

UNDERSTANDING MAGNETIC ENHANCEMENT IN HYDROCARBON RESERVOIRS

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Declaration of Originality

I hereby declare that this thesis “Understanding Magnetic Enhancement in Hydrocarbon reservoirs, using the Nisku as a case study” and the work presented here originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references.

Osamor Jude Chukwunwike (2020)

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ABSTRACT

A detailed magnetic study has been undertaken for over 115 samples of 12 wells in the Brazeau area of the Devonian Nisku formation, Alberta Canada. I report a range of magnetic results including room temperature hysteresis, first-order reverse curve (FORCs), low-temperature magnetometry, high-temperature magnetic susceptibility results, Scanning Electron Microscopy (SEM) results of samples from sour gas pools, sweet gas and oil pools, and dry well. The sour gas pools had the strongest magnetization, followed by the sweet oil and gas pools, while the dry well had the weakest magnetization from the room temperature results. There was observable strong magnetic enhancement at the hydrocarbon fluid contact for some wells particularly the sour gas wells, while some did not have anomalies exactly at the contacts but few meters away from the contact. These anomalies are suspected to be paleo-contacts. This observable magnetic enhancement was caused by inorganic precipitation of interacting single domain hematite (0.03-0.08 μm), multidomain magnetite with a vortex (3 μm above), and SP (<0.03 μm) greigite and pyrrhotite nanoparticle magnetic minerals at the hydrocarbon contacts. Iron oxide and sulphide minerals were revealed to be present in all the wells both from low and high-temperature measurements and also with the FORC analysis showing high coercivity ~100-350mT. From the data, iron sulphide greigite and pyrrhotite appears to be in dominant proportion alongside other minerals. I had the strong presence of siderite, greigite, and pyrite in the sour gas pools, and monoclinic pyrrhotite and maghemite in the sweet oil and gas pool and background presence of detrital magnetite, hematite, and siderite in the dry well. Authigenic magnetite and hematite were equally present in all the hydrocarbon wells. However, iron sulphide greigite and pyrrhotite appears to be in dominant proportion alongside other minerals.

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List of Publications & Conferences

Research abstract accepted at the AGU Geophysics, conference in Florida (2019)

The Geologist Association's poster presentation, 2nd prize best poster award (2019)

Identifying and understanding magnetic proxies & enhancement in hydrocarbon reservoirs using the novel Nisku carbonate formation, in Alberta Canada, as a case study (manuscript submitted)

Thermodynamic modelling of Anomalous magnetization in hydrocarbon reservoirs with additional greigite mineralogy and emphasis at the hydrocarbon contact using the Geochemist work bench (manuscript in preparation)

CHAPTER 1

1. Introduction

In hydrocarbon exploration, the use of seismic and well log data for interpretation cannot be overemphasized as it is one of the most valuable tools used. Acquiring this data can be very expensive as well as the complexities in the geology of the study area is still not fully resolved and understood. Given this, it is therefore imperative, to have a complementary cost-effective approach to exploration that would be of immense benefit to the industry. This chapter presents the use of a magnetic mineral characterization technique to identify hydrocarbon fluid contacts and also as a potential indicator of hydrocarbon presence in a full core.

A relationship between magnetic signatures and hydrocarbon generation was found by Donovan et al., (1984) where it was suggested that leakage from a petroleum or natural gas reservoir causes a chemically reducing environment in the overlying rocks and the consequent reduction of iron hydroxides and hematite to form magnetite causing a positive magnetic anomaly. This work by Donovan and subsequent authors (Foote 1984, Saunders and Terry 1985, Henry 1989, Machel and Burton 1993) have proposed the use of magnetism as a supportive method in hydrocarbon prospecting. Research in this area has spurred many authors to firmly establish a link between these two phenomena with some success.

Several studies have been conducted in investigating magnetic mineral formation around hydrocarbon plume environments (e.g. Reynolds et al., 1990; Machel and Burton, 1991a;1991b; Burton et al., 1993; Machel, 1995; Costanzo-Alvarez et al., 2000; Díaz et al., 2000; Aldana et al., 2003; Guzmán et al., 2011; Abubakar et al., 2016; Badejo, 2019). Alvarez et al. (2000), Aldana et al. (2003), and Guzmán et al. (2011) carried out magnetic tests on drill cuttings from 24 wells in Venezuela and observed increased magnetic susceptibilities in the hydrocarbon wells, which was linked to the presence of authigenic magnetite and iron sulphides. In these studies, magnetic anomalies had a direct correlation with extractable organic matter (EOM). It was then concluded that the leakage of hydrocarbon in the reservoir is responsible for increased magnetic susceptibility (Guzmán et al., 2011). A possible pitfall with this study is that samples from drill cuttings must have been contaminated by drilling fluids made of cement which would influence magnetic results.

Contrary to this, few studies in recent times have carried out magnetic tests on actual core samples to investigate magnetic mineralogy. (e.g., Liu et al., 2006; Emmerton et al., 2012; Emmerton et al., 2013; Emmerton, 2013; Abubakar, 2016; Badejo, 2018).

Liu et al. (2006), Emmerton et al. (2012), and Badejo (2019) investigated mass-dependent magnetic susceptibilities and magnetic hysteresis e.g. saturation magnetization (M_s) and remanent saturation magnetization (M_{rs}) in reservoir samples in China and the central North Sea UK respectively. The results from these studies showed an increase in

saturation magnetization and remanent saturation magnetization to be higher in oil-producing samples, and lower in dry wells “background samples”. This increase in saturation magnetization and remanent saturation magnetization in oil-producing wells was linked to the presence of (< 50 nm) fine-grained magnetite particles while larger particles (~30 µm) were observed in the dry formations.

Asides from the nano-particles found in the hydrocarbon-rich samples, larger framboids iron oxide minerals were also found which are made up of nano-particles alongside iron sulphides (greigite, pyrrhotite, pyrite, and siderite) Elmore et al., 1987; Kilgore and Elmore, 1989; Elmore and Crawford, 1990; Reynolds et al., 1991; Elmore et al., 1993a; Emmerton et al., 2012; Abubakar, 2016; Badejo, 2019). Badejo (2019) observed magnetic enhancement at the hydrocarbon contact for wells on the same hydrocarbon migration pathway in the central North Sea.

Recent works have established a clearer relationship between magnetism and hydrocarbons, using a wide range of methodologies and tools, combined with controlled laboratory experiments (Kars et al., 2012; Emmerton et al., 2013; Abubakar et al., 2016).

Using an extensive combination of geochemical and magnetic data of hydrocarbon samples, Emmerton (2013) provided a conclusive link between magnetism and oil biodegradation; Abubakar et al., (2015) integrated 2D seismic data, geochemical analysis, and mineral magnetic techniques to present direct evidence of the formation of magnetic minerals during hydrocarbon formation amongst others. Badejo (2019) used the magnetic signature of core samples with the premise of identifying hydrocarbon migration path routes came up with an observation that there are magnetic enhancements at the gas-oil and oil-water contacts of two notable wells of the Tay Formation on the North Sea (Figure 1), this observation brought about a dimension to this study.

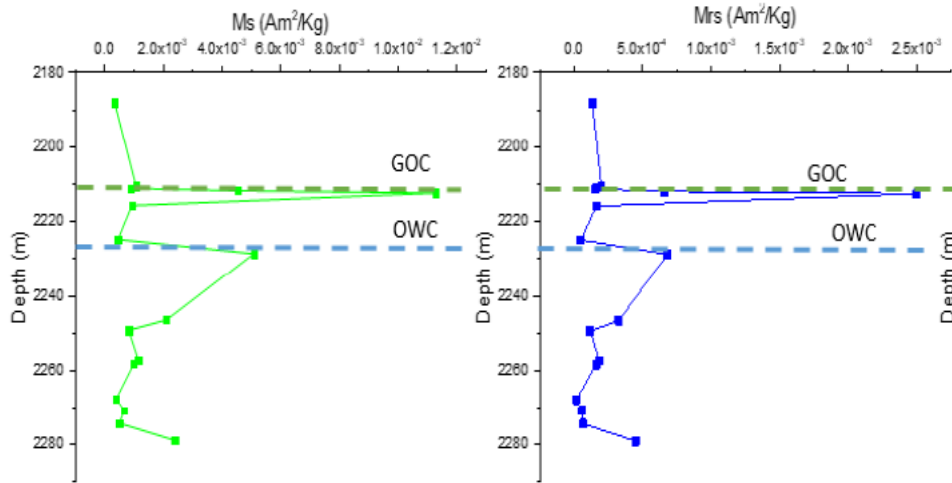


Figure 1: Plot of saturation magnetization (M_s) and saturation remanence magnetization (M_{rs}) vs depth. These are both measures of the total amount of magnetic minerals in the samples. These Figures show magnetic enhancements at OWC and GOC in wells 21-2/21-25.4 from the Tay Formation (Badejo, 2019).

Moving down the well, there is an enhancement in the magnetization at the depth interval 2220 m and 2230 m signifying the gas-oil contact and oil-water contact respectively (Figure 1) the contacts were identified independently by well log data, pressure data, and geological core description.

This is important because current methods of identifying and understanding complex hydrocarbon fluid contacts are disputed in the industry (Bora et al., 2011). Contrary to the diagrammatic representation of hydrocarbon-water contacts as always sharp and horizontal (Figure 2) most contacts are irregular and complex, posing a challenge in their identification (Dennis et al., 2000). A range of fluid contact exists as seen in (Figure 3). Brown (1992), described three kinds of non-horizontal contacts and their causes; hydrodynamic tilt is the reason for the type of hydrocarbon contact in (Figure 3b), reservoir heterogeneity causes the type of contact in (Figure 3c), and semipermeable barriers are responsible for the contact in (Figure 3d). Hence, hydrodynamic tilts in contacts; which is the water movement in the reservoir interval, differences in hydrocarbon permeability and saturation due to capillary effects on various pore systems and semi-permeable barrier all cause a non-horizontal tilt in the contact (Heasley et al., 2000)

If these contacts can be identified with precision by examining the nanometric magnetic minerals at fluid contacts, as suggested by Badejo (2019), this would, in turn, allow for effective reserve quantification in the future. Hence, understanding these magnetic enhancements at fluid contacts has the potential to help identify contacts and increase precision in estimating field reserves and field development.

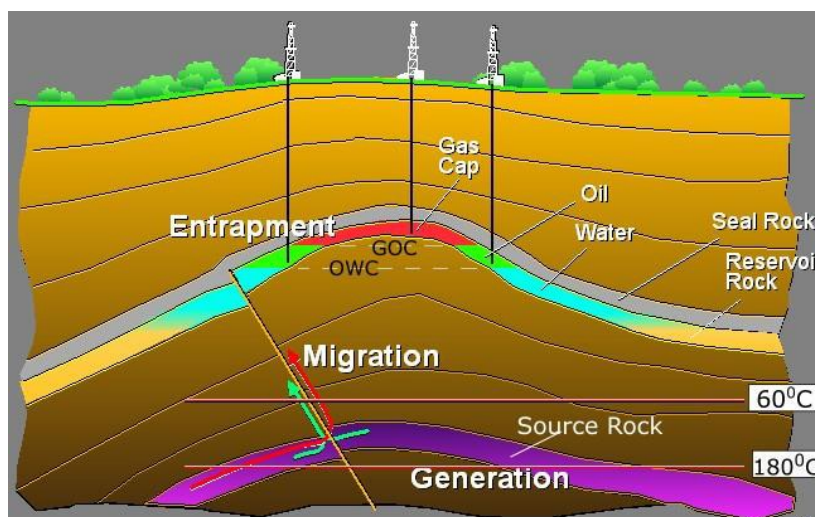


Figure 2: Petroleum system elements and processes (Modified from Fanarco, 2015).

This study focuses on the magnetic enhancement in hydrocarbon fluid contacts. Hydrocarbon fluid contact is defined as that interface that separates fluids of different densities in a reservoir. The effective identification of hydrocarbon fluid contact is important in reservoir volumetric calculation, characterization, and history matching. Oil is generated and expelled from the source rock during the burial at high temperature and pressure, after which migration occurs. In the event of hydrocarbon migration from the source to the reservoir, the hydrocarbon is trapped by a permeability barrier that prevents upward escape (Machel, 1991). This causes gas and oil to form bubbles at the high end of this trap, resulting in capillary pressure which prevents the hydrocarbon from expelling all the oil in the pore spaces. This effect creates a transition zone known as the reservoir.

As the burial depth increases, the source rock expels gas which migrates up-dip (Machel and Cole 1995). This migration occurs faster than oil. The gas charge migrates into the reservoir, dissolving the oil thereby creating a multiphase system as a function of temperature and pressure (Larter and di Primio, 2005). As temperature increases and pressure increases, the gas expels from the oil forming a gas cap above the oil with underlying formation water below the oil (Ahmed, 1989).

A fluid contact is, therefore, that interphase that separates fluids of different densities in a reservoir (Mohson, 1990), gas phase, oil phase water phase, etc. Most hydrocarbon fluid contacts are not always sharp or horizontal (Figure 1), some are gradational, making them irregular and complex, hence posing a challenge in effectively identifying them (Dennis *et al*; 2000). A range of fluid contact exists (Figure 3) which is peculiar with carbonate reservoirs because of its unique heterogeneity influenced by diagenesis which in turn affects hydrocarbon distribution. Also, depending on the lateral pressure, variation in the reservoir bed can be tilted or flat (Hubbert, 1953; Dennis *et al.*, 2000), in this case, the availability of pressure data (Repeat Formation Tester (RTF)) can help give more accurate precision of the exact depth interval of fluid contact.

Also, other conventional methods for identifying hydrocarbon fluid contact exists like the resistivity wireline logs. Resistivity logs help to identify oil-water contacts (OWC) and gas-water contacts (GWC) alone, as the resistivity of hydrocarbon is known to be much

higher than that of water (Kennedy et al; 1996). On the other hand, it cannot be used to determine gas-oil contact (GOC) because of the similarity between the resistivity of oil and gas. In this case, neutron porosity and density wireline logs are used; as gas is naturally less dense than oil and water and the neutron porosity derived for gas is very negligibly underestimated, this creates a gas effect in the logs, depicting the gas-oil contact (GOC). Also, geological description through routine core analysis by observing lithological changes and trends with depth can be used to predict hydrocarbon fluid contact in some cases.

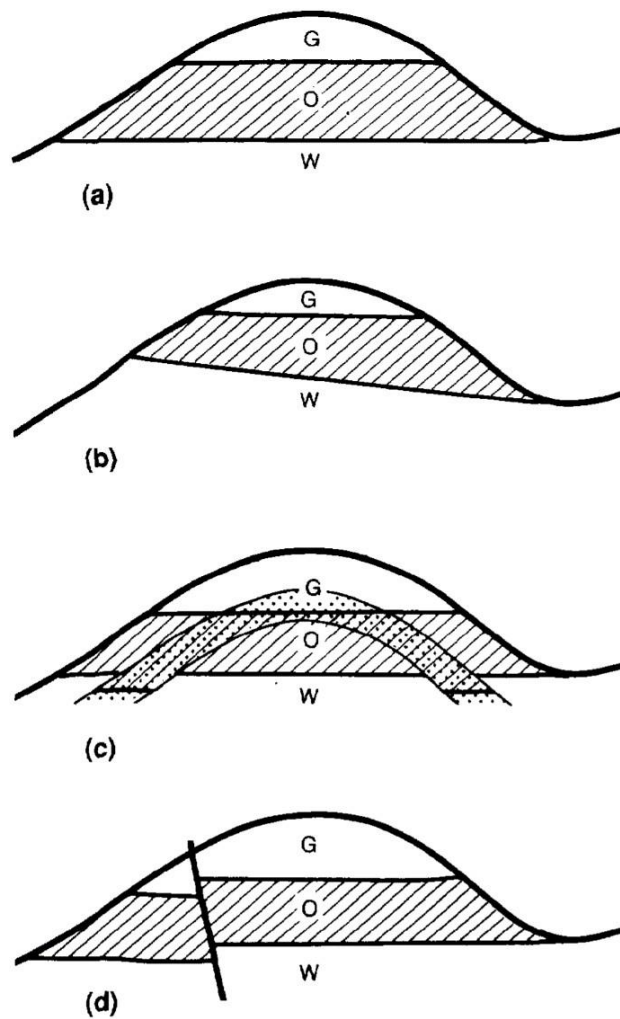


Figure 3: Geometries of fluid contacts. (a) Horizontal contacts (b) Tilted, flat contacts resulting from hydrodynamic conditions. (c) Contact elevation is constant for each lithology type, but pool contact is irregular due to reservoir heterogeneity. (d) Irregular contacts due to the semipermeable barrier in an otherwise homogeneous reservoir. (From Brown, 1992)

1.1 Study Aim

This thesis focuses on understanding these magnetic anomalies in hydrocarbon contacts as the causes of this enhancement are yet to be identified. Solving this problem required the use of data collected from the Nisku to undertake detailed, high-resolution sampling near fluid contacts. It revalidated earlier claims on the enhancement of magnetic signals at fluid contacts on the central North Sea. It required carrying out magnetic measurements on drill core samples collected from the Core Research Centre in Calgary and the University of Alberta Core facility. This would be the first time the carbonate samples from the Nisku formation are being studied magnetically as previous works have focused on great details of their chemistry (Machel et al., 1995) and diagenetic evolution (Machel and Buschekuehle 2008). Since the samples are of a different lithology; dominantly dolomites, limestones, and siltstone, this will also test the suitability of this method for a wide range of lithologies other than clastics. This is important because, it is estimated that more than 60% of the world's oil and 40% of the world's gas reserves are held in carbonate reservoirs the Middle East, for example, is dominated by carbonate fields, with around 70% of oil and 90% of gas reserves held within these reservoirs.

This study utilized mostly information from drill cores from the Brazeau study area of the Nisku as they are known to reveal more precise information about a formation than the conventional downhole logging methods alone. Burton et al. (1993) observed that magnetic anomalies can be detectable from cores making them valuable additions to subsurface methods for assessing the presence of hydrocarbon accumulations.

In a bid to understand magnetic enhancement in a hydrocarbon reservoir, within the scope of data available, this report provides answers to most of the following research questions of what processes are responsible for these magnetic enhancements at fluid contacts.

To provide answers to these questions, the abundance, size, morphology, and mineralogy of the magnetic minerals were determined. This was done using a combination of high and low-temperature magnetic measurements combined with magnetic hysteresis measurements and scanning and transmission electron microscopy.

1.1.1 Research Focus

With the current discovery by the Natural Magnetism Group of a phenomenon that shows magnetic enhancement at oil-water contacts (OWC), my thesis. aims at understanding the possible reasons for these enhancements by undertaking detailed, high-resolution sampling near fluid contacts on the Nisku play of the Western Canada Sedimentary Basin. This will be the first time the Nisku Formation is being studied magnetically as previous works have focused in great detail on their chemistry (Machel et al., 1995) and diagenetic evolution (Machel and Buschkuehle, 2008). The high level of geochemistry already completed makes them an excellent laboratory since the samples are of a different

lithology: predominantly dolomites, limestones, and siltstone, this will also test the suitability of this method for a wide range of lithologies.

The Nisku play is a carbonate system; previous works carried out by the NMG have been on sandstones, this would be a novel work on carbonates. Therefore, this work will allow me to further test the universality of this enhancement. Carbonate systems are particularly important because much of the world's oil is in carbonate systems, e.g. the Middle East on its own is dominated by carbonate fields, with around 70% of oil reserves in the Middle East are in Carbonate fields

1.1.2 Research Questions

In a bid to understand magnetic enhancement in a hydrocarbon reservoir, within the scope of data available, this project will provide answers to most of the following research questions:

1. What processes are responsible for these magnetic enhancements at fluid contacts?
2. How do these processes affect the magnetic mineralogy?
3. How stable are these magnetic enhancements for use as paleo-contact identifiers?
4. How do depth and temperature affect these processes?
5. Are these processes universal?
6. Can the process help us improve the yield from mature hydrocarbon reservoirs by helping us understand the production history?

To provide answers to these questions, the abundance, size, morphology, and mineralogy of the magnetic minerals will be determined. This will be done using a combination of high and low-temperature magnetic measurements combined with magnetic hysteresis measurements and scanning and transmission electron microscopy.

1.2. Hydrocarbon Exploration and Magnetism

In this section, fluid contacts with magnetic enhancement will be looked at.

1.2.1 Fluid Contacts

In a typical reservoir setting, the gas is found at the topmost part followed by oil which sits on the topwater, the reason for this difference in the arrangement of reservoir fluids is due to the difference in their densities (Fig. 3). There is a contact between gas, water, and oil-saturated zones in the reservoir, this is known as the oil-water contact (OWC), gas-oil contact (GOC), and gas water contact (GWC). The effective identification and markings of OWC, GOC, and GWC are essential for the volumetric calculation of an oil reserve (Chombart, 1960). In the identification and marking of OWC, GOC, GWC, several techniques such as resistivity logs, core analysis, mud logs, have all been developed in the past, these identification techniques are broken down into three stages for effective

quantitative interpretation of formation using well log data (Gevers and Watson, 1978), the first and second stage generates acoustic data for every 0.5ft and final stage collect the rock physics parameters, alongside a graph of density and velocity with depth to delineate hydrocarbon zones.

Another approach to identifying fluid contacts is the use of the acoustic log hydrocarbon indicator (William 1990), this is applied to clastic rocks, to differentiate between the water-bearing zone and the oil-bearing zone. The most recent is the simultaneous inversion to estimate subsurface rock properties such as shear impedance, density, and Poisson's ratio (Kim et al., 2004).

1.2.2 Formation of Magnetic Minerals and Magnetic enhancement in Hydrocarbon Environment

Donovan et al. (1979, 1984), Foote (1984), and Saunders and Terry (1985) initially proposed the use of an aeromagnetic survey as an exploration technique, after which soil magnetic susceptibility measurements and soil gas hydrocarbon studies were implemented (Saunders et al., 1989). However, the possible causes of these anomalies have still not been clearly understood.

A thorough review of published works to date by Reynolds et al., (1990), on the detection of magnetic anomalies suggested, has shown that some of the results were not properly substantiated (Reynolds et al., 1990); For example, an aeromagnetic survey conducted in a Cement Field in Oklahoma (Reynolds, 1982), reported magnetite as a contaminant rather than a magnetic mineral. Reynolds et al., (1990), also suggested that other surveys conducted in different hydrocarbon fields that had observable anomalies were either due to the metallic nature of bottom hole assembly equipment or as a result of natural phenomenon not associated with hydrocarbon seepage e.g. possible sedimentary deposition of magnetic minerals (Reynolds, 1982; Boardman, 1985; Fishman et al., 1989).

Also noteworthy is that hydrocarbon seepage could be responsible for creating magnetic minerals (Sassen et al., 1989; Reynolds et al., 1990). This seepage may be responsible for the destruction of natural remanent magnetization (Kilgore and Elmore, 1989), leaving behind some hydrocarbon fields with near-surface mineralization without any anomalous magnetization (Oehler and Sternberg, 1984).

Combustion metamorphism of prolific sedimentary rocks generates magnetic anomalies via the formation of magnetite, hematite, ilmenite, titanomagnetite, and other minerals in hydrocarbon source rocks at the surface or related to hydrocarbon leakage from reservoirs in the shallow subsurface (Cisowski and Fuller, 1987). Also, diagenetic chemical and microbial processes can cause anomalous magnetization in hydrocarbon seepage (Machel and Burton, 1991) as a geochemical study on the Nisku has buttressed how magnetite is produced by microbial activities or destroyed by desulphurization (Hans et al., 1991; Goldhaber and Reynolds, 1991) in processes associated with

hydrocarbon migration. It is however still inconclusive whether this effect can be identified from airborne surveys (Gay, 1992; Reynolds et al., 1990; Millegan, 1998; Stone et al., 2004). Morgan (1998) assumed that the weak aeromagnetic property in the oil fields of the Irish Sea was caused by complicated mixing and migration of fluids with hydrocarbons resulting in a reduction of magnetization in the sandstone formation.

Another possible cause of anomalous magnetization in petroleum systems is hydrocarbon migration (Liu et al., 2006). Works on the Mawangmiao oil field, Jiangnan Basin China had 47 samples in total collected from oil-producing wells (M46), dry well (M36) as well as some background samples to measure magnetic susceptibility, hysteresis parameters, to access secondary alteration of iron-bearing minerals associated with hydrocarbon migration, the results indicated that the magnetite susceptibility and saturation isothermal remanence magnetization (M_{rs}), saturation magnetization (M_s) of iron-bearing formation were dramatically enhanced. It was also observed that the grain sizes of the magnetic particles for the dry well (M36) and the background sample were coarse ($\sim 30 \mu\text{m}$) and of detrital origin which in contrast, alteration of hydrocarbon gave rise to ($\sim 25 \text{ nm}$) magnetic particles. The precise nature and mechanism of the formation of these finer grain particles were still unknown. At this time, the investigation of magnetization concerning soil geochemistry gives another clear indication of the causes of anomalous magnetization in a hydrocarbon environment (Emmerton et al., 2013). Wellcore samples were collected from Colombia, Indonesia, UK, and Canada; the percentage of oil components and the biodegradation state of the samples were compared to the magnetic susceptibility and mineralogy. From her findings, the process of biodegradation, removes aliphatic hydrocarbon from the oil, thereby reducing the oil quality after which, small magnetic grains get completely removed leaving larger magnetic grains in the presence of active bacteria. (Abubakar et al., 2015), demonstrated through controlled laboratory pyrolysis of known source rocks (Wessex Basin, UK) that magnetic minerals form during the same processes that generate hydrocarbon in a simulated 'oil kitchen'. The magnetic minerals formed during pyrolysis were found to be nanometric in size ($< 30 \text{ nm}$), with the potential to migrate with the oil.

CHAPTER 2

Review of Magnetism

2 Introduction

The second most fundamental force in the universe after gravity is magnetism. All magnetic materials are assigned to one of the three groups; diamagnetic, paramagnetic, or ferromagnetic and to a very large extent, most materials are diamagnetic, and those that do not possess permanent magnetic moments are usually classified as diamagnetic. In this study, magnetic minerals and their nanoparticle grain sizes were analyzed extensively. In this chapter, I provide a brief introduction to magnetism and magnetic minerals.

2.1 Review of Magnetization

2.1.1 Magnetization and Magnetic susceptibility

Magnetic susceptibility describes the response of a material to an external magnetic field and can be express mathematically as;

$$M = \chi H,$$

Where M= Induced magnetization (A/m)

H= Magnetic field (A/m)

χ = Magnetic susceptibility which is dimensionless in SI units

Magnetization M is the net magnetic moment (m) per unit volume, it has dimensions A/m.

The external magnetic field H and M are related by (Butler, 1992)

2.2 Classification of Magnetic Materials

Magnetic minerals can be classified as diamagnetic, paramagnetic, and ferromagnetic based on their response to applied fields. The property of these minerals is described by the spin and orbital motion of its electron, interaction, and possible response to magnetic fields (Butler, 1992).

2.2.1 Diamagnetism

Diamagnetism is an elemental property of all matter which are diamagnetic in the presence of an applied field, in response according to Lenz's Law to produce a field in the opposite direction to the applied field (Green, 1974). The effect is weak but can dominate if a rock does not contain minerals with other magnetic responses, a typical example is quartz.

2.2.2 Paramagnetism

Paramagnetic minerals have permanent magnetic moments due to unpaired electron spins, e.g. in the transition metals, the third shell is incomplete (Bohr, 1934). In an applied field, the atomic magnetic moments align with the field, but in a zero field, the moments are randomly aligned due to the thermal fluctuations. They do not retain a magnetic remanence. An example of a paramagnetic mineral is siderite at room temperature (Roberts et al., 2011).

2.2.3 Ferromagnetism

This is the term used to refer to magnetic behaviour found in substances with permanent magnetic moments. Unlike in paramagnetic materials, here the adjacent magnetic moment interacts strongly through quantum mechanical exchange coupling (Butler, 1992; Walden et al., 1999) to produce a spontaneous magnetization that exists in the absence of an external magnetic field. (Figure 2.1)

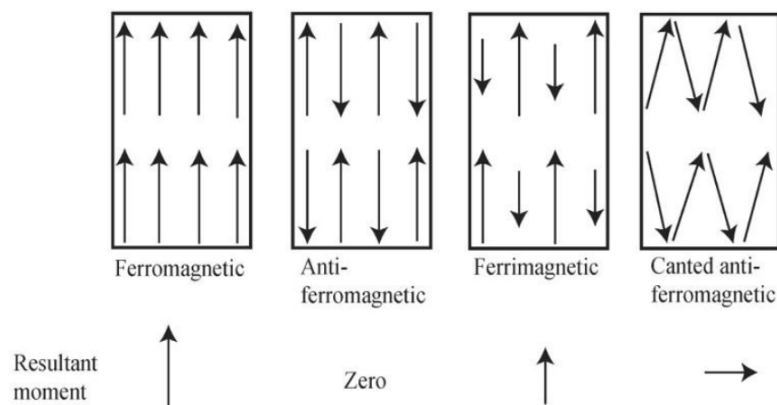


Figure 2.1: Schematic distribution of magnetic moment in crystals (McElhinny, 1973).

Ferromagnetic crystals are divided into regions called magnetic domains with domains aligned antiparallel to. (Kittel, 1949). These domains are controlled by competing for magnetic energies, the demagnetization energy (E_d), which makes them non-uniform, anisotropy energy (E_{anis}) which is the magnetic anisotropy, and the exchanged energy (E_{ex}) which aligns atomic magnets moments, and the external field energy (E_h) (Kittel, 1949).

