos Basin data. The unusual relationship between higher biodegradation in the deeper samples could be due to compartmentalization through the well. If the shallowest samples reside within one or two compartments with an aquifer supplying water to the deeper samples, increased biodegradation towards the oil-water contact would be expected. Using FT-IR indexes (Fig. 5.5) and GC fingerprinting (Table 5.3) the results suggest that the deepest samples (C541.75 and C616.48) show compartmentalization when compared to the shallower samples (Fig. 5.5) with a suggested oil-water contact closer to C541.75. The shallowest sample, C127.40 has significantly different characteristics that could be due to the oil residing in its own compartment (Fig. 5.5) but the presence of a higher contribution of higher plant material (Fig. 5.9) suggests an additional influence of more than one source rock most likely a tertiary Source within the shallow samples.

Hence, the chemical differences brought about by biodegradation and possibly source variations are potentially produced and certainly maintained by reservoir compartmentalization and chemical communication between the deeper and shallower samples is incomplete.

5.5 How do chemical variations relate to magnetisation through the well?

The samples from the Saltarín 1A well have been extensively geochemically analysed in the previous sections but in this section they are magnetically characterised to try to identify specifically what differences exist in the magnetic profile of the samples when compared to their geochemical signatures.

5.5.1 Magnetic characterisation

Magnetic susceptibility in the samples varied between $1.0\text{--}9.1 \times 10^{-4} \text{ m}^3\text{kg}^{-1}$ with the magnetic susceptibility decreasing with depth for these samples (Table 5.4).

Hysteresis parameter M_{rs}/M_s was significantly higher in the deepest sample (C616.48) but was also high in sample C541.68 relative to the shallowest samples (Table 5.4). H_{cr}/H_c ratios were higher in sample C147.25 (5.6) relative to the other samples, which varied between 2.4–2.9. On a Day plot (see Chapter 3) using grain boundaries for magnetite, the M_{rs}/M_s and H_{cr}/H_c ratios suggest samples C127.40 and C147.50 contain PSD-like grains whereas samples C541.75 and C616.48 are more SD-like in behaviour inferring smaller magnetic grains. The shallower samples also have much higher M_s values ($23.9\text{--}31.3 \times 10^{-3} \text{ Am}^2\text{kg}^{-1}$) compared to the deeper samples ($0.75\text{--}2.03 \times 10^{-3} \text{ Am}^2\text{kg}^{-1}$) (Table 5.4).

Table 5.4 Magnetic parameter summary for all the Colombian samples. The data is given for the oil stained samples.

Sample	χ ($10^{-4} \text{ m}^3\text{kg}^{-1}$)	H_{cr} (mT)	H_c (mT)	M_{rs}/M_s	M_s ($10^{-3} \text{ Am}^2\text{kg}^{-1}$)	MDF (mT)
C127.40	9.1	19.9	6.84	0.08	23.9	11
C147.25	3.4	28.2	5.02	0.05	31.3	14
C541.75	1.9	34.1	13.1	0.13	0.75	22
C616.48	1.0	57.9	23.8	0.28	2.03	48

The SIRM MDF's also varied dramatically with low MDF's between 11 mT and 14 mT for the shallow samples (C127.40 and C147.25) compared to the deeper samples, 22 mT and 48 mT for C541.75 and C616.48 respectively (Table 5.4).

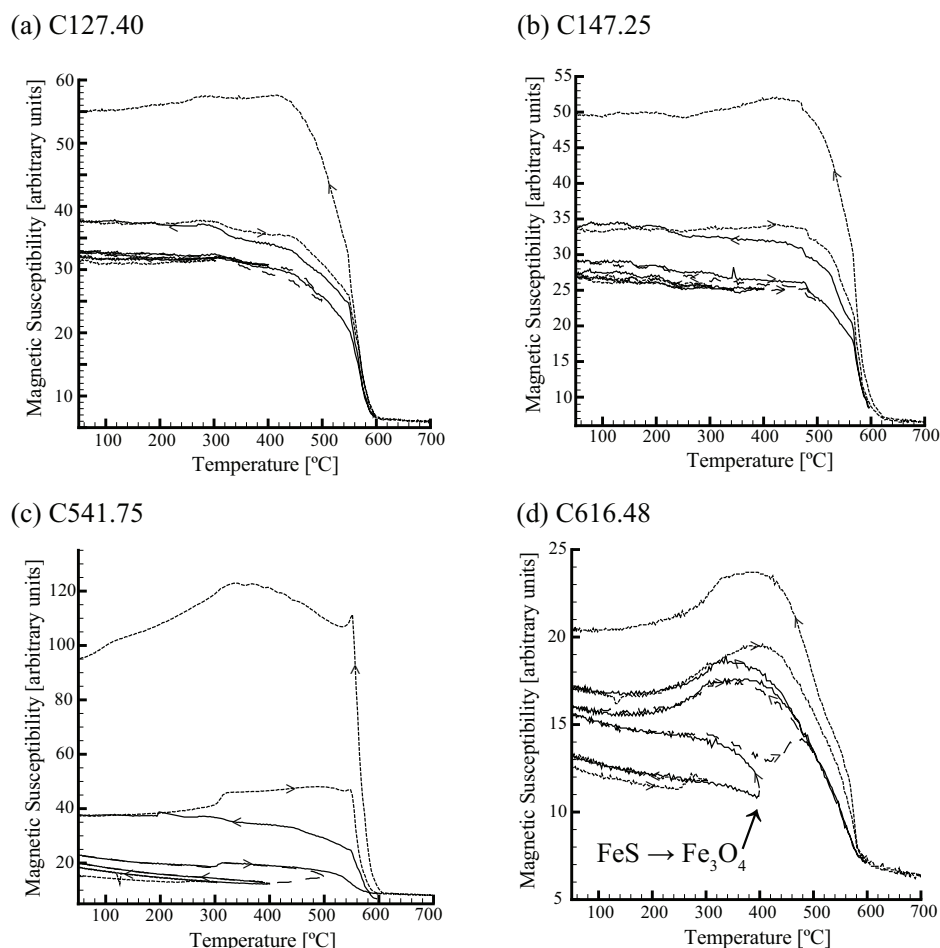


Figure 5.10. Magnetic susceptibility warming and cooling curves as a function of temperature, increasing the peak temperature in 100 °C cycles from 50°C to 700 °C in argon. (a) C127.40, (b) C147.25, (c) C541.75, and (d) C616.48. 300 °C, — 400 °C, -- 500 °C, — 600 °C and ... 700 °C.

High temperature magnetic susceptibility revealed similar behaviour in the shallowest samples (C127.40 and C147.25) (Fig. 5.10a,b) with the heating and cooling curves coinciding with an approximate Curie temperature of ~ 560 °C which is consistent with magnetite using the second derivative. The samples appear to become purer magnetite with heating. Sample C541.75, however, shows the formation of a new ferromagnetic mineral between 450-500 °C on the 500 °C cycle. The continued heating reveals the overall production of magnetite similar to that in the shallower samples but with the presence of a Hopkinson peak. A Hopkinson peak occurs when blocked stable SD grains become superparamagnetic (unblocked) grains at temperatures near the Curie temperature. Superparamagnetic grains have relatively higher susceptibilities and therefore produce a peak in high temperature susceptibility measurements. The deepest sample, C616.48 shows the continued production of new minerals on heating from 200 °C and 400 °C mostly. The overall result is a magnetite profile when cooled from 700 °C (Fig. 5.10d).

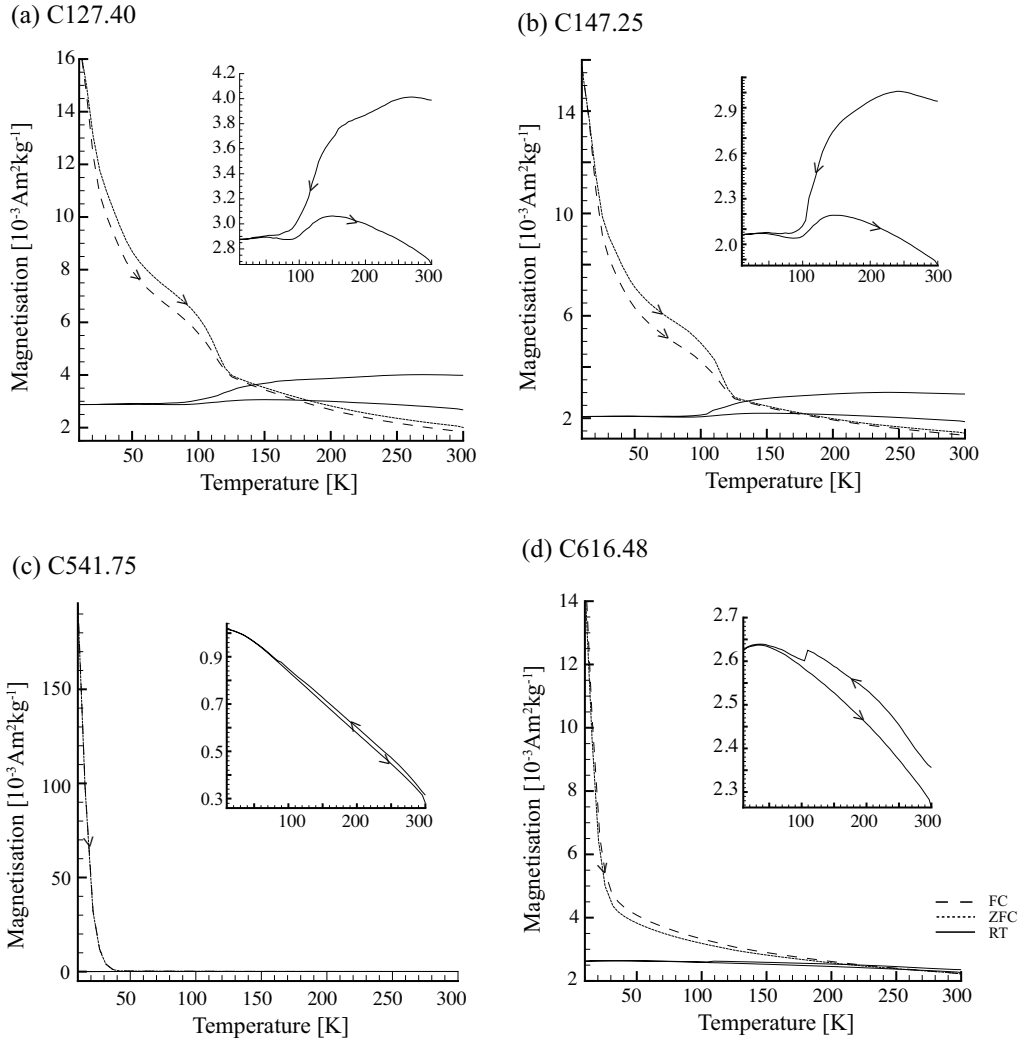


Figure 5.11. Zero field cooling (ZFC) and field cooling (FC) curves from 300 to 10 K in 10 K steps as well as room temperature remanence (RT) cooling and warming curves from 300-10 K in a zero field. (a) C127.40, (b) C147.25, (c) C541.75, and (d) C616.48. (FC ---, ZFC ····, RT warming →, RT cooling ←).

Figure 5.11 displays the warming and cooling curves of SIRM induced in different fields e.g., a field of 2.5 T at 10 K after field cooling (FC) (field = 2.5 T) and zero-field cooling (ZFC) whilst cooling from 300 K. The FC and ZFC curves as well as the room temperature (RT) cooling and warming curves are very similar for both the shallowest samples (Fig. 5.11a,b). The samples show a stronger remanence in the ZFC curve than the FC. FC remanences are usually larger than ZFC but the presence of multi domain magnetite can counter this (Carter-Stiglitz et al., 2006). The FC and ZFC curves reduce in magnetisation relatively steeply between 10-50 K and reveals a kink at both 50 K and ~ 110 K at the same point that the ZFC and FC converge. The RT cooling and warming curves diverge from 90 K with a large deflection in the warming curve at ~110 K. These characteristics show the presence of non-stoichiometric multi domain magnetite (Muxworthy & McClelland, 2000) and possibly some contribution from siderite or pyrrhotite.

Sample C541.75 shows a dramatic decrease in magnetisation in the FC and ZFC that overlap one another between 10-40 K representing possible pyrrhotite (Fig. 5.11c). It is difficult to differentiate between siderite (FeCO_3) and pyrrhotite (Fe_7S_8) in low temperature experimentation due to the presence of the Néel transition for siderite at ~ 37 K and a magnetic transition near ~ 35 K for pyrrhotite (Kars et al., 2011). The RT curves also decrease in magnetisation overall and show only a slight diversion at ~ 100 K. Sample C616.48 also shows a decrease in FC and ZFC between 10-30 K but the RT cooling and warming curves show significant divergence from ~ 95 K as well as a significant inflection at 100 K for the cooling curve. The RT curves also decrease in overall magnetisation with increasing temperature. This suggests the deeper samples contain of pyrrhotite and multi domain magnetite, present in slightly larger amounts in sample C616.48 (Fig. 5.11d), compared with samples C127.40 and C147.25, which show more multi domain magnetite.

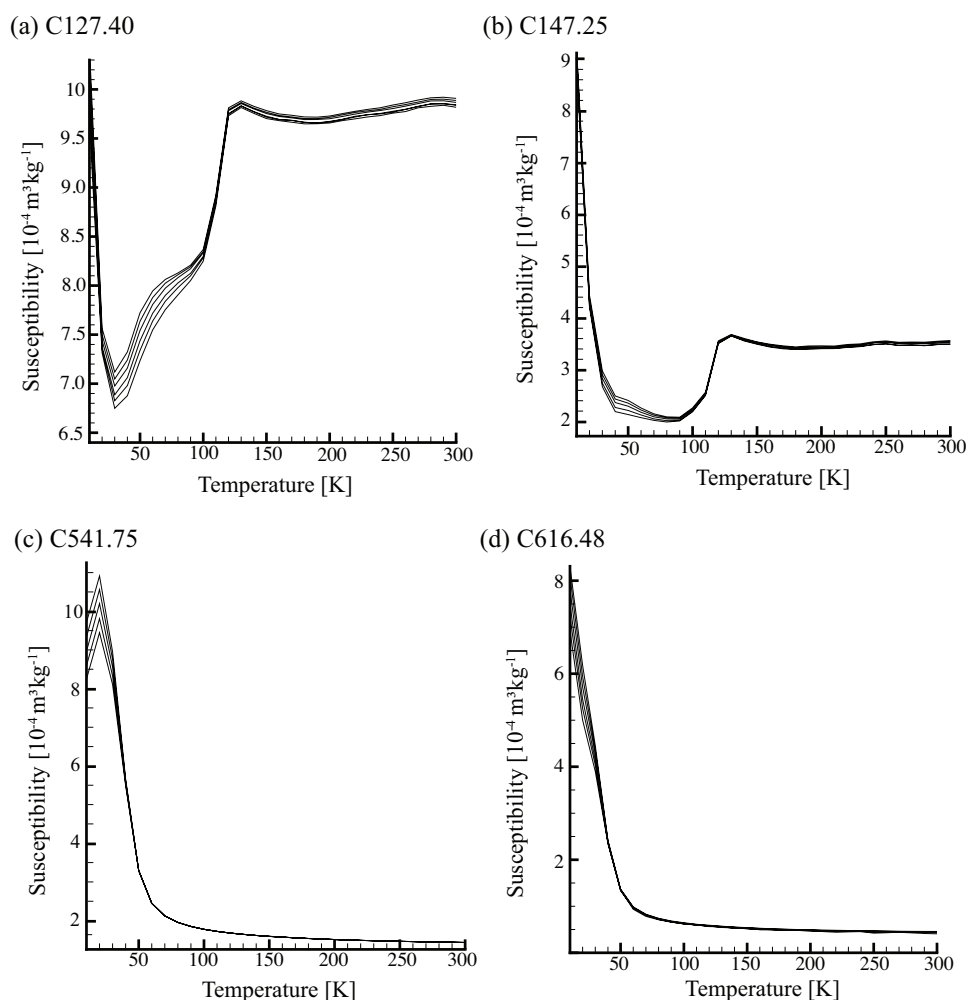


Figure 5.12. Susceptibility measurements for AC susceptibility at 7 frequencies between 10-300 K in 10 K steps at seven frequencies (1.0, 32.2, 10.0, 31.6, 100.1, 316.7, 997.3 Hz). (a) C127.40, (b) C147.25, (c) C541.75 and (d) C616.48.

AC susceptibility curves as a function of temperature and frequency show that the shallowest sample, C127.40 reveals deflections at ~ 30 K and 100 K (Fig. 5.12a) as well as a very strong

frequency dependency between 30-100 K. The largest inflection is at ~ 110 K suggesting a high presence of multi domain magnetite.

Sample C147.25 (Fig. 5.12b) shows a large abundance of multi domain magnetite (~ 110 K) and only a small frequency dependency at low temperatures. The deepest samples, C541.75 and C616.48 have similar behaviour with the dominance of frequency dependency below 30 K and a main deflection at ~ 50 K (Fig. 5.12c,d). Sample C541.75 also has a peak deflection at ~ 20 K. The AC susceptibility curves for these samples suggest low concentrations of magnetite and high concentrations of an iron sulphide (e.g., pyrrhotite) or siderite due to the low temperature frequency dependency.

The quantity of available material was too small to perform a magnetic extraction causing difficulty in Mossbauer spectroscopy and SEM/EDX analysis. Mössbauer spectroscopy was attempted on all the samples but due to low concentrations only two samples were successful (C147.25 and C616.48) (Fig. 5.13, Table 5.5).

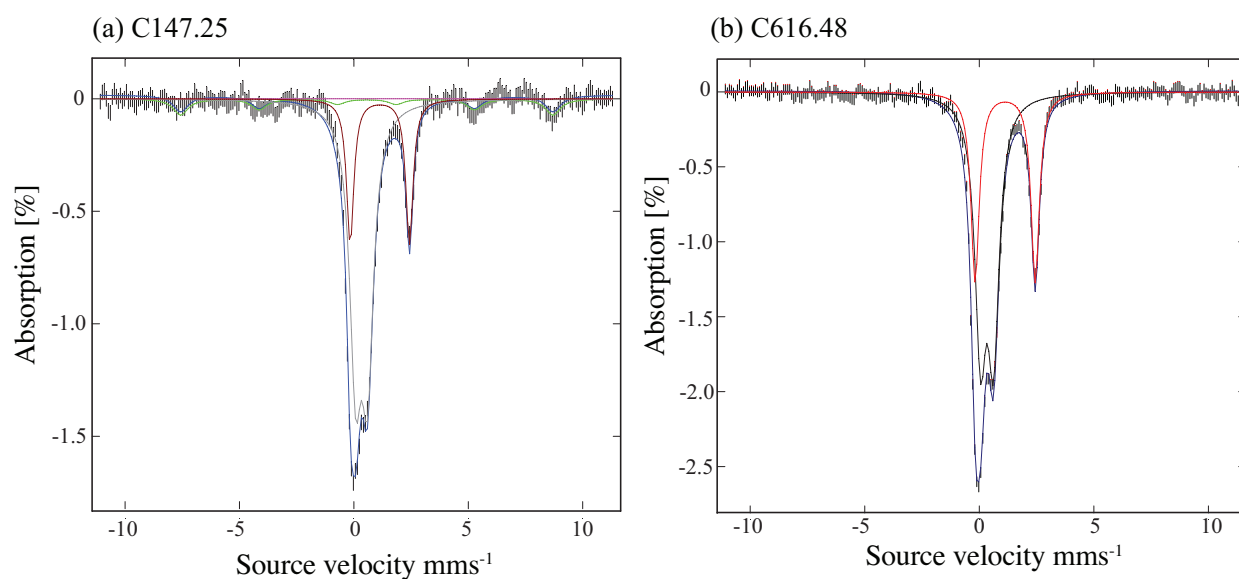


Figure 5.13. Mössbauer spectroscopy results with fitting curves for (a) C147.25 and (b) C616.48. Magnetic hyperfine parameters are quoted in Table 5.5.

The magnetic hyperfine parameters at room temperature show a central doublet with isomer shifts (IS) of 0.34 mms^{-1} and 1.13 mms^{-1} for sample C147.25 characteristic of Fe^{3+} and Fe^{2+} (Greenwood & Gibb, 1971). Sample C616.48 showed the same isomer shifts (Table 5.5). All components have much larger line widths (W) than expected for the stoichiometric chemical compounds ($W \sim 0.25\text{-}0.35 \text{ mms}^{-1}$). A sextet was identified within sample C147.25 with a field (B_{hf}) of 50.6 which represents non-stoichiometric magnetite (Vandenberghe et al., 2000). The quality of the fit in both

Mössbauer spectrums is low, however, the literature suggests that both samples contain oxidized versions of magnetite (Vandenberghe et al., 2000).

Table 5.5 Mössbauer spectroscopy for two sample; C147.25 and C616.48. Magnetic hyperfine parameters determined at room temperature.

Sample	Fits	QS (mms^{-1})	IS (mms^{-1})	B_{hf} (T)	W (mms^{-1})	Rel. Area %
C147.25	Doublet I	0.522	0.34	--	0.63	66.7
	Doublet II	2.59	1.13	--	0.38	22.8
	Sextet I	-0.001	0.57	50.6	0.80	10.5
C616.48	Doublet I	0.57	0.34	--	0.59	63.2
	Doublet II	2.63	1.13	--	0.44	36.8

QS – quadruple splitting, IS – isomer shift, B_{hf} = hyperfine field, W = width and Rel. Area % = relative proportion.

SEM and EDX analysis on the samples show the presence of framboidal material within the shallowest samples, C127.40 and C147.25 (Fig. 5.14).

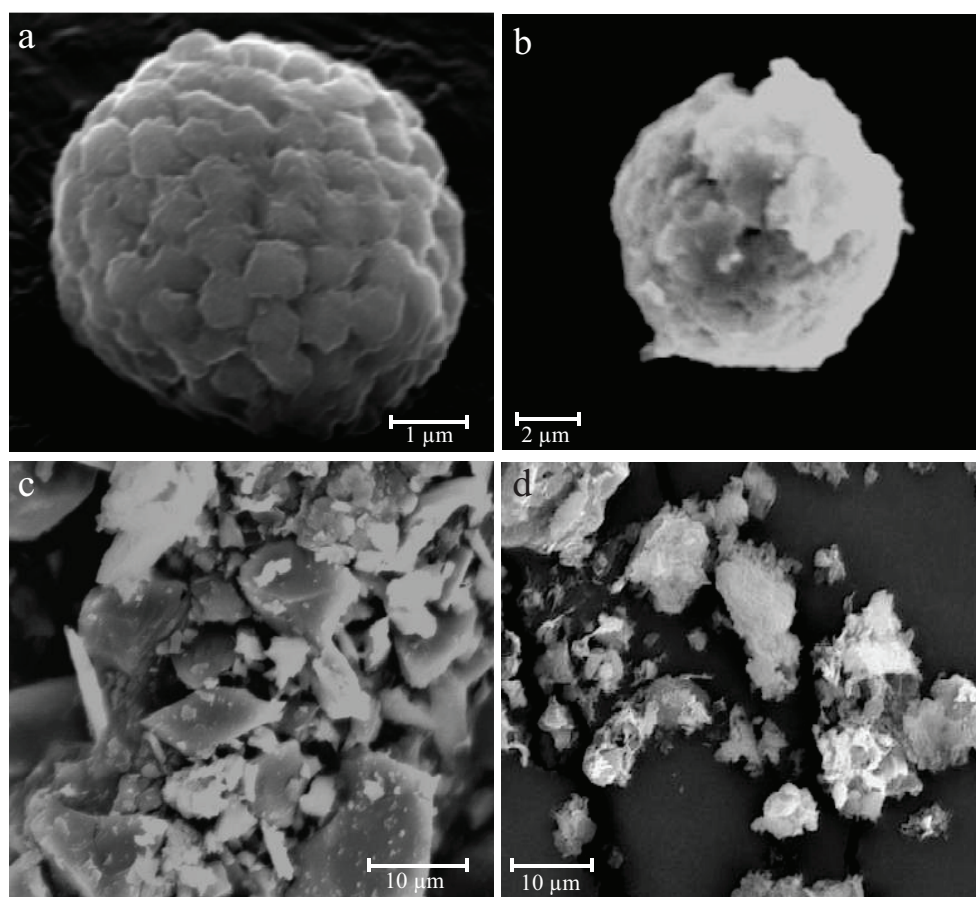


Figure 5.14. SEM images of samples; a) C127.40, b) C147.25, c) C541.68 and d) C616.48. Framboids were identified within samples C127.40 and C147.25.

The framboids almost certainly account for a proportion of the magnetic signal from these samples, however they do not necessarily dominate the signal. The framboids are abundant and range in size between 4 μm - 10 μm . EDX analysis reveals they are an iron sulphide, most probably pyrite (See section 1.3.3). Other magnetic grains were also identified within these two samples, mainly as iron oxides ranging in diameter between 1 - 5 μm . Conversely the deeper samples, C541.75 and C616.48 had no framboids present (Fig. 5.14). The magnetic minerals in the samples were hard to identify but it is thought that relatively small grains of mainly iron sulphides reside in the deeper samples, especially in C616.48.

5.5.2 How does the magnetic data relate to biodegradation?

As shown in the previous section (5.4), the level of biodegradation in the samples increases with depth and is most probably due to an oil water contact at depth. Also in Chapter 3 it was discussed how a relationship between biodegradation and magnetic susceptibility appears to exist over a variety of samples from across the world. To try to analyse this relationship further, the Colombian samples provide a set of samples that not only vary magnetically but also within oil chemistry, which has been determined to be due to biodegradation. It was concluded that the geochemical differences in the oils indicate compartmentalization (the shallow and deep samples are disconnected) and the magnetic data are investigated to see if it supports the geochemical interpretation.

Figure 5.15 is a plot of the Colombian samples compared with EOM%, biomarkers used for identifying biodegradation states in oils ($\text{Pr}/n\text{-C}_{17}$, $\text{Ph}/n\text{-C}_{18}$ and UCM/C_{29}) and magnetic susceptibility (χ). Figure 5.15 clearly shows that an increase in EOM coincides with a decrease in magnetic susceptibility as already identified in Chapter 3. To characterise this relationship further, biomarkers such as $\text{Pr}/n\text{-C}_{17}$, $\text{Ph}/n\text{-C}_{18}$ and UCM/C_{29} which all increase with increasing biodegradation (See Section 1.4.7.3) were correlated to magnetic susceptibility. The biodegradation parameters all have a strong negative correlation with magnetic susceptibility confirming the relationship observed in Chapter 3. Statistical analysis could not be conducted on the sample set because it only consists of four samples, which is not robust for confident statistical parameters.

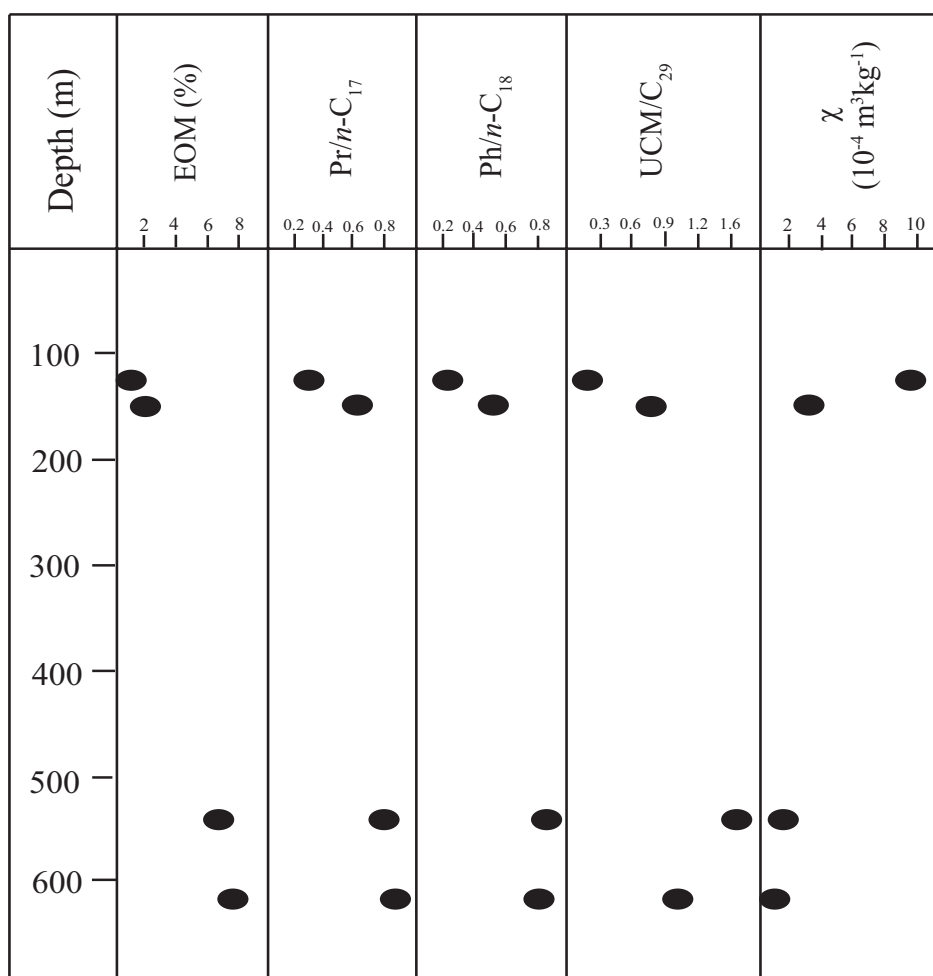


Figure 5.15. Plot of the four samples in this study versus EOM% and parameters used for assessing the degree of biodegradation in the oil (Pr/n-C₁₇, Ph/n-C₁₈ and UCM/C₂₉) and magnetic susceptibility (χ).

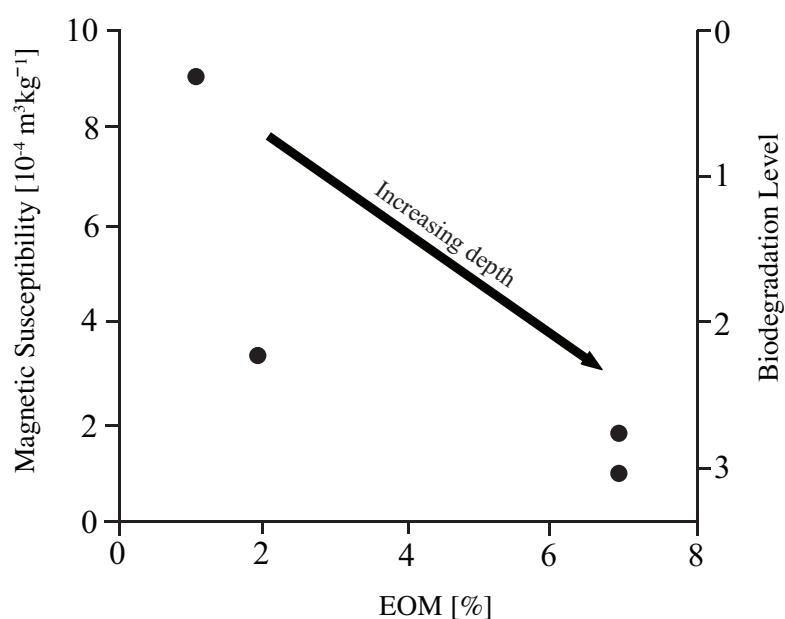


Figure 5.16. Magnetic susceptibility related to EOM% and biodegradation state for the Colombian samples using the Wenger scale of biodegradation (Wenger *et al.* 2001).

The overall biodegradation level of the oils taken from the Wenger Scale (See Section 1.4.6) and GC-MS fingerprinting (Section 5.3) definitely reveal a decrease in χ relative to an increase in biodegradation (Fig. 5.16).

5.6 Magnetic data discussion

Through magnetic characterisation, the samples broadly split into two sets of samples, the shallow samples (C127.40 & C147.25) and the deeper samples (C541.75 & C616.48). In terms of the shallowest samples, the framboids present, mainly iron sulphides as identified through EDX analysis are significant but do not necessarily dominate the magnetic signal due to the obvious presence of multi domain magnetite as seen in the MPMS data, Mössbauer spectroscopy and high temperature susceptibility measurements (Figs. 5.10-5.13). The framboids are maybe an indicator of the processes and associated environmental conditions occurring at shallow depths.

The deeper samples however, do not appear to have a significant abundance of multi domain magnetite but rather are dominated by a mineral, which shows significant low temperature dependency. There is considerable difficulty in identifying magnetic minerals in natural systems with magnetic transitions at temperatures < 40 K but combining all the magnetic data as well as SEM and EDX imaging, it is suggested an iron sulphide is the major magnetic mineral instead of an iron carbonate (siderite). In this case, pyrrhotite is most likely. The deeper samples also revealed no framboids present.

This detailed study proposes that the preferential removal of SD magnetite grains rather than the formation of multi domain magnetite by bacteria can explain why low abundances of magnetite are found within the more biodegraded deeper samples compared to the shallow samples which are still dominated by multi domain magnetite. This can be identified by the dramatic decrease in M_s between the shallower samples ($23.9\text{-}31.3 \times 10^{-3} \text{ Am}^2\text{kg}^{-1}$) and the deeper samples ($0.75\text{-}2.03 \times 10^{-3} \text{ Am}^2\text{kg}^{-1}$) (M_s Table 5.4). In addition, the relatively high abundance of iron sulphides within the deeper samples could also reflect the removal of magnetite by bacteria during biodegradation, whereas, the shallower samples which are less biodegraded have relatively smaller proportions of iron sulphides and larger abundances of multi domain magnetite. The iron sulphides present in the shallower samples exist as framboids. Perhaps the lack of bacteria at these sites allows the retention of pyrite (FeS_2) framboids as well as multi domain magnetite.

The magnetic susceptibility in this set of samples showed strong correlations with EOM% as seen in Chapter 3, but also revealed strong correlations for biodegradation biomarkers (Figs. 5.15, 5.16,

Table 5.6). Previously it was assumed that newly generated magnetite would strengthen magnetic signals in biodegraded samples (e.g., Díaz et al., 2006). These results suggest the opposite effect occurs and that it is the removal of magnetite and reduction in magnetic signal that leads to variation in oils.

5.7 Conclusions

Oils in the Llanos Foreland Basin display varying compositions that may reflect primary (source, maturity) or secondary (biodegradation, mixing) processes. A vertical succession from the Saltarín 1A well in the Llanos Foreland Basin, allows the geochemical characterisation of several organic matter impregnated sediments and, therefore, assessment of the main controls on oil chemistry. Biomarker data reveal that all Llanos Foreland oils are ultimately related to type-II kerogens that were deposited in an oxygen-poor environment. Moreover, there is no clear difference in maturity levels for the oils analysed.

The relatively low proportion of polar and asphaltene components, in addition to the retention of *n*-alkanes in all samples, suggests that the hydrocarbons have not experienced extreme levels of biodegradation. Some indications of biodegradation do exist, however, and it is surprising that a sample from the shallowest depth, which would be expected to be the most heavily degraded due to increased porosity, lower temperatures and water mobility is the least biodegraded of all the samples in this study. It is inferred that the shallowest sample resides within a distinct compartment with an aquifer supplying water to the deeper compartment leading to increasing biodegradation levels towards the oil-water contact. It is also notable that the shallow sample may contain relatively more contributions from a source rock that contains higher plant material as indicated by a greater relative abundance of C₂₉ steranes and the possible presence of oleanane. This may be a Tertiary source rock.

The increase in biodegradation (although relatively low) with depth allows for a detailed investigation into magnetisation and biodegradation. The shallow, least biodegraded samples (C127.40 and C147.25) were characterised by multi domain magnetite identified by semi-reversible Curie curves (Fig. 5.10), the inflections at ~120 K within RT SIRM cooling and warming curves (Fig. 5.11), hysteresis and SIRM data (Table 5.4) as well as iron sulphide framboids most probably pyrite or pyrrhotite as seen in SEM and EDX analysis. In contrast, the deeper more biodegraded samples (C541.75 and C616.48) were dominated by iron sulphides with low abundances of multi domain magnetite, moreover no framboids were identified. The presence of low temperature (< 40 K) magnetic transitions in the ZFC and FC curves (Fig. 5.11), the formation of ferromagnetic minerals on heating and SEM and EDX analysis confirm iron sulphides present, most probably

pyrrhotite. The very high coercivities (M_s) Table 5.4) and hysteresis parameters suggest very low abundances of multi domain magnetite within the deeper samples.

The overall magnetic susceptibility also varied over the samples between $1.0-9.1 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$. The magnetic susceptibility was correlated to EOM% and biodegradation biomarkers (Fig. 5.15). A strong negative linear correlation was identified in all cases (Table 5.6). It is proposed that this detailed study supports the idea of preferential removal of SD magnetite due to bacteria within oil impregnated sedimentary units as a main mechanism for anomalous magnetic signatures. It also concludes that magnetic framboids cannot be used as a tool for hydrocarbon identification due to their presence in many non-hydrocarbon associated environments as well as the lack of framboids within some hydrocarbon bearing sedimentary units.

Hence, the chemical differences brought about by biodegradation are potentially produced and certainly maintained by reservoir compartmentalization but the chemical communication between the deeper and shallower samples is incomplete. Magnetic characterisation also shows the incomplete removal of magnetite from the shallower less biodegraded samples relative to the iron sulphide dominated biodegraded deeper samples.

Chapter 6

Testing the universality of magnetic characterisations of hydrocarbon well cores in the North Sea, UK.

6.1 Introduction

Claims have been made that magnetic susceptibility (χ) anomalies found within oil producing well cores are characterised by iron oxide or iron sulphide framboids whereas similar χ anomalies found within dry well cores have no magnetic framboids associated with them (Foote, 1987; Foote, 1996; Liu et al., 1998b; Aldana et al., 1999; Costanzo-Alvarez et al., 2000; Liu et al., 2004; Costanzo-Alvarez et al., 2006; Díaz et al., 2006; Liu et al., 2006; Aldana et al., 2011; Guzman et al., 2011). An overview of these studies can be found in Chapter 1, Section 1.3.4. If this was an artefact for hydrocarbons it could be an interesting step towards a new identification technique. These studies, however, mainly concentrate on wells within specific areas in Colombia, Venezuela and China and well core cuttings sampled roughly every 15m. This hypothesis, therefore, has not been tested within many different geological environments nor investigated continuously through well cores.

Magnetic susceptibility profiling as part of wire line logging shows mixed results similar to variations identified in aeromagnetic studies. It has been suggested that magnetic susceptibility logging can be useful in identifying layer boundaries due to the magnetic mineral content differences, for example clays, sandstones and gravels. It can also be possible to correlate lithological facies by identifying different origins of the same material (e.g., sediments derived from mafic rocks), but with variable success (e.g., Chopra et al., 2002; Koptíková et al., 2010). However, there appears to be no direct correlation between hydrocarbon accumulations and magnetic susceptibility through wire line logging.

To study whether magnetic anomalies often recorded above hydrocarbon reservoirs are characterised by the same magnetic mineralogy and therefore could be used as a potential identification tool, cores from known hydrocarbon fields within the North Sea, UK, were analysed (Table 6.1) (a map and detailed descriptions of the oil fields are given in Section 2.1.2). Cores from both hydrocarbon producing and dry (no hydrocarbon shows) wells were investigated. The dry well cores were selected due to their vicinity to the Brent field (Table 6.1) and therefore provide a good basis for comparison in magnetic characterisation between oil producing and dry wells within the same geological formations and facies.

The method for collecting the well core samples involved an automated Bartington core logger and is described in detail in Section 2.2.5. Samples were taken from peak magnetic susceptibility values as well as background values and further characterised by SEM imaging and magnetic analysis. The magnetic susceptibility profiles are shown in Section 6.4 where they are also correlated to well log data.

Table 6.1 A list of well cores and depths analysed in this study.

Well	Sample name	Field	# of sample	Reservoir Age	H/C type	Drill Date	Depths (m)	Cores
9/09B-3	9B-	Bruce	4	Cretaceous/Jurassic	Condensate	1974	3540-4004	23
16/07A–A8	16/A8-	Brae	4	Jurassic	Oil/Condensate	1975	4645-4670	26
16/17-13	16/13-	Tiffany	2	Jurassic	Oil	1979	3942-4300	28
3/28A-4	3/28A-	Bressay	4	Tertiary	Oil	1978	1051-1153	25
211/29-C4	211-	Brent	5	Jurassic	Oil	1971	3422-3601	26
3/03-11	311-	...	1	...	...	1982	1335-3635	5
211/29-8A	211/8A-	...	1	...	...	1989	3330-3607	8

6.2 SEM imaging

Examples of SEM images are shown in Figure 6.1 and were used to help identify magnetic mineralogy. SEM interpretations are only suggestive of the magnetic material within the samples because only a subset of material is observed and very small grains (<500 nm) cannot be seen. The well core samples show a variety of different minerals within the samples, all dominated by quartz, feldspars, pyroxenes and olivines, all of which are typical of sandstones.

EDX analysis revealed all the samples were dominated by silicon and oxygen as expected in sandstones, as well as several other elements in most spectra such as Fe, Mg, Al, K and S. The EDX analysis often gave complex mineralogical profiles. Fe-rich spherical clusters or framboids were found within well cores 9/09B-3, 16/17-13 (Fig. 6.1c), 211/29-C4, 3/03-11(dry) (Fig. 6.1e) and 211/29-8A (dry) (Fig. 6.1f) ranging in size between 600 nm and 45 µm. The framboids were mainly dominated by iron and sulphur indicating an iron sulphide (pyrite or pyrrhotite), but iron-oxide framboids were also present. Identification of magnetic minerals within the samples was difficult but all samples contained small grains of iron oxides between 300 nm – 30 µm and the percentage of iron detected was between 9-26 %. There appears to be no difference between magnetic mineralogies in oil producing well samples or the dry well samples.

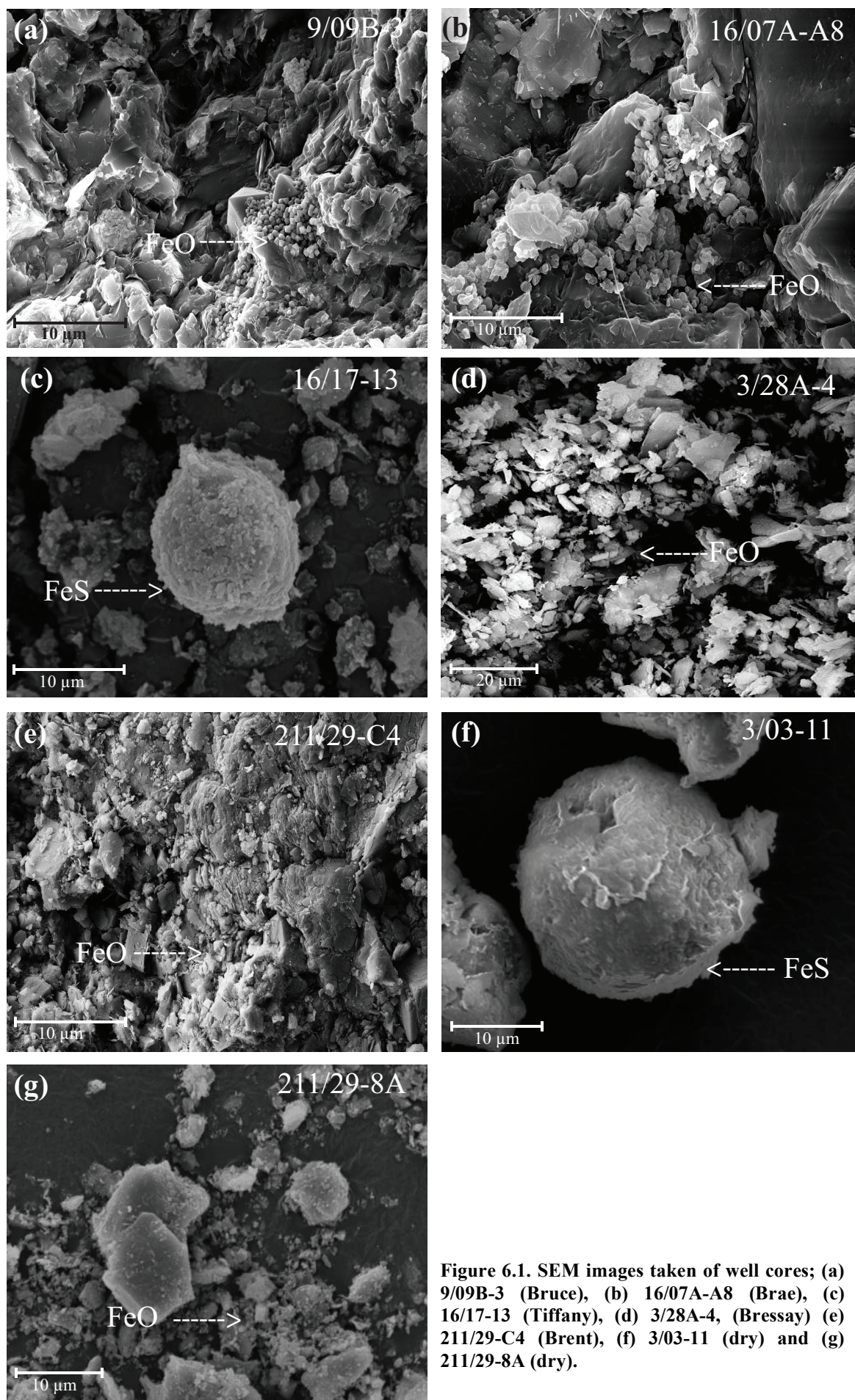


Figure 6.1. SEM images taken of well cores; (a) 9/09B-3 (Bruce), (b) 16/07A-A8 (Brae), (c) 16/17-13 (Tiffany), (d) 3/28A-4, (Bressay) (e) 211/29-C4 (Brent), (f) 3/03-11 (dry) and (g) 211/29-8A (dry).

6.3 Magnetic characterisation

The magnetic experimentation conducted on all the samples can be found in Appendix 2.2. Within this section, representative samples are shown for each oil producing well core with comparisons between background and anomalous χ samples. Dry (water wet) well cores are also evaluated and compared to hydrocarbon bearing cores. Anomalous and background magnetic susceptibility samples were selected by the method outlined in Section 2.2.5.

6.3.1 Room temperature experimentation

The samples were selected from the cores because of their relatively high χ but the absolute χ of the samples (Table 6.2) varied between well cores as well as within each sample set. Well core 3/28A-4 had χ anomaly values varying between $1.8\text{--}9.5 \times 10^{-5} \text{ m}^3\text{kg}^{-1}$ similar to well core 16/07A-A8 ($5.1\text{--}5.8 \times 10^{-5} \text{ m}^3\text{kg}^{-1}$) and 16/17-13 ($5.4 \times 10^{-5} \text{ m}^3\text{kg}^{-1}$). The χ anomaly values were much higher in well cores 211/29-C4 ($6.7\text{--}8.4 \times 10^{-4} \text{ m}^3\text{kg}^{-1}$) and 9/09B-3 ($1.7\text{--}4.7 \times 10^{-4} \text{ m}^3\text{kg}^{-1}$). Background samples were also taken for each well and varied between $1.5\text{--}9.5 \times 10^{-5} \text{ m}^3\text{kg}^{-1}$. The dry well cores had high χ values as well with well core 211/29-8A giving a similar magnetic susceptibility value to core 211/29-C4 ($7.84 \times 10^{-4} \text{ m}^3\text{kg}^{-1}$). Dry well core 3/03-11 had the highest χ of all the samples ($3.24 \times 10^{-3} \text{ m}^3\text{kg}^{-1}$).

Table 6.2 Summary of magnetic parameters measured from magnetic susceptibility and hysteresis data.

Well	Sample	χ ($10^{-4} \text{ m}^3\text{kg}^{-1}$)	H_{cr}/H_c	M_{rs}/M_s	M_s ($10^{-2} \text{ Am}^2\text{kg}^{-1}$)
9/09B-3	1	3.17	7.72	0.08	1.53
	2	4.68	3.05	0.14	1.95
	3 (B)	0.44	4.97	0.11	0.17
	4	1.74	6.37	0.13	0.66
16/07A-A8	1	0.58	2.01	0.18	0.60
	2 (B)	0.15	2.20	0.16	1.57
	3	0.51	2.83	0.16	1.68
	4	0.55	2.63	0.13	2.15
16/17-13	1	0.54	3.39	0.13	2.84
	2 (B)	0.43	3.70	0.11	0.92
3/28A-4	1	0.95	4.51	0.06	2.20
	2	0.18	3.50	0.16	0.83
	3	0.19	2.08	0.18	0.38
	4 (B)	0.16	2.59	0.08	0.32
211/29-C4	1 (B)	0.95	6.43	0.08	1.21
	2	8.41	7.38	0.02	13.4
	3	5.85	4.10	0.04	9.46
	4	7.87	7.27	0.03	2.17
	5	6.68	5.37	0.04	3.29
3/03-11	1	32.3	2.01	0.34	42.6
211/29-8A	1	7.84	7.17	0.02	3.40

6.3.1.1 Hysteresis

Room temperature hysteresis was dominated by paramagnetic behaviour similar to those described in Chapter 3. The samples were also magnetically weak, limiting the data retrievable from the samples. Table 6.2 displays the main parameters from the hysteresis data. This data were measured on an AGM and some of the samples were very close to the noise limit of $\sim 5 \times 10^{-11} \text{ Am}^2$.

A Day plot (Day et al., 1977) of room temperature hysteresis parameters shown in Figure 6.2 reveals the predominance of PSD-MD like grains in the wells (based on magnetite boundaries). MD-like behaviour within well cores 211/29-C4 and 9/09B-3 can be inferred as larger grain sizes relative to well cores 16/07A-A8, 16/17-13 and 3/28A-4 which show more PSD-like behaviour suggestive of relatively smaller grains (Fig. 6.2). The dry well cores (grey symbols, Fig. 6.2) showed variable behaviour with well core 3/03-11 showing SD-PSD-like grains and 211/29-8A with MD-like grains.

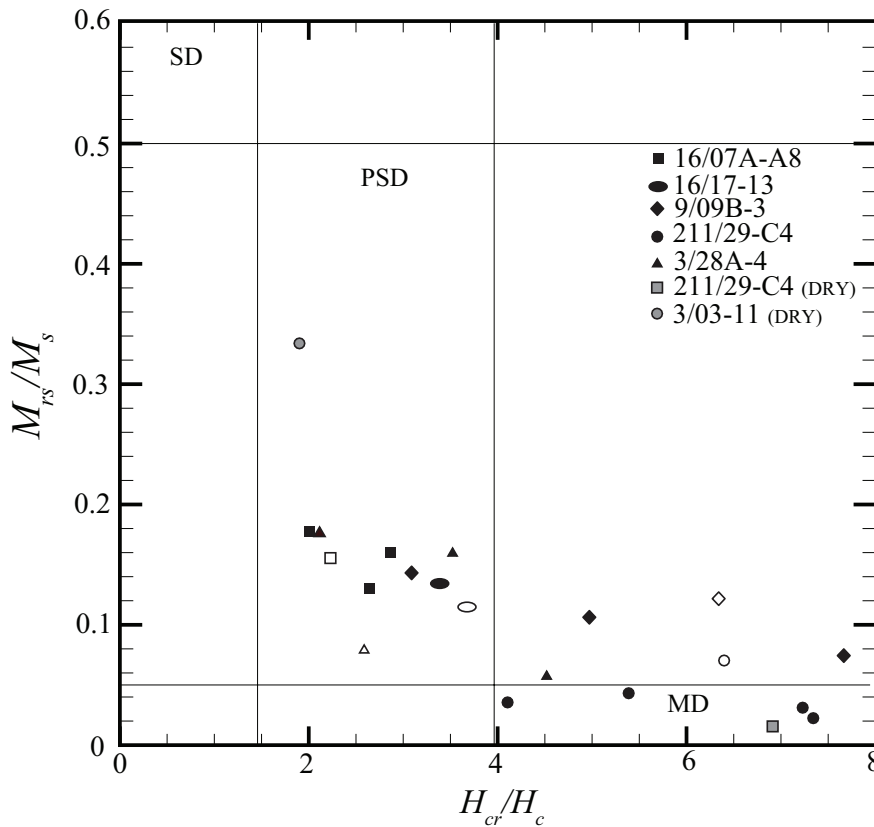


Figure 6.2. Day plot used to interpret grain sizes (SD, PSD and MD) for all well core samples at room temperature. Anomalous χ samples (closed symbols) and background samples (open symbols). The dry well cores are represented by grey symbols.

The well cores show variability in grain sizes within well cores as well as between each well. These variations are most probably due to the different geological facies within each well and can be hard to differentiate between. There appears to be no distinct difference between the dry and hydrocarbon wells within the hysteresis properties suggesting no dominating universal change in magnetic mineralogy due to hydrocarbons within well cores. Moreover, there is little variability between anomalous χ (closed symbols) and background (open symbols) samples for any of the well cores (Fig. 6.2).

6.3.1.2 Mössbauer spectroscopy

Only two samples were successfully measured in the Mössbauer due to the weak nature of the samples (low overall concentration of iron). Evaluations of the data were performed by a least squares fit to the data and are represented in Figure 6.3 and Table 6.3.

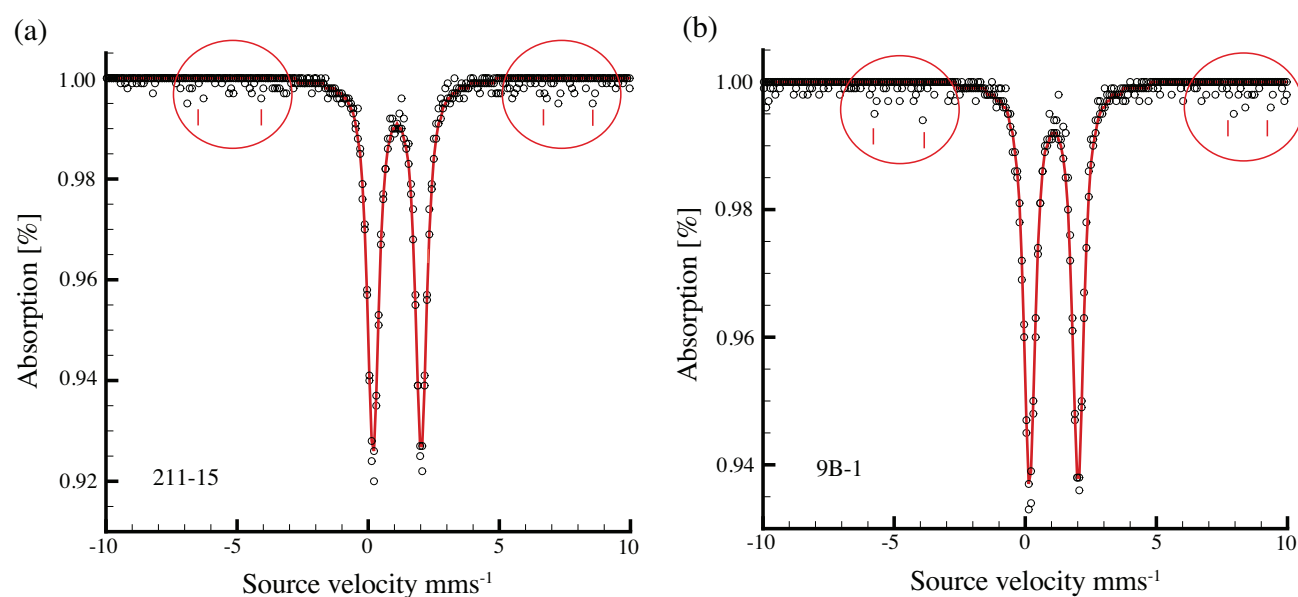


Figure 6.3. Mössbauer spectroscopy results with fitting for (a) Well core 211/29-C4 sample 4 and (b) Well core 9B/9-3 sample 1.

At room temperature the data show a quadruple splitting (QS) of 1.85 and 1.83 mm/s^{-1} and isomer shifts (IS) of 1.22 and 1.23 mm/s^{-1} for samples 9B-1 and 211-4 respectively (Table 6.3). These parameters suggest siderite (FeCO_3) as the main Fe carrier in both samples (Gil et al., 1992). Siderite is not magnetic at room temperature, therefore, although it is the dominant Fe carrier, there must be other magnetic minerals present to give the χ anomaly at room temperature. Two other peaks can potentially be identified but the exposure time was too low for a reliable fitting, these peaks would correspond to magnetite or maghemite.

Table 6.3 Mössbauer parameters for two samples; well core 9/9B-3-1 and well core 211/29-C4-15 at room temperature.

Sample	QS (mms ⁻¹)	IS (mms ⁻¹)	%
9/09B-3_1	1.85(1)	1.22(1)	100
211/29-C4_15	1.83(1)	1.23(1)	100

QS – quadruple splitting, IS – isomer shift and % relative proportion. Errors are quoted in parenthesis.

6.3.2 Low temperature experimentation

Low temperature experiments were conducted to try to determine magnetic mineralogy and grain sizes for both the anomalous χ and background samples of all the well cores.

6.3.2.1 Hysteresis

Low temperature hysteresis data were measured from 10-300 K every 20 K on a Princeton VSM at the IRM. The data revealed little difference in either ZFC or FC hysteresis through low temperatures for most samples, all giving a strong paramagnetic signal. After removal of the paramagnetic component, the data were often too noisy to convincingly identify open hysteresis loops, however, two samples (211/29-C4 -2 & -4) gave open hysteresis loops at low temperatures (<30 K) in a 1 TFC.

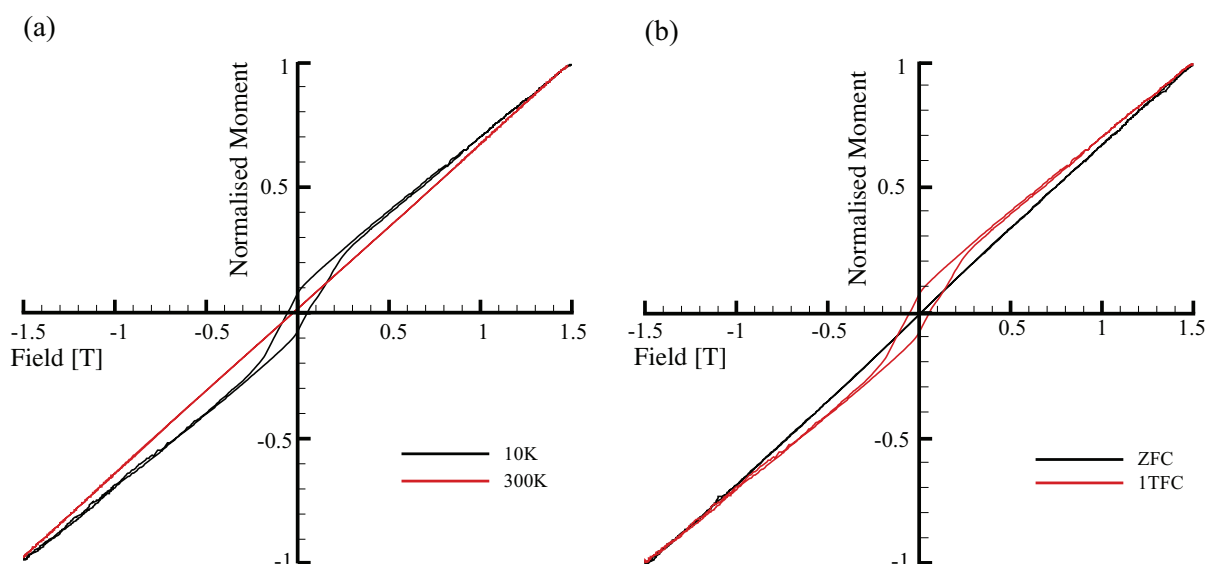


Figure 6.4. Hysteresis loops for well core 211/29-C4 sample 2. (a) Hysteresis loops at increasing temperatures of 10 K (black) and 300 K (red) in a 1TFC and (b) hysteresis loops at 10 K after ZFC (black) and 1TFC (red).

Figure 6.4a shows hysteresis loops at 10 K and 300 K in a 1 TFC for sample 211-2 and Figure 6.4b reflects the difference between the hysteresis after 1 TFC and ZFC at 10 K for the same sample. These results could reflect the presence of siderite identified through low temperature experimentation.

6.3.2.2 ZFC, FC and RT magnetisation curves

The same procedure for zero-field cooled (ZFC), field cooled (FC) and room temperature (RT) cooling and warming curves were followed as described in Chapter 2. Due to time constraints on the MPMS, not all samples had the full suite of measurements and only the FC and RT cooling curves were measured. The FC curve usually has a larger magnetisation than the ZFC curves and this behaviour was observed in all the samples whose ZFC and FC curves were measured (Fig. 6.5). Most of the samples showed the dominance of most probably siderite at low temperatures represented by the Néel transition at ~37 K (Jacobs, 1963) (Fig. 6.5). Figure 6.5 shows a steep remanence decay to almost zero at 37-38 K on both ZFC and FC warming for samples within well cores 9/09B- 3 and 211/29-C4 as well as well core sample 16/07A-A8-4 but to a lesser degree. At 10 K the FC SIRM intensity is also significantly greater than the ZFC SIRM intensity at 10 K in the same sample as identified in Figure 6.5a. As described by Frederichs *et al.* (2003) this difference is attributed to an additional thermal remanence acquired during cooling through the Néel temperature in a 2.5 T field.

Room temperature (RT) remanence curves on cooling and warming typically show a variable difference from 98-100 K to higher temperatures, and the RT cooling curve marks the Verwey transition (~110 K) indicating the presence of multi domain magnetite (Fig. 6.5). The exact temperature of the Verwey transition (110-120 K) depends on the stoichiometry of the magnetite present (Walz, 2002). In samples that show siderite present in the FC and ZFC curves (Fig. 6.5) the RT remanence curves may also show a marked increase at 37 K such as sample 211-5 (Fig. 6.5e). Several samples (well cores 9/09B-3, 16/07A-A8, 16/17-13 and 211/29-C4) also include a transition step at ~250 K marking the Morin transition (Morin, 1950) for hematite (Fig. 6.5c).

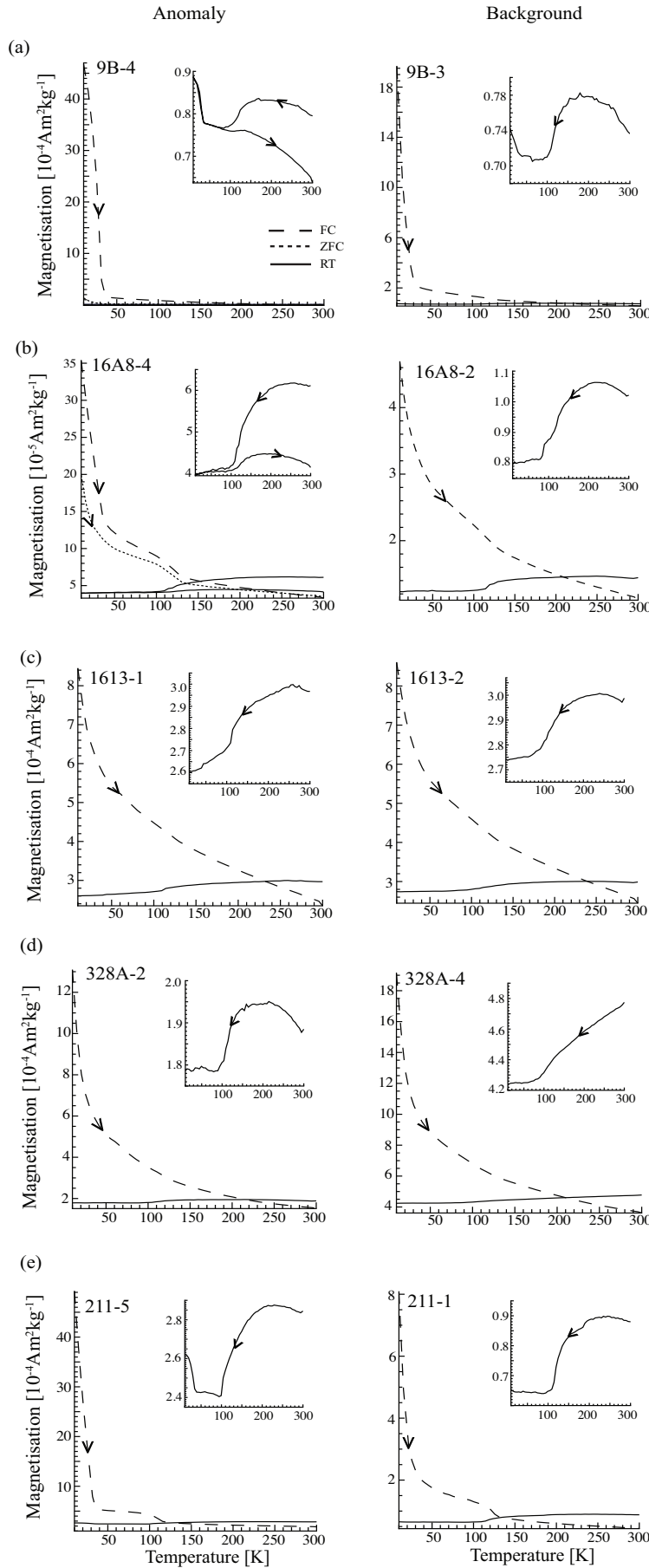


Figure 6.5. Zero field cooling (ZFC ---), Field Cooling (FC - -) curves and room temperature remanence curves (RT —) for well cores (a) 9/09B-3 (b) 16/07A-A8 (c) 16/17-13 (d) 3/28A-4 and (e) 211/29-C4. The inset is the magnified behaviour of the RT SIRM cooling curves.

The dry well core samples reveal overall similar behaviour to hydrocarbon bearing well cores but do show a distinct lack of multi domain magnetite within the RT SIRM cooling and warming curves. Moreover, the presence of most probably siderite, within both dry well cores, dominates the signal, especially within well core 211-8A-dry.

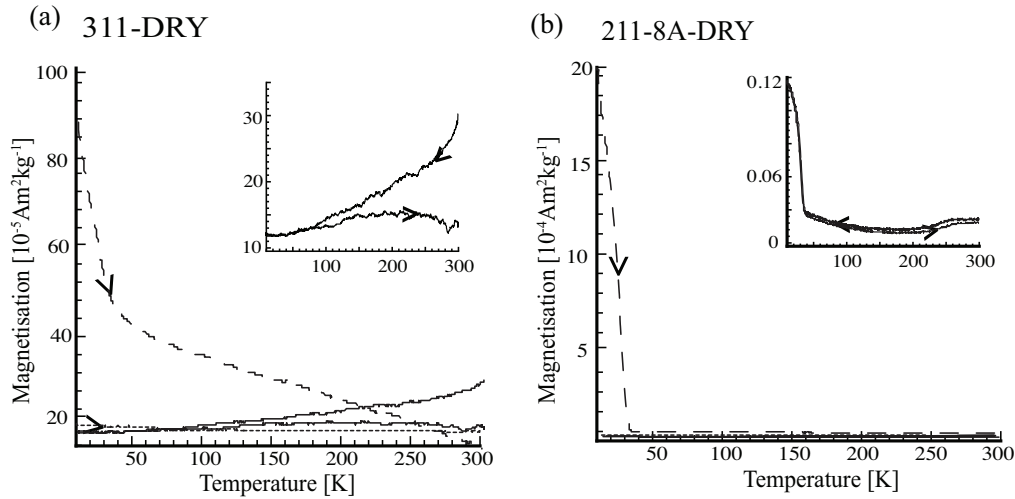


Figure 6.6. Zero field cooling (ZFC ---), Field Cooling (FC —) curves and room temperature remanence curves (RT —) for well cores (a) 3/03-11 (b) 211/29-C4. The inset is the magnified behaviour of the RT curves.

AC susceptibility curves were conducted on most samples, however, the dominance of paramagnetic minerals within the samples meant that no information could be extracted from the data even after a paramagnetic correction was applied. One sample, however, did yield meaningful data and Figure 6.7 shows the AC susceptibility curve as a function of temperature for well core 211/29-C4, sample 3.

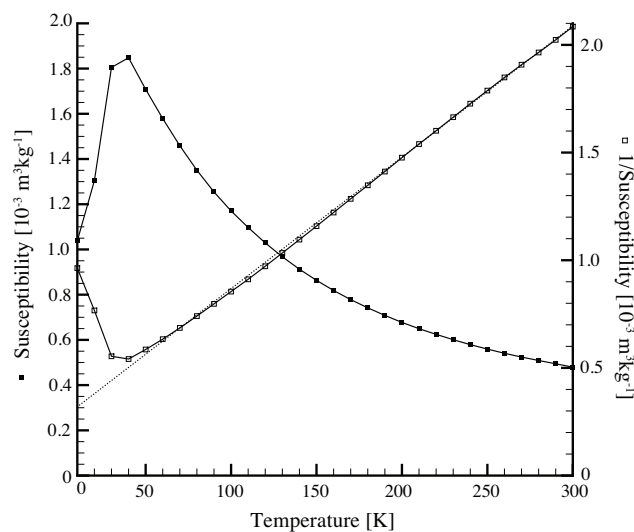


Figure 6.7. AC susceptibility curve as a function of temperature for well core 211/29-C4 sample 3. The graph shows both the magnetic susceptibility (χ) (•) and the inverse of magnetic susceptibility ($1/\chi$) (◦). The dotted line is a fit to the $1/\chi$ curve between 40-300 K.

There is a magnetic susceptibility increase from $1.04 \times 10^{-6} \text{ m}^3 \text{kg}^{-1}$ at 10 K to a peak value of $1.85 \times 10^{-6} \text{ m}^3 \text{kg}^{-1}$ at 40 K. Continued warming decreases the susceptibility linearly. The $1/\chi(T)$ curve shows a linear slope from ~ 37 K implying no impurities within the siderite (Frederichs et al., 2003) present in the sample.

6.3.3 High temperature experimentation

High temperature experiments were conducted on all the well core samples to identify differences in the sample behaviour undetected by low temperature experimentation.

6.3.3.1 High temperature susceptibility

High temperature mass susceptibility measurements were conducted in one continuous cycle from 50-700 °C in an argon atmosphere to try to limit oxidation. The mass susceptibility measurements showed some variation in behaviour in the samples and have been split into type A, B or C. Type A is characterised by a new ferrimagnetic mineral phase being produced around 400-550 °C represented by sharply increasing susceptibilities (Fig. 6.8a) most probably originating from the siderite within the samples. On cooling from 700 °C the change in slope between 530-590 °C indicates a Curie temperature for magnetite as well as enhanced susceptibility values for all samples after heating (Fig. 6.8b). Type B is similar to type A, but with additional formation of minerals from 300 – 400 °C and/or the formation of a mineral at ~ 300 °C on cooling. Type C behaviour is characterised by a steady warming curve with a Curie temperature indicative of magnetite (~ 580 °C) but with a large increase in susceptibility on cooling representing an almost irreversible Curie curve for magnetite. The formation of ferrimagnetic minerals on heating is mostly due from FeS_x to Fe_3O_4 at ~ 400 °C.

Well core 9/09B-3 showed type A behaviour in both the magnetic susceptibility anomaly and background samples similar to well core 16/07A-A8 (Fig. 6.8 a,b). Well core 211/29-C4 also had type A behaviour but with a large Hopkinson peak except for sample 211-1, which followed behaviour B (Fig. 6.8e) similar to well core 16/17-13 (Fig. 6.8c). Well core 3/28A-4 had behaviour type C for all the samples with some behaviour similar to type A as well (Fig. 6.8d). The background samples and the χ anomalous samples for each well core showed similar behaviour.

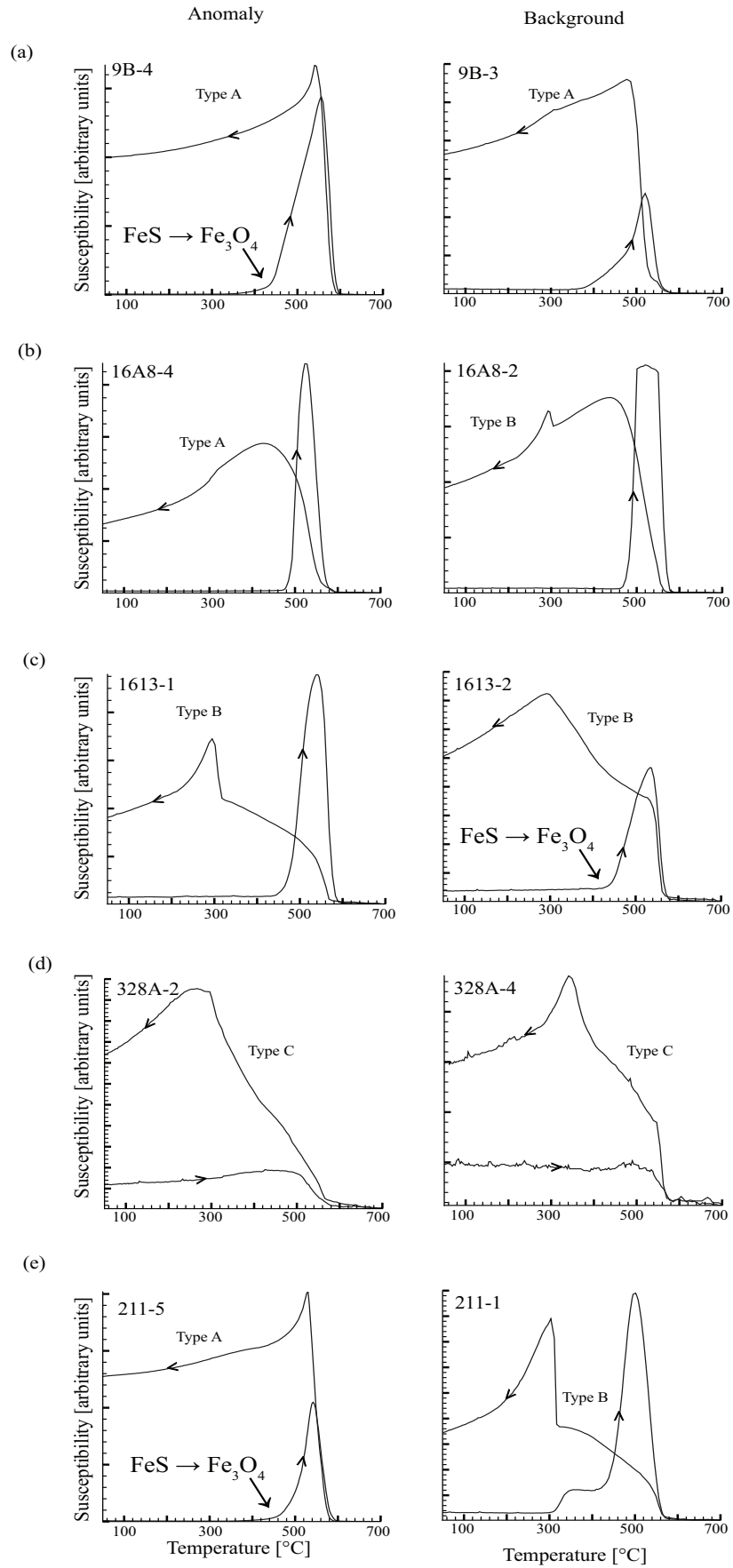


Figure 6.8. Magnetic susceptibility measurements as a function of temperature (up to 700 °C). The representative plots characterise the anomalously high magnetic samples (left) and the background samples (right). (a) 9/09B-3 (b) 16/07A-A8 (c) 16/17-13 (d) 3/28A-4 and (e) 211/29-C4.

The dry well cores (Fig. 6.9) showed similar behaviour as the hydrocarbon well cores (Fig. 6.8). Well core 3/03-11 had behaviour C (Fig. 6.9a) whereas the well core 211/29-8A revealed high temperature susceptibility behaviour like type A (Fig. 6.9b). There appears to be no difference between anomalous and background sample behaviour within hydrocarbon wells as well as no change in behaviour between hydrocarbon bearing or dry well cores.

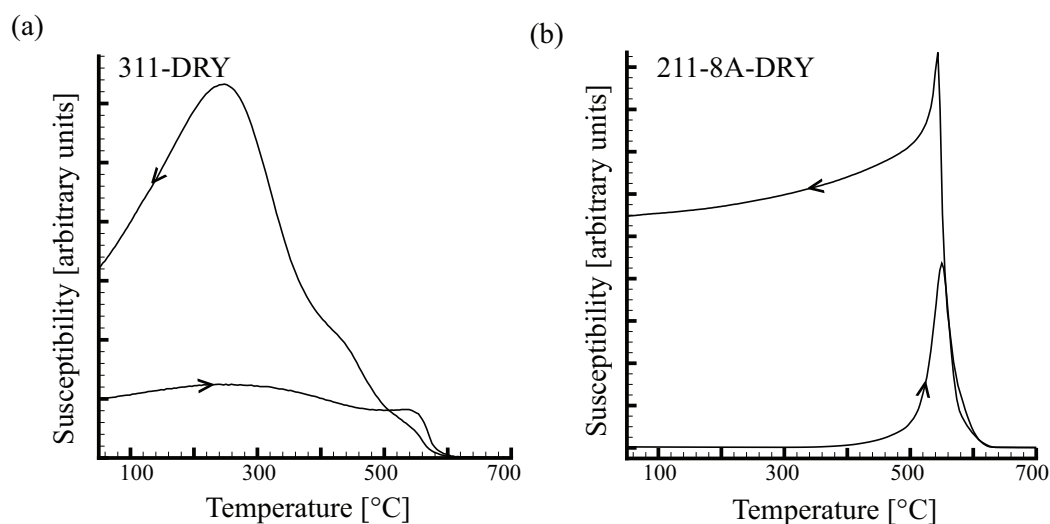


Figure 6.9. Magnetic susceptibility measurements as a function of temperature (up to 700 °C). The representative plots characterise the anomalously high magnetic samples for the dry well cores within this study, (a) 3/03-11 (b) 211/29-8A.

6.3.3.2 Hysteresis

High temperature hysteresis cycling was conducted from room temperature up to 600 °C in 100 °C cycles on a VSM at the IRM. All of the samples went from highly paramagnetic at room temperature to progressively more ferromagnetic with temperature. Figure 6.10a is a representative plot of hysteresis loops at 200 °C, 400 °C and 600 °C for the well core 9/09B-3 sample 1. Generally, the hysteresis loops did not change until 350 °C when the hysteresis loops began to represent a more ferromagnetic mineral.

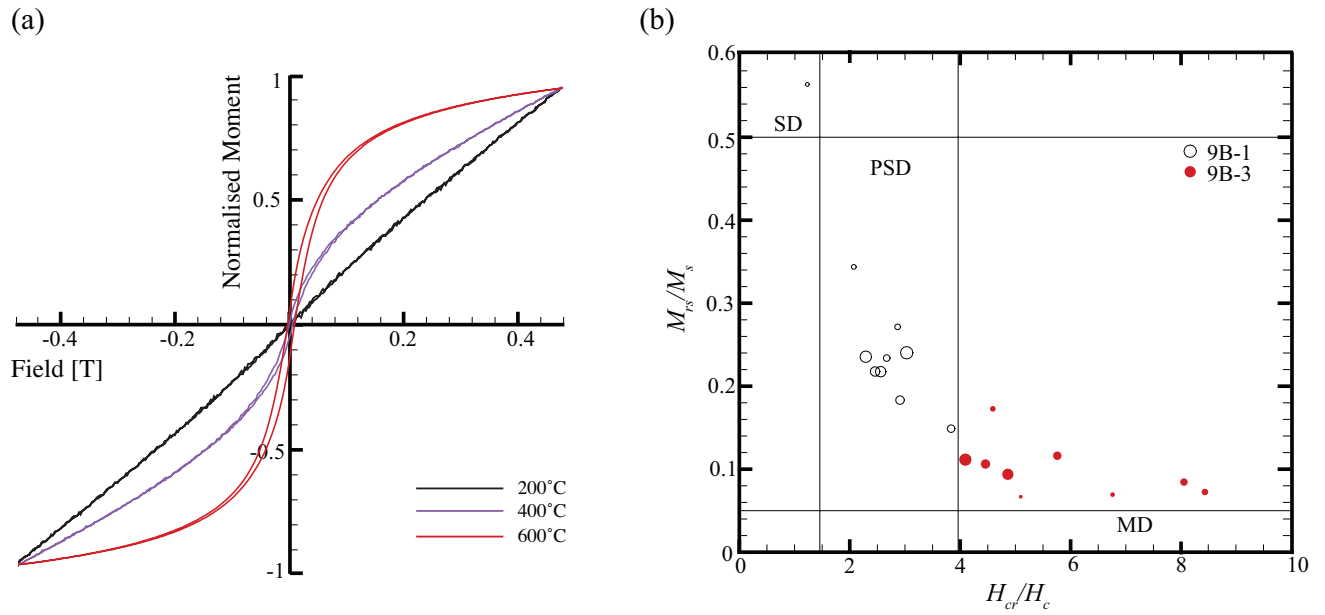


Figure 6.10. High temperature hysteresis measurements between 200-600 °C on well core 9/09B-3 (a) Hysteresis loops at 200 °C, 400 °C and 600 °C for 9B-1 and (b) a Day plot of hysteresis parameters for 9B-1 (anomalous χ) and 9B-3 (background). The size of the symbols increases with increasing temperature.