Below a critical size (d_0), the magnetic moments are aligned in a single crystal and are termed single domain structure (SD) (Kittel, 1948). For bigger magnetic grains, demagnetization energy (E_d) increases relatively breaking the structures into more domains giving rise to multiple domains (MD) (Muxworthy et al., 2006), separated by domain walls (Figure 2.2). This effect causes the structure termed the PSD pseudo-single domain (Verhoogen 1959).

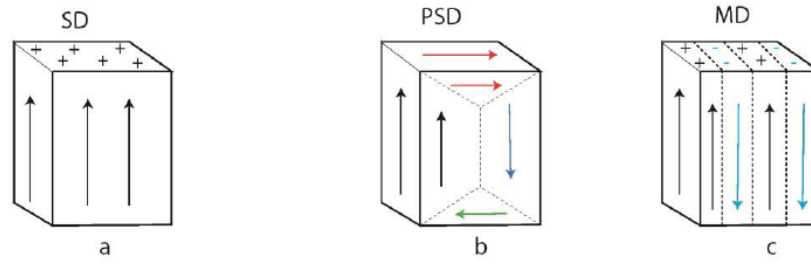


Figure 2.2: Diagrams showing a) single domain structure b) pseudo-single domain structure and c) multi-domain structure. The dashed line represents the domain wall and the arrow shows the direction of M_s in the domains (Dunlop and Özdemir, 1997) Multi-domain grains (MD) are much larger than SD grains, usually in a magnetically unstable state.

2.3 Magnetic Hysteresis

The magnetic behaviour as described in section 2.2 can be easily distinguished when a magnetic field is applied to it. (Figure 2.3) shows a simple magnetic hysteresis relationship.

When a ferromagnetic material is magnetized in one direction, it fails to relax back to zero when the applied magnetic field is removed. The lack of reversibility of the magnetic curve is known as magnetic hysteresis, which is due to the existence of permanent magnetizations in the material. The application of a strong magnetic field in a sample gives rise to a saturation magnetization (M_s). When the field is reduced to zero, the magnetization remaining in the sample is known as the saturation remanent magnetization (M_{rs}) (Figure 2.3), and the field at which the magnetization is reduced to zero is known as the coercive force (H_c) (Roberts et al., 2013), the field with which the Isothermal remanent magnetization (IRM) is reduced to zero is known as the remanence coercivity (H_{cr}) the whole of these parameters makes up the Hysteresis loop as shown in Figure 2.3

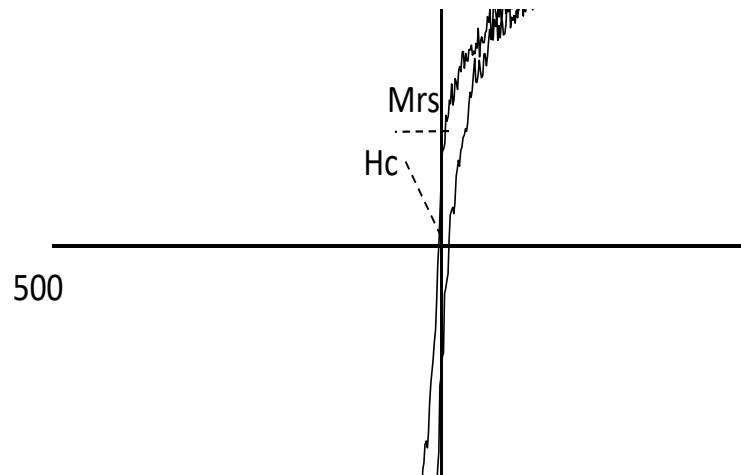


Figure 2.3: Magnetic Hysteresis plot for Ferromagnetic material showing hysteresis parameters, saturation magnetization (M_s), saturation remanence magnetization (M_{rs}), coercivity (H_c).

Multiple partial hysteresis loops form first-order reverse curve diagrams (FORC) (Roberts et al., 2000). These provide a comprehensive characterization of hysteresis behaviour and

are of effective use in the study of magnetic materials as first-order transition curves. FORC diagrams can be assumed to be a map of two distributions: on the x-axis, we have the coercivity distribution, and on the y-axis the inter-grain magnetostatic interaction distribution (Neel, 1954); the reality is a little more complex. For simple classification of samples into box-like SD, PSD, MD regions with arbitrary boundaries a Day plot is created showing a graphical M_r/M_s versus H_{cr}/H_c plot (Day, et al 1977).

2.4 Magnetic Remanence

This is the magnetization left in a material after an applied magnetic field is reduced to zero. There are several types of remanence, the most relevant ones to this study are isothermal remanent magnetization (IRM) and chemical remanent magnetization (CRM).

2.4.1 Isothermal remanent magnetization (IRM)

When a sample is exposed to a strong magnetic field at a constant temperature, Isothermal remanent magnetization can be induced. A typical case study is the hysteresis measurement in the laboratory. The capacity of a sample to possess isothermal remanent magnetization is largely dependent on the presence of magnetic grains in the sample with a coercive force, less than the applied field (Butler, 1992).

2.4.2 Chemical remanence magnetization (CRM)

This is the magnetization obtained during chemical changes in the rock formation, i.e., diagenesis. New minerals are formed during diagenesis leaving behind a magnetization in the rock called chemical remanence magnetization (Elmore et al., 2012; McCabe and Elmore, 1989; Robert et al., 2015). CRM can be subdivided into two: the pure growth CRM acquired from the growth of new minerals through a critical volume and the recrystallization CRM acquired from recrystallization or alteration of pre-existing mineral grains.

2.5. Magnetic Minerals Associated with Hydrocarbon

Magnetic minerals contribute to the magnetic signature of rocks. (Reynolds et al., 1990) and the most is the magnetite and titanomagnetite which applies to aeromagnetic surveys. This study focuses on magnetic minerals associated with hydrocarbons. Numerous magnetic minerals may be associated with hydrocarbons and associated non-hydrocarbon gases (predominantly H_2S and CO_2) e.g., magnetite, titanomagnetite, titanohematite, goethite, hematite, maghemite, monoclinic pyrrhotite, greigite, and others (Machel and Burton, 1991). The occurrence of magnetite (Fe_3O_4), monoclinic pyrrhotite (Fe_7S_8), and hematite (Fe_2O_3) is largely controlled by hydrocarbon (Machel et al., 1995). Magnetite and pyrrhotite are relatively abundant in near-surface diagenetic environments and they have strong magnetic remanences and susceptibilities (Clark, 1983). Hematite, on the other hand, is weakly magnetic but readily available in red beds. Other magnetic minerals exhibit weak magnetic susceptibilities in hydrocarbon diagenetic environments,

making their contribution to be small. Some common magnetic minerals of interest to this study are:

2.5.1 Magnetite (Fe_3O_4): It is one of the oxides of iron, its Curie temperature is $\sim 580^\circ\text{C}$ (Dunlop and Özdemir, 1997; Robert et al., 2011). This is the most common magnetic mineral in rocks. Magnetite changes to maghemite by the oxidation at room temperature. It is the strongest ferrimagnetic iron oxide mineral and it is relatively abundant in the earth's igneous, metamorphic and sedimentary settings. The crystal structure undergoes a transition to a monoclinic structure called the Verwey transition at $\sim 125\text{K}$ (Verwey, 1939). This transition is followed by a sharp drop in remanence which is indicative of magnetite in natural samples. When exposed to air, it undergoes an oxidation reaction at room temperature to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Dunlop and Özdemir, 1997). The newly formed maghemite shares magnetic similarity with magnetite, it also has an inverse spinel structure

2.5.2 Maghemite

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is the oxidized form of magnetite. This occurs when the magnetite is exposed to air. Its crystal structure is body-centered cubic (bcc) and shares magnetic similarity with magnetite. Upon heating at room temperature, maghemite becomes metastable and changes to hematite between $300\text{--}600^\circ\text{C}$ (Dunlop and Özdemir, 1997). Due to the unstable nature of maghemite at 350°C where it changes to hematite, its Curie temperature has become difficult to accurately determine.

2.5.3 Hematite ($\alpha\text{-Fe}_2\text{O}_3$): Hematite is readily abundant in all rock types amongst other iron oxides. Its crystal structure is hexagonal with alternating planes containing (Fe^{3+}) aligned in the opposite direction, which makes it antiferromagnetic and weaker than magnetite. The Morin transition for hematite is $\sim 260\text{K}$ and Curie temperature $\sim 675^\circ\text{C}$ (Evans and Heller, 2003). It is predominantly normally single domain SD and has a significant contribution from crystal defects and impurities (Dunlop and Özdemir, 1997).

2.5.4 Iron sulphides: Pyrrhotite (Fe_7S_8 , Fe_9S_{10}), Greigite (Fe_3S_4), and Pyrite (FeS_2)

The sulphide of iron called pyrite changes to pyrrhotite by desulphurization. Pyrrhotite (Fe_7S_8) is known to be magnetic pyrite because its colour is similar to pyrite and it is weakly magnetic. The magnetism increases as its iron content increase upon heating to $\sim 320^\circ\text{C}$ Curie temperature (Dekkers, 1988), when it starts to decompose to magnetite in the presence of air.

2.5.5 Greigite (Fe_3S_4) on the other hand is well known to form a precursor to Pyrite (FeS_2). It is thiospinel in nature, i.e., a sulphide with the inverse spinel crystal structure, like its iron oxide counterpart. Greigite is an authigenic ferromagnetic mineral that grows as a precursor to pyrite during early diagenetic sedimentary sulphate reduction (Roberts et al., 2011). The Curie temperature of greigite is at approximately $\sim 350^\circ\text{C}$ with a cubic crystal structure (Robert et al., 2011). Greigite lacks a low-temperature magnetic

transition. Greigite structure is metastable thermodynamically (Lennie and Vaughan, 2006) and is often present as an intermediary between the initial corrosion product of mackinawite and the final product pyrite.

2.5.5 Siderite Iron II Carbonate (FeCO_3)

It is a major source of iron commonly found in hydrothermal veins related to barite and separations in carbonates (Munoz et al., 2005) in an anoxic environment. Siderites are paramagnetic at room temperature. It is a common source of iron and can be identified by low-temperature experiments ($<40\text{K}$) due to Néel transition which ranges from 37K-38K. Siderite oxidizes to magnetite, maghemite, and hematite at the temperature of approximately above $\sim 490^\circ\text{C}$.

2.5.6 Titanohematites and titanomagnetites ($\text{Fe}_{2+}(\text{Fe}_{3+},\text{Ti})_2\text{O}_4$)

The Néel/Curie temperature of titanohematites varies from 300°C to 25°C with a linear decrease from titanium substitution (Sprain et al., 2016) and has similar magnetic strengths to hematite. Titanohematites found in sedimentary basins are by weathering in metamorphic rocks (Kennedy, 1981). Titanomagnetites are relatively abundant in basalts, igneous and metamorphic rocks. They undergo partial oxidation to form, titanohematite with reduced magnetic properties (Wechsler et al., 1984).

2.5.8 Pyrite (FeS_2)

Pyrite is the most abundant sulphide mineral in nature, also known as “fool’s gold”. The lattice crystal structure of pyrite and pyrrhotite are the most stable iron sulphides and considered to be the corrosion products seen in long exposures.

In the course of this study, magnetic minerals are usually identified by a low-temperature crystallographic transition, a high-temperature measurement curie temperature, and electron microscopy. The magnetic properties of these minerals and the temperature to which they can be identified can be summarised below.

Table 2.1: Magnetic property of the minerals vital for this study alongside their temperatures of identification. Tc is the curie temperature, Ms is saturation magnetization, low-temperature (LT) behaviour describes the low-temperature crystallographic transition of minerals on cooling remodified from (Evans and Heller 2003)

Mineral	Composition	Magnetic order at room temperature	Tc/Tn (°C)	Ms (Am ² /kg)	LT transition (K)	LT behaviour
Oxides						
Magnetite	Fe ₃ O ₄	Ferrimagnetic	~580	90	~125	Verwey transition
Hematite	αFe ₂ O ₃	Canted antiferromagnetic	675	0.4	~260	Morin transition
Maghemite	γFe ₂ O ₃	Ferrimagnetic	~600-650	~80		Hump on cooling
Titanohematite	Fe _y ²⁺ Fe _{3-2y} ³⁺ O _{3-2y}	Ferrimagnetic	150-200			Increase in remanence on cooling
Goethite	αFeOOH	Antiferromagnetic	120			Increase in remanence on cooling
Sulphides						
Greigite	Fe ₃ S ₄	Ferrimagnetic	~330	~20		No low-temperature behaviour
Hexagonal or monoclinic Pyrrhotite	Fe ₇ S ₈	Ferrimagnetic	320	~25	30-34	Besnus transition
Pyrite	FeS ₂	Paramagnetic				
Iron bicarbonate						
Siderite	FeCO ₃	Paramagnetic	-239.15			34 K in the presence of a field

2.6 Magnetism and Hydrocarbon

In this section, microbial and chemical processes responsible for the formation and destruction of magnetic minerals in reducing conditions caused by hydrocarbon invasion are discussed in detail.

Chemical and microbial processes are responsible for anomalous magnetization in hydrocarbon seepage environments (Burton et al., 1993). Lateral and vertical migration via the overlying beds during seal failure or fracture results in diagenetic changes resulting increase in dissolved sulphur and iron (Miller et al., 1987). This dissolution alongside changes in temperature, pressure, Eh which is the reduction potential that measures the oxidation or reduction state of a solution measured in volts (Rao et al, 2013), pH which defines the tendency of an environment to oxidize or reduce substrates and the value decreases from oxidizing to reducing environments(Mairer et al.,2009), pore water and dissolved inorganic carbon will influence the stability of certain magnetic minerals resulting in alteration and formation of new ones (Machel and Burton, 1991a; Machel, 1995).

The use of thermodynamic stability diagrams with thermodynamic models was used to predict the stability of magnetic minerals present from near-surface conditions to deep burial diagenetic conditions (6000 m) (Burton et al.,1993) caused by hydrocarbon seepage. I carried out similar thermodynamic models with the Geochemist Workbench including greigite that was never done from previous models into the database, 16 phase diagrams were created, and results were summarized. (Curtis et al., 1985; Katz et al., 1998; Lu et al., 1991; Moreau et al., 2005; Tohver et al., 2008) revealed how magnetic minerals changes due to the physical and chemical alteration that takes place in clay minerals. This is discussed in detail (see Chapter 4).

Hydrocarbon Infiltration: hydrocarbon invasion alters magnetic mineralogy in host rocks (Burton et al., 1993; Elmore et al., 1993; Machel, 1995; Emmerson et al., 2012; Abubakar et al., 2015; Badejo, 2019) during lateral or vertical migration, hydrocarbon invasion in host rocks alters magnetic mineralogy or the activity of microbes in the reservoirs can cause biodegradation to take place in then hydrocarbon(Richardson and Noltimier,1980; Ellwood and Pemberton, 1984; Elmore et al., 1987; McCabe et al., 1987; Ellwood and Crick, 1988; Peirce et al., 1998; Aldana et al., 2003; Costanzo-Alvarez, 2006; Díaz et al., 2000; Rijal et al., 2010; Emmerton et al., 2013).

Orogenic fluids help to transport hydrocarbon in the reservoir. They are known to be a very common source for chemical remagnetization (McCabe and Elmore, 1989; Stamatakis et al., 1996; Elmore et al., 2001; Elmore et al., 2012; Wilkinson et al., 2017). Orogenesis is a process that can influence the migration and transportation of magnetic minerals and basinal fluids vertically via fractures and faults and laterally via aquifers which results in chemical remagnetization and magnetic mineral alteration. (Elmore, 1989; Elmore et al., 2012).

2.6.1 Magnetic mineral diagenesis

Change in redox conditions influences the creation of new authigenic magnetic minerals and the destruction of detrital minerals in sedimentary environments. These new authigenic magnetic minerals form under a set of conditions that can subsequently change, for example, an increase in temperature, pressure, Eh, pH or weathering. At the occurrence of this, already existing minerals alter to form an equilibrium with the new one. Some studies have emphasized that Magnetic mineral diagenesis leads to secondary remanence magnetization through chemical remanence magnetization (McCabe and Elmore, 1989; Elmore et al., 2012). The action of externally derived fluids such as magmatic plumes, hydrothermal fluids, orogenic fluids, reservoir fluids, and hydrocarbon aid the geochemical processes that leads to the alteration of minerals during burial (Machel and Burton 1993; Elmore et al., 2012).

2.6.2 Remagnetization

Remagnetization occurs due to alterations caused by chemical changes in the environment. The type of chemical environment is, however, a key indicator of the nature of remagnetization that will take place. In sulphidic environments, iron sulphide minerals are formed, e.g., pyrite and some greigite and mackinawite (Robert et al., 2015) likewise in ferruginous environments iron oxides are formed (Robert et al., 2018) e.g. hematite, magnetite.

Also, several studies have discussed the possible factors enabling remagnetization in sedimentary environments which are;

Clay mineral diagenesis: (Curtis et al., 1985; Katz et al., 1998; Lu et al., 1991; Moreau et al., 2005; Tohver et al., 2008) revealed how magnetic minerals changes due to the physical and chemical alteration that takes places in clay minerals.

Hydrocarbon Infiltration: hydrocarbon invasion alters magnetic mineralogy in host rocks (Burton et al., 1993; Elmore et al., 1993; Machel, 1995; Emmerson et al., 2012; Abubakar et al., 2016; Badejo et al., 2019) during lateral or vertical migration, hydrocarbon invasion in host rocks alters magnetic mineralogy or the activity of microbes in the reservoirs can cause biodegradation to take place in hydrocarbon (Richardson and Noltimier, 1980; Ellwood and Pemberton, 1984; Elmore et al., 1987; McCabe et al., 1987; Ellwood and Crick, 1988; Peirce et al., 1998; ; Díaz et al., 2000; Aldana et al., 2003; Costanzo-Alvarez, 2006; Rijal et al., 2010. Emmerton et al., 2013.) Orogenic fluids: These fluids help to transport hydrocarbon in the reservoir. They are known to be a very extremely common source for chemical remagnetization (McCabe and Elmore, 1989; Stamatakis et al., 1996; Elmore et al., 2001; Elmore et al., 2012; Wilkinson et al., 2017). Orogenesis is a process that can influence the migration and transportation of magnetic minerals and basinal fluids vertically via fractures and faults and laterally via aquifers which results in chemical remagnetization and magnetic mineral alteration. (Elmore, 1989; Elmore et al., 2012)

2.6.3 Chemical Remagnetisation due to burial

Thermodynamic stability diagrams can be used to predict magnetic mineral assemblages (Burton et al., 1991; 1993). A proposed theoretical model attempting to explain the thermodynamic stability of common magnetic mineral assemblages at different diagenetic settings concerning proximity to hydrocarbon accumulation, depth, presence or absence of chemical species (HS^- , H_2S , or SO_4^{2-}), pH and Eh values (Table 2.2). This model predicts magnetic mineral stability as a function of depth and sulphur concentration. At 200°C and 600 bar pressure which connotes deep burial condition, hematite becomes unstable giving room for magnetite to be stable at low sulphur concentration, at high sulphur concentration, magnetite becomes unstable making pyrrhotite to be very stable (Table 2.2). This result illustrates how the stability of the magnetic minerals changes under reducing conditions and with increasing burial and their proximity to hydrocarbon seepage (low, high, and zero concentration levels). This inclusion of greigite into the model had its result output discussed in Chapter 5, which is not included below.

Table 2.2: Changes observed in minerals as they get buried deeper. LTS, MTS, and HTS denote total sulphur levels. The magnetic contrasts are shown concerning background levels, an increase (+) or a decrease (-). U=unstable, S=Stable; or replaced by MAG=magnetite, SID=siderite, PY=pyrite, PYR=pyrrhotite, and HEM=hematite. HC= hydrocarbon. The orange box highlights the conditions closest to the reservoir conditions in the Carbonate Nisku formation. Greigite was not included in previous calculations but have been included in these calculations by me. Table modified from Burton et al., (1993).

	No HC Plume			Distant from HC Plume				Near HC Plume		
	Hem	Mag	Pyrrh	Hem	Mag	Pyrrh	+/-	Hem	Mag	Pyrrh +/-
25 °C 1 bar	LTS	S	U	U	Mag/Sid	S/Sid	U +/-	U	U	U -
	MTS	S	U	U	Py	U	U -	U	U	U -
	HTS	S	U	U	Py	U	Py -	U/Py	U	U -
50 °C 150 bar	LTS	S	U	U	Mag/Sid	S/Sid	U +/-	U	U	U -
	MTS	S	U	U	Py	S/Sid	U -	U/Py	U	U -
	HTS	S	U	U	Py	U	S +	Py	U	S +/-
100 °C 300 bar	LTS	S	U	U	Mag	S/Sid	U +/-	U	U/Sid	U -
	MTS	S	U	U	Mag	S/Sid	U +/-	Py	U/Sid	U -
	HTS	S	U	U	Py	S/Pyrrh	S +	Py	U	S +/-
200 °C 600 bar	LTS	S	U	U	Mag	S/Sid	U +/-	Mag	S/Sid	U +/-
	MTS	S	U	U	Mag	S/Sid	U +/-	Mag	S/Sid	U +/-
	HTS	S	U	U	Mag	S/Pyrrh	S +	Mag/Pyrrh	S/Pyrrh	S +
High Eh/pH low S,var Fe ²⁺				pH >7.5 med/low Eh S,var Fe ²⁺				pH <7.5 med/low Eh S,var Fe ²⁺		

Table 2.2 suggests that magnetic minerals are most likely to alter with proximity to hydrocarbon seepage, this alteration further continues downwards as sediments are buried more deeply. The boxes highlighted in the table is relative to the burial levels and the sulphur concentration levels in the Nisku formation which is the study area focus of this thesis (see Chapter 3); very moderate to very high sulphur levels, close to the hydrocarbon plume at a temperature between 50°C and 100°C, at this depth interval, hematite is replaced with pyrite alongside and greigite as sulphur concentration

increases, the unstable nature of magnetite becomes evident as it changes to siderite, while increased sulphur concentration makes pyrrhotite stable, more discussion (see Chapter 4)

CHAPTER 3

NISKU GEOLOGY

3 Geology of the Devonian Nisku formation

The Nisku Formation of the Alberta Basin in the Western Canada Sedimentary Basin (Figure 3.1), is discussed in terms of the facies, members, diagenesis, and works that have been carried out on the formation. The Nisku Formation study area (Figure 3.1) was chosen for this research because detailed geochemical analysis of the play has been reported, e.g., Machel (1985) discussed its facies and diagenesis in detail, geochemical work was also done in Machel et al. (1997), Machel and Buschkuehle (2008) amongst another discussion of its reservoir characteristics and properties.

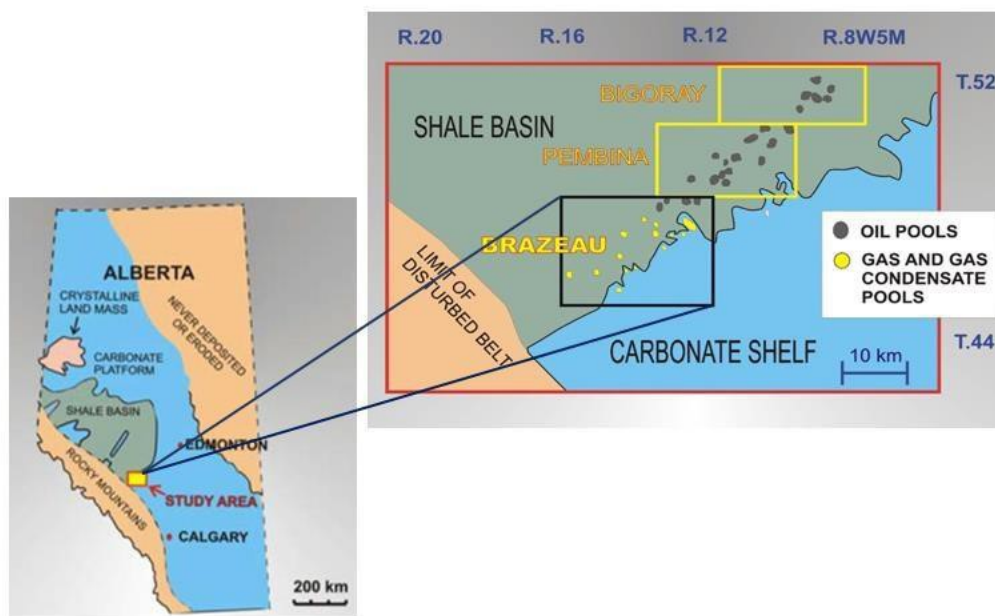


Figure 3.1: Schematic Map showing the location of the Nisku formation Geological Map of Alberta showing the Brazeau study area and environs with hydrocarbon pools showing the paleogeographic setting during deposition of the Nisku Formation (reproduced from Burton et al., 1995 and 2003).

3.1 Geological Background

The Nisku study area lies in a foreland basin which is 48 m (156 ft) thick at the type section. Its thickness ranges between 40 to 60 m (131 to 197 ft) thick throughout southern and central Alberta. The formation thins to 35 to 45 m (115 to 148 ft) where it overlies the Leduc carbonate complexes. In eastern Alberta, the Nisku Formation has been truncated by pre-Cretaceous erosion. In west-central Alberta thicknesses, greater than 100 m (328 ft) are encountered within the Winterburn Basin (Chevron, 1979). It is made up of light brown to light grey crystalline dolomite, with lesser amounts of brownish-grey dolomitic

siltstones, green shales, and anhydrite (CSPG, 2003). The Devonian Nisku Formation is of Frasnian age and belongs to the Winterburn Group. It is interpreted to have undergone 24 diagenetic stages, which are predominantly dolomitization and anhydritization (Manzano and Machel 1997). From 0 to 1000 m burial depth dolomitization took place in the Nisku Formation from fluids from the underlying Ireton Formation. 3000 m burial depth downwards anhydritization took place in the Nisku Formation or during late-stage diagenesis. Some of the build-ups of the Nisku are partially lithified during the deposition in the shallow phreatic environment, while the rest is subaerially exposed. The Nisku is located adjacent to the Rocky Mountains (Figure 3.1). During oil emplacement in the Nisku Formation, thermochemical sulphate reduction took place, resulting in the displacement of anhydrite in the deepest build up and formation of dead oil, sour gas, calcite, saddle dolomite, and elemental sulphur (Machel, 2004). The Nisku is divided into three study areas; the Brazeau, the Bigoray, and the Pembina area (Figure 3.1). These areas are divided according to the regions and provinces with which the Nisku spreads across. Brazeau area spreads across Manitoba from Alberta, then Pembina spreads towards the south-central region of the province of Manitoba and the Bigoray around central Alberta. More emphasis is laid on the Brazeau area as most of the wells examined magnetically were from this study area.

3.1.1 Stratigraphy

The Nisku Formation is about 40-60 m thick towards the West of the Leduc reef system and 50-70 m thick in Central Alberta. It thins out towards the Peace River Arch and slowly disappears towards the North East British Columbia (Machel et al. 1995; Upper et al., 2000). The Nisku formation is made up of bank facies, reef facies, and facies of the basinal slope system. The Nisku Formation in the Alberta subsurface conformably overlies the Ireton Formation of the Woodbend Group and is also overlain conformably by the Calmar Formation of the Winterburn Group (Machel 1985) (Figure 3.2). It was deposited in a slowly subsiding tectonic shelf which was developed in response to Late Frasnian regression (Watt, 1987). The carbonate ramp and basin configuration are also believed to be controlled by a relative rise in sea level (ERCB/AGS, 2008). Based on seismic data and character, the Upper Devonian (Frasnian) Nisku Formation has been divided into Nisku inner shelf, Nisku outer shelf, slope, and Winterburn Basin (Chevron, 1979).

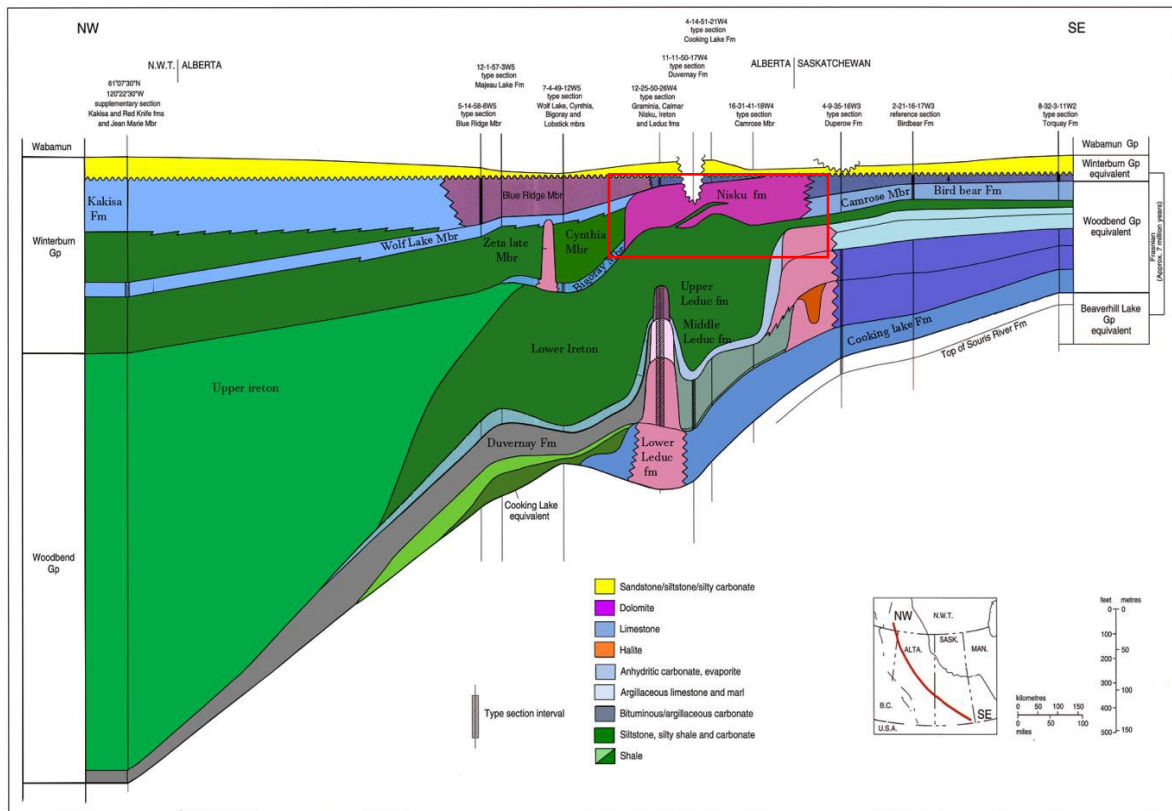


Figure 3.2: Tectono- stratigraphy and Schematic cross-section of the Devonian Nisku formation highlighted in red with all its members. Redrawn from Alberta Energy Regulator Devonian Wood bend/Winterburn strata 2003).