Figure 6.10b is a Day plot representing the progression of H_{cr}/H_c and M_{rs}/M_s ratios during heating for well core 9/09B-3 for an anomalous χ sample (9B-1) and the background sample (9B-3). The χ anomalous sample (9B-1) had predominantly PSD-like behaviour compared to MD-like behaviour in the background sample (9B-3). On heating (increasing size of symbols), the background sample 9B-3 revealed a possible bimodal distribution with the sample reaching smaller H_{cr}/H_c ratios towards PSD-like behaviour (Fig. 6.10b). The magnetic susceptibility anomalous sample 9B-1, however, showed no clear alteration of the sample throughout heating staying consistently within PSD-like behaviour.

6.4 Is there a correlation between magnetic susceptibility and well log data?

In an attempt to clarify whether there is a correlation between magnetic susceptibility and magnetic mineralogy and well log data, the corresponding data (see below) were plotted in Petrel (Figs. 6.12-6.17) and statistically analysed using SPSS software.

Well log data were given to this study from the current operators of the given hydrocarbon fields. The data were limited and it could not be obtained for well core 9/9B-3. Five specific well logs were given for nearly all the other wells and these were used to determine if correlations existed with magnetic susceptibility. A brief discussion is given on the individual well logs below;

1. A sonic log (DT) provides information on the geological formation, specifically increasing with an increase in effective porosity. Density logs (DEN) can provide information on a formations bulk density and can be used to infer lithology and porosity within a potential hydrocarbon reservoir in addition to sonic logs and neutron porosity logging (NEU).
2. A Gamma Ray log (GR) identifies naturally occurring gamma radiation. Different types of geological rocks emit differing amounts of gamma radiation with shales emitting much higher amounts of gamma radiation due to the Potassium and Uranium content in clay compared to sandstones, limestones and salts.
3. Resistivity logs (RES) measure the electrical resistivity of geological formations and are based on the theory that hydrocarbon fluids are resistive compared to saline formation water which acts as a conductor. High resistivity can therefore indicate hydrocarbon-bearing formations.

The magnetic susceptibility (SUSC) profiles were compared to well logging data; sonic (DT), gamma ray (GR), density (DEN), neutron (NEU) and resistivity (RES), to identify whether anomalous peaks in χ correlated to variations in the well logging characteristics. The results are plotted in Figures 6.12-6.17 and at first, show no obvious correlations, however, in nearly all well cores, broad areas of high GR (e.g., shales) correspond to generally high positive magnetic susceptibility. The GR logs are coloured to help interpret geological facies between sandstones (yellow) and muds/shales (grey). These broad areas are highlighted in red and are most probably due to the interplay of siliclastic admixture in carbonates as well as the concentration of diagenetic iron bearing minerals (Koptíková et al., 2010). Siderite nodules often found in mud-rich

sedimentary units were found within most of the cores, especially in well core 211/29-C4 (Brent field, Fig. 6.15). It is likely there is associated magnetite with these nodules, which could account for the elevated magnetic susceptibilities within mud-rich facies (Loope et al., 2012).

To analyse the data, SPSS software was used to statistically investigate the data using the nonparametric Spearman's rank correlation coefficient (R_s) (Borradaile, 2003) because the distribution of data were unknown. The whole cores were initially investigated and then repeated using moving windows of at least 20 points. The results (Table 6.4) showed correlations exist between magnetic susceptibility and nearly all of the properties investigated through the well logs for all of the cores at a 99% confidence level. However, care should be taken because a statistical significance in correlation only exists due to the number of data points. The data does not show a 'strong' correlation for any well logs versus magnetic susceptibility (Fig. 6.11). These results are interesting but most probably reflect the geological facies throughout the cores.

Table 6.4 Results for Spearman's rank correlation coefficient (R_s) for the magnetic susceptibility and other well log data for the entire well core.

Field	DT	GR	DEN	NEU	RES
Brae	.241*	.140*	-.060*	.211*	-.065*
Tiffany	.186*	.179*	.076*	.180*	.124*
Bressay	-.016	-.093*	-.142*	-.014	.168*
Brent	-.252*	.245*	...	...	.033
3/03-11 DRY	-.003	.432*	.303*	.159*	...
211/29-8A DRY	-.096*	.031	.281*	.015	...

* significant at 99% confidence level

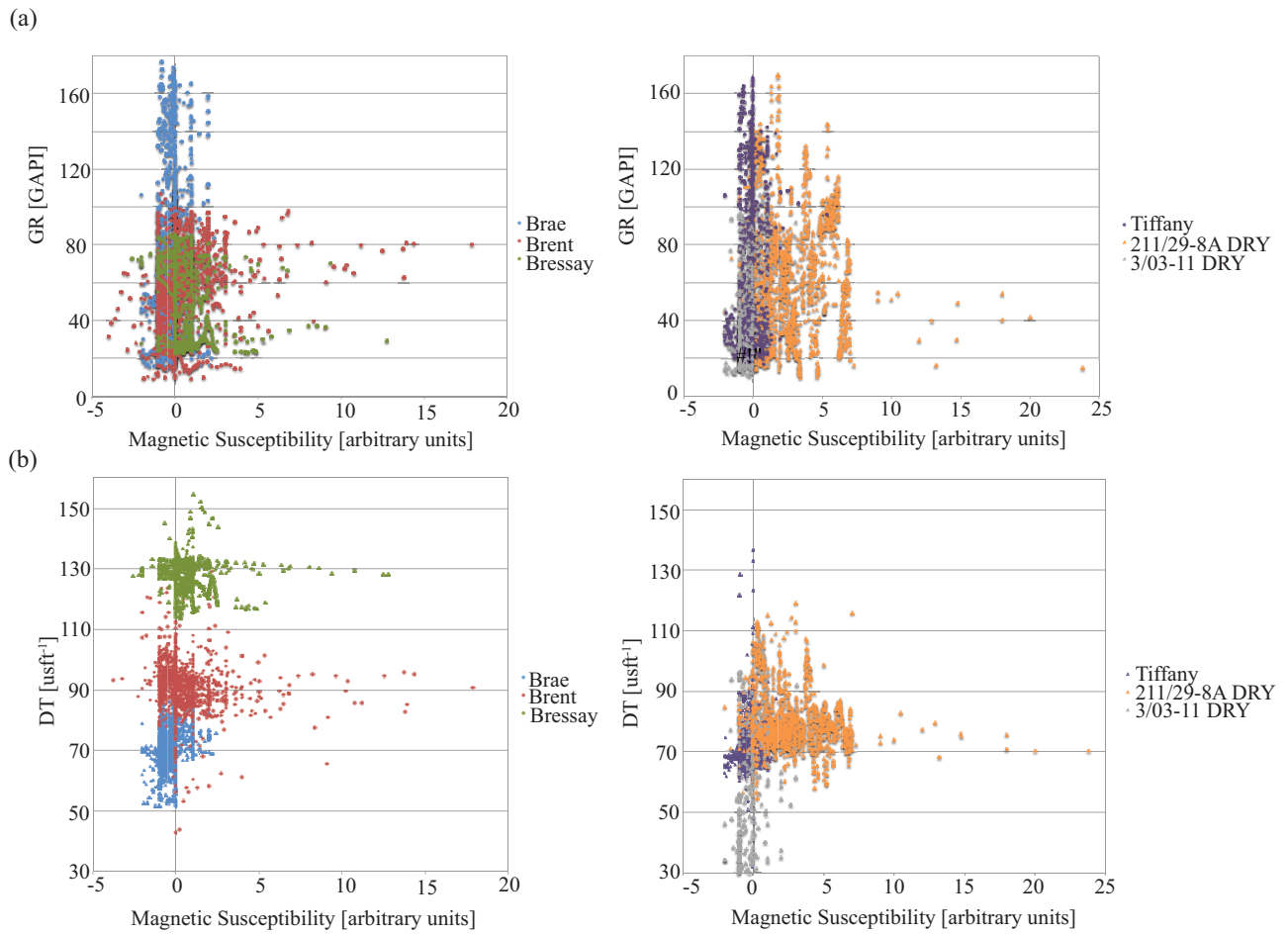


Figure 6.11. Bi plots of (a) Gamma Ray well logs (GR) versus magnetic susceptibility and (b) Sonic well logs (DT) versus magnetic susceptibility. The plots show that there is no strong correlation between these properties and that any significance in a low correlation is due to the number of data points.

Brae Field
Well core 16/07A-A8

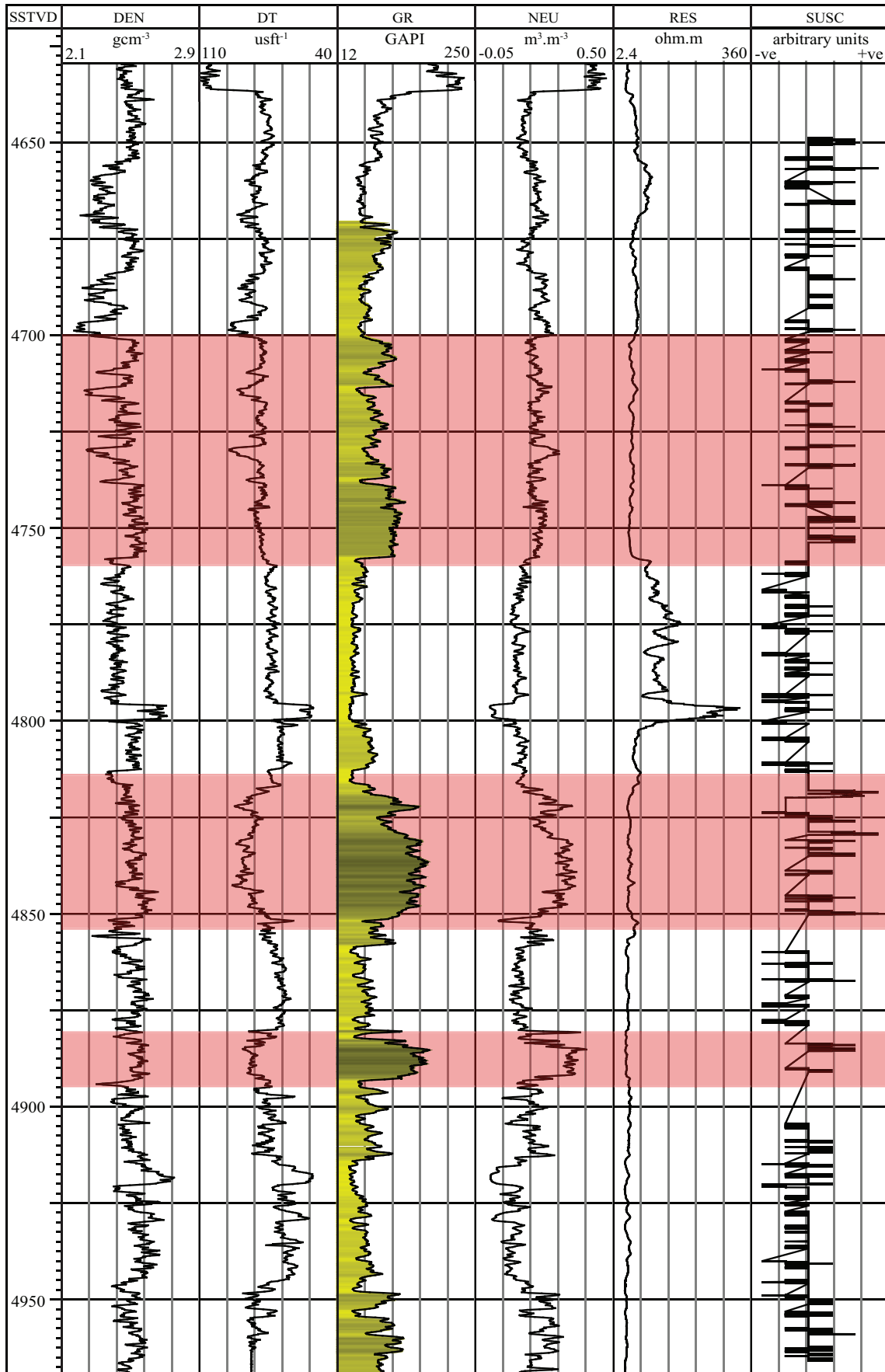


Figure 6.12. Well log data for well core 16/07A-A8. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron ($\text{m}^3 \cdot \text{m}^{-3}$), RES =resistivity (ohm.m) and SUC=magnetic susceptibility (arbitrary units).

Tiffany Field
Well core 16/17-13

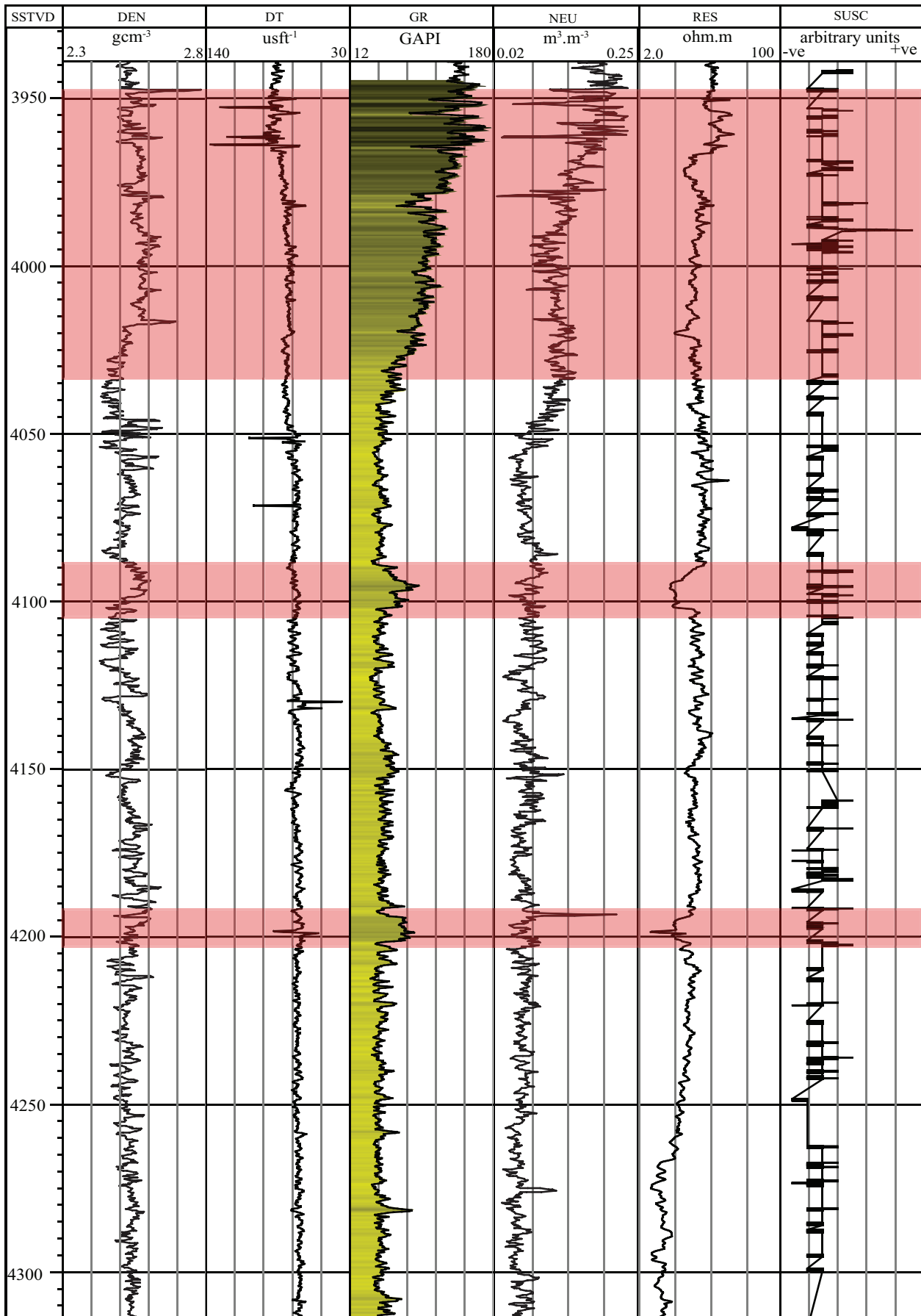


Figure 6.13. Well log data for well core 16/17-13. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (GAPI), NEU= neutron ($\text{m}^3 \cdot \text{m}^{-3}$), RES= resistivity (ohm.m) and SUSC=magnetic susceptibility (arbitrary units).

Bressay Field
Well core 328A-4

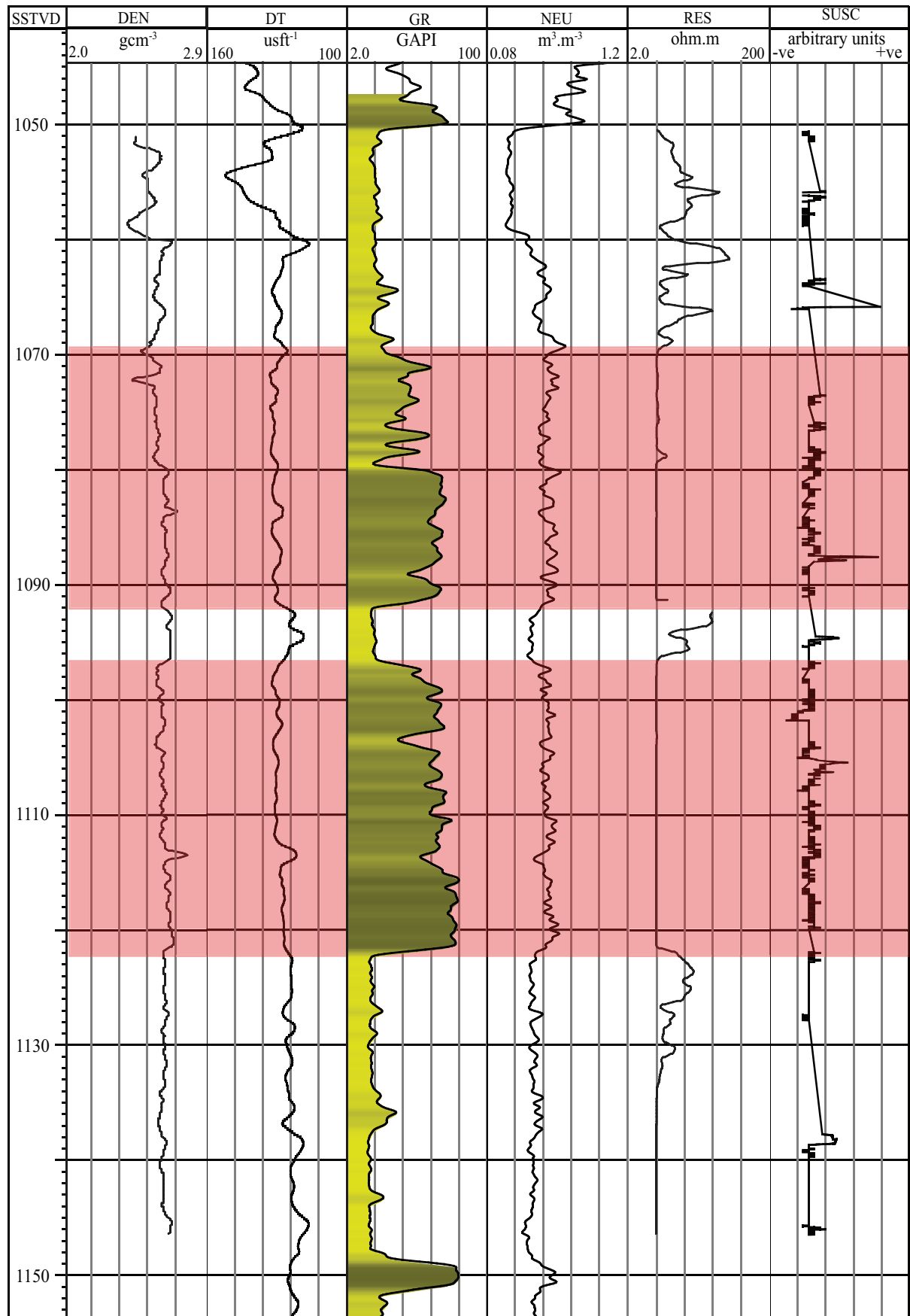


Figure 6.14. Well log data for well core 3/28A-4. DEN=density (gcm^{-3}), DT=sonic (usft^{-1}), GR=gamma ray (gAPI), NEU= neutron ($\text{m}^3 \cdot \text{m}^{-3}$), RES= resistivity (ohm.m) and SUC=magnetic susceptibility (arbitrary units).

Brent Field
Well core 211/29-C4

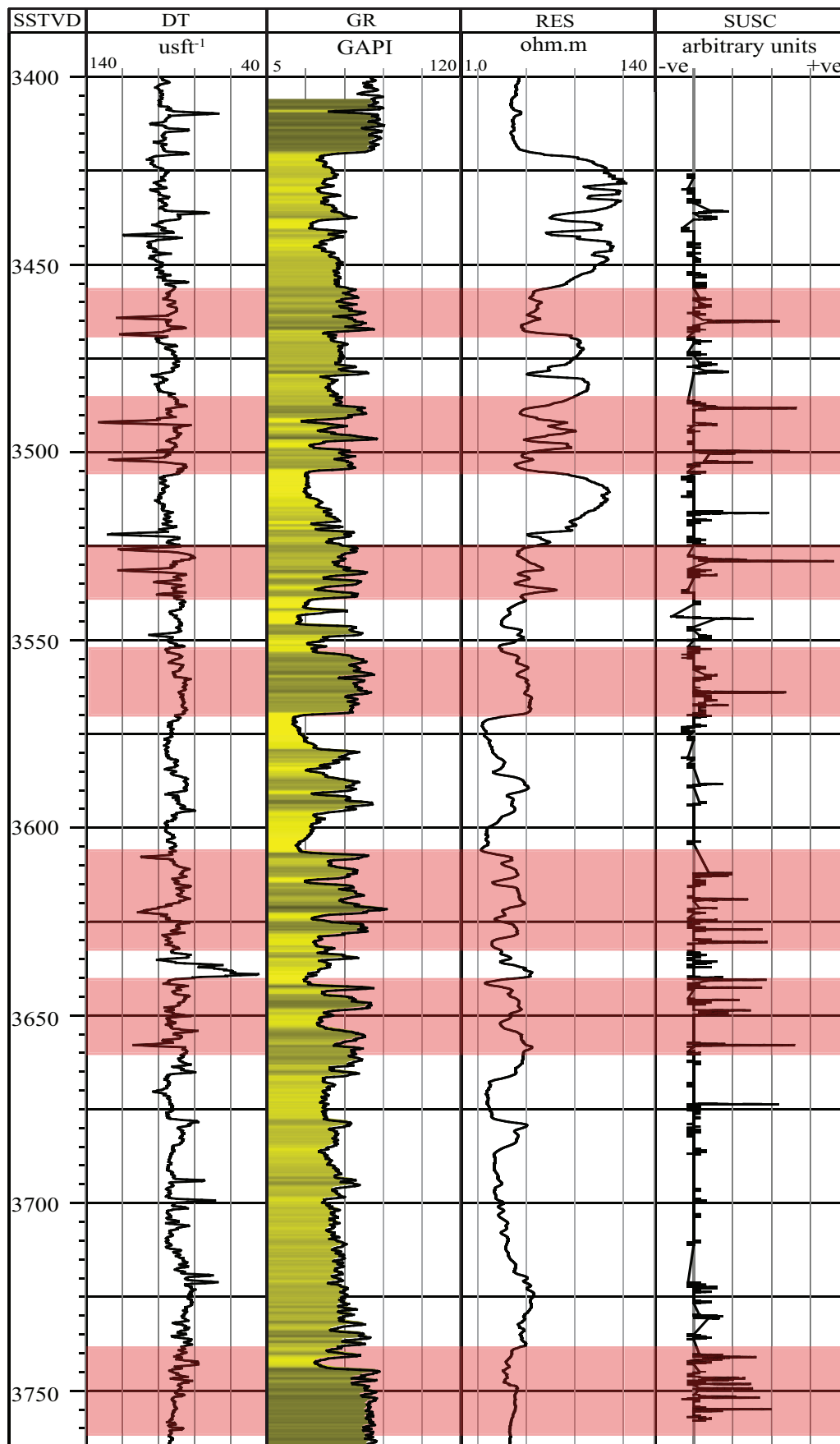


Figure 6.15. Well log data for well core 211/29-C4. DT=sonic (usft^{-1}), GR=gamma ray (gAPI), RES= resistivity (ohm.m) and SUSD=magnetic susceptibility (arbitrary units).

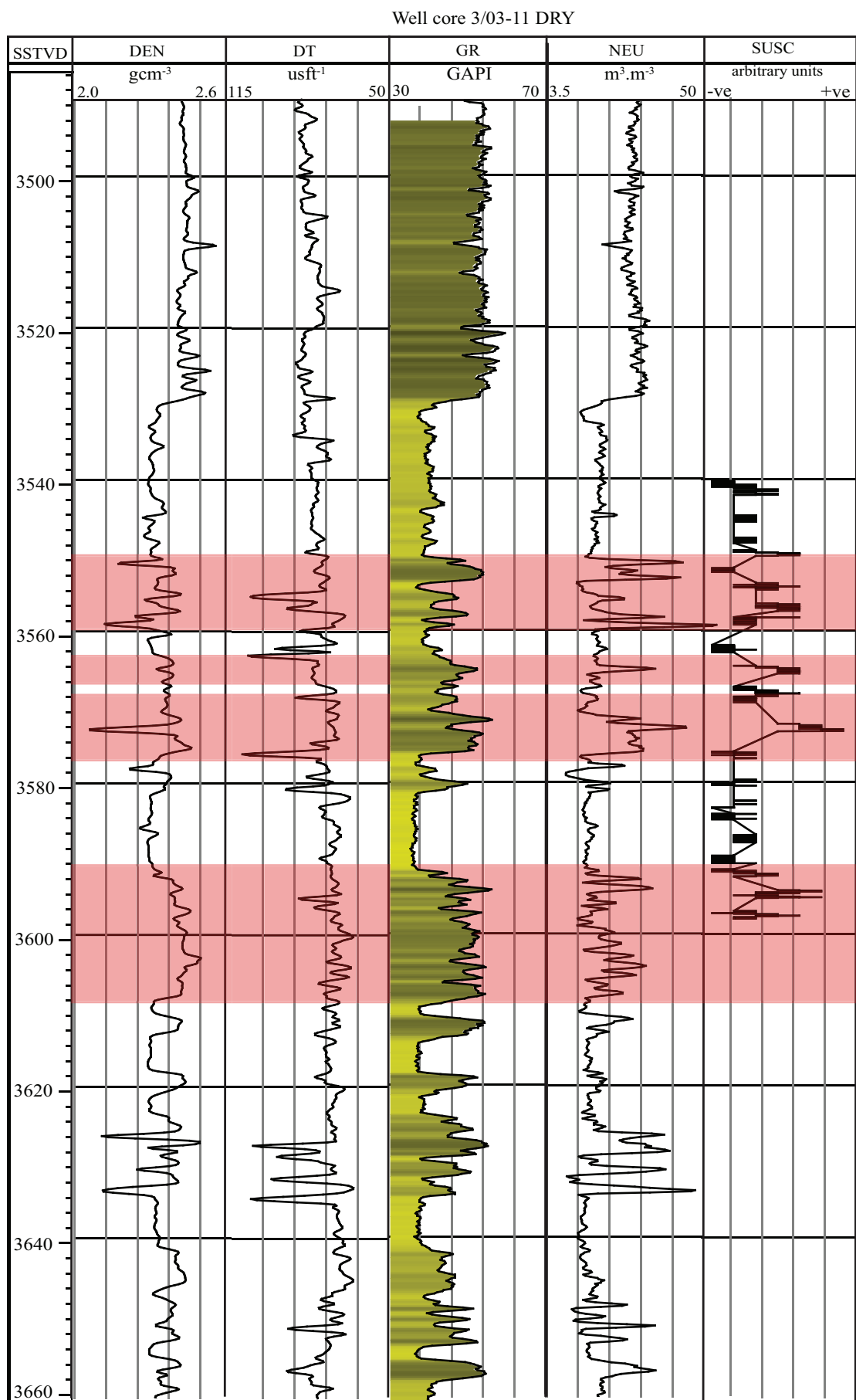


Figure 6.16. Well log data for well core 3/03-11. DEN=density (gcm⁻³), DT=sonic (usft⁻¹), GR=gamma ray (gAPI), NEU= neutron (m³.m⁻³) and SUCS=magnetic susceptibility (arbitrary units).

Well core 211/29-8A Dry

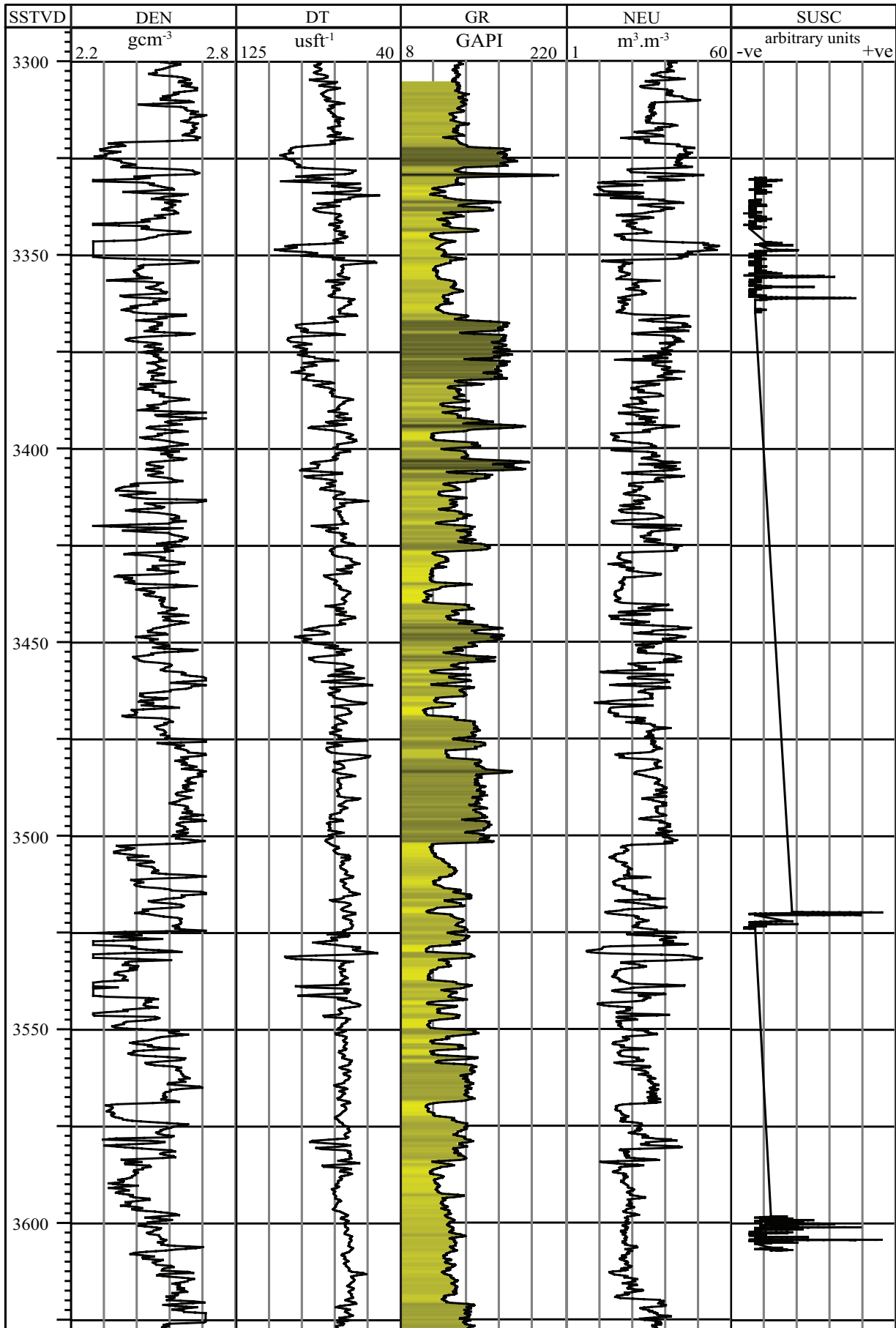


Figure 6.17. Well log data for well core 211/29-8A. DEN=density (gcm⁻³), DT=sonic (usft⁻¹), GR=gamma ray (gAPI), NEU= neutron (m³.m⁻³) and SUCS=magnetic susceptibility (arbitrary units).

If magnetic susceptibility was going to be used as a wire logging tool for hydrocarbon exploration, the peak magnetic susceptibility is the important factor when looking at correlations. To analyse this, the χ data for each core was normalised and compared to the other normalised well log properties. Figure 6.18 is an example from the Brent well core, which plots normalised magnetic susceptibility against the Spearman's correlation coefficient for each well log property. Each data point represents a moving window of 20 points in the magnetic susceptibility versus one of the well logs available. Evaluating the data points reveals that peaks in magnetic susceptibility (normalised magnetic susceptibility = 1.0) does not correspond to a given correlation coefficient for any of the well logs. The plot demonstrates that within this study there is a lack of any significant correlation for peak χ with any of the other well log correlation coefficients.

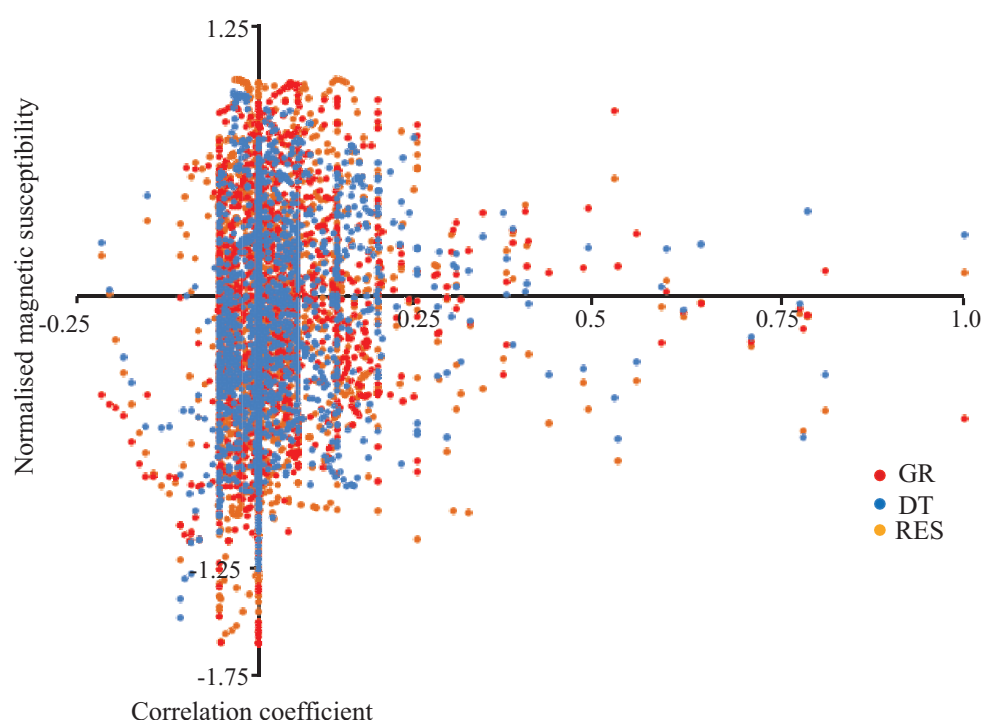


Figure 6.18. A plot representing normalised magnetic susceptibility versus the Spearman's correlation coefficient of well log data (GR, DT and RES) for the Brent well core, 211/29-C4.

Although there appears to be no statistical correlation between well logs and peak magnetic susceptibility, this could be potentially explained by the non-continuous nature of the cores as well as the low resolution of the magnetic susceptibility causing abrupt changes in χ compared to the other smooth well logs. It should also be noted that the data is limited and full well logs were not always ascertainable for each core as well as the low number of wells examined within this study.

6.5 Discussion

A combination of magnetic experimentation and SEM/EDX analysis has allowed a full rock magnetic characterisation of samples from both hydrocarbon bearing and dry well cores from the North Sea, UK. A detailed discussion follows comparing anomalously high magnetic susceptibility samples with background samples for each well (Section 6.5.1) and comparing the hydrocarbon saturated and dry well cores (Section 6.5.2).

6.5.1 Anomalous magnetic susceptibility

The well cores in this study showed varying numbers of anomalous magnetic susceptibility peaks and to differing magnitudes. The hydrocarbon bearing well core 211/29-C4 from the Brent Field had the strongest χ anomaly peaks ($8.4 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$) and well core 3/28A-4 from the Bressay Field had the lowest χ anomaly peaks ($1.8 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$) (Table 6.2). Samples from the χ anomalous peaks were compared to background samples for each well core (Figs. 6.2-6.10). Magnetic characterisation of these samples showed variation across all well cores as well as within each well core, such as the formation of a ferromagnetic mineral on heating (400-500 °C) within high temperature magnetic susceptibility curves with or without the formation of additional minerals on cooling (~300 °C) (Figs. 6.9 and 6.10). The formation of new minerals whilst heating is most likely a consequence of heating the original mineralogy, which is most likely siderite. There appears to be a strong abundance of siderite within some of the samples identified through the Néel transition in low temperature ZFC and FC curves (well cores 9/09B-3, 16/07A-A8 and 211/29-C4) (Figs. 6.5 and 6.6) as well as through Mössbauer spectroscopy (Fig. 6.3, Table 6.3) and AC susceptibility curves (Fig. 6.7). Iron oxides were also identified through RT SIRM cooling and warming curves (Figs. 6.5 and 6.6) as well as SEM imaging (Fig. 6.1) in all the samples and are thought to be mainly multi domain magnetite and small abundances of hematite. Across all the well cores there appears to be a wide range of magnetic minerals including, siderite, magnetite and hematite and are most probably due to their original geological facies and reveal a distinct lack of a specific magnetic mineral in association to hydrocarbons. The abundant siderite in the samples is most probably due to siderite nodules, which are common within sedimentary units (Klein & Beukes, 1989; Kholodov & Butuzova, 2008; Loope et al., 2012).

Comparing the anomalous magnetic susceptibility samples and the background samples, there does not appear to be a significant difference other than the concentration of magnetic minerals in the samples resulting in the χ differences. Both sets of samples for each well core share similar behavioural characteristics in ZFC, FC, RT SIRM curves (Fig. 6.5) high-temperature susceptibility

curves (Fig. 6.9) and within SEM and EDX analysis (Fig. 6.1). SEM analysis revealed the same magnetic mineralogy in both the anomalous χ samples and the background sample for each well core specifically revealing Fe-rich framboids in all the samples within well cores 9/09B-3, 16/17-13, 211/29-C4, 211/29-8A (dry) and 3/03-11(dry). Smaller grains are also likely to be present. This reveals a lack of specific magnetic characterisation within anomalous χ levels to try to characterise well cores associated with hydrocarbons.

6.5.2 Hydrocarbon bearing wells versus dry wells

The non-hydrocarbon bearing (dry) well cores (211/29-8A and 3/03-11) were characterised by similar magnetic mineralogy as the hydrocarbon bearing well cores and specifically the 211/29-C4 well core of the Brent Field, which share the same geological facies. Although these ‘dry’ cores have no hydrocarbon reservoirs the assumption has been made that migration of hydrocarbons have not occurred within these cores. This is potentially false and may explain why there are no differences in magnetic character between the ‘dry’ well cores and the hydrocarbon bearing well cores. The hysteresis parameters revealed a strong PSD-SD-like behaviour within well core 3/03-11 and a MD-like behaviour in well core 211/29-C4 (Fig. 6.2). These samples showed similar hysteresis parameters as the hydrocarbon well samples although the 3/03-11 well had the highest M_{rs}/M_s ratio of all samples within this study (Table 6.2). Similar behaviour within the high temperature susceptibility curves was also observed (Figs. 6.9 and 6.10). SEM images showed the presence of Fe-rich framboids in both the dry well cores (Fig. 6.1) mainly as iron sulphides as well as framboids present within some hydrocarbon bearing wells (9/09B-3, 16/17-13 and 211/29-C4). Specific anomalous characteristics such as described by Aldana *et al.* (1999) (framboids) were therefore not identified within this study. However, the FC, ZFC and RT SIRM curves (Figs. 6.5 and 6.6) revealed the presence of siderite and multi domain magnetite within the hydrocarbon bearing well cores close to the dry wells (well cores 211/29-C4 and 3/28A-4). Comparing this to the dry well cores, multi domain magnetite is not easily identifiable due to the overwhelming dominance of siderite within the samples, especially within well core 211/29-C4.

The results suggest, looking at the bigger picture of oil saturated and oil free sedimentary units, that compositional changes in the magnetic mineralogy due to hydrocarbons can be complex but potentially systematic. Figure 6.19 is a schematic describing the effect of hydrocarbon vicinity on magnetic mineralogy. Results within Chapters 3, 5 and 6 suggest that a biodegraded oil rich well core/seep will have a reduced magnetic signature due to the amount of oil present and to the destruction of single domain magnetite by bacteria within the oil (Well 2). With distance away from the hydrocarbon reservoir, (Well 1), carrier beds for the migrating hydrocarbons could hold a

positive magnetisation anomaly, The migrating hydrocarbons could cause alteration of the background signal by the formation of magnetite (possibly as framboids) around the hydrocarbon reservoir through the net transfer of electrons from altered organic matter to Fe (III) (Díaz et al., 2006). Finally, areas where there is little to no connection to the hydrocarbons, e.g., no migrating hydrocarbons (Well 3) the magnetic signal is only a record of the background signal. This behaviour has been identified within FC, ZFC and RT SIRM curves for two dry wells within this chapter most probably representing the migrational pathway cores (Well 1). This theory is supported by detailed magnetic stability research conducted by Burton *et al.* (1993), which revealed positive contrasts became more pronounced with greater proximity to a high concentration of hydrocarbons. In addition, this study shows that within the hydrocarbon reservoir itself, there is a negative contrast due to the bacteria present within the oil.

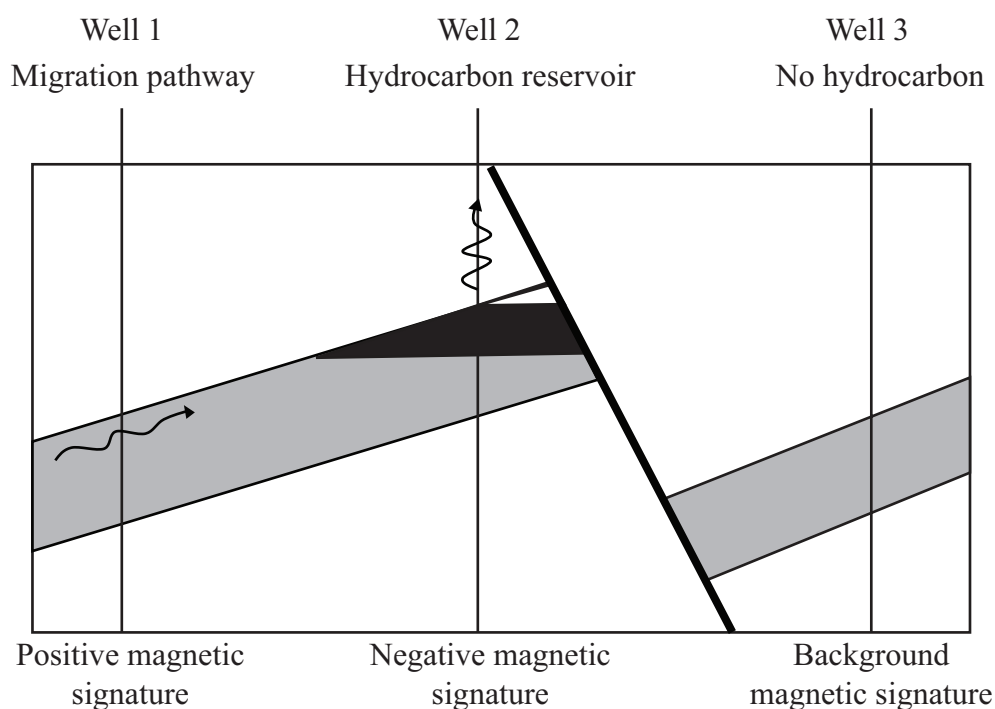


Figure 6.19. Schematic of variations in magnetic characterisation within well cores due to the vicinity and migration pathway of a hydrocarbon reservoir.

Finally, SPSS software was used to identify whether the magnetic susceptibility profiles of the well cores correlated to well log data (Figs. 6.12-6.17). A nonparametric Spearman's rank correlation coefficient (R_s) was used and the results showed correlations between magnetic susceptibility and nearly all well logs for all well cores taken over the whole cores at a significance of 99% (Table 6.4).

6.6 Summary

This study looked at the magnetic characteristics of samples throughout both hydrocarbon saturated well cores and non-hydrocarbon bearing (dry) well cores within the North Sea, UK. Anomalous magnetic susceptibility (χ) samples were identified using an automated Bartington Core logger (Chapter 2) and compared to background χ samples for each well core.

The well cores showed varying abundances of anomalous magnetic susceptibility peaks and to differing magnitudes. The hydrocarbon bearing well core 211/29-C4 from the Brent Field had the strongest χ anomaly peaks ($8.4 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$) and well core 3/28A-4 from the Bressay Field had the lowest χ anomaly peaks ($1.8 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$) (Table 6.2). Across all the well cores there was a wide range of magnetic minerals including, siderite, magnetite and hematite (Figs. 6.1-6.10) and are most probably due to original geological facies and reveal a distinct lack of a specific magnetic mineral in association to hydrocarbons. The abundant siderite in the samples is most probably due to siderite nodules, which are common within sedimentary units (Klein & Beukes, 1989; Kholodov & Butuzova, 2008; Loope et al., 2012).

Comparing the anomalous magnetic susceptibility samples and the background samples, there does not appear to be a significant difference other than the concentration of magnetic minerals in the samples. Both sets of samples for each well core share similar behavioural characteristics in low temperature and high-temperature curves (Figs. 6.5 and 6.8) and within SEM and EDX analysis (Fig. 6.1). This reveals a lack of specific magnetic characterisation within anomalous levels to try to characterise well cores better.

Moreover, the non-hydrocarbon (dry) well cores (211/29-8A and 3/03-11) were characterised by similar magnetic mineralogy as the hydrocarbon bearing well cores and specifically the 211/29-C4 well core of the Brent Field, which share the same geological facies. The assumption was made that the 'dry' well cores were not on a hydrocarbon migration pathway and could be considered 'oil free'. However, this may not be the case and may explain why there is no significant difference in magnetic characterisation between 'oil free' and hydrocarbon bearing well cores. The FC, ZFC and RT SIRM curves (Figs. 6.5 and 6.6) revealed the presence of siderite and multi domain magnetite within both dry well cores as identified within the hydrocarbon bearing well cores and similar behaviour within the high temperature susceptibility curves (Figs. 6.9 and 6.10). SEM images showed the presence of Fe-rich framboids in both the dry well cores (Fig. 6.1) mainly as iron sulphides as well as framboids present within some hydrocarbon bearing wells (9/09B-3, 16/17-13

and 211/29-C4) suggesting the presence of magnetic framboids was not characteristic of hydrocarbon bearing wells only.

The magnetic susceptibility profiles for the wells were plotted (except well core 9/09B-3) and compared to well log data (DT, GR, DEN, NEU, RES) (Figs. 6.12-6.17). The results showed correlations between magnetic susceptibility and nearly all of the properties investigated at a 99% confidence level (Table 6.4). However, the correlations are only significant because of the large number of data points. Broad areas of correlation identified on the well logs (Figs. 6.12-6.17) are most probably due to detrital magnetite within mud-rich sediments suggesting the correlations observed are due to geological facies changes.

Normalised magnetic susceptibility was investigated with respect to correlation coefficients for each well log property using a moving window of 20 points to identify whether χ peaks could be used for hydrocarbon identification (Fig. 6.18) through wire logging. All the well cores showed a lack of any significant correlation for anomalous χ with any of the other well log correlation coefficients. Moreover, specific anomalous characteristics such as described by Aldana *et al.* (1999) were therefore not identified within this study suggesting that at this stage, there are no universal characteristics that could be used to identify hydrocarbons through magnetisation logging tools. Although there appears to be no correlation with magnetic susceptibility peaks, it should be noted that the data were limited and full well logs were not always ascertainable for each core as well as the low number of wells examined within this study. There are many geological factors which affect any/all of the well logs and there may be a relationship between anomalous χ and some well log data, however, at present it is masked by many contributing factors and no easy solution is apparent. Due to the relationships determined in Chapters 3-5, it would suggest that any hydrocarbons, which leak through lower hydrocarbon reservoirs, should leave a magnetic trace and therefore be identifiable on a hydrocarbon migration pathway. It is very likely that hydrocarbons have migrated through the samples within this chapter, specifically the 'dry' well cores. Therefore, this study shows the relationship between migrating pathways (Well 1 - Fig. 6.19) and hydrocarbon reservoirs (Well 2 - Fig. 6.19). Unfortunately at this stage, the lack of suitable samples/data does not allow for the theory outlined in Figure 6.19, including no hydrocarbon well cores, to be investigated further within this study.

Chapter 7

Conclusions

7.1 Conclusions

7.1.1 Magnetisation and biodegradation

Combining the geochemical analysis with magnetic analysis for four sets of oil impregnated sedimentary rock samples from the UK, Canada, Colombia and Indonesia, allowed for the first time, a unique relationship between hydrocarbons and magnetisation to be established.

Biomarker data revealed that all oil samples were derived from mature type-II kerogen, deposited in oxygen-poor environments. The Colombian samples showed little biodegradation due to the retention of *n*-alkanes within their aliphatic fractions, compared to the UK, Canadian and Indonesian samples that displayed heavy to severe biodegradation with no *n*-alkanes retained. Pyrolysis data of the asphaltene fractions for these three sets of samples were consistent with a type II kerogen source. This study investigates the detailed magnetic characterisation of different oil bearing sediments with similar maturities and marine kerogen type II source rocks. The suite of samples available allows for the comparison of magnetic mineralogy with differing biodegradation levels within the oil, with increased biodegradation from low to high levels for Colombia, UK (OS), Canada, UK (MB & LC) and Indonesia samples respectively. Moreover, a vertical succession from the Saltarín 1A well in the Llanos Foreland Basin, allows the geochemical characterisation of several organic matter impregnated sediments and, therefore, assessment of the main controls on oil chemistry. Oils in the Llanos Foreland Basin display small varying compositions that may reflect primary (source, maturity) or secondary (biodegradation, mixing) processes. The relatively low proportion of polar and asphaltene components in addition to the retention of *n*-alkanes in all samples suggests that the hydrocarbons have not experienced extreme levels of biodegradation. Some indications of biodegradation do exist, however, and it is surprising that a sample from the shallowest depth, which would be expected to be the most heavily degraded due to increased porosity, lower temperatures and water mobility is the least biodegraded of all the samples in this study. It is inferred that the shallowest sample resides within a distinct compartment with an aquifer supplying water to the deeper compartment leading to increasing biodegradation levels towards the oil-water contact. It is also notable that the shallow sample may contain relatively more contributions from a source rock that contains higher plant material as indicated by a greater relative abundance of C₂₉ steranes and the possible presence of oleanane. Hence, the chemical differences brought about by biodegradation and possibly source variations are potentially produced and certainly maintained by reservoir compartmentalization and chemical communication between the deeper and shallower samples is incomplete.

Relationships between magnetic mineralogy and hydrocarbons have already been investigated (Elmore et al., 1987; McCabe et al., 1987; Kilgore & Elmore, 1989), but this more detailed magnetic study suggests this relationship is very complex, affected by a number of different factors especially biodegradation. Through these samples, a relationship between magnetic susceptibility (χ), the extractable organic matter (EOM %) and the relative abundance of aliphatic organic compounds in oil has been identified. The magnitude of mass normalised magnetic susceptibility varied between $10^{-4} \text{ m}^3\text{kg}^{-1}$ for the Colombian samples, 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for UK, 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for Canadian and 10^{-5} - $10^{-6} \text{ m}^3\text{kg}^{-1}$ for the Indonesian samples. A negative correlation between χ and EOM% for each given reservoir was identified with correlations between $R^2=0.7$ - 0.9 . Geological facies can have a large effect on the magnetic susceptibility of the rock unit, therefore, to remove these effects, negative regressions were determined for each set of samples and the data were normalized by the magnetic susceptibility at zero EOM content (e.g., background sample, χ_B). Using the normalised data, all the samples showed a strong negative linear regression in log space, which cannot be rejected at a 99% confidence level. Previously it was assumed that newly generated magnetite would strengthen magnetic signals in biodegraded samples. The results from this study suggest the opposite effect occurs and that it is the removal of magnetite and reduction in magnetic signal that leads to variation in oils. The magnitude of magnetic susceptibility appears to be dependent on not just the magnetic mineralogy of the original host rock (background samples) but also to the amount of hydrocarbon migration, accumulation and biodegradation within the rock. To try to distinguish whether the magnetic response was due to bacteria and/or migration, magnetic susceptibility was compared to individual oil components.

This study has identified a relationship between magnetic susceptibility and the relative abundance of aliphatic organic compounds in oil. The percentage of aliphatic and polar components within the oil is also indicative of biodegradation as the original aliphatic compounds are destroyed and polar compounds as well as asphaltenes become relatively more abundant as a consequence of biodegradation. A positive correlation for magnetic susceptibility and aliphatic percentages was identified through the change in magnetic susceptibility from oil free to oil impregnated for each sample ($\log_{10}\chi - (\log_{10}\chi/\log_{10}\chi_B)$). A negative correlation for polar and asphaltene compounds was also identified and these results conclude that magnetic susceptibility decreases with increasing effects of biodegradation, decreasing oil quality and cannot be rejected at a 99% confidence level. Biodegradation appears to remove both aliphatic hydrocarbons and magnetic susceptibility owing to the influence of bacterial metabolic activity that uses ferric iron minerals as electron acceptors. Magnetically, the more biodegraded samples (increasing biodegradation from Colombian, UK (OS),

Canadian, UK (MB & LC), Indonesian samples) display more multi domain characteristics, which can be inferred as larger magnetite grains as well as an increasing presence of hematite.

Further magnetic characterisation revealed that the high quality, low biodegradation oils from Colombia have a higher magnetic susceptibility and are dominated by pseudo-single domain grains of magnetite. The lower quality oils i.e., the UK, Canadian and Indonesian samples, displayed decreased magnetic susceptibility and pseudo-single domain to multi domain grains of magnetite and hematite. Therefore, with decreasing oil quality there is a progressive dominance of multi domain magnetite as well as the appearance of hematite. The additional presence of hematite in the more severely biodegraded samples and the lack of it within non-biodegraded samples suggests a later stage of biodegradation occurred most probably at the surface due to hematite being more stable in aerobic/oxidizing environments. Magnetite and pyrite/pyrrhotite framboidal material were found in all but the Canadian samples.

Correlations observed within this study suggest that bacteria play a key role in changing the magnetic signature of the host rock through anaerobic and aerobic biodegradation of the oil. There are several well-known bacteria (Heider et al., 1998) that readily use Fe ions in anaerobic processes within oil biodegradation (Bigge & Farrimond, 1998). The magnetic signature appears to become more MD-like with increased biodegradation, i.e., the signal of the rock is being dominated by larger magnetic particles, through the preferential removal of small SD grains and possibly the transformation of sulphide-rich framboids to oxide-rich framboids. The overall magnetisation is reduced, as is seen by the reduction in M_s , suggesting that more SD particles are being removed and MD particles formed. Iron sulphides also exist within all but the Canadian samples mainly as framboidal pyrrhotite most probably formed as a result of the generation of reduced sulphur by anaerobic sulphate-reducing bacteria which have been shown to also cause biodegradation of oils (Rueter et al., 1994). Furthermore, the results suggest that the progression of biodegradation within the oil is related to both the formation of multi domain magnetite and the overall reduction in magnetic susceptibility. The increase in biodegradation with depth within the Llanos Foreland Basin Saltarín 1A well allowed for further magnetisation and biodegradation characterisation. The shallow, least biodegraded samples (C127.40 and C147.25) were characterised by multi domain magnetite as well as iron sulphide framboids most probably pyrrhotite/pyrite identified by semi-reversible Curie curves, the inflections at ~120 K within RT SIRM cooling and warming curves, hysteresis and SIRM data as well as SEM and EDX analysis. In contrast, the deeper more biodegraded samples (C541.75 and C616.48) were dominated by iron sulphides with low abundances of multi domain magnetite. The presence of low temperature (< 40 K) magnetic transitions in the ZFC and FC curves, the formation of ferromagnetic minerals on heating and SEM

and EDX analysis confirm iron sulphides are present. The very high coercivities (M_s) and hysteresis parameters suggest very low abundances of multi domain magnetite within these samples. The deeper samples had no framboidal material. The overall magnetic susceptibility changes over the samples correlate with EOM% and biodegradation biomarkers. It is proposed that this detailed study supports the idea of preferential removal of SD magnetite due to bacteria within oil impregnated sedimentary units as a main mechanism for anomalous magnetic signatures. It also concludes that magnetic framboids cannot be used as a tool for hydrocarbon identification due to ambiguous presence in many non-hydrocarbon associated environments as well as the lack of framboids within some hydrocarbon bearing sedimentary units.

The results suggest by combining this study with other previous studies, that on a large spatial scale (Fig. 7.1), anomalous magnetic susceptibility can form above a reservoir due to the formation of secondary magnetic material through the net transport of electrons from altered organic matter possibly through leaking hydrocarbon gases and liquids.

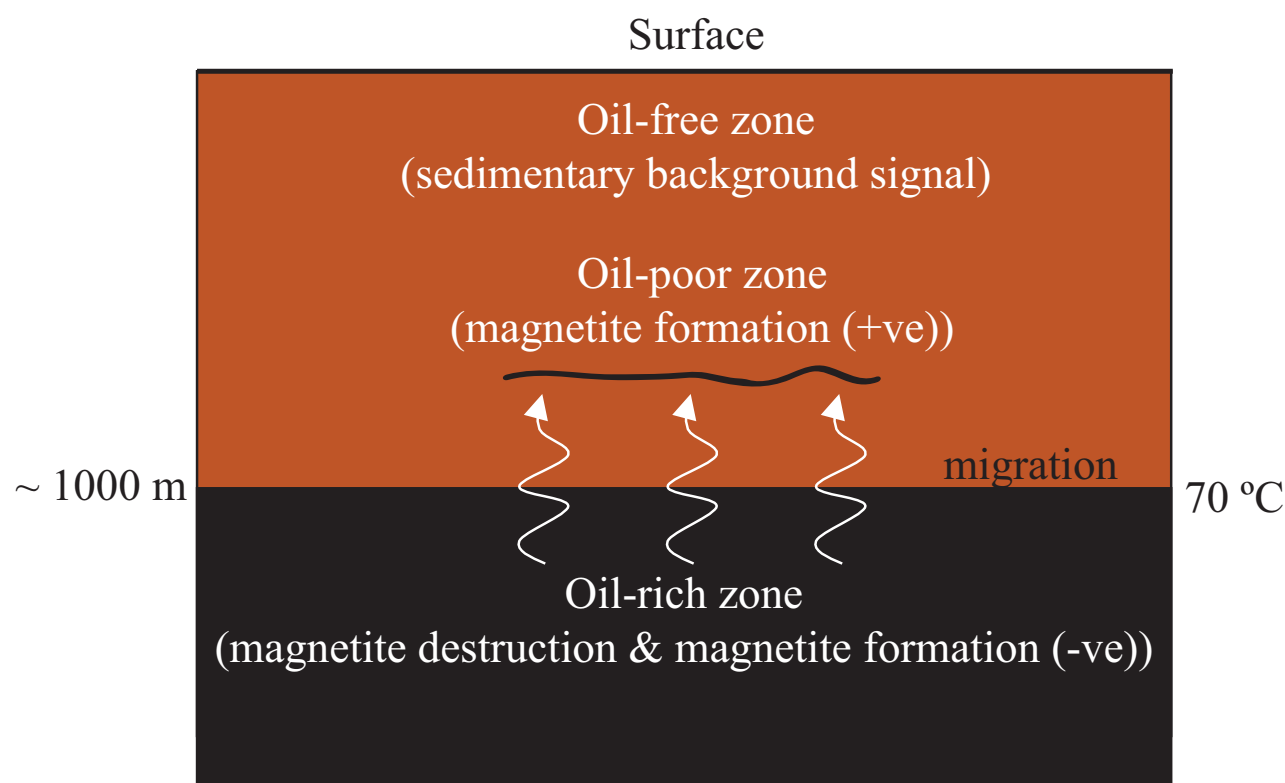


Figure 7.1. Schematic sketch showing the difference in magnetic mineralogy in an oil-rich and oil-poor zone.

However, within the reservoir and oil impregnated sedimentary units themselves, the host rock can hold its own anomalous magnetic susceptibility. The amount of oil saturation and biodegradation appears to decrease the magnetic signal through the presence of bacteria resulting in either the preferential removal of smaller magnetite grains or the formation of authigenic magnetite. This

complicated relationship may go some way as to explain why both high and low anomalies have been associated within hydrocarbon accumulations in the past (e.g., Donovan et al., 1979; Elmore et al., 1993; Reynolds & Goldkaber, 1993) (Fig. 7.1).

These findings reinforce the importance of bacteria within petroleum systems as well as providing a platform for the use of magnetisation as a hydrocarbon migration proxy. A relationship between hydrocarbons and their magnetic signatures has been alluded to for decades but this is the first study to combine extensive geochemical and magnetic data. These results suggest a very complex relationship between magnetisation and hydrocarbons through not only the change in magnetic signature within the host rock as a result of oil impregnation but also as a result of bacterial action.

7.1.2 Dating oil migration in the Wessex Basin

Hydrocarbon infiltration has been shown to cause a chemical remanent magnetisation (CRM) remagnetisation mainly through the formation of authigenic magnetite. The Mupe Bay intraformational conglomerate occupies an important position in the petroleum geology of the Wessex Basin because of its potential record of the timing of oil migration in the region. Yet two conflicting interpretations of the Mupe Bay outcrop are possible:

- i) The clasts represent previously oil stained and cemented boulders that were produced and transported in Wealden times before incorporation into a conglomeratic bed. The matrix of the conglomerate bed was then stained by later migrating oil, or
- ii) The clasts were transported unstained and both clasts and matrix were impregnated during a single oil-staining event at an undefined time after the bed was deposited in the Early Cretaceous.

Only the former scenario constrains the onset of oil migration in the Wessex Basin to the Early Cretaceous. Owing to the ambiguous nature of existing organic geochemical data, controversy exists over which interpretation is correct. There is a clear need for new methods and remagnetisation was investigated within this study.

Two key pieces of data are forthcoming. The first data set reflects the mineralogy and domain characteristics of the magnetite. The matrix is known to be more biodegraded than the clasts (Parfitt & Farrimond, 1998) and it may be possible that this biodegradation has resulted in relatively higher concentrations of multi domain authigenic magnetite within the matrix resulting in softer coercivity.

These differences between the clasts and matrix also support the theory of continued oil migration into the matrix.

Hematite was also identified within the clasts and is usually oxidized from magnetite. This suggests there was early incorporation of hydrocarbons into the clasts, which became oil cemented and subsequently isolated soon after oil migration. The early oil migration into the clasts could have insured early formation of magnetite and subsequent oxidation to hematite due to the isolation of the clasts from the matrix. The lack of hematite within the matrix supports this theory because biodegraded hydrocarbons are still actively seeping into the matrix allowing the formation of larger multi domain grains of magnetite but limiting the opportunity for oxidation. Magnetic susceptibility and hysteresis parameters differ before and after oil extraction in both the clasts and matrix however the magnitude of variation is larger within the matrix. The larger variations suggest the oil within the matrix is still mobile which can cause alteration in magnetic parameters. This is a result of unstable magnetic grains as well as their ability to realign in magnetic fields when 'mobile'. In contrast, the clasts show less variation because they are cemented oil sands allowing no movement of the magnetic grains and consequently are more stable.

The second data set comprises palaeodirection information. The data reveals that the matrix and clasts show different magnetic field orientations implying that the matrix and the clasts were stained by two separate oil migration events. This interpretation is supported by statistical analysis that indicates that the independence of the matrix and the clasts magnetisation cannot be rejected at a 95% confidence level.

A conglomerate test is normally performed on clasts owing to their random orientations as a result of transportation and incorporation into another host rock, however, in this study the clasts show the same orientation and therefore must have had their remanence recorded after incorporation into the sand matrix. This interpretation requires limited opportunity for biodegradation and magnetite formation before clast erosion, transport and deposition. Sedimentological data support this assertion and clasts are believed to have been transported only a small distance from Lulworth Cove (Wimbledon et al., 1996) and are considered to have been deposited into the matrix whilst soft due to their deformation (Miles et al., 1993; Wimbledon et al., 1996). Palaeomagnetic coordinates for the Cretaceous using the apparent polar wandering curve for Northern Eurasia are sporadic. Few very reliable constraints exist especially for the Early Cretaceous (Irving & Irving, 1982; Van der Voo, 1993; Torsvik et al., 2001), however, estimated mean palaeopoles from 140-120 Ma are between 73°N, 138°E and 77°N, 170°E with associated errors. The data gives a mean age for the CRM, and therefore staining, transport and incorporation of the clasts, as Early Cretaceous.

A final revelation is derived from the magnetic data from the matrix. The magnetic data for the Mupe Bay matrix shows the same magnetisation as today (-6° Declination, 65° Inclination) at 95% confidence, suggesting it is an active oil seep. This interpretation is concordant with other seeps along the Dorset coast, some of which are active at the present day, e.g. Bran Point (Watson et al., 2000). This study demonstrates the utility of magnetic data to constrain the timing of migration in petroleum basins. This data clearly supports the classic two-stage oil-staining event, which involves the onset of oil migration in the Wessex Basin in the Early Cretaceous. The matrix was stained at a later date and the Mupe Bay matrix continues to seep oil at the present day.

7.1.3 Well core magnetic characterisation

A combination of magnetic experimentation and SEM/EDX analysis has allowed a full rock magnetic characterisation of samples from both hydrocarbon bearing and dry well cores from the North Sea, UK. A detailed discussion follows comparing anomalously high magnetic susceptibility samples with background samples for each well (Section 6.5.1) and comparing the hydrocarbon producing and dry well cores (Section 6.5.2).

The well cores in this study showed varying numbers of anomalous magnetic susceptibility peaks and to differing magnitudes, for example $8.4 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $1.8 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$ for well cores 211/29-C4 and 3/28A-4 respectively. Samples from the χ anomalous peaks were compared to background samples for each well core. Magnetic characterisation of these samples showed variation across all well cores as well as within each well core, such as the formation of a ferromagnetic mineral on heating (400-500 °C) within high temperature magnetic susceptibility curves with or without the formation of additional minerals on cooling (~ 300 °C). There appears to be a strong abundance of siderite within some of the samples identified through the Néel transition in low temperature ZFC and FC curves (well cores 9/09B-3, 16/07A-A8 and 211/29-C4) as well as through Mössbauer spectroscopy and AC susceptibility curves. Iron oxides were also identified through RTSIRM cooling and warming curves as well as SEM imaging in all the samples and are thought to be mainly multi domain magnetite and small abundances of hematite. Across all the well cores there appears to be a wide range of magnetic minerals including, siderite, magnetite and hematite and are most probably due to their original geological facies and reveal a distinct lack of a specific magnetic mineral in association to hydrocarbons. The abundant siderite in the samples is most probably due to siderite nodules, which are common within sedimentary units (Klein & Beukes, 1989; Kholodov & Butuzova, 2008; Loope et al., 2012).

Comparing the anomalous magnetic susceptibility samples and the background samples, there does not appear to be a significant difference other than the concentration of magnetic minerals in the

samples resulting in the χ differences. Both sets of samples for each well core share similar behavioural characteristics in ZFC, FC, RT SIRM curves, high temperature susceptibility curves and within SEM and EDX analysis. SEM analysis revealed the same magnetic mineralogy in both the anomalous χ sample and the background sample for each well core specifically revealing Fe-rich framboids in all the samples within well cores 9/09B-3, 16/17-13, 211/29-C4, 211/29-8A (dry) and 3/03-11(dry). This reveals a lack of specific magnetic characterisation within anomalous χ levels to try to characterise well cores associated with hydrocarbons.

The non-hydrocarbon (dry) well cores (211/29-8A and 3/03-11) were characterised by similar magnetic mineralogy as the hydrocarbon bearing well cores and specifically the 211/29-C4 well core of the Brent field, which share the same geological facies. The hysteresis parameters revealed a strong PSD-SD-like behaviour within well core 3/03-11 and a MD-like behaviour in well core 211/29-8A. These samples showed similar hysteresis parameters and high temperature susceptibility behaviour as the hydrocarbon well samples. SEM images showed the presence of Fe-rich framboids in both the dry well cores mainly as iron sulphides as well as framboids present within some hydrocarbon bearing wells (9/09B-3, 16/17-13 and 211/29-C4). Specific anomalous characteristics such as described by Aldana *et al.* (1999) (framboids) were therefore not identified within this study. However, the FC, ZFC and RT SIRM curves revealed the presence of siderite and multi domain magnetite within the hydrocarbon bearing well cores close to the dry wells (well cores 211/29-C4 and 3/28A-4). Comparing this to the dry well cores, multi domain magnetite is not easily identifiable due to the overwhelming dominance of siderite within the samples, especially within well core 211/29-C4.

The results suggest, looking at the bigger picture of oil saturated and oil free sedimentary units, that compositional changes in the magnetic mineralogy due to hydrocarbons can be complex but potentially systematic. Results within Chapters 3, 5 and 6 suggest that an oil rich well core/seep will have a reduced magnetic signature due to the destruction of single domain magnetite by bacteria within the oil. With distance away from the hydrocarbons, small seepages of oil from below can cause alteration of the background signal by the formation of magnetite (possibly as framboids) above and below the hydrocarbon reservoir through the net transfer of electrons from altered organic matter to Fe (III) (Díaz *et al.*, 2006). Further distance from the oil reservoir/seep reduces the effect of hydrocarbons on the host rock and may cause small variations in magnetic mineralogy but it would no longer be sufficient enough to identify differences between hydrocarbon bearing and oil free sedimentary units, the magnetic signal is fundamentally only a record of the background signal. This behaviour has been identified within FC, ZFC and RT SIRM curves for two dry wells within Chapter 6. This theory is supported by detailed magnetic stability research conducted by Burton *et*

al. (1993), which revealed positive contrasts became more pronounced with greater proximity to a high concentration of hydrocarbons. In addition, this study shows that within the hydrocarbon reservoir itself, there is a negative contrast due to the bacteria present within the oil.

Finally, SPSS software was used to identify whether the magnetic susceptibility profiles of the well cores correlated to well log data. A nonparametric Spearman's rank correlation coefficient (R_s) was used and the results showed correlations between magnetic susceptibility and nearly all of the properties investigated at a 99% confidence level. The broad areas of correlation identified on the well logs are most probably due to the interplay of siliclastic admixture in carbonates as well as the concentration of diagenetic iron bearing minerals (Koptíková *et al.*, 2010). Siderite nodules often found in mud-rich sedimentary units were found within most of the cores and it is likely there is associated magnetite with these nodules, which could account for the elevated magnetic susceptibilities within mud-rich facies (Loope *et al.*, 2012).

Normalised magnetic susceptibility was investigated with respect to correlation coefficients for each well log property using a moving window of 20 points to identify whether χ peaks could be used for hydrocarbon identification. All the well cores showed a lack of any significant correlation for anomalous χ with any of the other well log correlation coefficients suggesting that magnetic susceptibility anomalies cannot be used as a tool for identifying hydrocarbons. Moreover, specific anomalous characteristics such as described by Aldana *et al.* (1999) were therefore not identified within this study suggesting that at this stage, there are no universal characteristics that could be used to identify hydrocarbons through magnetisation logging tools. Although there appears to be no correlation with magnetic susceptibility peaks, it should be noted that the data were limited and full well logs were not always ascertainable for each core as well as the low number of wells examined within this study. There are many geological factors which affect any/all of the well logs and there may be a relationship between anomalous χ and some well log data, however, at present it is masked by many contributing factors and no easy solution is apparent.

Due to the relationships determined in Chapters 3-5, it would suggest that any hydrocarbons, which leak vertically from lower hydrocarbon reservoirs, should leave a magnetic trace and therefore be identifiable on a hydrocarbon migration pathway. In Chapter 6, it is likely that hydrocarbons have migrated through the samples (Well 1 and 2 in Fig. 6.19). When hydrocarbons migrate, they can migrate vertically and/or laterally in a convoluted manor through carrier beds due to the presence of heterogeneities within the subsurface rock. When hydrocarbons begin to fill into a trap, the tortuous migration pathway will tend to fill from one side. Compositional changes within the oil can occur during filling as the source rock becomes more mature. Pulses of hydrocarbons can also cause

compositional variations if the reservoir is biodegraded with non-biodegraded oils entering. Within the reservoir and oil impregnated units themselves, the host rock can hold its own negative anomalous magnetic susceptibility due to the organic matter entering the system and the possible bacteria biodegrading the hydrocarbons. The hydrocarbons can accumulate until either the reservoir is filled to the spill point or there is capillary failure at the seal (e.g., at a sealing fault). Leaking hydrocarbons from such reservoirs can then leave a secondary trace as they move vertically towards the surface. The leaking hydrocarbons can cause a positive magnetic signature due to the formation of secondary magnetic material through the net transport of electrons from altered organic matter as suggested by Díaz *et al.* (2006) and/or the processes experienced by migrating hydrocarbons which cause a change in the the oil composition. This complicated relationship may go some way as to explain why both high and low anomalies have been associated within hydrocarbon accumulations in the past (e.g., Donovan et al., 1979; Elmore et al., 1993; Reynolds & Goldkaber, 1993).

Unfortunately at this stage, the lack of suitable samples/data does not allow for this theory to be investigated further within this study (See future work, Section 7.2).

7.2 Further work

Most of the future work from this research stems from the need for a large variability and suitability of samples.

If suitable samples could be obtained, similar magnetic and geochemical studies on the effect of magnetisation on source and maturity variations within oil would add to the database this study has initiated on biodegradation effects on magnetic mineralogy. In addition to this, more oil samples with known variations of aliphatic hydrocarbons, aromatic hydrocarbons and polar components would help determine exactly how rigid the correlations within this study are. A further test for the magnetic characterisation of hydrocarbons would involve a large sample set of varying contents of hydrocarbons varying from oil free to heavily saturated as well as differing oils in term of source maturity and biodegradation within a single geological formation. Such samples may be found within a compartmentalized reservoir or a set of oil reservoirs in close proximity along a well defined fill-to-spill path. The use of TEM and X-ray diffraction analysis could also help determine more strongly the magnetic mineralogy of the samples especially Fe-rich framboids.

Further work could also be done to look at the prospect of a proxy for identifying hydrocarbon migration pathways employing magnetic procedures. This is based on the theory outlined in Figure

6.19. Results within Chapters 3, 5 and 6 suggest that a biodegraded oil rich well core/seep will have a reduced magnetic signature due to the destruction of single domain magnetite by bacteria within the oil. With distance away from the hydrocarbon reservoir, carrier beds for the migrating hydrocarbons could hold a positive magnetisation change. The migrating hydrocarbons could cause alteration of the background signal by the formation of magnetite (possibly as framboids) around the hydrocarbon reservoir through the net transfer of electrons from altered organic matter to Fe (III) (Díaz et al., 2006). Finally, areas where there is little to no connection to the hydrocarbons, e.g., no migrating hydrocarbons the magnetic signal is only a record of the background signal. This theory could not be tested within this study due to a lack of suitable samples; a number of core samples would be needed from a single reservoir (oil saturated rock and oil free rock) as well as a general understanding of where the reservoir must have filled from to test the hypothesis.

Further work could also look at the effect of primary versus secondary migration. Primary migration should contain non-biodegraded hydrocarbons and should produce a positive magnetic signature compared to a negative magnetic anomaly associated with biodegraded hydrocarbon reservoirs. Secondary migration can lead to the formation of magnetite (possibly as framboids) around the hydrocarbon reservoir through the net transfer of electrons from altered organic matter to Fe (III) (Díaz et al., 2006), however, there could be a fundamental difference in the magnetic characterisation between these two migration pathways due to their migration histories.

Moreover, to try to understand correlations within well log data and magnetic susceptibility further studies using an automated Bartington core logger should be conducted. More continuous cores including a section of the reservoir itself would allow a detailed study of hydrocarbon effects within a single core. Taking continuous samples (not only at anomalous magnetic susceptibility values) as well as conducting the magnetic susceptibility analysis using a higher resolution than in this study to get very detailed information. This could result in a detailed understanding in terms of magnetic mineralogy within reservoir rocks and the effect of hydrocarbon migration through well cores.

References

- Aldana, M., Costanzo-Alvarez, V. & Díaz, M., 2003. Magnetic and mineralogical studies to characterize oil reservoirs in Venezuela. *The Leading Edge*, 22(6), pp.526-529.
- Aldana, M., Costanzo-Alvarez, V., Gomez, L., Gonzalez, C., Diaz, M., Silva, P. & Rada, M., 2011. Identification of magnetic minerals related to hydrocarbon authigenesis in Venezuelan oil fields using an alternative decomposition of isothermal remanence curves. *Studia Geophysica et Geodaetica*, 55(2), pp.343-358.
- Aldana, M., Costanzo-Alvarez, V., Vitiello, D., Colmenares, L. & Gomez, G., 1999. Framboidal magnetic minerals and their possible association to hydrocarbons: La Victoria oil field, southwestern Venezuela. *Geofisica Internacional*, 38(3), pp.137-152.
- Aubourg, C., Pozzi, J. P., Janots, D. & Sahraoui, L., 2008. Imprinting chemical remanent magnetization in claystones at 95 °C. *Earth and Planetary Science Letters*, 272(1-2), pp.172-180.
- Aubourg, C., Pozzi, J. P. & Kars, M., 2012. Burial, claystones remagnetization and some consequences for magnetostratigraphy. In: Elmore, R. D., Muxworthy, A. R., Aldana, M. M. & Mena, M. eds. *Remagnetization and Chemical Alteration of Sedimentary Rocks*. London: Geological Society London Special Publications. 371. pp.1-8.
- Audley-Charles, M. G., 1988. Evolution of the Southern margin of Tethys (North Australian region) from Early Permian to Late Cretaceous. In: Audley-Charles, M. G. & Hallam, A. eds. *Gondwana and Tethys*. Oxford: Geological Society London Special Publication. 37. pp.79-100.
- Bailey, M. E. & Dunlop, D. J., 1977. On the use of anhysteretic remanent magnetization in paleointensity determination. *Physics of the Earth and Planetary Interiors*, 13, pp.360-362.
- Balson, P., Butcher, A., Holmes, R., Johnson, H., Lewis, M. & Musson, R. 2002. North Sea Geology. In: BGS ed. *Strategic Environmental Assessment - SEA2 & SEA3*. BGS.
- Banerjee, S. K. & Moskowitz, B. M., 1985. Ferrimagnetic properties of magnetite. In: Kirschvink, J. L., Jones, D. S. & MacFadden, B. J. eds. *Magnetite Biomineralization and Magnetoreception in Organisms: A new magnetism*. Plenum Publishing Corporation. pp.17-41.
- Barwise, A. J. G., 1990. Role of nickel and vanadium in petroleum classification. *Energy & Fuels*, 4(6), pp.647-652.
- Bayona, G., Cortés, M., Jaramillo, C., Ojeda, G., Aristizabal, J. J. & Reyes-Harker, A., 2008a. An integrated analysis of an orogen-sedimentary basin pair: Latest Cretaceous-Cenozoic evolution of the linked Eastern Cordillera orogen and the Llanos foreland basin of Colombia. *Geological Society of America Bulletin*, 120(9-10), pp.1171-1197.
- Bayona, G., Valencia, A., Mora, A., Rueda, M., Ortiz, J. & Montenegro, O., 2008b. Estratigrafía y procedencia de las rocas del Mioceno en la parte distal de la cuenca antepais de los Llanos de Colombia. *Geología Colombiana*, 33, pp.23-46.
- Bazylinski, D. A., Frankel, R. B. & Konhauser, K. O., 2007. Modes of biomineralization of magnetite by microbes. *Geomicrobiology Journal*, 24(6), pp.465-475.
- Belkaaloul, N. K. & Aissaoui, D. M., 1997. Nature and origin of magnetic minerals within the Middle Jurassic shallow - water carbonate rocks of the Paris Basin, France: implications for magnetostratigraphic dating. *Geophysical Journal International*, 130(2), pp.411-421.
- Bell, P. E., Mills, A. L. & Herman, J. S., 1987. Biogeochemical conditions favoring magnetite formation during anaerobic iron reduction. *Applied and Environmental Microbiology*, 53(11), pp.2610-2616.
- Benthien, R. & Elmore, R., 1987. Origin of magnetization in the Phosphoria Formation at Sheep Mountain, Wyoming: A possible relationship with hydrocarbons. *Geophysical Research Letters*, 14(4), pp.323-326.