Due to the complex depositional history and environment, The Nisku Formation comprises bank facies, reefal facies, and basinal/slope facies (Figure 3.3). Facies changes in the prograding carbonate platform allowed for a finer subdivision of the Nisku Formation into constituent members, this is evident in the Pembina- Brazeau area which is located on the Nisku Shelf. Using log characteristics and lithologies from wells in the Brazeau area, the members of the Nisku Formation are Lobstick, Bigoray, Cynthia, Wolf Lake, Dismal Creek, and Zeta Lake.

3.1.2 Brazeau Area

The Brazeau Area is one of the geographical divisions of the Nisku Formation and is named after the Brazeau River (Machel et al., 2005). It is in the Alberta Basin west-southwest of Edmonton (Fig 3.1). In the downdip Brazeau Area, the Nisku reefs contain oil, sweet condensate, and then sour gas condensate in a general downdip direction (Figure 3.3). The initial volume of oil in place for the whole reef trend was originally estimated as 325.1 Mm³, with initially estimated reserves of 167 Mm³ and remaining reserves at 51.5 Mm³ (ERCB, 1985). Early estimates of gas reserves exceeded 14 Gm³ (Watts, 1987). It is important to note that almost the entire Nisku in the Brazeau Area is completely dolomitized as it has been earlier stated that reservoir properties are controlled by a complex sequence of diagenetic processes (Rennie et al., 1989).

Most core samples for this study were collected from the Brazeau Area of the Nisku Formation. Eleven (11) drill core samples were taken from Brazeau Area, one from the Pembina area and the last from the Bigoray Area. These samples were chosen because the Brazeau Area has most of the oil pools in the area, Machel (1985) and other researchers had previously carried out detailed work on the area, and samples were easily accessible.

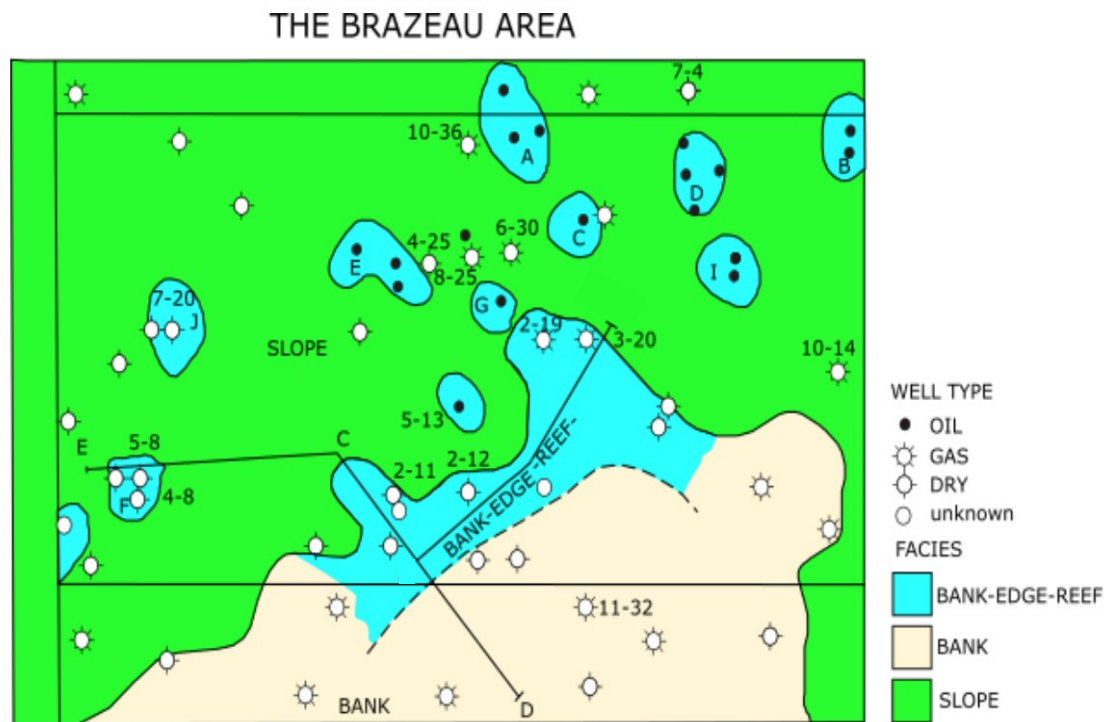


Figure 3.3: The study area (Brazeau Area) showing the facies and their distribution, wells, and line of section ECD (Fig. 3.6) (Redrawn from Machel, 1985).

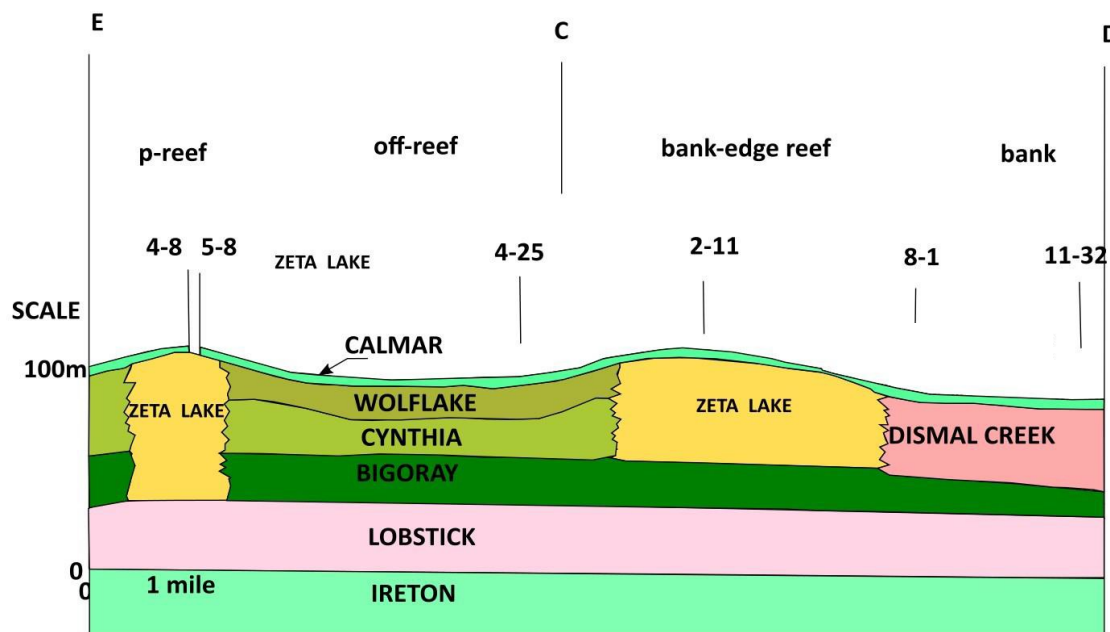


Figure 3.4: Cross section showing distribution and the stratigraphic relationship of all Nisku facies in the Brazeau Area (line of section ECD in Fig 3.5) 4-8, 5-8, 4-25, 2-11, 8-1, 11-32 are all wells.

3.2 Diagenesis in the Nisku Formation

Diagenesis refers to the physical, chemical, and biological changes that happen to sediments after they have been deposited and during the process of lithification, which in carbonate rocks strongly alters the reservoir properties (MacKenzie et al., 1965). In the Nisku, intermediate burial diagenesis is the most important factor because this has altered the porosity and permeability of the Zeta Lake Member (Anderson, 1985; Machel, 1985; Watts, 1987a). Machel (1985; 2003) identified over 19 distinctive diagenetic phases and processes, following combined interpretation of stratigraphic, petrographic, and geochemical data. The relative timing of these diagenetic phases is based on principles of superposition and cross-cutting (Machel and Buschkuehle, 2008). The diagenetic history of the Nisku Formation is shown in Figure 3.7 (e.g., stages I-V) and are summarised below.

During shallow burial of up to 300 m in the Late Devonian, the carbonate sediments underwent lithification to limestone, by different calcite cements. In the late Devonian and Mississippian, during burial from about 300 m to 1500 m, most Nisku reefs were extensively dolomitized to so-called grey matrix dolomite (Machel and Burton, 1991); for every reef encountered in the diagenetic phase, 23% of replacive anhydride was present with a milky white, nodule texture.

After a long duration of sequential deposition, erosion, and non-deposition, the Nisku reef underwent burial fairly rapidly from 2000 m to a maximum depth of about 4500 m to 6000 m (depending on the location within the study area) during the Late Cretaceous and Early Tertiary. This will be further explained in detail at each stage.

3.2.1 Diagenetic Stage I (phases 1-6, 7a)

This diagenetic stage encompasses deposition and shallow burial up to about 300 m during the near end of the Devonian period. The reef mound was poorly lithified in the upper part and partially lithified in the lower part. At 300 m burial depth, reefal and non-reefal strata were lithified (Upper et al., 2000).

3.2.2 Diagenetic Stage II (phases 7b, 8-10)

The stage represents a combination of rapid, shallow to intermediate burial conditions, 300 to 1100 m. This burial depth was reached in the Mississippian period in most of the study area. Chemical compaction, matrix dolomitization, and replacive anhydritisation are major events in this diagenetic stage. Chemical compaction started near the end of the Devonian period and continued throughout the Mississippian period (Machel et al., 1995).

3.2.3 Diagenetic Stage III: This stage encompasses a long period of non-deposition, minor sedimentation, and erosion (Machel 1987).

3.2.4 Diagenetic Stage IV (phases 11-14)

This stage encompasses intermediate to deep burial events, from 1500-2500 m in the Bigoray area and 2000-3400 m in the Brazeau area, signifying a repetition of rapid burial during the Late Cretaceous and early Tertiary. The burial limit of this stage was reached near the end of the late Cretaceous period. Regional structural deep in this stage is responsible for the variation in depth between North East and South West of the study area. Oil generation and migration took place during this stage. Hydrocarbons were derived from the underlying and adjacent strata, which then requires vertical and lateral migration into the Nisku reservoirs (Schmitt and Batzle 2010).

3.2.5 Diagenetic Stage V (phases 14-19)

Deep and maximum burial occurred in stage five, from 3000-3500 m in the Bigoray area and 4500-5000 m in the Brazeau area. The significant event in this stage was thermochemical sulphate reduction in the deepest build-up at 135-160°C, resulting in the formation of oxidizing liquid and gaseous hydrocarbon to bitumen, and reduction of anhydrides to hydrogen sulphides and elemental sulphur, which in turn promoted the formation of saddle dolomite and white calcite spar. Structural deformation, including tilting and sub-vertical faulting, occurred during Stage V, coinciding with the Laramide Orogeny in the Rocky Mountain region, 200-400 km to the west (Upper et al., 2000).

The vast majority of diagenetic fabrics exist in the limestone buildups of the updip Bigoray area (Figure 3.1). Further downdip, many of the limestone-diagenetic features are also present, but pervasive matrix dolomitization and anhydritisation have destroyed them in most locations (Machel, 1983).

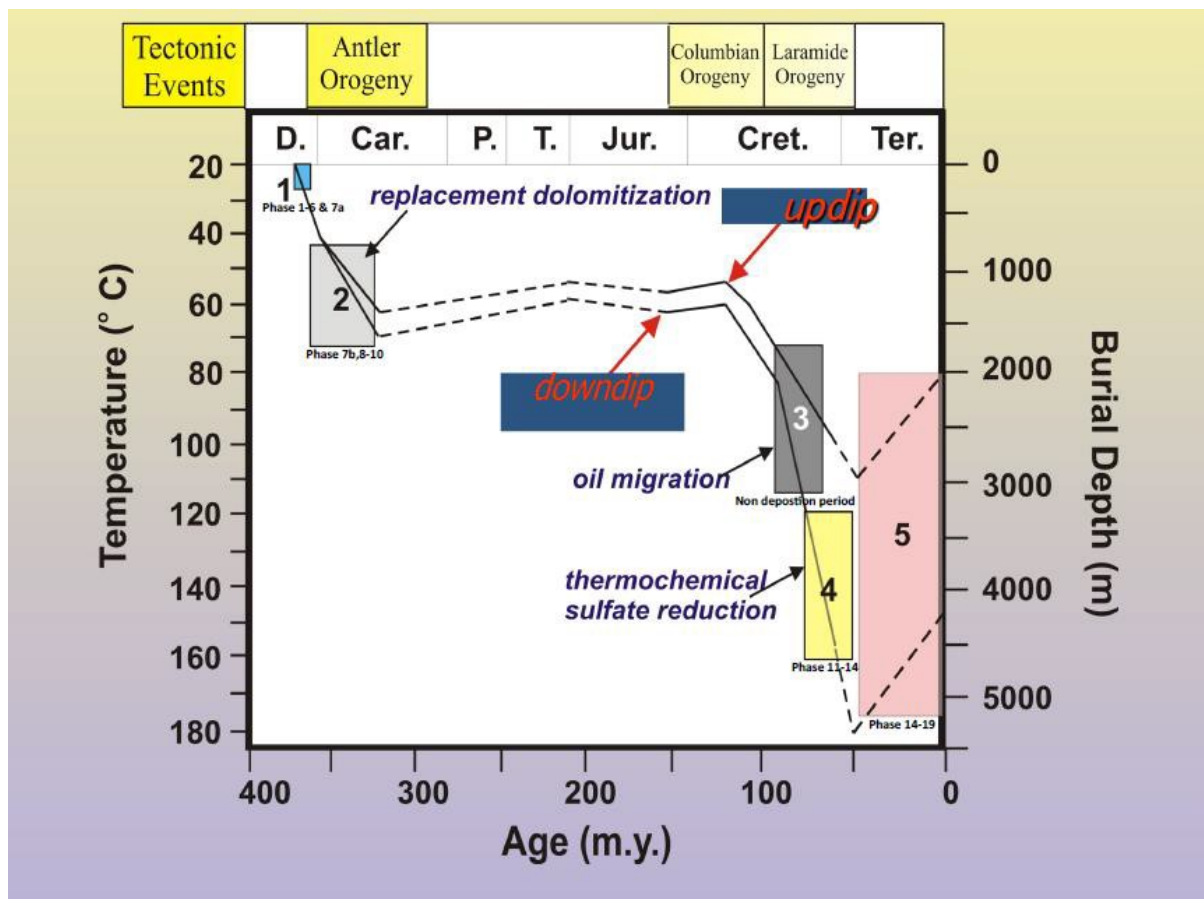


Figure 3.5: Schematic diagram of the diagenetic stages and burial history in the Nisku and their respective events, age, burial depths, and temperature (Machel, 1985).

PHASE	---- TIME ---->	STAGE
1	Micrite envelopes	I
2	Anhydrite I, Dolomite I	
3	Dissolution I	
4	Pyrite I	
5	Calcite I	
6	Calcite II	
7	Calcite III	
8	Calcite IV	
9	Dolomite II	II
10	Dissolution II	
11	Pressure solution	
12	Dolomite III	
13	Pyrite II	
14	Fractures I	
15	Calcite V	
16	Secondary anhydrite	
17	Fractures II	III
18	Hydrocarbons	
19	Fractures III, Dissolution III	IV
20	Dolomite IV and V	
21	Elemental sulfur	
22	Calcite VI, Calcite VII	
23	Pyrite III, Sphalerite	
24	Fractures IV, Tertiary anhydrite	V

Figure 3.6: Diagenetic sequence of the Nisku Formation (the diagenetic phases are grouped into five stages), from Machel and Buschkuehle (2008).

3.3 The Nisku Petroleum System

Petroleum System

A petroleum system encompasses a pod of active source rock and all genetically related oil and gas accumulations; it includes all the geological elements and processes that are essential if an oil and gas accumulation is to exist (Magoon and Dow, 1994). The essential elements of a petroleum system include the following: source rock, reservoir rock, and seal rock, overburden rock, and the two processes are: trap formation and generation-migration—an accumulation (Magoon and Dow, 1994). The Cynthia Member of the Nisku Formation and the underlying Ireton Formation are the main source rocks in the Brazeau area (Chevron, 1979; Machel, 1985), as indicated by carbon isotope and total organic content data. The Zeta Lake Member is the reservoir rock and the calmer member is the caprock (Figure 3.4). The source rock of hydrocarbons in the Nisku is the underlying Ireton Formation and the off-reef Calmar Formation, the reservoir rock is the Zeta Lake Member while the caprock is the Calmar Formation (Machel et al., 1995).

The petroleum system in the Brazeau area is commonly referred to as the “Nisku Petroleum System”. This naming of the petroleum system does not follow the convention proposed by Magoon and Beaumont (1999) in which the source, reservoirs, and certainty symbols are used in naming and characterizing the petroleum system. This is because

there has been uncertainty about the main source of the hydrocarbon in the area (Chevron, 1979; Allan and Creany, 1991; Reinson et al., 1993; Creamy et al., 1994), hence a generic name (Nisku Petroleum System) is used.

3.3.1 Source Rock

The Cynthia Member of the Nisku Formation and the underlying Ireton Formation are the main source rock in the Brazeau area (Chevron, 1979; Machel, 1985). The Cynthia Member consists of dark grey, calcareous, silty shale with moderate fissility. It conformably overlies the Bigoray Member and underlies the Wolf Lake Member (Figure 3.4). The increase in API gravity of oils from northeast to southwest in the West Pembina area also supports local sourcing from the Cynthia Member (Creany et al., 1994) because of the impact of migration. The geochemical similarity between the Cynthia Member and the Duvernay Formation has hinted at the possibility of the Duvernay being a potential source. Some oils in the Nisku generally are also a part of the Duvernay petroleum system (ERCB, 1985).

3.3.2 Reservoir

The Zeta Lake Member of the Nisku Formation forms the main reservoir in the Brazeau area. It is made up of grey-brown, very fossiliferous, reefoid, massive dolomite with variable secondary vuggy porosity. The highest porosity and permeability values in the Nisku Formation were obtained from the Zeta Lake member with average horizontal and vertical permeability higher than 50 mD and average porosities up to 8.6% (Bachu et al., 2008). The Zeta Lake Member diachronously overlies the Bigoray Member of the Nisku Formation and is conformably overlain by the Calmar Formation (Figure 3.4). The reefs of the Zeta Lake Member have been intensely dolomitized.

3.3.3 Seal

In the study area, the dolomitic shales and siltstones of the Calmar Formation form the top seal while the calcareous shale and argillaceous limestone of the Ireton Formation provides a bottom seal (Chevron 1979). The Ireton Formation is conformably overlain by platform carbonates of the Nisku Formation (Bachu et al., 2008).

Two plays are identified in the Brazeau area (Reinson et al., 1993):

The Nisku shelf margin play: This includes all gas pools and prospects in the Zeta Lake reefs that developed in the outer shelf margin of the Nisku Formation. In this play, the Zeta Lake reef forms the reservoir, the Cynthia and Calmar member provides vertical seals, the Cynthia provides lateral seals, and the Cynthia Member is the named source rock in this play (Chevron, 1979; Machel, 1985).

The Nisku isolated reef play: This play includes all gas-bearing pools and prospects in the downslope Zeta Lake Member reefs of the Nisku Formation in west-central Alberta. The isolated Zeta Lake reefs form the main reservoir of this play and the other elements

are like that of the Nisku shelf margin play, but the Ireton Formation is suggested as an additional source rock (Machel 1985).

3.3.2 The Brazeau Area Petroleum System

The shallowest (up-dip) part of the play in the Brazeau Area in North East, which contains sweet oil pools (labelled A, B, C, D, E, G, I, L in [Figure 3.6](#)) and the deepest (down-dip) part of the play in South West, which contains sour gas pools (labelled Y, K, CA, CB in [Figure 3.6](#)). Migration in the study area is from South-West to North-East ([Figure 3.1](#)). The southwestern part of the basin is buried more deeply than the Northeastern part of the basin, hence sour gas is present where the depth of oil generation has been exceeded and the depth of thermal maturation and thermochemical sulphate reduction has been reached (Machel, 2004). Facies are intercalated between the carbonate shelf margin and shale basin, such that hydrocarbon distribution is controlled by two factors;

1. Facies/reservoir type distribution. This implies that some parts of the basin are made up of reefs while some parts are made up of isolated reefs within the shale basin.
2. Burial depth: It is more deeply buried, the southwestern part of the basin is characterized by thermochemical sulphate reduction. The very shallow, northeastern part of the basin is characterized by heavy oil. The part of the study area with intermediate burial depth has a mixture of sweet and sour crude (i.e. pools M, F, and J in [Figure 3.6](#)), caused by thermal maturation generating some H₂S.

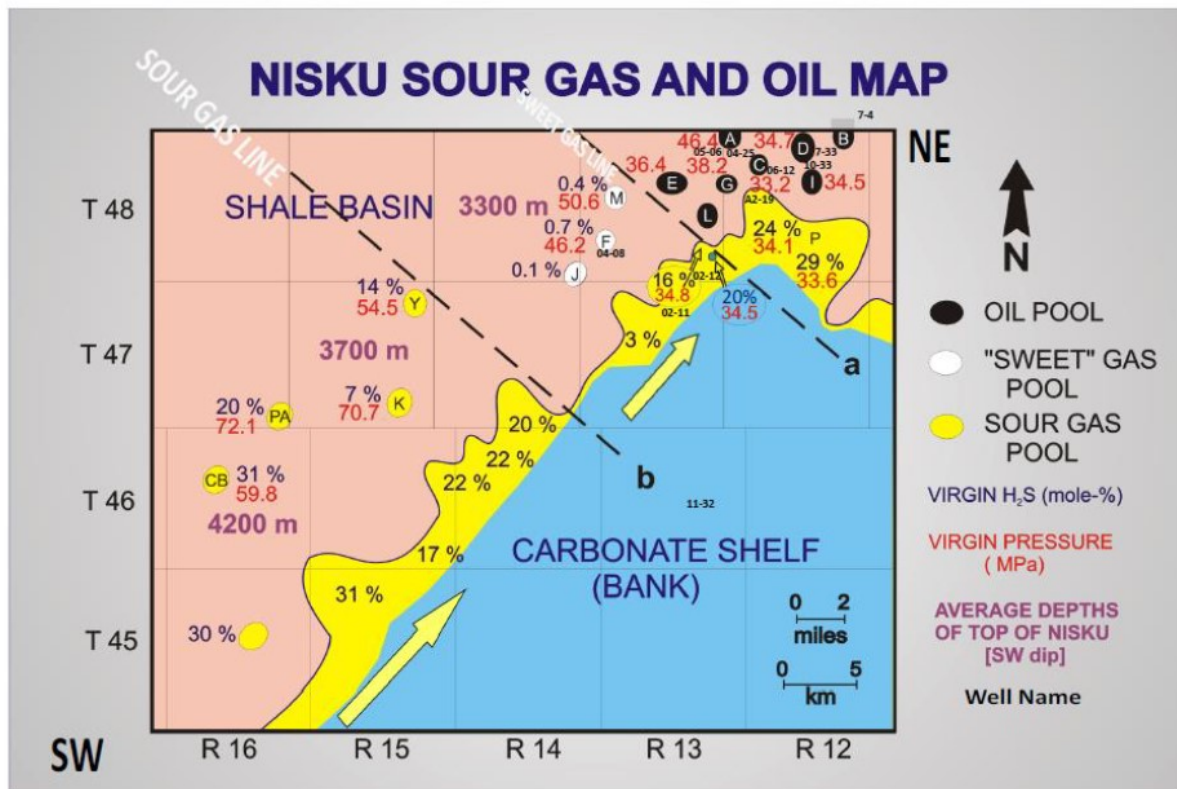


Figure 3.1: Present-day map showing the Nisku sour gas and oil pool and the wells examined in this study with their pressure and mol concentration of H₂S and the migration of sour gas up-dip (yellow arrows). From Machel (1995).

3.4. Sampling strategy and Methodology

Hydrocarbon saturated core samples were collected for this study at the University of Alberta Core facility and the Core Research Centre in Calgary, Canada (Figure 3.7). The sampling interval with which the core sampling was done was at the depth of + or -3m. The well log data-informed position and depth interval for core sampling. Well log data, pressure data, and geological description was used to identify the depth interval of the hydrocarbon contact which informed the core sampling depth used in this study. The location of the drillcores used, their geometry, and the geological description can be found in Chapter 5, the logs and pressure data can be found in Appendix 2.

Ideally, the basis for identifying contacts was from the resistivity logs, high resistivity connotes the presence of hydrocarbon while low resistivity means low in hydrocarbon signifying the dominance of the water zone (Figure 3.64). From the pressure data in Appendix 2, the change in pressure gradient vs depth was used to identify the contact. I also used physical geological evaluation and description to identify the hydrocarbon contacts. The assistance of Prof. Han Machel on our first visit to the core research center in Calgary came in handy with this. As an expert in the field, he started with geologically examining well located in 02-12-48-13W5, which from his previous publication (Machel et al., 1993) showed hydrocarbon to start at 3201m. Upon geological examination, from the top of the drill core, we found white saddle dolomite, calcite cement, and some elemental sulphur to appear not at the top of the drill core but at exactly that same depth interval of 3201m, which was ascribed to be influenced by diagenesis. According to Hans, the depth interval where saddle dolomite begins to form is the beginning of the water leg, which makes it the hydrocarbon contact. This same approach was used in sampling the other wells, unfortunately not all the wells had this calcite and saddle dolomite feature in them, the logs did not capture them either, this made it difficult to identify the hydrocarbon contacts. The hydrocarbon contact was expressly seen on two wells 02-12-48-13W5 and 02-19-48-12W5 which were both located on the bank edge reefs (Figure 5.17). Some of these samples were chiselled out of the core (Figure 3.64) due to the hardness of the carbonate formation and put in a cellophane bag; these bags were non-reactive with the rock sample. I collected over a hundred samples from twelve (12) wells, the location of the wells are from the Brazeau study area of the West Canada sedimentary basin (Figure 5.17), Resistivity log was gotten from two (2) wells. The samples were collected and stored in the bags. I travelled from Canada to the Institute for Rock Magnetism in Minneapolis where magnetic measurements were carried out on them, the rest of the samples were then transported to Imperial College London for magnetic measurements.



Figure 3.64: Schematic of sampling methodology and strategy for well 02-12 with sampling done at +3m interval



Figure 3.7: Photographic view of carbonate core sampling of the Nisku play for magnetic experiments at the Core storage facility of the University of Alberta

3.4.1 Methodology

Over a hundred samples were called from the 12 wells (Appendix 2), No single magnetic measurement method can alone truly identify the size and magnetic mineralogy of a sample. Magnetic measurements must therefore be done in combinations. Below are the methods used and what they are used for:

1. Low-temperature measurements: crystallographic transitions e.g., Verwey transition in magnetite at ~120 K (Verwey, 1939), Morin transition in hematite ~260 K (Morin, 1950), Besnus transition ~30-34K in monoclinic pyrrhotite (Besnus and Meyer, 1964), hump in cooling for maghemite.
2. High-temperature measurements: Curie temperature, inversion temperatures.
3. Room temperature measurements: the grain size, mineralogy
4. Mossbauer spectrometry: the grain size, mineralogy
5. Scanning electron microscopy (SEM): mineralogy, grain size, but not always scalable to bulk magnetic measurements, due to sample heterogeneity.

3.4.2 Magnetic instrumentation.

I have undertaken magnetic measurements at both the NMG laboratory and the Institute for rock magnetism, University of Minnesota. I won a Visiting Fellowship from the Institute for Rock Magnetism worth \$4000 for a 10-day visit.

3.4.3 Magnetic hysteresis measurements

Magnetic hysteresis loops were measured on a Princeton Measurements Vibrating Sample Magnetometer (VSM). The VSM was also used to measure FORC (first-order reverse curve) diagrams. These helped to determine the magnetic mineralogy, grain size, and domain state of the grains.

To further characterize the mineralogy and grain size, I made low-temperature hysteresis and first-order reversal curve (FORC) measurements using the low-temperature Princeton vibrating sample magnetometer (VSM) at the Institute for Rock Magnetism in the USA, as the NMG laboratory at Imperial College London only has the room-temperature and high-temperature furnace option.

3.4.4 Low-temperature thermomagnetometry measurements

Low-temperature measurements were carried out at the Institute for Rock Magnetism in Minneapolis and Imperial College using a Quantum Magnetic Property Measurement System (MPMS). The MPMS was used to carry out low-temperature measurements (300-10K) for the identification of magnetic minerals. Low-temperature crystallographic transitions in this experiment were used to identify the magnetic minerals present. Abubakar et al., (2015) and Badejo (2019) have individually shown that low-temperature

magnetic measurements are required to fully quantify the magnetic mineralogy, as many of the magnetic minerals (over 80 % of the total) are nanoparticles < 30 nm in size, that are either superparamagnetic)

3.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) imaging of four test samples was carried out with the compositional analysis equally done. SEM was carried out for imaging of the magnetic minerals present in the samples. I carried out magnetic extraction because the relative abundance of these minerals was less than 1%, and this extraction helped to increase mineral abundance for imaging by passing it through the Frantz electromagnetic separator. The EDX analysis was at a spot size of about 1 μ m.

CHAPTER 4

THERMODYNAMIC MODELLING OF IRON MINERALS AT THE HYDROCARBON FLUID CONTACT

4 Introduction

Hydrocarbon presence can change the thermodynamic equilibrium state of minerals, resulting in the alteration of the magnetic mineralogy of the host rock. This alteration of magnetic mineralogy can lead to both enhancement and reduction in the total magnetization (Burton et al., 1993; Machel, 1995; Emmerton et al., 2013).

In thermodynamic modelling, it is possible to change a range of parameters, e.g., for example, ion concentration, temperature, pressure, pH, and Eh.

Eh is the reduction potential which measures the oxidation or reduction state of a solution measured in volts (Rao et al., 2013). The greater the depth in the reservoir, the more reducing the system is (Machel and Burton 1993). Eh measures the tendency of an environment to oxidize or reduce substrates and the value decreases from oxidizing to reducing environments (Mairer et al., 2009). Standard Eh in near-surface to deep burial conditions ranges from 142 to 295mv. On the other hand, pH measures the acidity and the basicity of the system. It is on a scale of 0-14. 0-7 scale connotes acidity, pH 7 is neutral, while pH 7-14 connotes alkalinity, the pH of crude oil is between the scale of 9-11 (Hutin et al., 2016).

The activity is a measure of the effective concentration of species in a mixture. The values of the activities used in this study were standard concentration used in Geochemistry for hydrocarbon systems. (Machel and Burton 1993) adopted these activity coefficients for the 1993 model.

In this chapter, I modelled the thermodynamics of what happens at the hydrocarbon contact and the possible minerals that are formed in the process depending on the environment, i.e., sulphidic, which is deeper. I present thermodynamic modelling, in the form of thermodynamic stability diagrams for selected iron and sulphide minerals common to diagenetic settings ranging from near-surface to 4000 m of depth. Such modelling was initially attempted by Machel and Burton (1993) using SUPCRT92 thermodynamic modelling tools, but greigite was excluded because the importance of greigite was not appreciated at that time. The presence of greigite is important as the precipitation of iron sulphides has been previously linked to the presence of hydrocarbons (Reynolds et al., 1990; Reynolds et al., 1991; Costanzo-Alvarez et al., 2000; Mena and Walther, 2012). The new modelling was done with the Geochemist Workbench. The Geochemist Workbench is an integrated geochemical modelling package used for balancing chemical reactions, calculating stability diagrams and equilibrium states of natural waters. Tracing reaction processes, modelling reactive transport, plotting the results of these calculations, and storing the related data (Bethke et al., 2008). It is standard geochemical modelling in aqueous systems used to create Eh-pH diagrams and calculate speciation. This programme was written in C++. In the software, time marching algorithms are employed as the simulation procedure in which the model at each time step evaluates the transport equations separately from the Chemical model known in the

field of reactive transport modelling as the operator splitting method. My current proficiency in python programming language has opened my understanding of this concept to a larger extent. In the time marching programs, the programs automatically divide the modelling domain into nodal blocks, this phenomenon is regarded as discretization because it separates the domains into discrete parts. Each nodal block has fixed dimensions $\Delta x, \Delta y$, and Δz in a linear domain Δr , $\Delta \theta$, and Δy in a radial domain, or Δr and $\Delta \theta$ in a spherical domain. The properties of the entire nodal block carry a single value of porosity, permeability, temperature, pH, and so on which are the inputs yielding a more robust output. The nodal blocks fit together to form the domain over which the transport equations are solved. The nodal blocks or points may be referred to as nodes, this can be built with python combining both the front end and the back-end features. These constraints are the same as the ones used in (Burton et al., 1993) with SOLEMNQ for predicting the anomalous magnetization in hydrocarbon seepage environment. These constraints are representative of the subsurface thermodynamic condition used to predict the depth, pressure, and concentration of hydrocarbon in the subsurface whose resultant magnetic mineralogy is modelled as the output. Other notable geochemical publications addressing subsurface condition uses these constraints as well (Roberts et al., 2020). 25°C and 1bar represent subsurface depth intervals of 0-1000m called the near-surface condition, 50°C, and 150bar represents depth interval 1500 -2500m known as the shallow burial condition, intermediate burial condition is 100°C and 200bar, at depth of 2500-3500m, while the deep burial condition is 4000m to 6000m, at 200°C and 600 bar pressure.

The stability diagrams were made using similar constraints (Machel and Burton 1993), this was between 25°C and 1bar to 100°C and 300 bar, aqueous sulphur species activities (HS^- , H_2S or SO_4^{2-}) from 10^{-2} to 10^{-14} , bicarbonate activities of 10^{-1} to 10^{-4} , pH values from 5 to 11 and Eh values from -0.1 to -1.5V, divalent iron activities of 10^{-4} to 10^{-6} as these are standard realistic thermodynamic constraints for hydrocarbon plumes. I included ferromagnetic greigite into the database using the Gibbs free energy (Ghiorso et al., 1983; Ning et al., 2018). There is no limit to the number of kinetic redox reactions you can consider in a single simulation. These conditions are typical of carbonate systems and can be used to predict the growth of new authigenic minerals in a system from surface to the depth interval where the hydrocarbon contact is. The thermodynamic stability diagrams estimate the expected geochemical conditions of magnetic minerals present for various hydrocarbon systems from surface conditions to deep burial conditions. According to the predictions, there are several striking trends in magnetic mineral assemblage and resultant magnetic properties of the rocks which have a close relationship with (1) increasing temperature and pressure, i.e., increasing burial depth, showing increased direct proportionality with the enhancement of magnetic minerals and growth of new authigenic magnetic minerals. (2) magnetic susceptibility at surface condition is lower, but at greater depth, it increases, showing direct correlation with magnetic susceptibility increase as seen in the high-temperature magnetic measurements (3) core samples taken around hydrocarbon traps show increased magnetic susceptibility, which is in close

relationship with the high magnetic susceptibility results found in rock samples invaded with hydrocarbon from magnetic measurements, when in comparison with samples from dry wells showing very low and weak magnetic susceptibility readings (Chapter 5).

4.1 Defined Thermodynamic constraints

In this study, the defined constraints used in this model are in Table 2.51. These are the same as used in Burton et al. (1993). In Table 2.52, I added greigite terms into the database to have a comparative observation when compared with magnetic results in Chapter 5. These chosen constraints are standard for thermodynamic modelling of hydrocarbon systems (Burton et al., 1993). This modelling is very effective in this study as experimentally carrying out the phase behaviour of the minerals in the laboratory would be challenging.

Table 2.51 Equations used to define input boundaries for my stability diagrams:

1. $\text{FeO}_4 + 3\text{HCO}_3^- + 5\text{H}^+ + 2\text{e}^- = 3\text{FeCO}_3 + 4\text{H}_2\text{O}$ 2. $\text{Fe}_2\text{O}_3 + 2\text{HCO}_3^- + 4\text{H}^+ + 2\text{e}^- = 2\text{FeCO}_3 + 3\text{H}_2\text{O}$ 3. $3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^- = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ 4. $\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}^- = 3\text{Fe}^{2+} + 4\text{H}_2\text{O}$ 5. $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$ 6. $\text{Fe}_2\text{CO}_3 + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^-$ 7. $\text{FeS} + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{S}$ 8. $\text{FeS}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Fe}^{2+} + 2\text{H}_2\text{S}$ 9. $\text{FeS}_2 + 2\text{H}^+ + 2\text{e}^- = \text{Fe}^{2+} + 2\text{HS}^-$ 10. $\text{FeS}_2 + 2\text{H}^+ + 2\text{e}^- = \text{FeS} + \text{H}_2\text{S}$ 11. $\text{FeS}_2 + \text{H}^+ + 2\text{e}^- = \text{FeS} + \text{HS}^-$ 12. $\text{Fe}_3\text{O}_4 + 3\text{HS}^- + 5\text{H}^+ + 2\text{e}^- = 3\text{FeS} + 4\text{H}_2\text{O}$	13. $3\text{FeS}_2 + 4\text{H}_2\text{O} + 4\text{e}^- = \text{Fe}_3\text{O}_4 + 6\text{HS}^- + 2\text{H}^+$ 14. $2\text{FeS}_2 + 3\text{H}_2\text{O} + 2\text{e}^- = \text{Fe}_2\text{O}_3 + 4\text{HS}^- + 2\text{H}^+$ 15. $2\text{FeS}_2 + 3\text{H}_2\text{O} + 2\text{e}^- + 2\text{H}^+ = \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{S}$ 16. $\text{FeS}_2 + \text{HCO}_3^- + \text{H}^+ + 2\text{e}^- = \text{FeCO}_3 + 2\text{HS}^-$ 17. $\text{FeS}_2 + \text{HCO}_3^- + 3\text{H}^+ + 2\text{e}^- = \text{FeCO}_3 + 2\text{H}_2\text{S}$ 18. $\text{FeS} + \text{HCO}_3^- = \text{FeCO}_3 + \text{HS}^-$ 19. $\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- = 4\text{H}_2\text{O} + \text{HS}^-$ 20. $\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- = 4\text{H}_2\text{O} + \text{HS}^-$ 21. $\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}$ 22. $\text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 38\text{H}^+ + 30\text{e}^- = 2\text{FeS}_2 + 19\text{H}_2\text{O}$ 23. $\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^- = \text{FeS}_2 + 8\text{H}_2\text{O}$
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Table 2.52: New Addition of constraints for greigite which was not part of Machel and Burton 1993

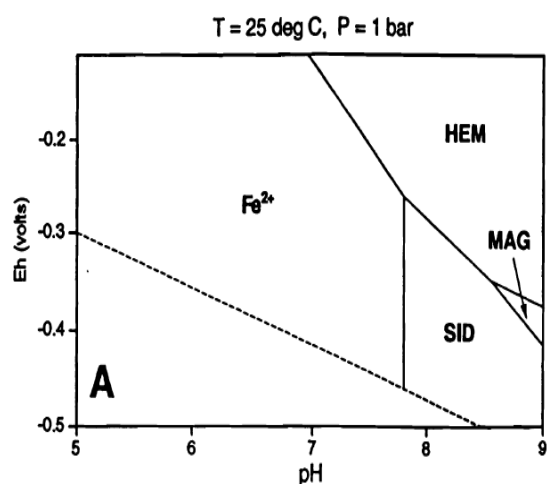
New Addition of constraints for greigite which was not part of Machel and Burton 1993 from (Rickard et al., 2006; Ning et al., 2014).	1. $\text{Fe}_3\text{S}_4 + 4\text{H}^+ = \text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{HS}^-$ 2. $\text{Fe}_3\text{S}_4 + \text{HCO}_3^- + \text{H}^+ + 2\text{e}^- = 3\text{FeCO}_3 + 2\text{HS}^-$ 3. $\text{Fe}_3\text{S}_4 + 4\text{H}_2\text{O} + 4\text{e}^- = \text{Fe}_3\text{O}_4 + 4\text{HS}^- + 2\text{H}^+$ 4. $\text{Fe}_3\text{S}_4 + 2\text{H}_2\text{O} = 0.5\text{H}^+ + 0.5\text{SO}_4^{2-} + 3\text{Fe}^{2+} + 3.5\text{HS}^-$ 5. $\text{Fe}_3\text{S}_4 + 1.75\text{H}^+ + \text{H}_2\text{O} = 3\text{Fe}^{2+} + 3.5\text{HS}^- + 0.25\text{SO}_4^{2-}$
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Table 2.5 3: Gibbs free energy values (cal/mol) for minerals used in the thermodynamic constraints from Johnson et al 1992, Greigite Gibbs free energy was calculated and derived from publications (Rickard et al., 2006; Ning et al., 2014) and also calculated with the RXN software package in Geochemist Workbench

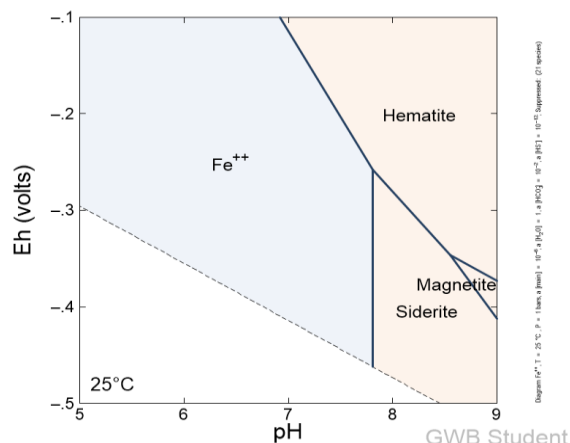
Mineral or Aqueous species	Machel and Burton (1993) cal/mol	This thesis (cal/mol)
Magnetite (Fe ₃ O ₄)	-242574	-242574
Hematite (Fe ₂ O ₃)	-178155	-178155
Siderite (FeCO ₃)	-162414	-162414
Pyrrhotite (FeS)	-24084	-24084
Pyrite	-38293	-38293
Greigite		-74541109
Fe ²⁺	-21870	-21870
H ₂ S	-6673	-6673
HS ⁻	+2860	+2860
SO ₄ ²⁻	-177930	-177930
HCO ₃ ⁻	-140282	-140282
H ₂ O	-56688	-56688
H ⁺	0	0
O _{2(g)}	0	0
H _{2(g)}	0	0

4.1.1 Testing Geochemist Workbench Model against Machel and Burton 1993

I used Geochemist Workbench to extend the work previously done. I created a new database on the Geochemist Workbench with newly defined constraints as seen in (Table 2.51, Table 2.52, Table 2.5 3) to test these results with the same defined constraints in (Machel and Burton 1993 a) which gave the following results below. At 25°C, 1 bar pressure, at increased iron concentration and intermediate sulphur concentration (Figure 4.1) without greigite constraints defined in the model, hematite is replaced by magnetite and siderite as the Eh reduces. At reduced increased iron concentration, low sulphur and increased carbonate concentration (Figure 4.2), hematite and siderite are formed. At increased iron and increased sulphur levels (Figure 4.3) pyrite is formed as a replacement of hematite, at 50°C 150 bar, low sulphur levels, and increased iron concentration, (Figure 4.4), magnetite replaces hematite.

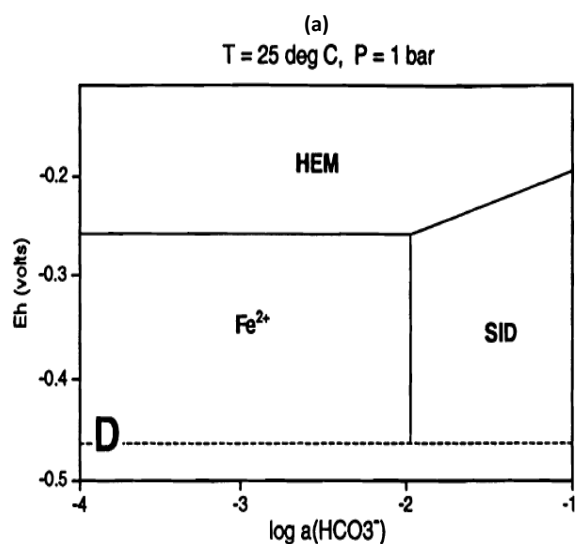


Burton 1993 et al

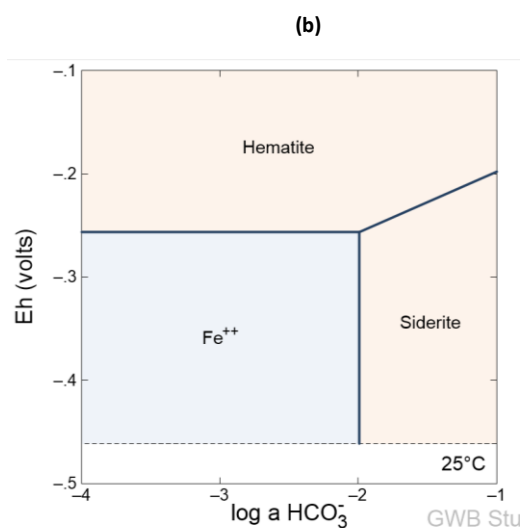


This study

Figure 4.1: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at near-surface thermodynamic conditions of 25°C and 1bar with varying Fe²⁺, HCO₃⁻ and HS⁻ levels. aFe²⁺=10⁻⁶, HCO₃⁻=10⁻², HS⁻=10⁻¹² for a) Burton 1993 model using SUPCRT92 and b) Geochemist Workbench respectively



Burton 1993 et al



This Study

Figure 4.2: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at near-surface thermodynamic conditions of 25°C and 1bar with varying Fe²⁺, HCO₃⁻ and HS⁻ levels aFe²⁺=10⁻⁶, HCO₃⁻=10⁻², HS⁻=10⁻¹², pH 7.8 for (a) Burton 1993 model using SUPCRT92 and (b) Geochemist Workbench respectively

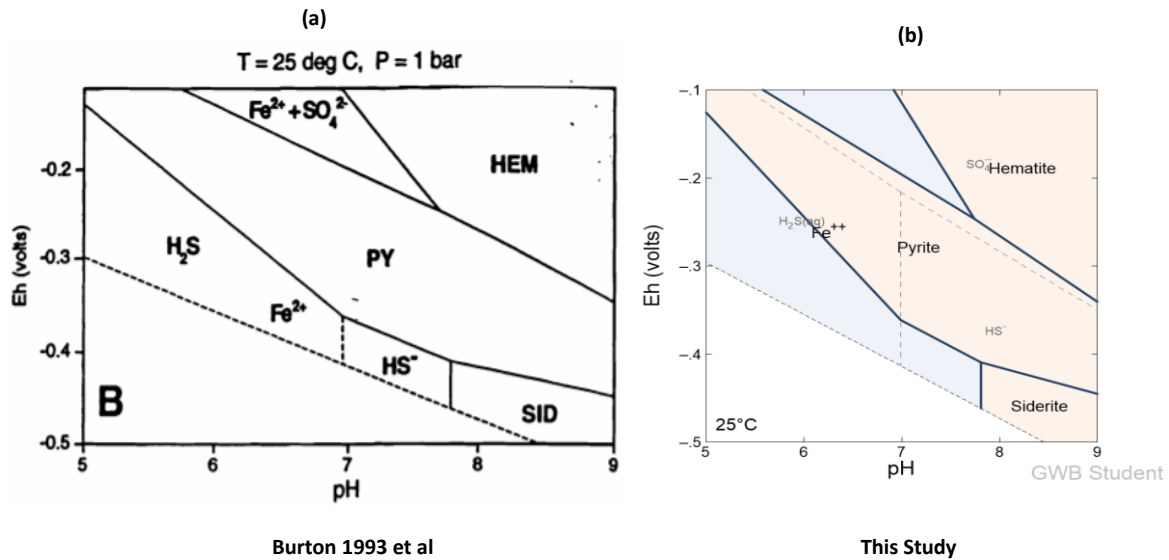


Figure 4.3: predictive thermodynamic constraints above the hydrocarbon contacts. Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring above the contact at near-surface burial conditions of 25°C and 1 bar with varying Fe^{2+} , and HS^- levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{H}_2\text{O}=0.5$, pH 9, $\text{HS}^-=10^{-5}$ for (a) Burton 1993 model using SUPCRT92 and (b) Geochemist Workbench respectively

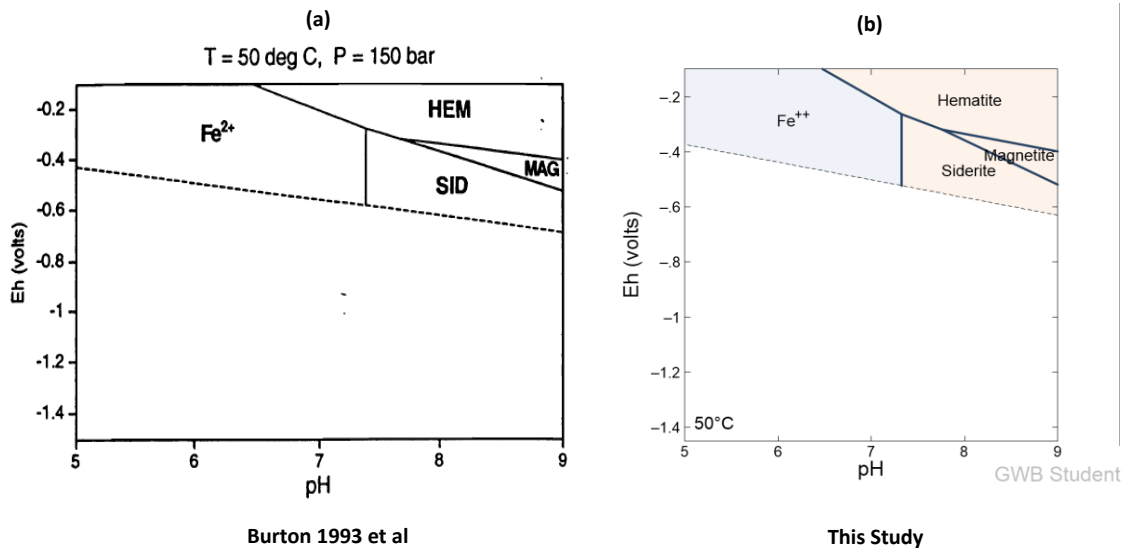


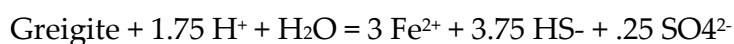
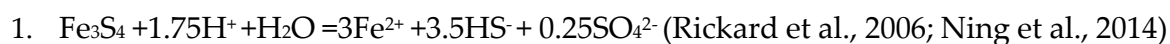
Figure 4.4: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at intermediate burial thermodynamic conditions of 50°C and 150 bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$, $\text{HS}^-=10^{-12}$ for a) Burton et al 1993 model using SUPCRT92 and b) Geochemist Workbench respectively

After carrying out the following checks and tests with the newly created database on Geochemist Workbench, I got the following results (Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4) with the input constraints, this confirms that the results of Burton and Machel (1993) are repeatable. The equation used to define boundaries in my stability diagrams are (Table 2.51).

4.2 Greigite addition into the Geochemist Workbench database:

Greigite is an iron sulphide mineral, which is magnetically strong and thermodynamically metastable (Lennie and Vaughan et al., 2006). The aqueous reaction resulting in the

precipitation of greigite when hydrocarbon reacts with water and dissolved iron mineral in the presence of hydrogen sulphide was accounted for the reaction to take place. For the model to work effectively, the ion equation involving greigite dissolution in water alongside its ion species needed to be balanced. RXN software package on Geochemist Workbench helped to model a balanced equation. I calculated the Gibbs free energy of greigite and log K values for each of the temperature conditions examined and ACT2 of the software package helped with the thermodynamic modelling of the constraints and outputs.



Log K's:

0 C: -27.0468	150 C: -28.3652
25 C: -27.4356	200 C: -28.4662
60 C: -27.8263	250 C: -28.4564
100 C: -28.1328	300 C: -28.3672

Polynomial fit:

$$\log K = -27.05 - .01689 T + 7.47\text{e-}5 T^2 - 1.625\text{e-}7 T^3 + 1.75\text{e-}10 T^4$$

$$\text{Log K at 25 C} = -27.4356$$

Assumptions implicit in equilibrium equation from ACT 2:

$$\text{temperature} = 25 \text{ }^\circ\text{C}$$

$$\text{activity of Fe}^{++} = 1$$

$$\text{activity of HS}^- = 1$$

$$\text{activity of SO}_4^{--} = 1$$

$$\text{activity of H}^+ = 1$$

$$\text{activity of H}_2\text{O} = 1$$

Equilibrium equation:

$$\text{Reactants are favoured, } \Delta G = -311.880 \text{ kJ/mol}$$

4.3 Application of new Models

In the early 1990s, Burton et al. (1993) used SUPCRT 92 to carry out geochemical modelling. I used Geochemist Workbench on different codes to do the same thing but my modification varied because of the addition of greigite. Initially, I compare the two codes and then try to determine what difference the addition of greigite does. In some conditions, the formation of greigite was not favourable, and the results are very similar to that of Burton et al. (1993).

4.3.1 Near Surface Thermodynamic Modelling

At near-surface conditions, no greigite was formed, these conditions, therefore, reproduced Burton et al. 1993 model with SUPCRT92. At surface and near-surface conditions, (25°C and 1bar) in the “plume environment” rich in hydrocarbon with relatively high pH of a typical reservoir system. If the sulphur level (HS^-) is low, hematite is replaced by magnetite at intermediate EH values and pH greater than 8.5, and siderite at pH values between 7.8 and 8.5. At high sulphur levels, hematite is replaced by pyrite at increasing (HS^-) and some very negligible greigite, which is still dominated by pyrite, but at greater depth pyrite formed still at increasing sulphur levels. (Figure 4.5; Figure 4.6). At relatively low pH levels, in surface plume environments. ($\text{pH} < 7.5$), if sulphur is low or intermediate, hematite, magnetite and pyrrhotite become unstable and dissolve. At low Fe^{2+} , they all dissolve, and high iron Fe^{2+} (10^{-4}) they are replaced by pyrite. Regardless of the Fe^{2+} levels, magnetite and pyrrhotite are unstable. The depth interval synonymous for near-surface thermodynamic conditions is 0-1000 m. Greigite was added into the database including the other constrains in Figure 4.7A and Figure 4.7B takes other constraints into consideration including greigite.

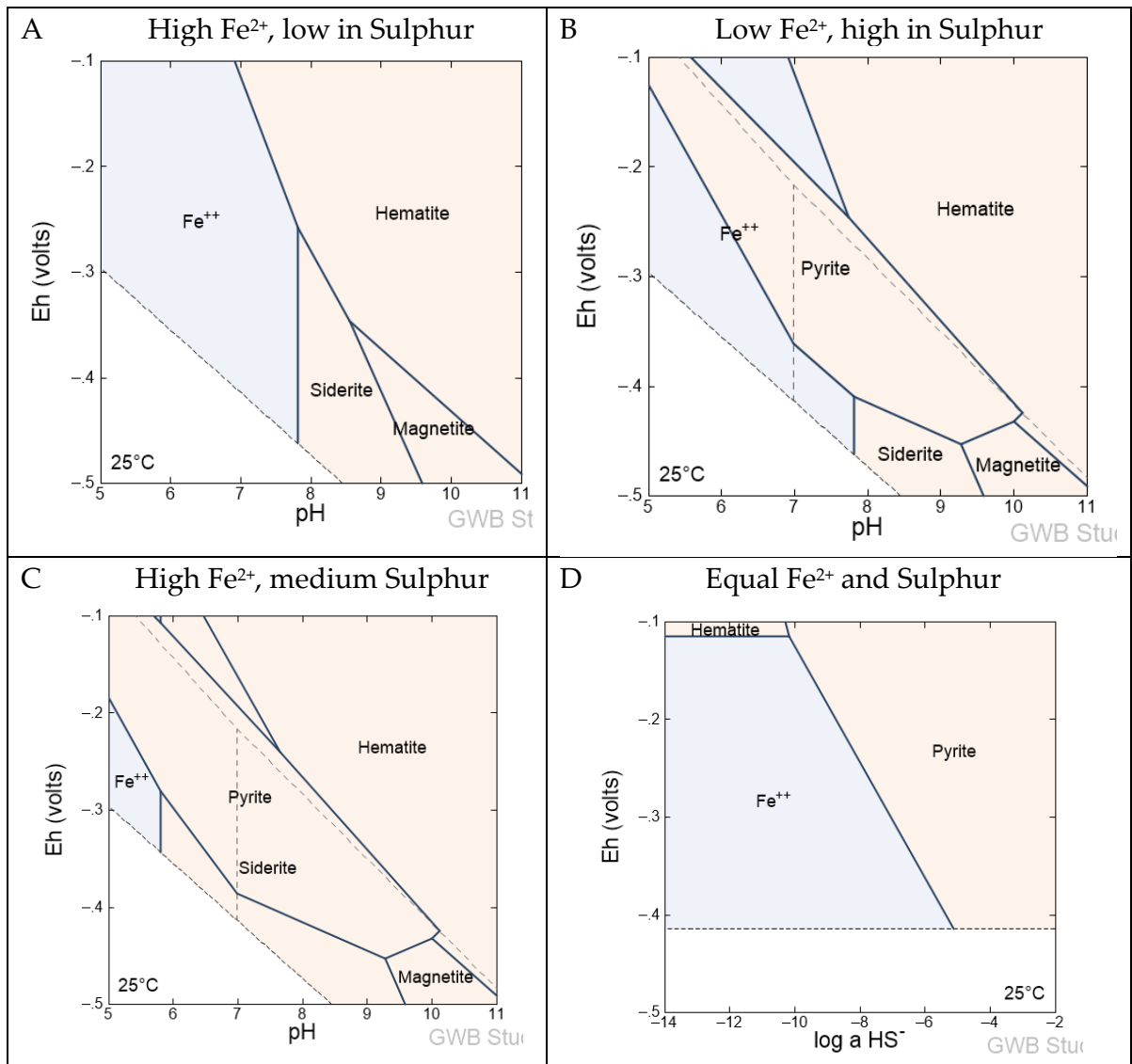


Figure 4.5: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at near surface thermodynamic conditions of 25°C and 1bar with varying Fe²⁺, HCO₃⁻ and HS⁻ levels. A) $a_{Fe^{2+}}=10^{-6}$, $HCO_3^-=10^{-2}$, $HS=10^{-12}$ B) $a_{Fe^{2+}}=10^{-6}$, $HCO_3^-=10^{-2}$, $HS=10^{-6}$ C) $a_{Fe^{2+}}=10^{-4}$, $HCO_3^-=10^{-2}$, $HS=10^{-6}$ D) $a_{Fe^{2+}}=10^{-6}$, pH 7. The dash lines represents the speciation of new minerals formed.