- Berkowitz, N., 1997. *Fossil hydrocarbons: Chemistry and Technology*. San Diego: San Diego Academic press.
- Bigge, M. A. & Farrimond, P., 1998. Biodegradation of seep oils in the Wessex Basin - a complication for correlation. In: Underhill, J. R. ed. *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society London Special Publications. 133. pp.373-386.
- Blanc, P. & Connan, J., 1994. Preservation, degradation and destruction of trapped oil. In: Magoon, L. B. & Dow, W. G. eds. *The petroleum system-from source to trap*. Tulsa, OK: American Association of Petroleum Geologists Memoir. 60. pp.237-247.
- Bleaney, B. I. & Bleaney, B., 1957. *Electricity and Magnetism*. Oxford: Oxford University Press.
- Borradaile, G., 2003. *Statistics of Earth Science data- Their Distribution in Time, Space and Orientation*. Germany: Springer.
- Braun, R. L. & Burnham, A. K., 1992. PMOD: a flexible model of oil and gas generation, cracking and exsolution. *Organic Geochemistry*, 19(1-3), pp.161-172.
- Brooks, P. W., Fowler, M. G. & Macqueen, R. W., 1988. Organic geochemistry of Western Canada Basin tar sands and heavy oils. *Organic Geochemistry*, 12, pp.519-538.
- Brothers, L. A., Engel, M. H. & Elmore, R. D., 1996. The late diagenetic conversion of pyrite to magnetite by organically complexed ferric iron. *Chemical Geology*, 130, pp.1-14.
- Buchanan, J. G., 1998. The exploration history and controls on hydrocarbon prospectivity in the Wessex basin, southern England, UK. In: Underhill, J. R. ed. *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society London Special Publications. 133. pp.19-37.
- Burton, E. A., Machel, H. G. & Qi, J., 1993. Thermodynamic constraints on anomalous magnetization in shallow and deep hydrocarbon seepage environment. In: Aïssaoui, D. M., McNeill, D. F. & Hurley, N. F. eds. *Applications of Paleomagnetism to Sedimentary Geology*. Society of Economic Paleontologists and Mineralogists Special Publication. 49. pp.193-207.
- Butler, 1992. *Paleomagnetism: Magnetic domains to geological terranes*. Blackwell.
- Canfield, D. E. & Berner, R. A., 1987. Dissolution and pyritization of magnetite in anoxic marine sediments. *Geochimica et Cosmochimica Acta*, 51(3), pp.645-659.
- Carter-Stiglitz, B., Moskowitz, B., Solheid, P., Berquó, T. S., Jackson, M. & Kostrov, A., 2006. Low-temperature magnetic behaviour of multi-domain titanomagnetites: TM0, TM16, and TM35. *Journal Geophysical Research*, 111(B12S05), pp.1-12.
- Chadwick, R. A., 1993. Aspects of basin inversion in Southern Britain. *Journal of Geological Society*, 150(2), pp.311-322.
- Chopra, P., Papp, E. & Gibson, D. 2002. Geophysical Well Logging. In: Papp, E. ed. *Geophysical and remote sensing methods for Regolith exploration*. CRC LEME.
- Cioppa, M. T. & Symons, D. T. A., 2000. Timing hydrocarbon generation and migration: paleomagnetic and rock magnetic analysis of the Devonian Duvernay Formation, Alberta, Canada. *Journal of Geochemical Exploration*, 69-70, pp.387-390.
- Coates, J., 2000. Interpretation of Infrared Spectra, A Practical Approach. In: Meyers, R. A. ed. *Encyclopedia of Analytical Chemistry*. Chichester: Wiley. pp.10815-10837.
- Collinson, D. W., 1965. Depositional Remanent Magnetization in sediments. *Journal of Geophysical Research*, 70(18), pp.4663-4668.
- Collinson, D. W., 1983. *Methods in rock magnetism and paleomagnetism – techniques and instrumentation*. London: Chapman and Hall.
- Connan, J., 1984. Biodegradation of crude oils in reservoirs. In: Brooks, J. & Welte, D. H. eds. *Advances in Petroleum Geochemistry*. London: Academic Press. 1. pp.299-335.
- Cooper, D. C., Picardal, F., Rivera, J. & Talbot, C., 2000. Zinc immobilization and magnetite formation via ferric oxide reduction by *Shewanella putrefaciens* 200. *Environmental Science & Technology*, 34(1), pp.100-106.

- Cooper, M., Addison, F., Alvarez, R., Coral, M., Graham, R. H., Hayward, A. B., Howe, S., Martinez, J., Naar, J., Peñas, R., Pulham, A. J. & Taborda, A., 1995a. Basin development and tectonic history of the Llanos basin, Eastern Cordillera, and Middle Magdalena Valley, Colombia. *American Association of Petroleum Geologists Bulletin*, 79(10), pp.1421-1443.
- Cooper, M., Addison, F., Alvarez, R., Hayward, A., Howe, S., Pulham, A. J. & Taborda, A., 1995b. Basin development and tectonic history of the Llanos Basin, Colombia. In: Tankard, A. J., Suarez, R., Welsink, H.J., ed. *Petroleum basin in South America: American Association of Petroleum Geologists Memoir* 62. pp.659-665.
- Cornford, C., Christie, O., Endresen, U., Jensen, P. & Myhr, M. B., 1988. Source rock and seep oil maturity in Dorest, Southern England. *Organic Geochemistry*, 13(1-3), pp.399-409.
- Cortes, J. E., Rincon, J. M., Jaramillo, J. M., Philp, R. P. & Allen, J., 2010. Biomarkers and compound-specific stable carbon isotope of n-alkanes in crude oils from Eastern Llanos Basin, Colombia. *Journal of South American Earth Science*, 29(2), pp.198-213.
- Costanzo-Alvarez, V., Aldana, M., Aristeguieta, O., Marcano, M. C. & Aconcha, E., 2000. Study of magnetic contrasts in the Guafita oil field (south-western Venezuela). *Physics and Chemistry of the Earth*, 25(5), pp.437-445.
- Costanzo-Alvarez, V., Aldana, M., Diaz, M., Bayona, G. & Ayala, C., 2006. Hydrocarbon-induced magnetic contrasts in some Venezuelan and Colombian oil wells. *Earth Planets Space*, 58, pp.1401-1410.
- Davidson, J. 1991. Geology and prospectivity of Buton Island, S.E. Sulawesi, Indonesia. In: Indonesian Petroleum Association. Proceedings of the 20th Annual Convention, Jakarta, 209-233.
- Day, R., Fuller, M. & Schmidt, V. A., 1977. Hysteresis properties of titanomagnetites - grain size and compositional dependence. *Physics of the Earth and Planetary Interiors*, 13(4), pp.260-267.
- Dengo, C. A. & Coy, M. C., 1993. Structure of the Eastern Cordillera of Colombia: Implications for Trap Styles and Regional Tectonics. *American Association of Petroleum Geologists Bulletin*, 77, pp.1313-1337.
- Díaz, M., Aldana, M., Costanzo-Alvarez, V., Silva, P. & Perez, A., 2000. EPR and magnetic susceptibility studies in well samples from some Venezuelan oil fields. *Physics and Chemistry of the Earth*, 25(5), pp.447-453.
- Díaz, M., Aldana, M., Jiménez, S., Sequera, P. & Costanzo-Alvarez, V., 2006. EPR and EOM studies in well samples from some Venezuelan oil fields: correlation with magnetic authigenesis. *Revista Mexicana de Física*, 52(3), pp.63-65.
- Didyk, B. M., Simoneit, B. R. T., Crassell, S. C. & Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature*, 272, pp.216-222.
- Donovan, T. J., Forgey, R. L. & Roberts, A. A., 1979. Aeromagnetic detection of diagenetic magnetite over oil-fields. *American Association of Petroleum Geologists Bulletin*, 63(2), pp.245-248.
- Doust, H. & Noble, R. A., 2008. Petroleum systems of Indonesia. *Marine and Petroleum Geology*, 25(2), pp.103-129.
- Dunlop, D. J., 1973. Theory of the magnetic viscosity of lunar and terrestrial rocks. *Reviews of Geophysics and Space Physics*, 11, pp.855-901.
- Dunlop, D. J. & Özdemir, O., 1997. *Rock Magnetism: Fundamentals and Frontiers*. Cambridge: Cambridge University Press.
- Dzou, L. I., Holba, A. G., Ramón, J. C., Moldowan, J. M. & Sinniker, D., 1999. Application of new diterpane biomarkers to source, biodegradation and mixing effects on Central Llanos Basin oils, Colombia. *Organic Geochemistry*, 30(7), pp.515-534.
- Elmore, R., Engel, M., Crawford, L., Nick, K., Imbus, S. & Sofer, S., 1987. Evidence for a relationship between hydrocarbons and authigenic magnetite. *Nature*, 325, pp.428-430.

- Elmore, R., Kelley, J., Evans, M. & Lewchuk, M. T., 2001. Remagnetization and orogenic fluids: testing the hypothesis in the central Appalachians. *Geophysical Journal International*, 144, pp.568-576.
- Elmore, R. D. & Crawford, L., 1990. Remanence in authigenic magnetite - testing the hydrocarbon - magnetite hypothesis. *Journal of Geophysical Research*, 95(B4), pp.4539-4549.
- Elmore, R. D., Imbus, S. W., Engel, M. H. & Fruit, D., 1993. Hydrocarbons and magnetization in magnetite. In: Aissaoui, D. M., McNeill, D. F. & Hurley, N. F. eds. *Applications of Paleomagnetism to Sedimentary Geology*. Society of Economic Paleontologists and Mineralogists Special Publication. 49. pp.181-191.
- Elmore, R. D. & Leach, M. C., 1990. Remagnetization of the Rush Springs Formation, Cement, Oklahoma: Implications for dating hydrocarbon migration and aeromagnetic exploration. *Geology*, 18, pp.124-127.
- England, W. A., 1994. Secondary migration and accumulation of hydrocarbons. In: Magoon, L. B. & Dow, W. G. eds. *The Petroleum System-From Source to Trap*. American Association of Petroleum Geologists Memoir 60, Tulsa, pp.211-217.
- England, W. A., Mackenzie, A. S., Mann, D. M. & Quigley, T. M., 1987. The movement and entrapment of petroleum fluids in the subsurface. *Journal of Geological Society London*, 144, pp.327-347.
- Ensminger, A., Albrecht, P., Ourisson, G. & Tissot, B., 1977. Evolution of polycyclic alkanes under the effect of burial (Early Toarcian Shales, Paris Basin). In: Campos, R. & Goni, J. eds. *Advances in Organic Geochemistry 1975*. Madrid: Enadimsa. pp.45-52.
- Evans, M. A. & Elmore, R. D., 2006. Fluid control of localized mineral domains in limestone pressure solution structures. *Journal of Structural Geology*, 28(2), pp.284-301.
- Evans, M. A., Elmore, R. D. & Lewchuk, M. T., 2000. Examining the relationship between remagnetization and orogenic fluids: central Appalachians. *Journal of Geochemical Exploration*, 69-70, pp.139-142.
- Evans, M. E. & Heller, F., 2003. *Environmental magnetism: principles and applications of enviromagnetics*. Amsterdam: Academic Press.
- Faivre, D. & Schuler, D., 2008. Magnetotactic bacteria and magnetosomes. *Chemistry Review*, 108, pp.4875-4898.
- Fan, P., King, J. D. & Claypool, G. E., 1987. Characteristics of biomarker compounds in Chinese crude oils. In: Kumar, R. K., Dwivedi, P., Banerjee, V. & Gupta, V. eds. *Petroleum Geochemistry and Exploration in the Afro-Asian Region*. Rotterdam: Balkema. pp.197-202.
- Farrimond, P., Eglinton, G. & Brassell, S. C., 1989. The Cenomanian/Turonian anoxic event in Europe: an organic geochemical study. *Marine and Petroleum Geology*, 7(1), pp.75-89.
- Fisher, R. A., 1953. Dispersion on a sphere. *Proceedings of the Royal Society London, Series A*(217), pp.295-305.
- Fletcher, K. J., 2003. The Central Brae Field, Blocks 16/07a, 16/07b, UK North Sea. In: Gluyas, J. G. & Hitchens, H. M. eds. *United Kingdom Oil and Gas Fields, Commemorative Millennium Volume*. Geological Society London Memoirs 20. pp.183-190.
- Foote, R. S., 1987. Correlations of borehole rock magnetic properties with oil and gas producing areas. *Association of Petroleum Geochemical Explorationists Bulletin*, 3(1), pp.114-134.
- Foote, R. S., 1996. Relationship of near-surface magnetic anomalies to oil- and gas-producing areas. In: Schumacher, D. & Abrams, M. A. eds. *Hydrocarbon Migration and Its near-Surface Expression*. American Association of Petroleum Geologists Memoirs. 66. pp.111-126.
- Frankel, R. B. & Blakemore, R. P., 1980. Navigational Compass in Magnetic Bacteria. *Journal of Magnetism and Magnetic Materials*, 15-18, pp.1562-1564.
- Frederichs, T., Dobeneck, T., Bleil, U. & Dekkers, M. J., 2003. Towards the identification of siderite, rhodochrosite, and vivianite in sediments by their low-temperature magnetic properties. *Physics and Chemistry of the Earth*, 28, pp.669-679.
- Fredrickson, J. K., McKinley, J. P., Bjornstad, B. N., Long, P. E., Ringelberg, D. B., White, D. C., Krumholz, L. R., Suflita, J. M., Colwell, F. S., Lehman, R. M., Phelps, T. J. & Onsott, T. C.,

1997. Pore-size constraints on the activity and survival of subsurface bacteria in a Late Cretaceous shale-sandstone sequence, northwestern New Mexico. *Geomicrobiology Journal*, 14, pp.183-202.
- Fritsche, W. & Hofrichter, M., 2008. Aerobic Degradation by Microorganisms. In: Rehm, H. J. & Reed, G. eds. *Biotechnology: Environmental processes II*. Second ed. Weinheim, Germany: Wiley-VCH Verlag GmbH. 11b. pp.144-167.
- Gapeyev, A. K. & Tsel'movich, V. A., 1988. *Stages of oxidation of titanomagnetite grains in igneous rocks (in Russian)*. Viniti N, Moscow.
- Garner, N. & Cioppa, M. T., 2006. Late Paleozoic remagnetization of the Trenton Formation in Ordovician petroleum reservoirs of southwestern Ontario. *Journal of Geochemical Exploration*, 89(1-3), pp.119-123.
- Gautier, D. L., 2005. Kimmeridgian shales total petroleum system of the North Sea Graben province. *U.S. Geological Survey Bulletin*, 2204-C, pp.1-24.
- Gay, S., 1992. Epigenetic versus syngenetic magnetite as a cause of magnetic anomalies. *Geophysics*, 57(1), pp.60-68.
- Gil, P. P., Pesquera, A. & Velasco, F., 1992. X-ray diffraction, infrared and Mossbauer studies of Fe-rich carbonates. *European Journal of Mineralogy*, 4, pp.521-526.
- Gonçalves, F. T. T., Mora, G. A., Córdoba, F., Kairuz, E. C. & Giraldo, B. N., 2002. Petroleum generation and migration in the Putumayo Basin, Colombia: insights from an organic geochemistry and basin modeling study in the foothills. *Marine and Petroleum Geology* 19, pp.711-725.
- Gonzalez, F., Aldana, M., Costanzo-Alvarez, V., Diaz, M. & Romero, I., 2002. An integrated rock magnetic and EPR study in soil samples from a hydrocarbon prospective area. *Physics and Chemistry of the Earth*, 27(25-31), pp.1311-1317.
- Greenwood, N. N. & Gibb, T. C., 1971. *Mössbauer Spectroscopy*. Chapman and Hall.
- Guzman, O., Costanzo-Alvarez, V., Aldana, M. & Diaz, M., 2011. Study of magnetic contrasts applied to hydrocarbon exploration in the Maturin Sub-Basin (eastern Venezuela). *Studia Geophysica et Geodaetica*, 55(2), pp.359-376.
- Hamilton, W., 1979. Tectonics of the Indonesian Region. *U.S. Geological Survey Professional Paper* 1078.
- Hansel, C. M., Benner, S. G., Neiss, J., Dohnalkova, A., Kukkadapu, R. K. & Fendorf, S., 2003. Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow. *Geochimica et Cosmochimica Acta*, 67(16), pp.2977-2992.
- Head, I. M., Jones, M. & Larter, S. R., 2003. Biological activity in the deep subsurface and the origin of heavy oil. *Nature*, 426, pp.344-352.
- Heider, F. & Dunlop, D. J., 1987. Two types of chemical remanent magnetization during the oxidation of magnetite. *Physics of the Earth and Planetary Interiors*, 46, pp.24-45.
- Heider, J., Spormann, A. M., Beller, H. R. & Widdel, F., 1999. Anaerobic bacterial metabolism of hydrocarbons. *Fems Microbiology Reviews*, 22(5), pp.459-473.
- Hesselbo, S. P., 1998. Basal Wealden of Mupe Bay: a new model. In: Underhill, J. R. ed. *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society London Special Publications. 133. pp.349-353.
- Hetzel, W. 1936. Verslag van het onderzoek naar het voorkomen van asfaltgesteenten op het eiland Boeton. *Verslag en Mededelingen betreffende Indies Delfstofkunde en hare toepassingen*. Dienst van den Mijnbouw in Nederlandsch-Indi. Batavia.
- Huang, W. Y. & Meinschein, W. G., 1979. Sterols as ecological indicators. *Geochimica et Cosmochimica Acta*, 43(5), pp.739-745.
- Huang, Y., Street-Perrott, F. A., Perrott, F. A., Metzger, P. & Eglinton, G., 1999. Glacial-interglacial environmental changes inferred from the molecular and compound-specific $\delta^{13}\text{C}$ analyses of sediments from Sacred Lake, Mt Kenya. *Geochimica et Cosmochimica Acta* 63(9), pp.1383-1404.

- Irving, E. & Irving, G. A., 1982. Apparent polar wander paths Carboniferous through Cenozoic and the assembly of Gondwana. *Geophysical Surveys*, 5(2), pp.141-188.
- Isaksen, G. H. & Bohacs, K. M., 1995. Geological controls on source rock geochemistry through relative sea level; Triassic, Barents Sea. In: Katz, B. J. ed. *Petroleum Source Rocks*. New York: Springer. pp.25-50.
- Ivakhnenko, O. P. & Potter, D. K., 2004. Magnetic susceptibility of petroleum reservoir fluids. *Physics and Chemistry of the Earth*, 29(13-14), pp.899-907.
- Jacobs, L. S., 1963. Metamagnetism of siderite (FeCO_3). *Journal of Applied Physics*, 34(4), pp.1106-1107.
- Jiles, D., 1991. *Magnetism and Magnetic Materials*. London: Chapman and Hall.
- Karlin, R., Lyle, M. & Heath, G. R., 1987. Authigenic magnetite formation in suboxic marine sediments. *Nature*, 326(6112), pp.490-493.
- Kars, M., Aubourg, C. & Pozzi, J. P., 2011. Low temperature magnetic behaviour near 35 K in unmetamorphosed claystones. *Geophysical Journal International*, 186(3), pp.1029-1035.
- Katz, B., Elmore, R., Cogoini, M. & Ferry, S., 1998. Widespread chemical remagnetization: orogenic fluids or burial diagenesis of clays? *Geology*, 26(7), pp.603-606.
- Kerlogue, A., Cherry, S., Davies, H., Quine, M. & Spotti, G., 1994. The Tiffany and Toni oil fields, Upper Jurassic submarine fan reservoirs, South Viking Graben, UK North Sea. *Petroleum Geoscience*, 1, pp.279-285.
- Kholodov, V. N. & Butuzova, G. Y., 2008. Siderite formation and evolution of sedimentary iron ore deposition in the Earth's history. *Geology of Ore Deposits*, 50(4), pp.338-361.
- Kilgore, B. & Elmore, R. D., 1989. A study of the relationship between hydrocarbon migration and the precipitation of authigenic magnetic minerals in the Triassic Chugwater Formation, Southern Montana. *Geological Society of America Bulletin*, 101(10), pp.1280-1288.
- Killops, S. & Killops, V., 2005. Long-term fate of organic matter in the geosphere. In: Killops, S. & Killops, V. eds. *Introduction to Organic Geochemistry*. Second ed. Oxford: Blackwell. pp.117-162.
- Kirkland, D. W. & Evans, R., 1981. Source-rock potential of evaporitic environments. *American Association of Petroleum Geologists Bulletin*, 65, pp.181-190.
- Kirschvink, J. L. & Gould, J. L., 1981. Biogenic magnetite as a basis for magnetic field detection in animals. *Biosystems*, 13(3), pp.181-201.
- Kittel, C., 1949. Physical theory of ferromagnetic domains. *Reviews of Modern Physics*, 21(4), pp.541-583.
- Kittel, C., 1967a. Diamagnetism and paramagnetism. In: Johnson, S. & McFadden, P. eds. *Introduction to Solid State Physics*. 3rd ed. New York: John Wiley & Sons, Inc. pp.297-318.
- Kittel, C., 1967b. Ferromagnetism and antiferromagnetism. In: Johnson, S. & McFadden, P. eds. *Introduction to Solid State Physics*. New York: John Wiley & Sons, Inc. pp.321-257.
- Klein, C. & Beukes, N. J., 1989. Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the early Proterozoic transval supergroup, South Africa. *Economic Geology*, 84(7), pp.1733-1774.
- Koptíková, L., Bábek, O., Hladil, J., Kalvoda, J. & Slavík, L., 2010. Stratigraphic significance and resolution of spectral reflectance logs in Lower Devonian carbonates of the Barrandian area, Czech Republic; a correlation with magnetic susceptibility and gamma-ray logs. *Sedimentary Geology*, 225, pp.83-98.
- Krumholz, L. R., 2000. Microbial communities in the deep subsurface. *Hydrogeology Journal*, 8(1), pp.4-10.
- Lake, S. D. & Karner, G. D., 1987. The structure and evolution of the Wessex Basin, Southern England: an example of inversion tectonics. *Tectonophysics*, 137(1-4), pp.347-178.
- Larter, S. R., Wilhelms, A., Head, I. M., Koopmans, M., Alplin, A., Di Primio, R., Zwach, C., Erdmann, M. & Telnaes, H., 2003. The controls on the composition of biodegraded oils in the deep surface – part 1: biodegradation rates in petroleum reservoirs. *Organic Geochemistry*, 34, pp.601-613.

- Leblanc, G. & Morris, W. A., 1999. Aeromagnetics of southern Alberta within areas of hydrocarbon accumulation. *Bulletin of Canadian Petroleum Geology*, 47(4), pp.439-454.
- Lees, G. M. & Cox, P. T., 1937. The geological basis of the search for oil in Great Britain by the D'Arcy Exploration Co. Ltd. *Journal of the Geological Society*, 93, pp.156-190.
- Lijmbach, G. W. 1975. On the origin of petroleum In: Applied Science Publishers. Proceedings of the 9th World Petroleum Congress, London, 357-369.
- Liu, Q., Chan, L., Liu, Q., Li, H., Wang, F., Zhang, S. X., Xia, X. H. & Cheng, T. J., 2004. Relationship between magnetic anomalies and hydrocarbon microseepage above the Jingbian gas field, Ordos basin, China. *American Association of Petroleum Geologists Bulletin*, 88(2), pp.241-251.
- Liu, Q. S., Chan, L. S., Yang, T., Xia, X. H. & Cheng, T. J., 2006. Magnetic enhancement caused by hydrocarbon migration in the Mawangmiao Oil Field, Jiangnan Basin, China. *Journal of Petroleum Science and Engineering*, 53(1-2), pp.25-33.
- Liu, Q. S., Cheng, T. J. & Liu, S. G., 1998a. Comprehensive evaluation of mechanism of "chimney effect" using principles of magnetism, geochemistry and mineralogy. *Chinese Science Bulletin*, 43(9), pp.743-748.
- Liu, Q. S., Liu, S. G., Qu, Z. & Hou, W. G., 1998b. Magnetic and mineralogical characteristics of hydrocarbon microseepage above oil/gas reservoirs of the Tuoko region, northern Tarim Basin, China. *Science China D*, 41(2), pp.121-129.
- Loope, D. B., Kettler, R. M., Weber, K. A., Hinrichs, N. L. & Burgess, D. T., 2012. Rinded iron-oxide concretions: hallmarks of altered siderite masses of both early and late diagenetic origin. *Sedimentology*, 59, pp.1769-1781.
- Lovley, D., Stolz, J., Nord Jr, G. L. & Phillips, E. J. P., 1987. Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism. *Nature*, 330, pp.252-254.
- Lovley, D. R., 1990. Magnetite formation during microbial dissimilatory iron reduction. *Iron Biominerals*, pp.1-16.
- Machel, H., 1995. Magnetic mineral assemblages and magnetic contrasts in diagenetic environments—with implications for studies of palaeomagnetism, hydrocarbon migration and exploration. In: Turner, P. & Turner, A. eds. *Palaeomagnetic Applications in Hydrocarbon Exploration*. Geological Society London Special Publication. 98. pp.9-29.
- Machel, H., 1996. Magnetic contrasts as a result of hydrocarbon seepage and migration. In: Schumacher, D. & Abrams, M. A. eds. *Hydrocarbon migration and its near-surface expression*. American Association of Petroleum Geologists Memoirs. 66. pp.99-109.
- Machel, H. & Burton, E. A., 1991. Chemical and microbial processes causing anomalous magnetization in environments affected by hydrocarbon seepage. *Geophysics*, 56(5), pp.598-605.
- Mackenzie, A. S., Disko, U. & Roullkotter, J., 1983. Determination of hydrocarbon distributions in oils and sediment extracts by gas chromatography-high resolution mass spectrometry. *Organic Geochemistry*, 5, pp.57-63.
- Mackenzie, A. S., Leythaeuser, D., Mouller, P., Quigley, T. M. & Radke, M., 1988. The movement of hydrocarbons in shales. *Nature*, 331, pp.63-65.
- Mackenzie, A. S., Patience, R. L., Maxwell, J. R., Vandenbroucke, M. & Durand, B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin France - I. Changes in the configuration of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochimica et Cosmochimica Acta*, 44, pp.1709-1721.
- Mackenzie, A. S. & Quigley, T. M., 1988. Principles of geochemical prospect appraisal. *American Association of Petroleum Geologists Bulletin*, 72, pp.399-415.
- Matthews, A., 1976. Magnetite formation by the reduction of hematite with iron under hydrothermal conditions. *American Mineralogist*, 61, pp.927-932.
- McCabe, C. & Elmore, R. D., 1989. The occurrence and origin of late Paleozoic remagnetization in the sedimentary rocks of North America. *Reviews of Geophysics*, 27(4), pp.471-194.

- McCabe, C., Jackson, M. & Saffer, B., 1989. Regional patterns of magnetite authigenesis in the Appalachian basin: Implications for the mechanism of Late Palaeozoic remagnetisation. *Journal of Geophysical Research*, 94(B8), pp.10,429-10,443.
- McCabe, C., Sassen, R. & Saffer, B., 1987. Occurrence of secondary magnetite within biodegraded oil. *Geology*, 15(1), pp.7-10.
- McCabe, C., Van der Voo, R. & Ballard, M., 1984. Late Paleozoic remagnetization of the Trenton limestone. *Geophysical Research Letters*, 11(10), pp.979-982.
- McCabe, C., Van der Voo, R., Wilkinson, B. H. & Devaney, K., 1985. A middle/late Silurian paleomagnetic pole from limestone reefs of the wabash formation, Indiana, USA. *Journal of Geophysical Research*, 90(B4), pp.2959-2965.
- McCabe, C., Vandervoo, R., Peacor, D. R., Scotese, C. R. & Freeman, R., 1983. Diagenetic magnetite carries ancient yet secondary remanence in some Palaeozoic sedimentary carbonates. *Geology*, 11(4), pp.221-223.
- McKirdy, D. M., Aldridge, A. K. & Ipma, P. J. M., 1983. A geochemical comparison of some crude oils from pre-Ordovician carbonate rocks. In: Bjoroy, M., Albrecht, C., Cornford, C., de Grast, K., Erlington, G., Galinov, E., Leythueuser, D., Pelet, R., Rullkotter, J. & Socers, G. eds. *Advances in Organic Geochemistry*. Chichester: John Wiley & Sons. pp.99-107.
- McKirdy, D. M., Kantsler, A. J., Emmett, J. K. & Aldridge, A. K., 1984. Hydrocarbon genesis and organic facies in Cambrian carbonates of the Eastern Officer Basin, South Australia. In: Palacas, J. G. ed. *Petroleum Geochemistry and Source Rock potential of Carbonate Rocks*. Tulsa, OK: American Association of Petroleum Geologists Geology. pp.13-31.
- Mello, M. R., Telnaes, N., Gaglianone, P. C., Chicarelli, M. I., Brassell, S. C. & Maxwell, J. R., 1987. Organic geochemical characterization of depositional palaeoenvironments of source rocks and oils in Brazilian marginal basins. *Organic Geochemistry*, 13, pp.31-45.
- Miles, J. A., Downes, C. J. & Cook, S. E., 1993. The fossil oil seep in Mupe Bay, Dorset: a myth investigated. *Marine and Petroleum Geology*, 10, pp.58-70.
- Moldowan, J. M., Dahl, J., Huizinga, B. J., Fago, F. J., Hickey, L. J., Peakman, T. M. & Taylor, D. W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. *Science*, 265(5173), pp.768-771.
- Moldowan, J. M., Seifert, W. K. & Gallegos, E. J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rock. *American Association of Petroleum Geologists Bulletin*, 69, pp.1255-1268.
- Moldowan, J. M., Sundararaman, P. & Schoell, M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of S. W. Germany. *Organic Geochemistry*, 10, pp.915-926.
- Mora, A., Parra, M., Strecker, M., Kammer, A., Dimaté, C. & Rodríguez, F., 2006. Cenozoic contractional reactivation of Mesozoic extensional structures in the Eastern Cordillera of Colombia. *Tectonics*, 25(TC2010), pp.1-19.
- Morin, J., 1950. Magnetic susceptibility of α -Fe₂O₃ and Fe₂O₃ added titanium. *Physics Review*, 78, pp.819-820.
- Mossop, G. D., 1980. Geology of the Athabasca oil sands. *Science*, 207, pp.145-152.
- Murray, A. P., Summons, R. E., Boreham, C. J. & Dowling, L. M., 1994. Biomarker and n-alkane isotope profiles for tertiary oils: relationship to source rock depositional setting. *Organic Geochemistry*, 22, pp.521-542.
- Muxworthy, A. R. & McClelland, E., 2000. Review of the low-temperature magnetic properties of magnetite from a rock magnetic perspective. *Geophysical Journal International*, 140(1), pp.101-114.
- Néel, L., 1949. Théorie du traînage magnétique des ferromagnétiques en grains fins avec applications aux terres cuites. *Annales de Géophysique*, 5, pp.99-136.
- Néel, L., 1955. Some theoretical aspects of rock magnetism. *Advanced Physics*, 4, pp.191-243.

- O'Brien, V. J., Moreland, K. M., Elmore, R. D., Engel, M. H. & Evans, M. A., 2007. Origin of orogenic remagnetizations in Mississippian carbonates, Sawtooth Range, Montana. *Journal of Geophysical Research*, 112(B06103), pp.1-19.
- Obermajer, M., Osadetz, K., Fowler, M., Li, M. & Snowdon, L. R., 2004. Variable alteration in heavy crude oils of west-central Saskatchewan, Canada. *Organic Geochemistry*, 35, pp.469-491.
- Oliver, J., 1986. Fluids expelled tectonically from orogenic belts: Their role in hydrocarbon migration and other geologic phenomena. *Geology*, 14, pp.99-102.
- Osypov, K., Nicholas, D., Woodward, M., Zdraveva, O., Qiao, F., Yarman, E., Vyas, M., Yang, Y., Liu, Y. & vanova, N. 2011. From quantifying seismic uncertainty to assessing E&P risks and the value of information. *SEG Annual Meeting*. San Antonio, Texas: Society of Exploration Geophysicists.
- Özdemir, Ö., Xu, S. & Dunlop, D. J., 1995. Closure domains in magnetite. *Journal Geophysical Research*, 100(B2), pp.2193-2209.
- Palmer, S. E., 1993. Effect of biodegradation and water washing on crude oil composition. In: Engel, M. H. & Macko, S. A. eds. *Organic Geochemistry*. New York: Plenum Press. pp.511-533.
- Palmer, S. E. & Russel, J. A. 1988. The five oil families of the Llanos basin. III Simposio Bolivariano de Exploracion Petrolera en las Cuencas Subandinas, Caracas, Colombia, 724-754.
- Parfitt, M. A. & Farrimond, P., 1998. The Mupe Bay oil seep: a detailed organic geochemical study of a controversial outcrop. In: Underhill, J. R. ed. *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society London Special Publications. 133.
- Parkes, J. & Maxwell, J. R., 1993. Some like it hot (and oily). *Nature*, 365, pp.694-695.
- Permanyer, A., Douifi, L., Lahcini, A., Lamontagne, J. & Kister, J., 2002. FTIR and SUVF spectroscopy applied to reservoir compartmentalization: a comparative study with gas chromatography fingerprints results. *Fuel*, 81, pp.861-866.
- Permanyer, A., Rebufa, C. & Kister, J., 2007. Reservoir compartmentalization assessment by using FTIR spectroscopy. *Journal of Petroleum Science and Engineering*, 58, pp.464-471.
- Peters, K. E., Fraser, T. H., Amris, W., Rustanto, B. & Hermanto, E., 1999. Geochemistry of crude oils from eastern Indonesia. *American Association of Petroleum Geologists Bulletin*, 83(12), pp.1927-1942.
- Peters, K. E., Walters, C. C. & Moldowan, J. M., 2005a. Biodegradation parameters. In: Peters, K. E., Walters, C. C. & Moldowan, J. M. eds. *The Biomarker Guide II. Biomarkers and Isotopes in Petroleum Systems and Earth History*. Cambridge: Cambridge University Press. 2. pp.645-705.
- Peters, K. E., Walters, C. C. & Moldowan, J. M., 2005b. Maturity-related biomarker parameters. In: Peters, K. E., Walters, C. C. & Moldowan, J. M. eds. *The Biomarker Guide II. Biomarkers and Isotopes in Petroleum Systems and Earth History*. Cambridge: Cambridge University Press. 2. pp.608-635.
- Peters, K. E., Walters, C. C. & Moldowan, J. M., 2005c. Organic chemistry. In: Peters, K. E., Walters, C. C. & Moldowan, J. M. eds. *The Biomarker Guide I. Biomarkers and Isotopes in the environment and human history*. Cambridge: Cambridge University Press. 1. pp.18-43.
- Peters, K. E., Walters, C. C. & Moldowan, J. M., 2005d. Source- and age-related biomarker parameters. In: Peters, K. E., Walters, C. C. & Moldowan, J. M. eds. *The Biomarker Guide II. Biomarkers and Isotopes in Petroleum Systems and Earth History*. Second ed. Cambridge: Cambridge University Press. 2. pp.483-602.
- Pigram, C. J. & Panggabean, H., 1984. Rifting of the northern margin of the Australian continent and the origin of some micro-continents in Eastern Indonesia. *Tectonophysics*, 107, pp.331-353.

- Price, P. L., O'Sullivan, T. & Alexander, R. 1987. The nature and occurrence of oil in Seram, Indonesia. In: Indonesian Petroleum Association. Proceedings of the Indonesian Petroleum Association Sixteenth Annual Convention, Jakarta, Indonesia, 141-173.
- Ramón, J. C. & Dzou, L. I., 1999. Petroleum geochemistry of Middle Magdalena Valley, Colombia. *Organic Geochemistry*, 30(4), pp.249-266.
- Ramón, J. C., Dzou, L. I., Hughes, W. B. & Holba, A. G., 2001. Evolution of the Cretaceous organic facies in Colombia: implications for oil composition. *Journal of South American Earth Science* 14, pp.31-50.
- Rangel, A., Giraldo, B., Magoon, L., Sarmiento, L., Bartels, H., Mora, C., Córdoba, F., Luna, O. & Reyes, J. 1996. Oil potential of the cretacic megasequence and associated oil families in the Middle Magdalena Valley-Colombia. *Memorias del V Congreso Latinoamericano de Geoquímica Orgánica*, Cancún, México, 105.
- Ranger, M. & Pemberton, S., 1997. Elements of a stratigraphic framework for the McMurray Formation in South Athabasca area, Alberta. *Canadian Society of Petroleum Geologists, Memoir*, 18, pp.263-291.
- Rankey, E. C. & Mitchell, J. C., 2003. That's why it's called interpretation: Impact of horizon uncertainty on seismic attribute analysis. *The Leading Edge*, 22(9), pp.820-828.
- Rathey, R. P., & Hayward, A. B., 1993. Sequence stratigraphy of a failed rift system: the Middle Jurassic to Early Cretaceous basin evolution of the Central and Northern North Sea. In: Parker, J. R. ed. *Petroleum geology of Northwest Europe: Proceedings of the 4th Conference*. Geological Society, London. pp.215-249.
- Reynolds, R., Fishman, N. S. & Hudson, M. R., 1991. Sources of aeromagnetic anomalies over Cement oil field (Oklahoma), Simpson oil field (Alaska), and the Wyoming-Idaho-Utah thrust belt. *Geophysics*, 56(5), pp.606-617.
- Reynolds, R., Fishman, N. S., Wanty, R. B. & Goldhaber, M. B., 1990a. Iron sulfide minerals at Cement oil-field, Oklahoma-implications for magnetic detection of oil-fields. *Geological Society of America Bulletin*, 102(3), pp.368-380.
- Reynolds, R. & Goldhaber, M., 1993. Sulfidization and magnetization above hydrocarbon reservoirs. In: Aissaoui, D. M., McNeill, D. F. & Hurley, N. F. eds. *Applications of Paleomagnetism to Sedimentary Geology*. Society of Economic Paleontologists and Mineralogists Special Publication. 49. pp.167-179.
- Reynolds, R., Webring, M., Grauch, V. J. S. & Tuttle, M., 1990b. Magnetic forward models of Cement oil field, Oklahoma, based on rock magnetic, geochemical, and petrologic constraints. *Geophysics*, 55(3), pp.344-353.
- Reynolds, R. L., Fishman, N. S., Hudson, N. R., Karachewski, J. A. & Goldhaber, M. B., 1985. Magnetic minerals and hydrocarbon migration: Evidence from Cement (Oklahoma), North Slope (Alaska), and the Wyhoming-Adaho-Utah thrust belt. *EOS (American Geophysical Union Transaction)*, 66(867).
- Riediger, C. L., Fowler, M. G., Snowdon, L. R., MacDonald, R. & Sherwin, M. D., 1999. Origin and alteration of Lower Cretaceous Mannville Group I oils from the Provost oil field, east Central Alberta, Canada. *The Bulletin of Canadian Petroleum Geology*, 47, pp.43-62.
- Rijal, M. L., Appel, E., Petrovsky, E. & Blaha, U., 2010. Change of magnetic properties due to fluctuations of hydrocarbon contaminated groundwater in unconsolidated sediments. *Environmental Pollution*, 158(5), pp.1756-1762.
- Rijal, M. L., Porsch, K., Appel, E. & Kappler, A., 2012. Magnetic signature of hydrocarbon-contaminated soils and sediments at the former oil field Hanigsen, Germany. *Studia Geophysica et Geodaetica*, 56, pp.889-908.
- Roberts, A., 1995. Magnetic properties of sedimentary greigite (Fe₃S₄). *Earth and Planetary Science Letters*, 134(3-4), pp.227-236.
- Roeder, D. & Chamberlain, R. L., 1995. Eastern Cordillera of Colombia: Jurassic-Neogene crustal evolution. In: Tankard, A. J., Suarez, R. & Welsink, H. J. eds. *Petroleum Basins in South America*. American Association of Petroleum Geologists Memoir. 62. pp.633-645.

- Ross, A. S., Farrimond, P., Erdmann, M. & Larter, S. R., 2010. Geochemical compositional gradients in a mixed oil reservoir indicative of ongoing biodegradation. *Organic Geochemistry*, 41, pp.307-320.
- Rubinstein, I., Sieskind, O. & Albrecht, P., 1975. Rearranged sterenes in a shale: occurrence and simulated formation. *Journal of the Chemical Society Perkin Transactions I*, pp.1833-1836.
- Rubinstein, I. & Strausz, O. P., 1977. The origin of the oil sand bitumens of Alberta: a chemical and a microbiological simulation study. *Geochimica et Cosmochimica Acta*, 41(9), pp.1341-1353.
- Rueter, P., Rabus, R., Wilkes, H., Aeckersberg, F., Rainey, F. A., Jannasch, H. W. & Widdel, F., 1994. Anaerobic oxidation of hydrocarbons in crude oil by new types of sulphate-reducing bacteria. *Nature*, 372, pp.455-458.
- Saffer, B. & McCabe, C., 1992. Further studies of carbonate remagnetisation in the Northern Appalachian basin. *Journal of Geophysical Research*, 97(B4), pp.4331-4348.
- Sakaguchi, T., Burgess, J. G. & Matsunaga, T., 1993. Magnetite formation by a sulfate-reducing bacterium. *Nature*, 365, pp.47-49.
- Sánchez, C. & Permanyer, A., 2006. Origin and alteration of oils and oil seeps from the Sinú-San Jacinto Basin, Colombia. *Organic Geochemistry*, 37, pp.1831-1845.
- Sarmiento, L. F. & Rangel, A., 2004. Petroleum systems of the Upper Magdalena Valley, Colombia. *Marine and Petroleum Geology*, 21, pp.373-391.
- Sassen, R., McCabe, C., Kyle, J. R. & Chinn, E. W., 1989. Deposition of magnetic pyrrhotite during alteration of crude oil and reduction of sulfate. *Organic Geochemistry*, 14, pp.381-392.
- Saunders, D. F., Burson, K. R. & Thompson, C. K., 1991. Observed relation of soil magnetic susceptibility and soil gas hydrocarbon analyses to subsurface hydrocarbon accumulations. *American Association of Petroleum Geologists Bulletin*, 75(3), pp.389-408.
- Sawlowicz, Z., 1993. Pyrite framboids and their development: a new conceptual mechanism. *Geologische Rundschau*, 82, pp.148-156.
- Scalan, R. S. & Smith, J. E., 1970. An improved measure of the odd-even predominance in the normal alkanes of sediment extracts and petroleum. *Geochimica et Cosmochimica Acta*, 34, pp.611-620.
- Schiefelbein, C. & Cameron, N., 1997. Sumatra/Java oil families. In: Fraser, A. J., Matthews, S. J. & Murphy, R. W. eds. *Petroleum Geology of Southeast Asia*. Geological Society London Special Publications. 126. pp.143-126.
- Schowalter, T. T., 1979. Mechanisms of secondary hydrocarbon migration and entrapment. *American Association of Petroleum Geologists Bulletin*, 63(5), pp.723-760.
- Scotese, C., Van der Voo, R. & McCabe, C., 1982. Paleomagnetism of the upper Silurian and lower Devonian carbonates of New York State: evidence for secondary magnetizations residing in magnetite. *Physics of the Earth and Planetary Interiors*, 30, pp.385-395.
- Seifert, W. K. & Moldowan, J. M., 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. *Physics and Chemistry of the Earth*, 12, pp.229-237.
- Selley, R. C., 1992. Petroleum seepages and impregnations in Great Britain. *Marine and Petroleum Geology*, 9, pp.226-244.
- Selley, R. C., 1997. *Elements of Petroleum Geology*. New York: Academic Press.
- Selley, R. C. & Stoneley, R., 1987. Petroleum habitat in South Dorset. In: Brooks, J. & Glennie, K. W. eds. *Petroleum geology of North West Europe*. London: Graham and Trotman. pp.139-148.
- Sephton, M. A. 1992. *Migrated hydrocarbons in the Wessex basin*. MSc, University of Newcastle Upon Tyne.
- Smith, R. B. & Silver, E. A., 1991. Geology of Miocene collision complex, Buton, eastern Indonesia. *Geological Society of America Bulletin*, 103(5), pp.660-678.
- Sparks, N. H. C., Mann, S., Bazylinski, D. A., Lovely, D. R., Jannasch, H. W. & Frankel, R. B., 1990. Structure and morphology of magnetite anaerobically-produced by a marine

- magnetotactic bacterium and a dissimilatory iron-reducing bacterium. *Earth and Planetary Science Letters*, 98(1), pp.14-22.
- Springer, M. V., Garcia, D. F., Conçalves, F. T. T., Landau, L. & Azevedo, D. A., 2010. Diamondoid and biomarker characterisation of oils from the Llanos Orientales Basin, Colombia. *Organic Geochemistry*, 41, pp.1013-1018.
- Stainforth, J. G. & Reinders, J. E. A., 1990. Primary migration of hydrocarbons by diffusion through organic matter networks, and its effect on oil and gas generation. *Organic Geochemistry*, 16(1-3), pp.61-74.
- Stoneley, R. & Selley, R. C. 1986. A Field Guide to the Petroleum Geology of the Wessex Basin. *Department of Geology Imperial College, London*.
- Struijk, A. P. & Green, R. T., 1991. The Brent Field, Block 211/29, UK North Sea. In: Abbotts, I. L. ed. *United Kingdom Oil and Gas Fields, 25 Years Commemorative Volume*. Geological Society Memoir. 14. pp.63-72.
- Suk, D., Peacor, D. & Van der Voo, R., 1990. Replacement of pyrite framboids by magnetite in limestone and implications for palaeomagnetism. *Nature*, 345, pp.611-613.
- Suk, D., Van der Voo, R., Peacor, D. R. & Lohmann, K. C., 1993. Late Paleozoic remagnetization and its carrier in the Trenton and Black River carbonates from the Michigan basin. *The Journal of Geology*, 101(6), pp.795-808.
- Tauxe, L., with contributions from Butler, R., van der Voo, R. and Banerjee, S., 2010. Fisher Statistics. *Essentials of paleomagnetism*. University of California Press. pp.207-225.
- Ten Haven, H. L., de Leeuw, J. W., Bullkötter, J. & Sinninghe Damste, J. S., 1987. Restricted utility of the pristane/phytane ratio as a paleoenvironmental indicator. *Nature*, 330, pp.641-643.
- Tissot, B., Durand, B., Espitalie, J. & Combaz, A., 1974. Influence of the nature and diagenesis of organic matter in formation of petroleum. *American Association of Petroleum Geologists Bulletin*, 58, pp.499-506.
- Tissot, B. P. & Welte, D. H., 1984. *Petroleum Formation and Occurrence*. Berlin: Springer.
- Todd, S. P., Dunn, M. E. & Barwise, A. J. G., 1997. Characterizing petroleum charge systems in the Tertiary of SE Asia. In: Fraser, A. J., Matthews, S. J. & Murphy, R. W. eds. *Petroleum Geology of Southeast Asia*. Geological Society London Special Publication. 126. pp.25-47.
- Torsvik, T. H., Van der Voo, R., Meert, J. G., Mosar, J. & Walderhaug, H. J., 2001. Reconstructions of the continents around the North Atlantic at about the 60th Parallel. *Earth and Planetary Science Letters*, 187, pp.55-69.
- Underhill, J. R., 2001. Controls on the genesis and prospectivity of Paleogene paleogeomorphic traps, East Shetland Platform, UK North Sea. *Marine and Petroleum Geology*, 18, pp.259-281.
- Underhill, J. R., & Partington, M. A., 1993. Jurassic thermal doming and deflation in the North Sea: implications of the sequence stratigraphic evidence. In: Parker, J.R. ed. *Petroleum geology of Northwest Europe: Proceedings of the 4th Conference*, Geological Society, London. pp.337-345.
- Underhill, J. R. & Paterson, S., 1998. Genesis of tectonic inversion structures: seismic evidence for the development of key structures along the Purbeck-Isle of Wight Disturbance. *Geological Society London*, 155, pp.975-992.
- Underhill, J. R. & Stoneley, R., 1998. Introduction to the development, evolution and petroleum geology of the Wessex Basin. In: Underhill, J. R. ed. *Development, evolution and petroleum geology of the Wessex Basin*. Geological Society London Special Publications. 133. pp.1-18.
- Van der Voo, R., 1993. *Paleomagnetism of the Atlantis, Tethys and Iapetus Oceans*. Cambridge University Press.
- Van Kaam-Peters, H. M. E., Köster, J., van der Gaast, S. J., Dekker, M., de Leeuw, J. W. & Damsté, S., 1998. The effect of clay minerals on diasterane/sterane ratios. *Geochimica et Cosmochimica Acta*, 62, pp.2923-2929.

- Vandenbergh, R. E., Barrero, C. A., da Costa, G. M., Van San, E. & De Grave, E., 2000. Mossbauer characterization of iron oxides and (oxy)hydroxides: the present state of the art. *Hyperfine Interactions*, 126, pp.247-259.
- Vandenbergh, R. E., Van San, E. & De Grave, E., 2001. About the Morin transition in hematite in relation with particle size and aluminium substitution. *Czechoslovak Journal of Physics*, 51(7), pp.663-675.
- Venkatachalapathy, R., Veerasingam, S., Basavaiah, N. & Ramkumar, T., 2010. Comparison between petroleum hydrocarbon concentrations and magnetic properties in Chennai coastal sediments, Bay of Bengal, India. *Marine and Petroleum Geology*, 27, pp.1927-1935.
- Venkatachalapathy, R., Veerasingam, S., Basavaiah, N., Ramkumar, T. & Deenadayalan, K., 2011. Environmental magnetic and petroleum hydrocarbons records in sediment cores from the north east coast of Tamilnadu, Bay of Bengal, India. *Marine Pollution Bulletin*, 62, pp.681-690.
- Villamil, T., 2003. Regional hydrocarbon systems of Colombia and western Venezuela: Their origin, potential, and exploration. In: Bartolini, C., Buffler, R. T. & Blickwede, J. eds. *The Circum-Gulf of Mexico and the Caribbean: Hydrocarbon habitats, basin formation, and plate tectonics*. American Association of Petroleum Geologists Memoir. 79. pp.697-734.
- Wakeham, S. G., 1990. Algal and bacterial hydrocarbons in particular matter and interfacial sediment of the Cariaco Trench. *Geochimica et Cosmochimica Acta*, 54, pp.1325-1336.
- Walton, D., 1983. Viscous magnetization. *Nature*, 305, pp.616-619.
- Walz, F., 2002. The Verwey Transition - a Topical Review. *Journal of Physics*, 14, pp.R285-R340.
- Waples, D. W. & Machihara, T., 1990. Application of sterane and triterpane biomarkers in petroleum exploration. *Bulletin of Canadian Petroleum Geology*, 38, pp.357-380.
- Watson, D. F., Hindle, A. D. & Farrimond, P., 2000. Organic geochemistry of petroleum seepages within the Jurassic Bencliff Grit, Osmington Mills, Dorset, UK. *Petroleum Geoscience*, 6(4), pp.289-297.
- Wechsler, B. A., Lindsley, D. H. & Prewitt, C. T., 1984. Crystal structure and cation distribution in titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$). *American Mineralogist*, 69, pp.754-770.
- Wenger, L. M., Davis, C. L. & Isaksen, G. H., 2001. Multiple controls on petroleum biodegradation and impact on oil quality. *Society of Petroleum Engineers-Reservoir Evaluation Engineering*, 5, pp.375-383.
- Wenger, L. M. & Isaksen, H. G., 2002. Control of hydrocarbon seepage intensity on level of biodegradation in sea bottom sediments. *Organic Geochemistry*, 33, pp.1277-1292.
- Whitman, W. B., Coleman, D. C. & Wiebe, W. J. 1998. Prokaryotes: the unseen majority. National Academy of Sciences of the United States of America 6578-6583.
- Wimbledon, W. A., Allen, P. & Fleet, A. J., 1996. Penecontemporaneous oil-seep in the Wealden (early Cretaceous) at Mupe Bay, Dorset, U.K. *Sedimentary Geology*, 102, pp.213-220.
- Wirjosujono, S. & Hainim, J. A. 1975. Cenozoic sedimentation in Buton Island. Regional Conference of Geology and Mineral Resources, S.E. Asia, Jakarta, 109-119.
- Wisniowiecki, M., Van der Voo, R., McCabe, C. & Kelly, W. C., 1983. A Pennsylvanian paleomagnetic pole from the mineralized Late Cambrian Bonnetterre Formation, southeast Missouri. *Journal of Geophysical Research*, 88(B8), pp.6540-6548.
- Zhang, C. L., Vali, H., Romanek, C. S., Phelps, T. J. & Liu, S. V., 1998. Formation of single-domain magnetite by a thermophilic bacterium. *American Mineralogist*, 83(11-12), pp.1409-1418.
- Zumbege, J. E., 1984. Source rocks of the La Luna Formation (Upper Cretaceous) in the Middle Magdalena Valley, Colombia. In: Palacas, J. C. ed. *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*. American Association of Petroleum Geologists. 18. p.127.

Appendix

Appendix 1: Organic geochemistry **257**

- 1.1 Aliphatic hydrocarbon chromatograms 258
- 1.2 FTIR spectra and asphaltene chromatograms 279

Appendix 2: Magnetic experimentation **297**

- 2.1 Oil impregnated samples 298
- 2.2 Well core samples 319

Appendix 1

Organic geochemistry

1.1	Aliphatic hydrocarbon chromatograms	258
1.2	FTIR spectra and asphaltene chromatograms	279

Appendix 1

Organic Geochemistry

1.1 Aliphatic hydrocarbon chromatograms

TIC chromatogram: Total Ion Current chromatogram of the aliphatic extract

***m/z* 191 chromatogram:** Ion extraction 191 to identify hopanes within the aliphatic fractions

***m/z* 217 chromatogram:** Ion extraction 217 to identify steranes within the aliphatic fractions

***m/z* 57 chromatogram:** Ion extraction 57 to identify *n*-alkanes within the aliphatic fractions

Compounds identified and labelled on the chromatograms:

***m/z* 191**

H₂₇₋₃₀ ($\beta\alpha/\alpha\beta$): C₂₇₋₃₀ $\beta\alpha$ moretane/ C₂₇₋₃₀ $\alpha\beta$ hopane

Ts: C₂₇ 18 α trisnorhopane

Tm: C₂₇ 17 α trisnorhopane

TT27-28: C₂₇ & C₂₈ tricyclic terpanes

C₂₉ Ts: C₂₉ - 18 α - 30-norneohopane

***m/z* 217**

C₂₇₋₂₉ $\alpha\alpha\alpha$ (S/R): C₂₇₋₂₉ $\alpha\alpha\alpha$ S / C₂₇₋₂₉ $\alpha\alpha\alpha$ R sterane isomerization

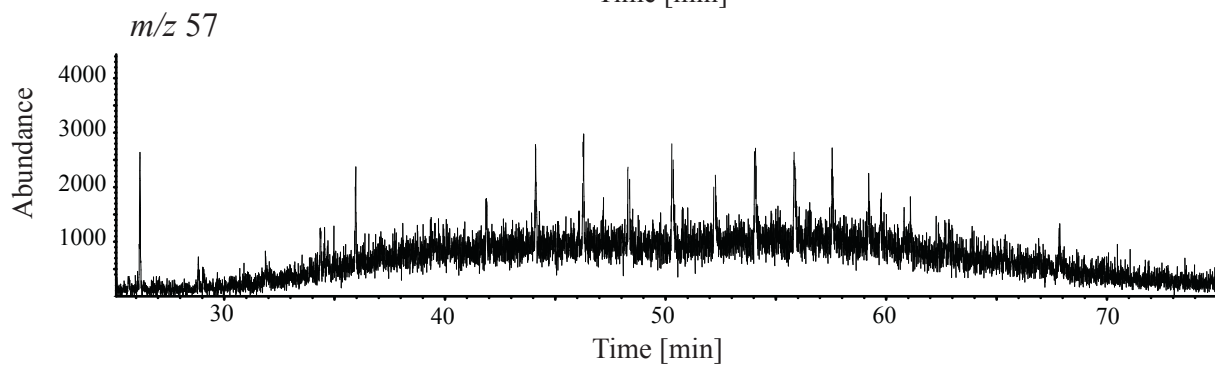
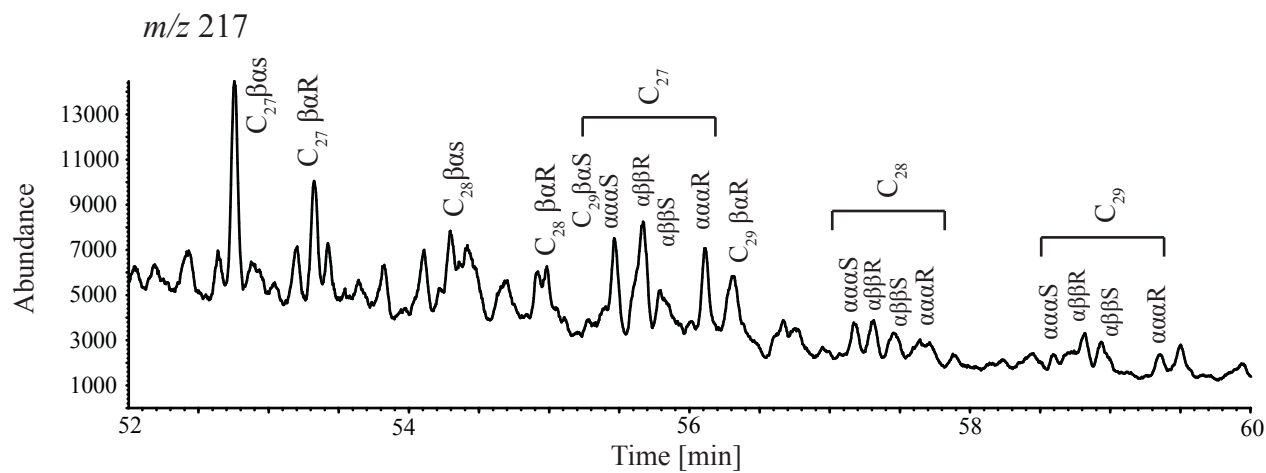
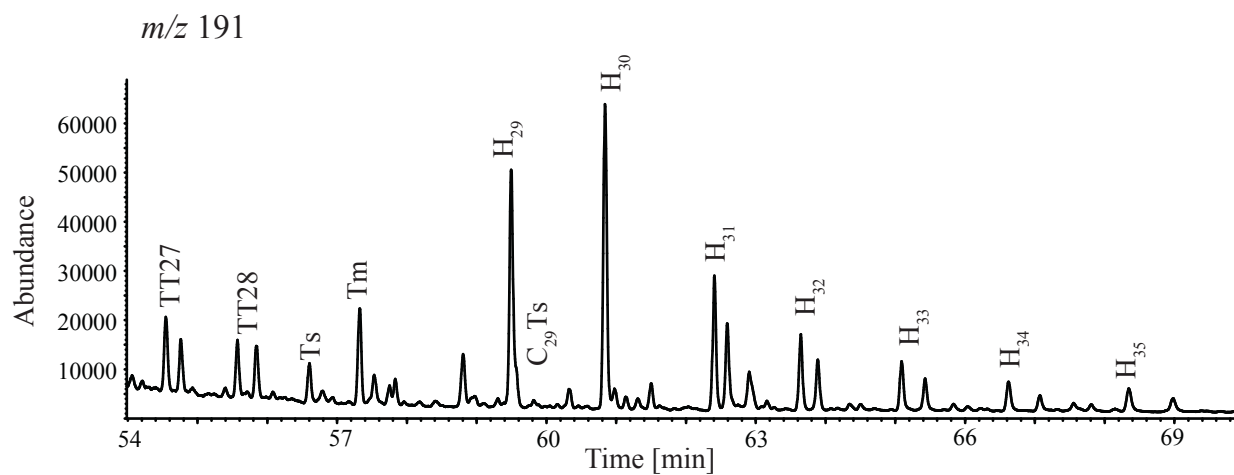
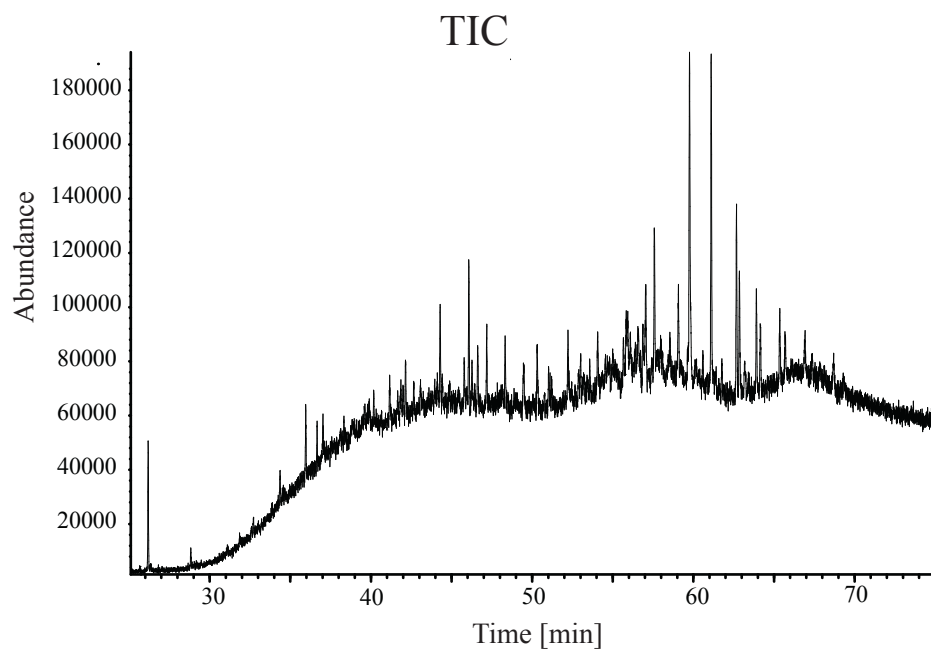
C₂₇₋₂₉ $\alpha\beta\beta$ (20S/R): C₂₇₋₂₉ $\alpha\beta\beta$ S / C₂₇₋₂₉ $\alpha\beta\beta$ R sterane nuclear isomerization

***m/z* 57**

C₉-C₃₀: C₉-C₃₀ *n*-alkanes

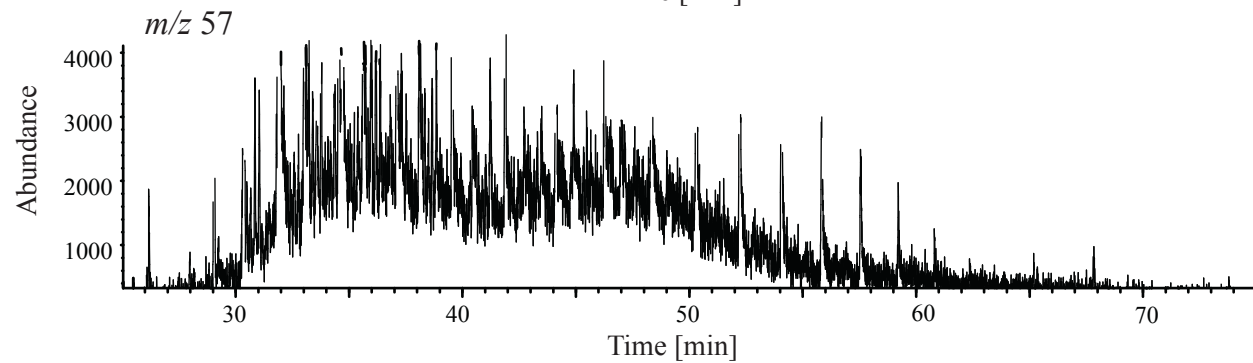
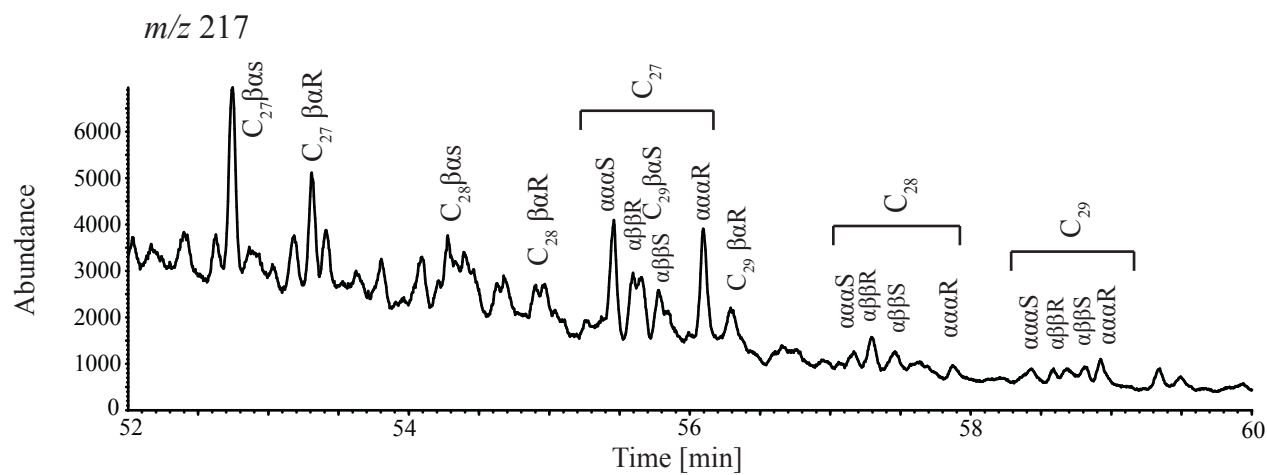
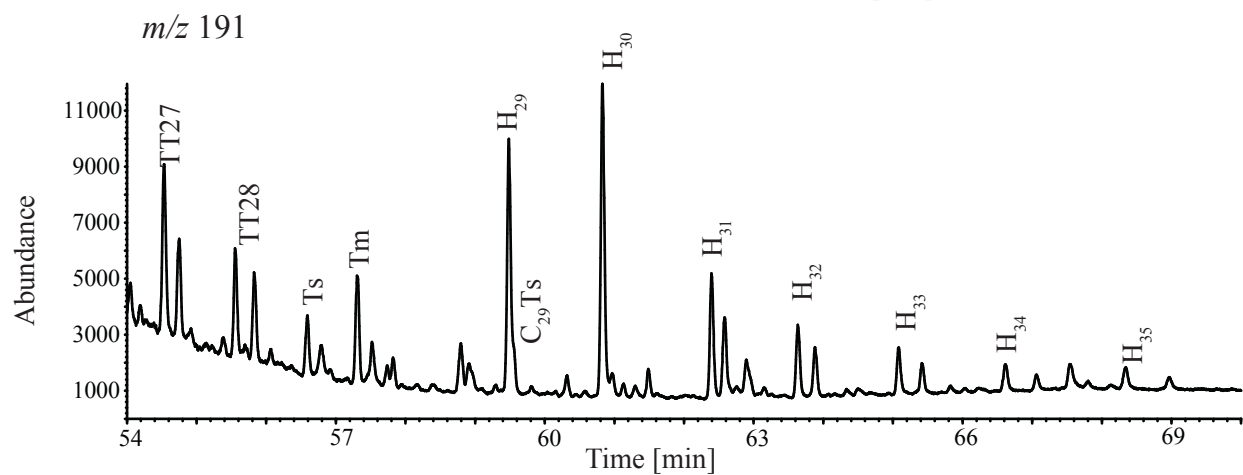
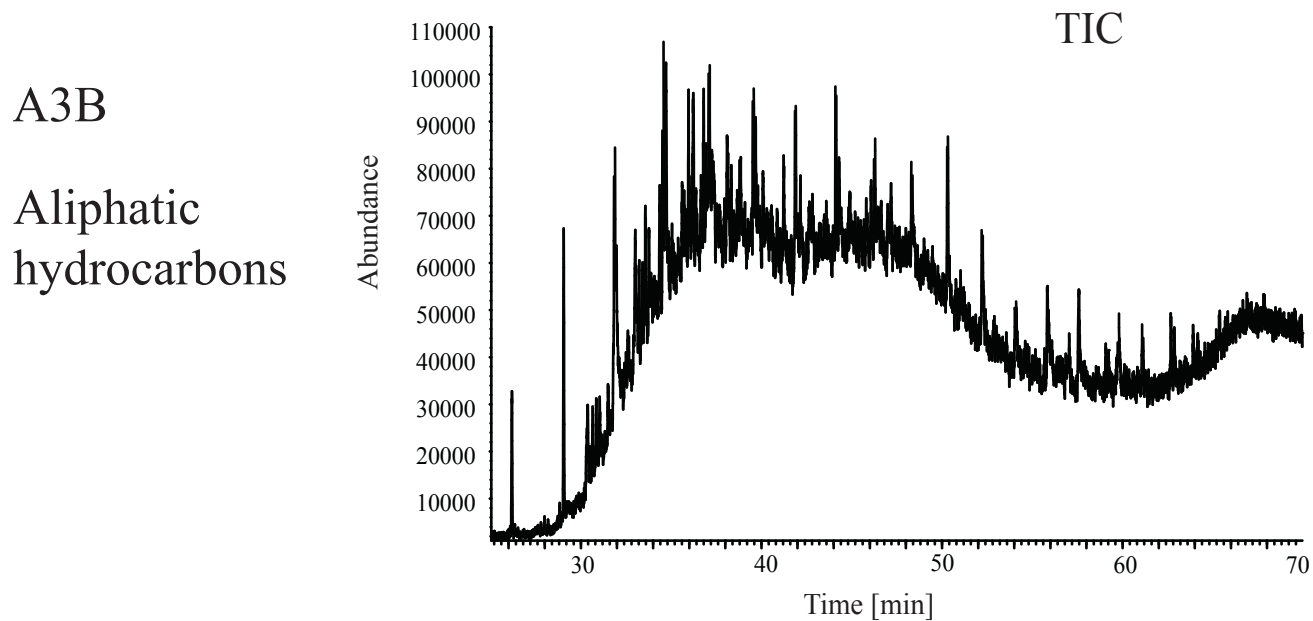
A1B

Aliphatic
hydrocarbons

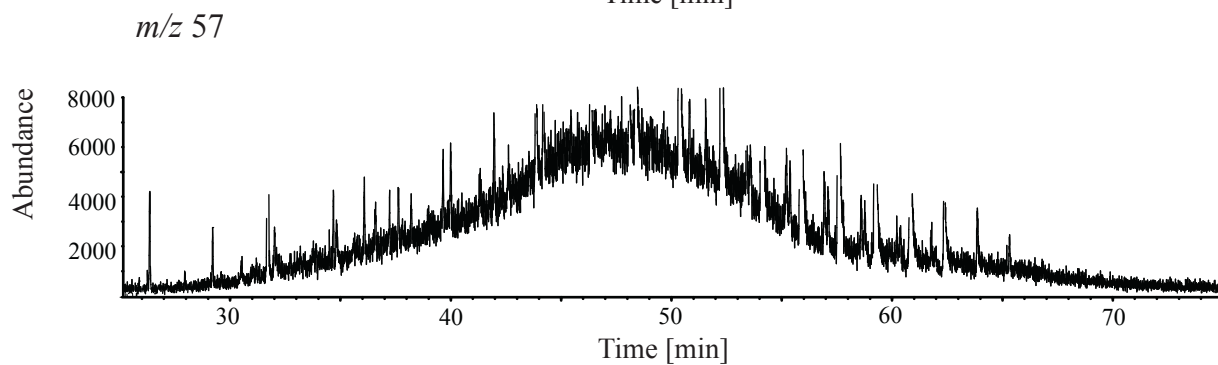
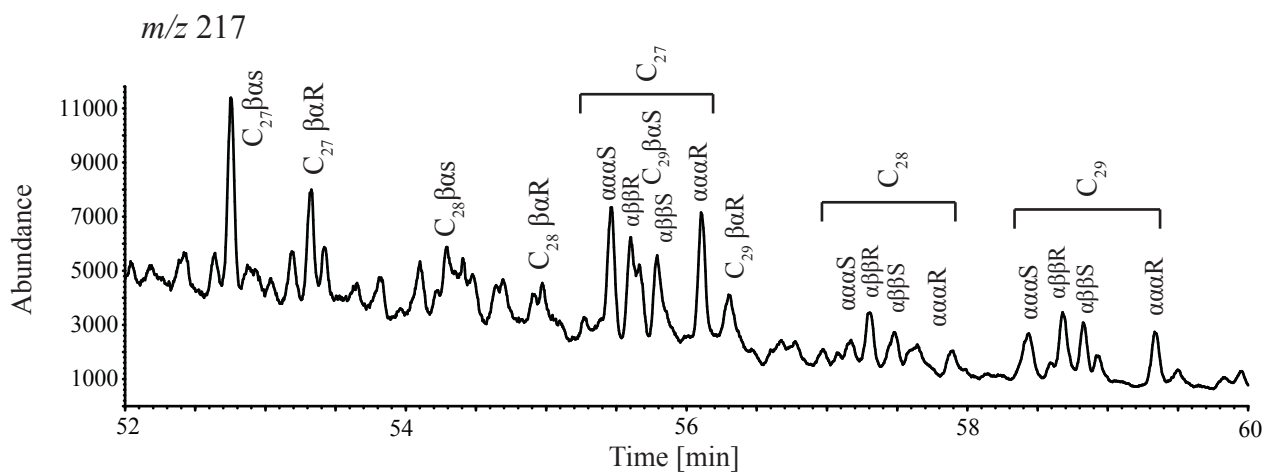
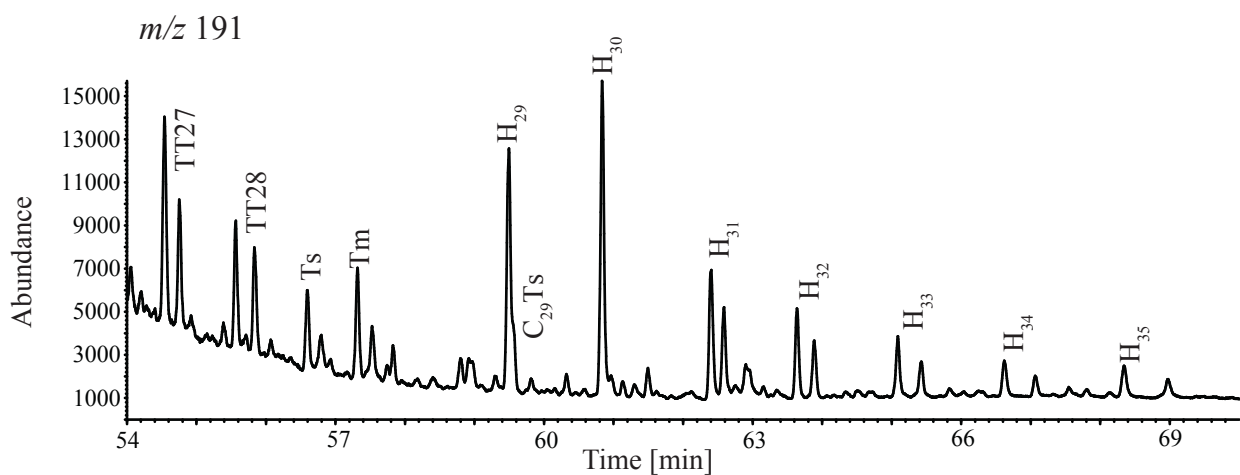
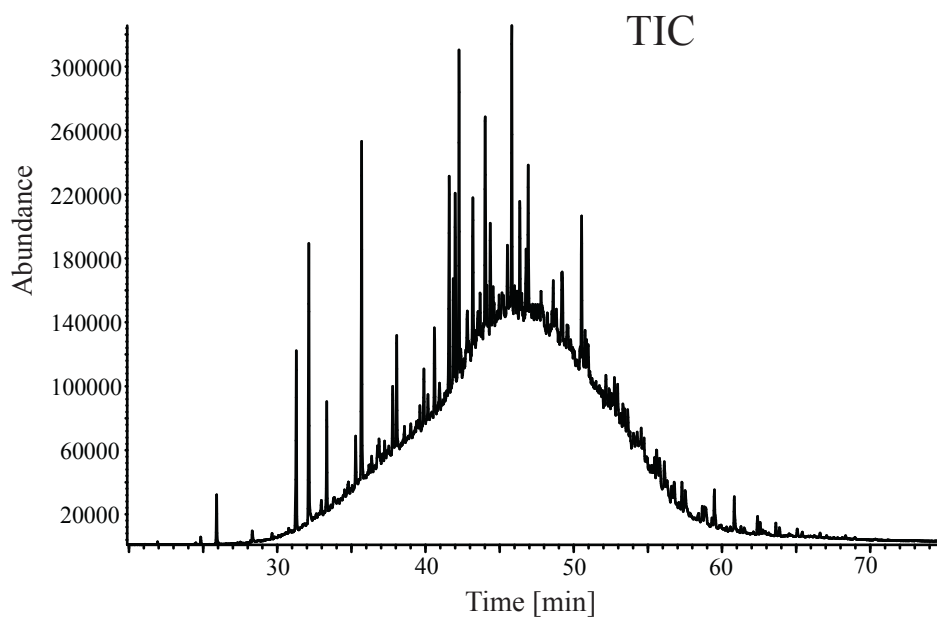