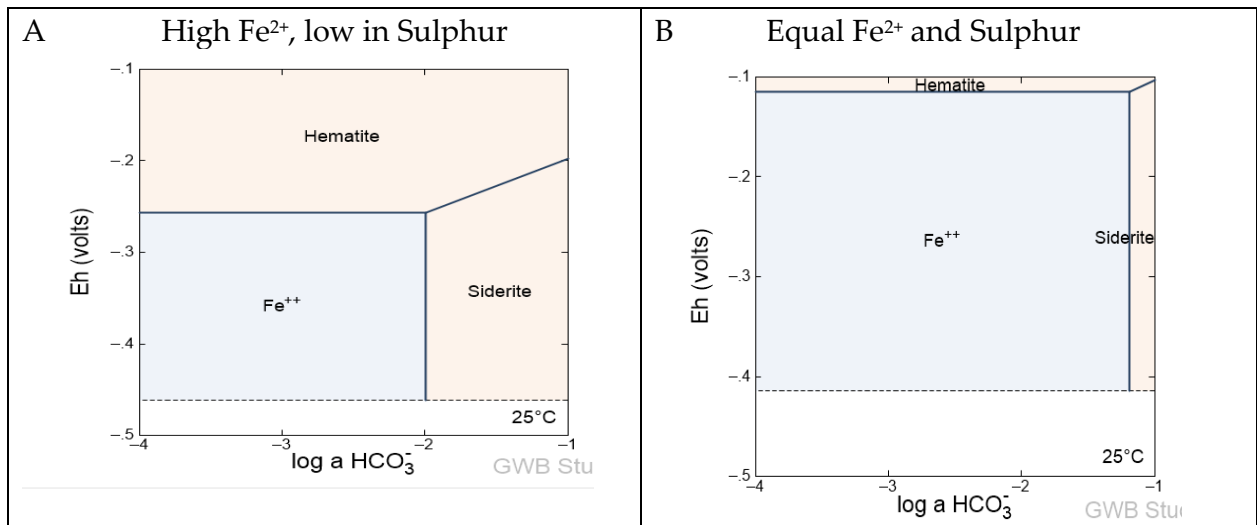


Figure 4.6: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at near-surface thermodynamic conditions of 25°C and 1bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $\text{HS}^- = 10^{-12}$ pH 7.8 B) $\text{HS}^- = 10^{-6}$, pH 7.0

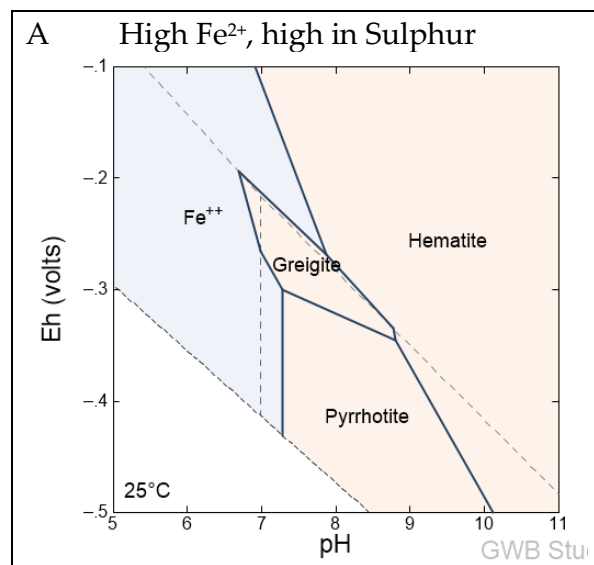


Figure 4.7: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at near-surface thermodynamic conditions of 25°C and 1bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $\text{HS}^- = 10^{-5}$, pH 7.8 with greigite added into database.

4.3.2 Shallow Burial modelling condition:

Under shallow burial conditions, 50°C and 150bar at high pH, 1000m to 2500m and low sulphur (HS^-), hematite is replaced with magnetite, at pH >8 and intermediate Eh conditions, and by siderite at pH between 7.5 and 8 and at lower Eh. At high sulphur condition and intermediate Eh, hematite is replaced by pyrite. With the inclusion of greigite into the database, at increasing sulphur condition and intermediate Eh, pyrite and greigite precipitates, as the sulphur condition increases, more greigite is formed replacing pyrite. Magnetite experiences stability at pH >8 and intermediate Eh condition, at lower

pH it is replaced by siderite. Lower pH implies, low or no hydrocarbon presence. The presence of siderite from the magnetic result was seen on background samples or dry wells with no hydrocarbon presence, this is what the thermodynamic modelling can predict too. At intermediate sulphur and Eh conditions, magnetite is stable at pH>8.3, at low Eh, it is replaced by siderite. Magnetite is usually very unstable, low and intermediate sulphur levels makes pyrrhotite to be unstable too. In high sulphur rich environments like the sour gas pool, thermodynamic sulphur conditions (HS^-) is high, pyrrhotite is stable and can replace pyrite at low Eh (Figure 4.8; Figure 4.9; Figure 4.10)

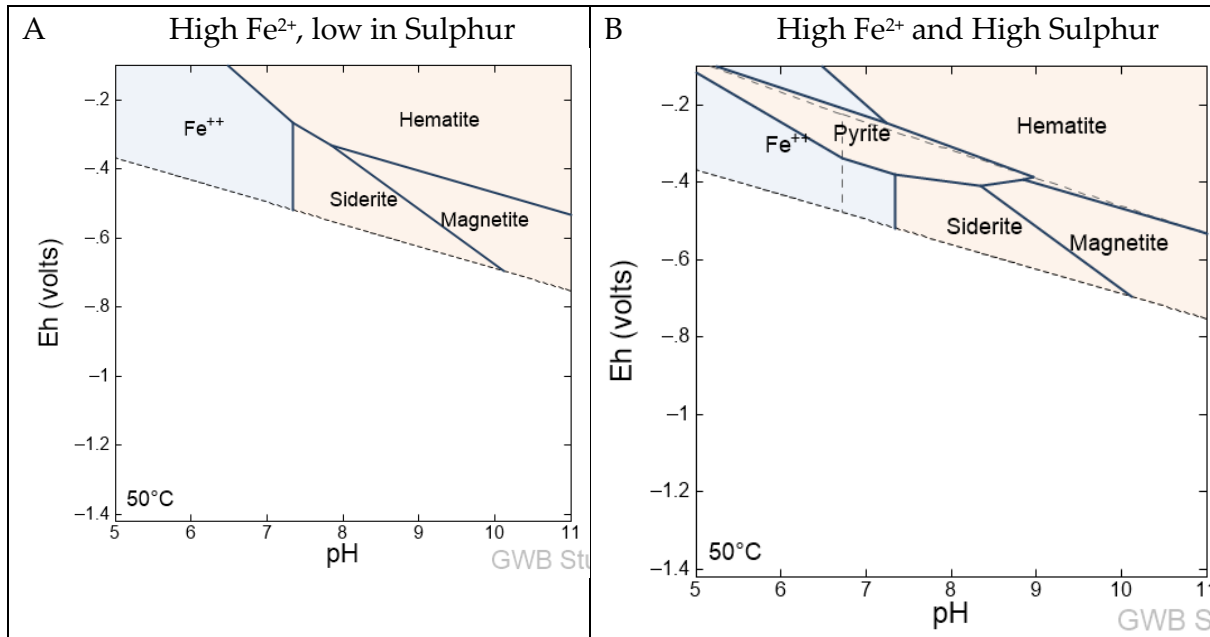


Figure 4.8: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at shallow burial thermodynamic conditions of 50°C and 150 bar with varying Fe^{2+} , HCO_3^- and HS^- levels. A) $\text{Fe}^{2+}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ B) $\text{HS}^-=10^{-6}$.

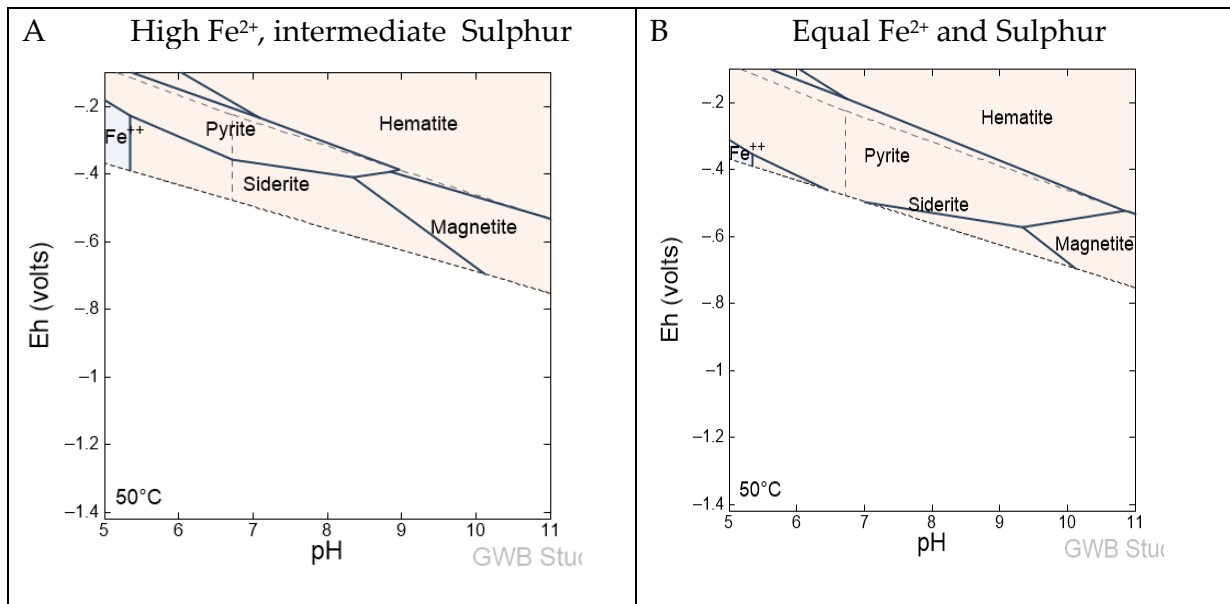


Figure 4.9: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at shallow burial thermodynamic conditions of 50°C and 150 bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a\text{Fe}^{2+}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $a\text{Fe}^{2+}=10^{-4}$, $\text{HS}=10^{-6}$ B) $a\text{Fe}^{2+}=10^{-4}$, $\text{HS}=10^{-4}$, $\text{HCO}_3^-=10^{-2}$

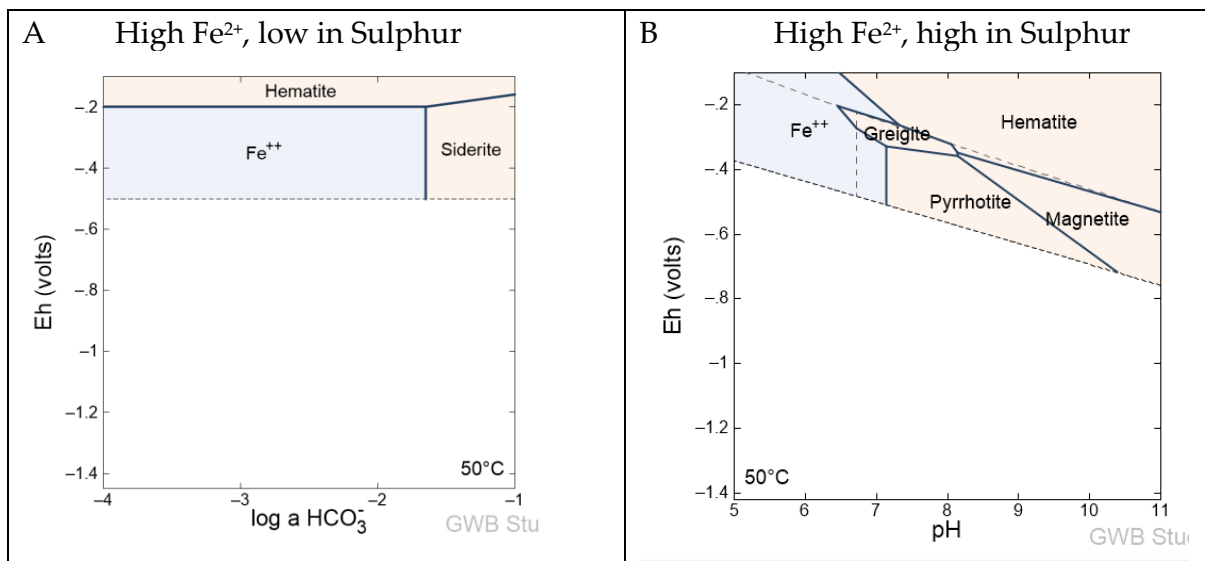


Figure 4.10: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at shallow burial thermodynamic conditions of 50°C and 150 bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a\text{Fe}^{2+}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $\text{HS}=10^{-2}$

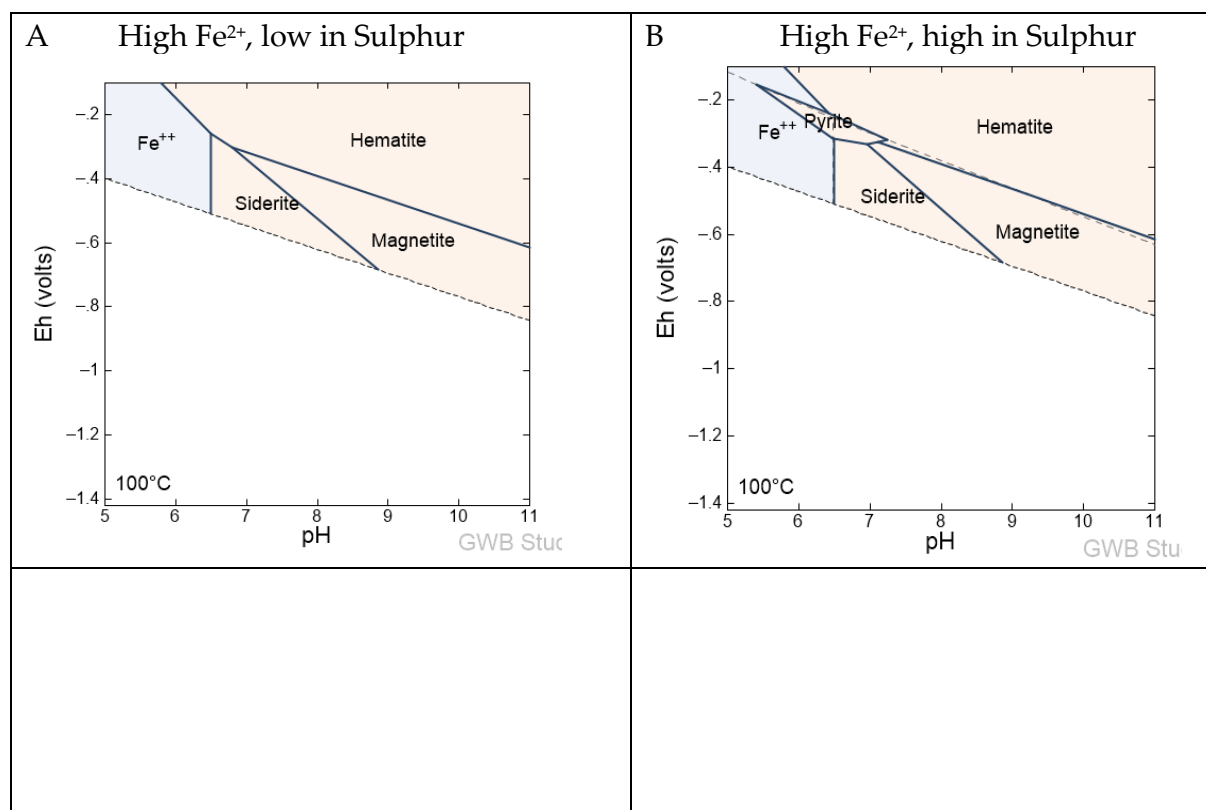
At shallow depth (50°C, 150 bar), in low pH sub environments, intermediate Eh, the unstable property of hematite is seen as it dissolves under low sulphur condition. Even as at intermediate sulphur conditions, hematite dissolves, but at low Eh and pH much > 6 and high Fe^{2+} , pH > 7.2. At low Fe^{2+} hematite is replaced by pyrite. At high sulphur condition hematite is replaced by greigite and pyrite, and with increasing sulphur condition, we have more pyrite formed alongside some greigite, magnetite is readily unstable on the condition as it dissolves at all sulphur conditions (Figure 4.10). The unstable characteristics of pyrrhotite are evident at low and intermediate sulphur levels,

it becomes stable when sulphur is high. When the pH is < 5.4 , which is readily not a usual condition, pyrrhotite becomes unstable and dissolves to Fe^{2+} and H_2S .

4.3.3 Intermediate burial condition

Under intermediate burial conditions (100°C , 300bars) (Figure 4.12), at relatively high pH, low sulphur conditions, hematite is replaced by magnetite. At high sulphur conditions, hematite is replaced by pyrite and greigite. The Stability of magnetite under intermediate burial condition is evidence at intermediate Eh and low sulphur condition respectively, but it replaced by siderite at low Eh levels. When sulphur levels are high, magnetite is stable under intermediate Eh values but replaced by pyrrhotite at increased Eh conditions. At high sulphur conditions, pyrrhotite is stable and can replace pyrite at low Eh. Greigite, on the other hand, is stable at high sulphur conditions, and more pyrite is formed as the sulphur condition increases.

At intermediate and high sulphur conditions, hematite is replaced by pyrite and greigite and pyrrhotite. Magnetite is replaced by siderite at higher pH > 7 . At high sulphur and low Eh conditions, pyrrhotite is stable. At a very low pH < 5.2 , pyrrhotite can form to replace pyrite. Pyrrhotite can become unstable and dissolve to form aqueous Fe^{2+} and H_2S (Figure 4.11). Intermediate burial condition (100°C , 300 bars) is a typical subsurface condition of the sour gas pools of the Nisku, at the depth interval when magnetic enhancement was observed. This thermodynamic conditions/constraints with the presence of hydrocarbon alter the mineralogy of the host rock, leading to the growth of new authigenic minerals. The depth interval is at 2500-3500m.



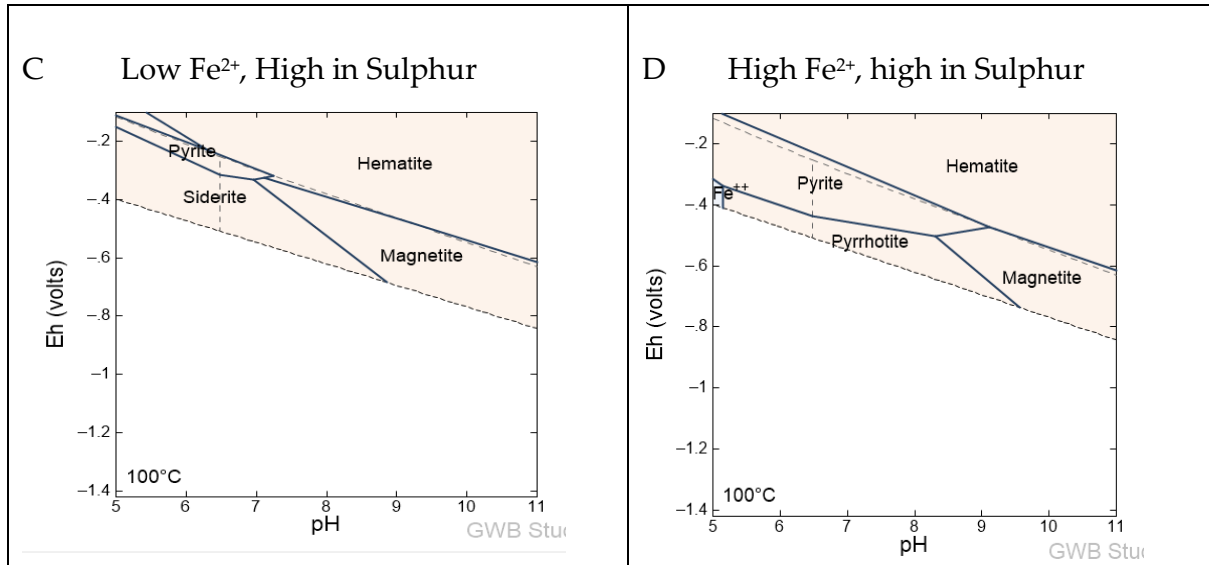


Figure 4.11: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at intermediate burial conditions of 100°C and 300 bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a\text{Fe}^{2+}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $\text{HS}^-=10^{-12}$, pH 7 B) $\text{HS}^-=10^{-5}$

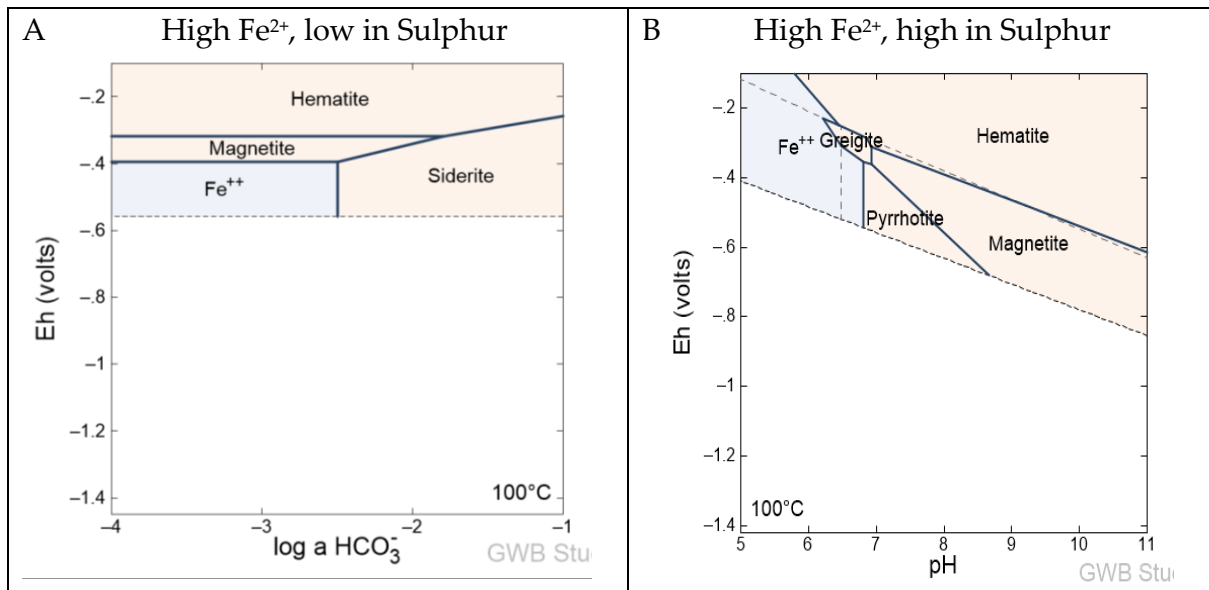


Figure 4.12 Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at intermediate burial conditions of 100°C and 300 bar with varying Fe^{2+} , HCO_3^- and HS^- levels. $a\text{Fe}^{2+}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $\text{HS}^-=10^{-12}$ B) $\text{HS}^-=10^{-6}$ C) $a\text{Fe}^{2+}=10^{-4}$, $\text{HS}^-=10^{-6}$ D) $a\text{Fe}^{2+}=10^{-4}$, $\text{HS}^-=10^{-4}$

4.3.4 Deep burial condition

Under deep burial conditions (200°C, 600 bars), 2500m to 3500m, under high pH and intermediate Eh condition and at all sulphur levels, hematite is most likely to be replaced by magnetite. The stability of magnetite is confirmed at intermediate Eh conditions, intermediate, and low sulphur conditions. Interestingly under deep burial condition, at high sulphur and intermediate Eh, magnetite remains stable, whereas, at low Eh, magnetite is replaced by pyrrhotite (Figure 4.13). The unstable nature of iron sulphide mineral pyrrhotite is seen under deep burial conditions at low intermediate sulphur conditions, however, at high sulphur and low Eh conditions, pyrrhotite is stable. Hematite could potentially be replaced by siderite over a small range of pH (5.3 to 5.6) or possibly undergo dissolution at low pH < 5.3. At pH above 5.8 and high sulphur, hematite is replaced by magnetite or by pyrrhotite at much lower pH < 5.8 and Eh conditions. At pH > 5.6, intermediate Eh condition, and low sulphur condition magnetite is stable. Magnetite is possibly replaced by siderite at low Eh. At higher Sulphur conditions, and intermediate Eh, magnetite is stable, but replaced by pyrrhotite at low Eh and low pH < 5.8. At low, and intermediate sulphur the unstable nature of pyrrhotite is seen, it becomes stable at high sulphur conditions and low Eh.

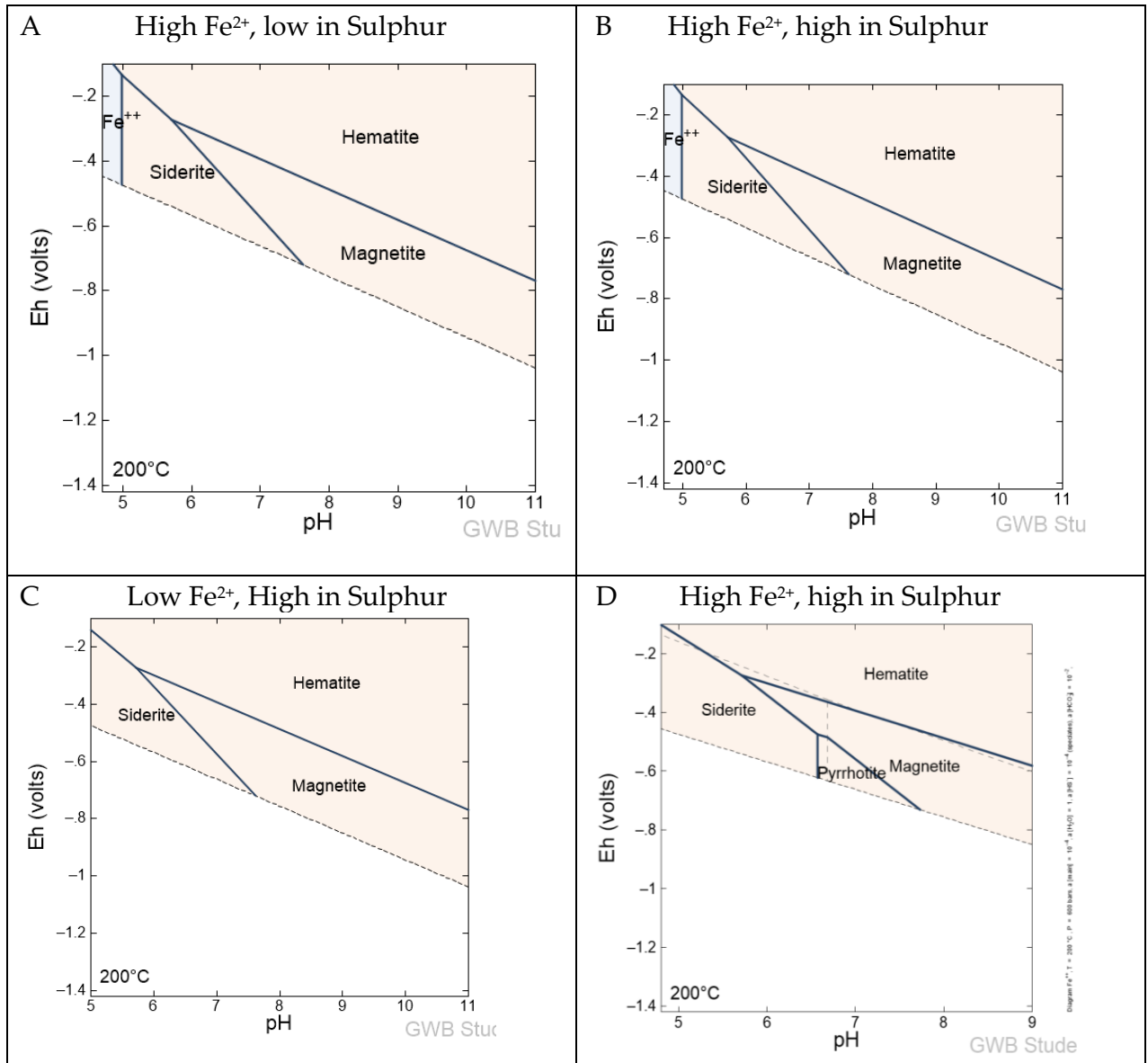


Figure 4.13: Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at deep burial thermodynamic conditions of 200°C and 600bar with varying Fe²⁺, HCO₃⁻ and HS⁻ levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{HCO}_3^-=10^{-2}$ A) $\text{HS}^- = 10^{-12}$ B) $\text{HS}^- = 10^{-6}$ C) $a_{\text{Fe}^{2+}}=10^{-4}$, $\text{HS}^- = 10^{-6}$ D) $a_{\text{Fe}^{2+}}=10^{-4}$, $\text{HS}^- = 10^{-4}$.

4.3.5 Summary of Comparison with Machel and Burton 1993 Model

The results are almost identical with Machel and Burton except for cases where greigite was formed and greigite seem to form at intermediate and shallow depth and certain Eh and pH. Intermediate burial condition is the proposed depth interval where I found greigite from my magnetic results. Greigite does not form at deep burial conditions. We are then going to look at the hydrocarbon contacts.

4.4 Redox Conditions favouring the Enhancement of Magnetic minerals, pH, Eh, H₂O, HS⁻

The pH of crude oil is between 9.0-11.00 (Hutin et al., 2016), which implies that crude has high alkalinity. The more biodegraded it becomes, the lower the pH becomes (Emmerton, 2012). The activity of reducing bacteria plays a vital role in reducing the pH of crude oil, for its acidic nature to be observed (Bell et al., 1987; Emmerton et al., 2012). The pH of water, on the other hand, is 7, which signifies neutrality. Water can neutralize, the alkalinity or acidity of a solution. Above the hydrocarbon contact, at shallow depth, crude oil has increased pH conditions, and at the contact, the pH reduces because of the influence of increased biodegradation and water at shallow depth and greater depth, thermodynamics reaction with the presence of water at the gas-water contact. For this study, intermediate burial condition is the focus, because the predictive depth interval is 2500 m to 3500 m. The depth interval where hydrocarbon contact was found for the Nisku was at 3201 m. Several diagenetic studies in sulphidic environments have also shown and predicted that iron-bearing detrital mineral assemblages undergo a radical alteration of the iron-bearing minerals. Hydrogen sulphide as a by-product of thermochemical sulphate reduction reacts with the released Fe²⁺ from iron mineral dissolution or iron oxyhydroxide minerals to form iron sulphide minerals greigite, pyrite (Machel and Burton 1995; Roberts et al., 2015, Roberts et al., 2018).

4.5.1 Above the contact:

The environments around which magnetic mineral diagenesis occurs and the environment that favours these diagenetic processes are quite important. In the assumption that the water concentration above the transition zone is not as much as it is at the transition and below the transition zone (Figure 4.61). The thermodynamic constraints in consideration are e.g. Eh, pH, HS⁻, H₂O as seen in (Figure 4.14)

pH 9-11, $\text{HS}^- = 10^{-5}$, $\text{Fe}^{2+} = 10^{-6}$,

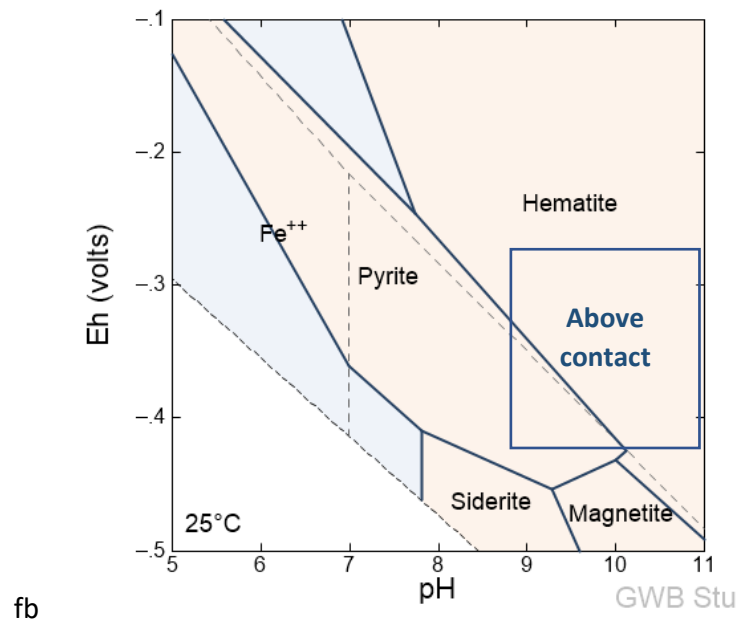


Figure 4.14: Predictive thermodynamic constraints above the hydrocarbon contacts. Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring above the contact at near-surface burial conditions of 25°C and 1 bar with varying Fe^{2+} , and HS^- levels. $a_{\text{Fe}^{2+}} = 10^{-6}$, $\text{H}_2\text{O} = 0.5$, pH 9, $\text{HS}^- = 10^{-5}$. The activation of water is not lower than 0.5 because the model above the hydrocarbon contact predicts the condition where hydrocarbon concentration is low.

4.5.2 At the Hydrocarbon contact

At the contact, the pH of the saltwater will further alter the already existing pH of hydrocarbon, hence reducing the overall pH of the mixture, bringing it further down below neutral, making it more acidic in concentration, this condition alongside the dissolved detrital mineral, which releases Fe^{2+} , which also reacts with H_2S produced from thermochemical sulphate reduction (TSR) favours the growth of the new authigenic minerals. This could be the reason why iron sulphide greigite, was formed at a much lower pH (Figure 4.61). This, therefore, implies that at lower pH, ferrimagnetic mineral precipitation is favourable. At higher the pH, ferrimagnetic minerals are not favourably formed (Figure 4.15).

pH= 7, HS= 10^{-5} , $\text{Fe}^{2+}= 10^{-6}$,

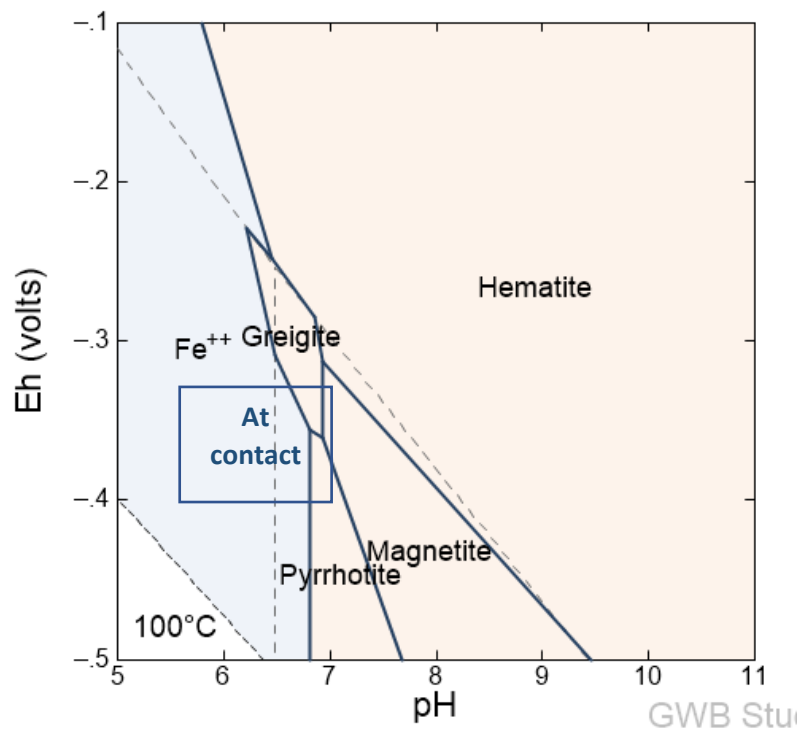


Figure 4.15: Predictive thermodynamic constraints above the hydrocarbon contact at pH 7. Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring at the contact at near-surface burial conditions of 100°C and 150 bar with varying Fe^{2+} , and HS levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{H}_2\text{O}=1$, pH 7, $\text{HS}=10^{-5}$, $\text{HCO}_3^- =10^{-2}$

4.5.3 Below the hydrocarbon contact

At this thermodynamic condition, it is assumed that the concentration of water increases. The hydrocarbon in this phase has a large concentration of water with dissolved minerals. Water in this phase is very hydrocarbon-rich, the pH of this solution will increase almost as it was above the hydrocarbon contact before the water transition zone was reached. The pH is almost close to neutral or neutral or exceeds pH 7 below the transition zone (Figure 5.16) except when it is close to a zone, where water no longer exists, then the pH rises above 7 and water concentration in the solution reduces at much greater depth and higher temperatures (Figure 5.16)

pH= 9-11, HS= 10^{-12} , Fe^{2+} = 10^{-6}

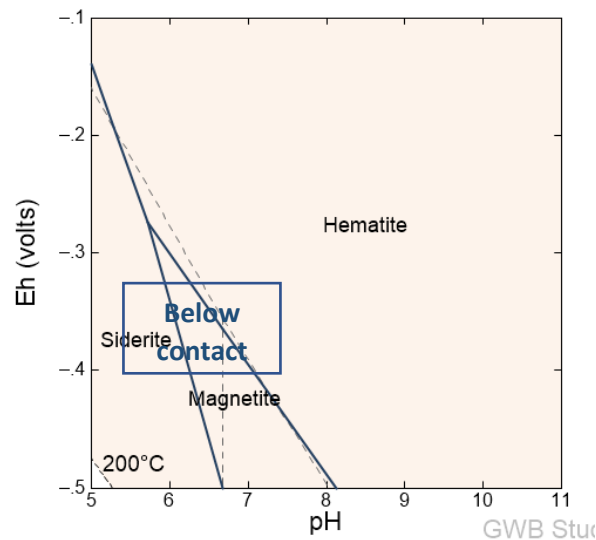


Figure 5.16: Predictive thermodynamic constraints below the hydrocarbon contacts. Thermodynamic stability diagrams illustrating magnetic mineral diagenesis occurring above the contact at near-surface burial conditions of 200°C and 600 bar with varying Fe^{2+} , and HS^- levels. $a_{\text{Fe}^{2+}}=10^{-6}$, $\text{H}_2\text{O}=1$, pH 9-11, $\text{HS}^-=10^{-12}$

For wells 02-12-28 and A2-19 on the bank edge reef in the sour gas pool, where I observed magnetic enhancement at their hydrocarbon contact, it had the characterized presence of iron sulphide greigite and pyrrhotite as seen from the high-temperature magnetic results, SEM and room temperature results and FORC diagrams (Chapter 5). The thermodynamic condition in the subsurface from the magnetic result was used to create a thermodynamic model with iron sulphide greigite inputted. The initial temperature, pressure, and redox potential from previous models that had no greigite input in the geochemical model were not particularly in close sync with the magnetic results I have from my room temperature measurements until greigite was included to explain the process. Room temperature magnetic results predicted the presence of paramagnetic pyrite, thermodynamic models also predict pyrite growth. Greigite precipitation was not seen in samples located in the sweet oil pools but in the sour gas pool only. Details are addressed in the discussion section.

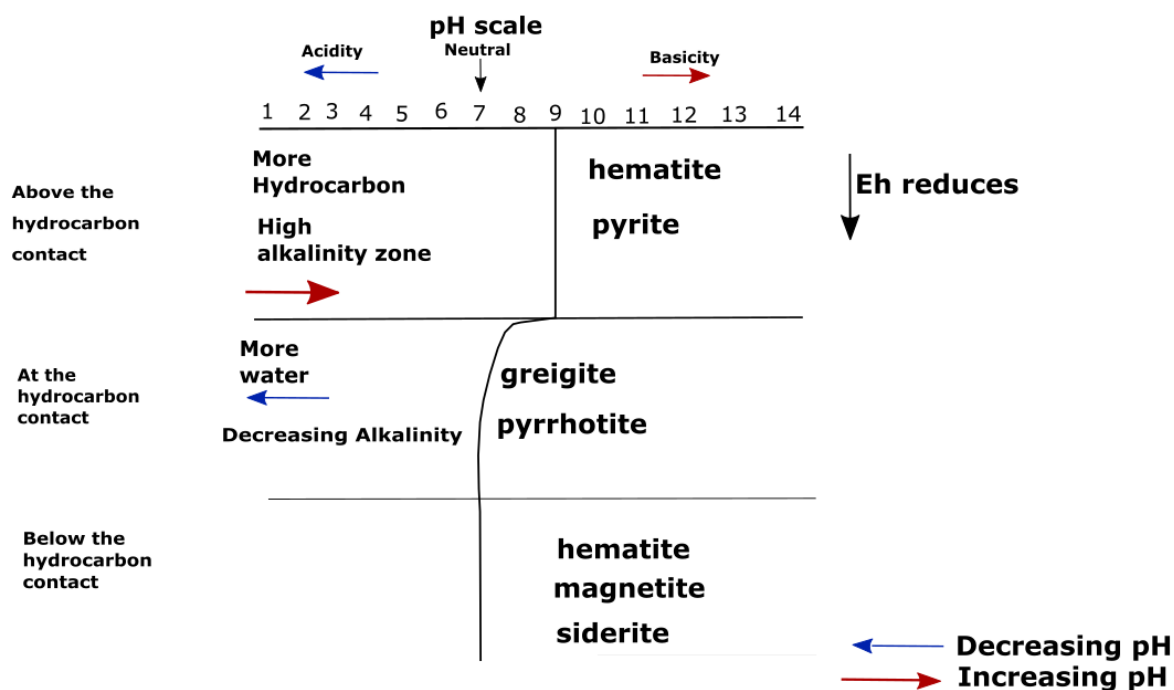


Figure 4.61: Chemistry of magnetic mineral precipitation in the reservoir, above the hydrocarbon contact, at the hydrocarbon contact and below the hydrocarbon contact

4.6 Discussion

Above the hydrocarbon contact, and at reduced Eh and increasing sulphur concentration, hematite is gradually replaced by pyrite at a pH range of 9-11, (Figure 4.14) at the hydrocarbon contact, rich in water concentration at pH is 7, water neutralizes the hydrocarbon solution making the pH further drop, which results in the formation of greigite and pyrrhotite, both are strong iron sulphide magnetic minerals, the solution becomes more acidic in concentration, the more acidic the solution is, the stronger the minerals formed, this appears to be the cause of the increased magnetic enhancement found at the hydrocarbon contact, the impact of water as not just a universal solvent, but at as a reducing agent has an impact with this process. Water impacts the reduction in the hydrogen ion concentration, making the solution more acidic in concentration favouring the precipitation of these strong magnetic minerals. This effect could also have played a major role with (Emmerton et al., 2013) observation on how biodegraded crude oil becomes more acidic and giving rise to increased magnetic anomalies geochemically. Greigite is a strongly magnetic mineral from the sulphide group, comparing the predictive results of magnetic minerals formed from geochemical modelling with magnetic measurements gives a pointer as to what kinds of magnetic minerals are expected as a rule of thumb to precipitate during diagenesis. Unfortunately, the magnetic

results of the Nisku seem to defy this claim, not until when greigite was included in the model. From magnetic results in Chapter 5 of this thesis, magnetic enhancement was found at the hydrocarbon fluid contacts for two wells on the bank edge reef which are known to be hydrologically contagious e.g. Well 02-12 and A2-19. (Machel and Burton 2003) and are both sour gas wells with 20% sulphur concentration (Machel and Burton 1991; Machel and Burton 1995). Magnetic results also predict the presence of iron sulphide greigite and pyrrhotite to be the mineralogy combination responsible for influencing the increased and positive magnetic anomaly identified at the hydrocarbon contacts. Pyrite is naturally stable, with increased sulphur concentration, ferromagnetic greigite parameters from thermodynamics literature (brothers et al., 1996; Derack et al., 1996; Ning et al., 2004) was included in the database of the thermodynamic model, to understand the how the growth of greigite would affect pyrite which from the results showed that greigite was formed. Pyrite is a precursor to greigite (Roberts et al., 2015; Roberts et al., 2018) pyrite forms under increasing sulphur concentration in the system. Pyrite is precipitated from the thermodynamic modelling, but the strong ferromagnetic property of greigite would overshadow the paramagnetic nature of pyrite in the system. Arguably, the Fe^{2+} and Fe^{3+} are produced from magnetite and hematite when they dissolve. This produced Fe^{2+} and Fe^{3+} reacts with H_2S to enable remagnetisation and growth of new authigenic minerals depending on the environment (Figure 5.17). In Sulphidic environment, pyrite is formed, for methanic environment, greigite is formed and it is stable (Elmore et al., 2012, Roberts et al., 2018). Insufficient sulphur available to react with Fe^{2+} and Fe^{3+} would lead to a shortage of formation of pyrite and enhance the formation of greigite. This phenomenon would be the case for the Nisku sour gas pools on the bank edge reef.

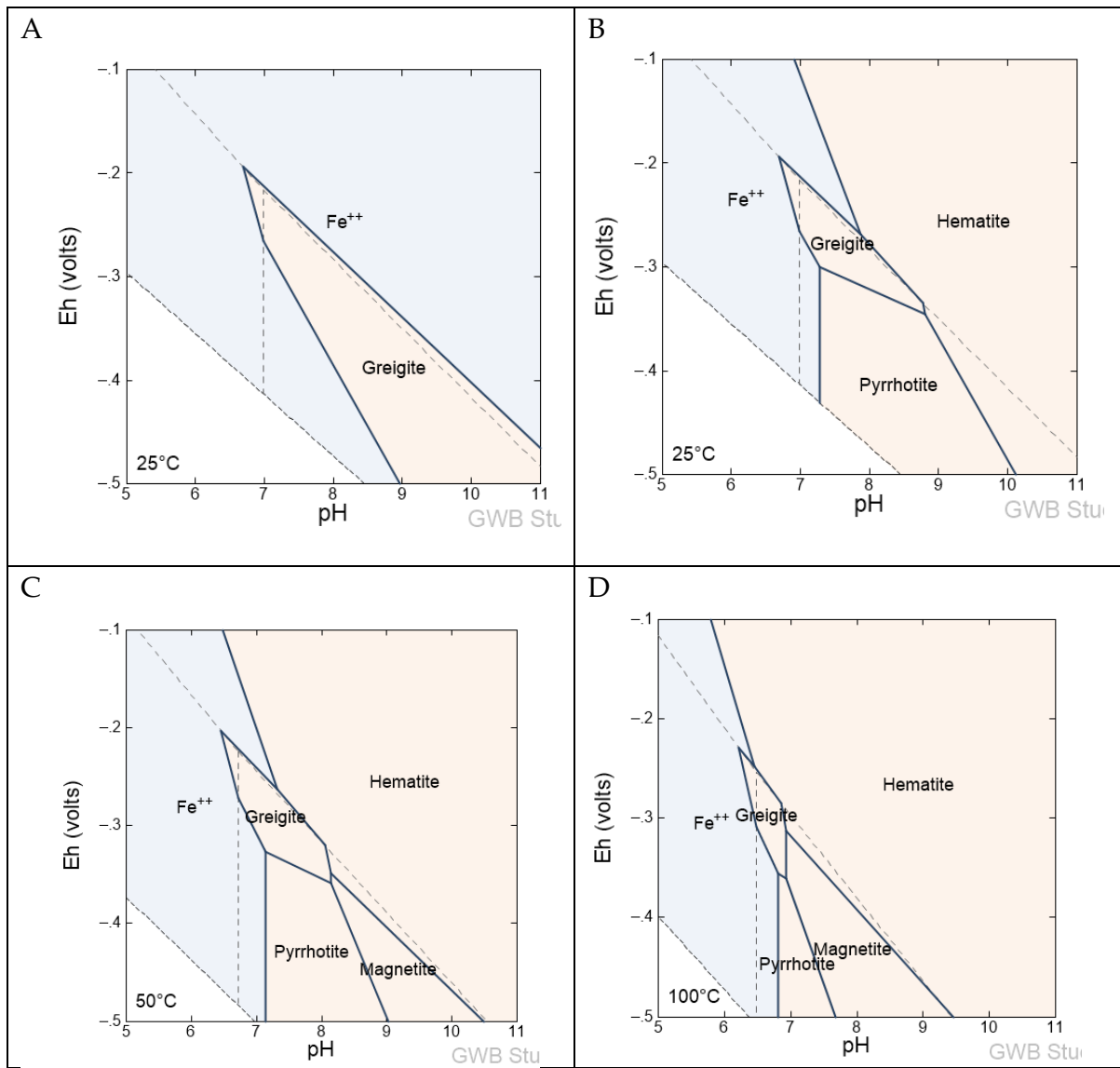


Figure 5.17: Thermodynamic stability diagram predicting the growth and precipitation of authigenic greigite from 25°C, 1bar, near surface condition to intermediate burial condition 100°C,300bar. $a_{Fe^{2+}} = 10^{-6}$, $a_{HCO_3^-} = 10^{-2}$ is the same across board A) 25°C, 1bar , $HS = 10^{-5}$ with greigite alone included in the database, B) 25°C, 1bar , $HS = 10^{-5}$ C) 50°C, 150 bar , $HS = 10^{-5}$, D) 100°C, 300 bar , $HS = 10^{-5}$

4.7 Summary

In summary, predicted changes in the magnetic susceptibility would be greatly observed in a hydrocarbon-rich environment which shows trends with increasing depth. The decrease in magnetic susceptibility will be very predominant in surface or near-surface environment, or at shallow depth, but with increasing depth, susceptibility increases. This trend with increasing depth is seen in the model as hematite, dissolves and is replaced by pyrite at the near-surface condition or shallow depth, but with increased burial condition and increased sulphide concentration and reduced pH, and increased H₂O concentration, which signified the oil and water transition zone, new growth of authigenic sulphide minerals greigite and pyrrhotite was formed as a replacement of hematite. The summary of the stability diagrams from thermodynamic modelling gives a clear indication of how an increase in temperature and pressure conditions is of direct proportionality with increased burial conditions in the subsurface, towards the enhancement of magnetic signals, this implies that magnetic signal enhancement increases with depth and at increasing temperature and pressure conditions. The thermodynamic metastable nature of greigite could be the possible reason why the greigite did not precipitate at greater depth in the model. Thermodynamic stability diagrams common for iron oxides and sulphides can hence help predict magnetic mineral assemblages and associated changes in magnetic susceptibility for a range of thermodynamic conditions and these predictions are based on assumptions that equilibrium is attained thermodynamically, which would require (Table i).

1) Sufficient supply of necessary reactants. H₂S and iron ionically represented HS⁻, Fe²⁺

Every depth interval in the subsurface is represented from the modelling experiment. The thermodynamic processes that inform the minerals that are formed are accounted for.

2) Biological influences on reactions are usually very insignificant

The nature of the thermodynamic environment influences the type of minerals formed i.e. rich sulfidic environments lead to the formation of ferrimagnetic iron sulphide minerals at greater depths. The temperature, pressure, redox potential, Eh, and pH, affects the thermodynamic stability of the host rocks and the authigenic magnetic minerals formed.

Table i: Showing the mineralogy at every depth interval with thermodynamic modelling capturing the zones and the predicted mineral precipitated as output.

Zones		Depth (m)	Condition	Output Mineralogy
Above contact	Near surface	0-1000	25°C, 1bar	hematite,siderite
At contact	Shallow burial	1500-2500	50°C ,100bar	greigite, pyrrhotite
At contact	Intermediate	2500-3500	100°C, 200bar	greigite, pyrrhotite
Below contact	Deep burial	4000-6000	200°C, 600bar	hematite

CHAPTER 5

IDENTIFYING MAGNETIC PROXIES IN HYDROCARBON RESERVOIRS

5.1 Introduction

This chapter builds on current research findings, in an attempt to identify a set of magnetic proxies which can be used to identify the presence of magnetic minerals in reservoirs and the causes of magnetic enhancement at the hydrocarbon-water contact by determining the mineralogy, morphology, grain sizes of the minerals presence and its relative abundance by calibrating the rock magnetic results.

5.1.1. Identifying the Hydrocarbon fluid contacts

The gas-water contact (GWC) and oil-water contact (OWC) depth interval were picked from the resistivity well log data obtained from the Alberta Energy regulator Canada; the resistivity of hydrocarbon is higher than that of water (Ahmed, 1989). Some wells did not have clear oil-water contacts (e.g., Wells 04-08-48-13W5, 06-25-50-12W5, 07-33-4-12W5, and 05-06-49-12W5). Core lithological description was also used to identify the gas-water contact and oil-water contact to substantiate the chosen depth. For the gas wells, white saddle dolomite was formed at the top of the water leg in the reservoir alongside some yellowish elemental sulphur (e.g., in wells on the bank edge reef; Machel and Cole 1995). I also obtained pressure data using the Repeat formation tester (RFT). The pressure gradient per depth in the well was interpreted and used to identify hydrocarbon contacts. The pressure gradient in the well from top depth is homogenous until a new phase is reached, and the pressure gradient changes and the depth interval where this deviation is seen is identified to be a hydrocarbon fluid contact. The GWC and OWC are identified by the neutron and density logs. The point where the neutron and density log crosses each other is used to identify the gas transition zone, the density of the gas is low and the resistivity on the order hand increases, because hydrocarbon is less conductive than water. The point they cross each other is the transition zone. (Figure 5)

5.2 Sampling and Methodology

5.2.1 Sampling

I investigated a total of 115 samples (from 12 wells in the Nisku formation) sampled from the Core Research Centre in Calgary and the University of Alberta Core store facility. These samples were taken from the GWC and OWC identified in Figure 5.1. Low-temperature measurement was carried out at the Institute for Rock Magnetism in Minneapolis and Imperial College. I used a suite of low-temperature, room temperature, and high-temperature measurements to effectively characterize the magnetic mineralogy of the samples, as no single measurement identifies the magnetic signature. First, a Princeton Measurements Vibrating Sample Magnetometer (VSM) was used to measure hysteresis loops and FORC (First-order reverse Curve) measurements at room temperature. This helped to determine the magnetic mineralogy, grain size and domain state of the grains. High-temperature measurements were carried out with the Agico Kappabridge to measure magnetic susceptibility as a function of temperature (30°C-

700°C) in the presence of argon because of its inert nature and to prevent oxidation from taking place. The cooling temperature obtained alongside the heating and cooling curve was used to identify the magnetic mineral present in the samples. A Quantum Design Magnetic Property Measurement System (MPMS) was used to carry out low-temperature measurements (down to 10 K) for the identification of magnetic minerals. Low-temperature crystallographic transition in this experiment was used to identify the magnetic minerals present. It was important to carry out this array of magnetic measurements at low temperatures as previous work (Emmerton 2012; Abubakar 2016; Badejo et al., 2019) has shown that low-temperature magnetic measurements are required to fully characterize the magnetic mineralogy, as many (>80%) of the magnetic minerals are nanoparticles < 30 nm in size, that are either superparamagnetic or “magnetically invisible” at room temperature. Mössbauer spectroscopy was used to characterize the magnetic mineralogy in samples. Low-temperature measurement was also carried out on one sample with the VSM. Scanning Electron Microscopy (SEM) imaging of four test samples was carried out (Figure 5.16) with accompanying compositional analysis carried out using Energy Dispersive X-Ray (Spectroscopy) EDX to optically determine the morphology and grain sizes of oxides of iron and sulphur present in the samples. I picked these samples, from the depth intervals where I found spikes in form of the increased magnetic anomaly of the room temperature results.

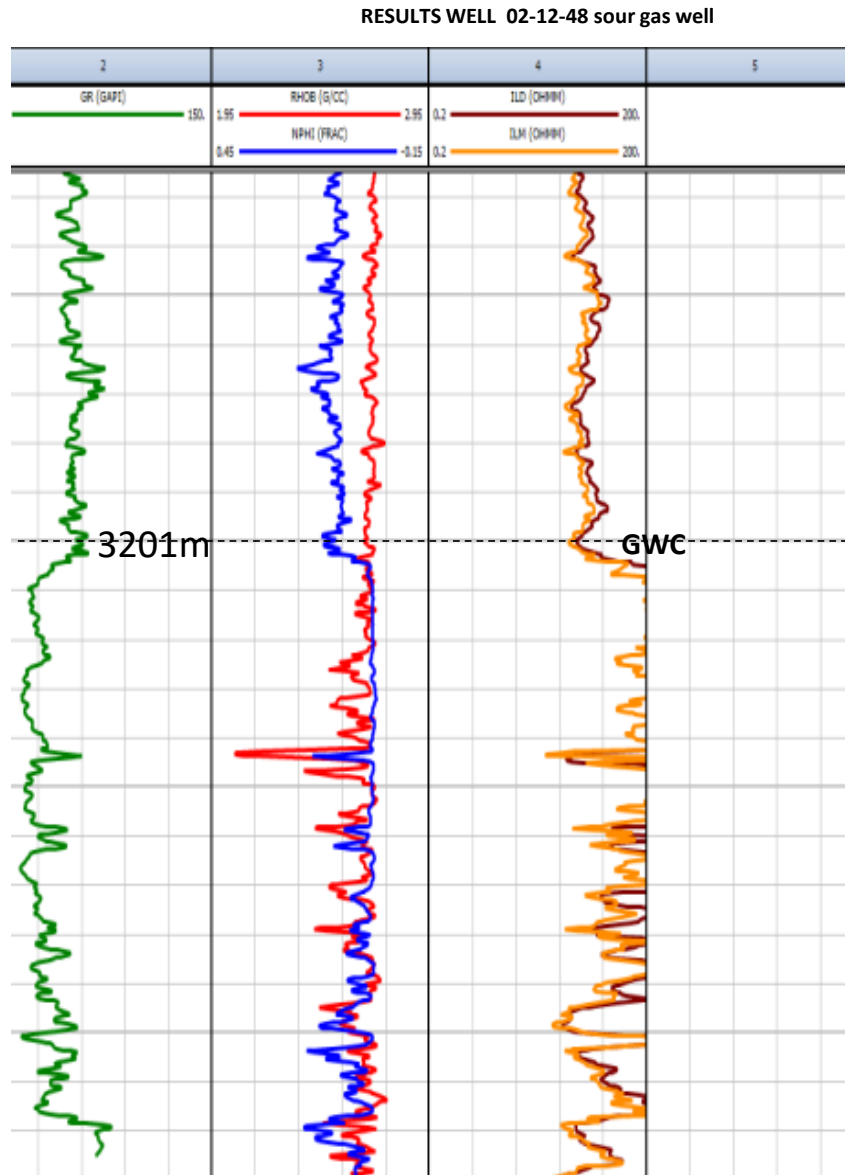


Figure 5.1: Example of composite logs of the Nisku sour gas (Well 02-12-48) used to identify the presence or absence of hydrocarbon fluid contacts. The cross over in RHOB (density) and NPHI (neutron) logs indicates the gas-water contact as hydrocarbon is less dense than water and it also indicates a change in lithology (consistent with the GR log). The Gamma Ray (GR) log helps to interpret the lithology of the formation, sandstone and carbonates have low GR values. The increase in ILD and ILM (resistivity log) signifies the presence of hydrocarbon, as hydrocarbon is less conductive than water.