A3B

Aliphatic
hydrocarbons

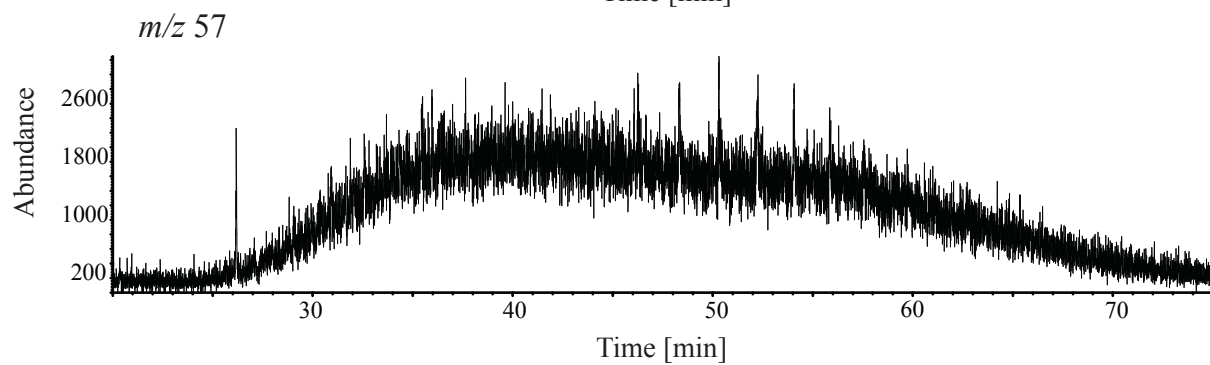
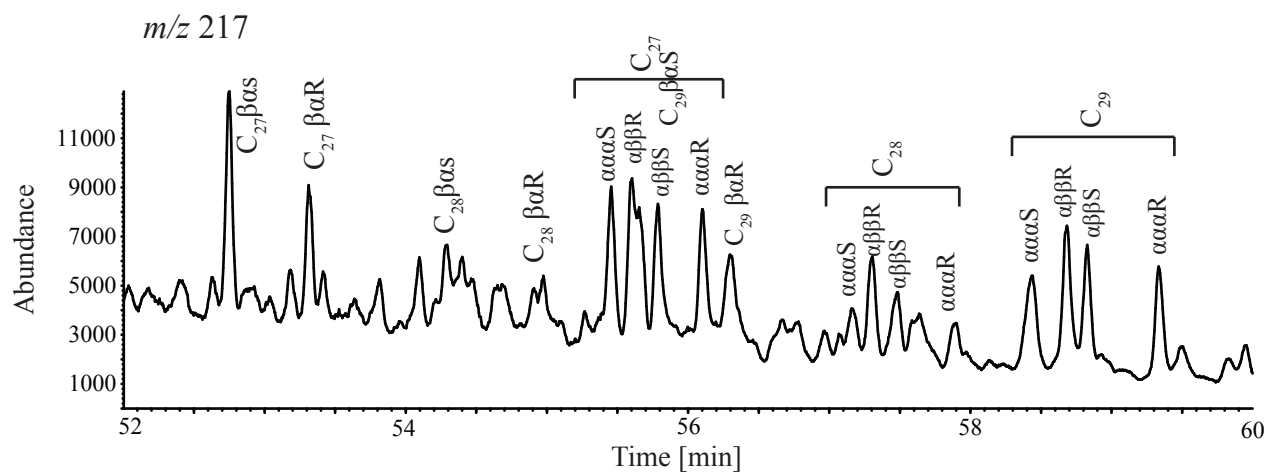
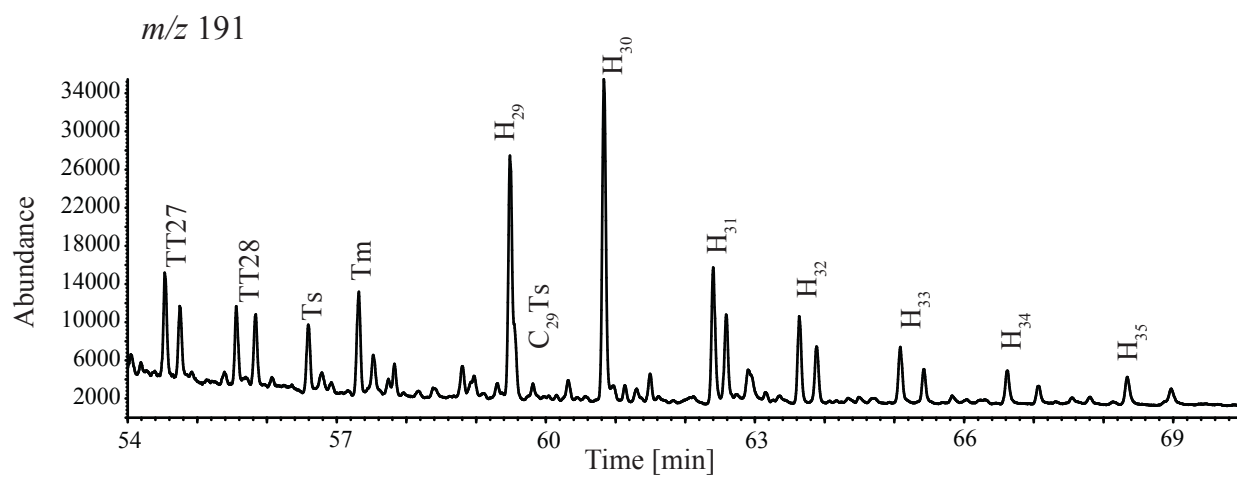
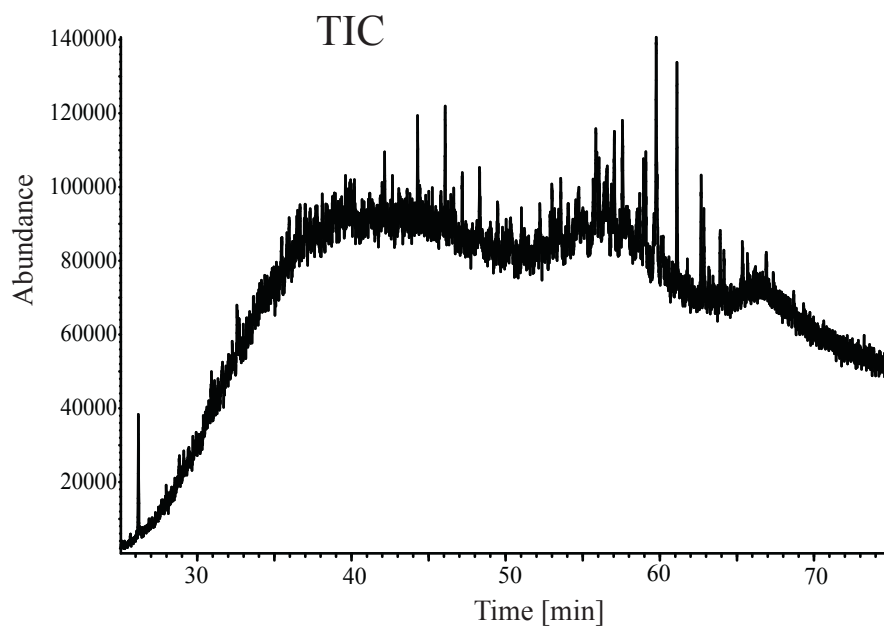


Aliphatic hydrocarbons



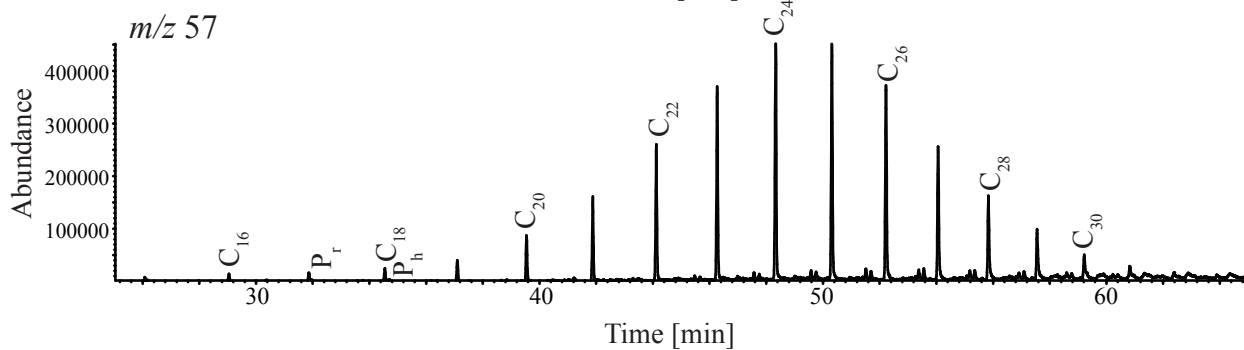
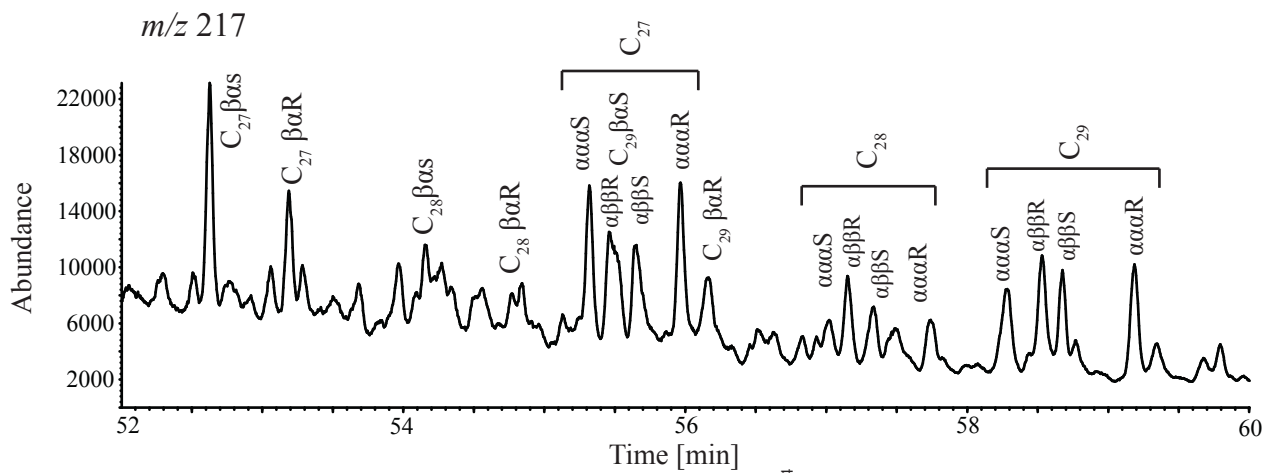
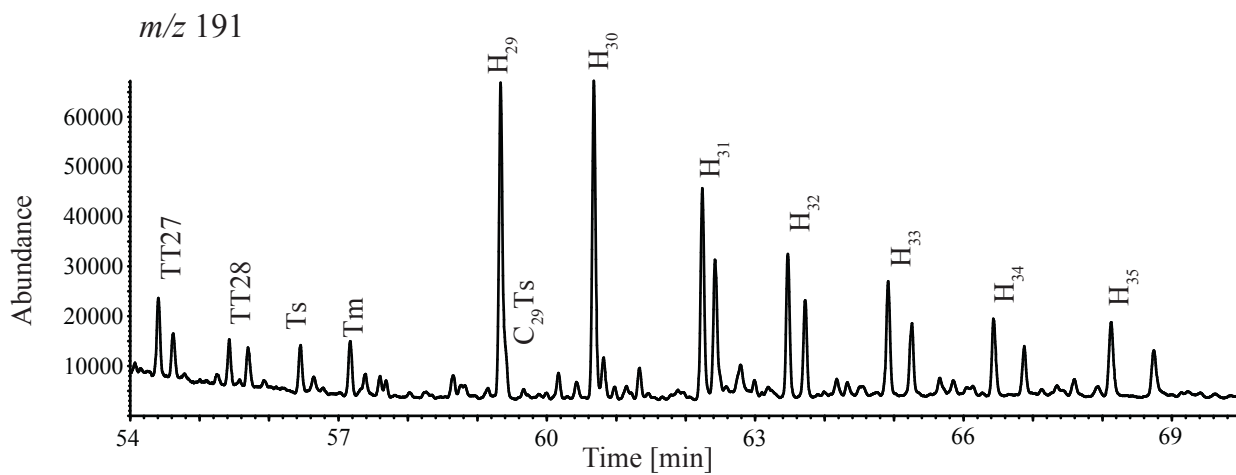
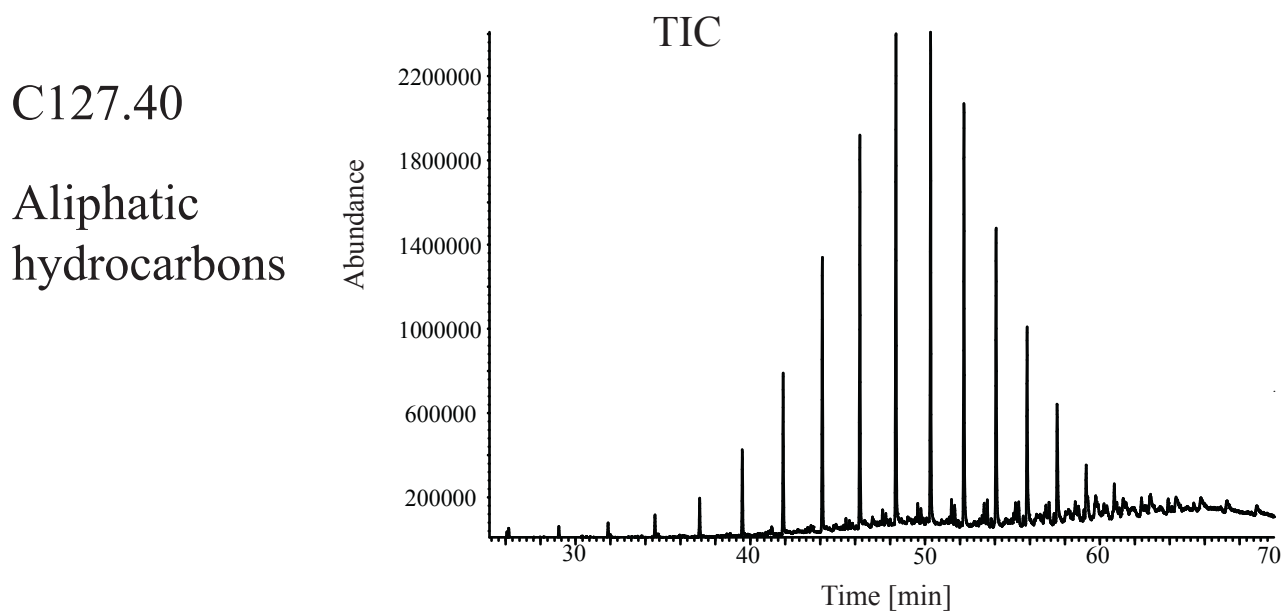
A827.75

Aliphatic
hydrocarbons



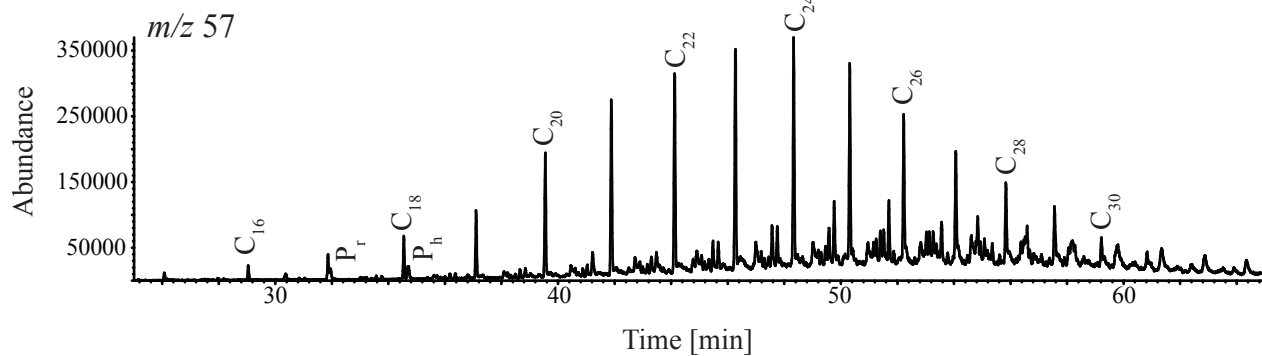
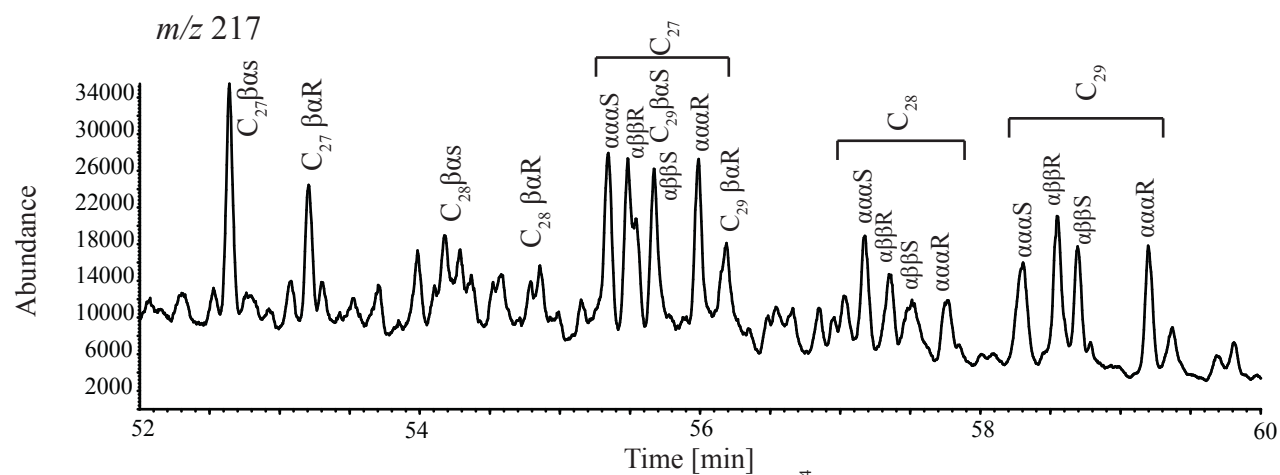
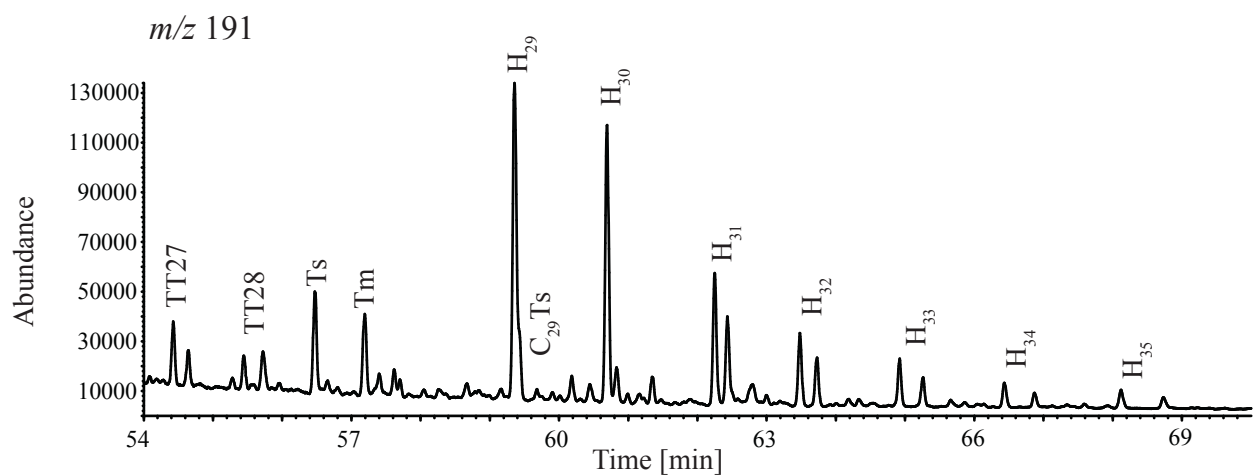
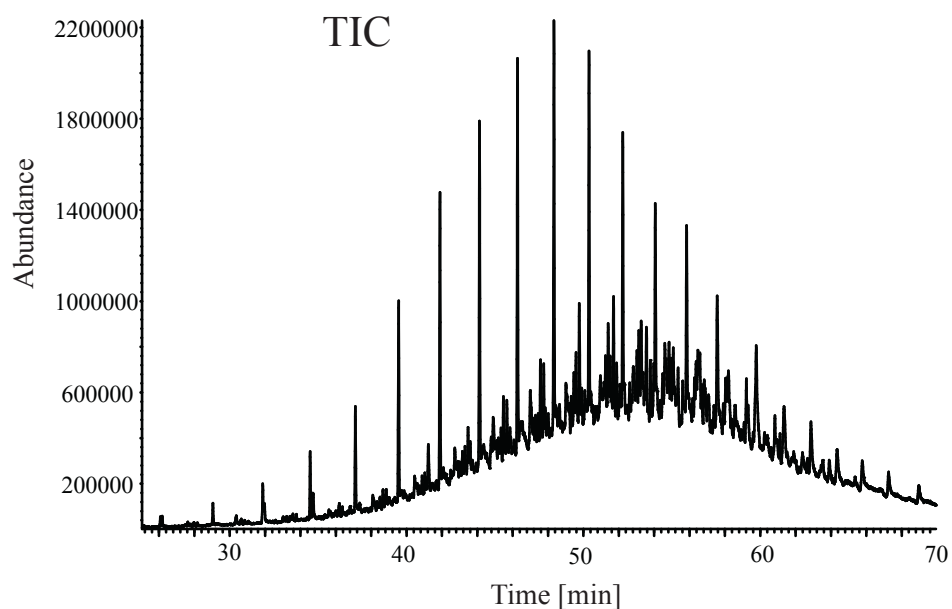
C127.40

Aliphatic
hydrocarbons



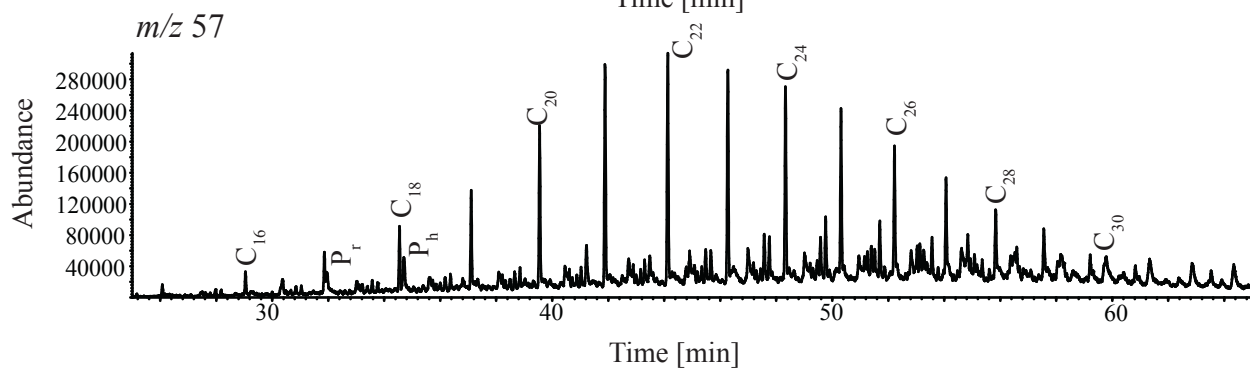
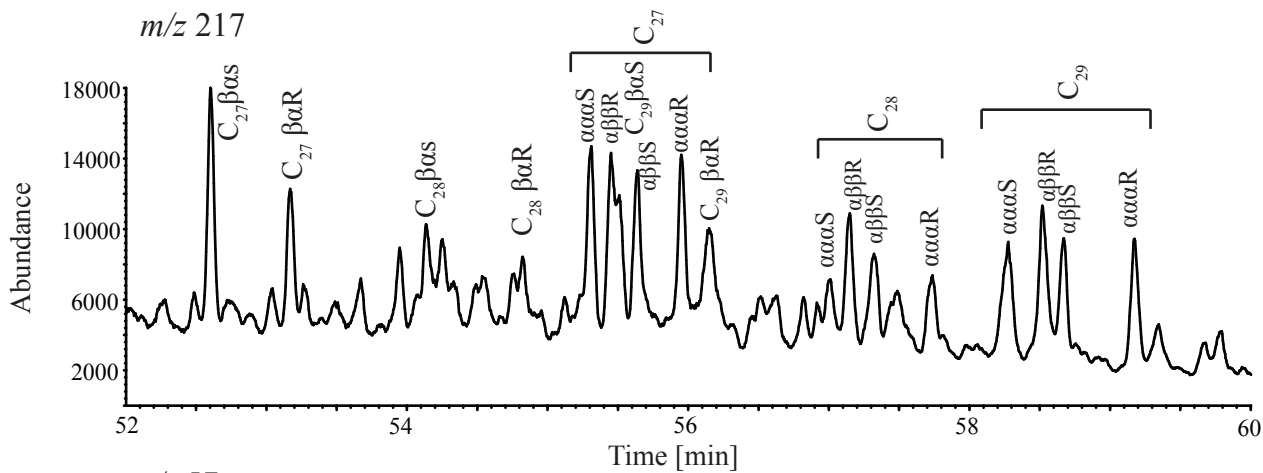
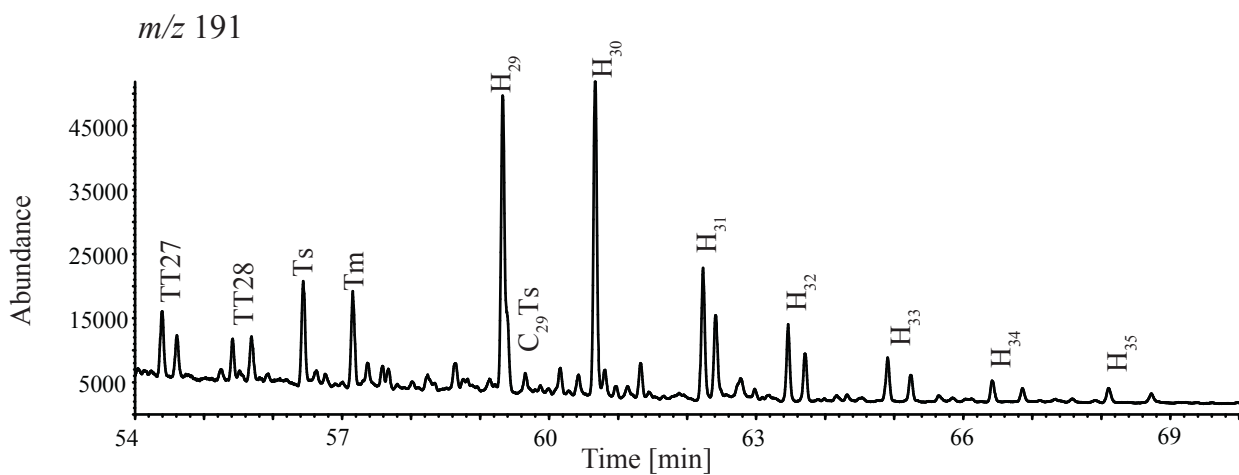
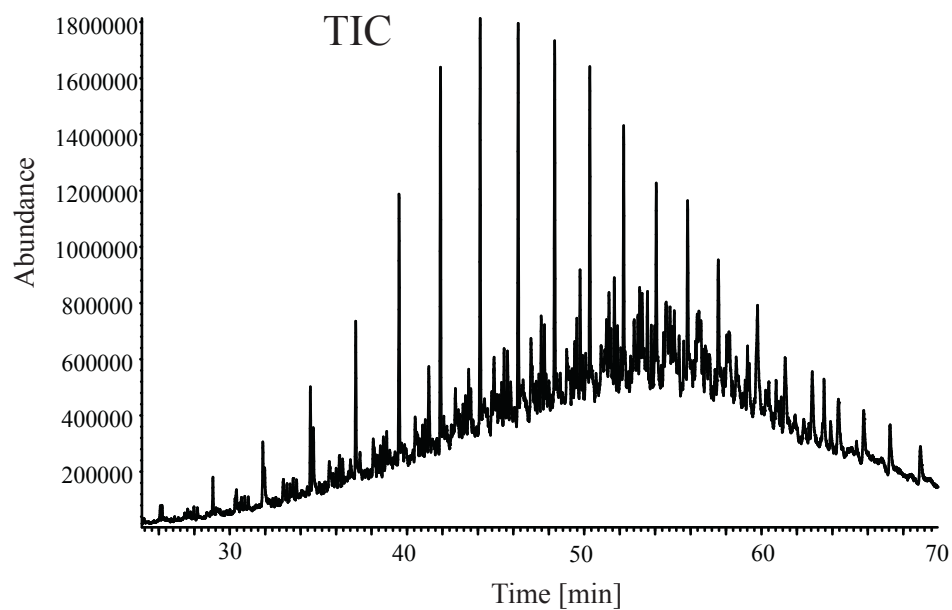
C147.25

Aliphatic
hydrocarbons



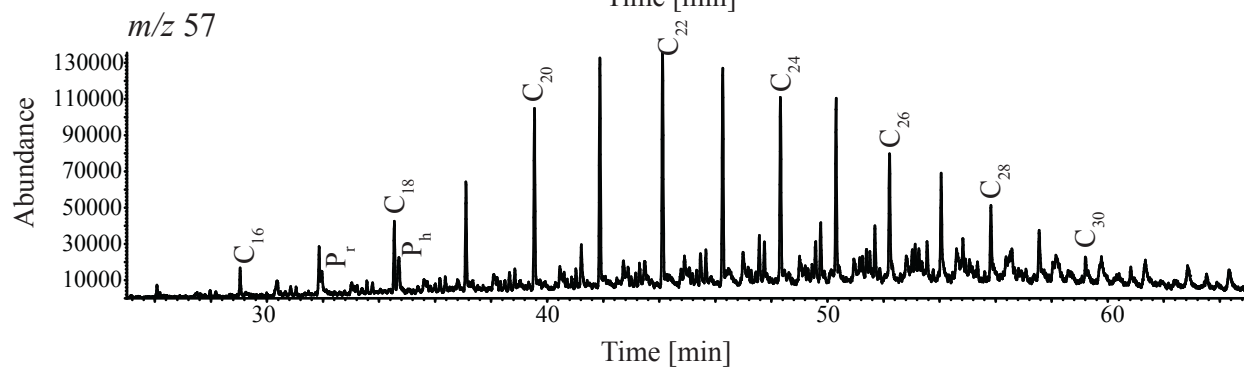
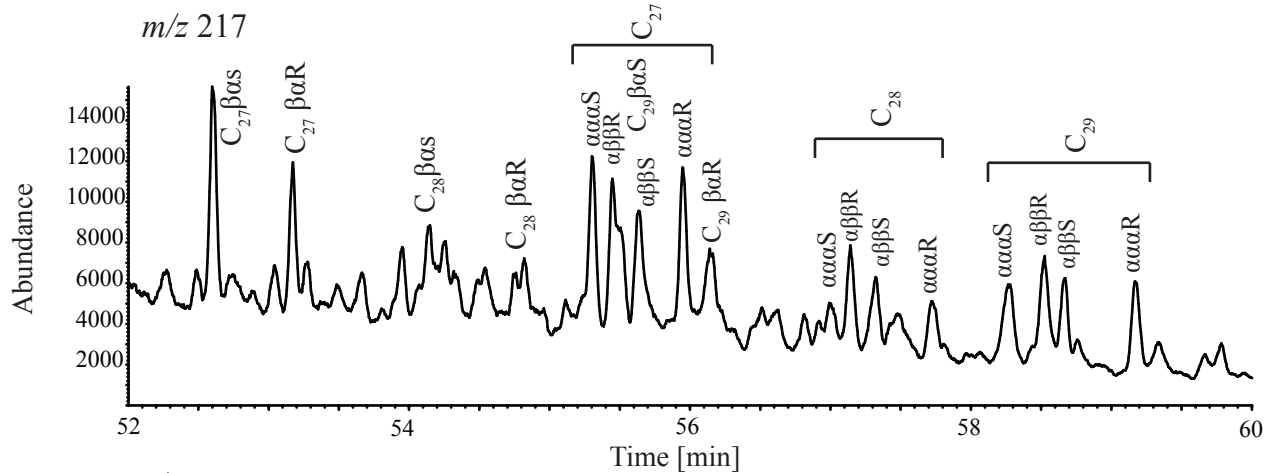
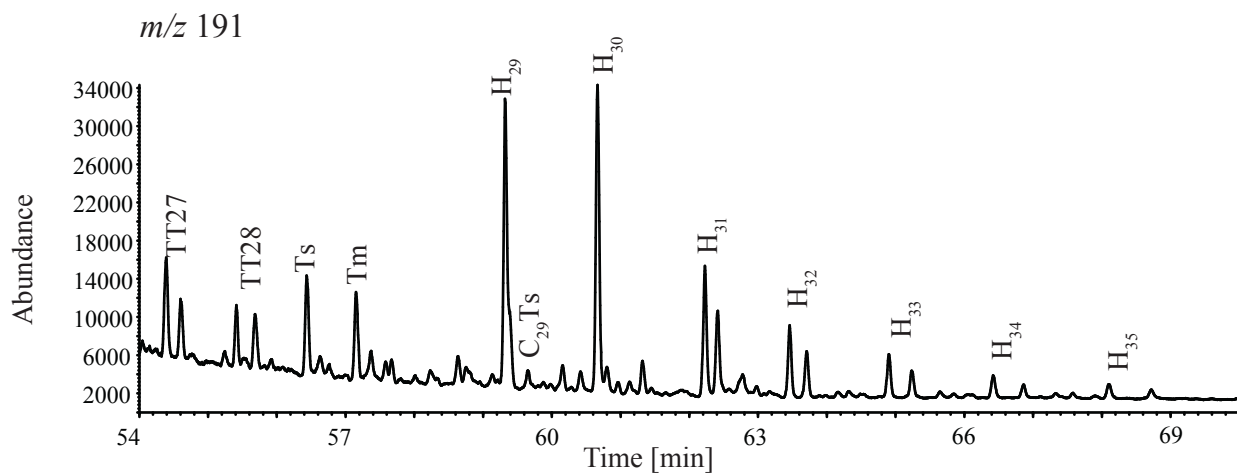
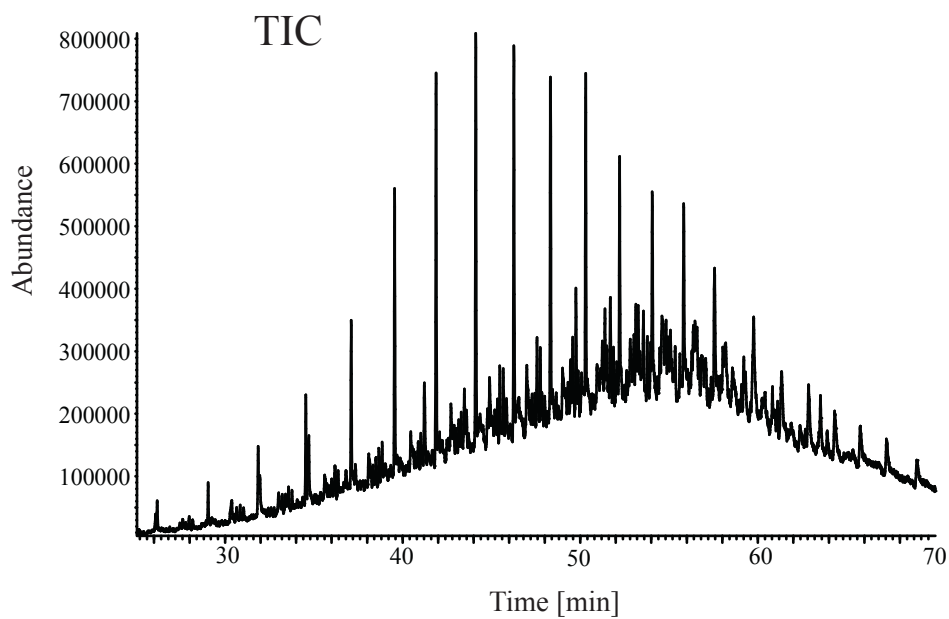
C541.75

Aliphatic
hydrocarbons



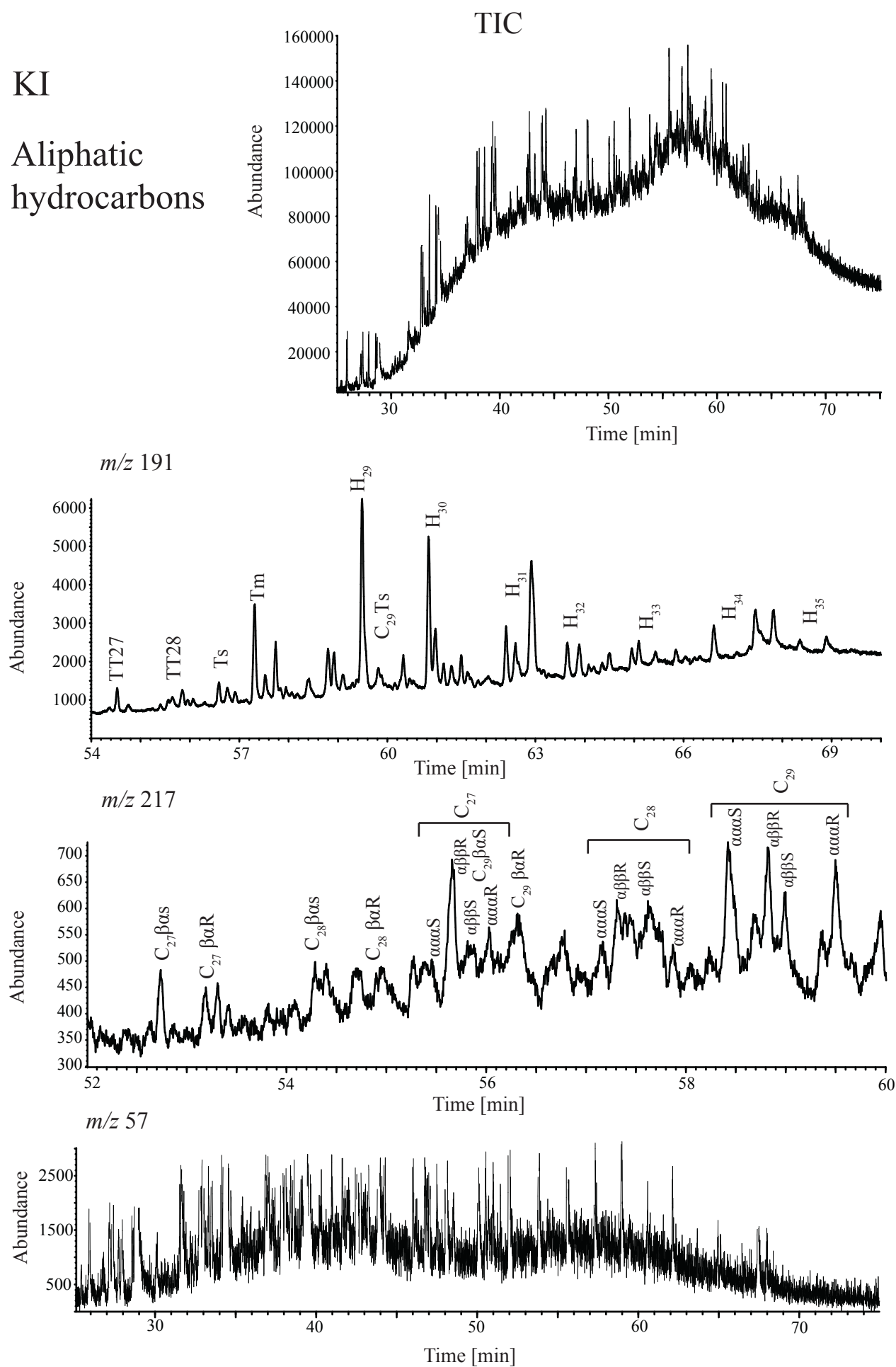
C616.48

Aliphatic
hydrocarbons

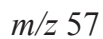
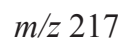
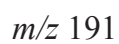


KI

Aliphatic
hydrocarbons

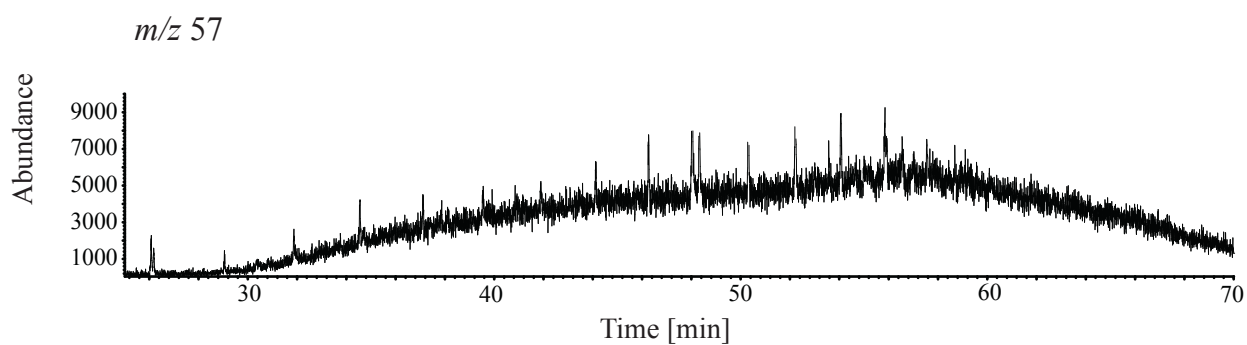
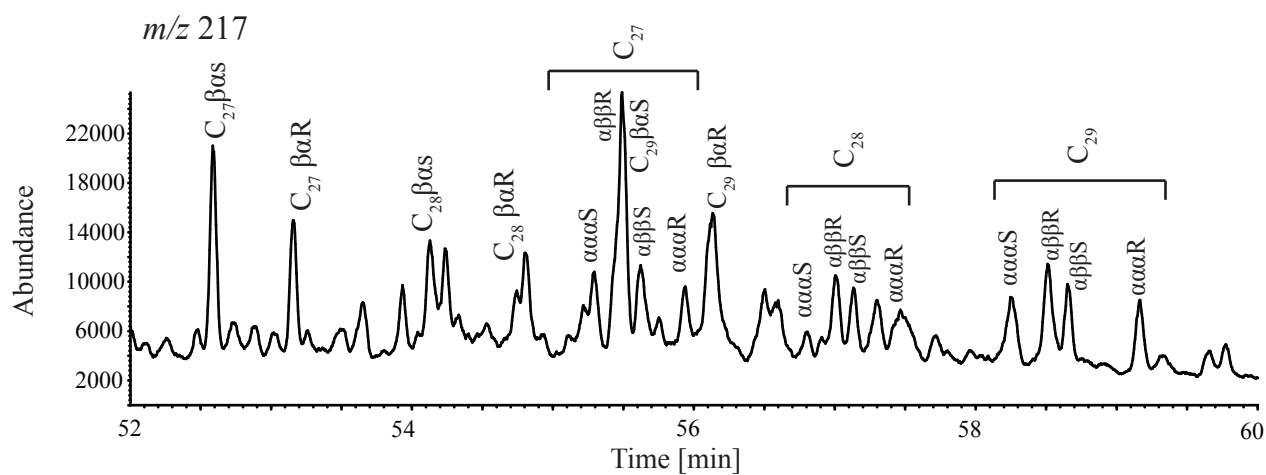
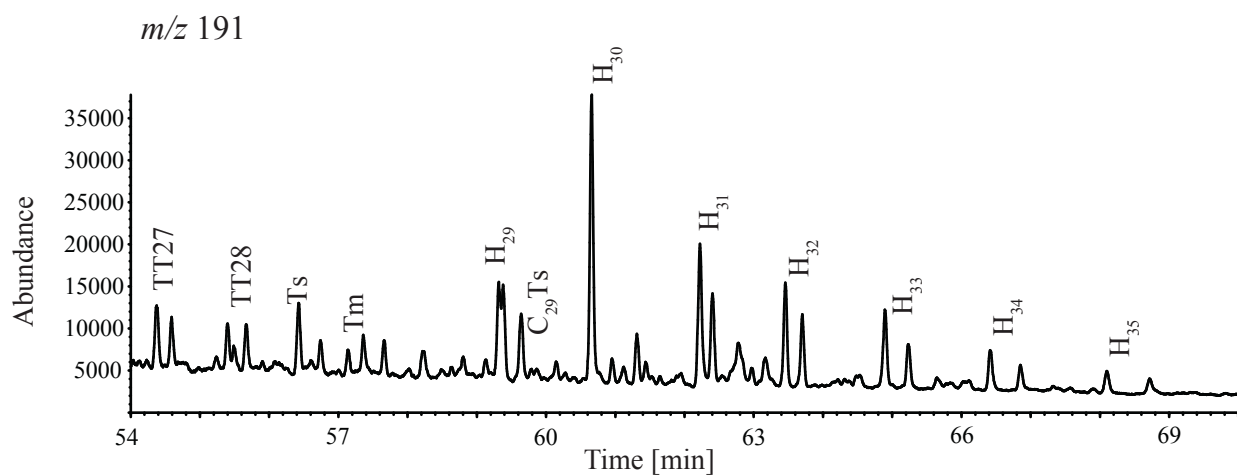
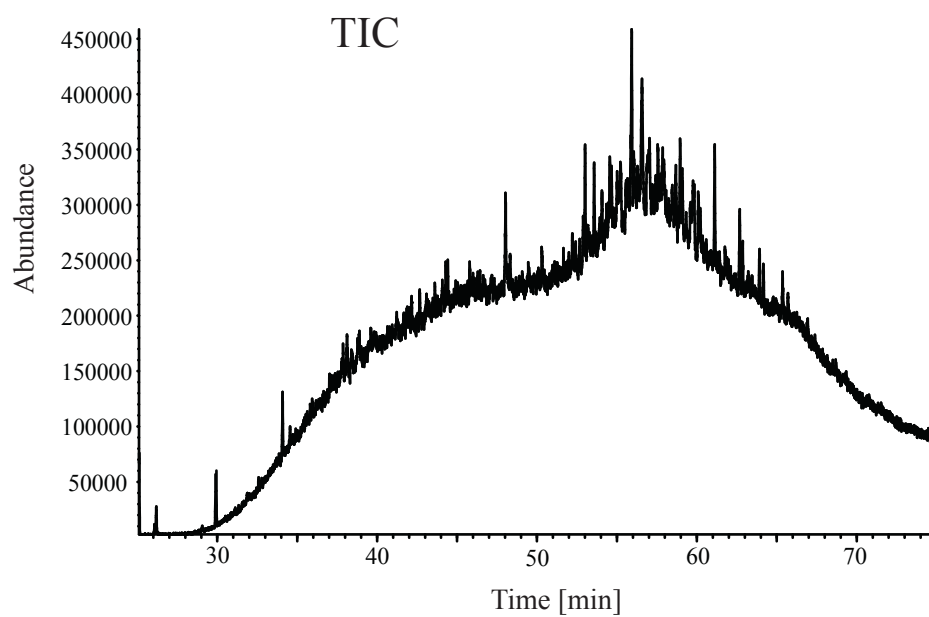


Aliphatic hydrocarbons



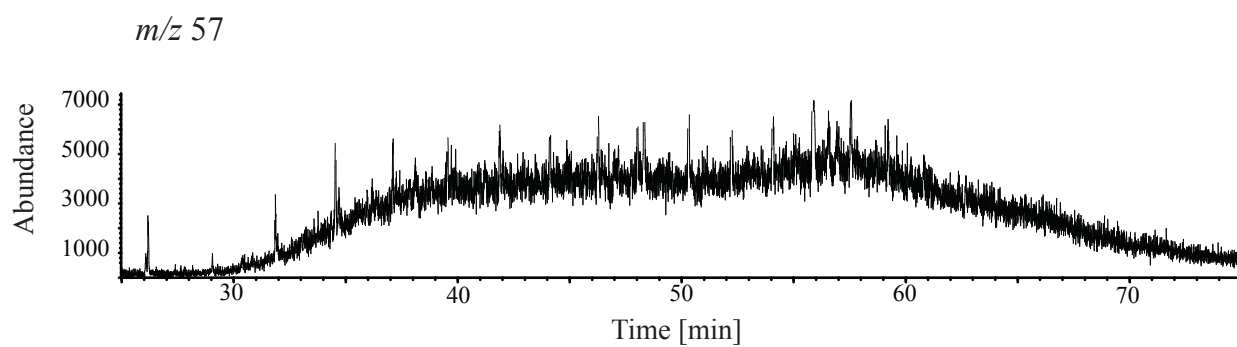
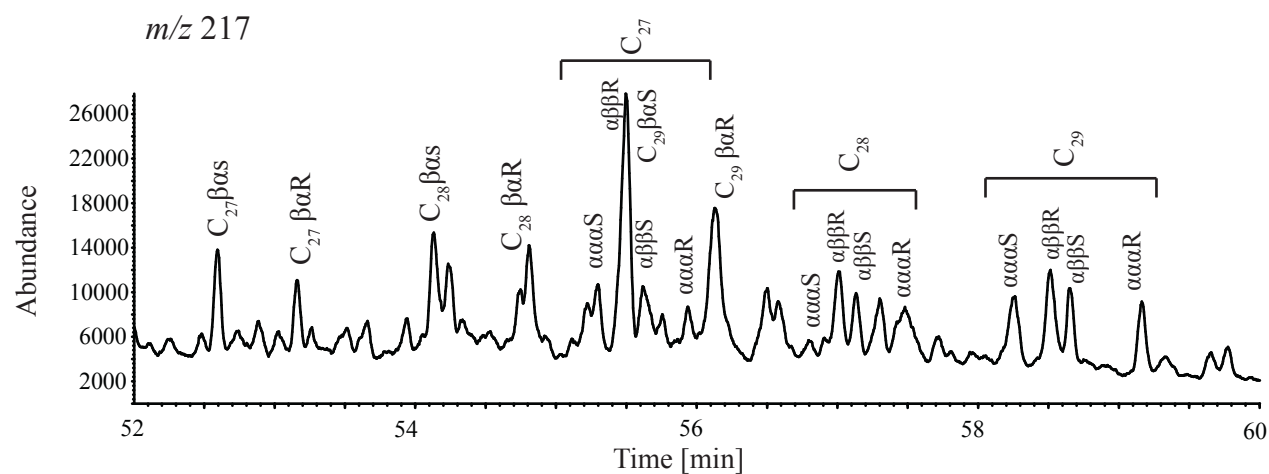
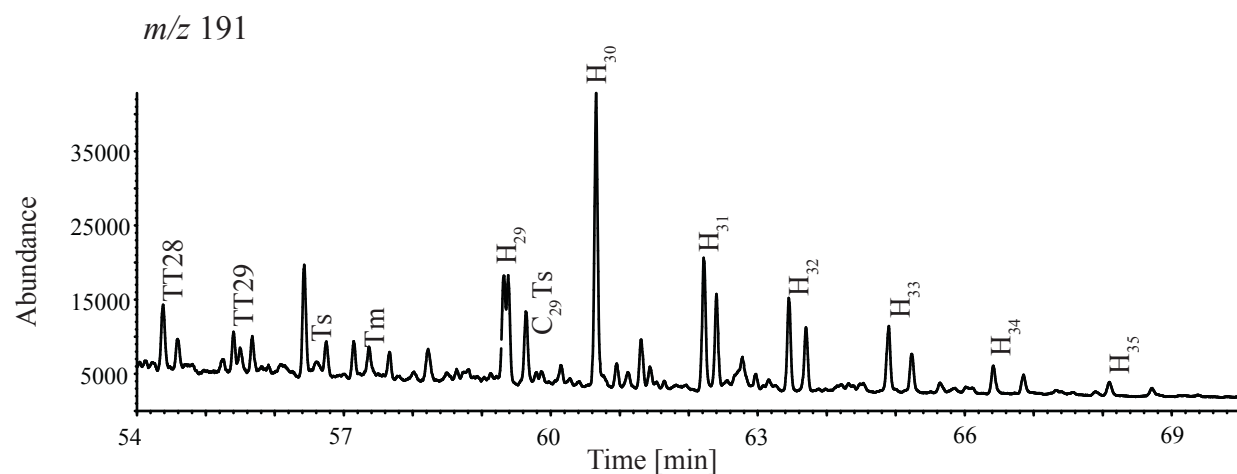
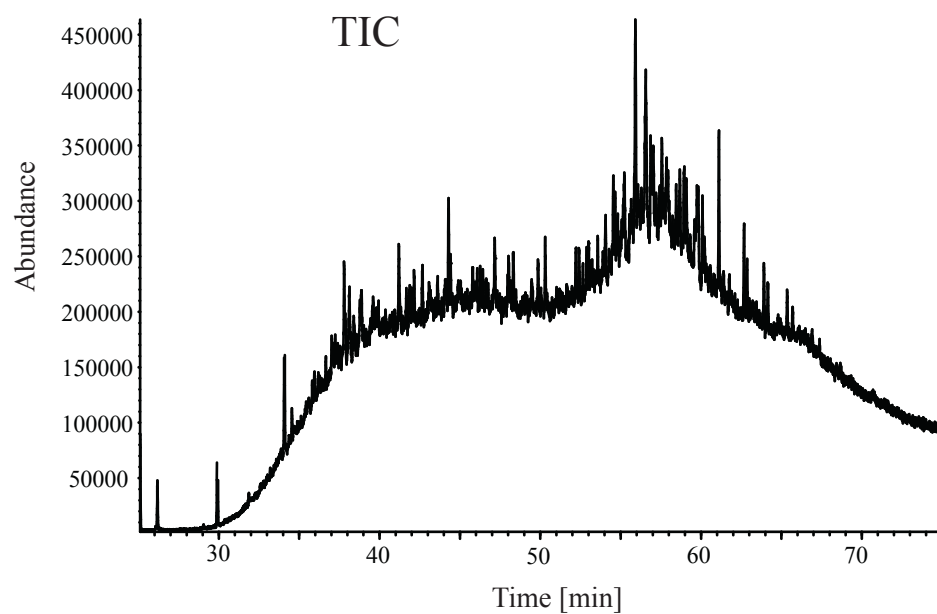
OS2

Aliphatic
hydrocarbons



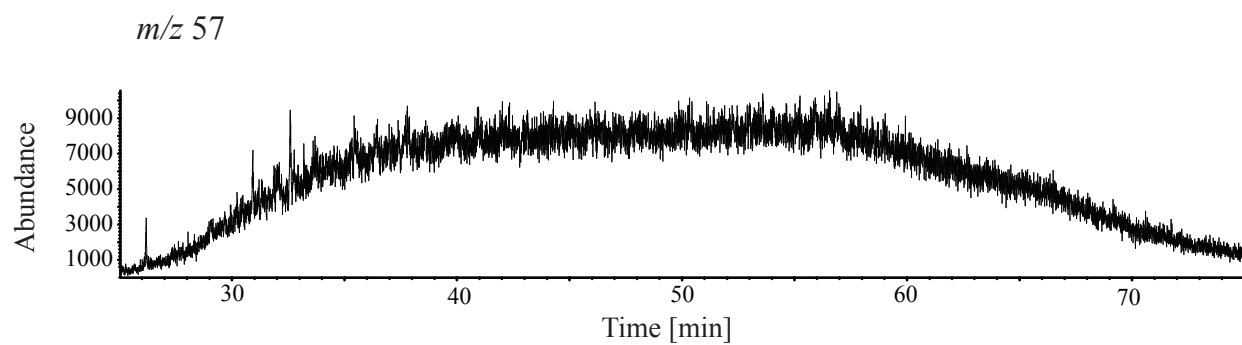
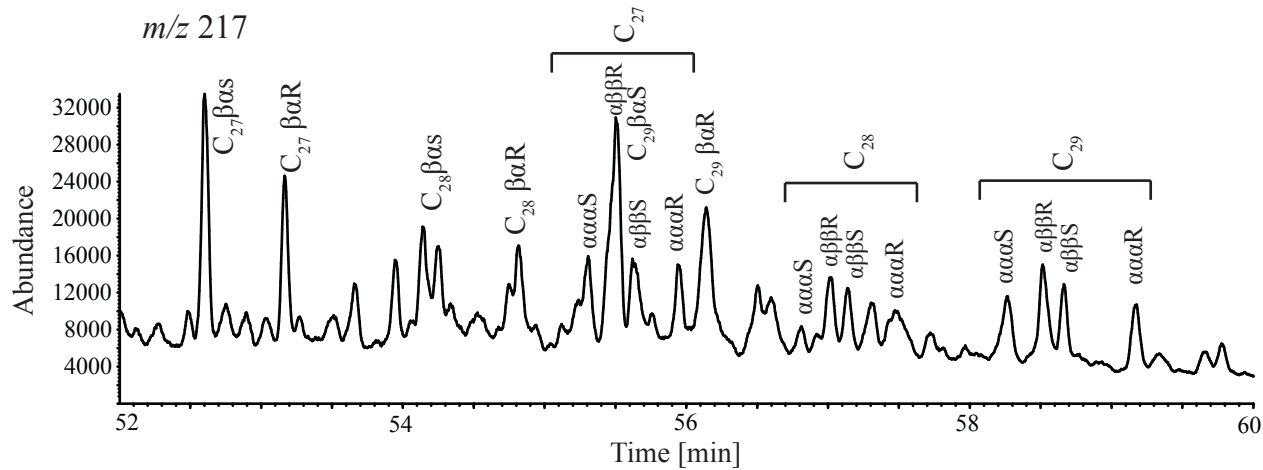
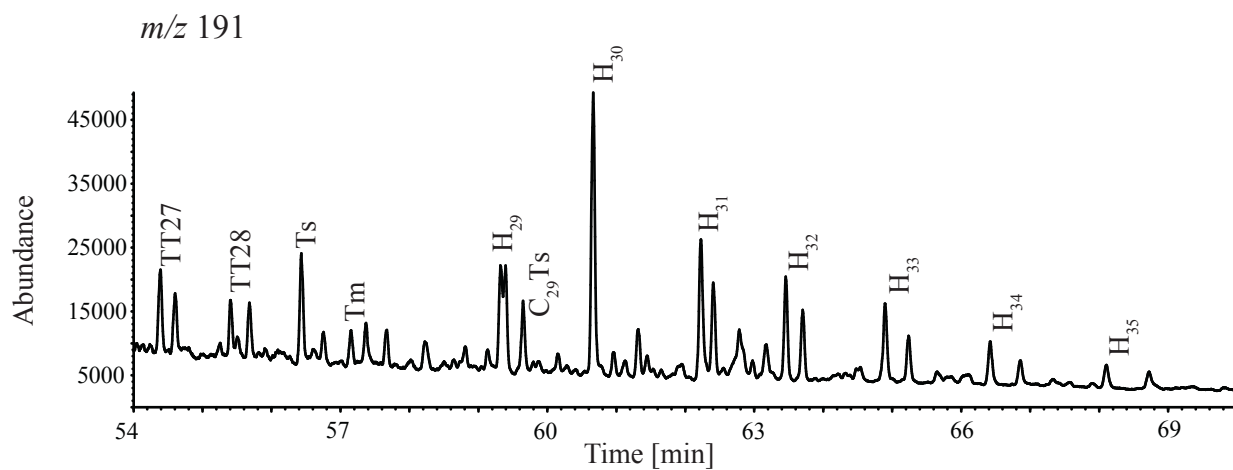
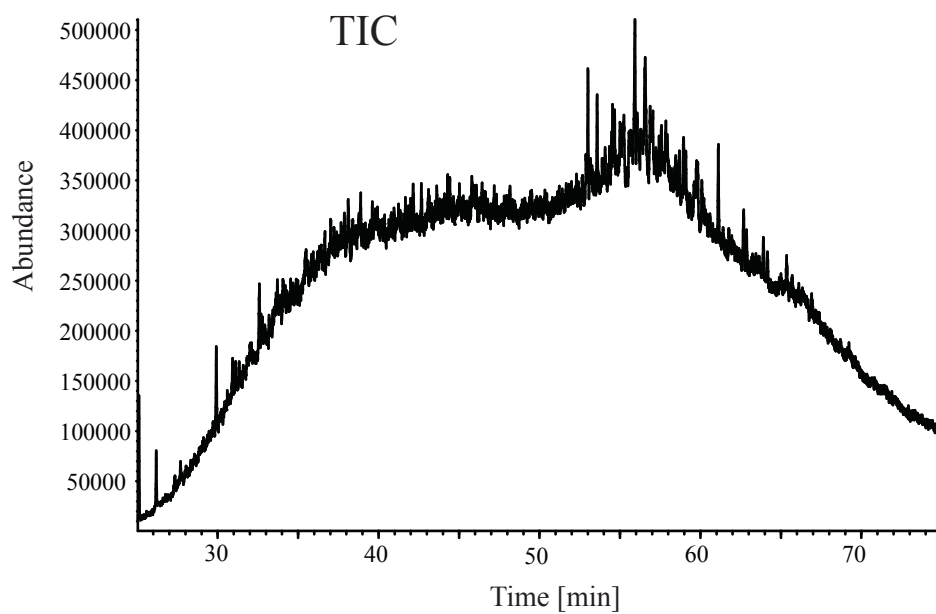
OS3

Aliphatic
hydrocarbons



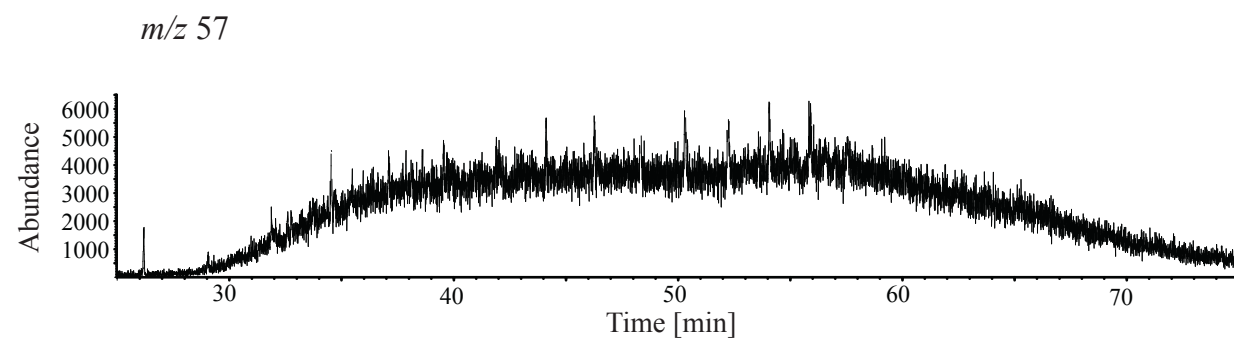
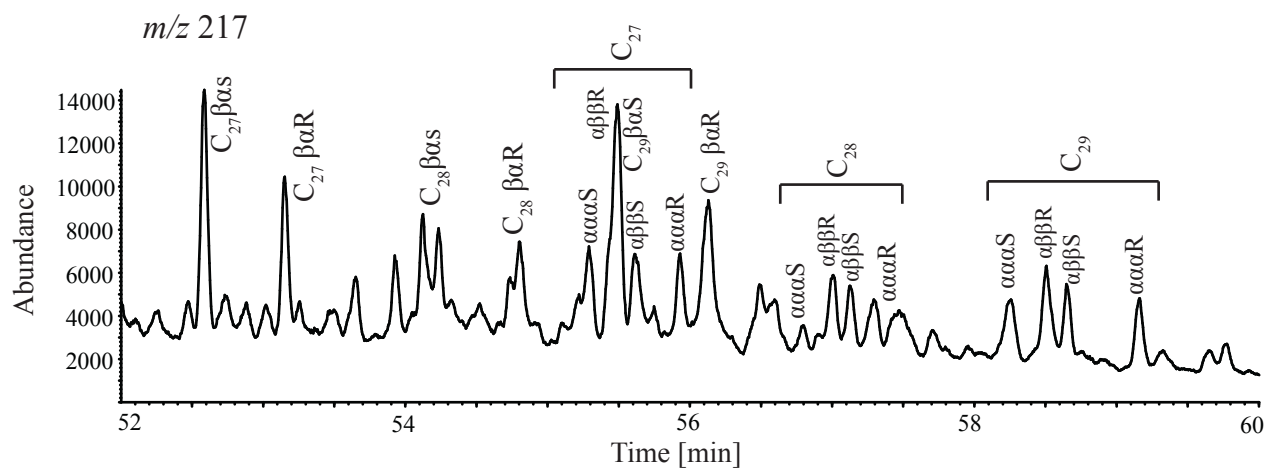
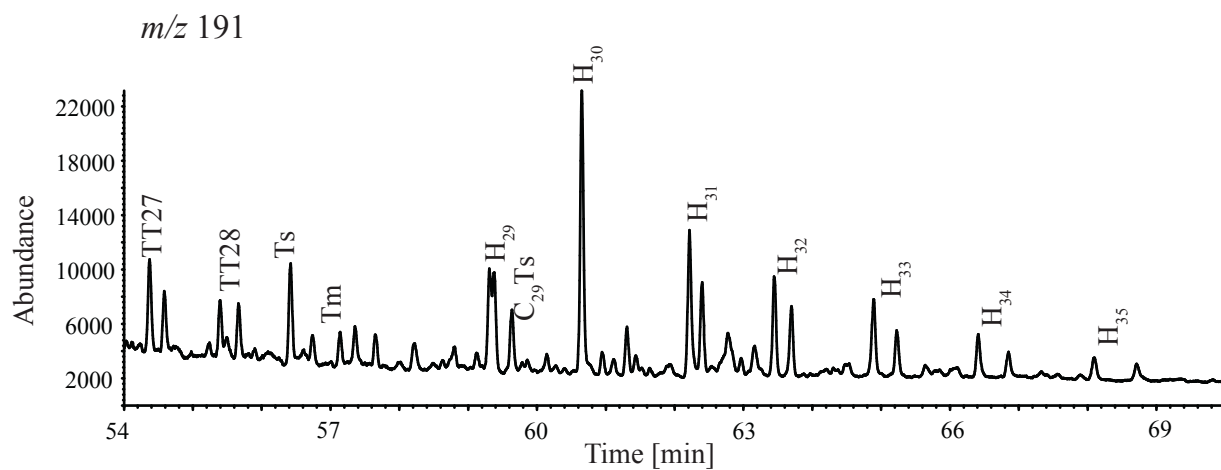
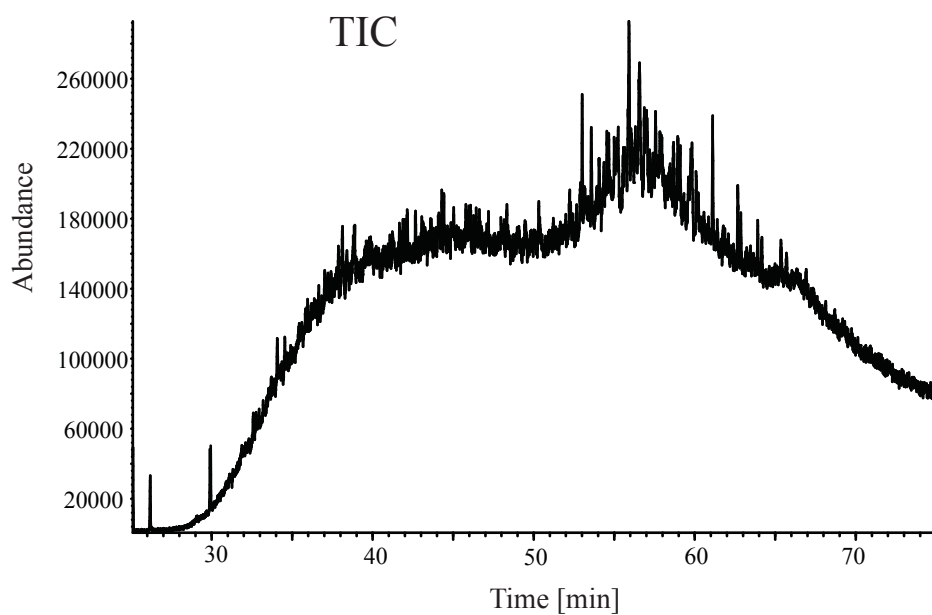
OS4

Aliphatic
hydrocarbons



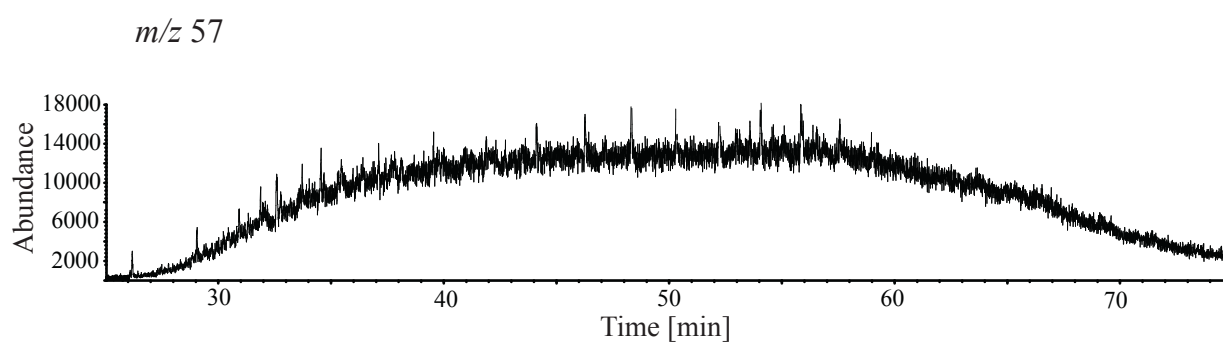
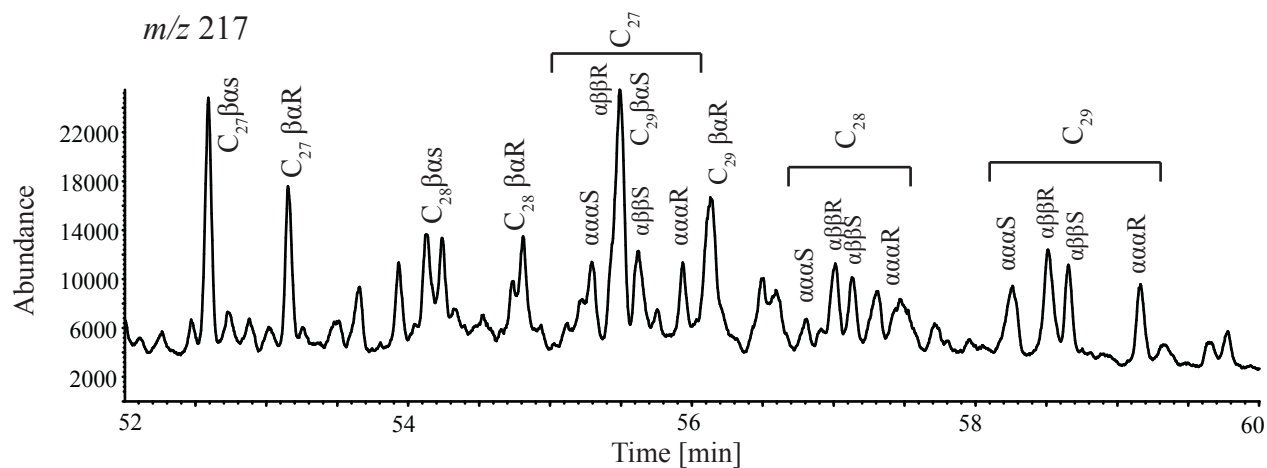
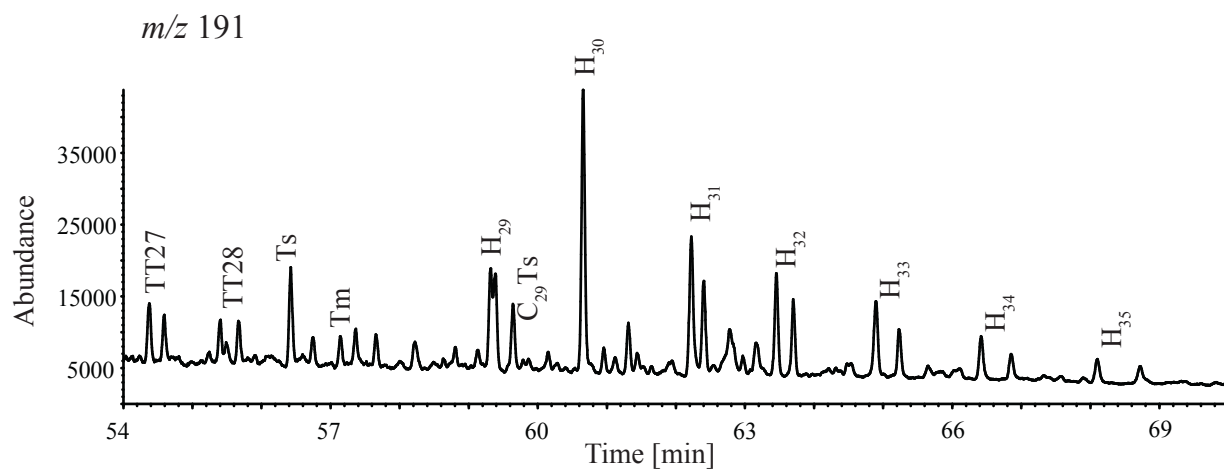
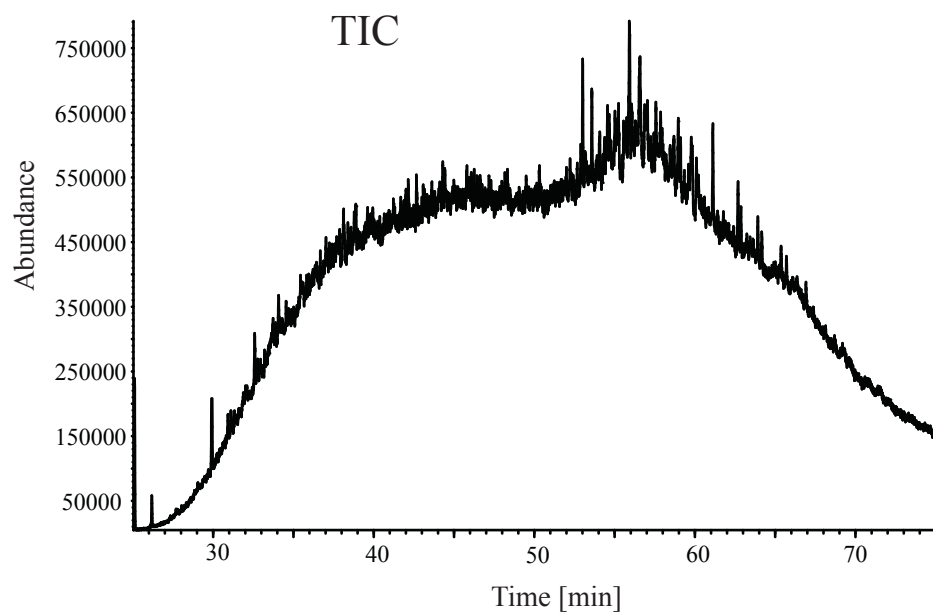
OS5

Aliphatic
hydrocarbons



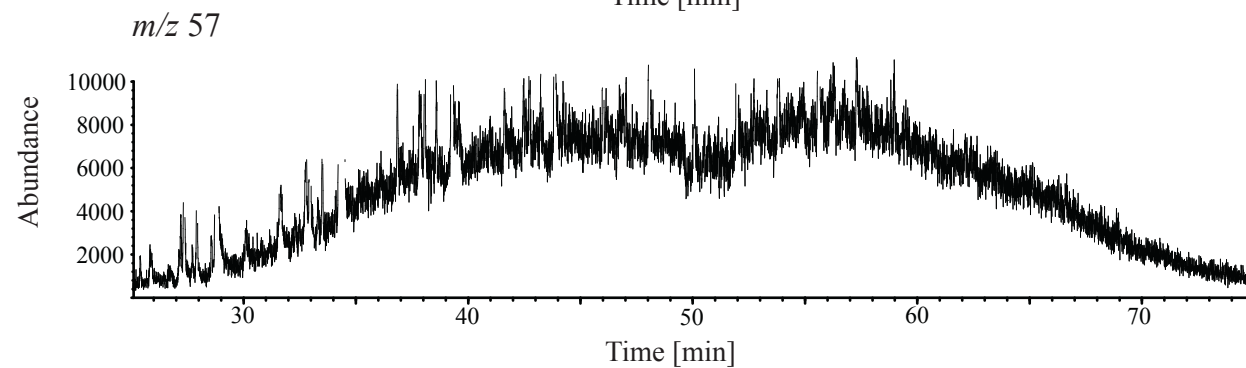
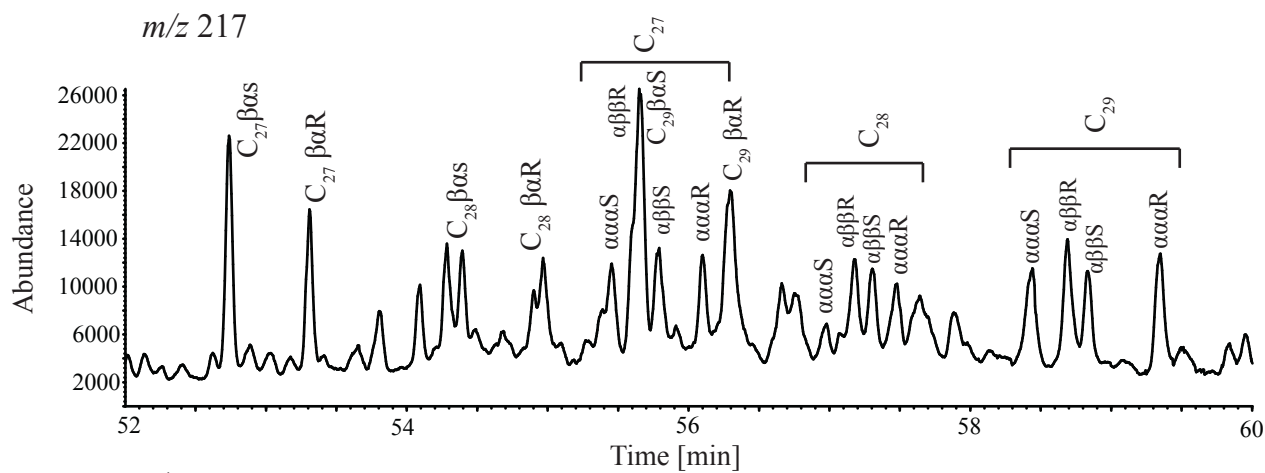
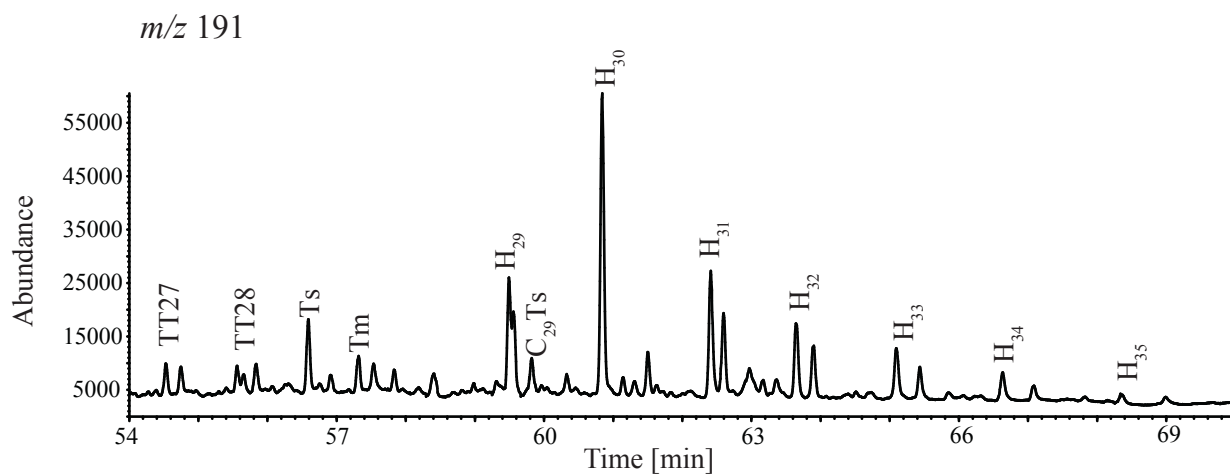
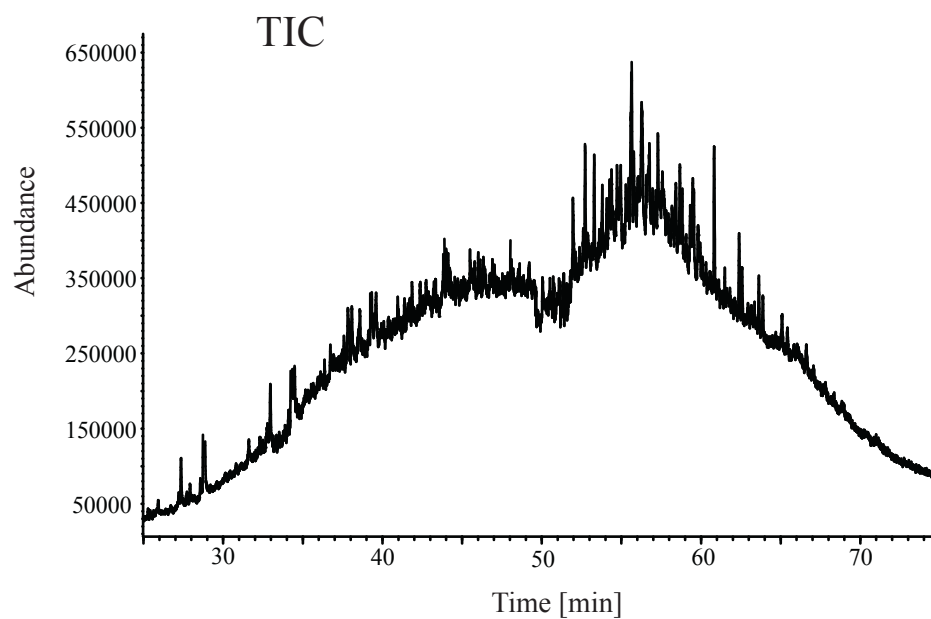
OS6

Aliphatic
hydrocarbons



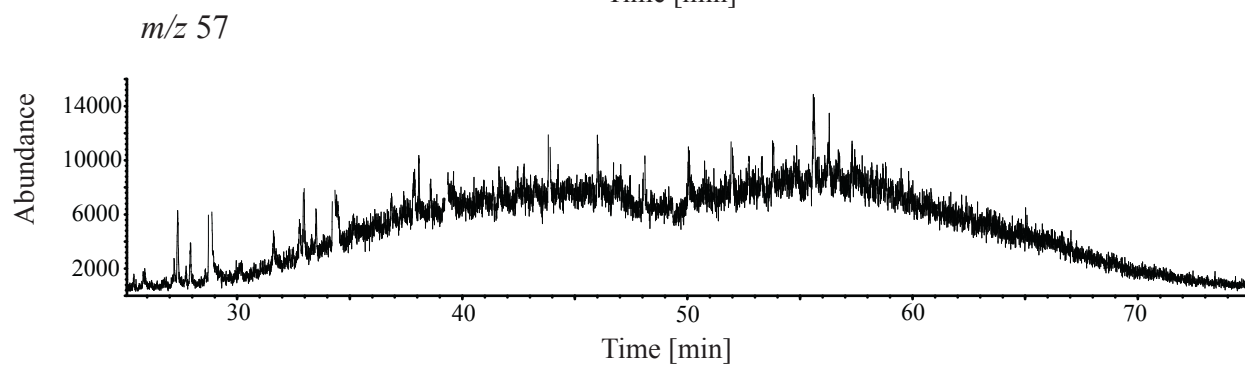
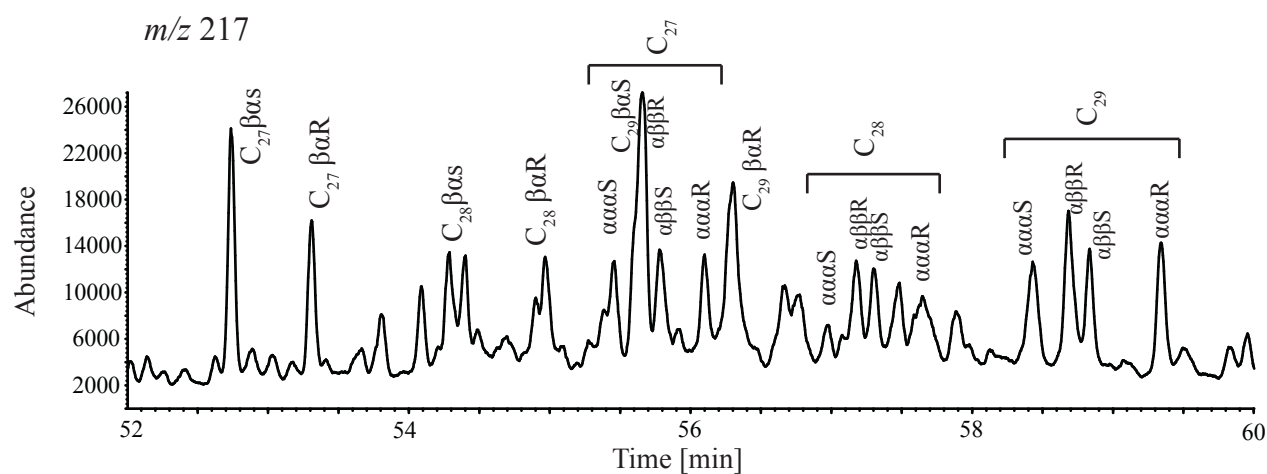
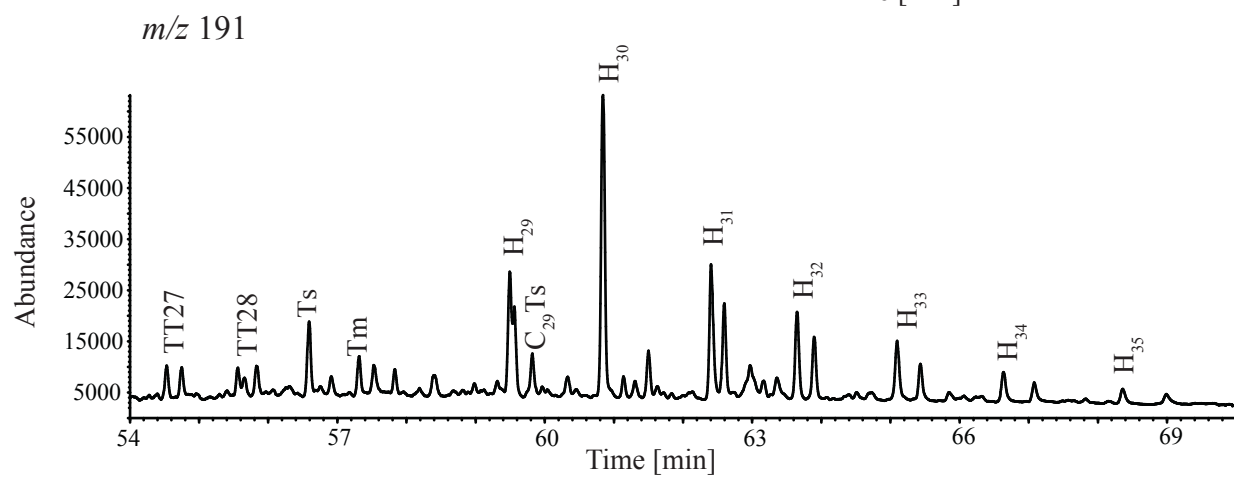
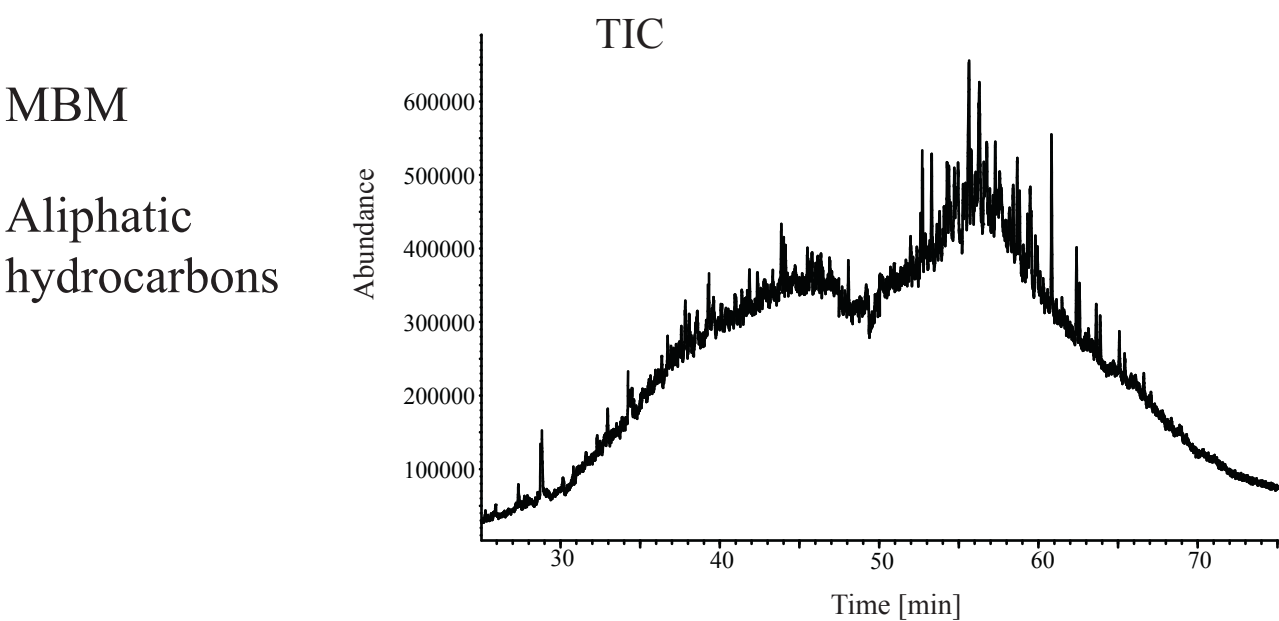
MBC

Aliphatic
hydrocarbons



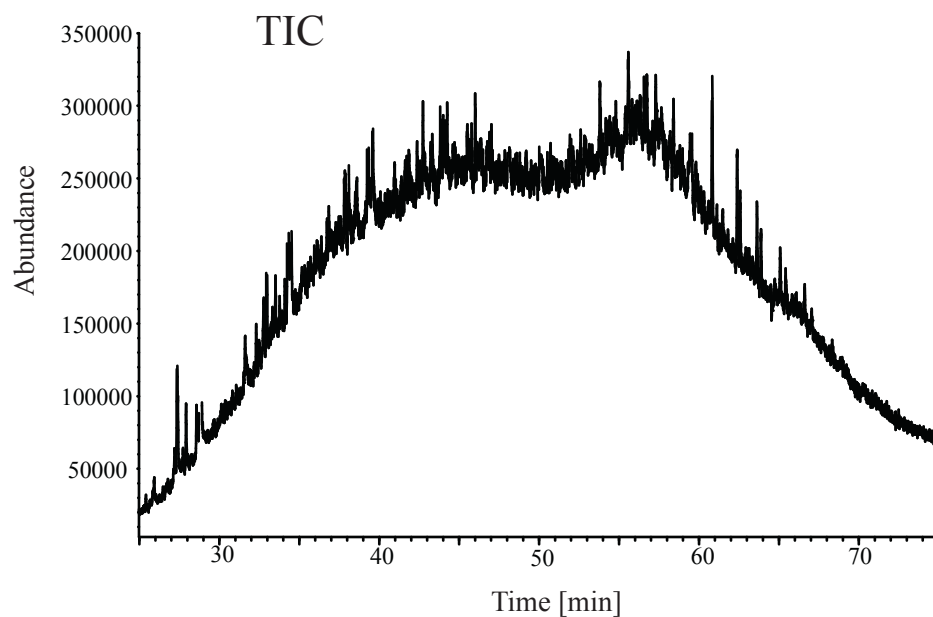
MBM

Aliphatic
hydrocarbons

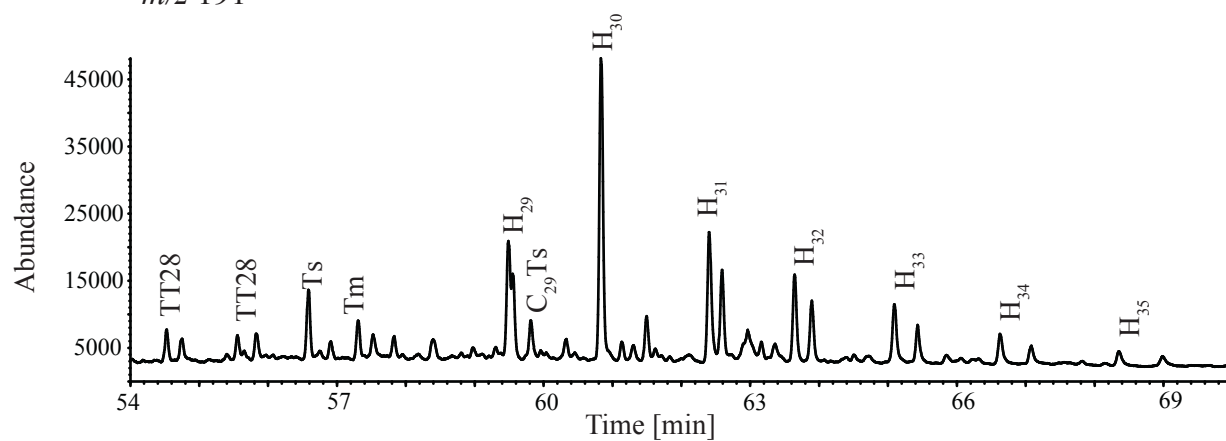


LC

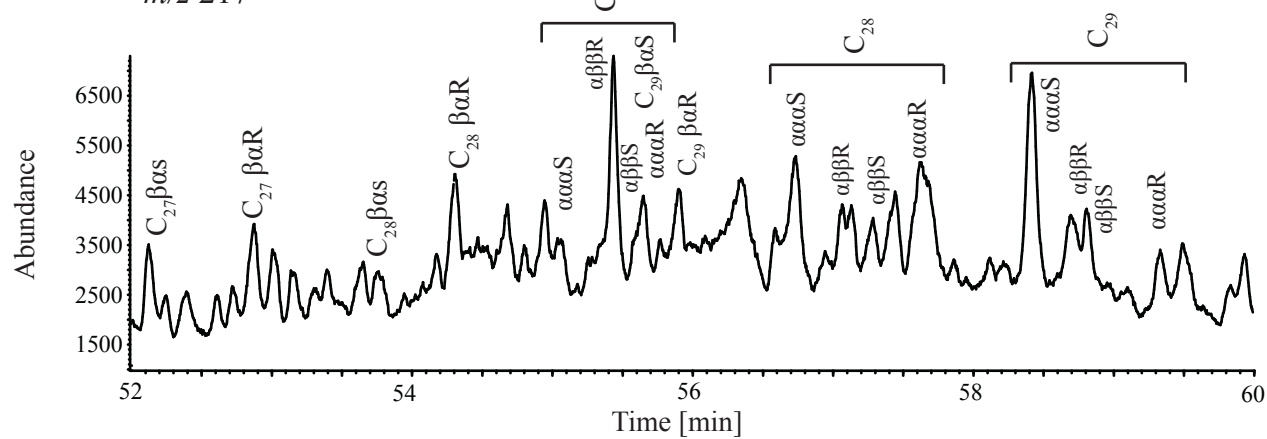
Aliphatic
hydrocarbons



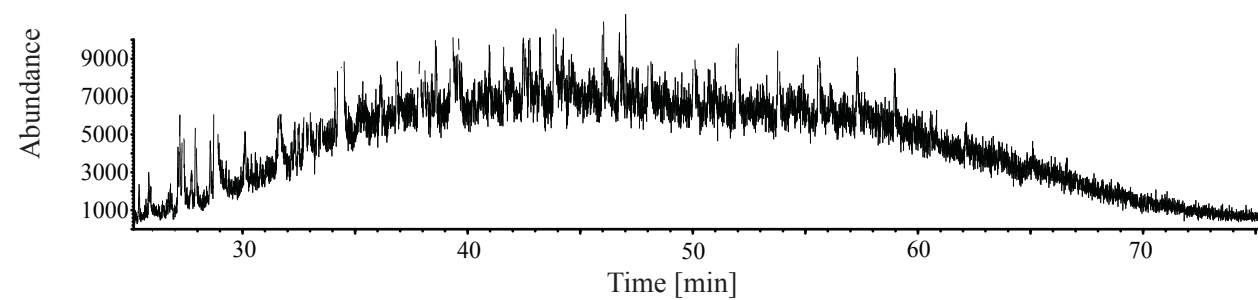
m/z 191



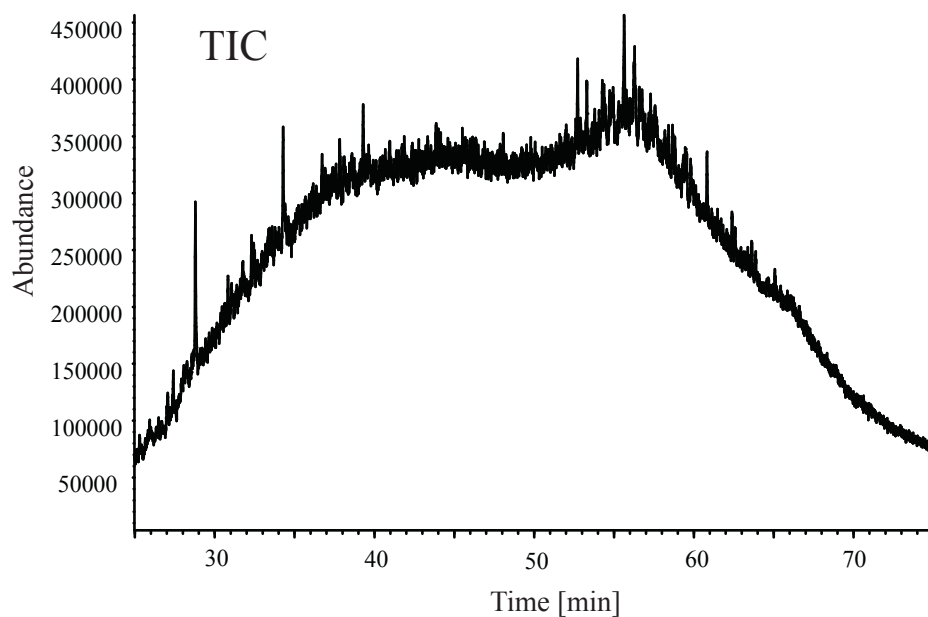
m/z 217



m/z 57



Aliphatic hydrocarbons



Chromatogram showing the abundance of various compounds over time. The x-axis represents Time [min] from 54 to 69. The y-axis represents Abundance from 2000 to 18000. The peaks are labeled as follows:

Compound	Approximate Time [min]	Approximate Abundance
TT27	54.5	5000
TT28	55.5	5000
Ts	56.5	10000
Tm	57.5	4000
H ₂₉	59.5	9000
C ₂₉ Ts	60.0	6000
H ₃₀	60.5	18000
H ₃₁	62.5	10000
H ₃₂	63.5	7000
H ₃₃	65.0	5000
H ₃₄	66.5	4000
H ₃₅	68.5	2000

Organic Geochemistry

1.2 FTIR spectra and asphaltene chromatograms

FTIR Spectra: Spectra analysis for FT-IR between $500\text{-}4000\text{cm}^{-1}$ wavelengths

TIC chromatogram: Total Ion Current chromatogram of the whole asphaltene extract

***m/z* 57 chromatogram:** Ion extraction 57 to identify *n*-alkanes within the asphaltene fractions

Compounds identified and labelled on the chromatograms:

FTIR:

C-H Sat: methylene/methyl bands ($2960\text{-}2860\text{ cm}^{-1}$, $\sim 1470\text{ cm}^{-1}$, $\sim 1380\text{ cm}^{-1}$)

C=O ($\sim 1700\text{ cm}^{-1}$)

C=C ($\sim 1510\text{ cm}^{-1}$)

N-O ($\sim 1540\text{ cm}^{-1}$)

C-O ($1150\text{-}1200\text{ cm}^{-1}$)

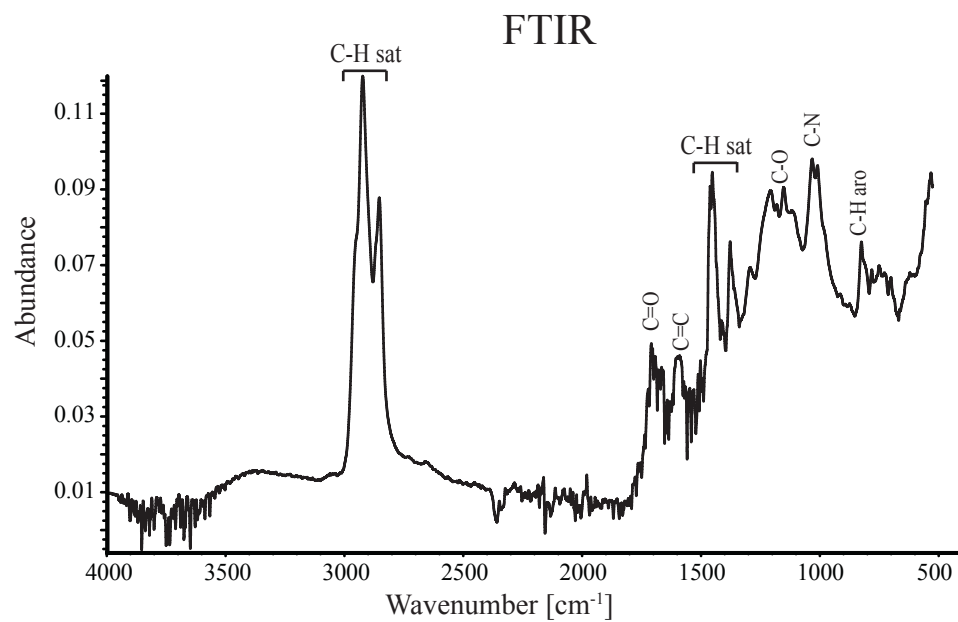
C-N ($1090\text{-}1020\text{ cm}^{-1}$).

C-H aro: aromatic ring related vibrations ($900\text{-}670\text{ cm}^{-1}$)

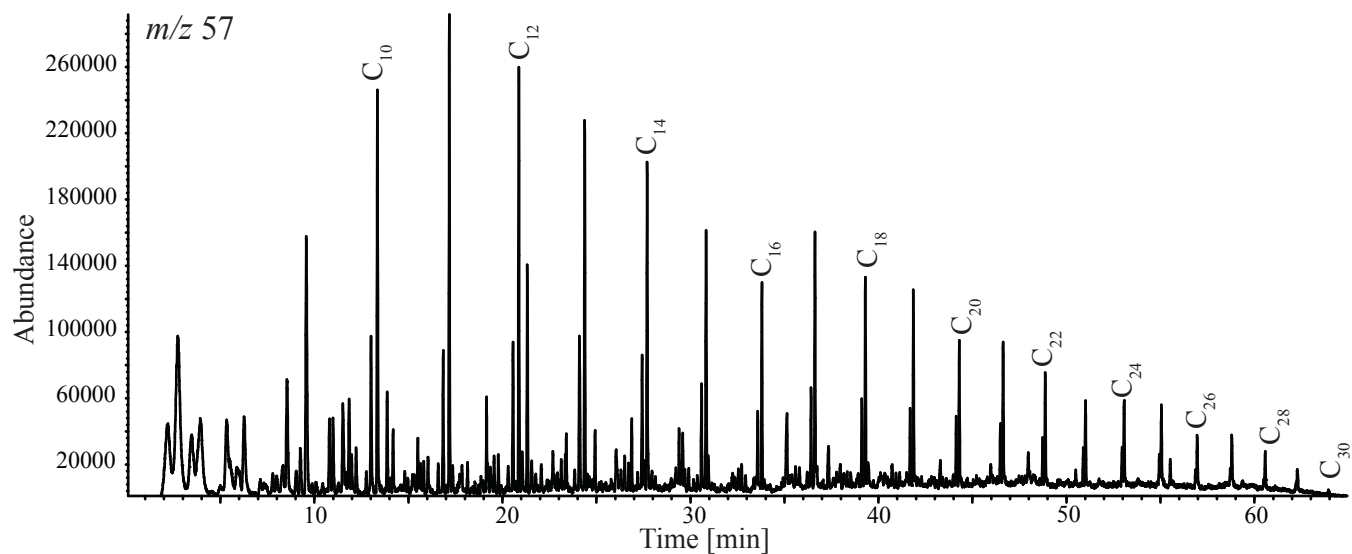
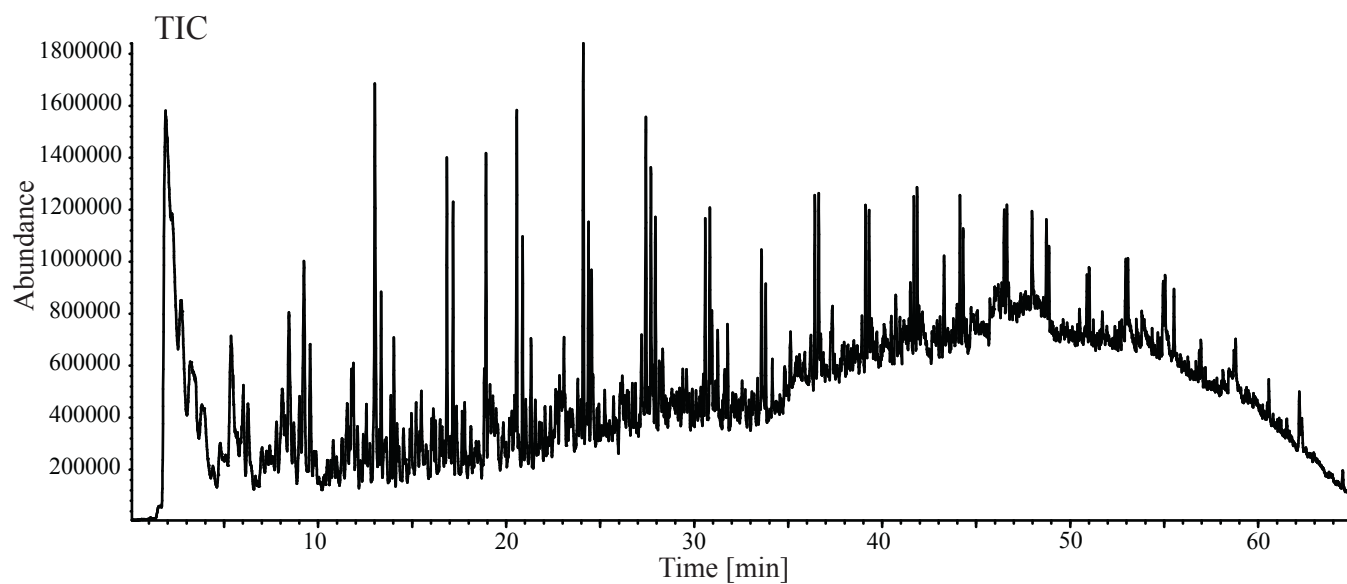
m/z 57

C₉-C₃₀: *n*-alkanes between C₉-C₃₀

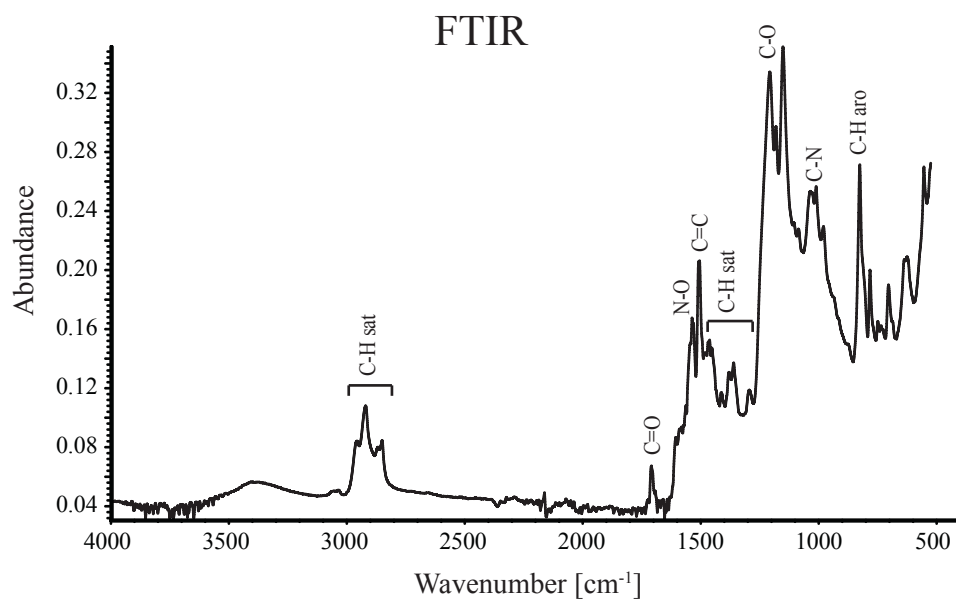
A1B



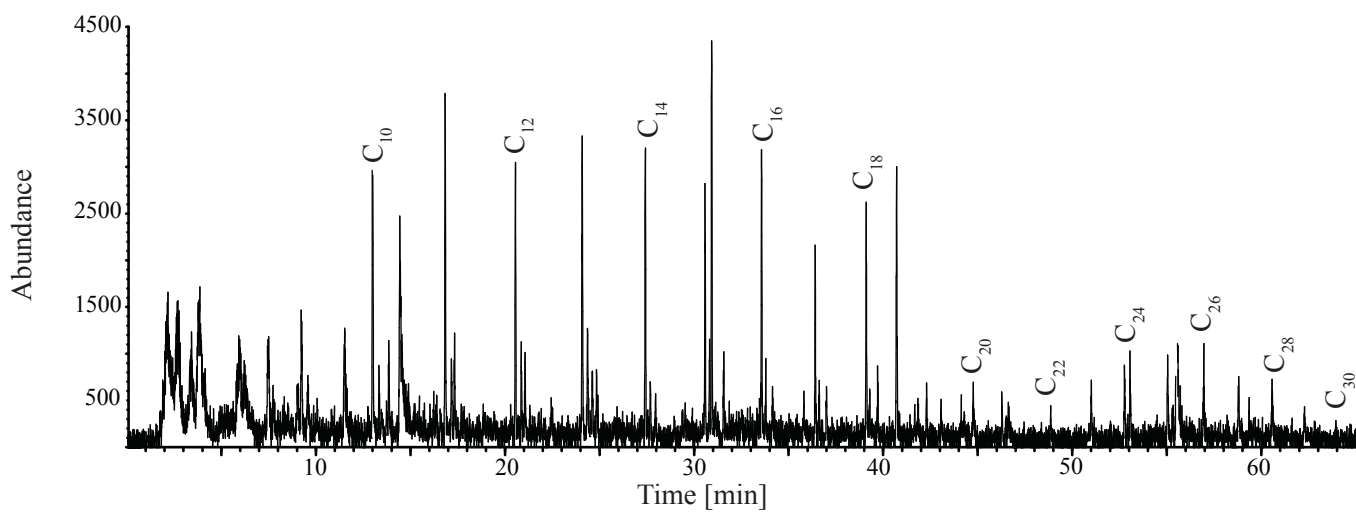
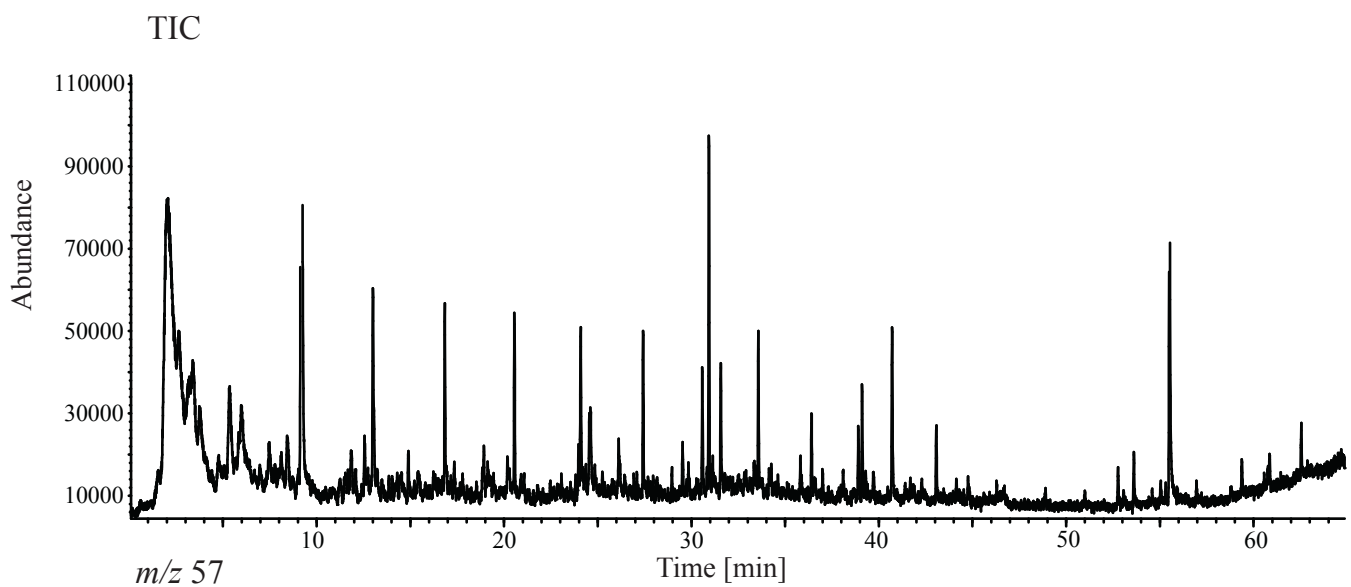
Asphaltene Pyrolysis



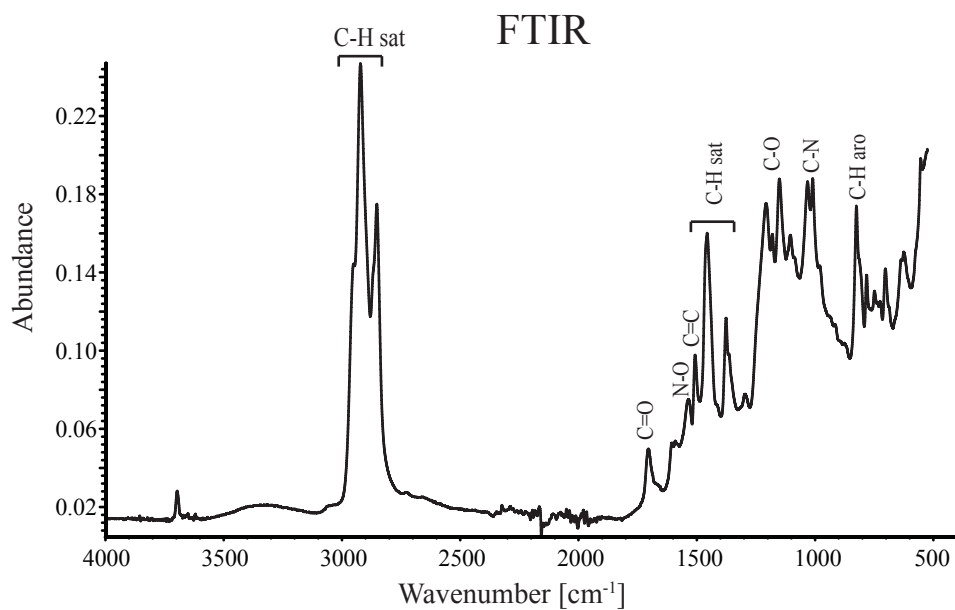
A3B



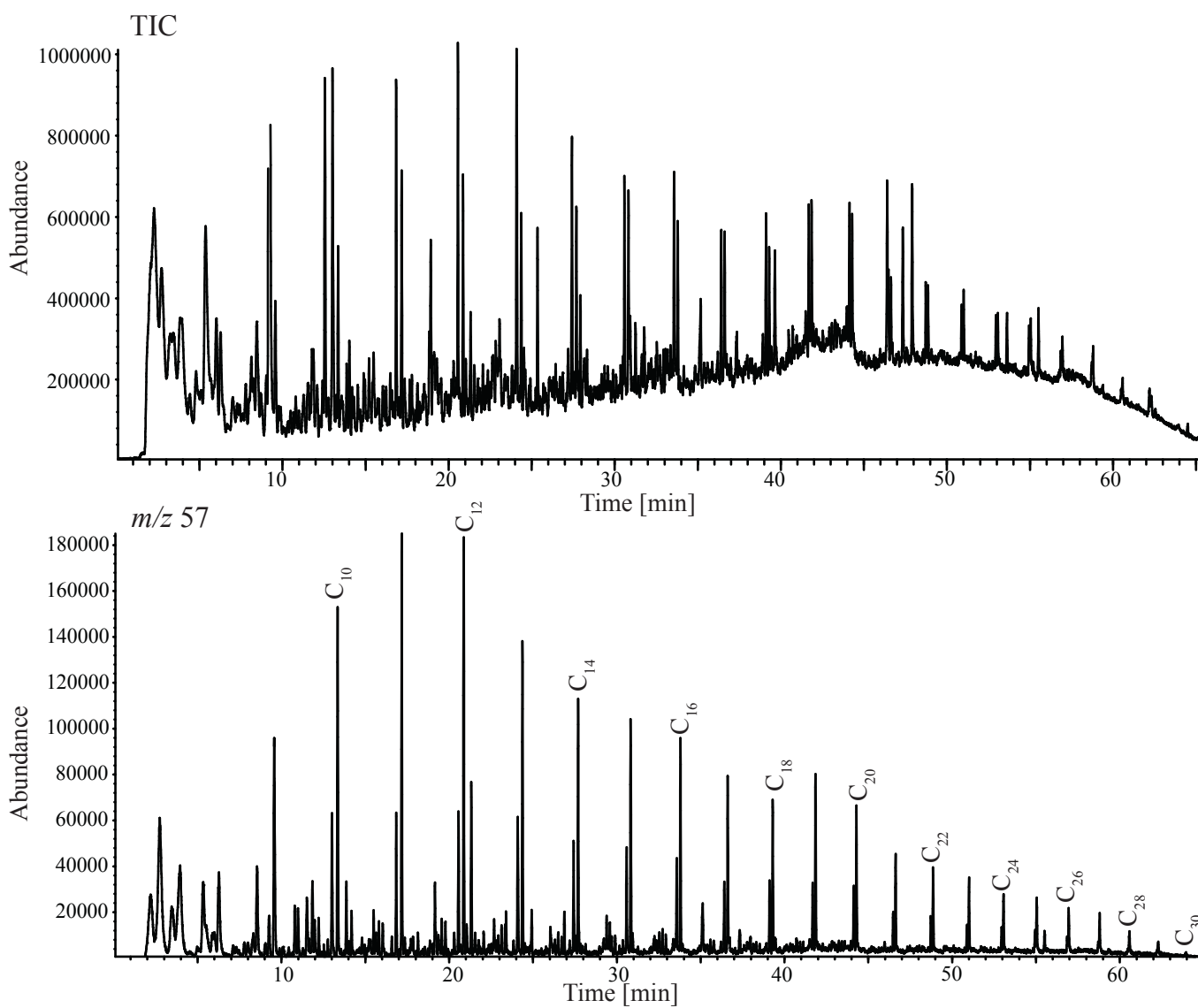
Asphaltene Pyrolysis



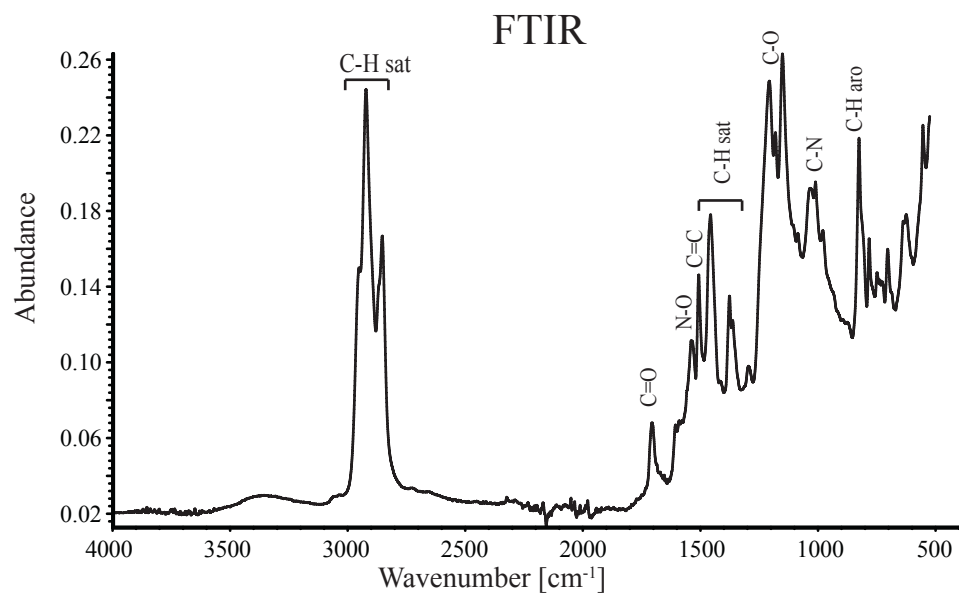
A827.32



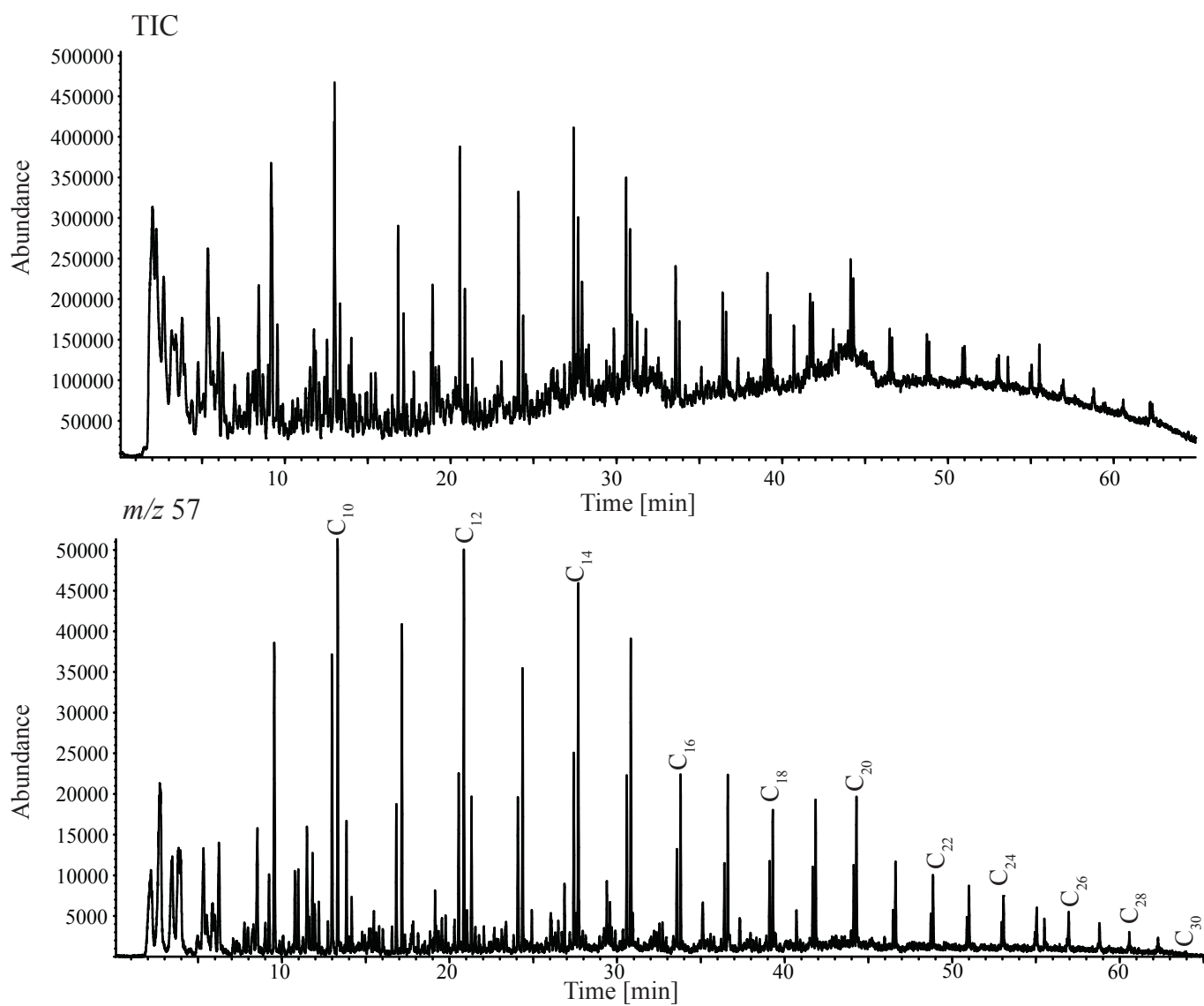
Asphaltene Pyrolysis



A827.75



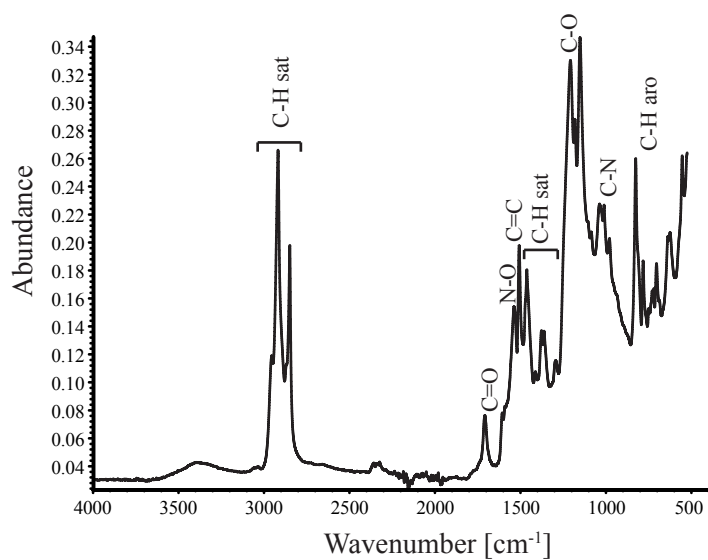
Asphaltene Pyrolysis



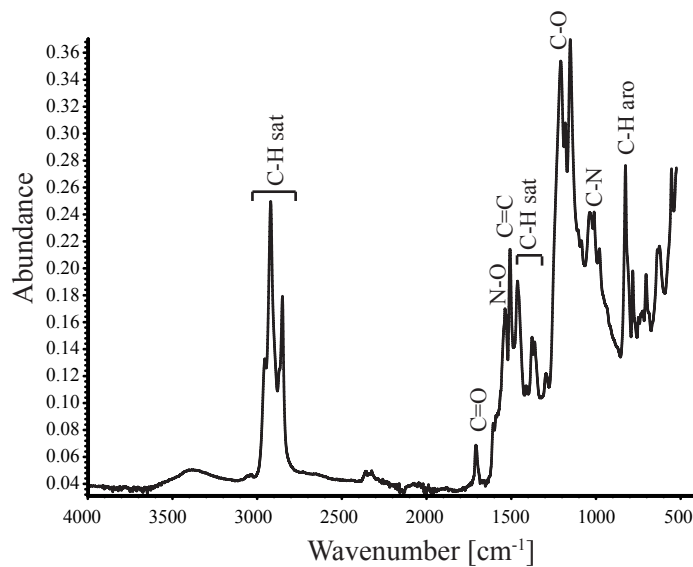
Colombia FTIR

No asphlatenes present

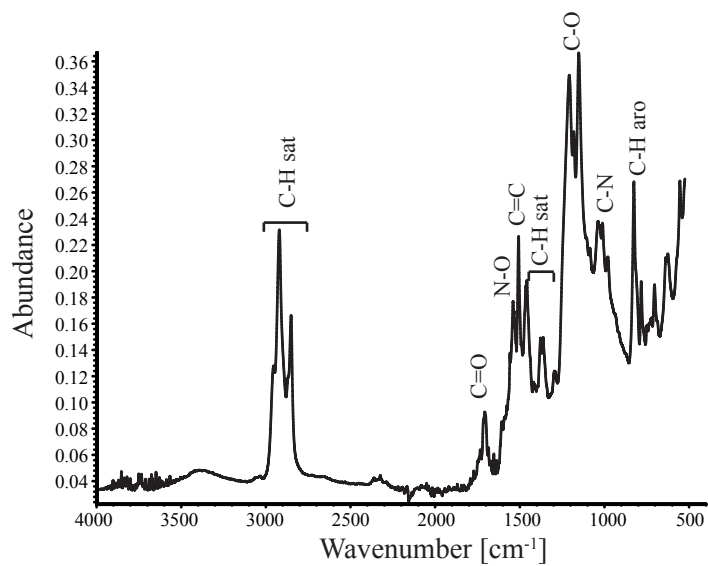
C127.40



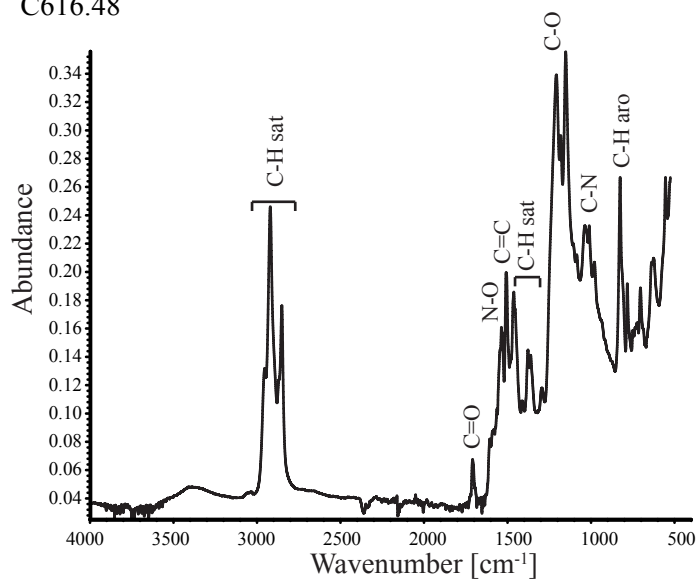
C541.75



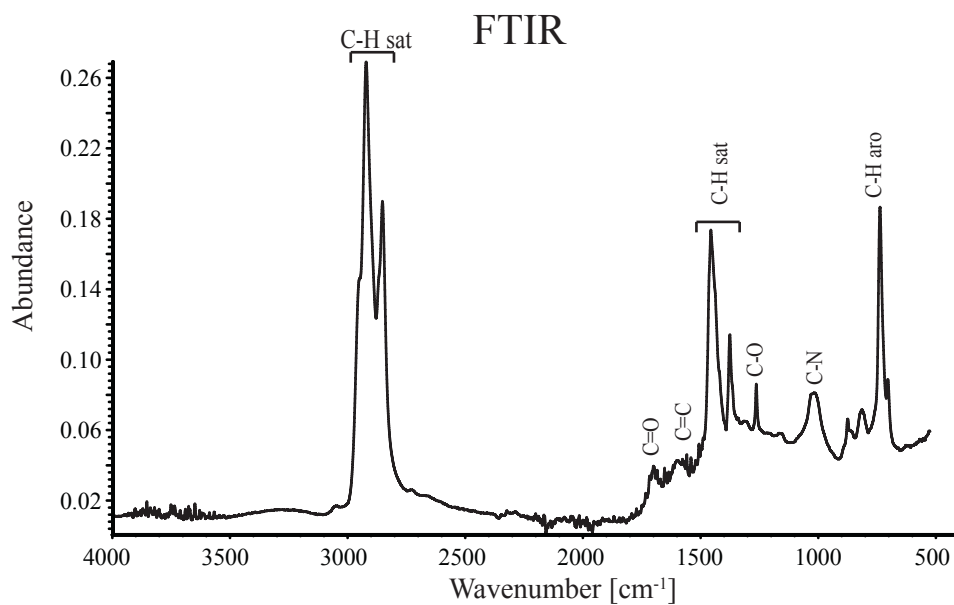
C147.25



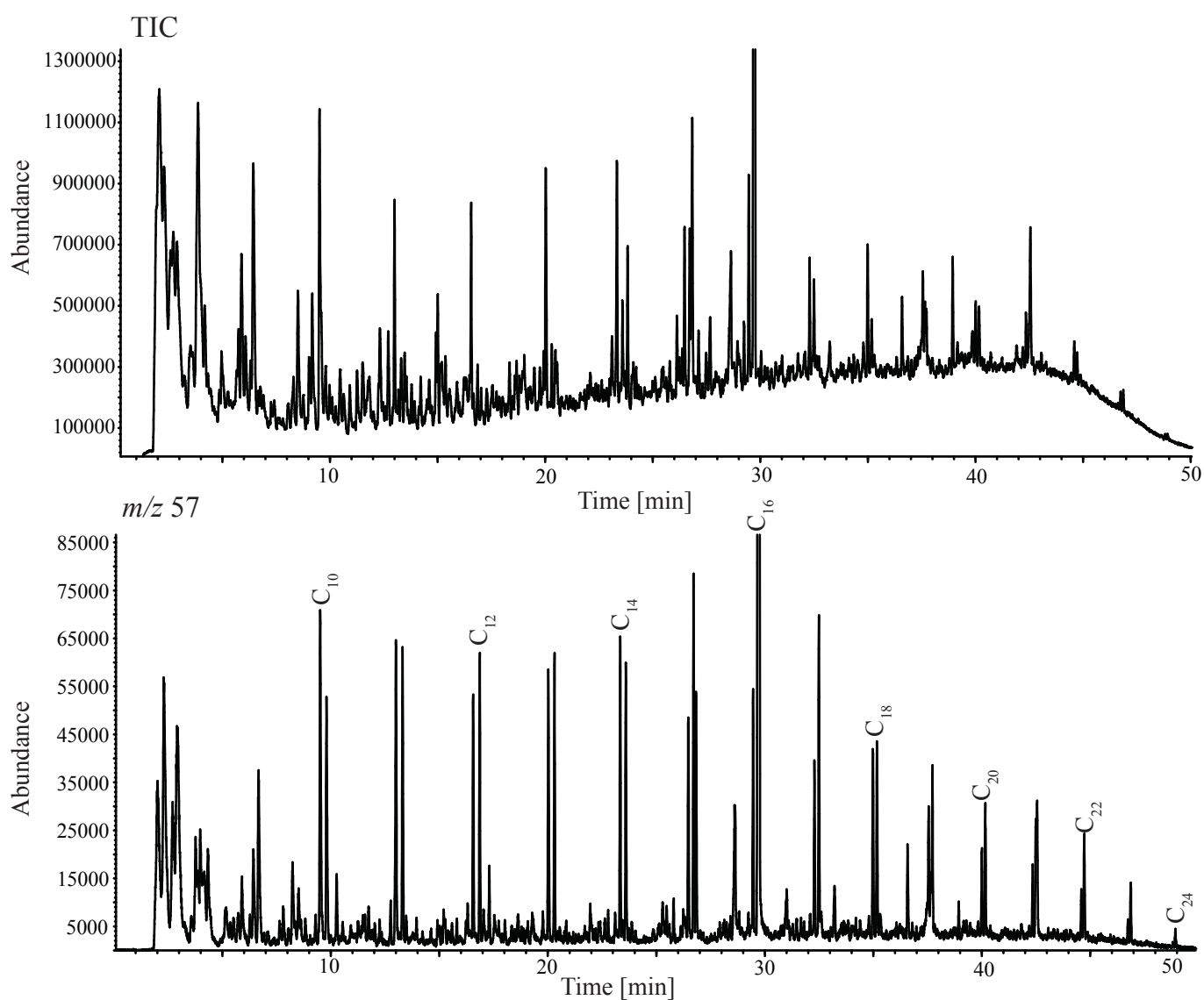
C616.48



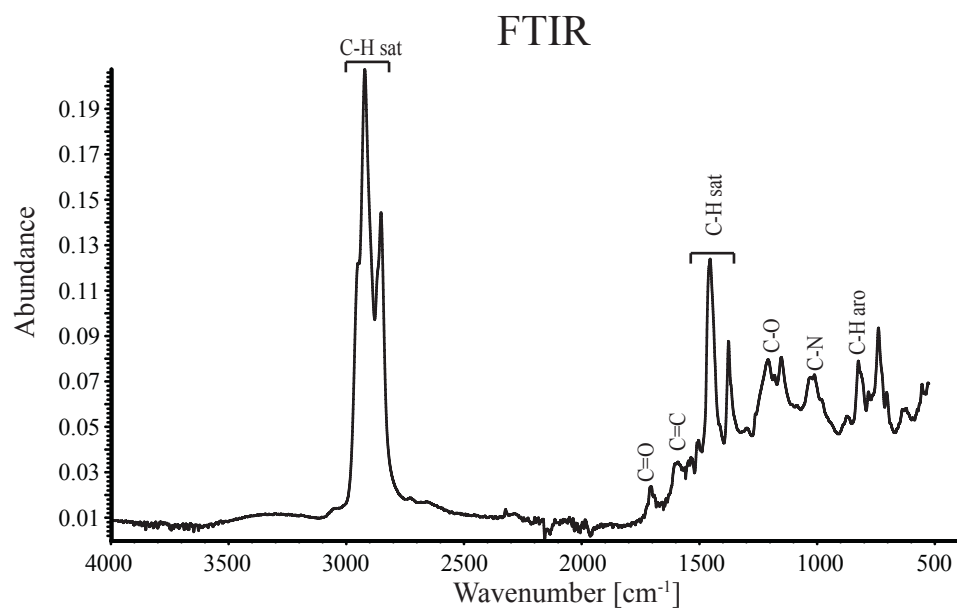
KI



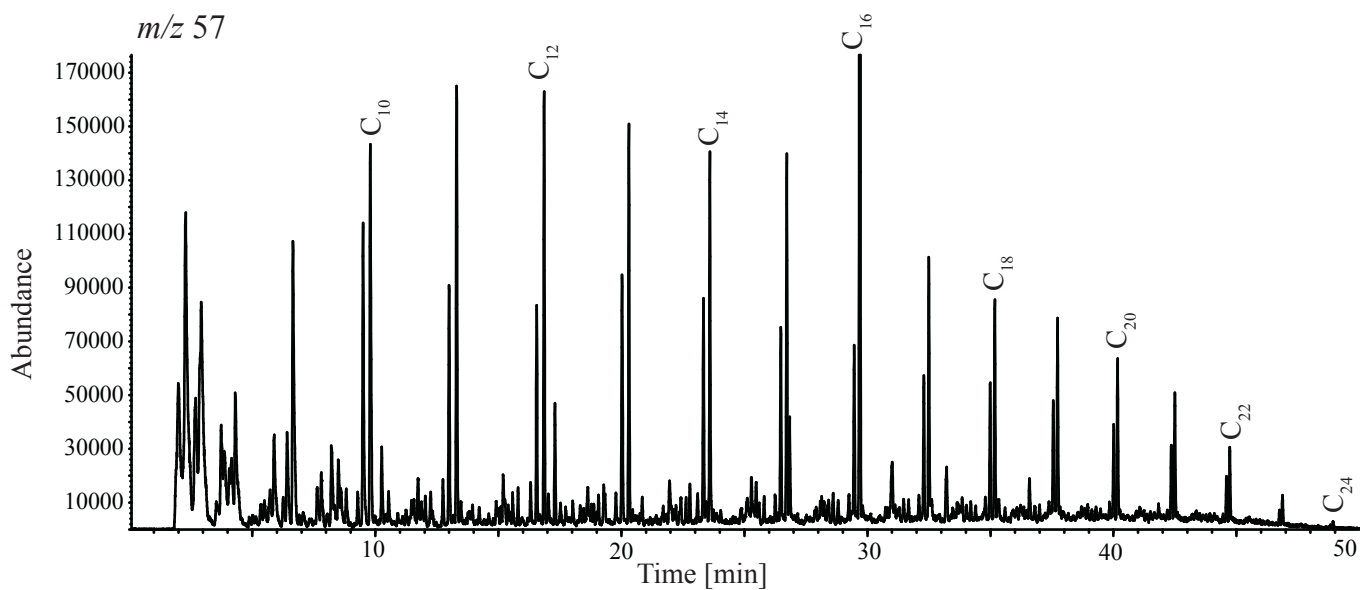
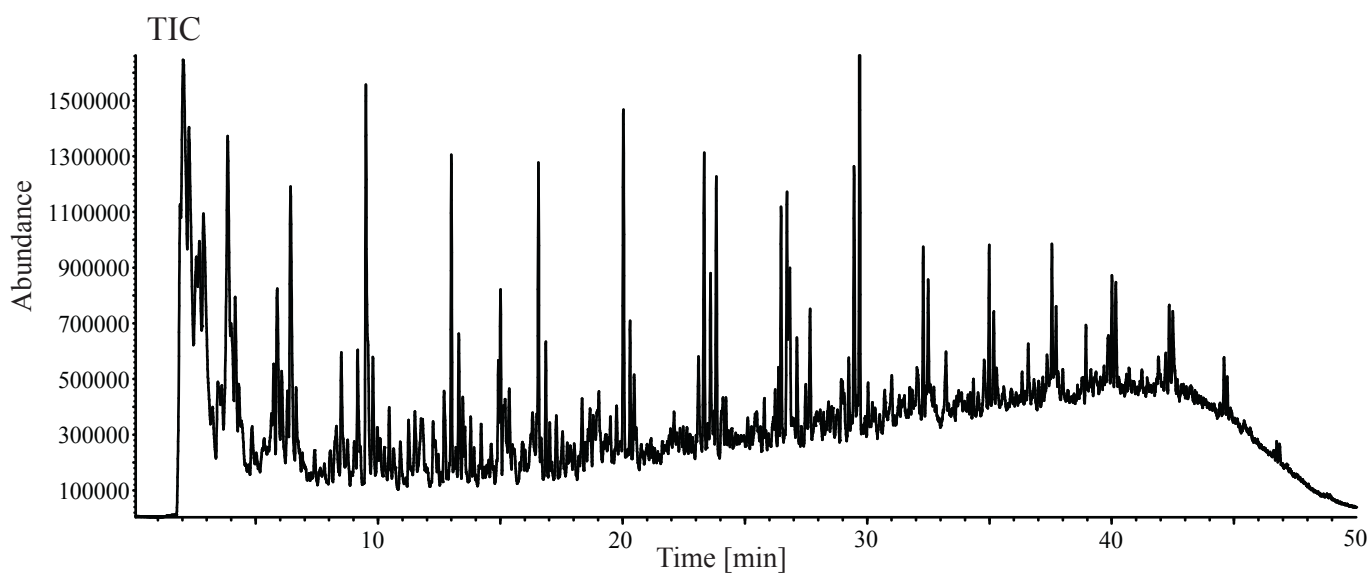
Asphaltene Pyrolysis