5.2.2.1 Magnetic Hysteresis measurements

Room-temperature measurements on a VSM were carried out at Imperial College London and the Institute for Rock Magnetism, Minneapolis, USA. The saturation magnetization (M_s), remanent saturation magnetization (M_{rs}), coercivity (H_c), and high field slope (H_{fs}) were estimated from the measured hysteresis loops.

First Order reverse curve (FORC) diagrams are used to identify the domain-state distributions within a sample (Roberts et al., 2000; Roberts et al., 2014). A FORC diagram is calculated from a class of partial-hysteresis curves (Roberts et al., 2000). The x-axis represents the coercivity distribution while the y-axis describes the magnetic-interaction

distribution within the sample (Roberts et al., 2000). The ‘irregular’ measurement protocol by Zhao et al. (2015) was used for all the measured FORCs, because of its ability to identify magnetostatic interactions that regular FORCS are not able to capture.

5.2.2.2 Low-temperature measurements

Low-temperature remanence measurements as a function of temperature were performed with the Magnetic property measurement system (MPMS) at the University of Minnesota’s Institute for Rock Magnetism in Minneapolis. as follows: 1) cooling from 300 K to 10 K in the presence of a 2.5 T field (FC) and subsequent measuring of the remanence on warming back to 300 K; 2) after cooling to 10 K, in absence of magnetic field (ZFC), a 2.5 T field SIRM was applied and the remanence was measured on warming to 300 K. This FC and ZFC sequence helps to identify the presence of siderite (Jacobs, 1963; Frederichs et al., 2003) and nanometric particles (< 30 nm). 3) a room temperature saturation isothermal magnetization (RT SIRM) was imparted with a 2.5 T field and the remanence was then measured upon cooling to 10 K (RT SIRM cooling) and on warming back to 300 K (RT SIRM warming). These measurements help to identify the magnetic minerals present in the samples based on mineral-specific crystallographic transitions, e.g., the Verwey transition in magnetite at 125 K (Verwey, 1939), the Morin transition in hematite at 263 K (Morin, 1950), the Besnus transition in monoclinic pyrrhotite at 30-34 K (Bensus and Meyer, 1964; Dekkers et al., 1989) and to identify nanometric particles (< 30 nm) that are magnetically invisible at room-temperature due to high thermal energy, i.e., particles that are said to be superparamagnetic at room temperature and are effectively “magnetically transparent”.

5.2.2.3 High-temperature Measurements

High-Temperature susceptibility measurements were also carried out with the Agico Kappa bridge at the Institute for Rock Magnetism Minneapolis and Imperial College to measure susceptibility as a function of temperature (30-700°C). These measurements were conducted in the presence of Argon because of its inert nature and to prevent oxidation from taking place. Mineralogy of the samples is identified based on their Curie temperature and thermomagnetic behaviour (Dunlop and Özdemir, 1997). The Curie Temperature (T_c) for magnetite is 580°C, that for hematite is 675°C, that for greigite is 330°C, and that for monoclinic pyrrhotite is 320°C (Dunlop and Özdemir, 1997).

5.2.2.4 Scanning Electron Microscopy (SEM)

To aid magnetic characterization, which can be non-unique, I undertook some SEM imaging. The purpose was to look at iron oxide and sulphide minerals present in the samples to validate the magnetic results. The morphology and grain sizes of oxide and sulphide magnetic minerals can be seen as well, together with the EDX analysis showing composition. As the abundance of magnetic minerals was much less than 1%, magnetic

extraction was carried out to increase the magnetic mineral abundance for imaging. To achieve this, samples were ground to an even grain size, and passed through a Frantz electromagnet magnetic separator four times to reduce the abundance of non-magnetic materials following the protocol developed by Chang et al. (2012), as the initial SEM carried out without magnetic extraction did not yield good microscopic results. Samples were ground and coated in gold for imaging energy dispersive X-ray (EDX) analysis on the Zeiss LEO Gemini 1525 scanning electron microscope (SEM) at the Dept. of Materials, Imperial College London. The EDX analysis had a spot size of about 1 μm . The optical tests help to determine the morphology and grain sizes of oxides of iron and sulphur present in the samples.

5.3. Room temperature magnetic results

5.3.1 Magnetic Hysteresis, Coercivity and High-field Susceptibility (Hfs)

Mass-normalized room-temperature hysteresis loops, e.g. in Figure 5.2, samples from depth interval 3201m of Well 02-12-48 were measured together with measurements of coercivity and high field susceptibilities. The samples exhibited very weak magnetic behaviours, and most of the loops were not closed. Signal to noise ratio (SNR) was low with strong paramagnetic behaviour. For simple classification of samples into a box-like single domain (SD), pseudo-single domain (PSD), or multidomain (MD) region with arbitrary boundaries, a Day plot is created showing a graphical M_{rs}/M_s versus H_{cr}/H_c plot (Dunlop, 2002).

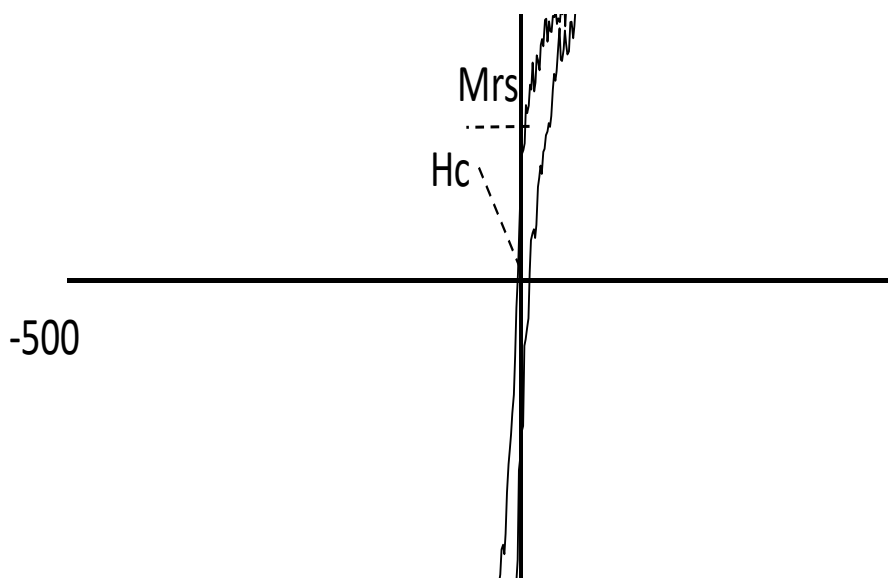


Figure 5.2: Representative hysteresis loop showing a strong paramagnetic behaviour within the sample 3201 from well 02-12-48

Table 5.1 how the results of the saturation magnetization, coercivities, high field slope pool location, and the percentage concentration of H_2S for all the wells examined in this study. Saturation magnetization, remanence magnetization, and coercivity were obtained for each well. The sour gas pools had the highest saturation magnetizations (M_s), with the

dry gas pools the lowest (Table 5.2). The hydrocarbon generated from the source has the potential to transport tiny nanoparticle magnetic minerals through the pore spaces of the rocks (Abubakar et al., 2015) and deposit them in the reservoir, hence the reason for the increased magnetization in the sour gas pool.

Table 5.1: Measured values of Ms, Mrs, Hc (mT), High field slope (hfs) in wells in the Nisku study area. The high field slope helps to differentiate between paramagnetic and diamagnetic components, with positive high field slope (hfs) indicating the presence of suspected paramagnetic minerals (pyrite or siderite), which corresponds to increased saturation magnetization. Hydrocarbon-bearing wells are roughly arranged from east to west. Note: Well 07-04-49-25W5 is a dry well

Well name	Pool type	Sample	Hc (mT)	Mrs (Am ² /kg)	Ms (Am ² /kg)	high-field slope (Hfs)	Magnetic Property (Hfs)	suspected Mineralogy (Hfs)
Well 05-06-49-12W5	sweet pool	10121	3.5	4.74E-08	7.53E-07	-2.52E-12	diamagnetic	calcium carbonate
Well 05-06-49-12W5	sweet pool	10121R	9.5	9.57E-08	7.76E-07	-2.55E-12	diamagnetic	calcium carbonate
Well 05-06-49-12W5	sweet pool	10021	8.4	9.31E-08	7.71E-07	-2.66E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	10062	10.1	8.42E-07	6.22E-06	-6.33E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	10066	0.4	1.21E-06	7.18E-06	-2.38E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	10066B	7.6	7.74E-07	5.12E-06	-2.42E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	10066RB	7.6	7.33E-07	4.77E-06	-2.03E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	10113	17.5	3.56E-08	8.00E-07	-6.68E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	10122	11.5	2.19E-08	2.52E-07	-1.61E-12	diamagnetic	calcium carbonate
Well 07-33-48-12W5	sweet pool	101351	5.1	2.60E-07	1.99E-06	1.02E-12	paramagnetic	pyrite or siderite
Well 07-33-48-12W5	sweet pool	10157	10.1	1.44E-07	8.03E-07	1.75E-11	paramagnetic	pyrite or siderite
Well 07-33-48-12W5	sweet pool	10169	9.0	8.90E-08	3.71E-07	-4.06E-12	diamagnetic	calcium carbonate
Well 07-04-49-25W5	dry well	10092	2.1	8.37E-08	1.65E-06	6.76E-11	paramagnetic	pyrite or siderite
Well 07-04-49-25W5	dry well	10180	7.6	1.90E-07	2.84E-06	1.12E-10	paramagnetic	pyrite or siderite
Well 07-04-49-25W5	dry well	10240	10.1	1.58E-07	1.98E-06	2.30E-10	paramagnetic	pyrite or siderite
Well A2-19-12W5	sour gas	3150	10.0	8.22E-07	8.18E-06	-3.34E-14	diamagnetic	calcium carbonate
Well A2-19-12W5	sour gas	3150R	12.6	2.94E-07	1.26E-06	-5.82E-12	diamagnetic	calcium carbonate
Well A2-19-12W5	sour gas	3152	10.1	2.62E-07	1.16E-06	-4.04E-12	diamagnetic	calcium carbonate
Well A2-19-12W5	sour gas	3153R	15.1	2.91E-07	1.15E-06	-1.78E-11	diamagnetic	calcium carbonate
Well A2-19-12W5	sour gas	3159	7.6	1.18E-06	9.50E-06	-5.43E-11	diamagnetic	calcium carbonate
Well A2-19-12W5	sour gas	3160	22.6	8.41E-07	2.13E-06	4.50E-12	paramagnetic	pyrite or siderite
Well A2-19-12W5	sour gas	3163	12.6	7.29E-07	8.15E-06	7.39E-14	paramagnetic	pyrite or siderite
Well A2-19-12W5	sour gas	3163R	20.1	6.69E-07	1.93E-06	1.90E-11	paramagnetic	pyrite or siderite
Well A2-19-12W5	sour gas	3177	10.0	5.67E-07	2.55E-06	-7.85E-12	diamagnetic	calcium carbonate
Well A2-19-12W5	sour gas	3177R	5.1	9.54E-08	1.59E-06	6.65E-11	paramagnetic	pyrite or siderite
Well A2-19-12W5	sour gas	3177RR	4.8	1.89E-07	3.10E-06	1.51E-10	paramagnetic	pyrite or siderite
Well 02-12-48	sour gas	3180	5.1	2.03E-07	1.82E-06	-8.74E-12	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3192	7.6	3.10E-07	1.47E-06	-1.38E-11	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3201	7.6	9.34E-07	1.26E-05	-1.6E-11	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3201R	7.6	9.24E-07	1.14E-05	-1.38E-11	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3219	5.1	4.81E-06	5.72E-05	-2.22E-11	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3225	4.1	5.15E-07	2.36E-06	-9.32E-12	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3228	2.0	2.39E-07	1.95E-06	-2.02E-11	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3228R	7.6	3.48E-07	1.60E-06	-3.26E-11	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3246	18.0	5.01E-07	3.08E-06	-1.30E-12	diamagnetic	calcium carbonate
Well 02-12-48	sour gas	3255	5.0	1.59E-07	3.29E-07	-1.11E-11	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3334	12.0	2.36E-07	9.50E-07	-2.71E-11	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3353	10.0	6.04E-07	1.48E-06	-4.75E-12	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3353R	15.1	2.91E-07	1.15E-06	-1.78E-11	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3365	10.0	7.92E-08	1.60E-07	-8.01E-12	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3372	27.6	5.56E-07	3.99E-06	-1.08E-11	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3372R	2.6	-5.95E-08	1.27E-06	-4.88E-12	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3372RR	12.6	5.22E-07	1.72E-06	-2.04E-11	diamagnetic	calcium carbonate
Well 04-08-48-13W5	sweet pool	3380	10.1	7.96E-08	5.24E-07	2.19E-14	diamagnetic	pyrite or siderite
Well 04-08-48-13W5	sweet pool	3384	15.1	1.75E-07	1.15E-06	2.44E-11	paramagnetic	pyrite or siderite
Well 04-08-48-13W5	sweet pool	3393	17.6	3.67E-07	1.09E-06	-1.6E-12	diamagnetic	calcium carbonate
Well 06-25-50-12W5	sweet pool	8233	15.4	5.98E-08	4.53E-07	-8.77E-14	diamagnetic	calcium carbonate
Well 06-25-50-12W5	sweet pool	8233R	20.9	1.44E-07	4.60E-07	3.04E-13	paramagnetic	pyrite or siderite
Well 06-25-50-12W5	sweet pool	8233RR	16.5	1.16E-07	4.75E-07	3.13E-13	paramagnetic	pyrite or siderite
Well 06-25-50-12W5	sweet pool	8233RRR	10.6	6.96E-08	5.23E-07	2.39E-12	paramagnetic	pyrite or siderite
Well 06-25-50-12W5	sweet pool	8233RRRR	13.6	6.64E-08	4.82E-07	3.23E-13	paramagnetic	pyrite or siderite
Well 06-25-50-12W5	sweet pool	8293	17.3	3.32E-08	3.78E-07	-1.04E-11	diamagnetic	calcium carbonate
Well 06-25-50-12W5	sweet pool	8293R	15.2	5.20E-08	3.84E-07	-1.04E-11	diamagnetic	calcium carbonate
Well 06-25-50-12W5	sweet pool	8409	10.0	-4.29E-08	1.79E-07	-1.15E-11	diamagnetic	calcium carbonate

Given the data for the measured saturation magnetization (Ms), remanence saturation magnetization (Mrs), coercivities (Hc) and high field slope (Hfs), large positive high-field slope values signify the presence of paramagnetic minerals (pyrite or siderite), negative slope indicates the magnetic signal is low in ferromagnetic (in the broad sense) and paramagnetic material, and the diamagnetic signal is dominating in the wells studied. The magnetic property and the suspected mineralogy column are both functions of the high field slope readings (Table 5.1). Two of these wells (Well 02-12-48 and A2-19-12W5) are on the same migration pathway. They are hydrologically contagious (Machel and Burton 2003). The measured Ms, Mrs and Hc values cannot be used to distinguish the sweet or sour oil wells or gas well as they appear to be similar across the board. Some of the

samples in the wells had high M_s values, e.g., M_s value $5.72 \times 10^{-5} \text{ Am}^2/\text{kg}$ corresponds to $2.22 \times 10^{-11} \text{ Am}^2/\text{kg}$ high field slope, while some samples in the same well had very low M_s values. The high M_s values correspond to negative high field slope while the low M_s values correspond to positive high field slope which indicates the presence of ferromagnetic or paramagnetic minerals. All materials are diamagnetic, but the increased presence and proportion of paramagnetic or ferromagnetic magnetic minerals (pyrite or siderite) is responsible for increased M_s values while the suspected absence of paramagnetic minerals components is responsible for decreased M_s value, the absence of ferromagnetic or paramagnetic component is what makes diamagnetism dominant. The proportion of these paramagnetic and diamagnetic components cannot be estimated but can be qualitatively analysed. Peaks in M_s , M_{rs} , and susceptibility were noticed at hydrocarbon fluid contacts (e.g. for wells 02-12-48 and A2-19-12W5). There is no relationship observed for M_s values between wells on the same hydrocarbon migration pathway (e.g. Wells 02-12 -48 and A2-19-12W5). The migration trend is inferred to be lateral, except for sweet pools with a very low sulphur concentration on the isolated reefs in between the bank shelf margin and the shale basin in the NE up-dip direction, in which all samples have very high coercivity values (H_c) (e.g. Wells 04-08-48-13W5, 06-25-50-12W5, 07-33-4-12W5, 05-06-49-12W5). These high coercivities could be due to the increasing presence of iron sulphides (Horng, 2018), while the low coercivities in the sour gas pools could be due to magnetic phases of authigenic origin (Costanzo-Alvarez et al., 2000). The saturation magnetization is generally higher in wells in the shale basin up-dip (Wells 04-08-48-13W5, 06-25-50-12W5, 07-33-4-12W5, 06-25-50-12W5) compared to wells charged laterally (Wells 02-12 -48 and A2-19-12W5) on the bank edge reef. This is not unexpected as magnetic mineral formation due to the presence of hydrocarbon has been shown to produce either a positive or negative magnetic anomaly, which can lead to noticeable increases or decreases in relative susceptibility along with the profile (Burton et al., 1993; Machel, 1995). For example, a positive magnetic anomaly would be observed if magnetite was precipitated in a layer with pyrite and/or hematite present before the

invasion of oil, while a negative anomaly would be observed if the invasion of oil led to the precipitation of siderite (Table 5.1).

Table 5.2: Average room- temperature magnetic measurement result for all the wells examined in this study, showing the average saturation magnetization, coercivity, and the percentage of H₂S concentration in the pools. The H₂S % concentration was derived from Machel and burton (1995)

Nisku room temperature magnetic results					
Well Name	Magnetization Am ² /kg	Hc(mT)	Pool	Location	H ₂ S (%)
02-12-48-12W5	3.05E-06	7	sour gas	Carbonate shelf(Band edge reef)	20%
07-33-48-12W5	2.04E-06	9	oil pool	shale basin	0%
A2-19-48-13W5	1.45E-06	18	sour gas	Carbonate shelf(Band edge reef)	20%
04-08-48-13W5	1.02E-06	13	sweet gas pool	shale basin	0.70%
05-06-49-12W5	7.17E-07	7	oil pool	shale basin	0%
06-25-50-12W5	6.42E-07	15	oil pool	shale basin	0%
07-04-49-25W5	3.55E-07	7	Dry well	shale basin	0%

In Table 5.2, wells are ranked according to their average magnetic enhancement, with the sour gas pool having the higher magnetic intensity and dry wells having the lower magnetic intensity. The sweet oil and gas pools had intermediate magnetic enhancement when compared to the sour-gas and dry wells.

The average saturation magnetization of the sour gas pool for well 02-12-48 is eight times stronger than the average saturation magnetization in the dry well 07-04-49, and the dry well has higher coercivity than the sour gas well (Table 5.2)

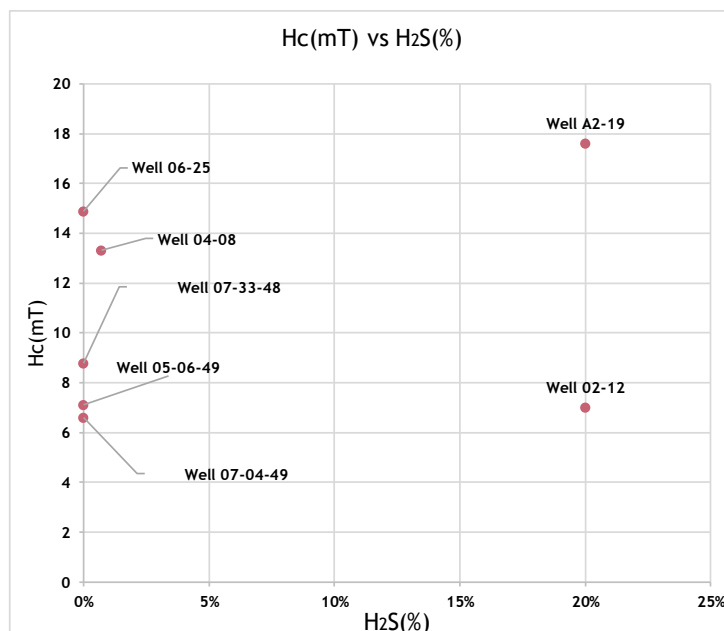


Figure 5.3: Graph of Coercivity (mT) vs H₂S (%) concentration. H₂S concentration (%) was derived from Machel and Burton (1995).

Given the data for measured coercivity in comparison with the concentration of H_2S in all the wells. A key observation is that wells rich in sulphur concentration possess low coercivity (e.g. well 02-12-48-12W5 in Figure 5.3), confirming the possibility of magnetically soft minerals (e.g. greigite and magnetite) being present. Higher coercivities (e.g. wells 04-08-48-13W5, 06-25-50-12W5) signify the presence of magnetically hard minerals (e.g. hematite) (Janna et al., 2015). The lithology has a distinct spatial distribution. Saddle dolomite occurs only in the water-bearing part of the pool, which suggests it formed after the gas-water contact. This implies that saddle dolomite can form an aqueous solution. Elemental sulphur occurs in the gas water transition zone intergrown with saddle dolomite, suggesting it formed after the gas water transition zone was developed (Machel and Burton 1995; Burton et al., 2003).

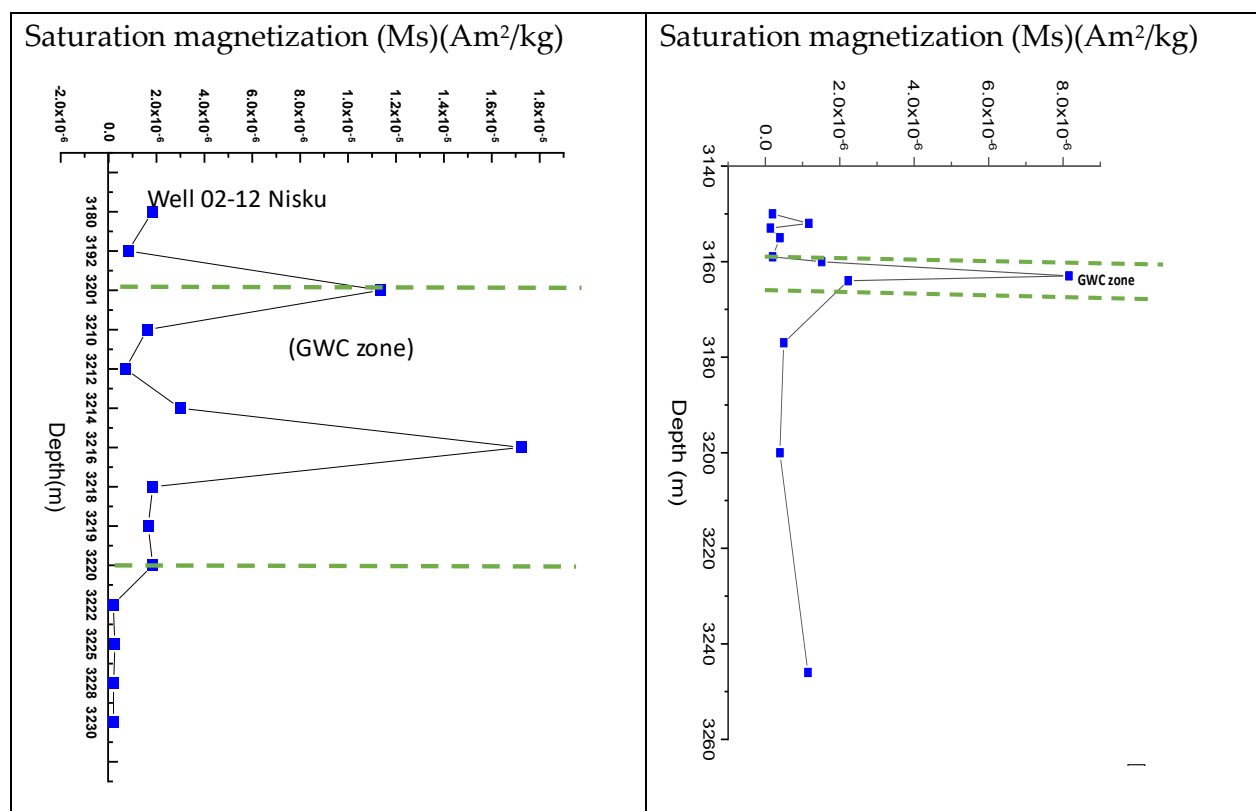


Figure 5.4: Saturation magnetization (Ms) against depth (m) with the gas-water contact (GWC) highlighted for wells in the carbonate shelf margin bank edge reef: a) 02-12-48-12W5 and b) A2-19-48-13W5. The gas-water contact zone is marked by a distinct peak highest within the zone, this spike is speculated to be the paleo-contact.

It is clear from that for the gas pool, magnetism is greatly enhanced at the gas-water contact (GWC), for example in Wells 02-12-48-12W5 and A2-19-48-13W5 located at the bank edge reef (Fig. 5.4). The absolute values for wells 02-12-48-12W5 are to the order of magnitude of magnetic anomalies $10^{-5} Am^2/kg$ in comparison to wells A2-19-48-13W5 which is to the order of $10^{-6} Am^2/kg$. Well, 02-12 is more strongly magnetic than A2-19-48-13W5 which are both located on the bank edge reef, on the other hand, magnetic enhancement is not seen at the OWC for the wells in the isolated reefs located in the shale

basin area Figure 5.5 and Figure 5.6. This appears to be a possible pitfall in the observation of magnetic enhancement at the hydrocarbon contact (Badejo et al., 2020) and poses a threat to the universality of this study. Also, some spikes in magnetization are not associated with the hydrocarbon contact in these wells, probably due to the combination of paramagnetic and diamagnetic behaviour of magnetic minerals present in the samples. The dominance of paramagnetic behaviour in any measured sample results in increased saturation magnetization while the dominance of diamagnetic behaviour in samples results in decreased saturation magnetization whether it is found on the fluid contact or not.

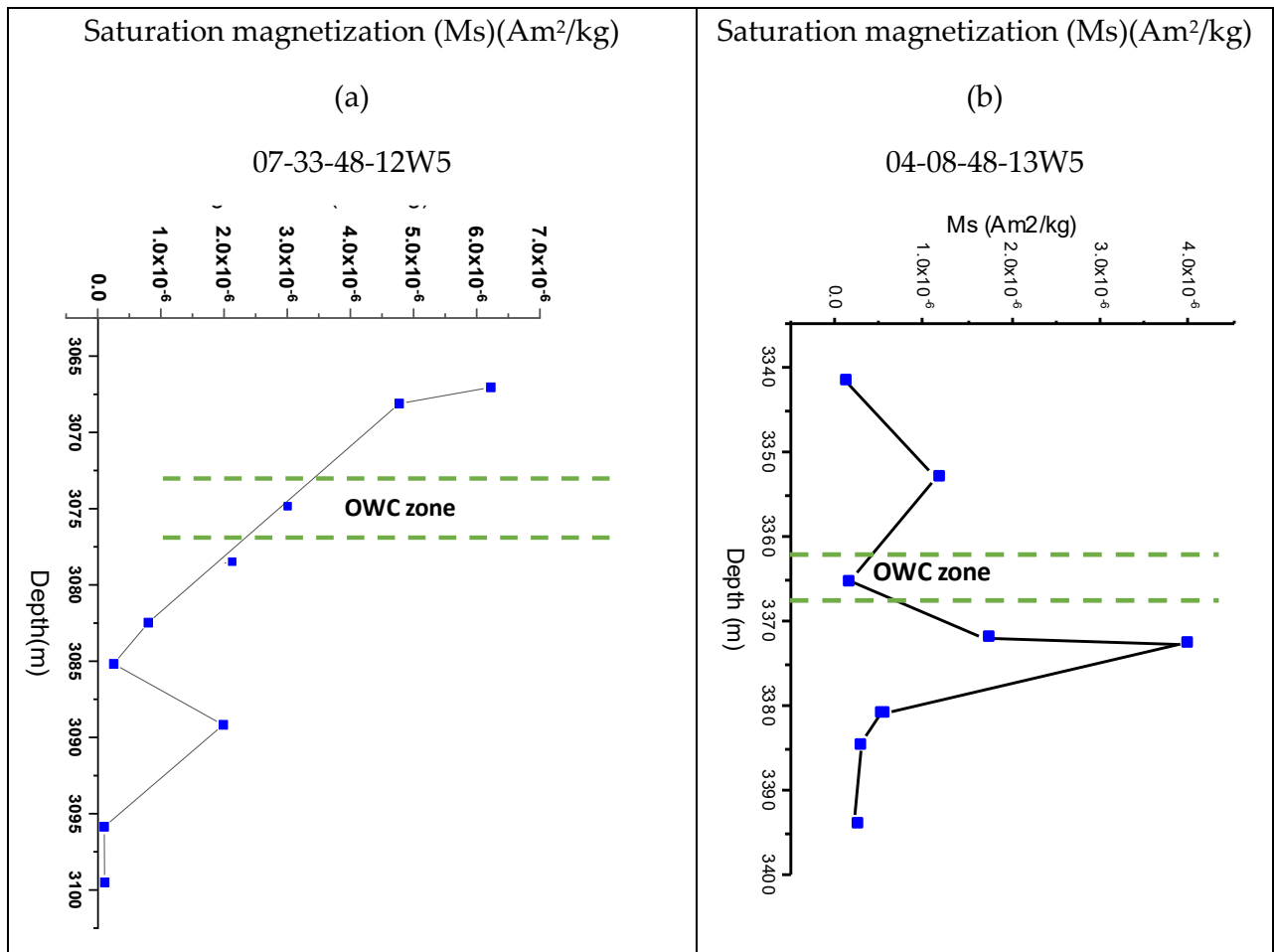


Figure 5.5: Saturation magnetization (M_s)(Am^2/kg) against depth (m) showing oil-water contact (OWC) for wells in the shale basin: a) 07-33-48-12W5, b) 04-08-48-13W5. Error margin $\pm 6m$ SD. Note, these wells are located in sweet oil pools.