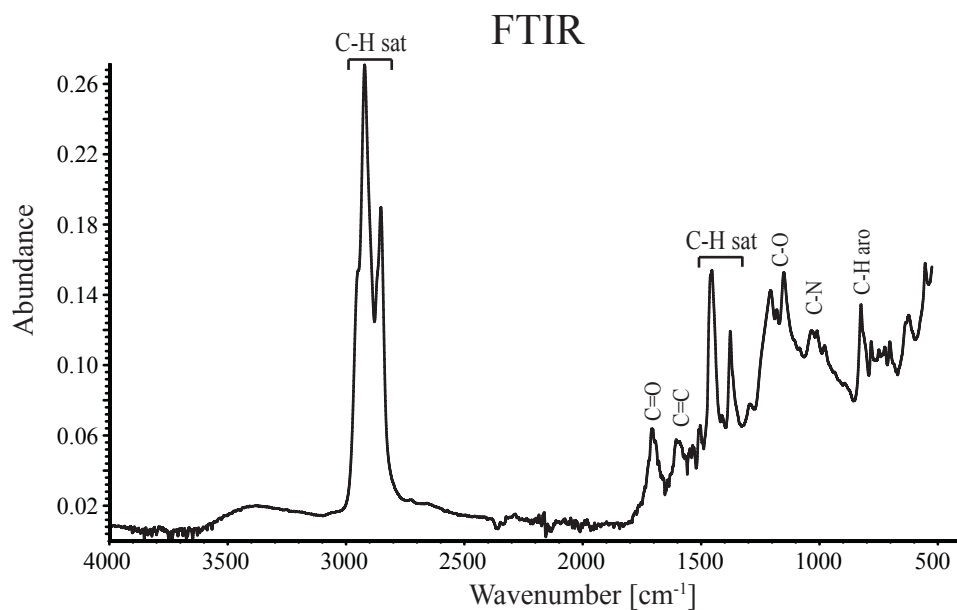
LI



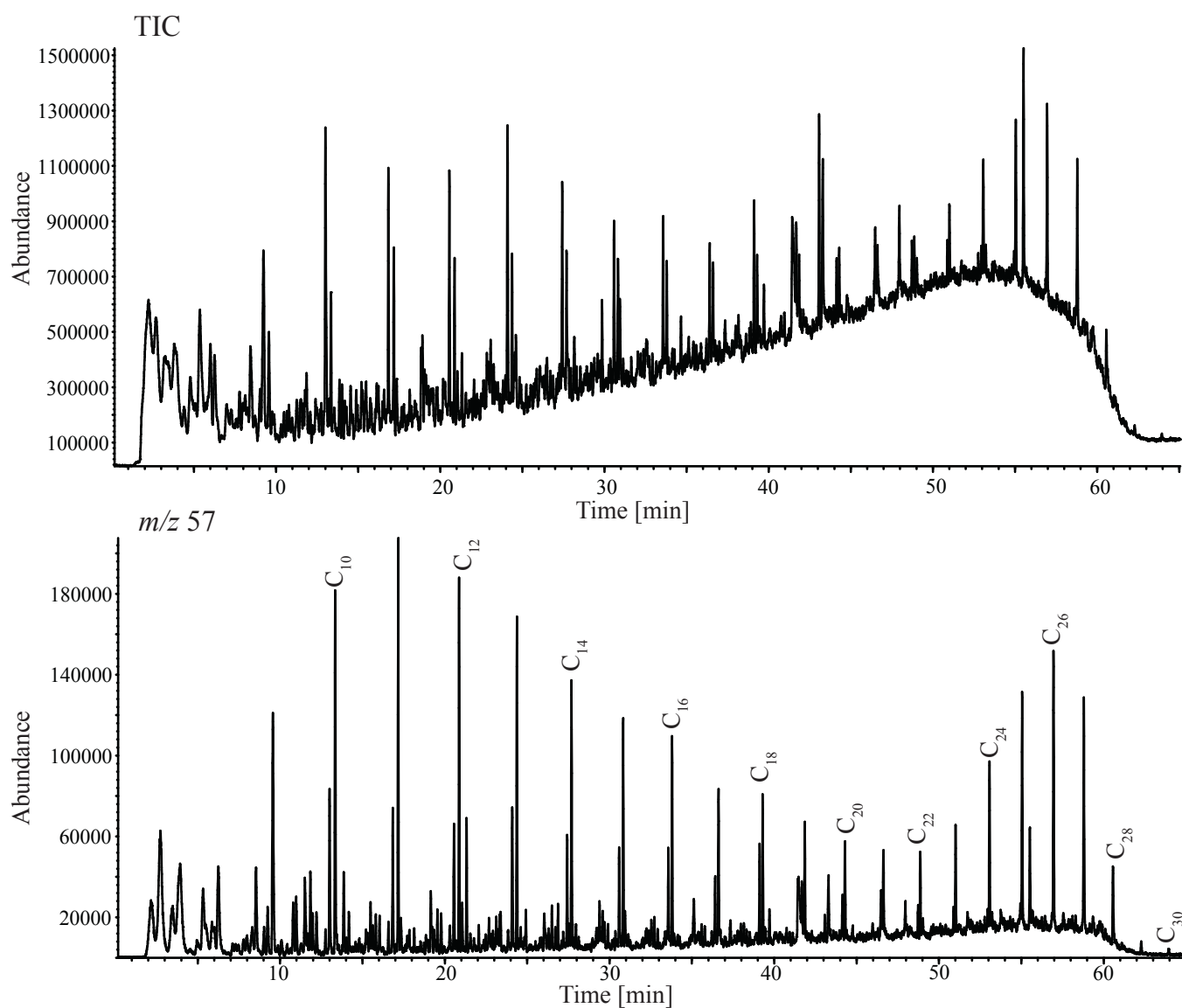
Asphaltene Pyrolysis



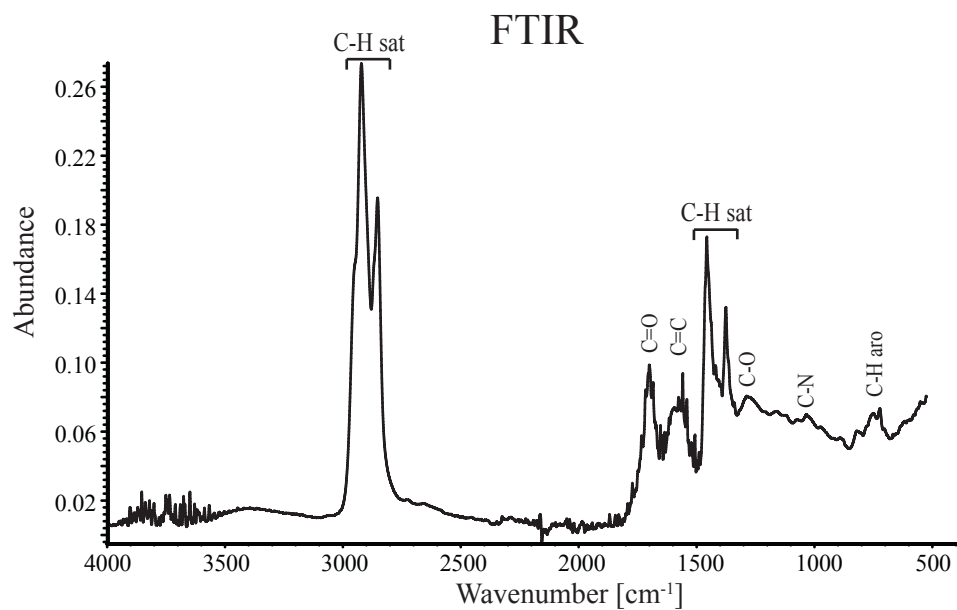
OS2



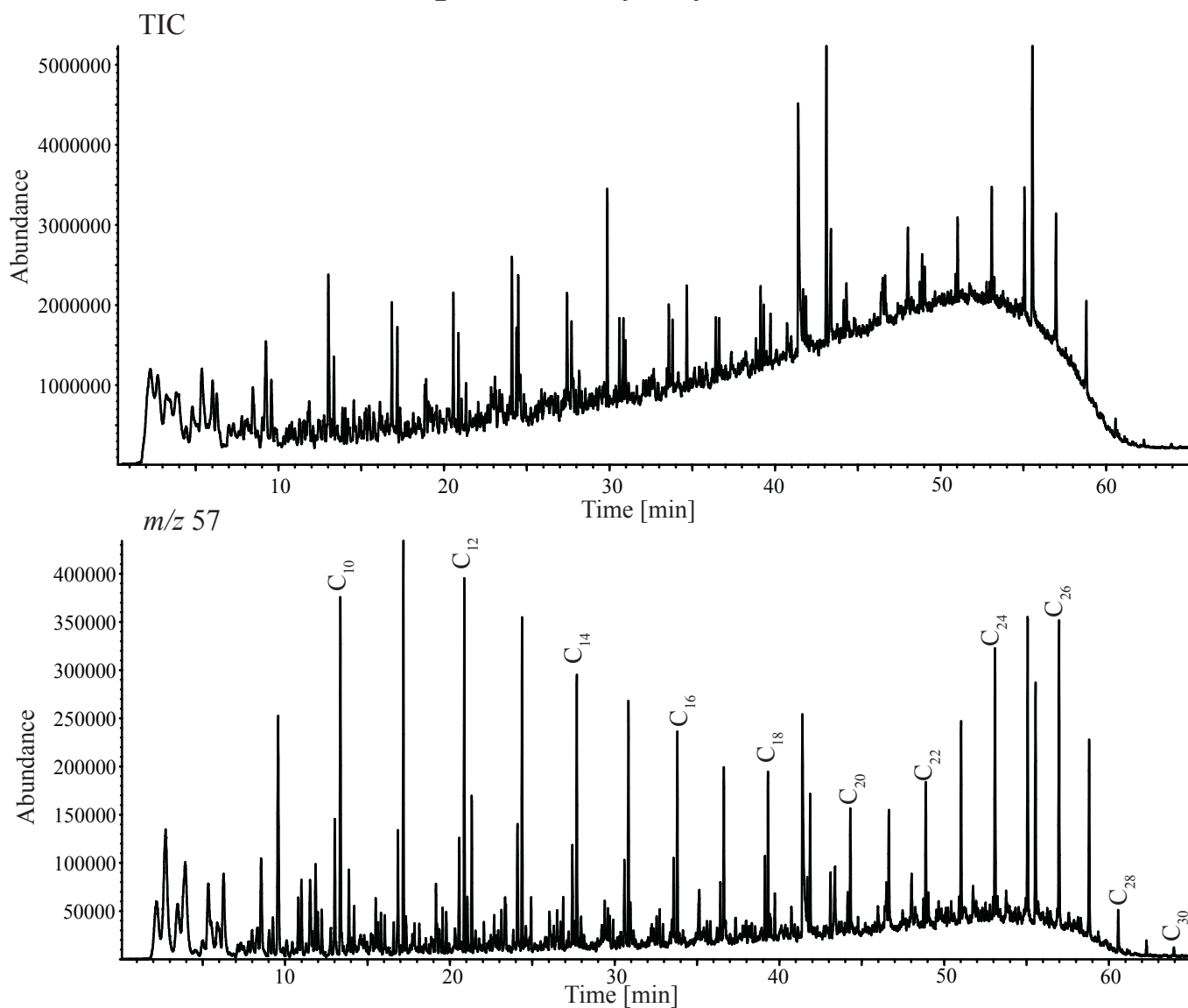
Asphaltene Pyrolysis



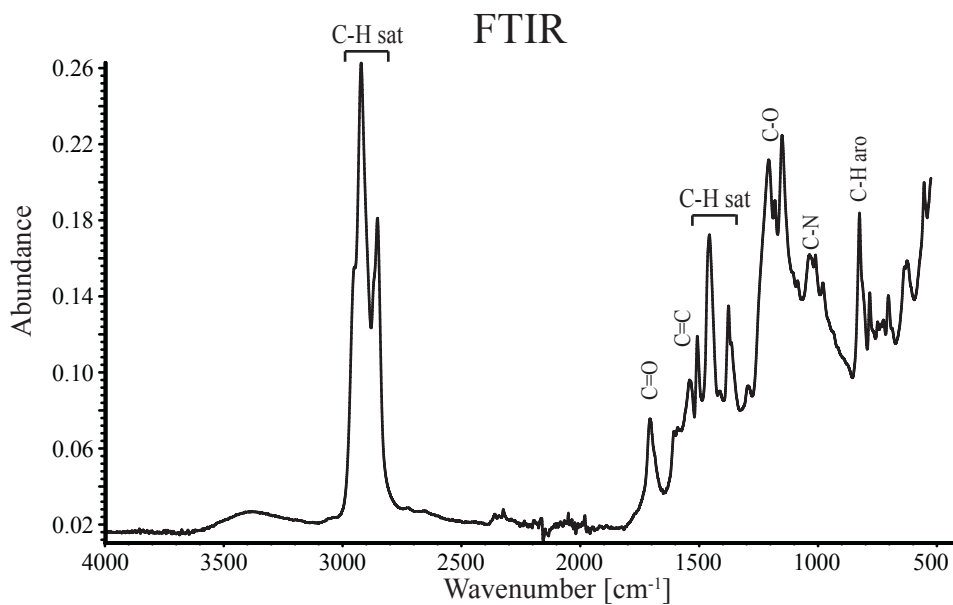
OS3



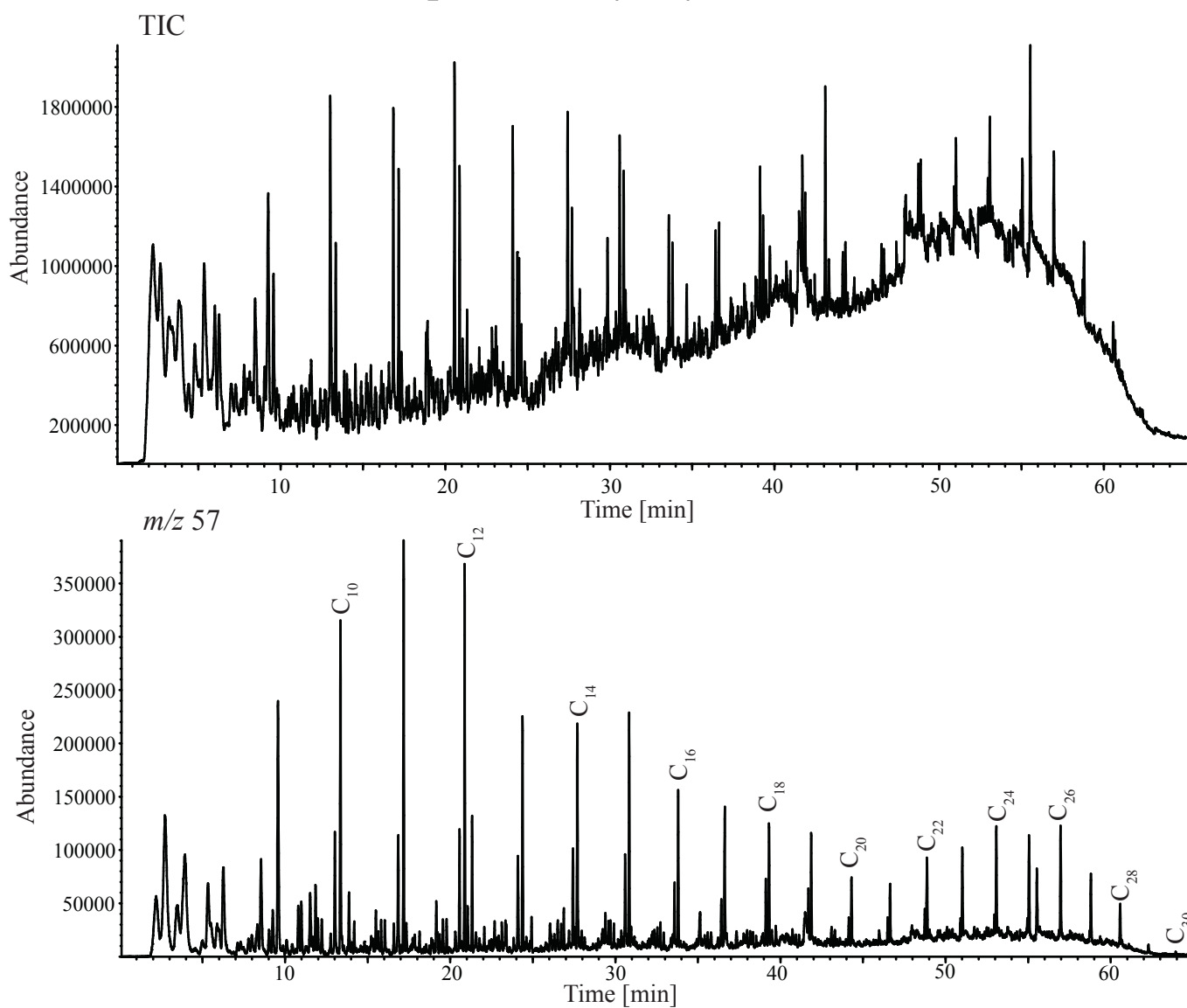
Asphaltene Pyrolysis



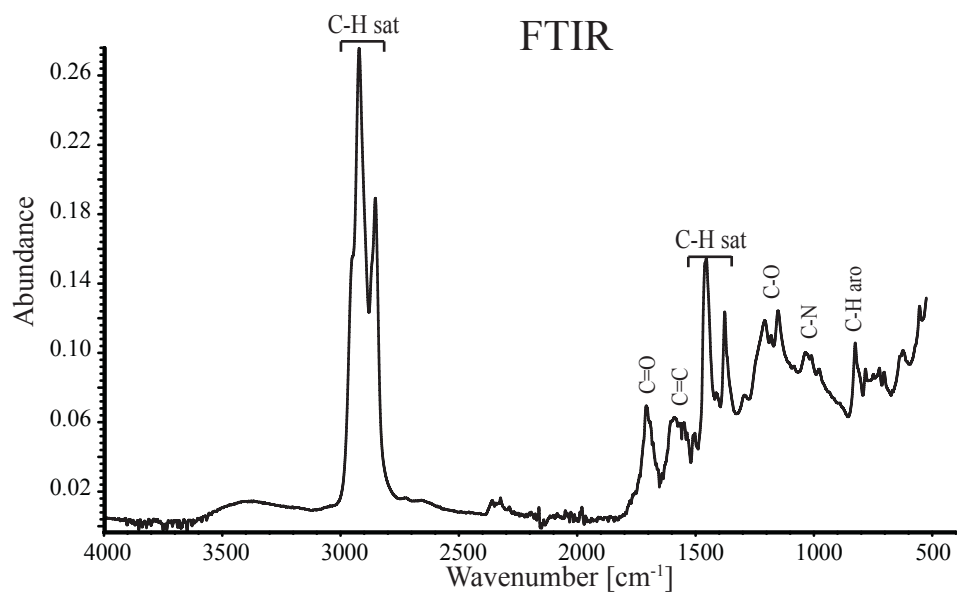
OS4



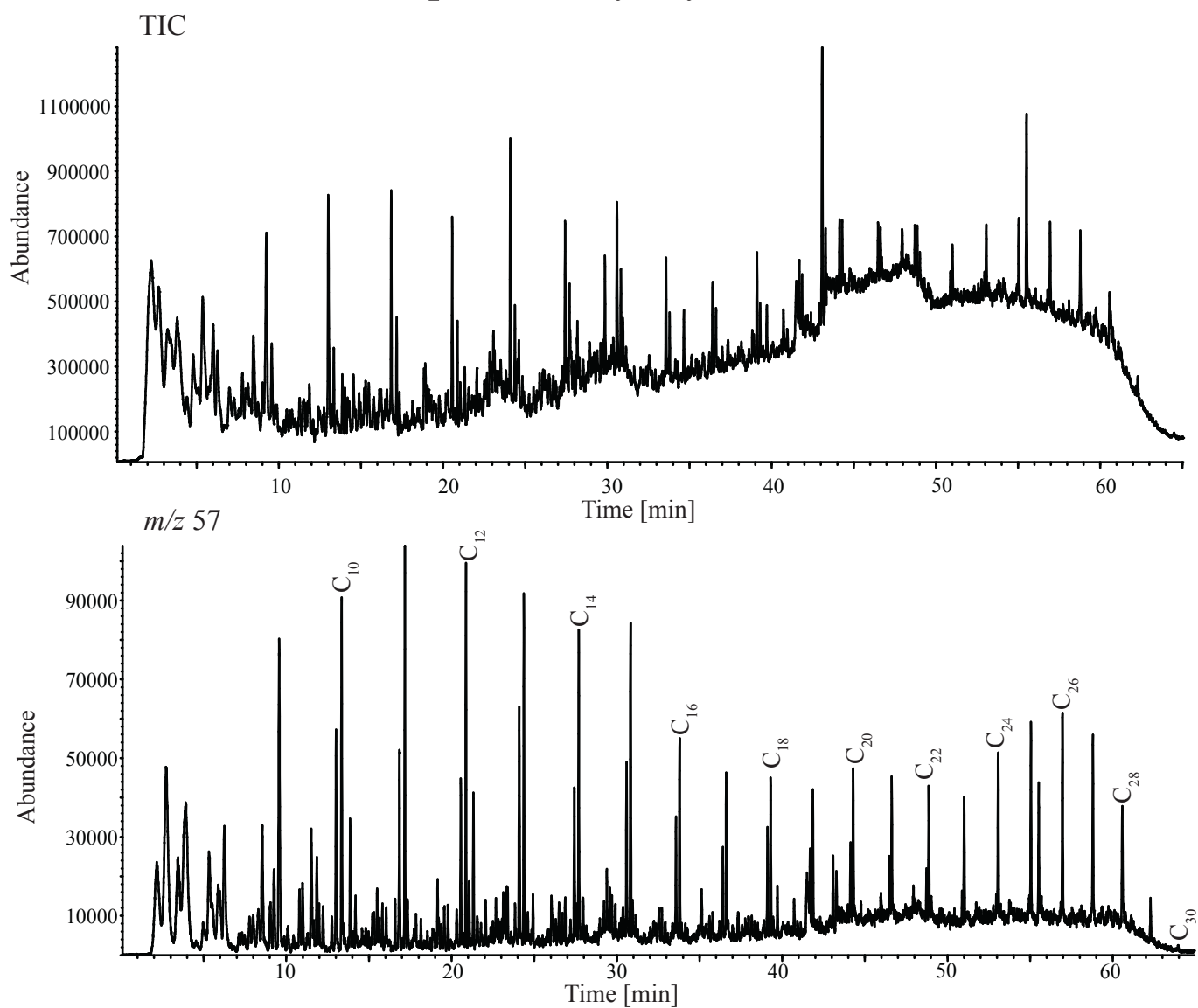
Asphaltene Pyrolysis



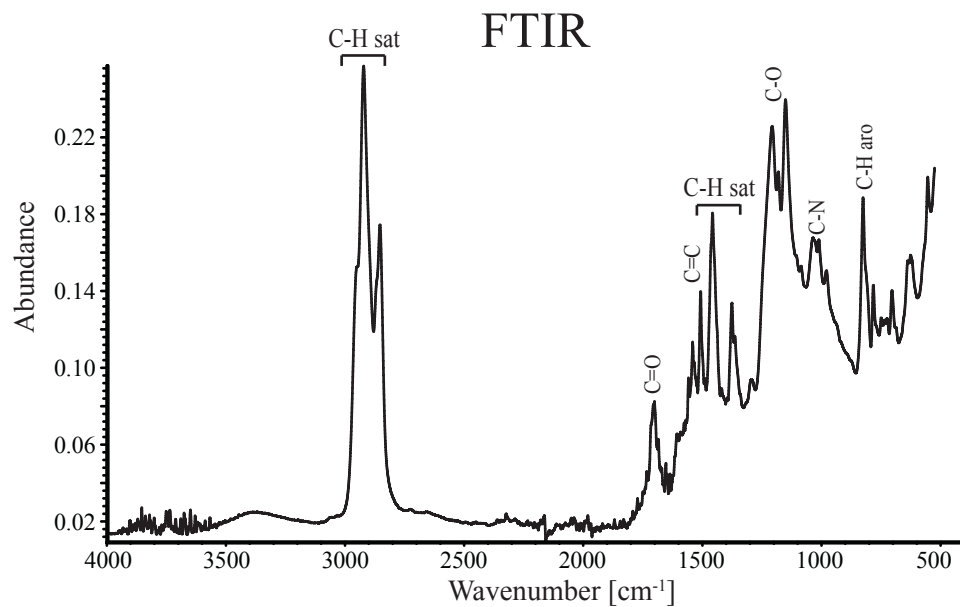
OS5



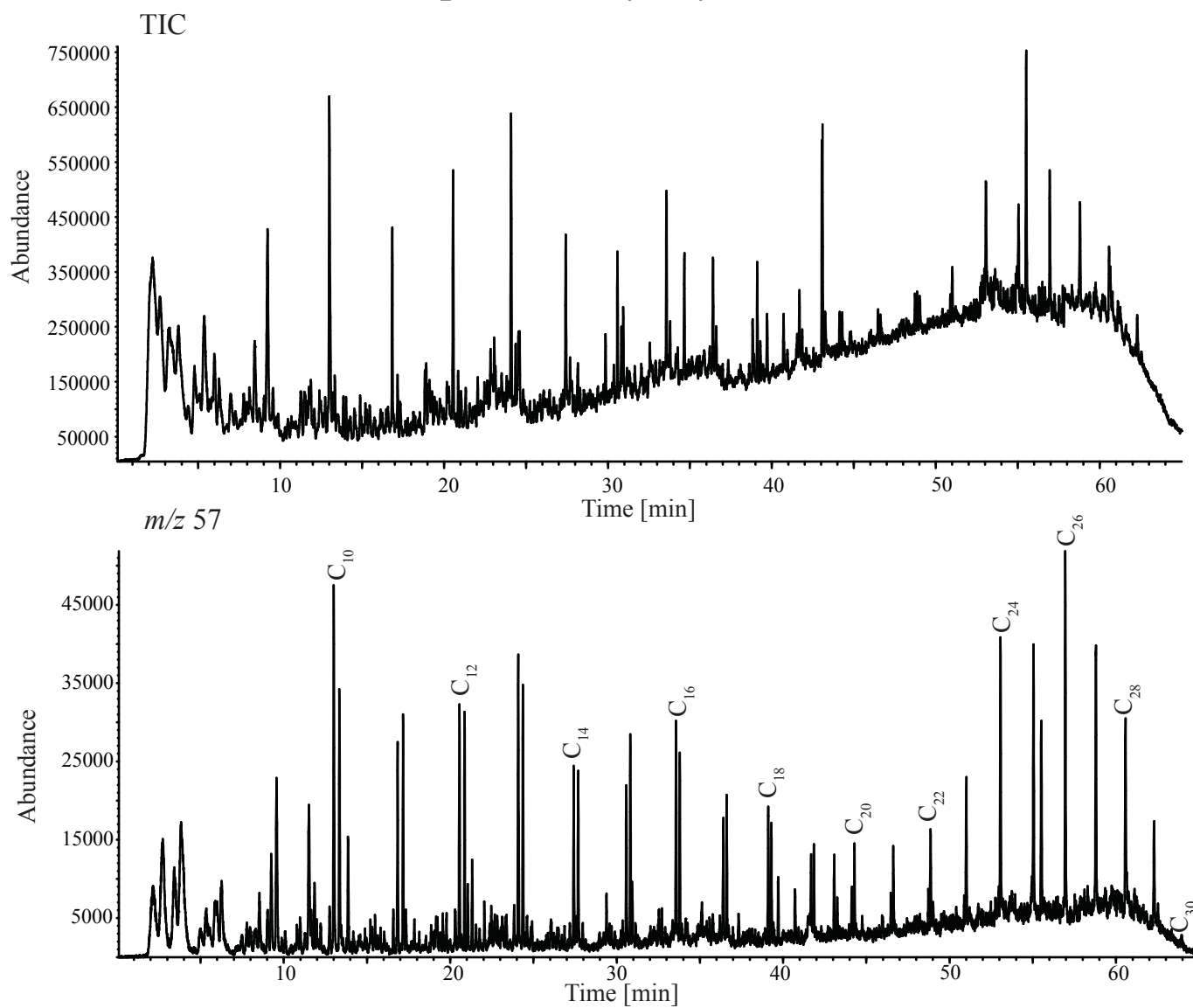
Asphaltene Pyrolysis



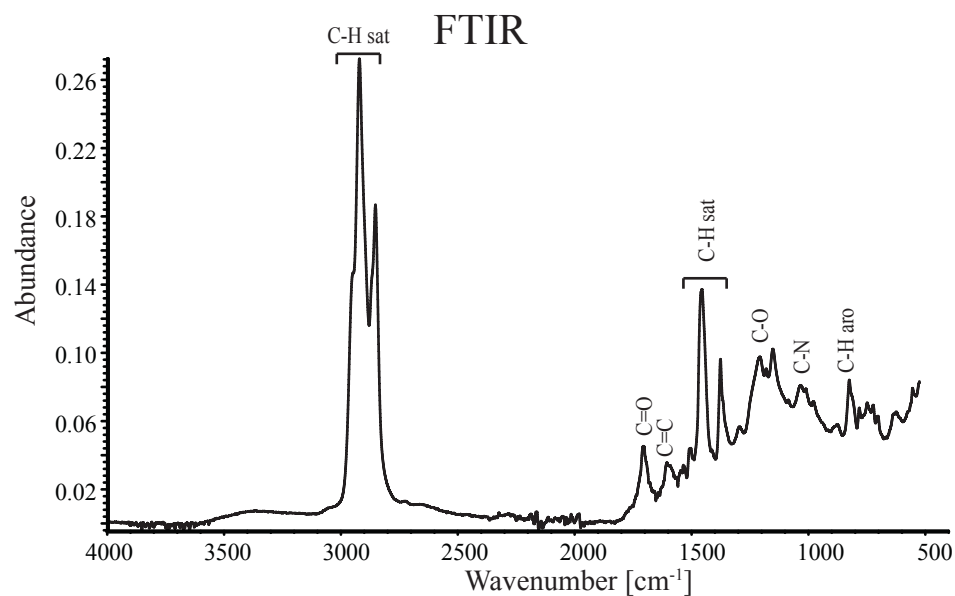
OS6



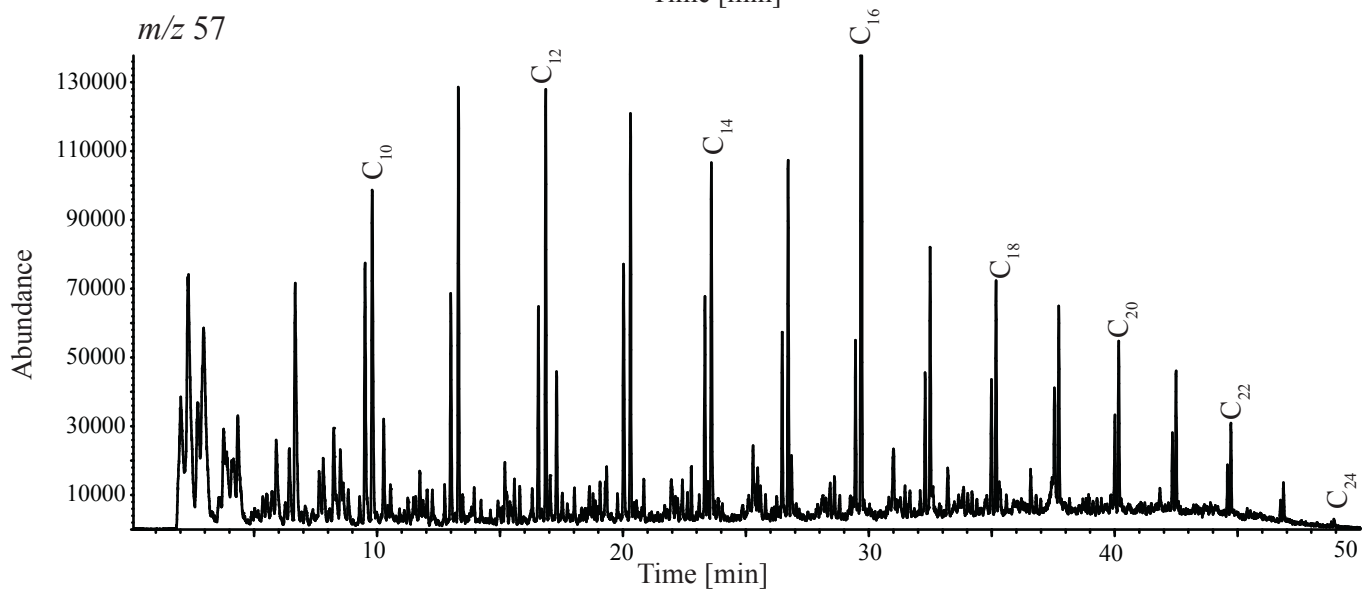
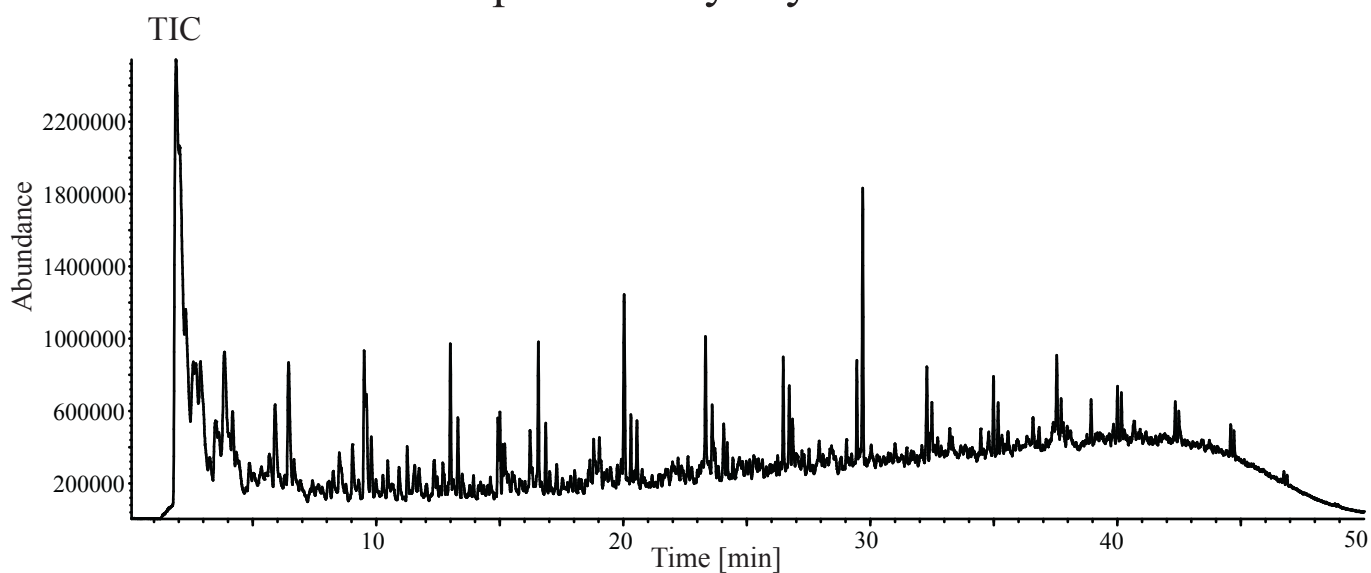
Asphaltene Pyrolysis



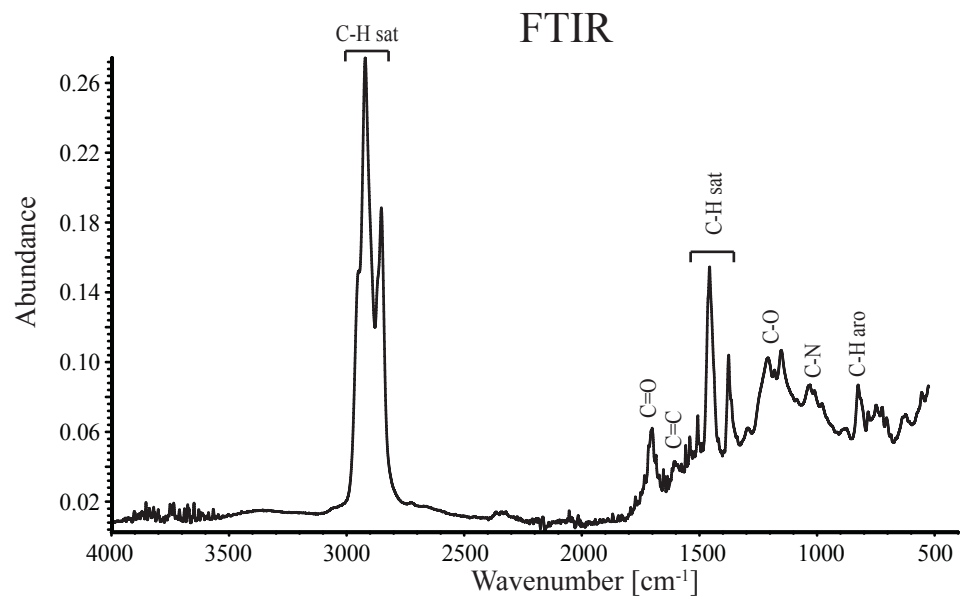
MBC



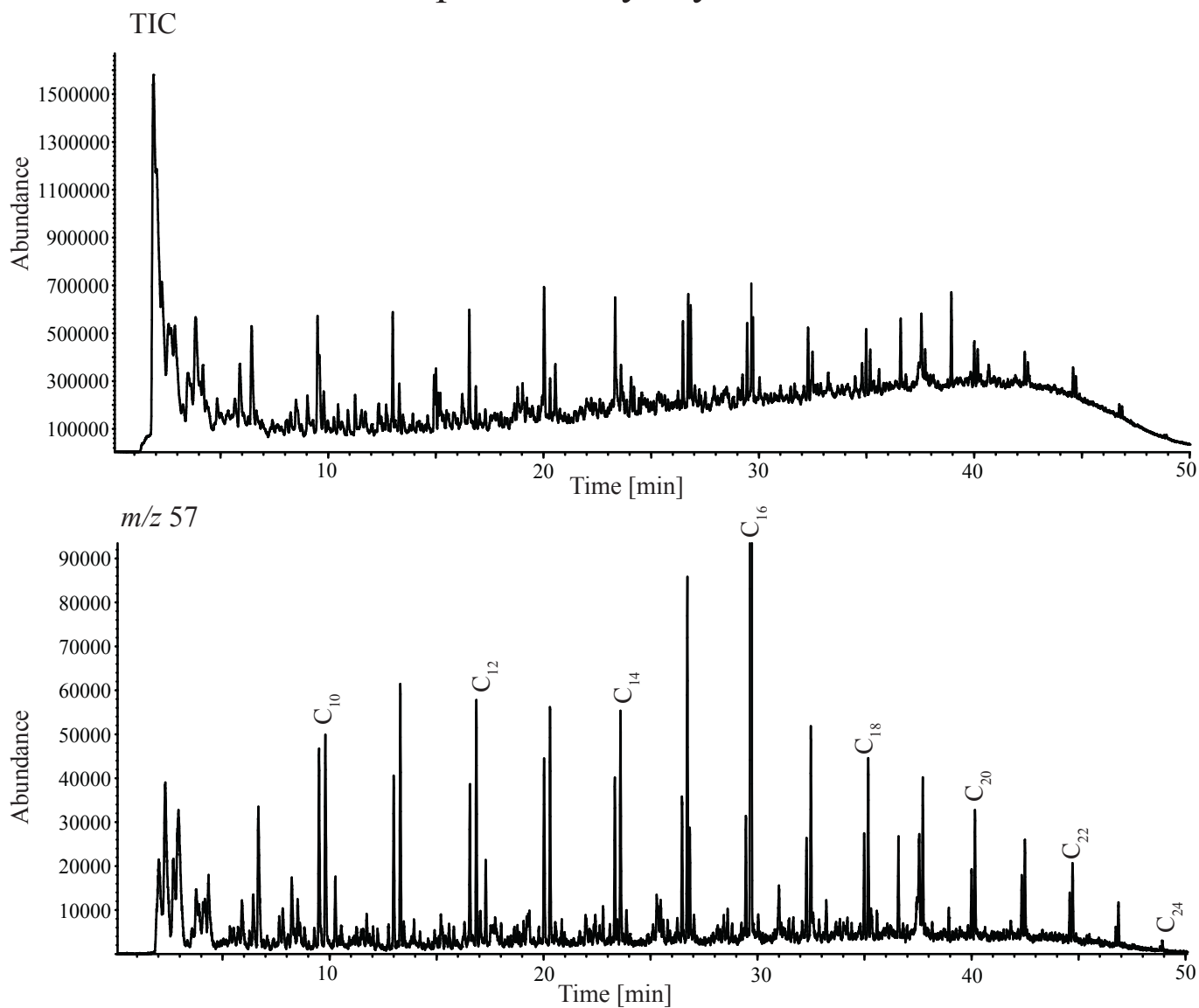
Asphaltene Pyrolysis



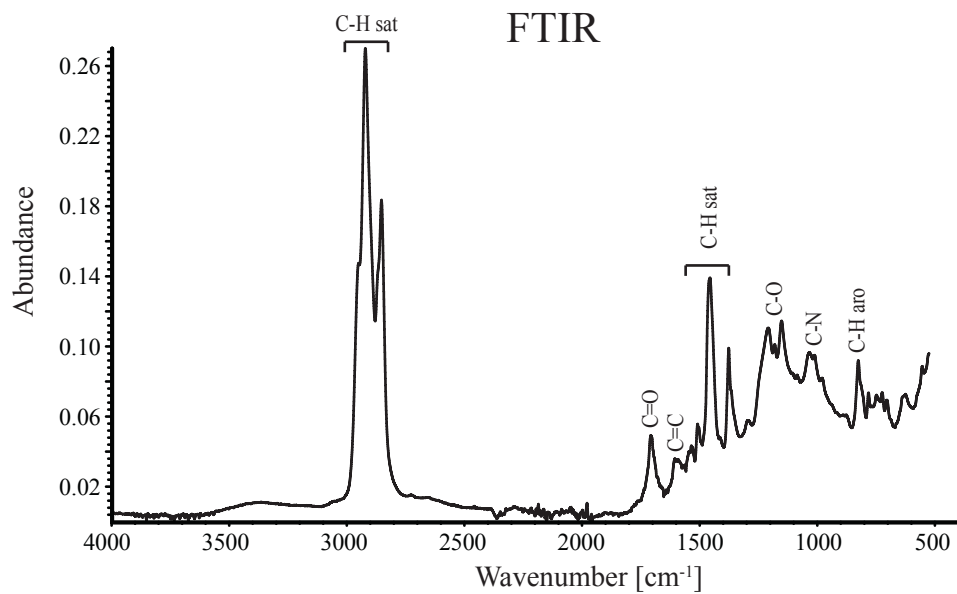
MBM



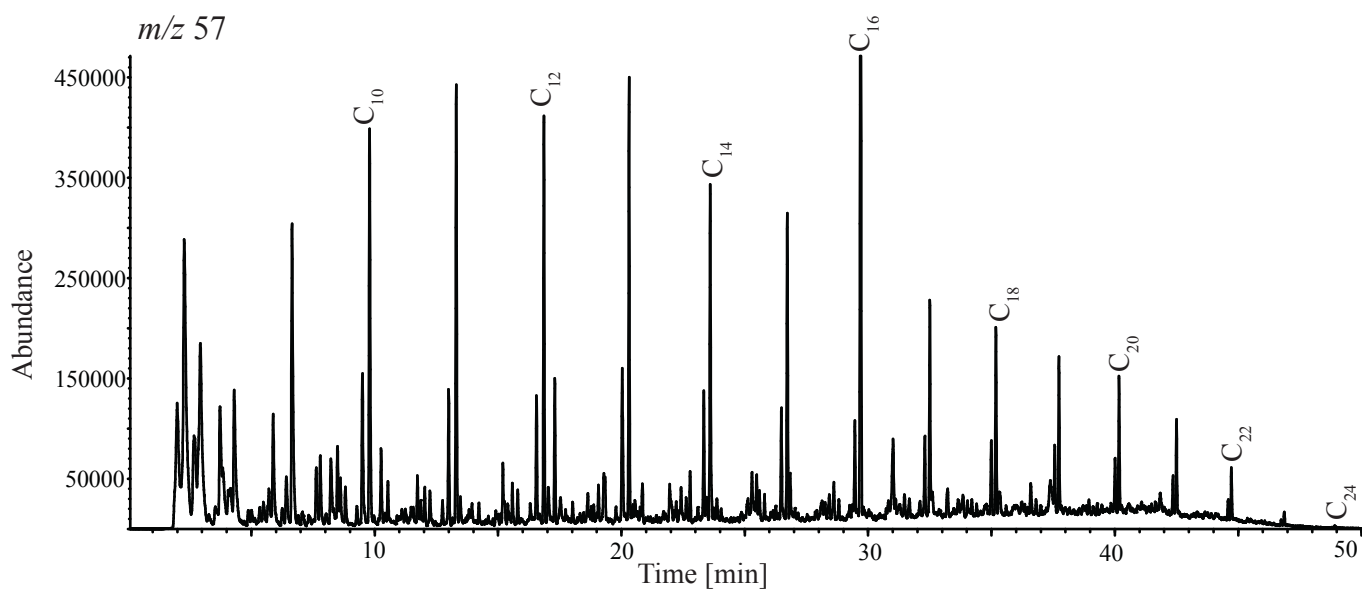
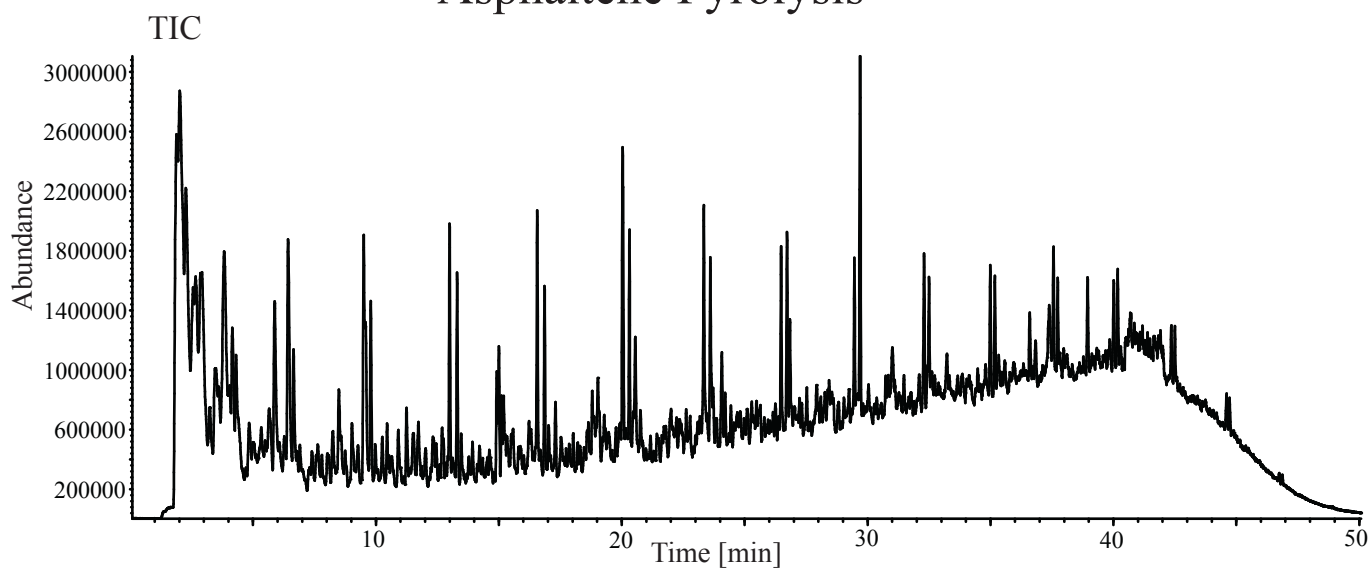
Asphaltene Pyrolysis



LC



Asphaltene Pyrolysis



Appendix 2

Magnetic experimentation

2.1 Oil impregnated samples	298
2.2 Well core samples	319

Appendix 2

Magnetic experimentation

2.1 Oil impregnated samples

(a) High temperature susceptibility curves

100 °C cyclic warming and cooling curves from 50 °C to 700 °C or one cycle warming and cooling curves from 50 °C to 700 °C (cooling $\leftarrow$). (300°C $\cdots$, 400°C --- , 500 °C $- - -$, 600 °C --- and 700 °C $\cdots$). OS1-OS6 have the oil stained (---) and cleaned ($- \cdot - \cdot$) sand curves.

(b) MPMS data

Zero field cooling (ZFC) and field cooling (FC) curves from 300 to 10 K in 10 K steps as well as room temperature remanence (RT) cooling and warming curves from 300-10 K in a zero field. (FC $- - -$ ZFC $\cdots$ RT warming $\rightarrow$, cooling $\leftarrow$).

(c) Hysteresis

Hysteresis loops for both oil stained (---) and cleaned (oil-free) samples ($\cdots$).

(d) SIRM curves

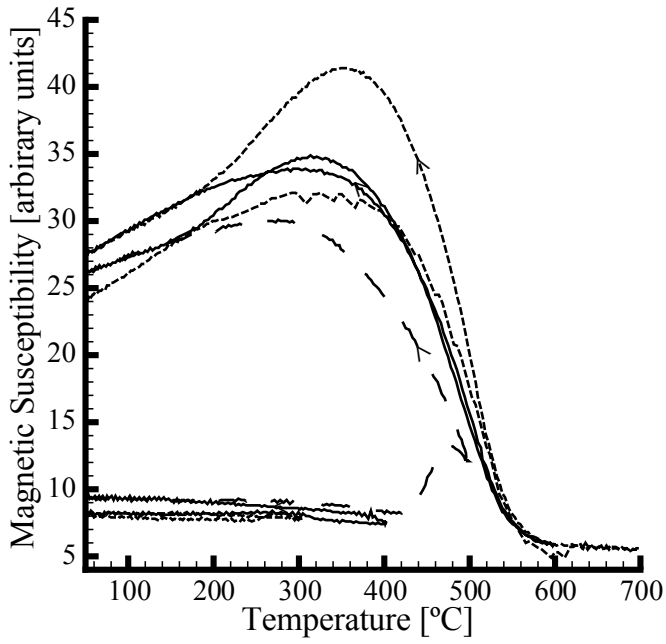
SIRM curves for oil stained (squares) and ‘cleaned’ oil-free (triangles) samples and corresponding MDF’s.

(e) AC Susceptibility as a function of temperature

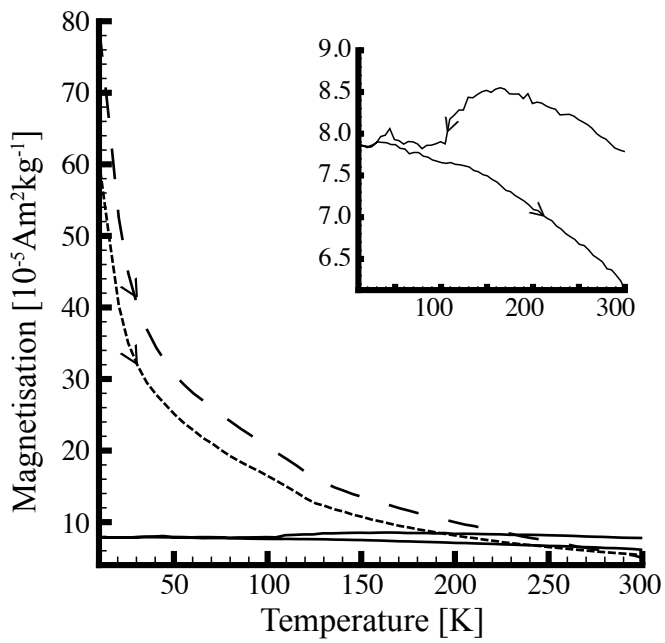
Susceptibility measurements for AC susceptibility at 7 frequencies between 10-300 K in 10 K steps at seven frequencies (1.0, 32.2, 10.0, 31.6, 100.1, 316.7, 997.3 Hz)

A1B magnetic experimentation

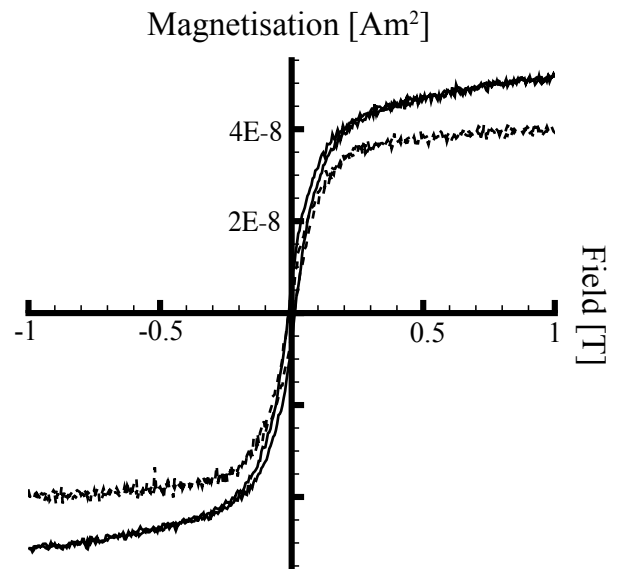
(a)



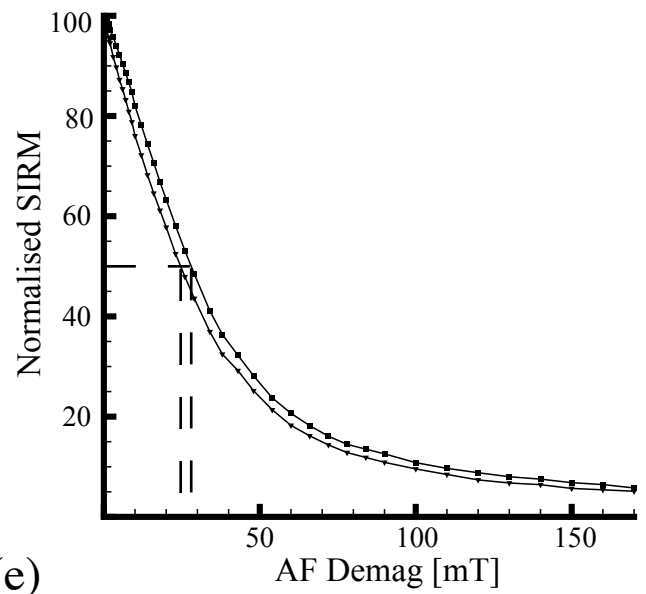
(b)



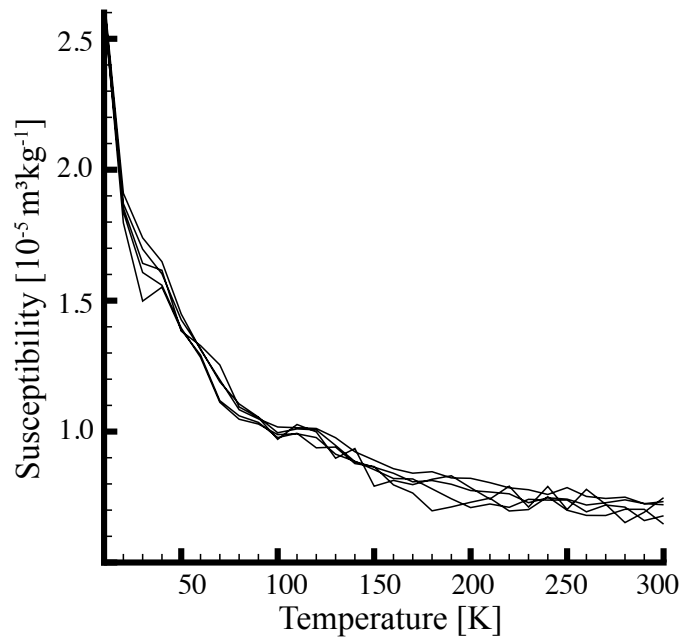
(c)



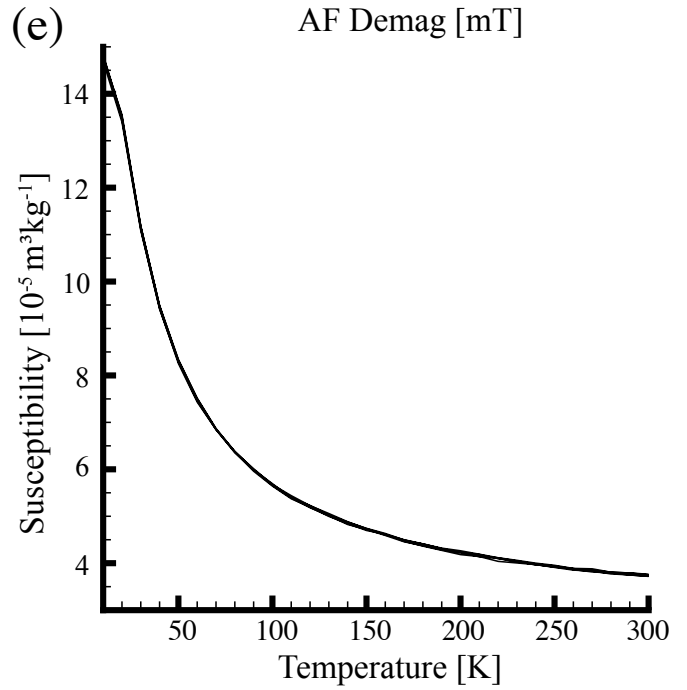
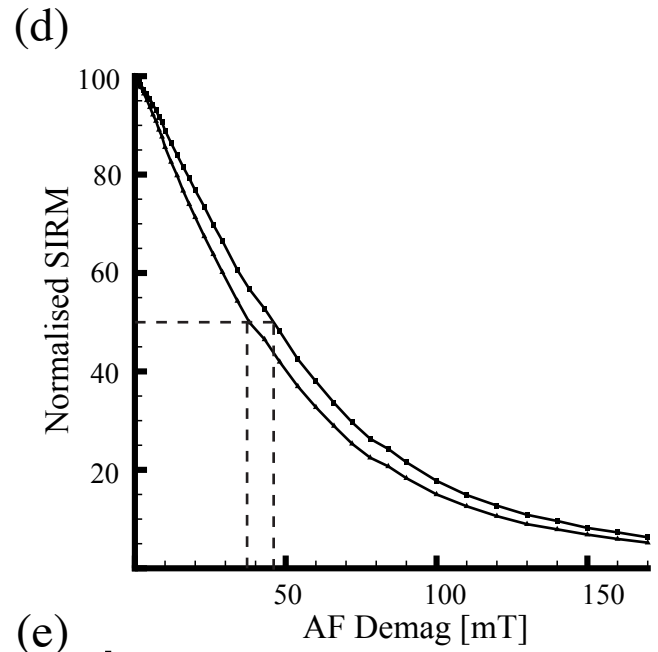
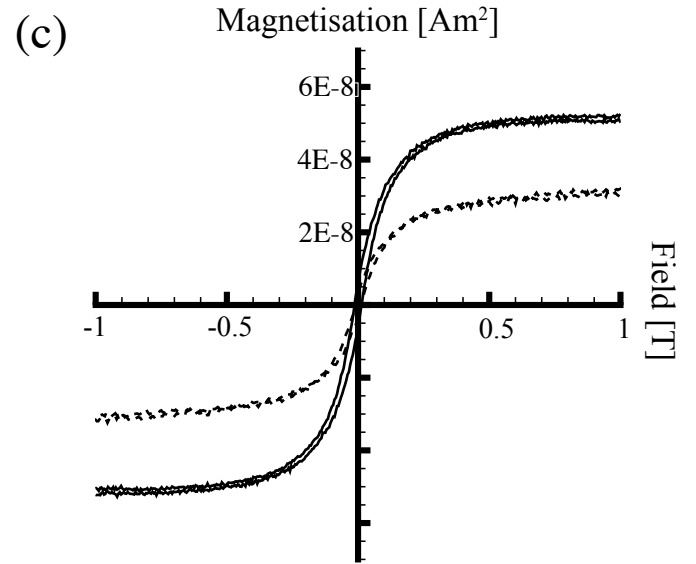
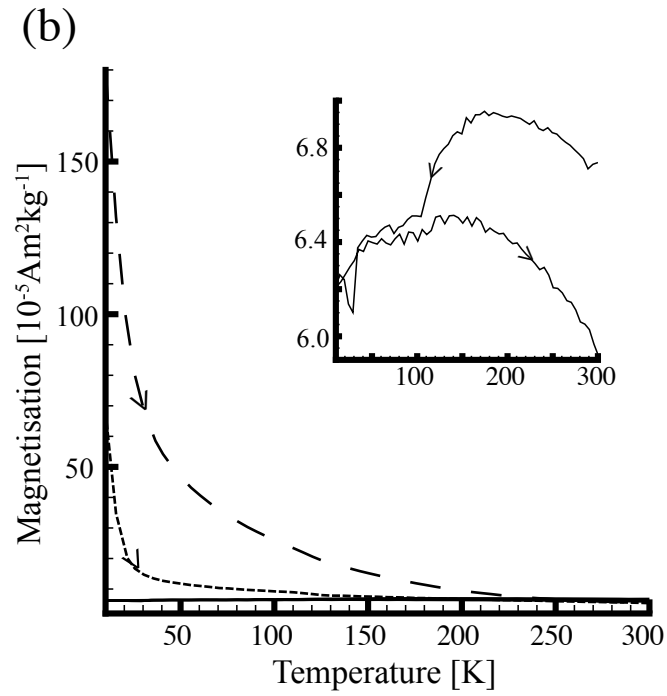
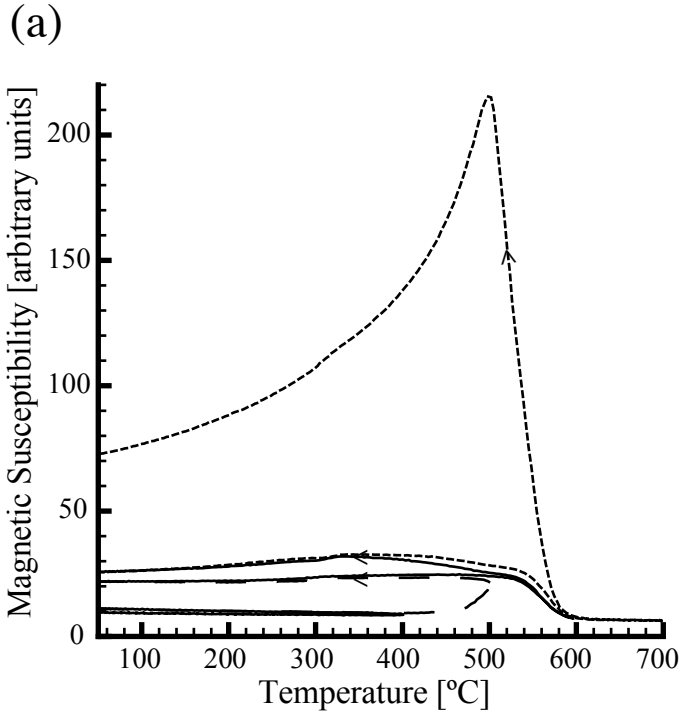
(d)



(e)

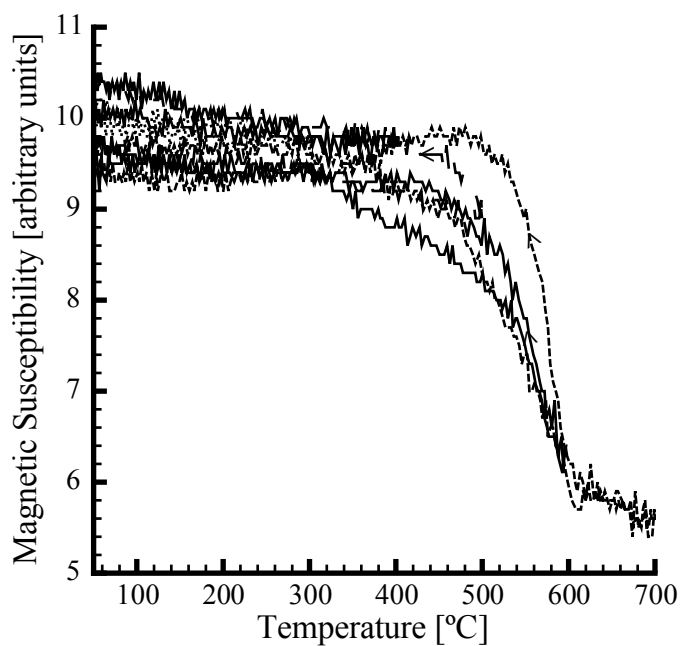


A3B magnetic experimentation

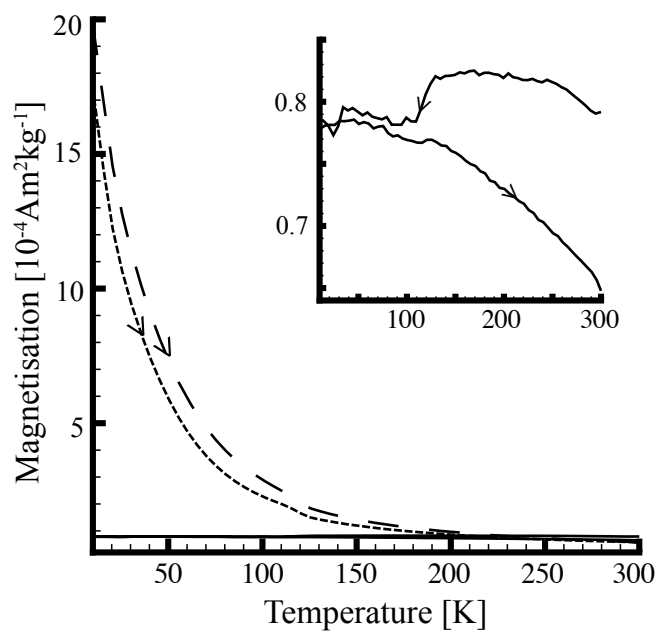


A827.32
magnetic experimentation

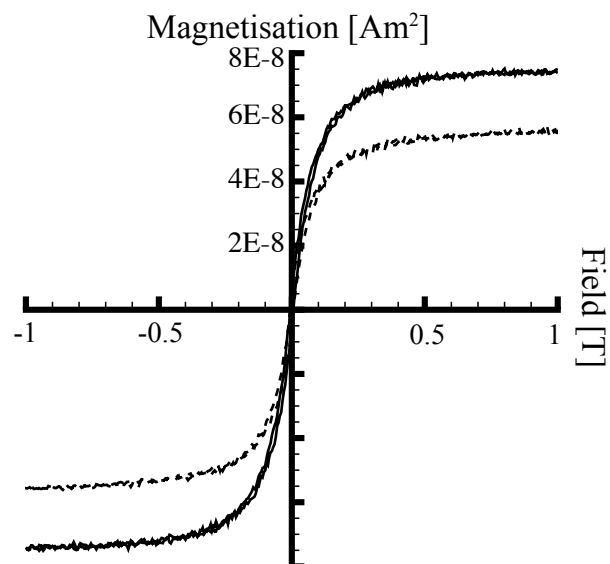
(a)



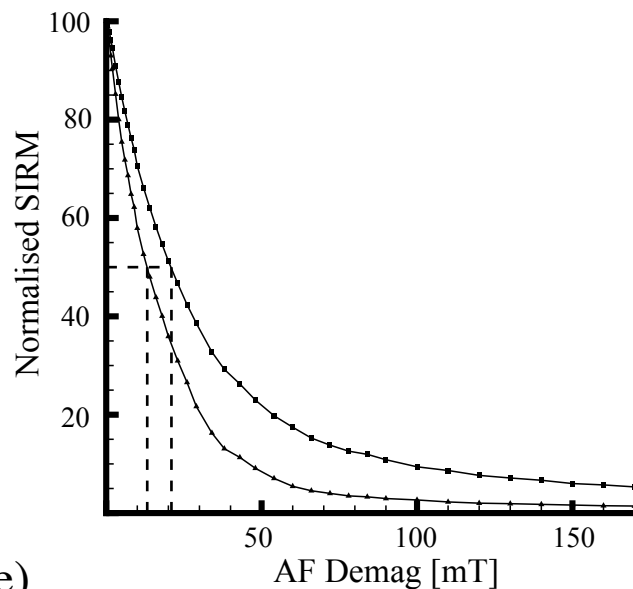
(b)



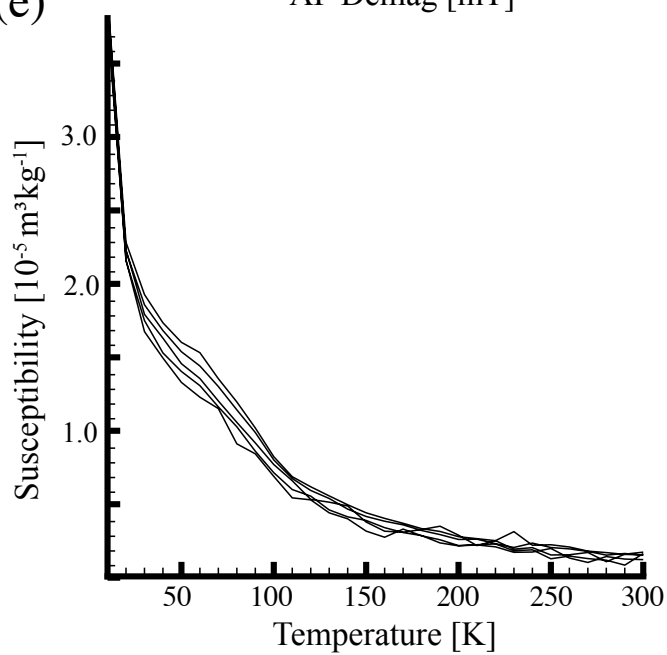
(c)



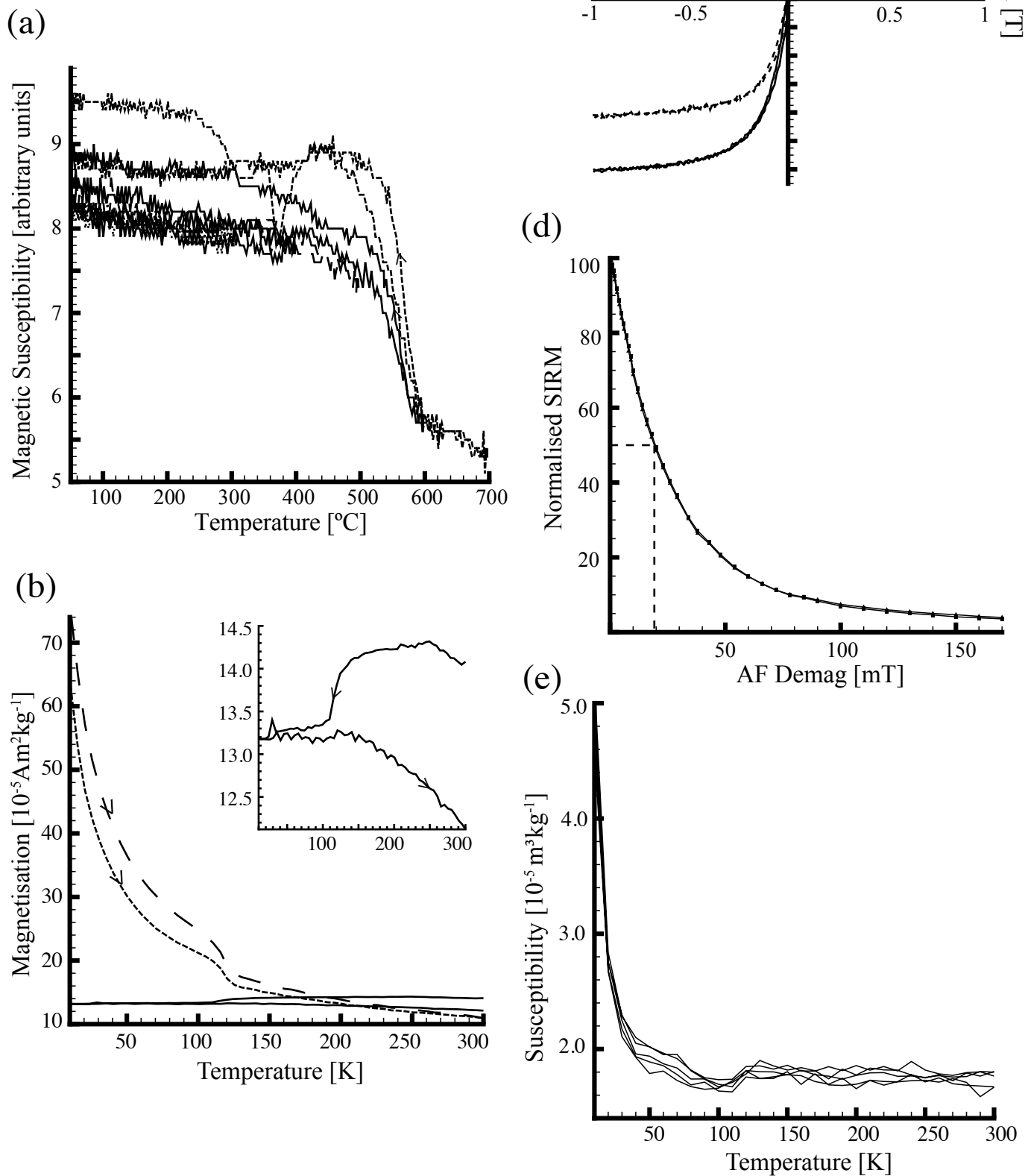
(d)



(e)

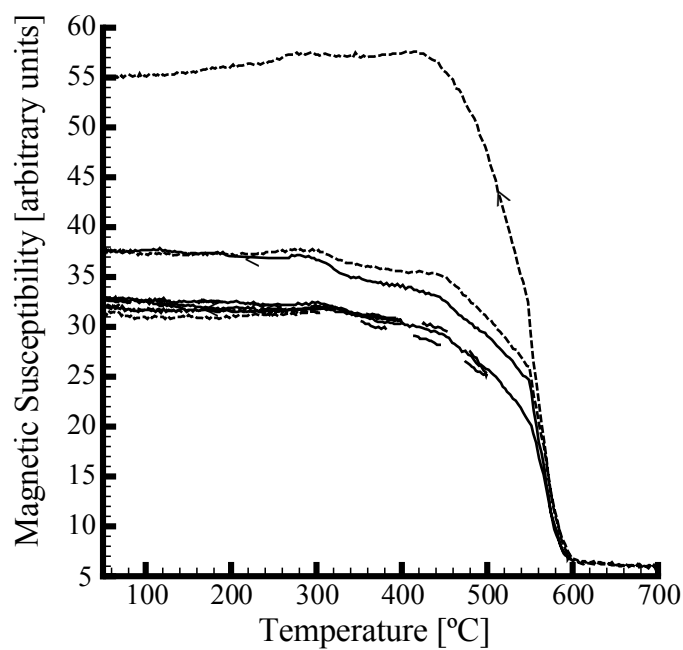


A827.75 magnetic experimentation

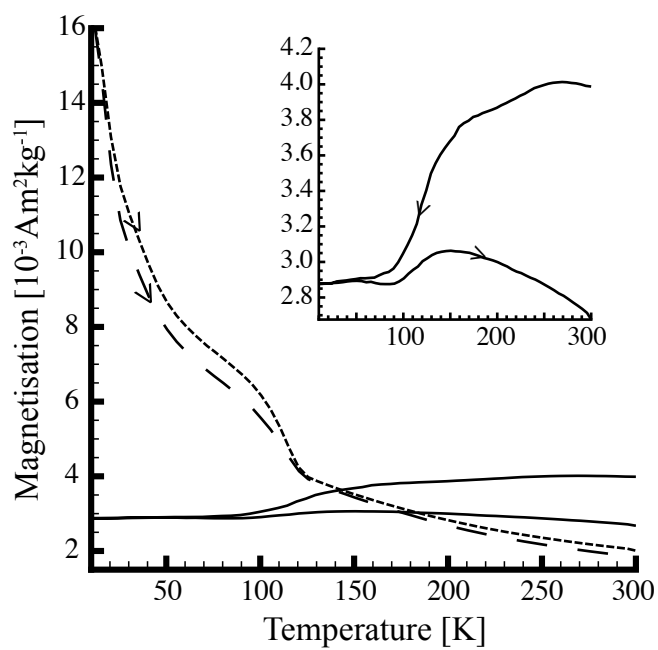


C127.40
magnetic experimentation

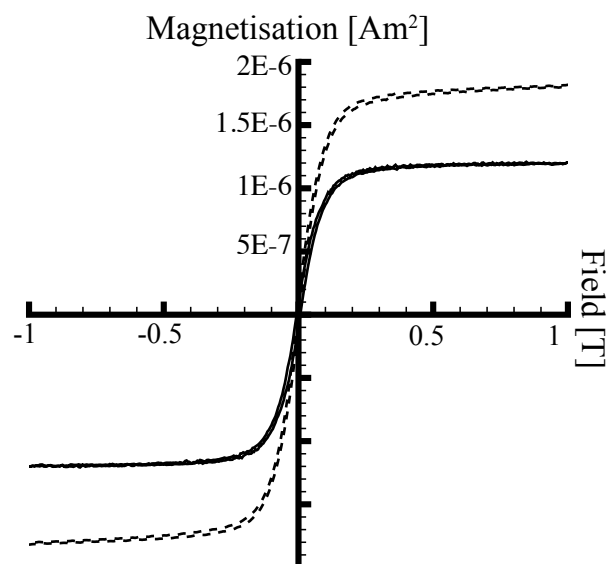
(a)



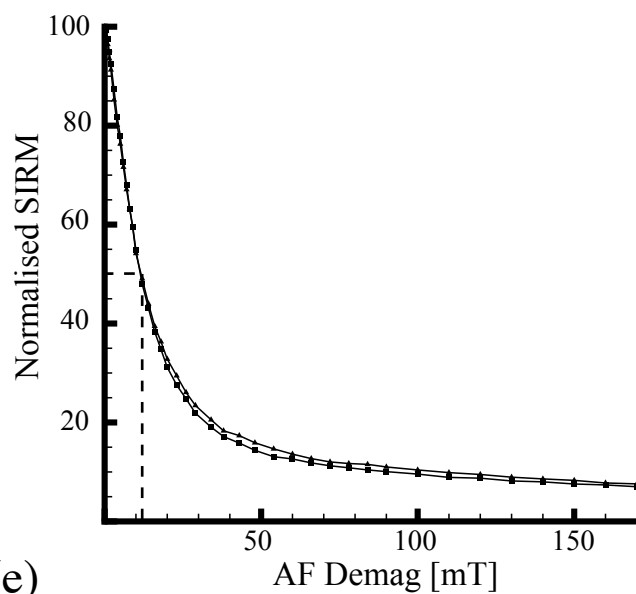
(b)



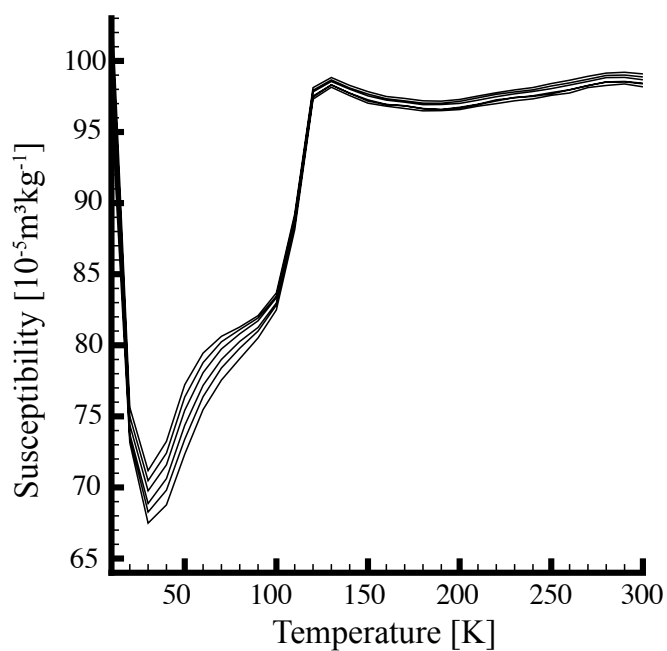
(c)



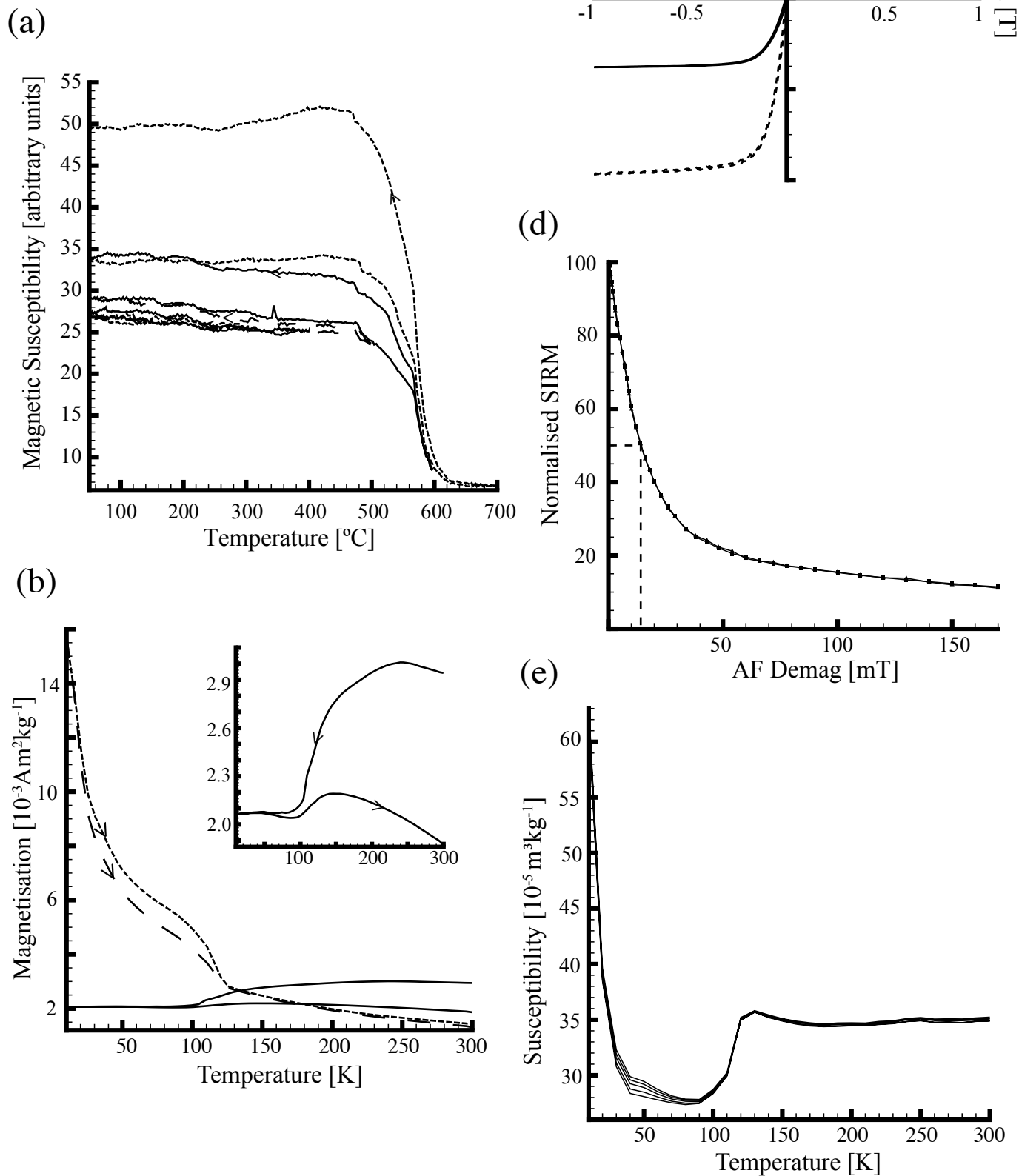
(d)



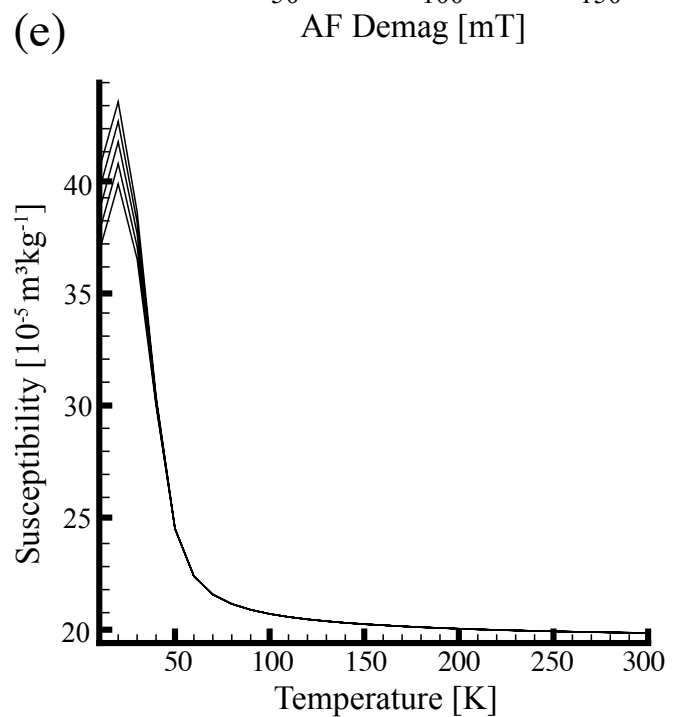
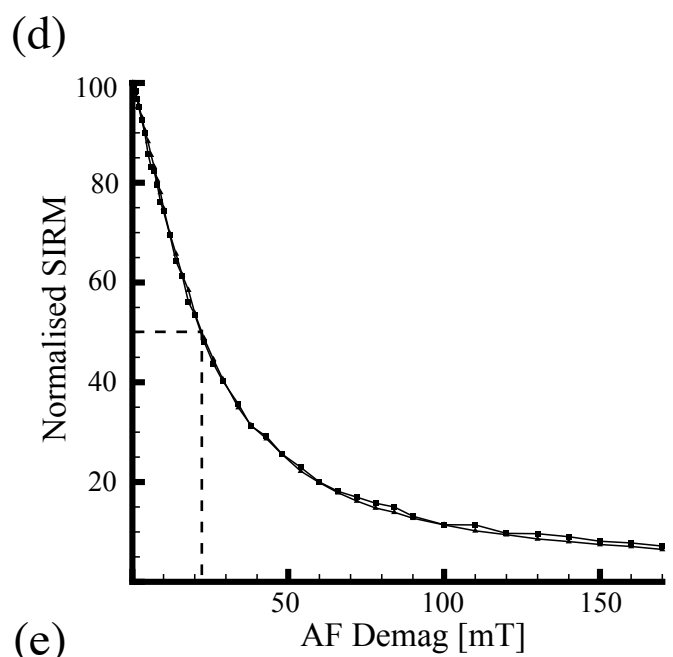
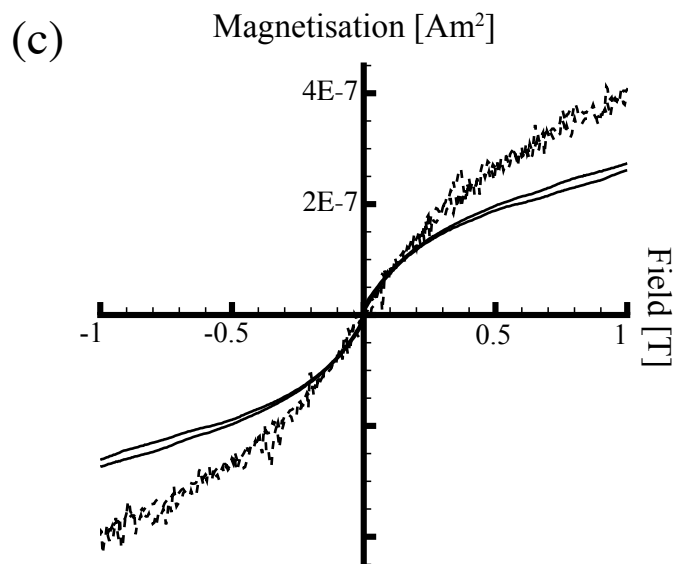
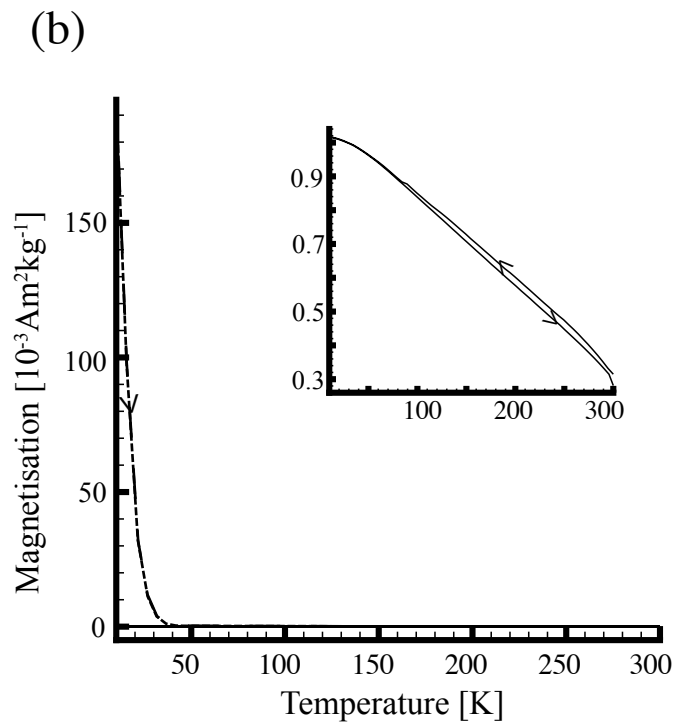
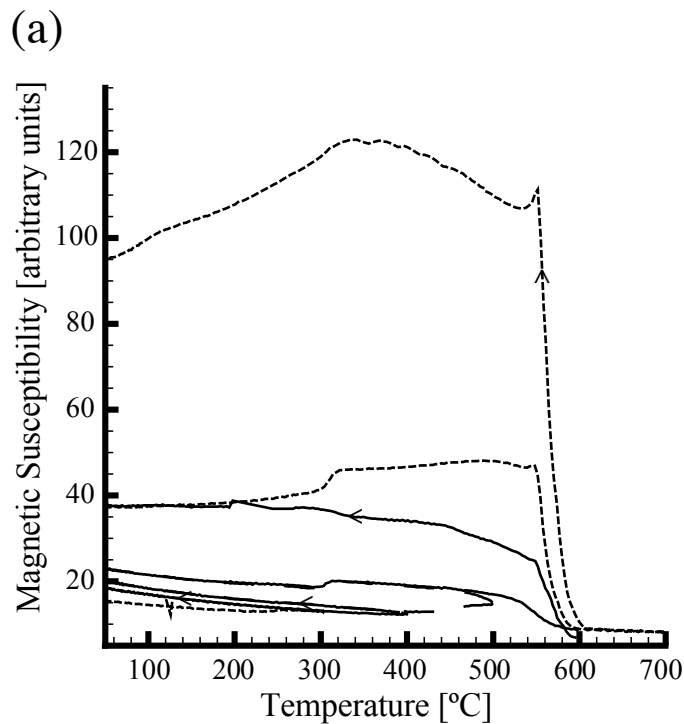
(e)



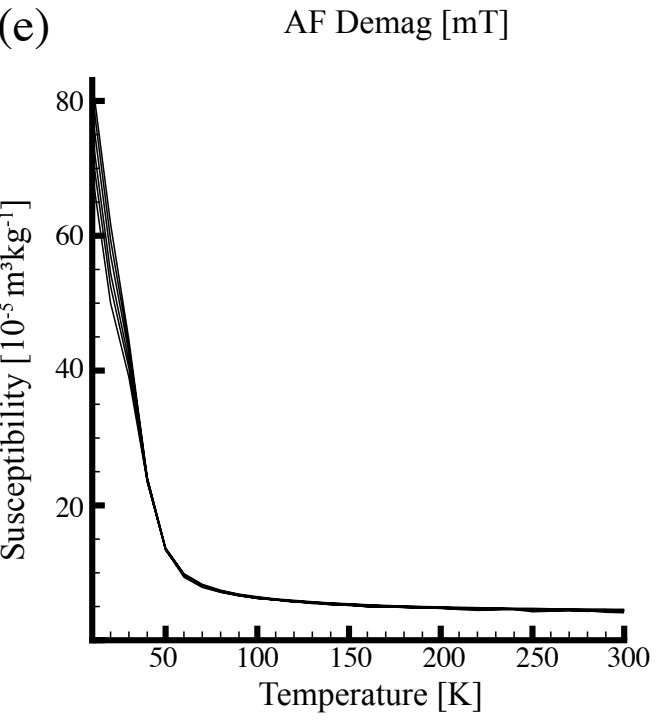
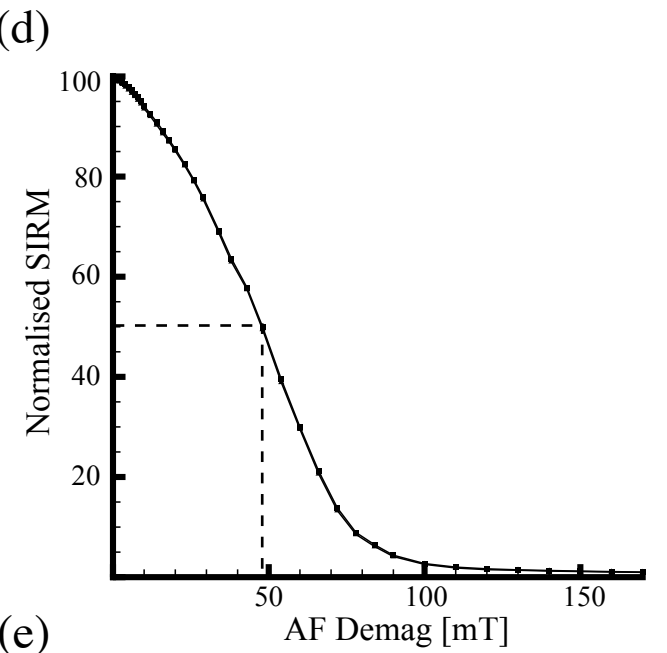
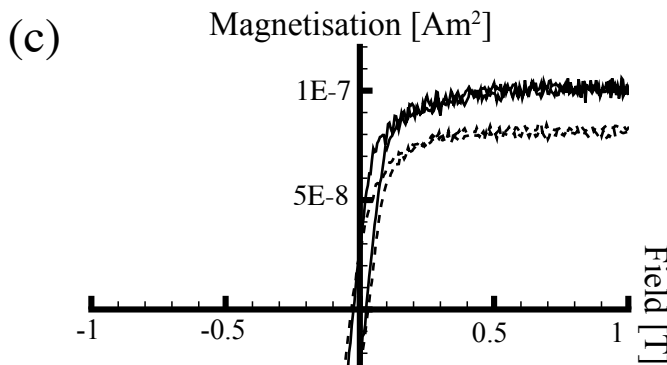
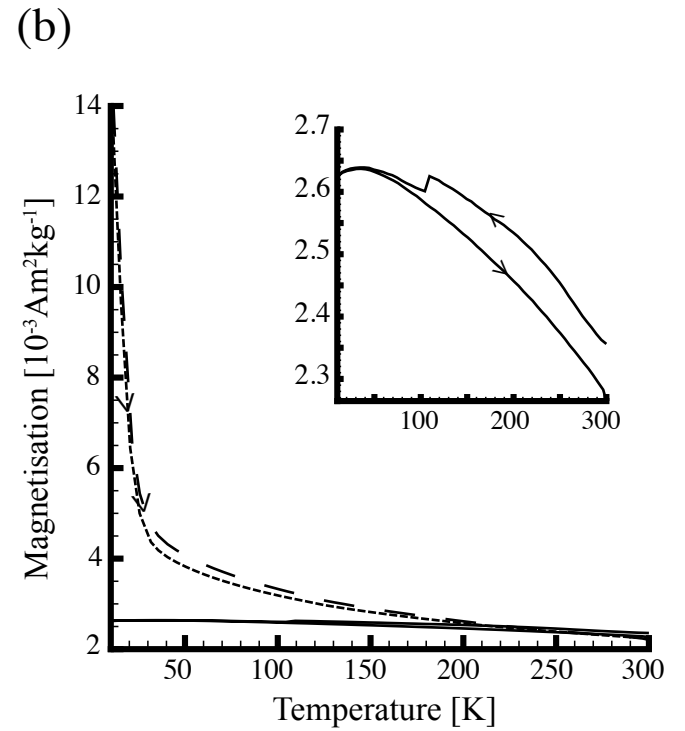
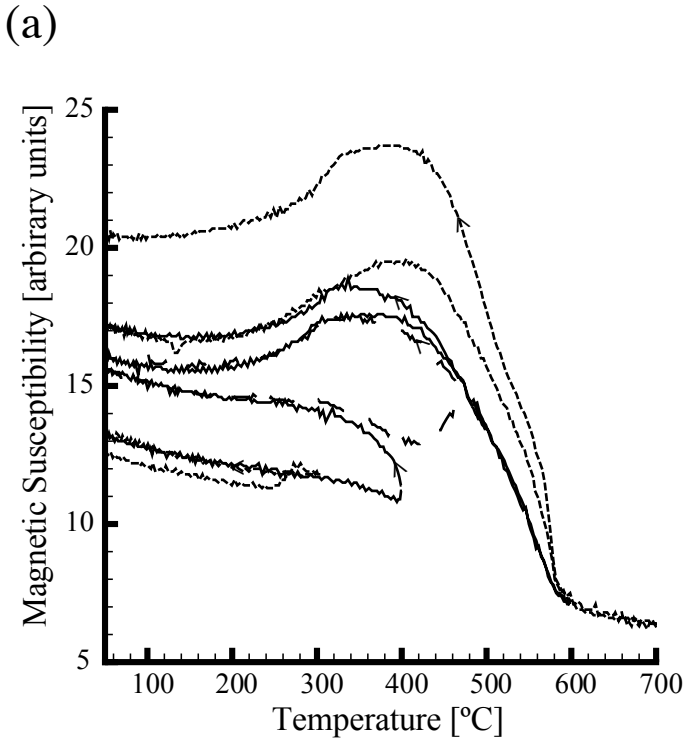
C147.25 magnetic experimentation



C541.75
magnetic experimentation

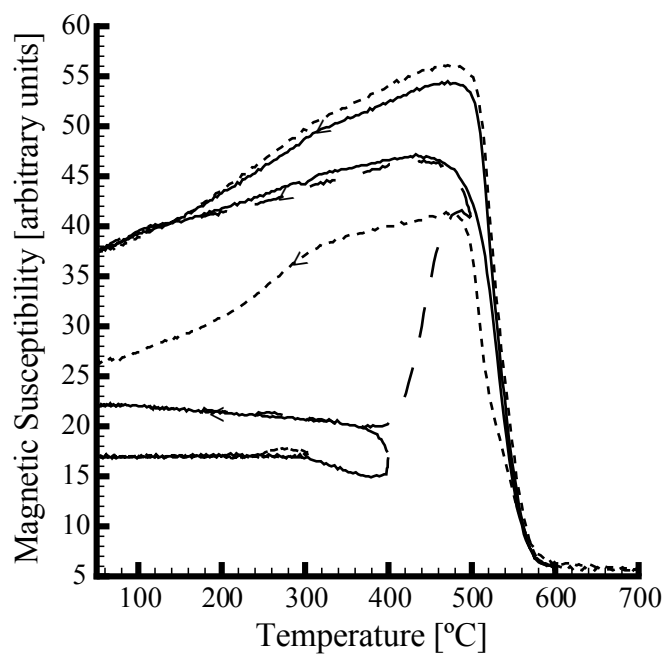


C616.48
magnetic experimentation

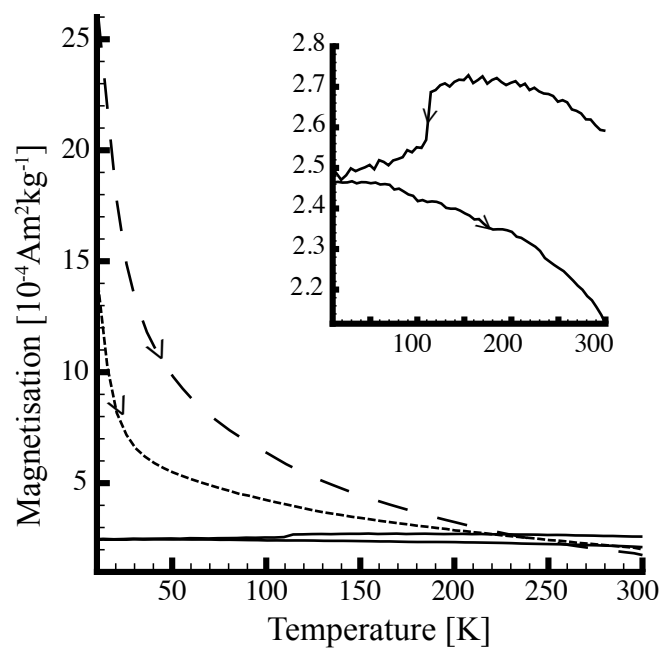


KI magnetic experimentation

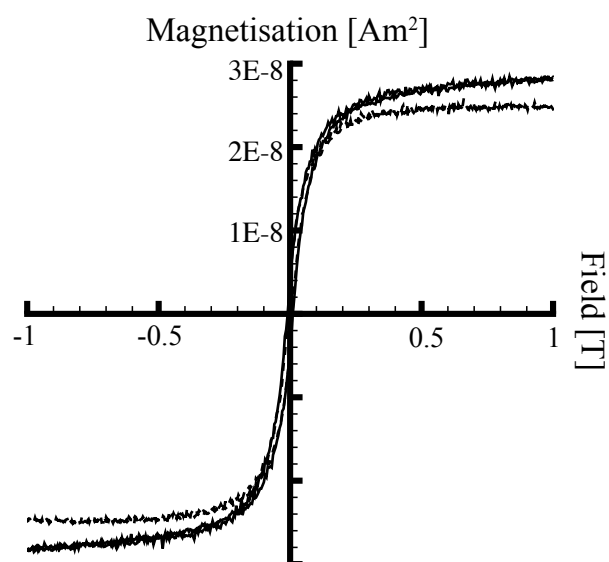
(a)



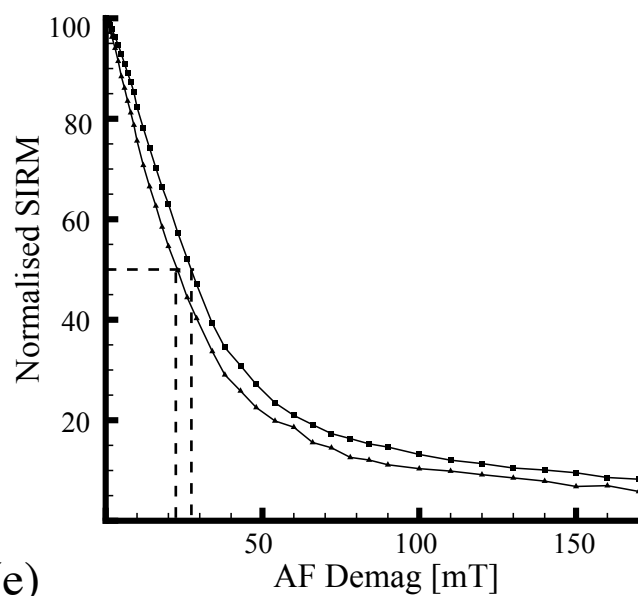
(b)



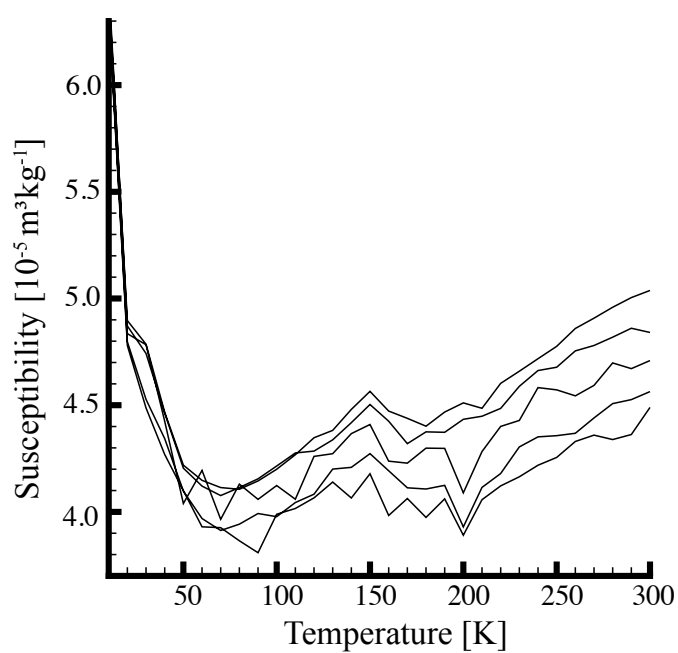
(c)



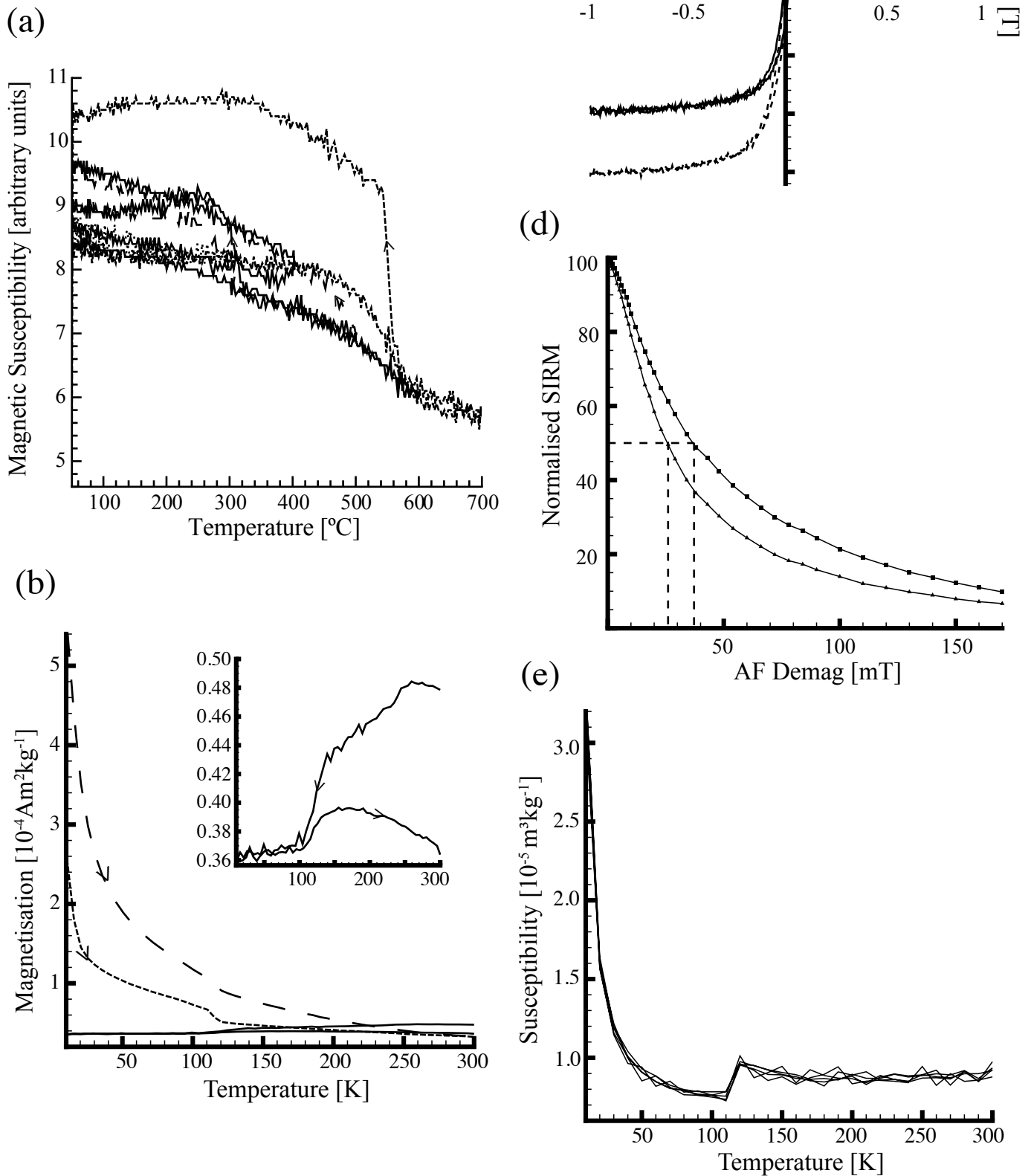
(d)



(e)

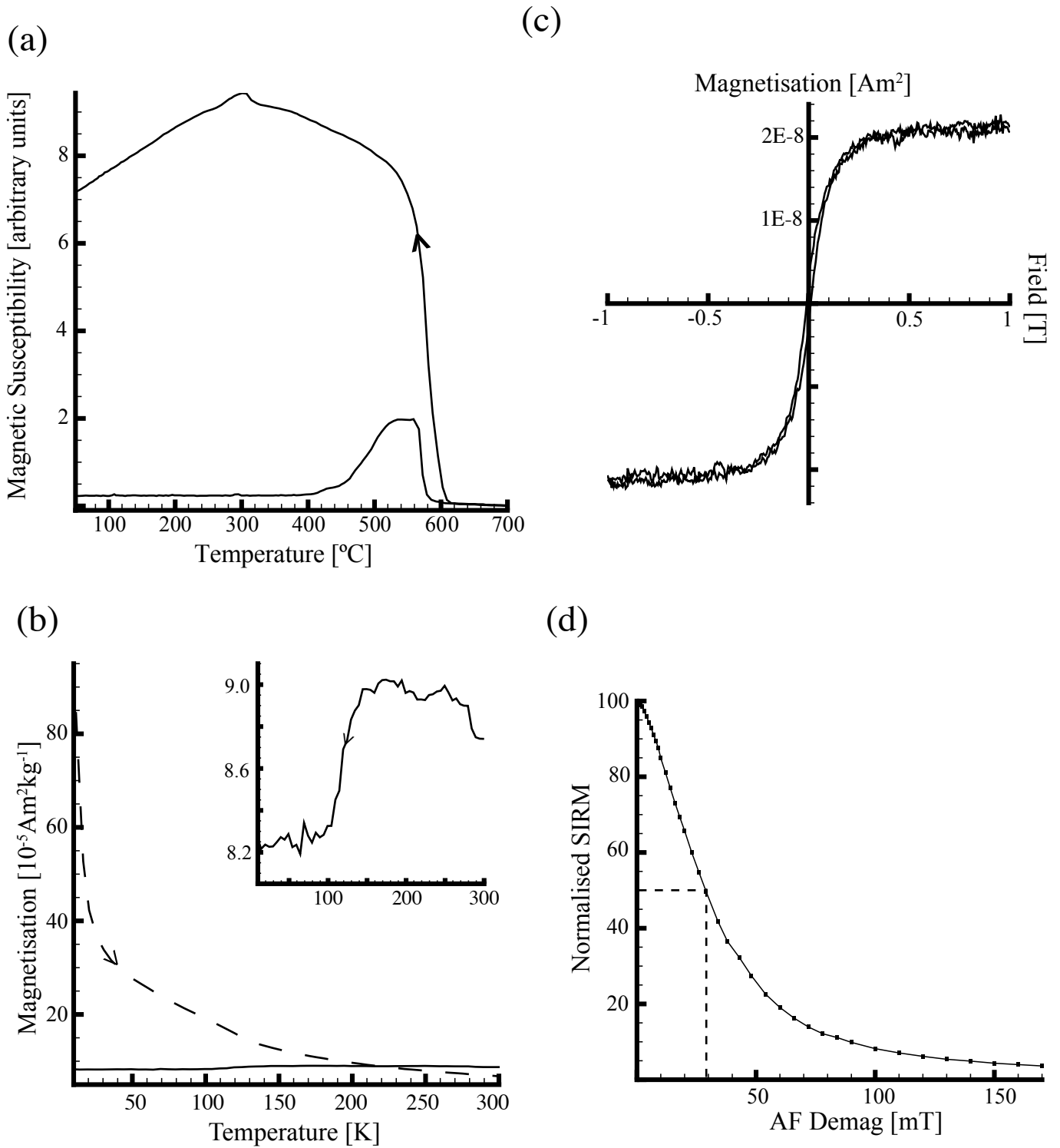


LI magnetic experimentation



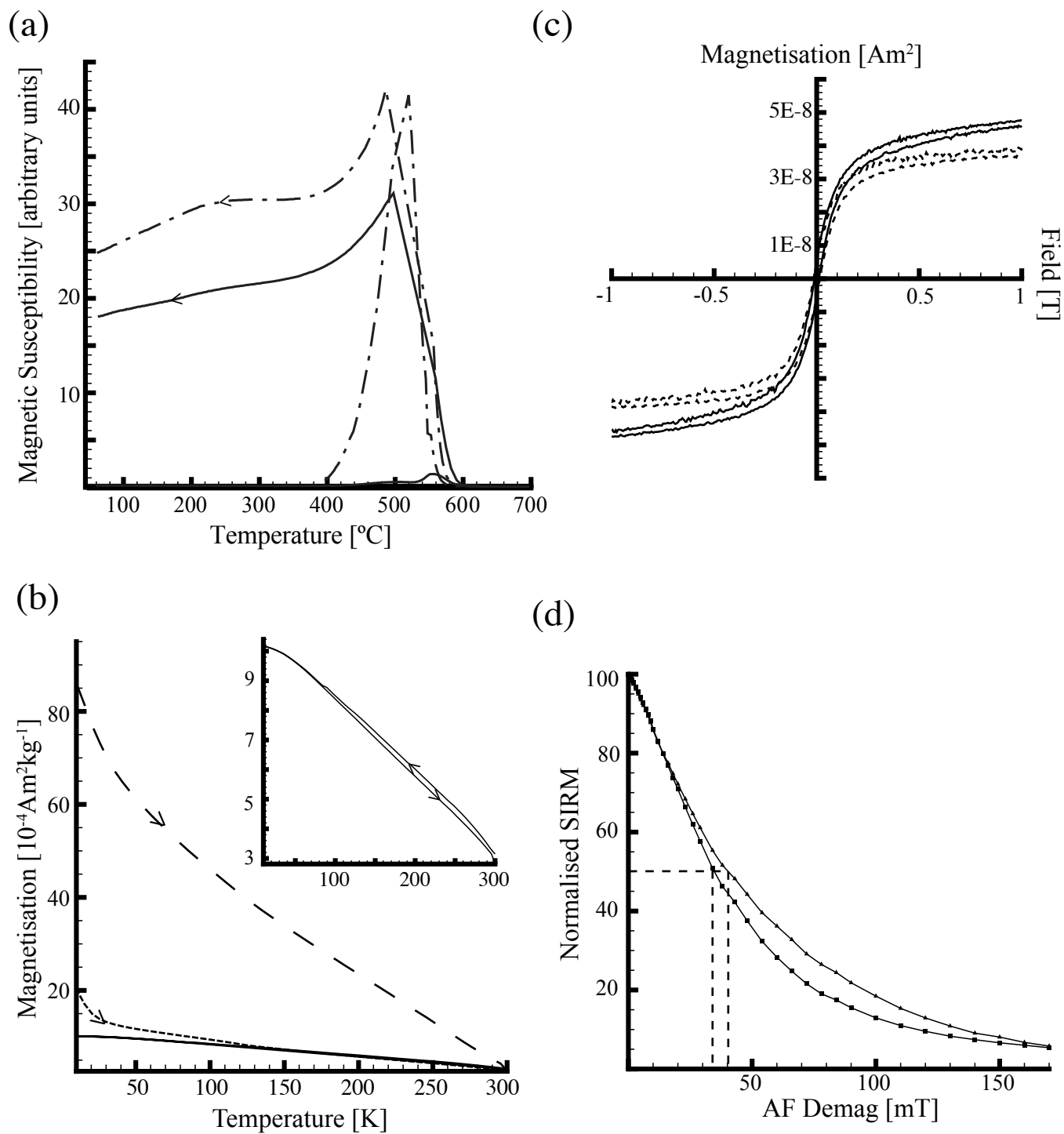
OS1

magnetic experimentation

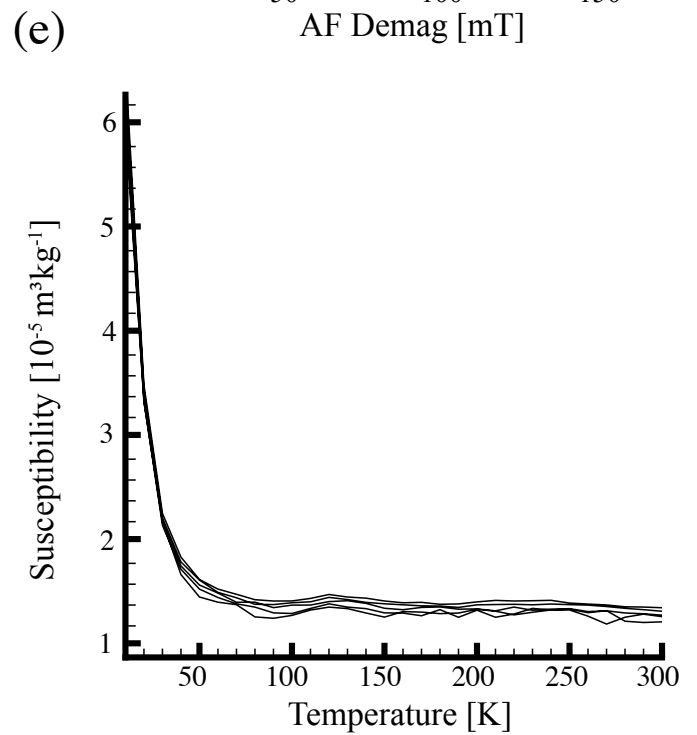
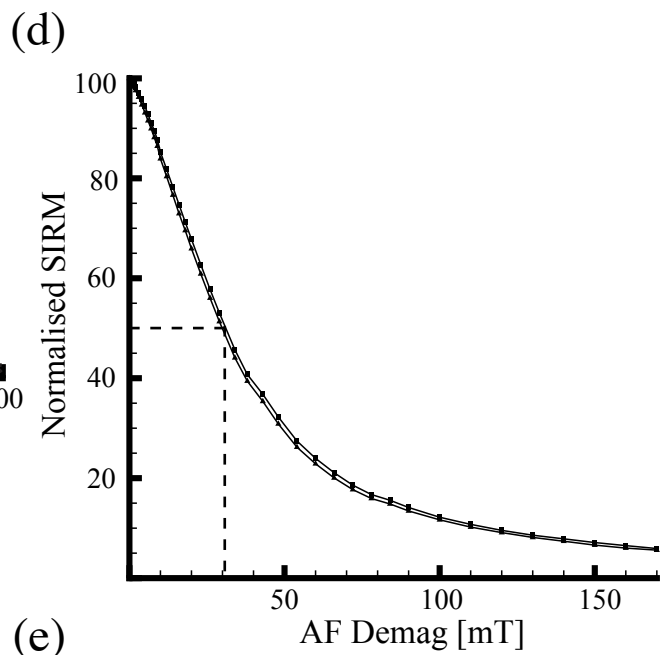
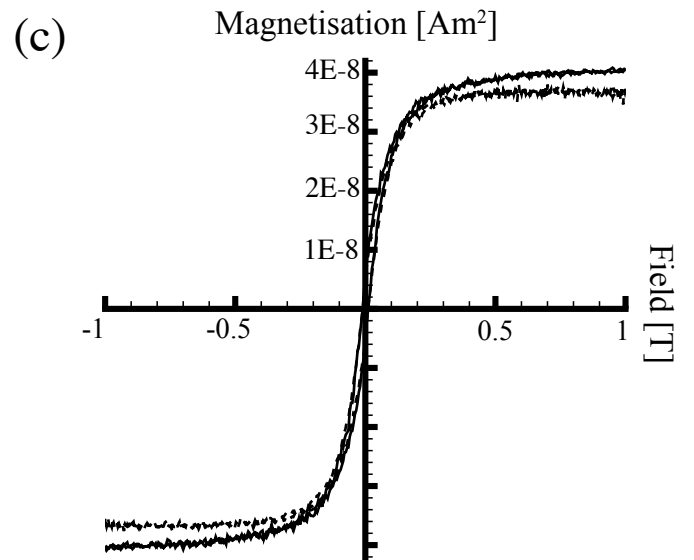
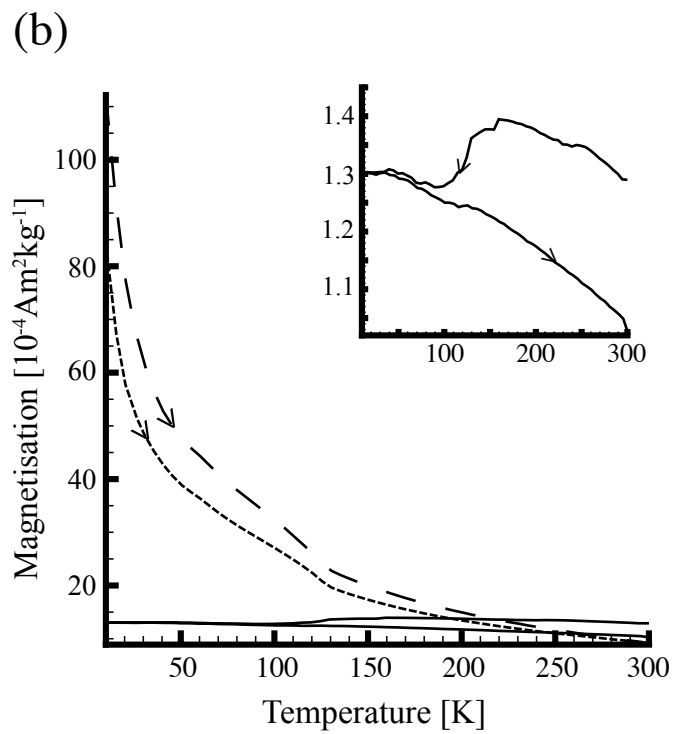
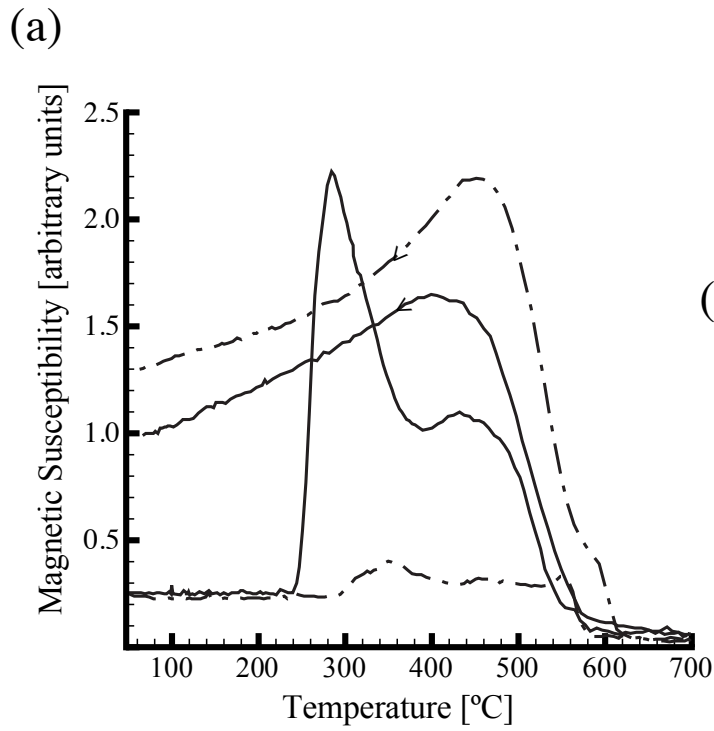


OS2

magnetic experimentation



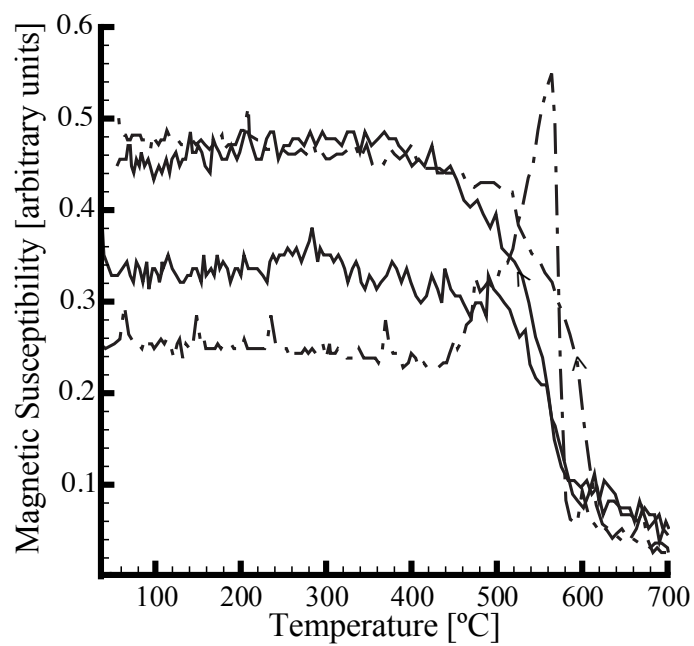
OS3 magnetic experimentation



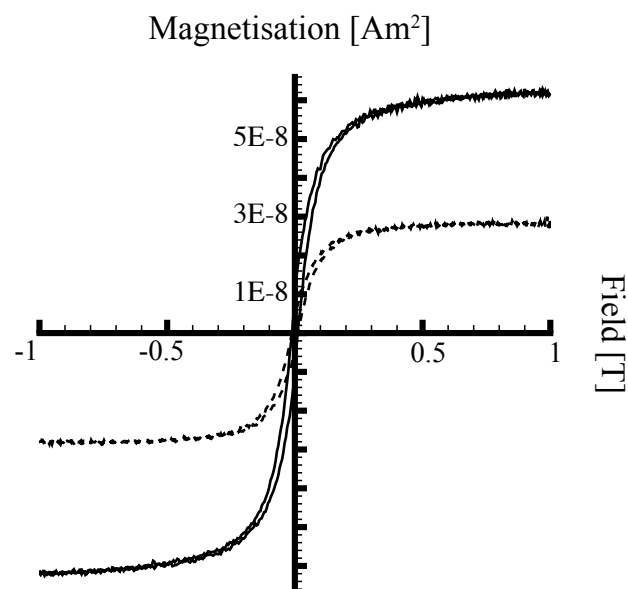
OS4

magnetic experimentation

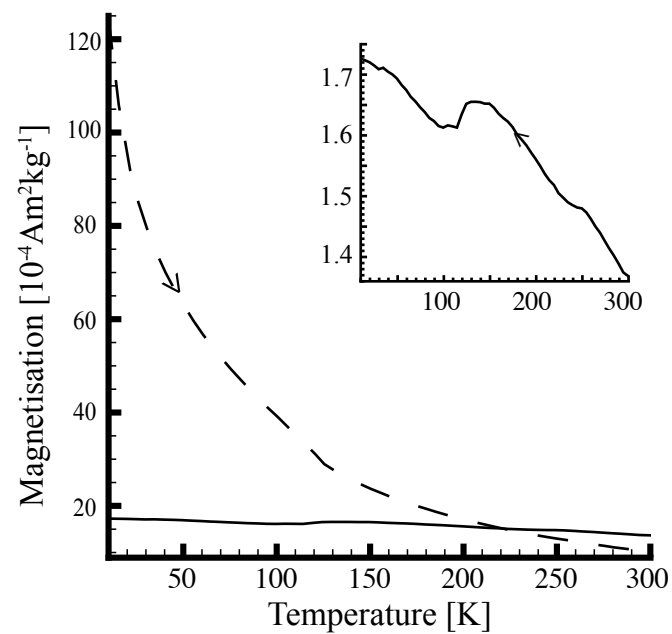
(a)



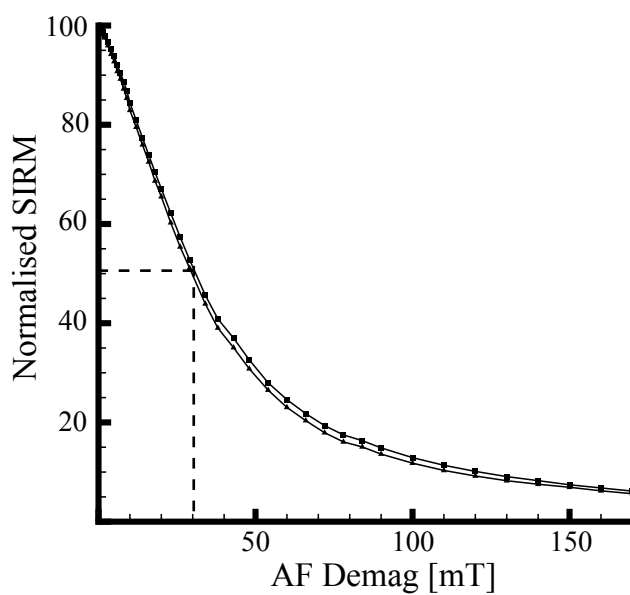
(c)



(b)



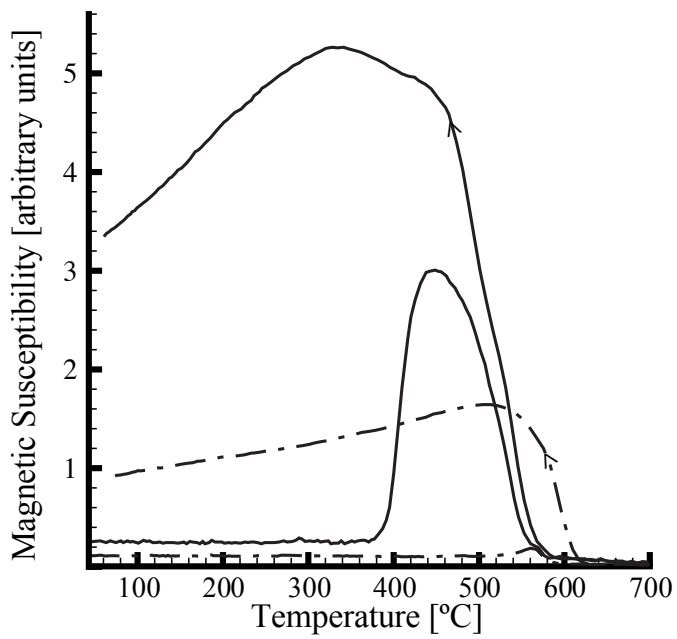
(d)



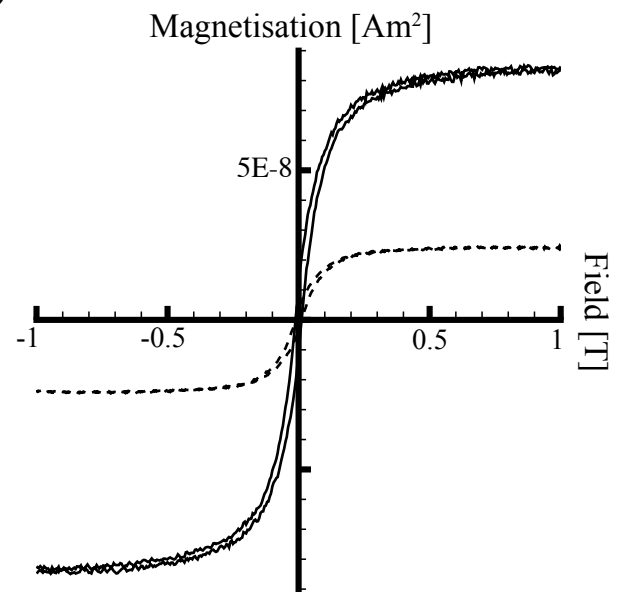
OS5

magnetic experimentation

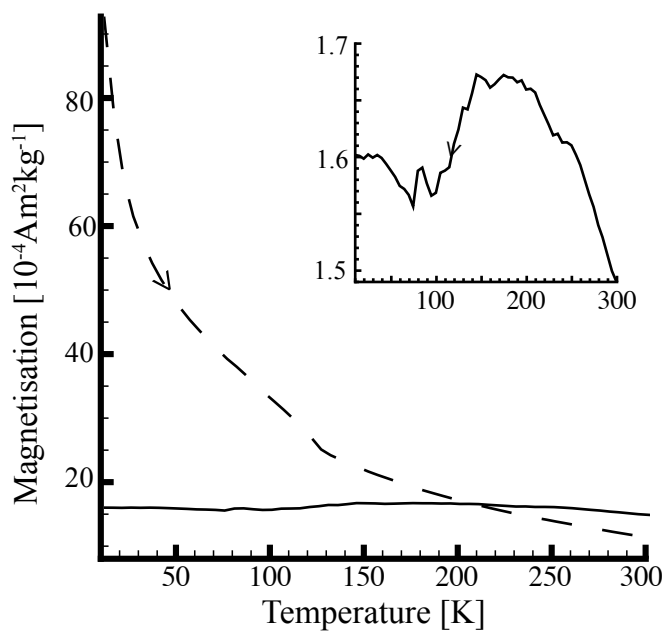
(a)



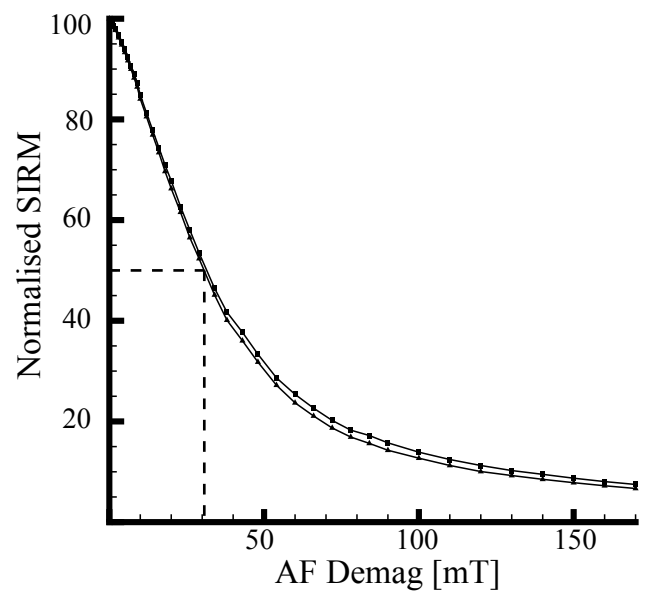
(c)



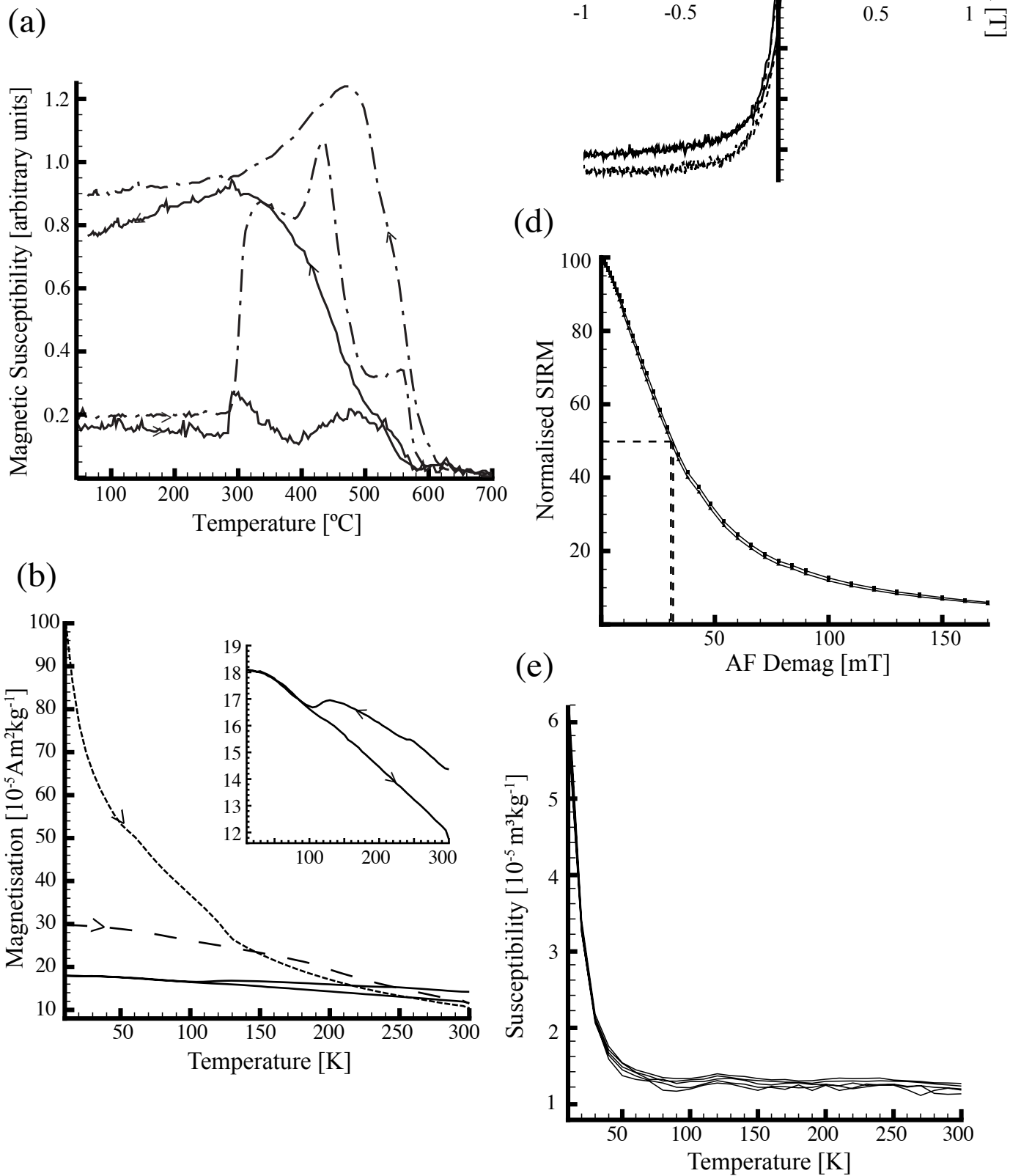
(b)



(d)

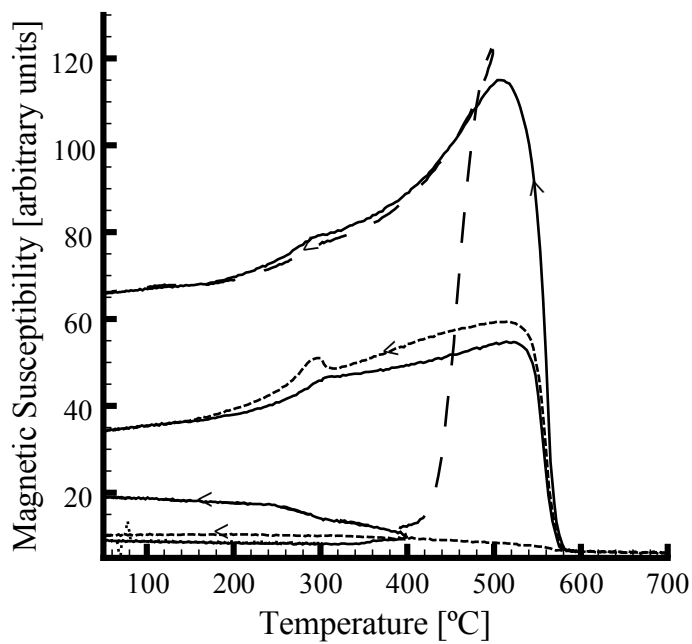


OS6 magnetic experimentation

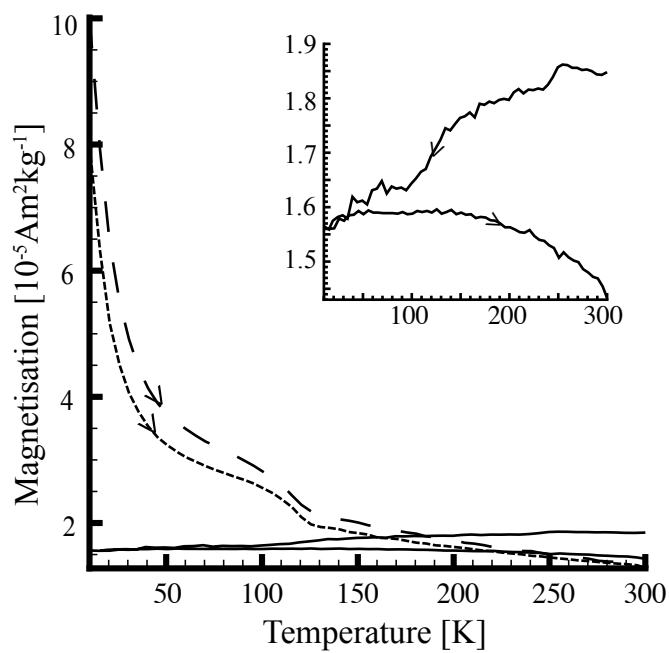


MBC
magnetic experimentation

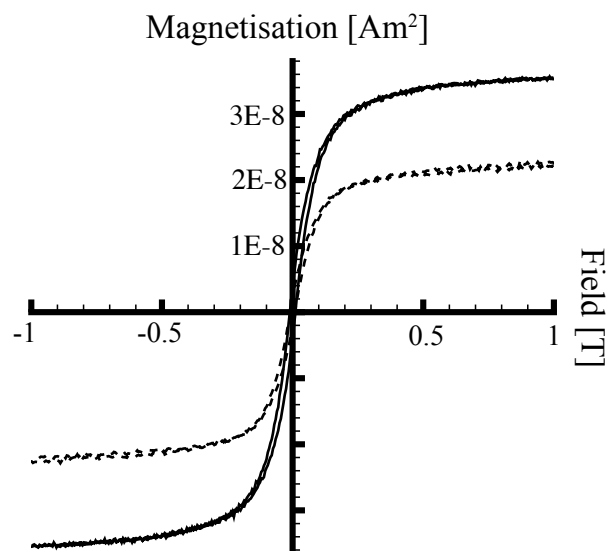
(a)



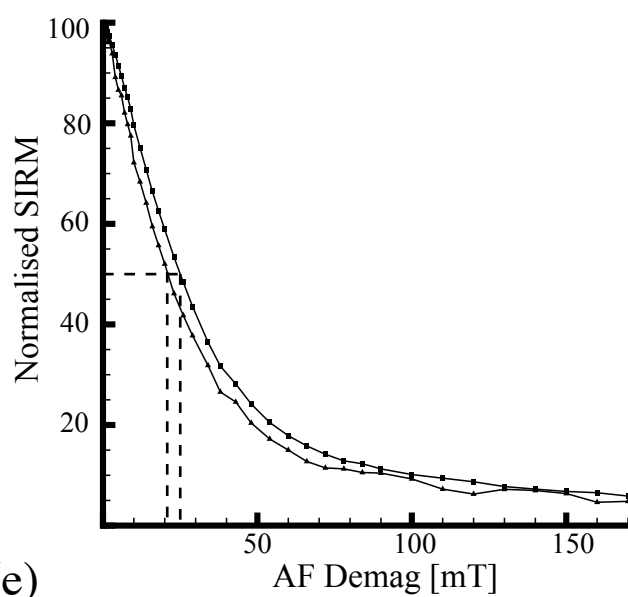
(b)



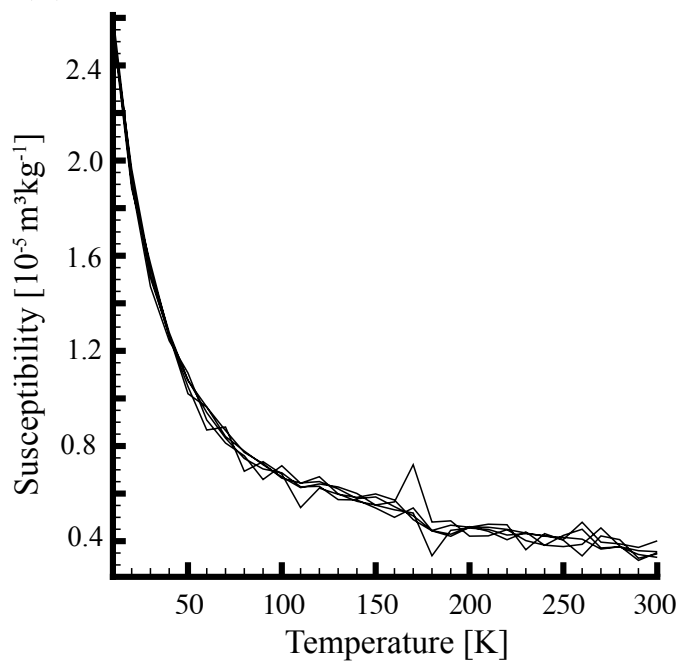
(c)



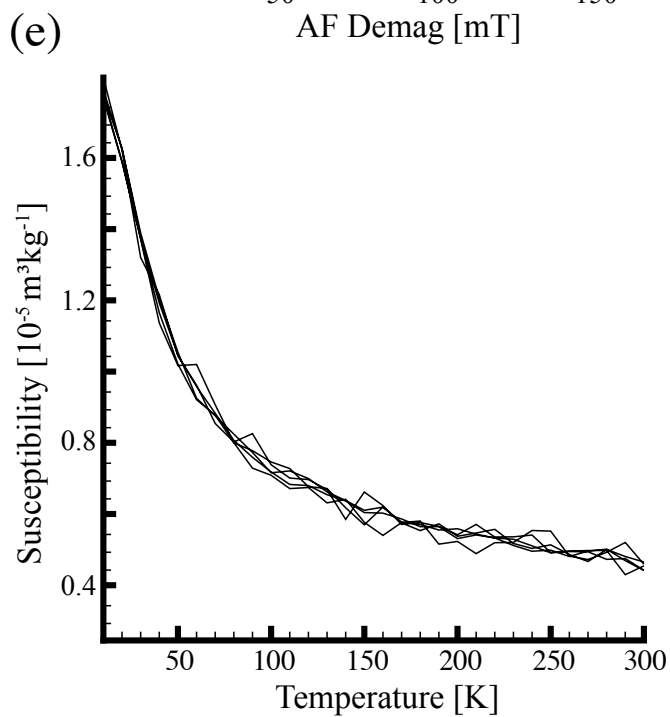
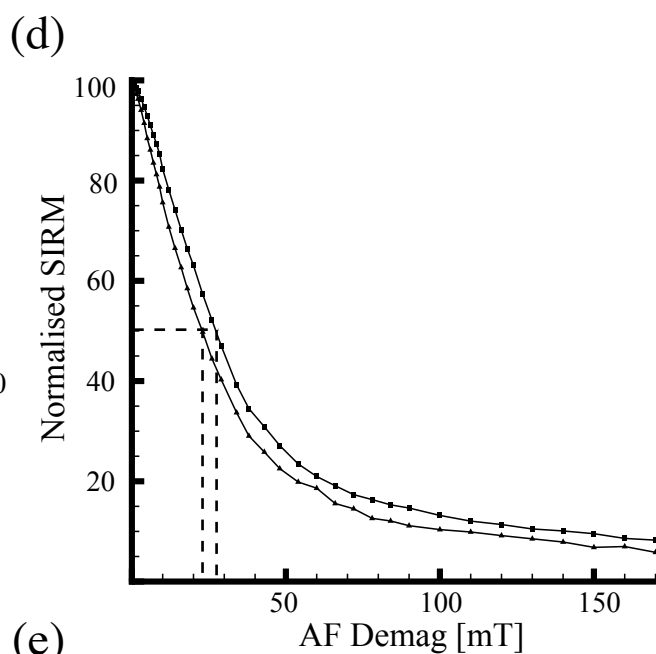
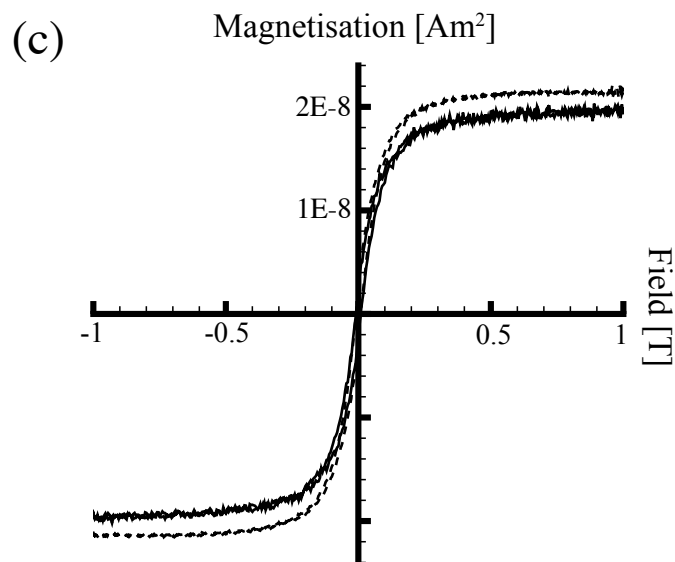
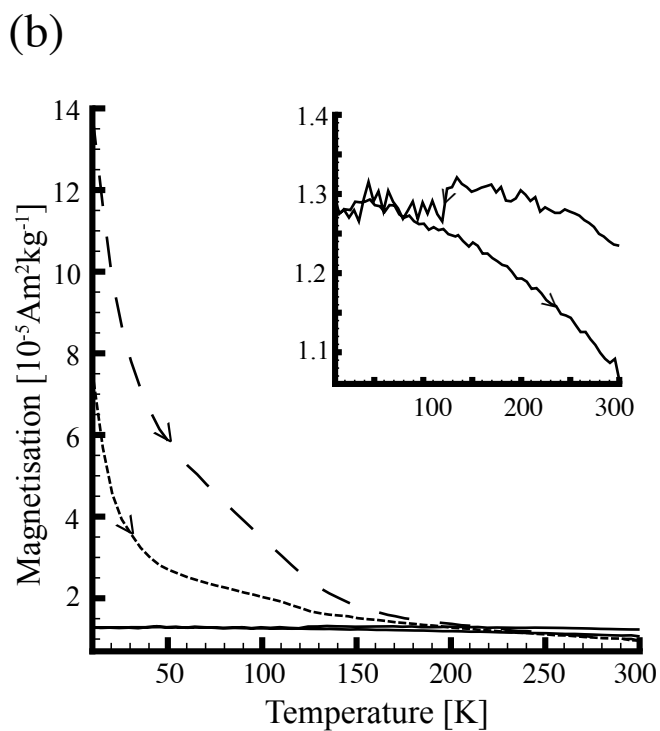
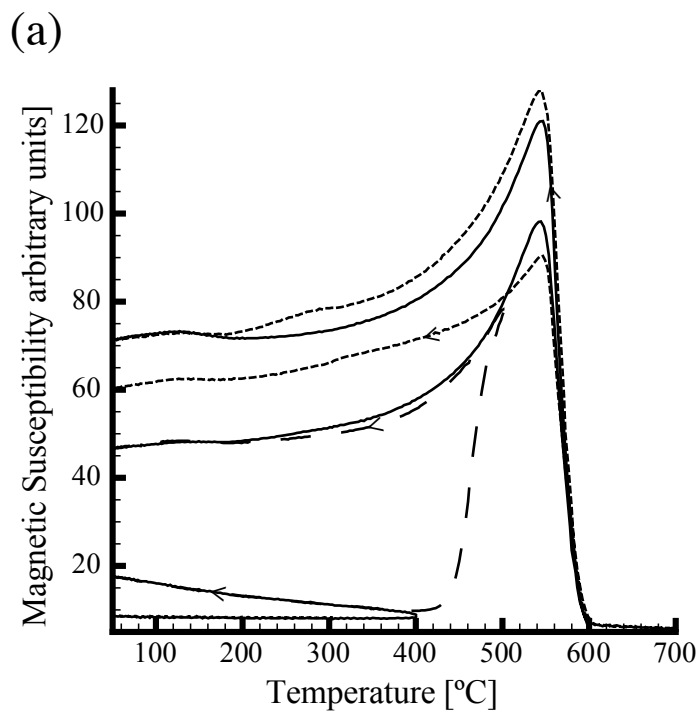
(d)



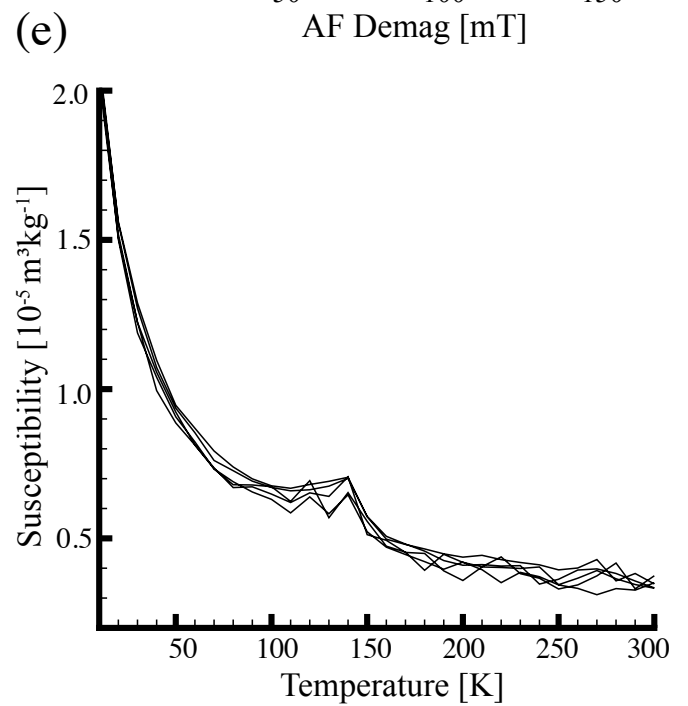
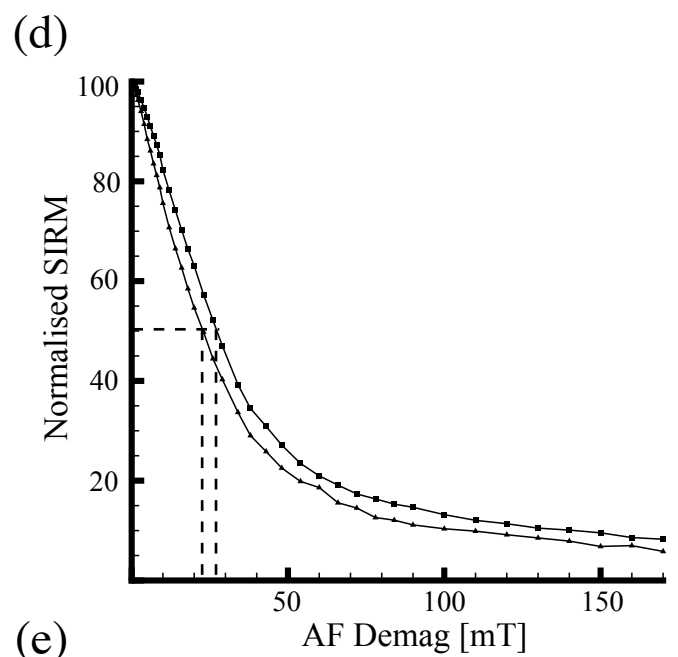
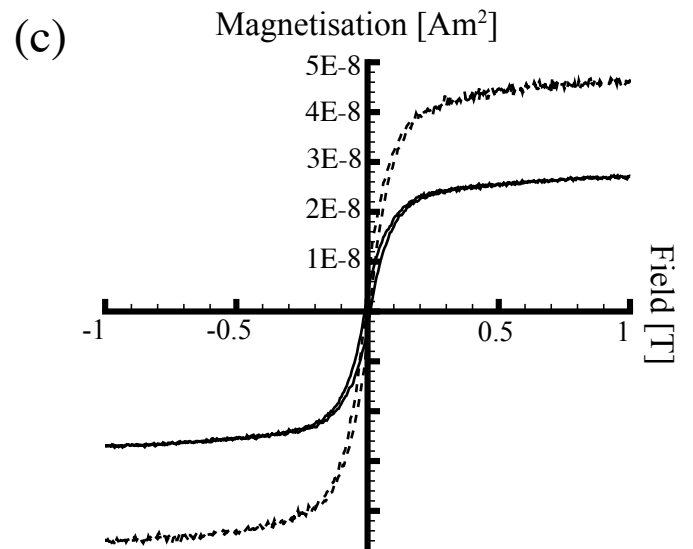
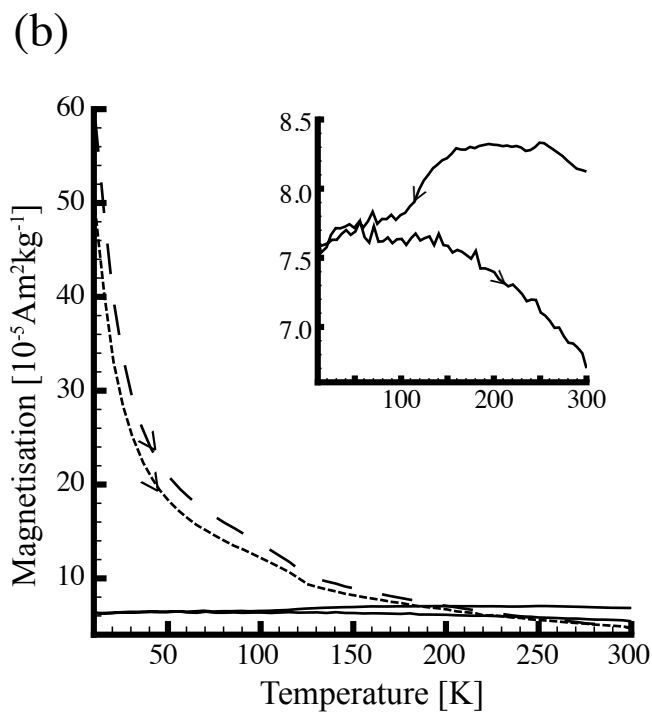
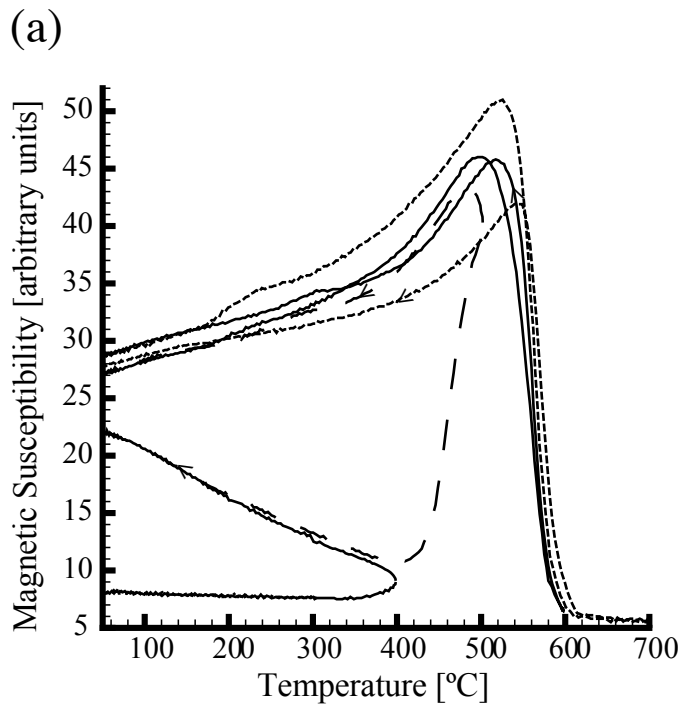
(e)



MBM magnetic experimentation



LC magnetic experimentation



Magnetic experimentation

2.2 Well Core samples

(a) Hysteresis

Hysteresis loop for the well core samples (—).

(b) High temperature susceptibility

One cycle warming and cooling curves from 50 °C to 700 °C. Warming (—) and cooling (---).

(c) MPMS data

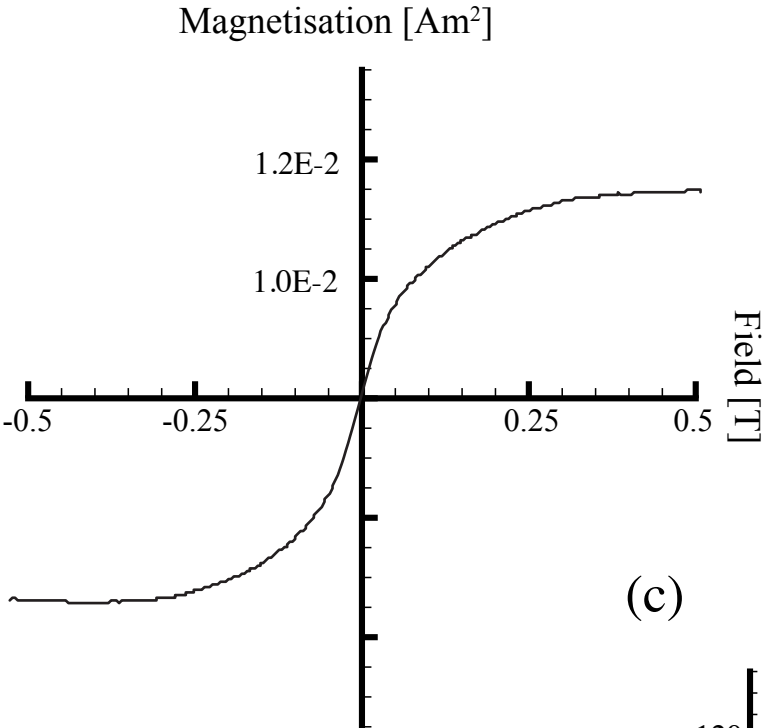
Zero field cooling (ZFC) and field cooling (FC) curves from 300 to 10 K in 10 K steps as well as room temperature remanence (RT) cooling and warming curves from 300-10 K in a zero field. (FC - - - ZFC ···· RT warming →, cooling ←).

(d) AC Susceptibility as a function of temperature

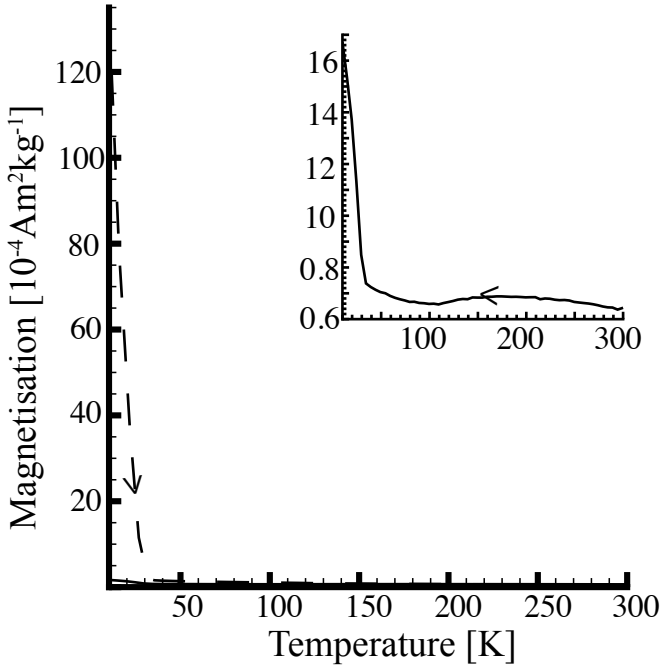
Susceptibility measurements for AC susceptibility at 7 frequencies between 10-300 K in 10 K steps at seven frequencies (1.0, 32.2, 10.0, 31.6, 100.1, 316.7, 997.3 Hz)

9/09B-3 - 1 magnetic experimentation

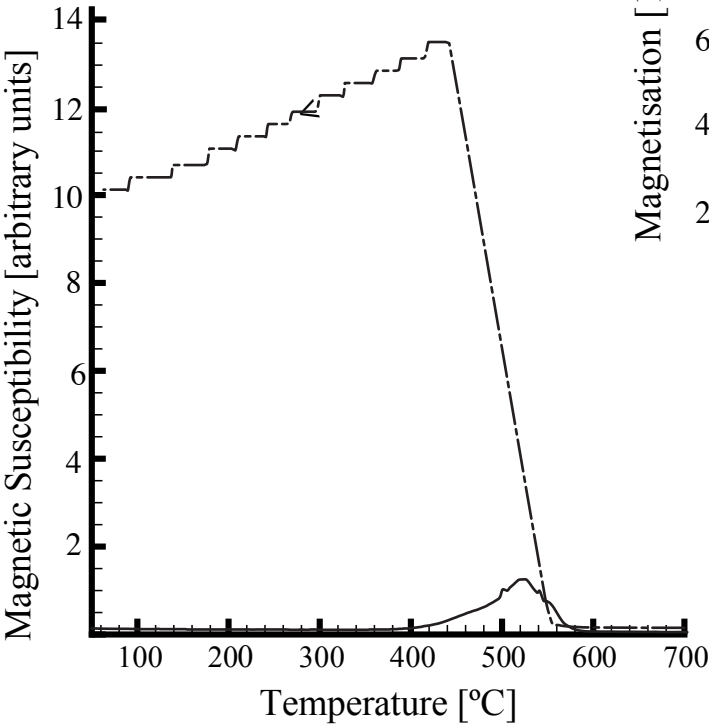
(a)



(c)



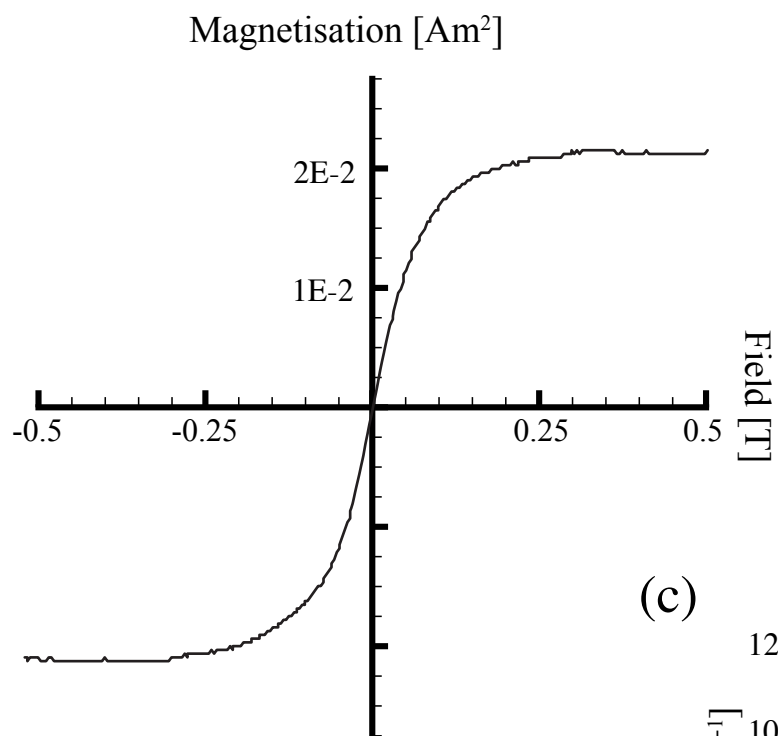
(b)



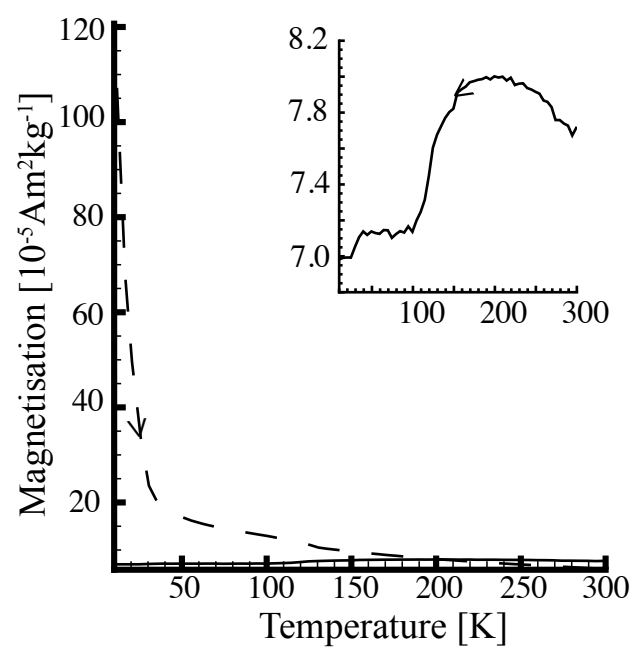
9/09B-3 - 2

magnetic experimentation

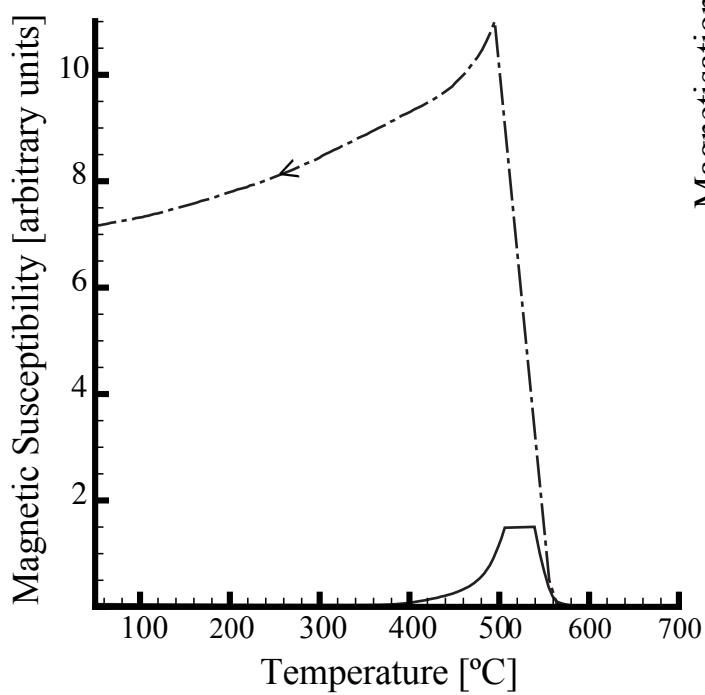
(a)



(c)



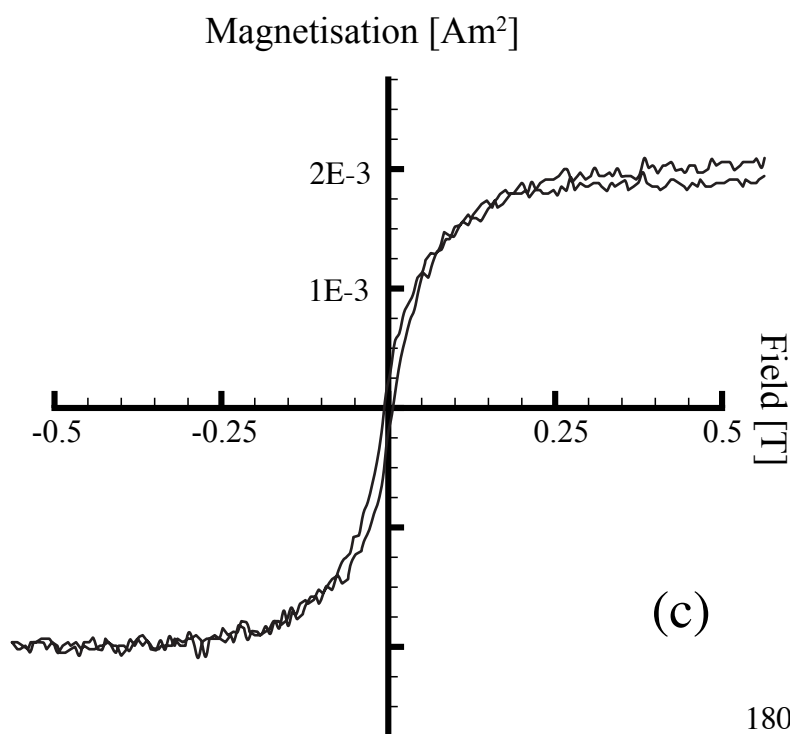
(b)



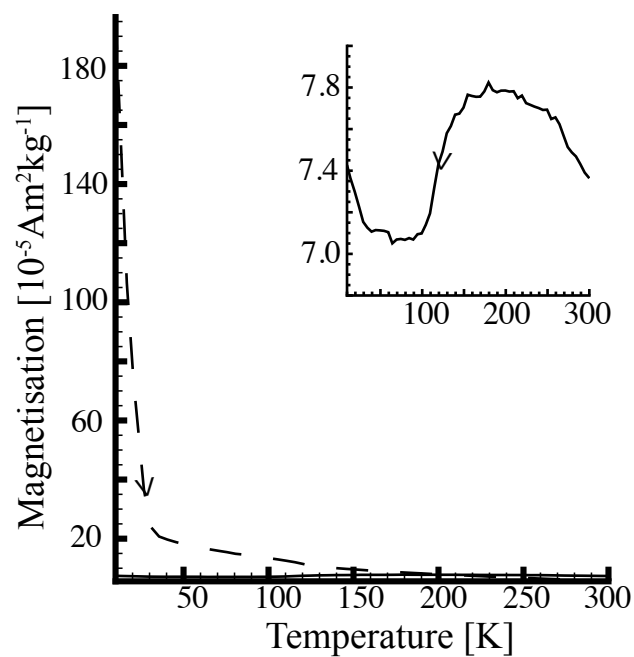
9/09B-3 -3

magnetic experimentation

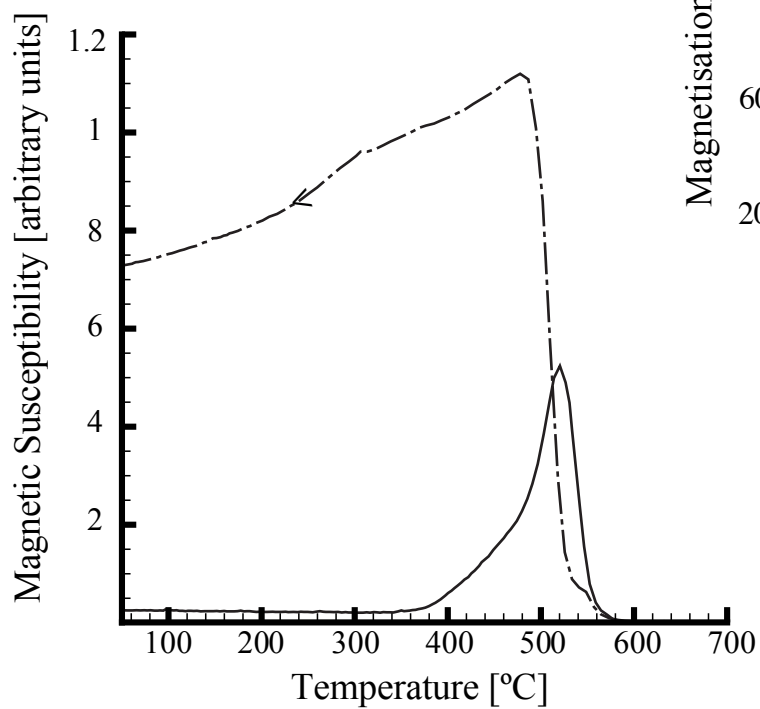
(a)



(c)



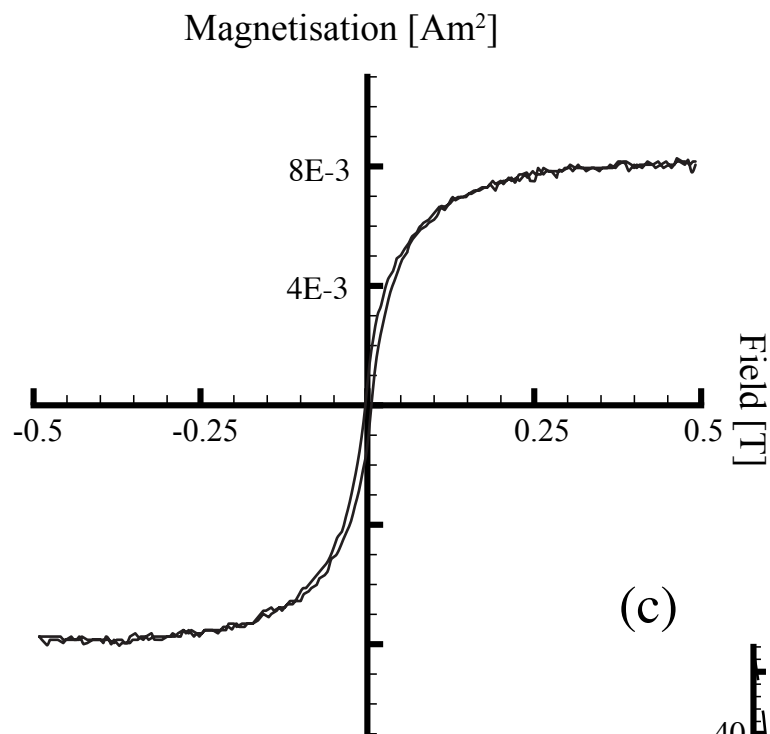
(b)



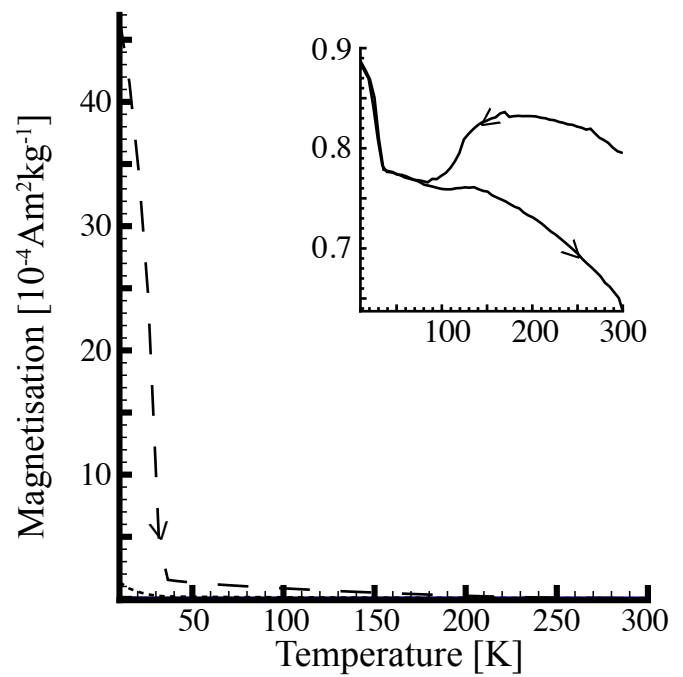
9/09B-3 -4

magnetic experimentation

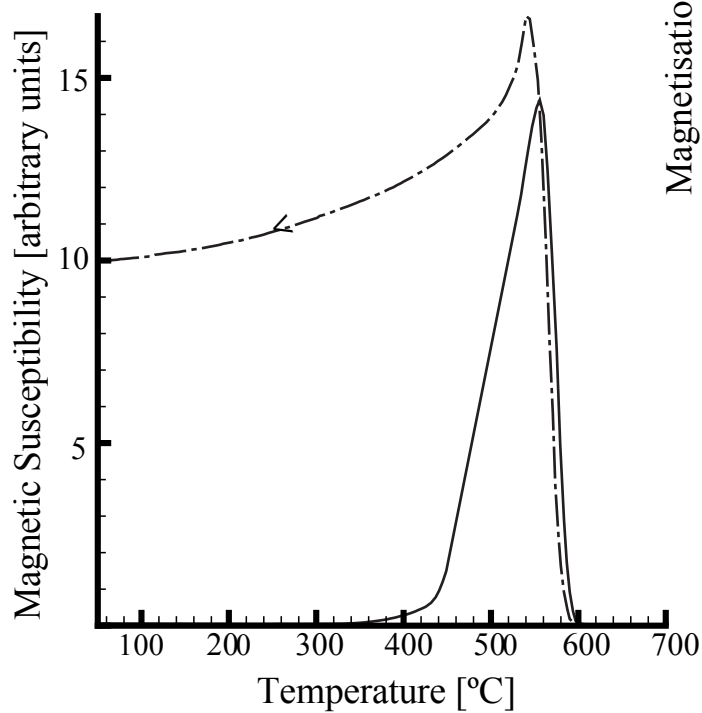
(a)



(c)



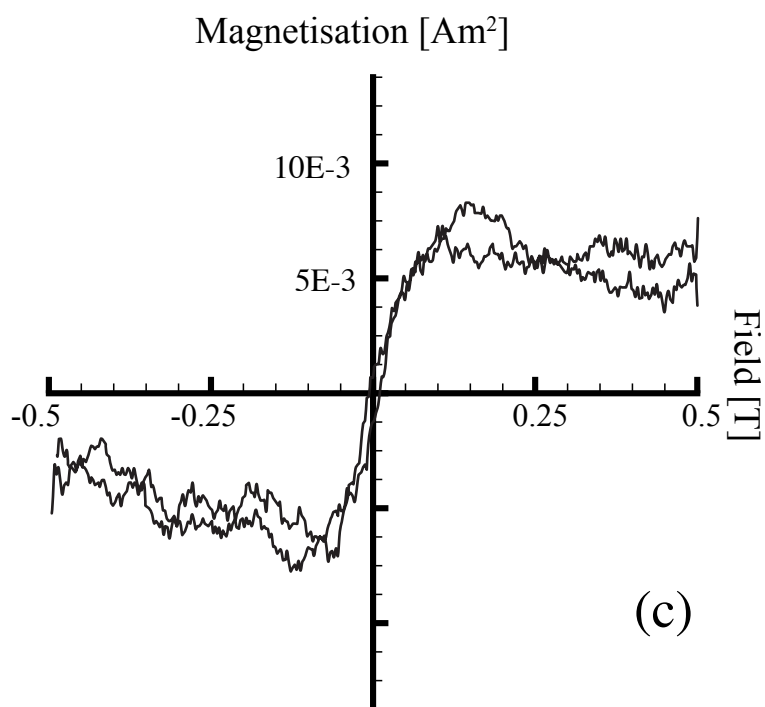
(b)



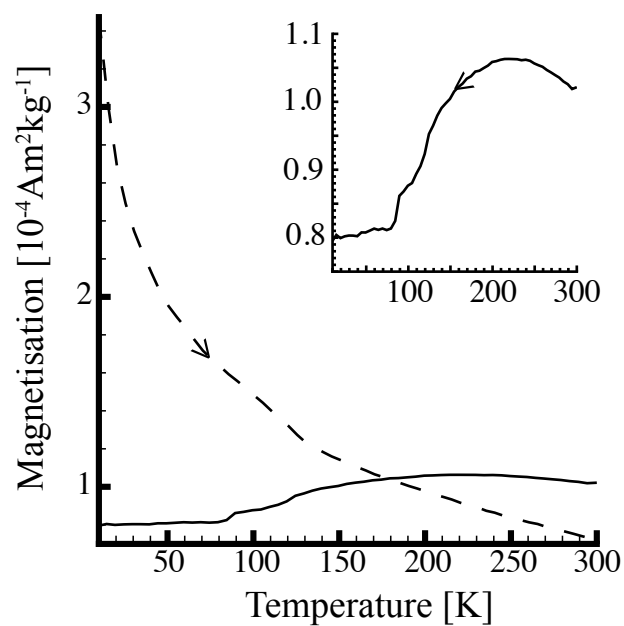
16/07A-A8 -1

magnetic experimentation

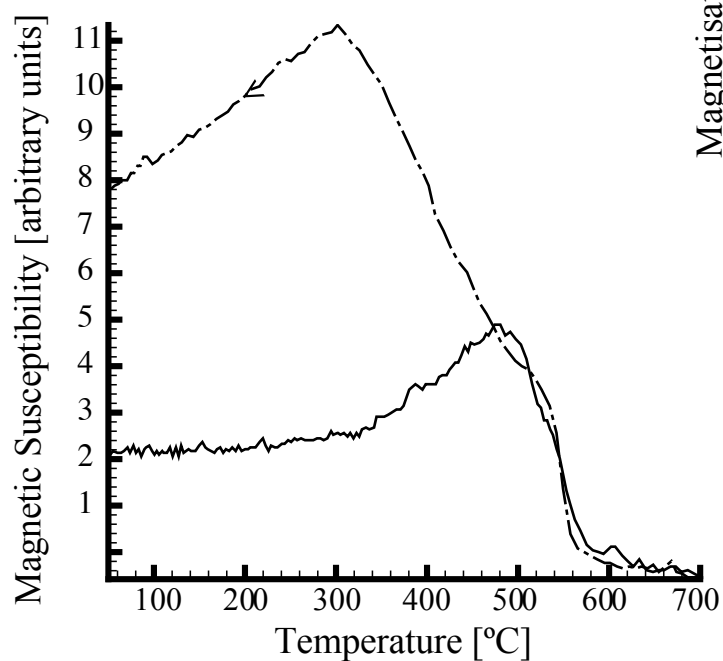
(a)



(c)



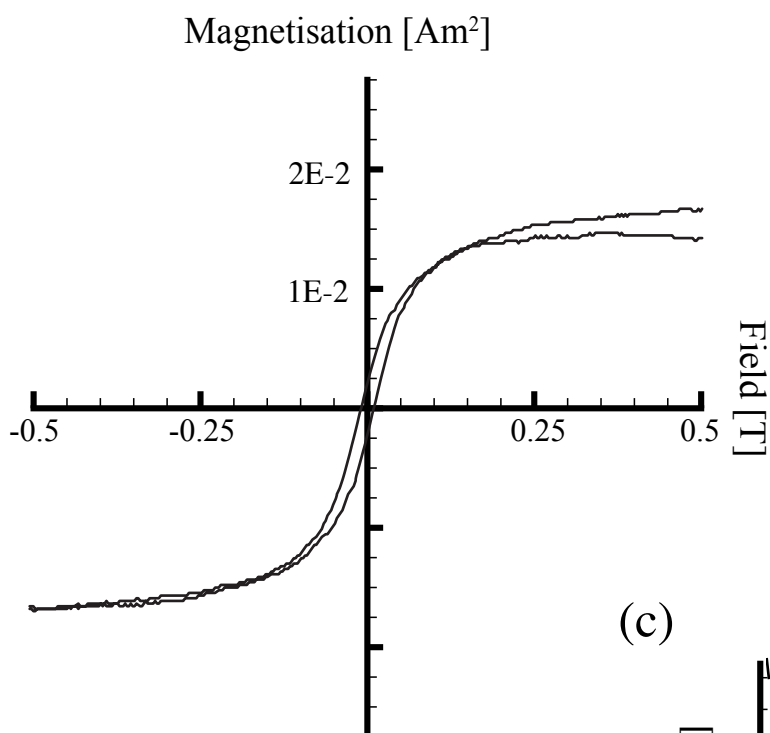
(b)



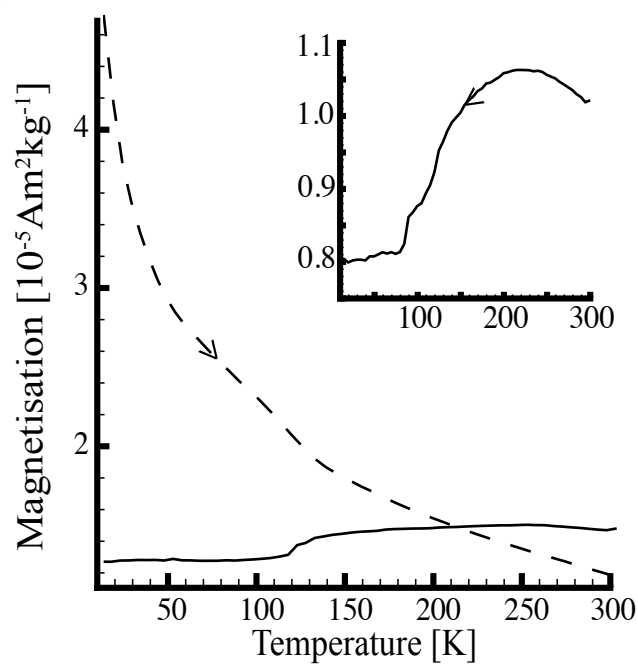
16/07A-A8 -2

magnetic experimentation

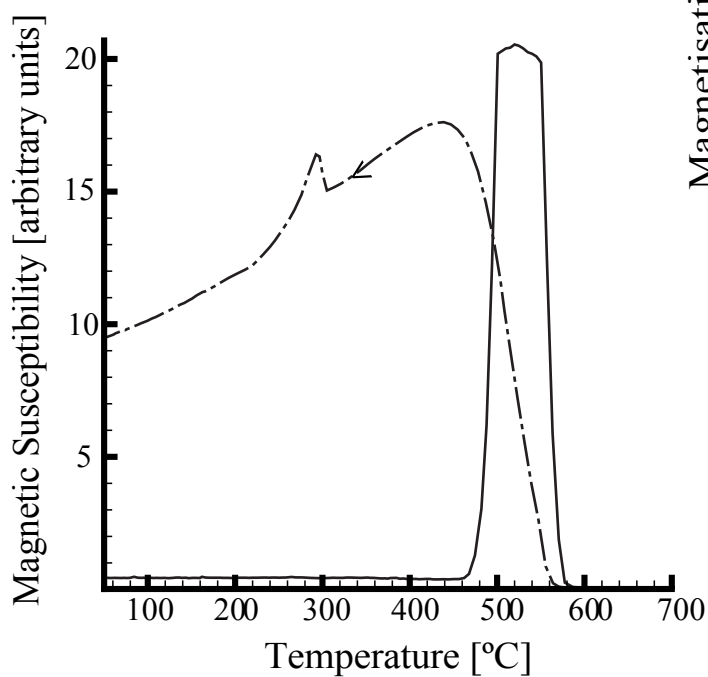
(a)



(c)



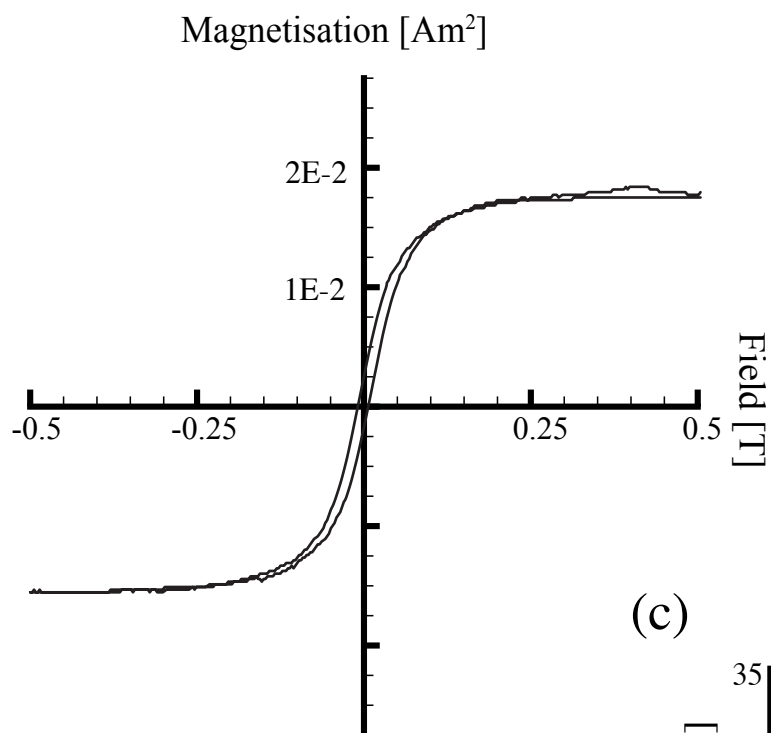
(b)



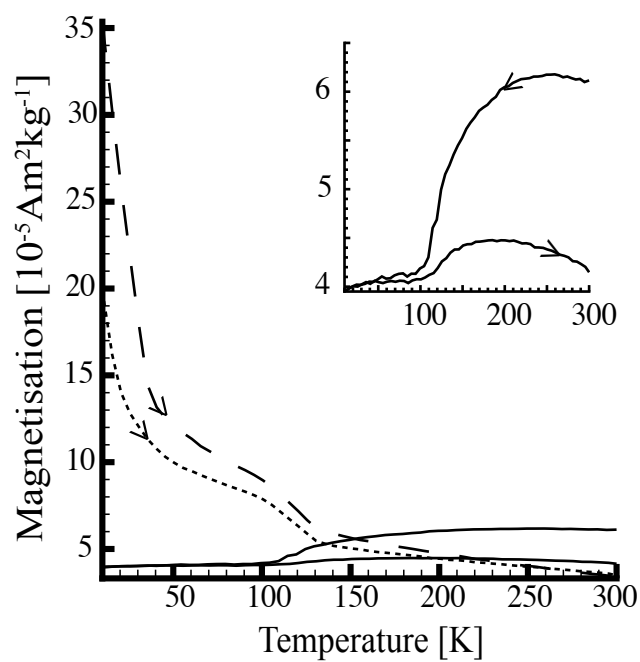
16/07A-A8 -3

magnetic experimentation

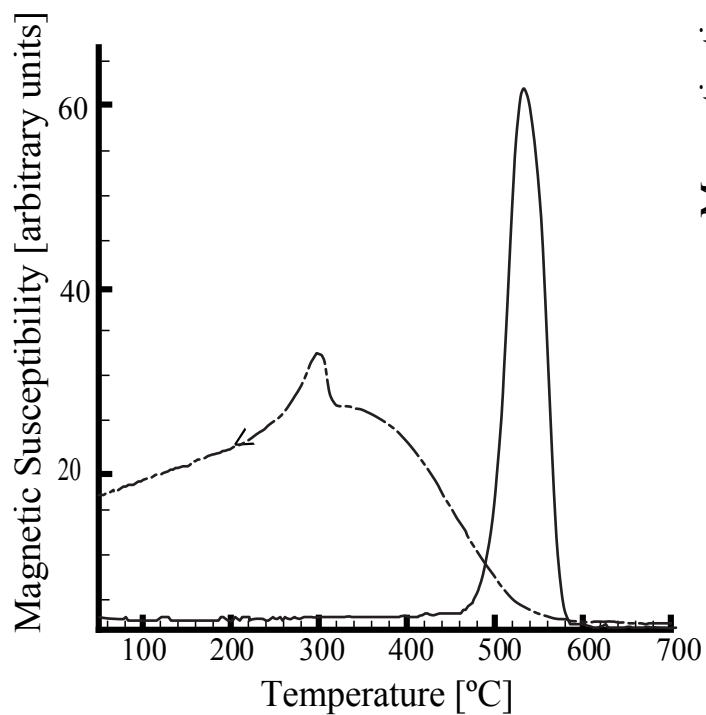
(a)



(c)



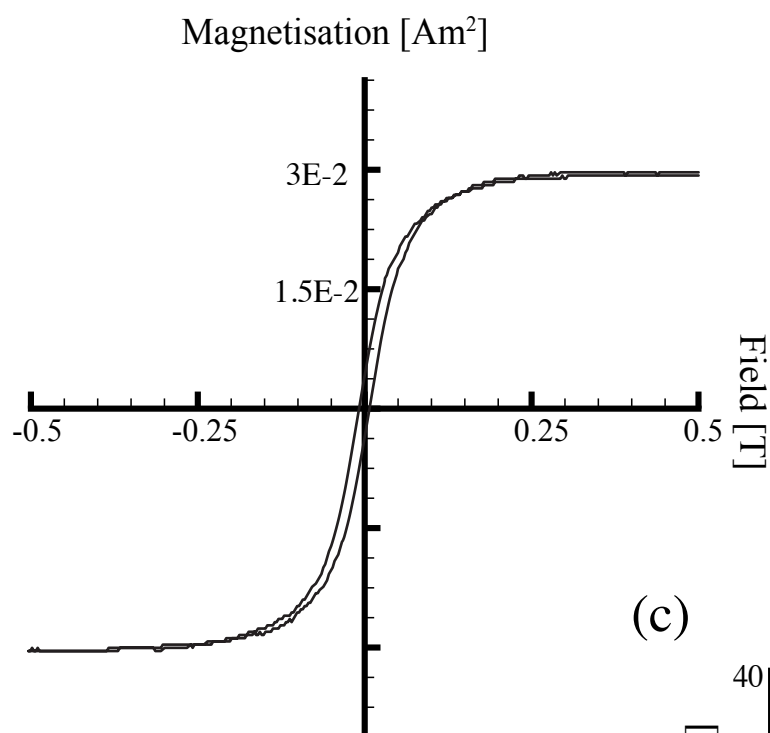
(b)



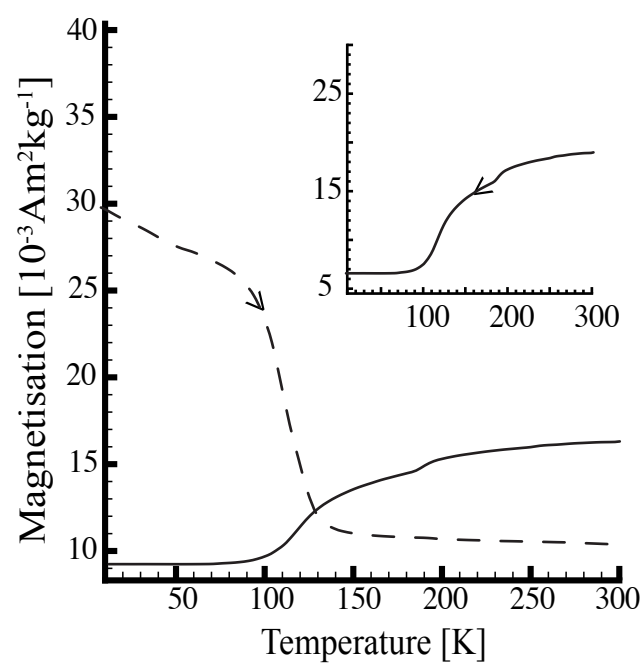
16/07A-A8 -4

magnetic experimentation

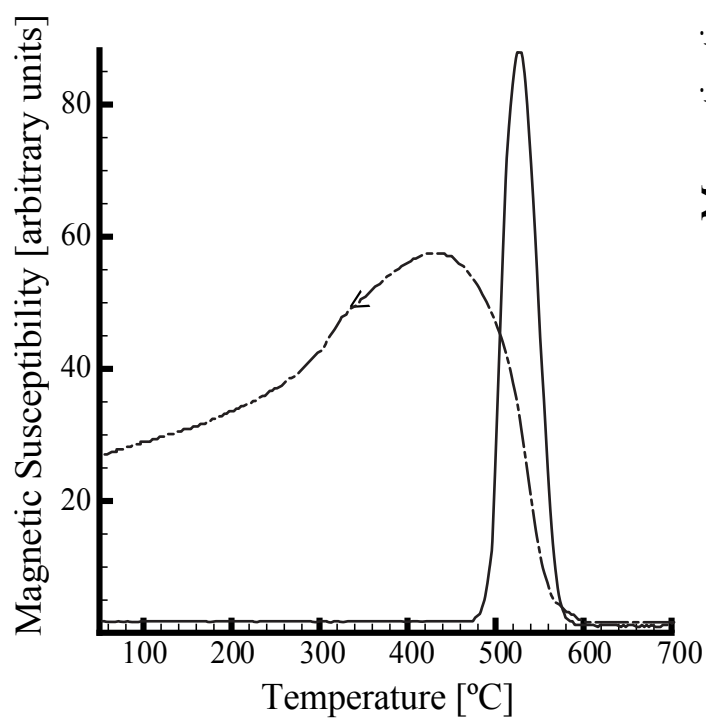
(a)



(c)



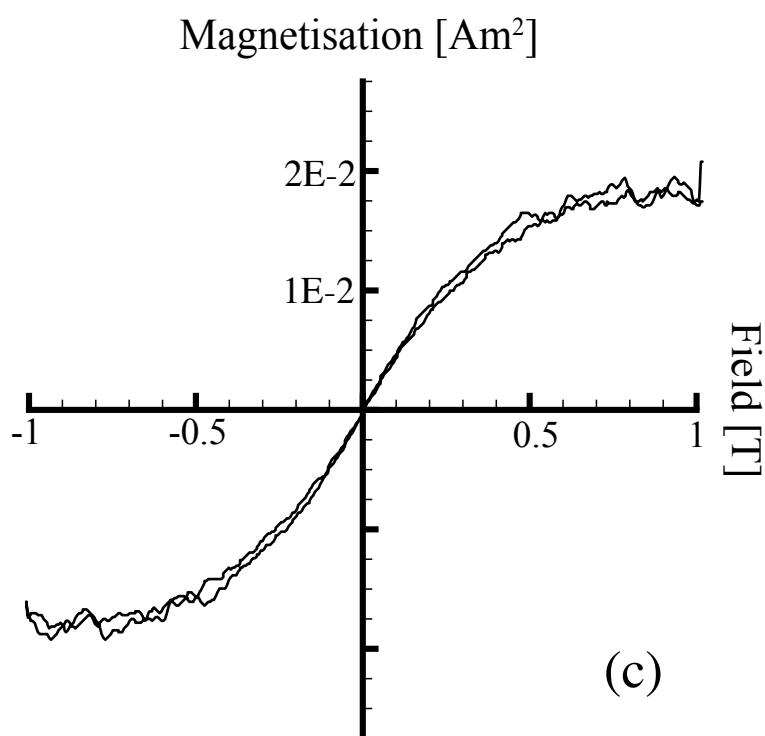
(b)



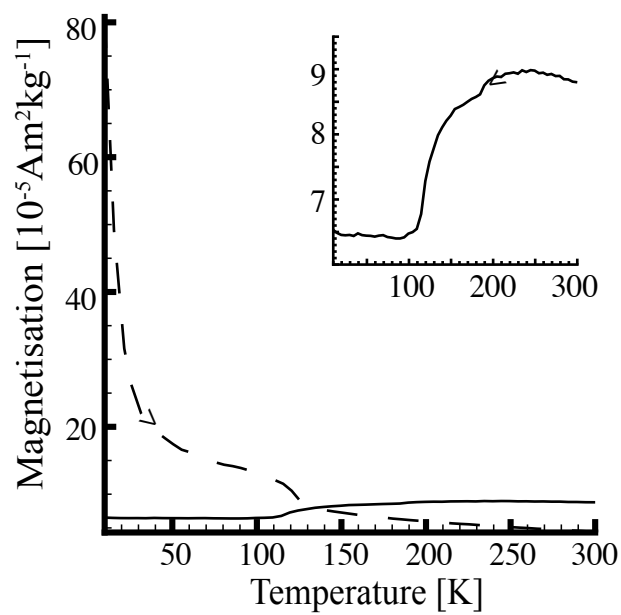
211/29-C4 - 1

magnetic experimentation

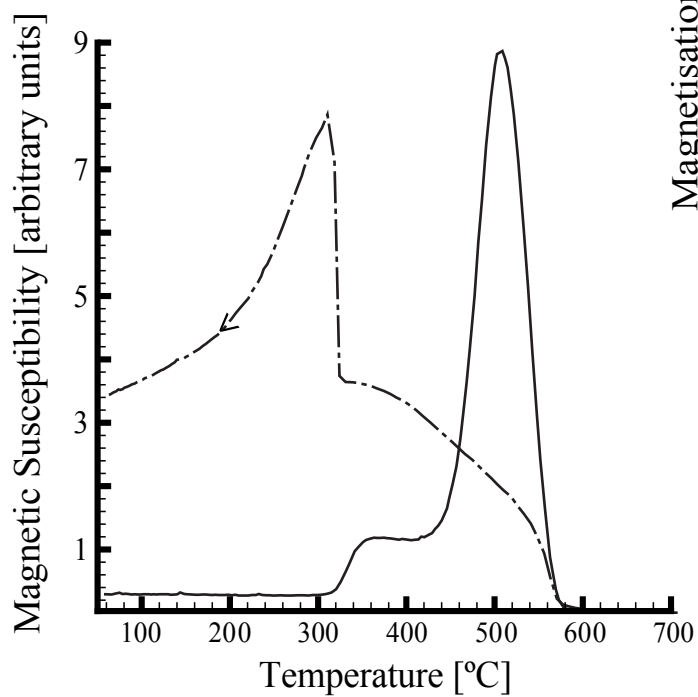
(a)



(c)



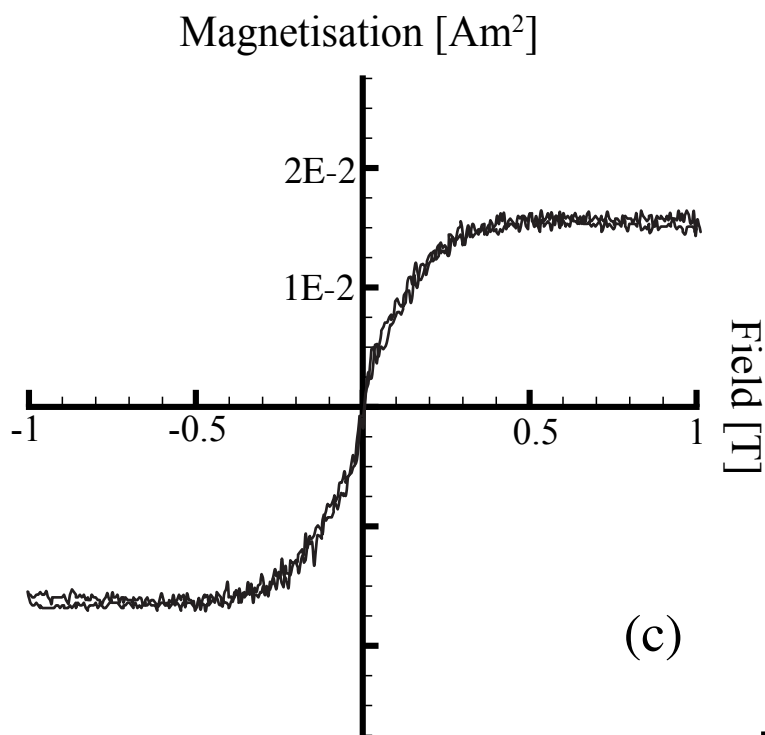
(b)



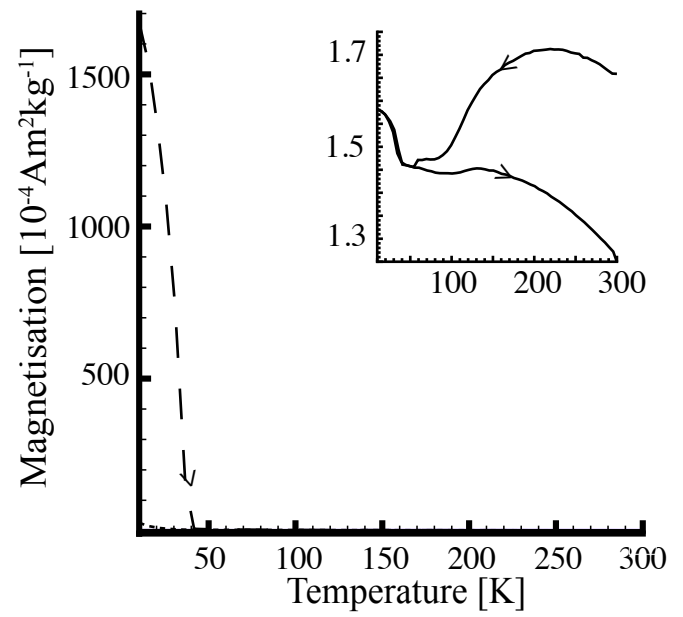
211/29-C4 - 2

magnetic experimentation

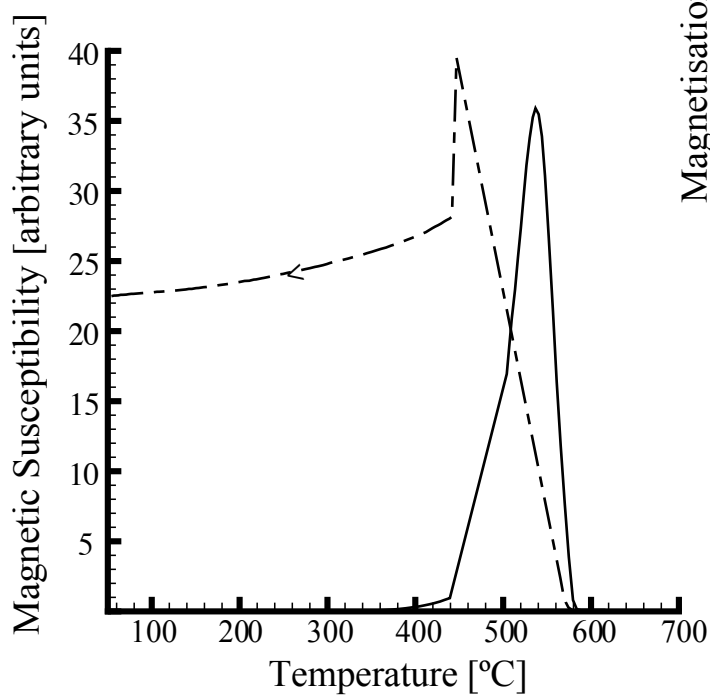
(a)



(c)



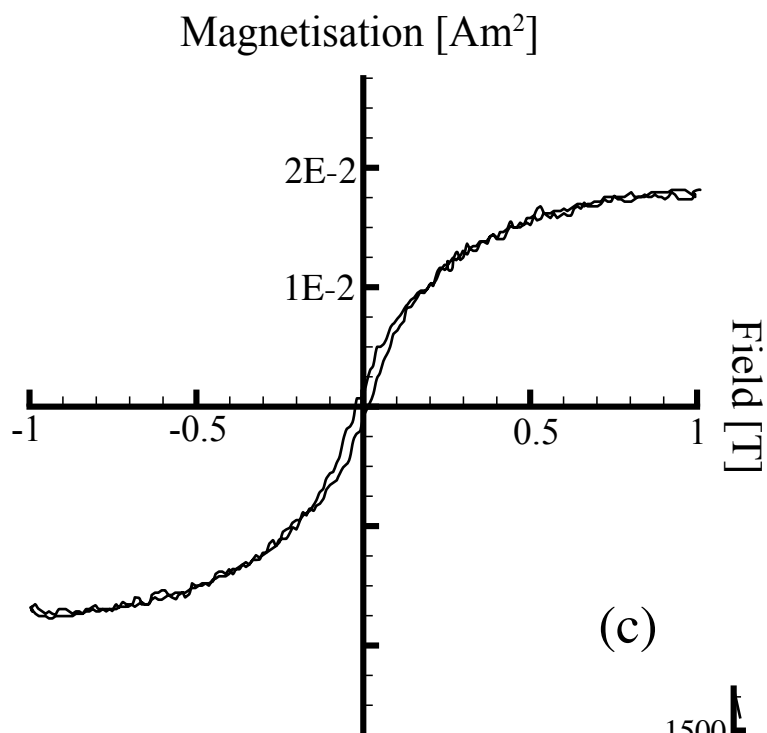
(b)



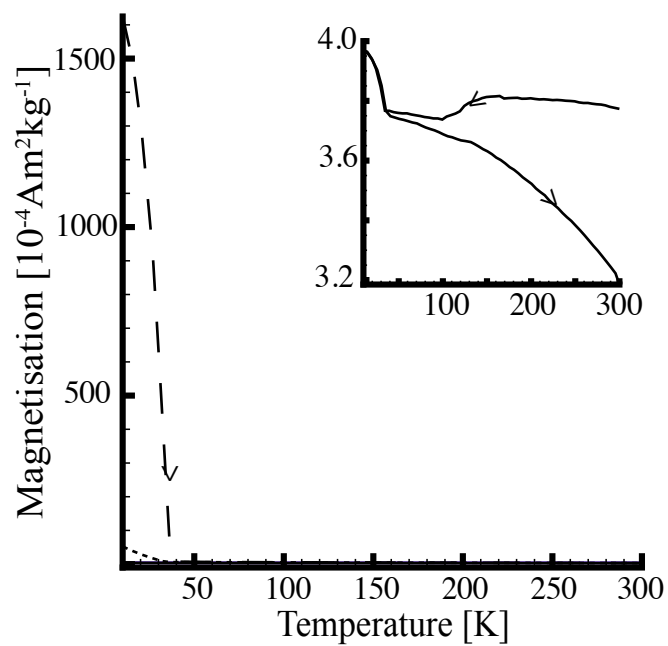
211/29-C4 - 3

magnetic experimentation

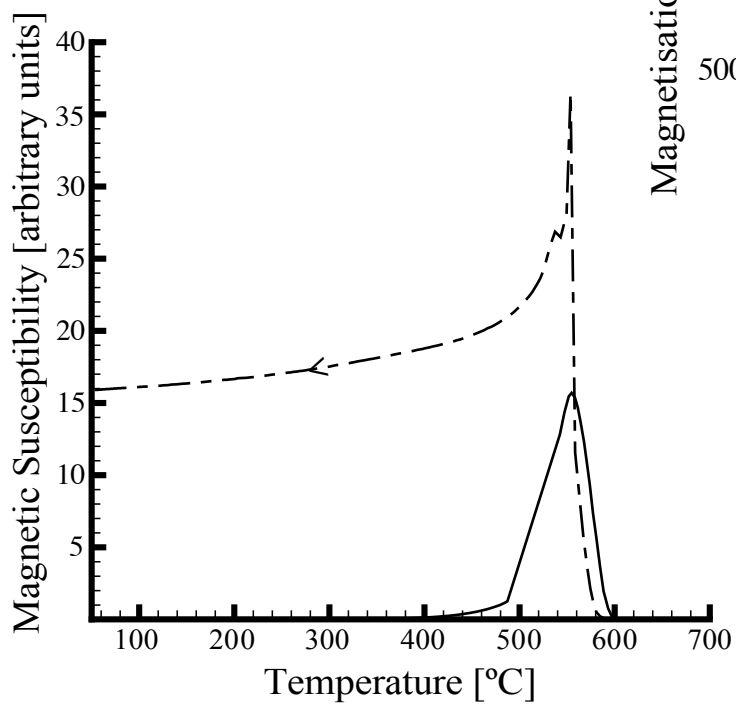
(a)



(c)



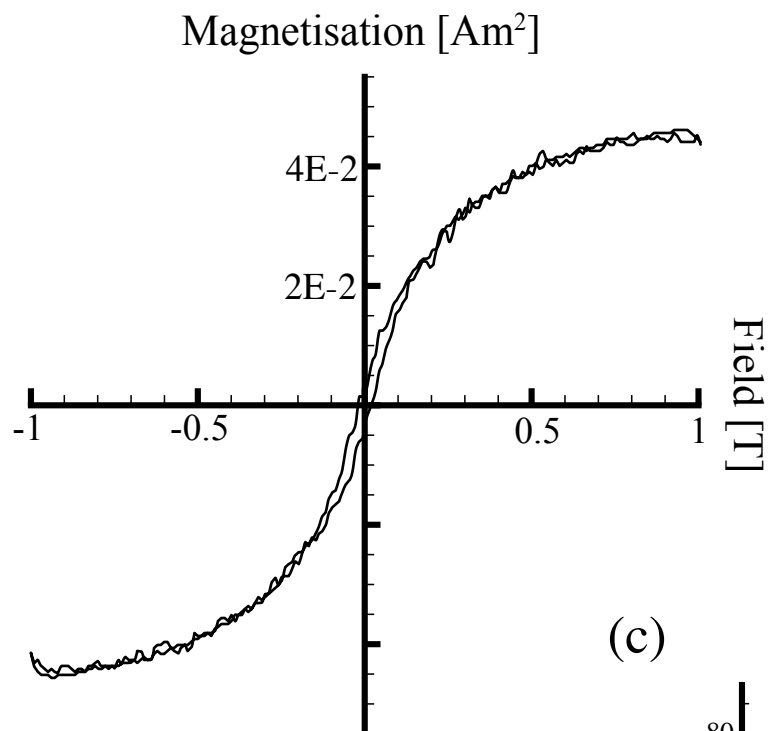
(b)



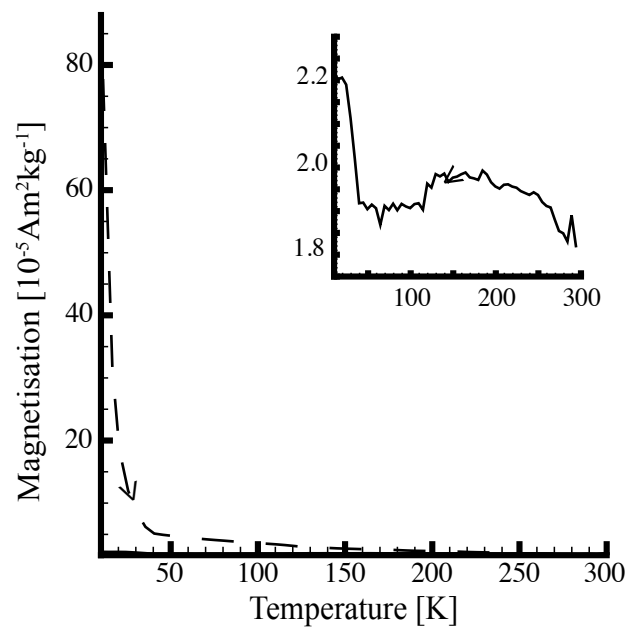
211/29-C4 - 4

magnetic experimentation

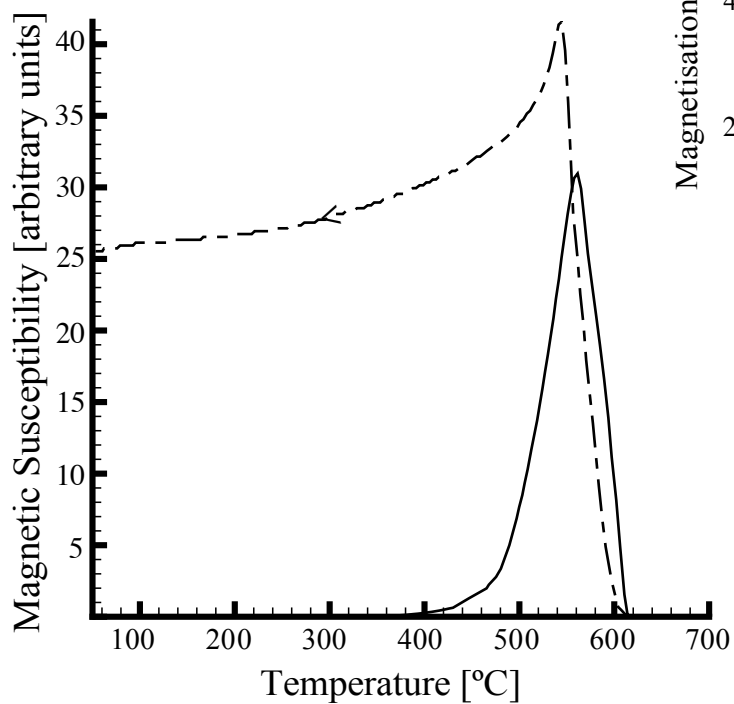
(a)



(c)



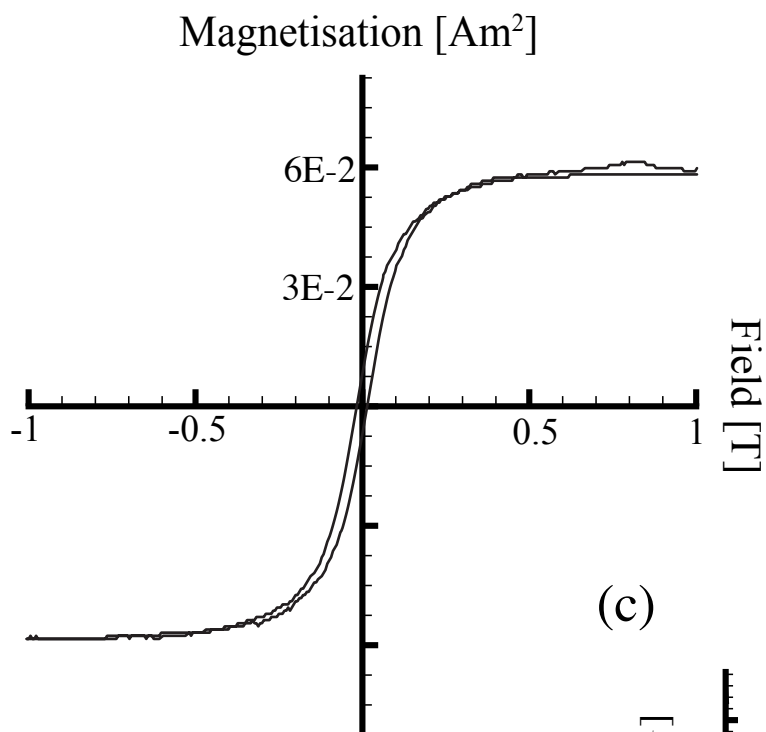
(b)



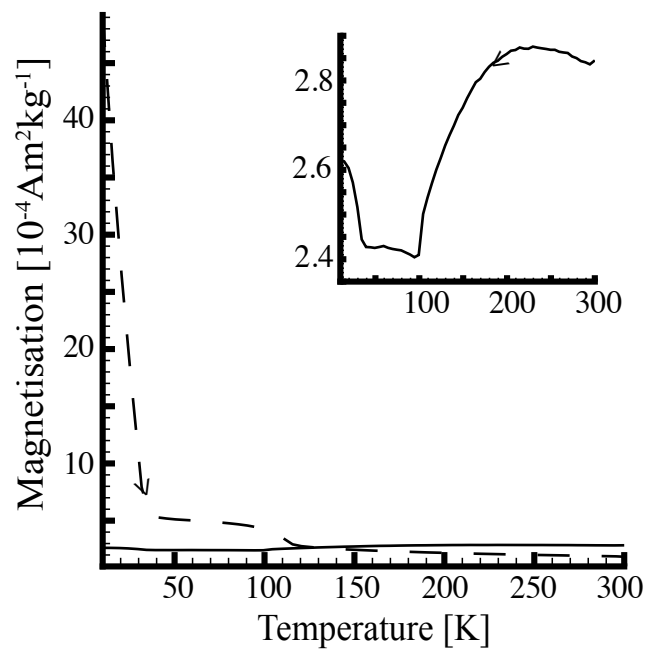
211/29-C4 - 5

magnetic experimentation

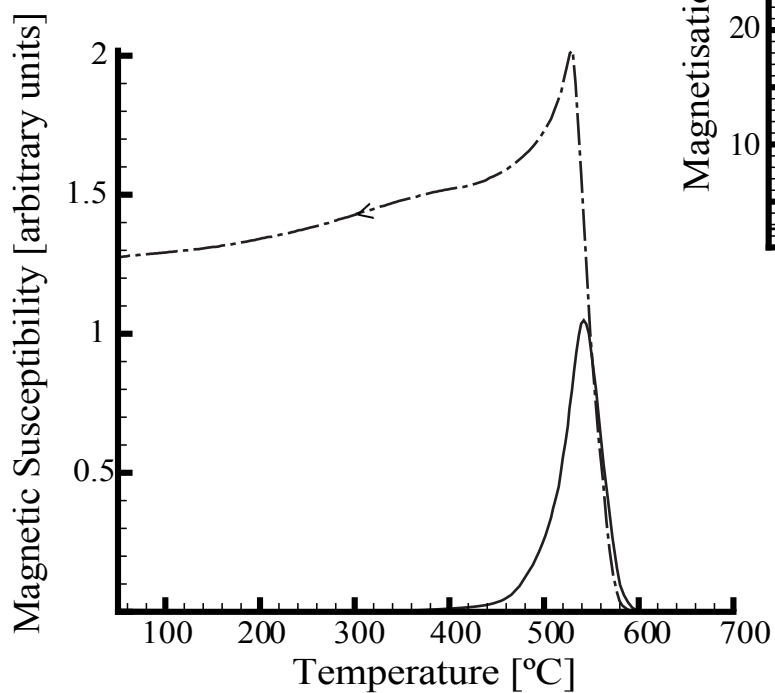
(a)



(c)



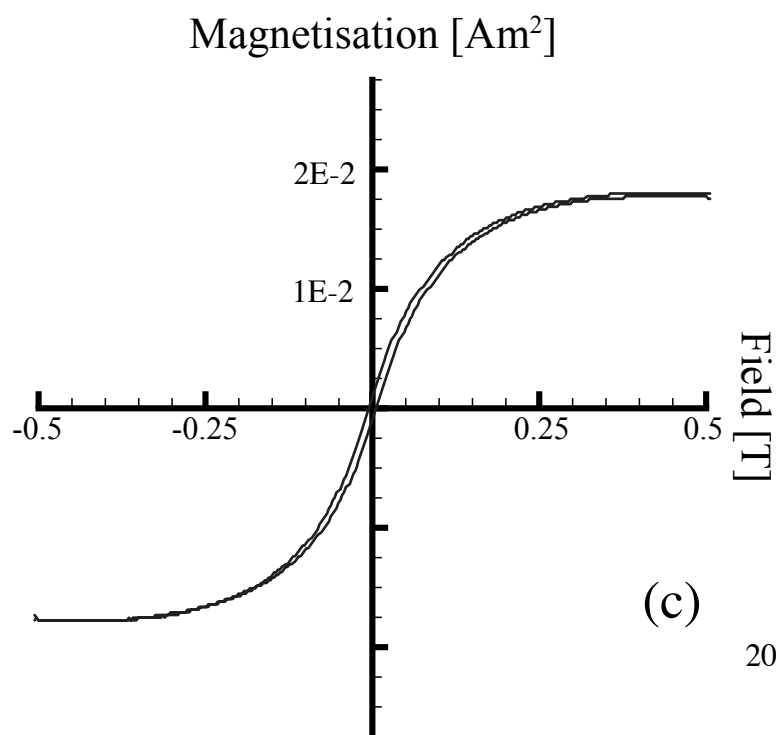
(b)



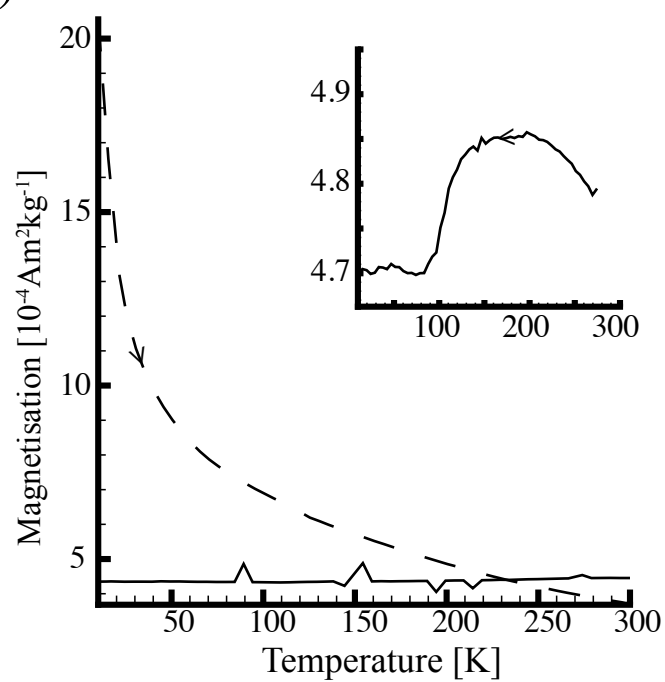
3/28A-4 -1

magnetic experimentation

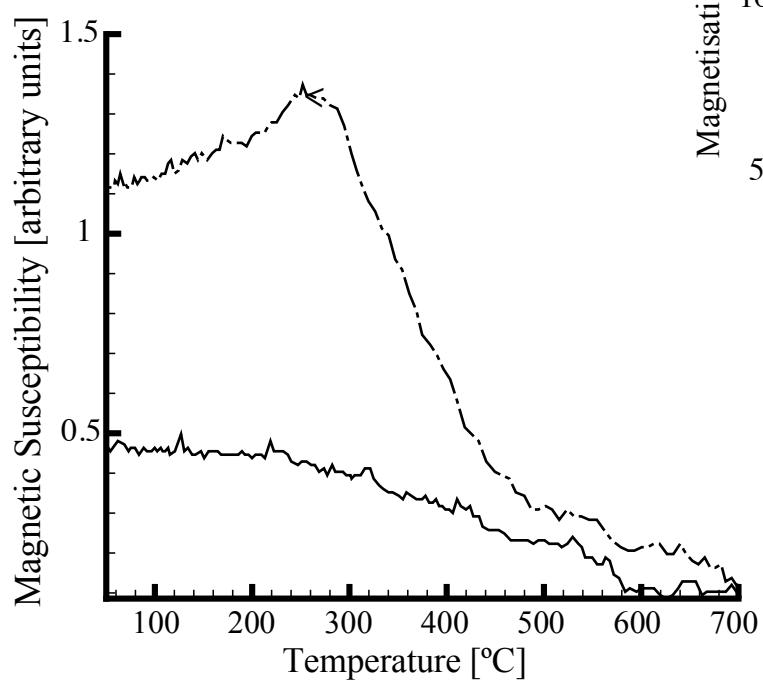
(a)



(c)



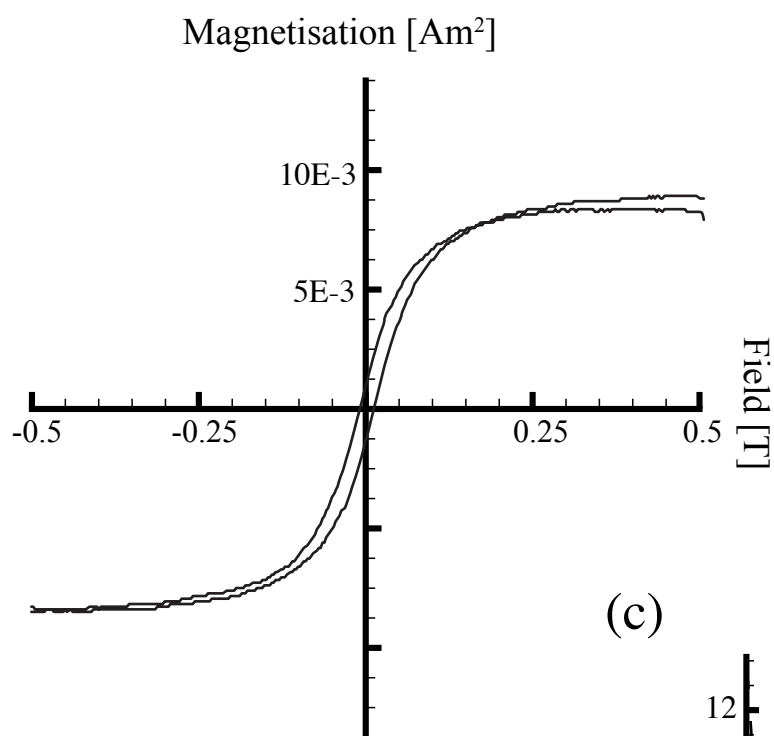
(b)



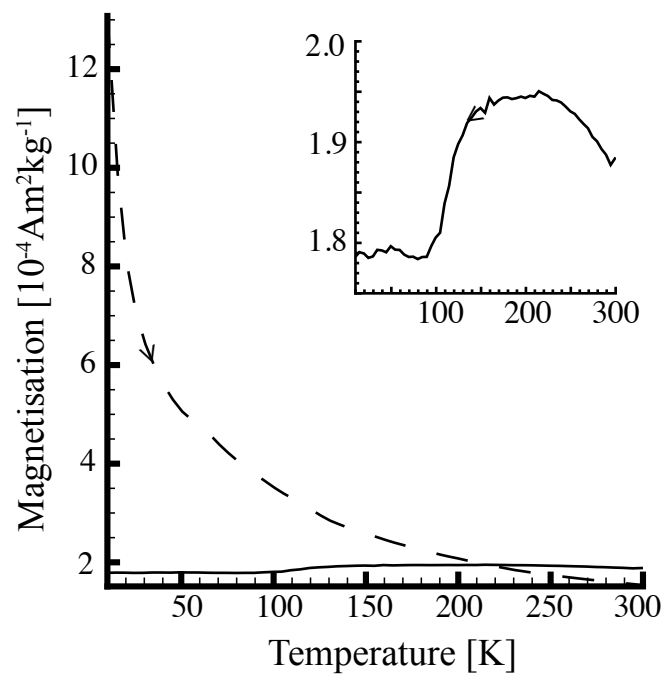
3/28A-4 -2

magnetic experimentation

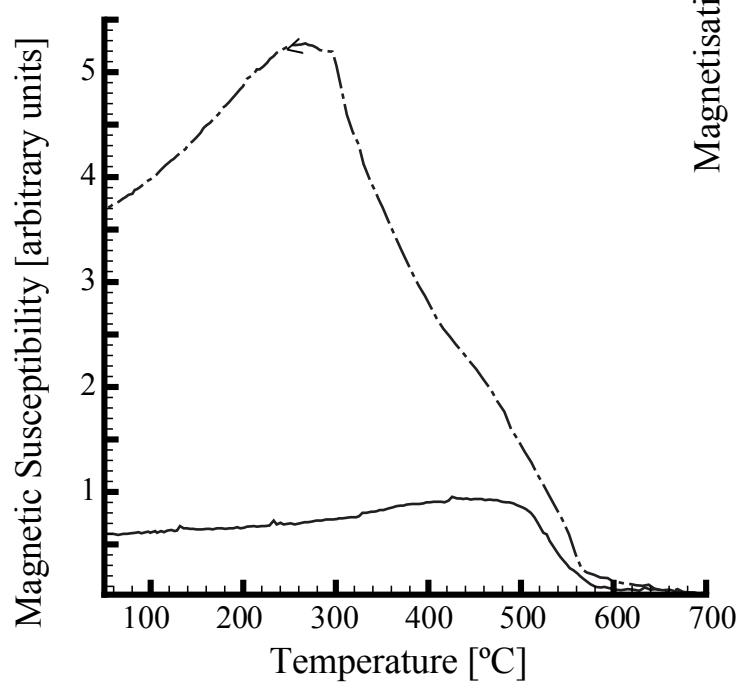
(a)



(c)

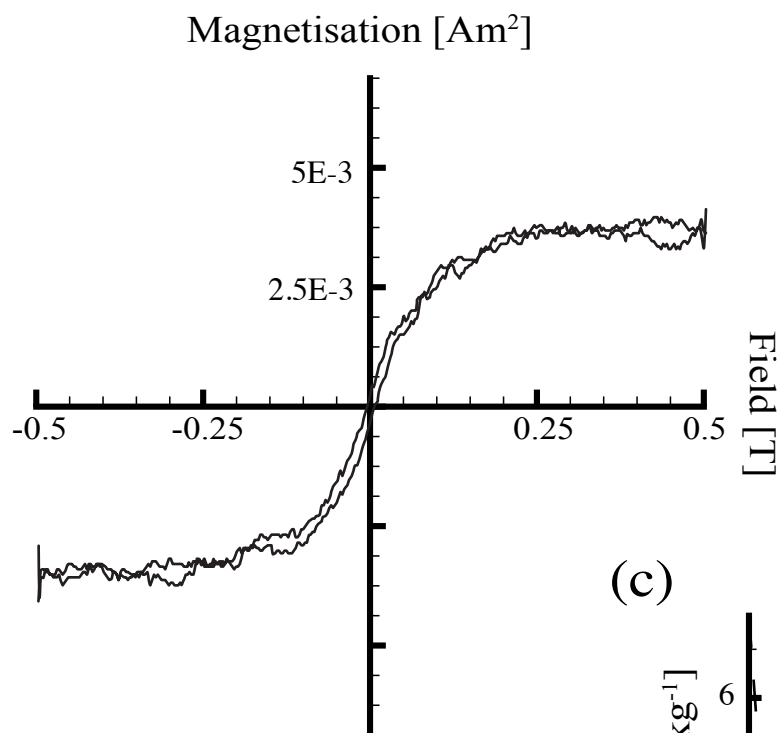


(b)

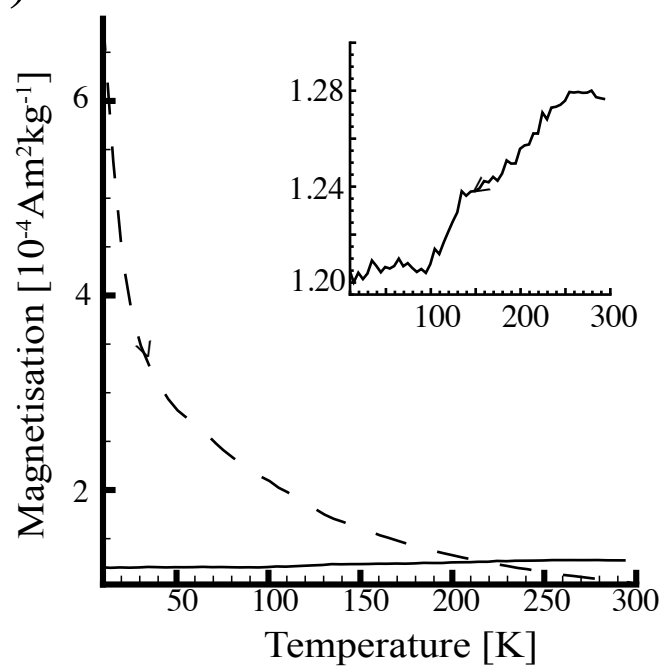


3/28A-4 -3 magnetic experimentation

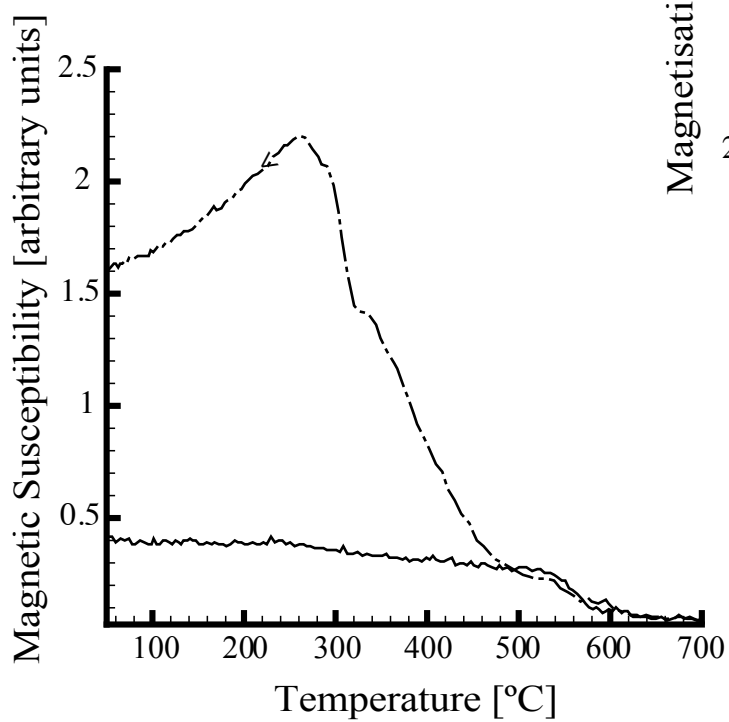
(a)



(c)

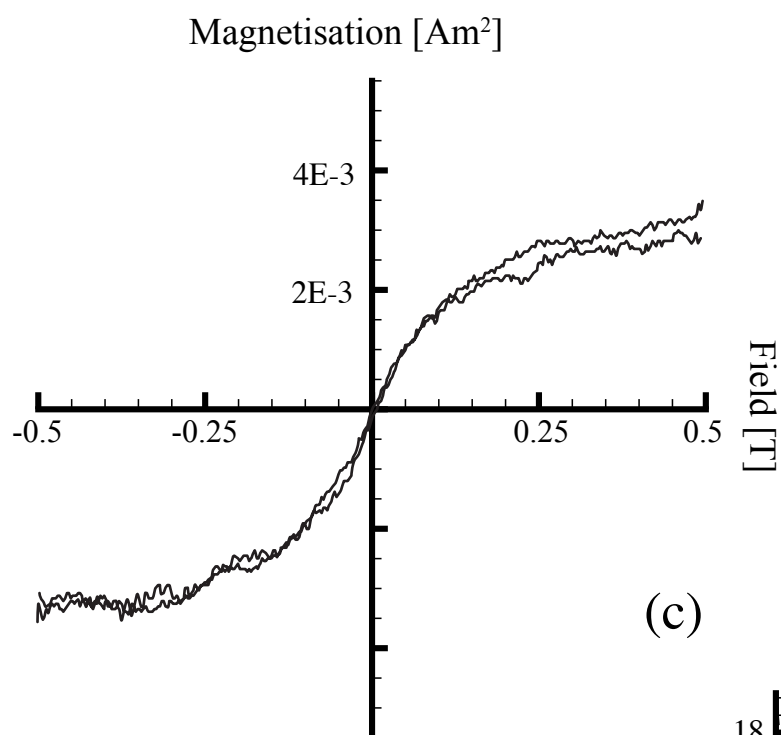


(b)

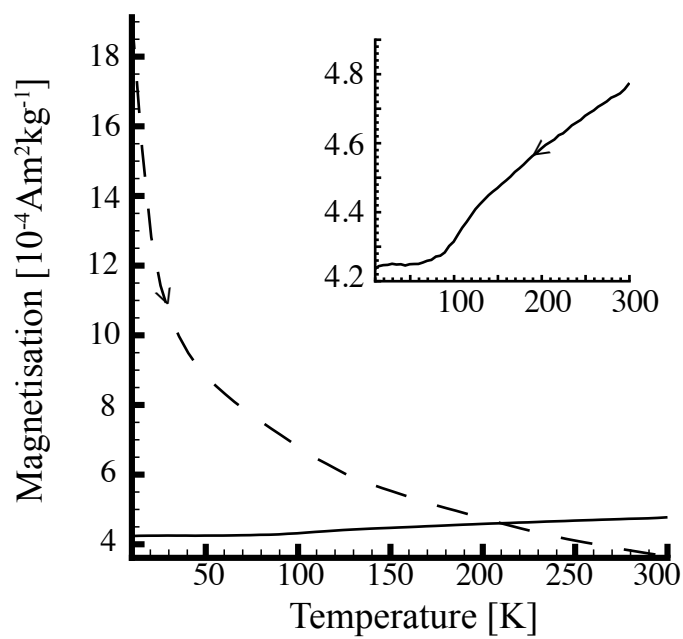


3/28A-4 -4 magnetic experimentation

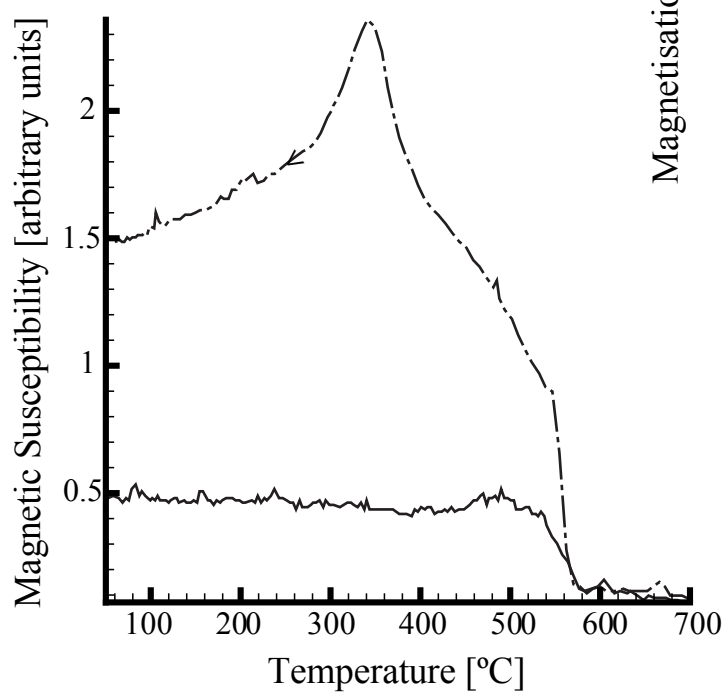
(a)



(c)



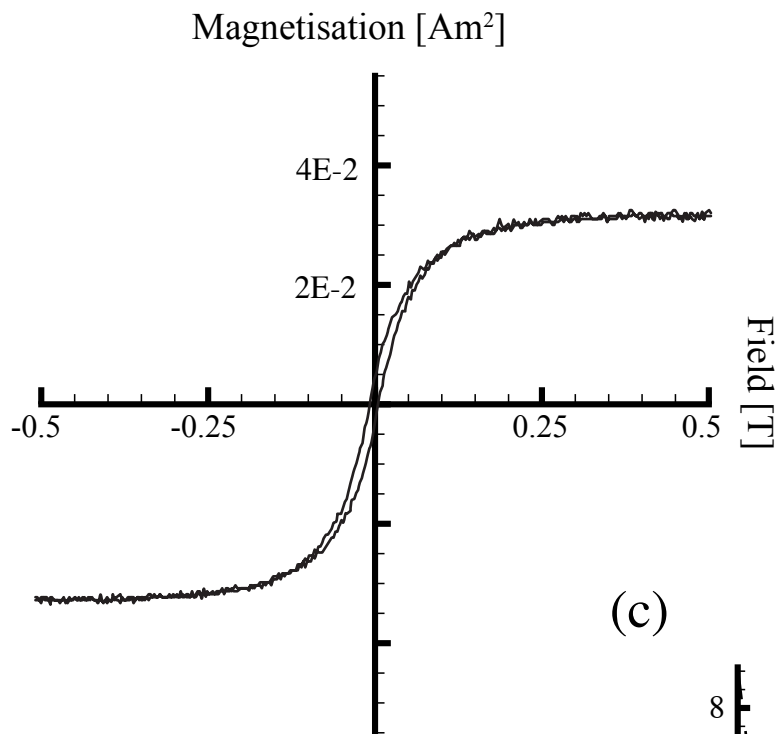
(b)



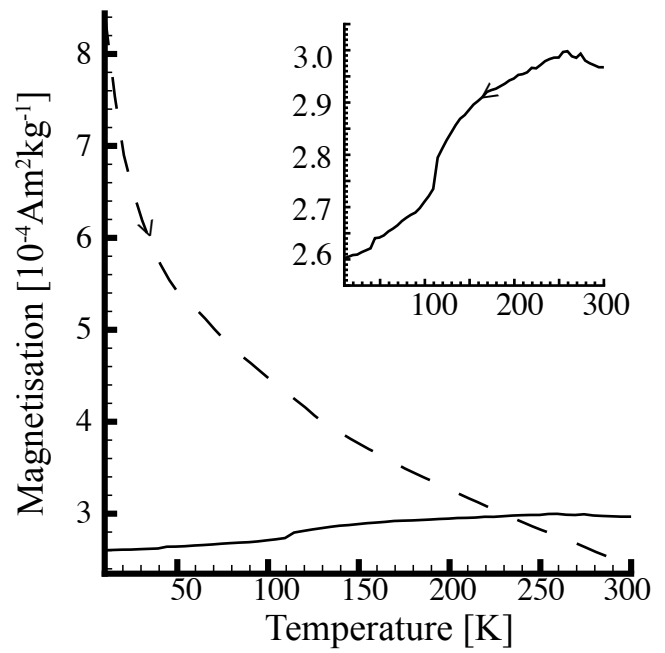
16/17-13 -1

magnetic experimentation

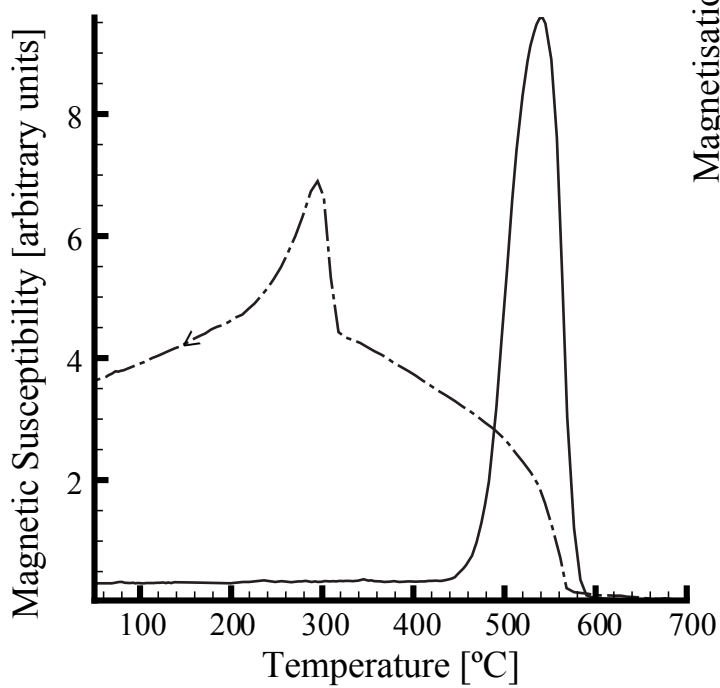
(a)



(c)



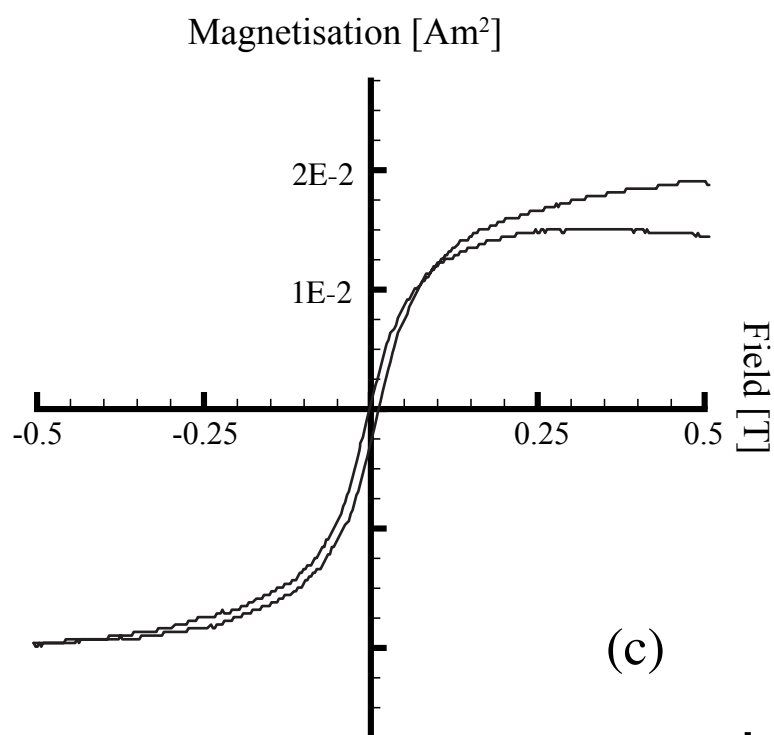
(b)



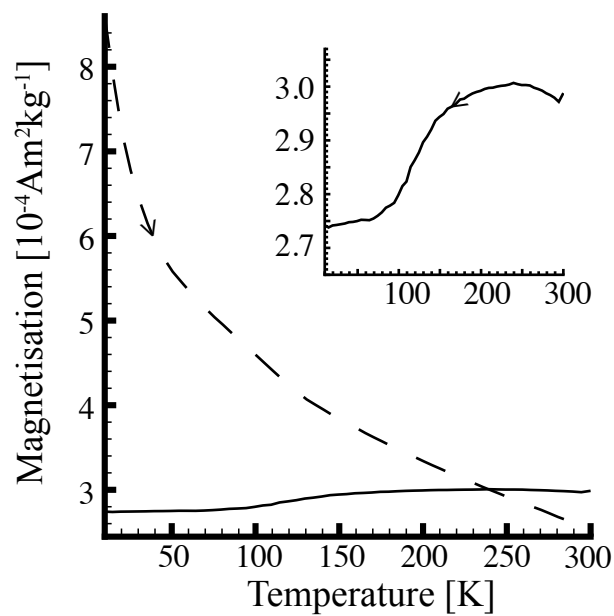
16/17-13 -2

magnetic experimentation

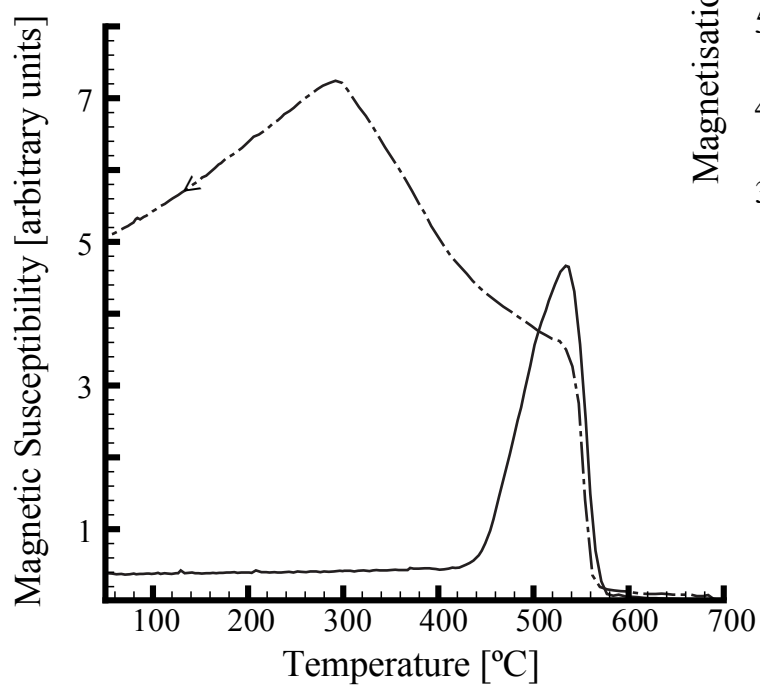
(a)



(c)

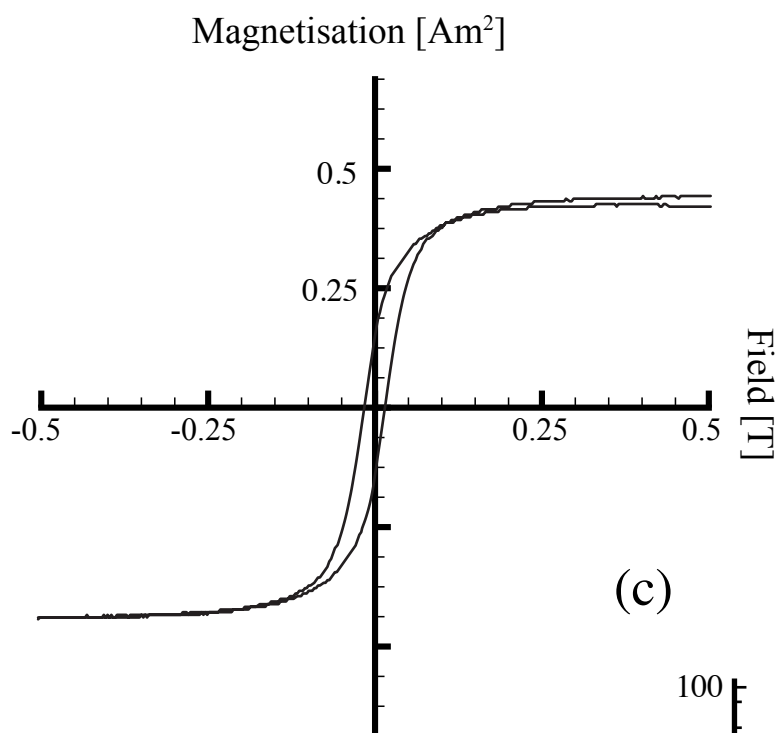


(b)

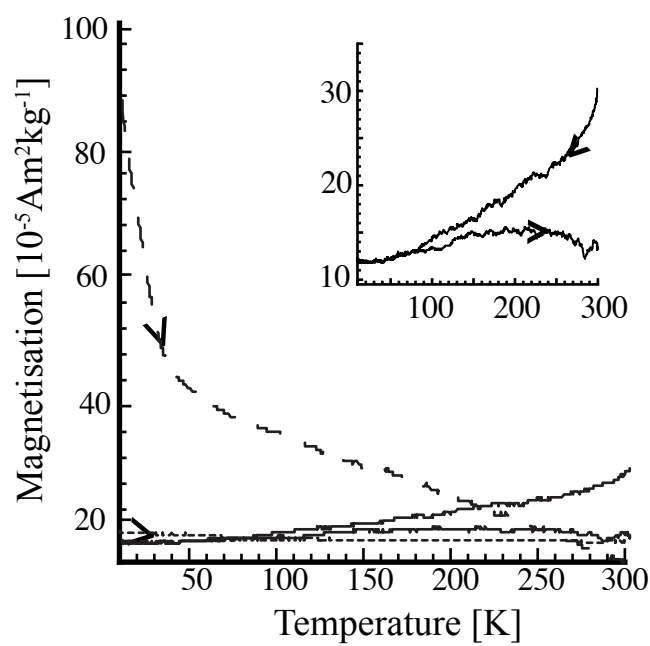


3/03-11 (DRY) magnetic experimentation

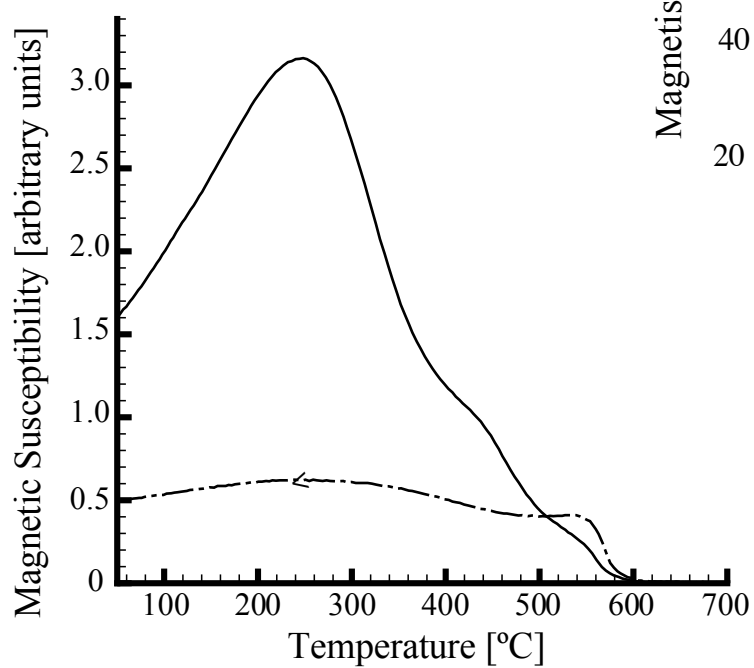
(a)



(c)

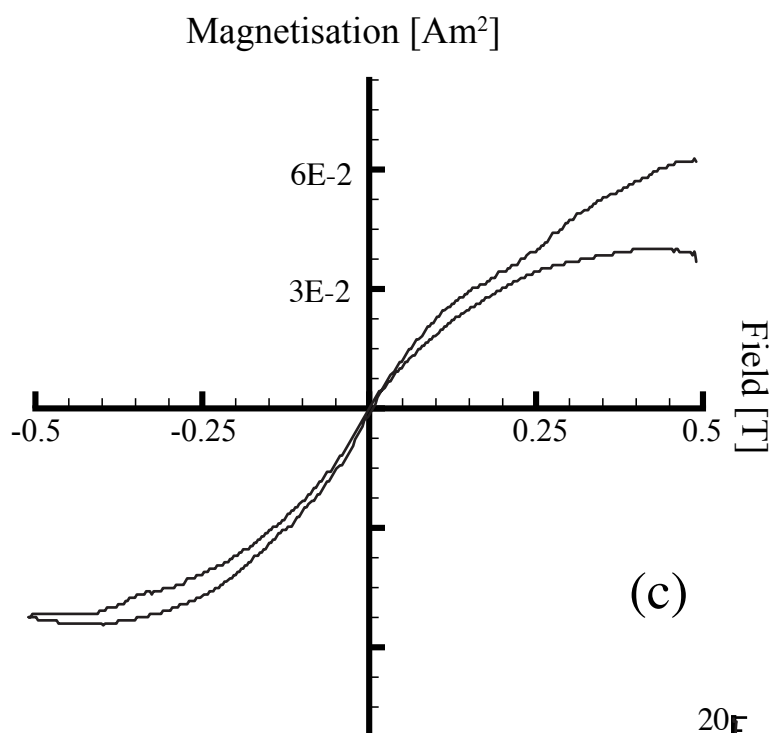


(b)

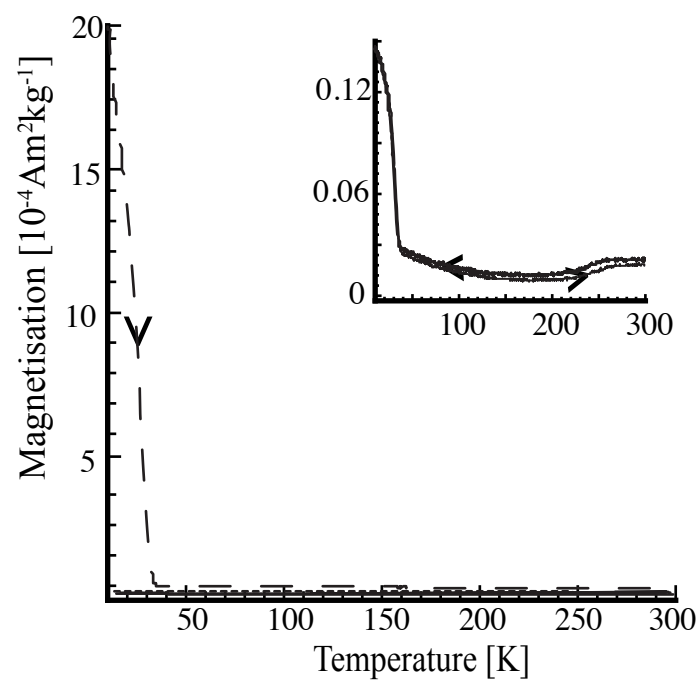


211/29-8A (DRY) magnetic experimentation

(a)



(c)



(b)