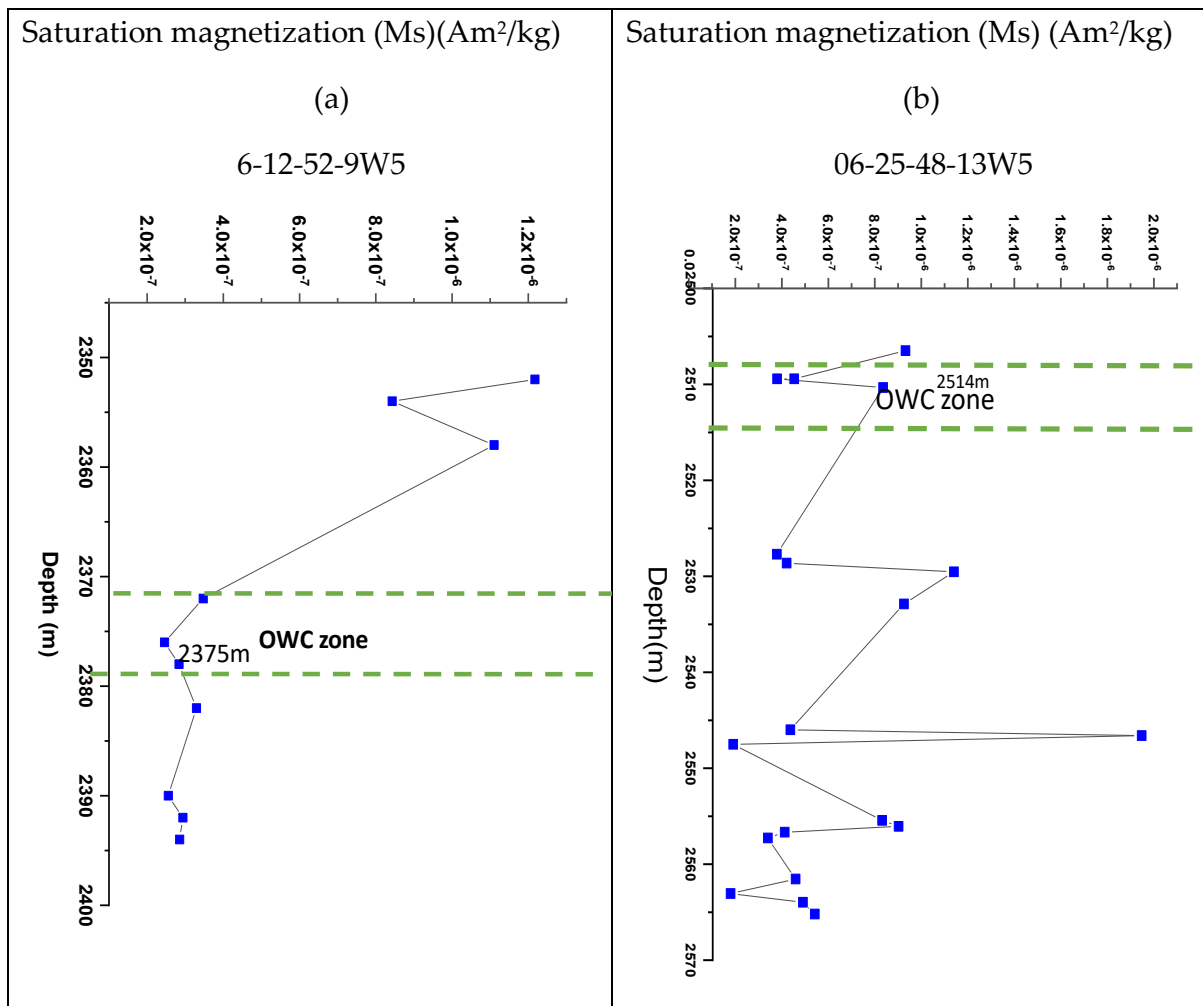


Figure 5.6: Saturation magnetization (Ms) against depth (m) showing oil-water contact (OWC) for wells in the shale basin. a) 06-12-52-9W5, b) 06-25-48-13W5. Error margin + or -6m SD.

This leaves some unanswered questions as to the reason why magnetic enhancement was not found at hydrocarbon fluid contacts, as it is on other parts of the Brazeau area. Does the geological configuration of the sedimentary basin, play a vital role in this? Could the fact that these wells are not on the bank edge reef, but on the isolated reef in the shale be a possible factor? The foreland basinal structure of Nisku formation could result in a tilted hydrocarbon contact, as the position of the sweet wells is in the up-dip direction. Also, could the fact that these wells in the up-dip direction are found on an isolated reef, and are not hydrologically contagious, be a factor? Wells on the bank edge reef which are porous and permeable, and migration is lateral. Could the depth intervals where spikes are greatly enhanced by the new hydrocarbon contact? Could fluid inclusion be needed to investigate this hypothesis?

5.3.2 First order reverse curve (FORC)

FORC diagrams were used to identify the domain-state distributions within the samples (Roberts et al., 2000; Roberts et al., 2014). It was calculated from a class of partial-hysteresis curves (Roberts et al., 2000). As a first approximation, the x-axis represents the coercivity distribution while the y-axis describes the magnetic-interaction distribution within the sample (Roberts et al., 2000). The ‘irregular’ measurement protocol by Zhao et al. (2015) was used for all the FORCs. Multiple hysteresis loops form. For simple classification of samples into a box-like single domain (SD), pseudo-single domain (PSD), and multidomain (MD) regions with arbitrary boundaries, a Day plot is created showing a graphical M_{rs}/M_s versus H_{cr}/H_c plot (Dunlop, 2002).

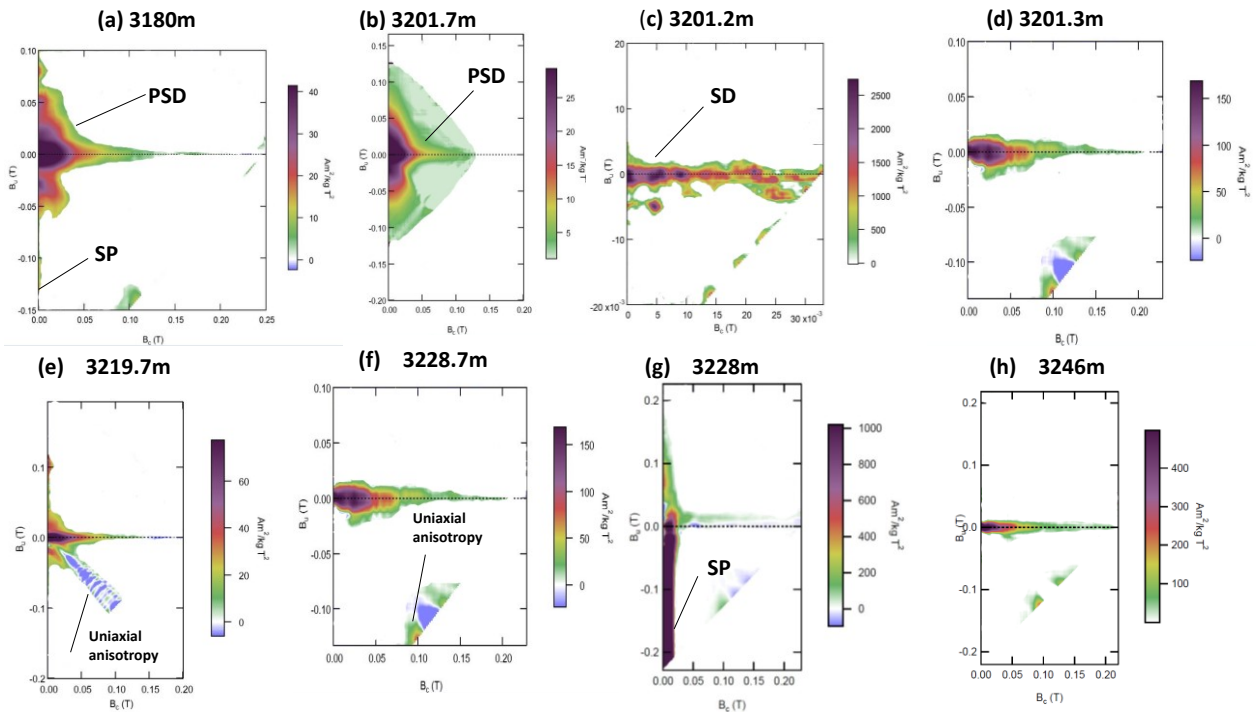


Figure 5.7: FORC diagrams for samples in well 2-12 of the Nisku sour gas pool at room temperature showing their respective magnetostatic interaction (B_u) and coercivities (B_c). a) FORC diagram suggests the presence of a mixture of PSD/MD and SP grains (3180 m); b) FORC diagram suggests the presence of PSD/MD grain with a vortex (3201.7 m, at GWC); c) FORC diagram suggests the presence of SD grains (3201.2 m); d) FORC diagram suggests the presence of SD grains with some SP grains (3201.3 m); e) FORC diagram suggests the presence of non-interacting SD grain with multiaxial anisotropy (3219.7 m); f) FORC diagram suggests the presence of SD grains with anisotropy (3228.7 m); g) FORC diagram suggests the presence of SP grains with anisotropy (3228.0 m); h) FORC diagram suggests the presence of SD grain (3246 m). VARIFORC parameters (Egli, 2013) for FORC smoothing are $sc,0 = 1.2$, $sc,1 = 3$, $sb,0 = 3$, $sb,1 = 5$, and $\lambda c = 1$ $\lambda b = 1$. SD grains have grain size $0.03\text{--}0.08\mu\text{m}$, SP grains have grain size $<0.03\mu\text{m}$

FORC distributions (e.g., Roberts et al., 2000; Muxworthy and Roberts, 2007) were also measured and representative plots are shown in Figure 5.7. Figure 5.7a-b depicts interacting with single domain grains with vortex, and Figure 5.7b shows the presence of multi-domain grains. Figure 5.7c-d shows the presence of interacting single domain grains in a suspected greigite sample, and Figure 5.7e shows the presence of a single domain grain with stretched peaks. Figure 5.7f shows the presence of interacting single domain

grains, in Figure 5.7g an SP grain is suspected to be present within the negative region, and Figure 5.7h shows the presence of interacting single domain grains. High coercivities in FORC diagrams depict the presence of iron oxides or sulphides (Muxworthy *et al*, 2012; Harrison *et al*, 2018).

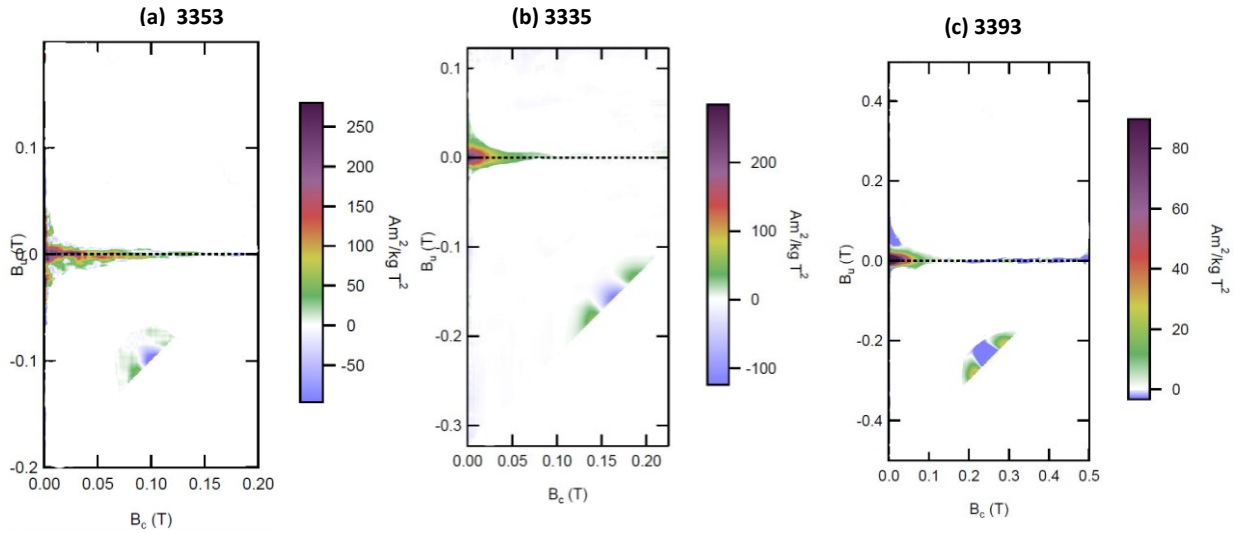


Figure 5.8: Representative FORC diagrams for well 04-08-48 in a sweet oil pool. a) FORC diagram suggests the presence of SP grains (3353 m, at OWC); b) FORC diagram suggests the presence of interacting SD grain with vortex structure or multi-axial anisotropy (3335 m); c) FORC diagram suggests the presence of SD grain (3393 m). VARIFORC parameters (Egli, 2013) for smoothing FORCs are $sc,0 = 3$, $sc,1 = 3$, $sb,0 = 4$, $sb,1 = 3$ and $\lambda c = \lambda b = 0.1$.

FORC distributions (e.g., Roberts *et al.*, 2000; Muxworthy and Roberts, 2007) and representative plots are shown for sweet pools as seen in Figure 5.8a depicts interacting single domain grains, Figure 5.8b shows the presence of interacting single- domain grains with multi-axial anisotropy, and Figure 5.8 shows the presence of single-domain grains in a suspected greigite sample, High coercivities in FORC diagrams depict the presence of iron oxides or sulphides.

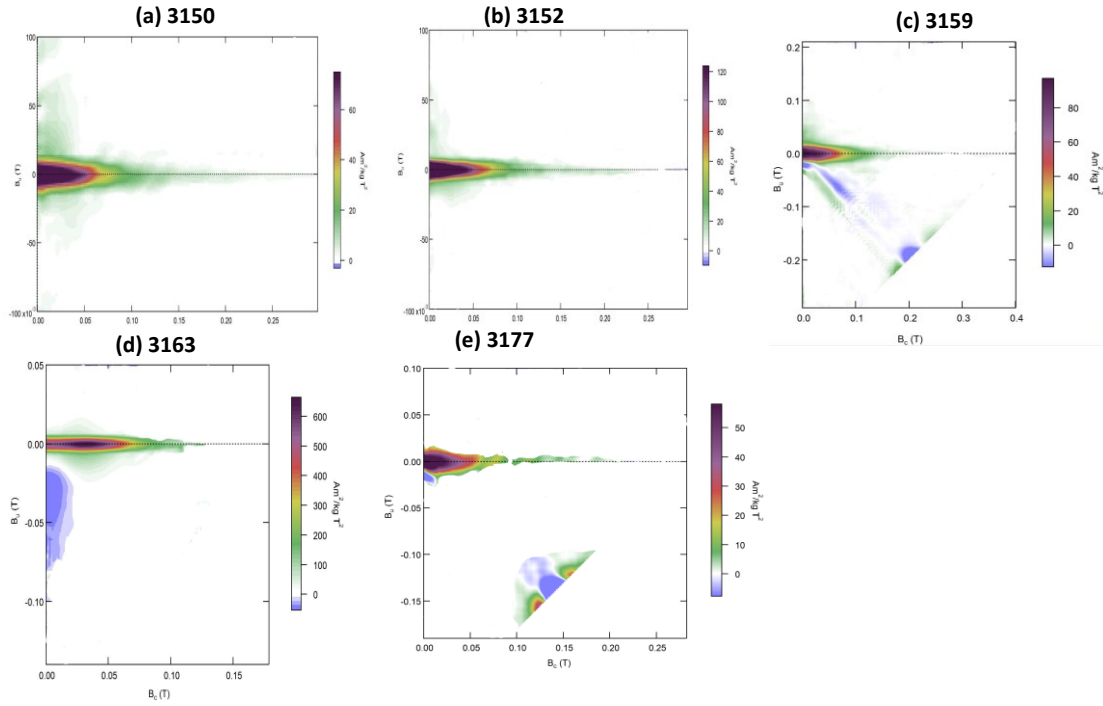


Figure 5.9: Representative FORC diagrams of samples from the gas-water contact of well A2-19 of the Nisku sour gas pool at room temperature; showing their respective magnetostatic interaction (B_u) and coercivities (B_c). a) FORC diagram suggests the presence of SD grain and SP grain with multiaxial anisotropy (3150 m); b) FORC diagram suggests the presence of a mixture of SD grain and SP grains with multiaxial anisotropy (3152 m); c) FORC diagram suggests the presence of a mixture of SD grain and SP grains with multiaxial anisotropy (3159 m); d) FORC diagram suggests the presence of a mixture of SD grain and SP grains with multiaxial anisotropy (3163 m at GWC); FORC diagram suggests the presence (3177 m). VARIFORC parameters (Egli, 2013) for FORC smoothing

Given the above FORC diagrams from well A2-19, Figure 5.9a, taken from above the GWC, depicts relaxing single domain grains not completely superparamagnetic but small enough that thermal energy is enough to reduce its coercivity, so it is starting to relax to its axis. The grain size is around 30 nm. Figure 5.9d shows data from the sample collected at the GWC, and exhibits interacting single domain grains a little away from the origin, indicative of the presence of greigite or pyrrhotite iron sulphide minerals approximately 80 nm in size. It has a negative region signifying uniaxial anisotropy.

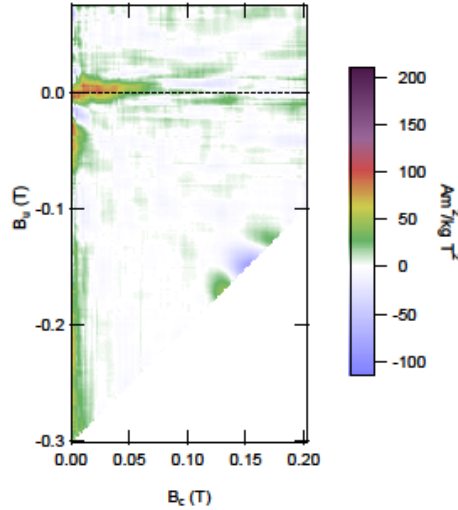


Figure 5.10: FORC diagram from dry well 07-04-49 with characteristic SP grain suspected. VARIFORC parameters (Egli, 2013) for FORC smoothing are $sc,0 = 1.2$, $sc,1 = 3$, $sb,0 = 3$, $sb,1 = 5$, and $\lambda c = 1$ $\lambda b = 1$. Note Well 07-04-49 is a dry well.

In addition to the results from the sour gas pools, samples from the sweet pools located in the shale basin were also characterized. This was very important as adequate knowledge of the magnetic behaviour of samples from the oil-water contact will aid a better understanding of the magnetic behaviour of precipitated samples in pools low in sulphur concentration (e.g. Well 04-08-48-13W5, located in the sweet gas pool of the Brazeau area in which the sulphur concentration is less than 1%; Upper et al. (2000).

5.3.3 Low -temperature magnetic measurements

From the results shown in Figure 5.11(a-b), low-temperature crystallographic transition shows the suspected presence of siderite, the presence of magnetite at Verwey transition $\sim 120\text{K}$ (Verwey, 1930) and hematite at Morin transition $\sim 263\text{K}$ (Morin, 1950), Figure 5.11(c) also displays the suspected presence of hematite at Curie temperature of $\sim 660^\circ\text{C}$. Figure 5.11 (d-e) shows magnetite at Verwey transition of $\sim 120\text{K}$, hematite at Morin transition $\sim 260\text{K}$, hump on cooling shows maghemite with a low-temperature warming curve of saturation isothermal remanence induced at 10K after both zero-field and (2.5T). These results display the characterized magnetic mineralogy for Well 02-12-48 of the Nisku sour gas pool located in the Brazeau area. This carbonate shelf margin is situated down-dip from the line a (Chapter 3), at 20% H_2S concentration level. The $\sim 120\text{k}$ Verwey transition characterizes magnetite in a sample at low temperature, $\sim 260\text{k}$ Morin transition characterizes hematite, hump on cooling signifies hematite, and Néel transition $\sim 37\text{k}$ characterizes pyrrhotite.

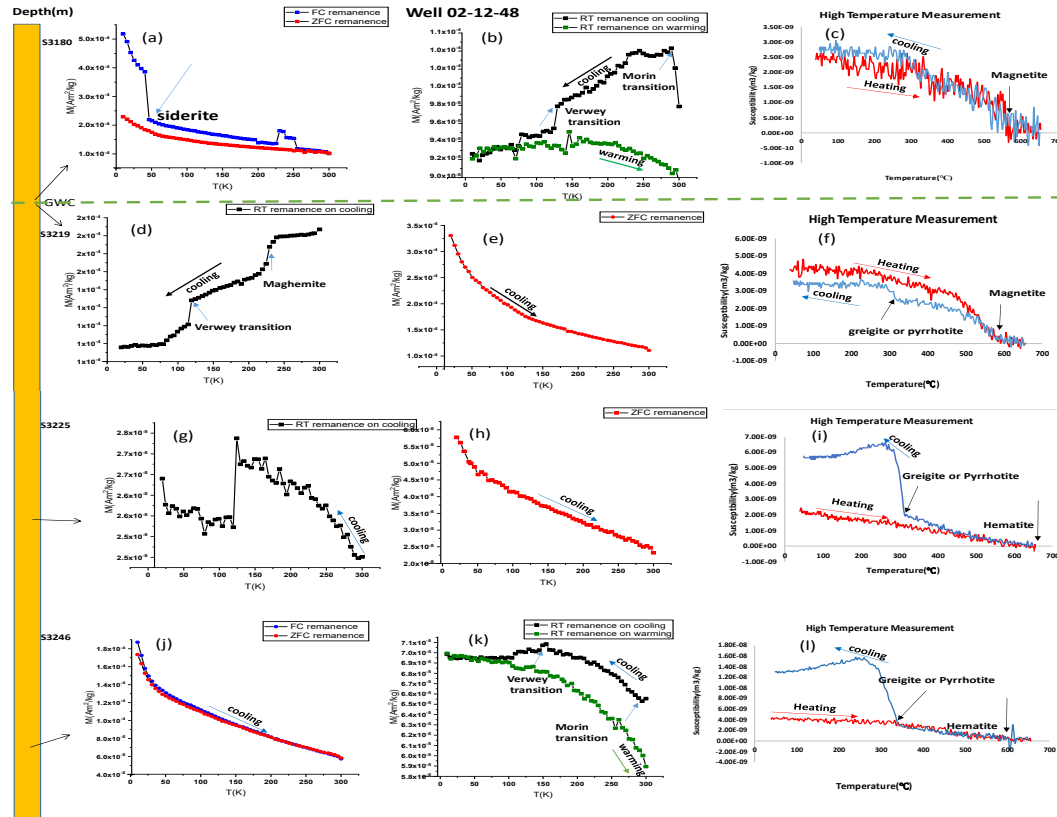


Figure 5.11: LT experiments (cycling cooling, cycling warming, FC and ZFC), HT susceptibility experiments for samples in well 02-12-48. a-c) Results for sample at 3180 m, at GWC; a) LT experiments suggest the presence of siderite; b) RT remanence on cooling suggests the presence of magnetite, hematite or goethite, c) HT experiment suggests the presence of hematite. d-f) Results for sample at 3219 m; d) LT suggests the presence of magnetite, maghemite, and hematite, e) zero-field cooling curve, f) HT experiment suggests the presence of magnetite. g-i) Results for sample at 3225 m; g) LT experiments suggest the presence of magnetite, h) zero-field cooling curve, i) HT experiment suggests the presence of hematite, greigite or pyrrhotite. j-l) Results for sample at 3246 m; j) FC ZFC remanence on cooling, k) LT experiments suggests the suspected presence of magnetite and hematite, l) HT susceptibility experiments show the suspected presence of hematite, greigite or pyrrhotite. For the HT susceptibility measurements, the samples were heated in argon.

From the results shown in Figure 5.12(a-b) Low-temperature crystallographic transition shows the suspected presence of siderite, it shows the suspected presence of magnetite at Verwey transition of $\sim 120\text{K}$ (Verwey,1930) and hematite at Morin transition $\sim 263\text{K}$ (Morin,1950). Figure 5.12(c) also shows the suspected presence of hematite at Curie temperature $\sim 660^\circ\text{C}$. Figure 5.12(d-e) shows the suspected presence of magnetite at Verwey transition $\sim 120\text{K}$, hematite at Morin transition $\sim 260\text{K}$ and hump on cooling showing the suspected presence of maghemite.

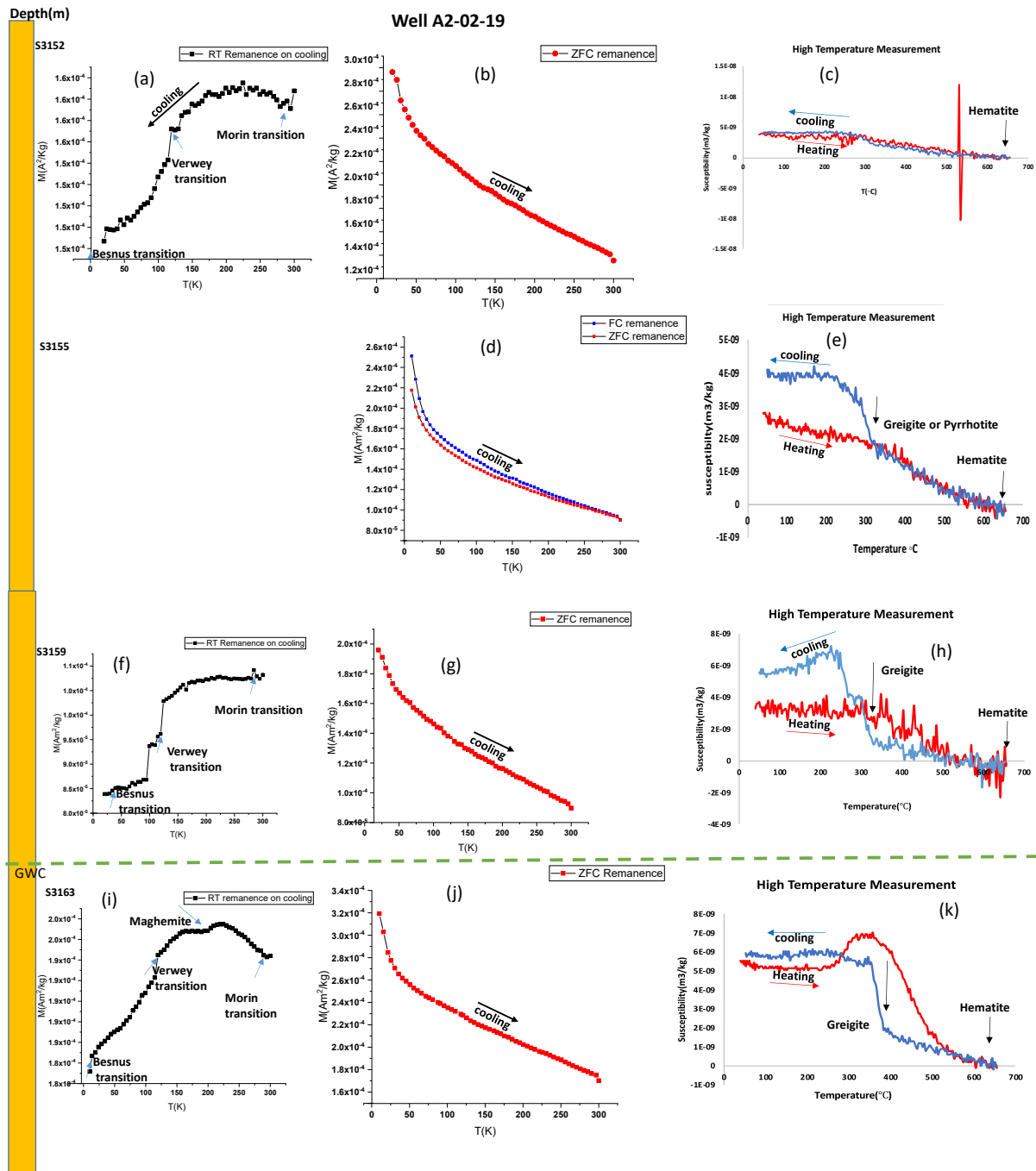


Figure 5.12: LT experiments (cycling cooling, cycling warming, FC and ZFC), HT susceptibility experiments for samples in well A2-02-19. a-c) Results for sample at 3152 m; a) LT experiments suggest the presence of pyrrhotite, magnetite, and hematite, b) Zero field cooled remanence with the suspected presence of magnetite and c) HT experiment suggests the presence of hematite. d-e) Results for sample at 3155 m; d) LT field cooled/zero-field cooling e) HT experiment suggests the presence of hematite, greigite, or pyrrhotite. f-h) Results for sample at 3159 m at GWC; f) LT experiments suggest the presence of pyrrhotite, magnetite, and hematite. g) zero-field remanence on cooling, h) HT experiment suggests the presence of hematite, greigite, or pyrrhotite. i-k) Results for sample

at 3163 m at the GWC i) LT experiments suggest the presence of pyrrhotite, magnetite, maghemite and hematite, j) zero-field remanence on cooling, k) HT experiment suggests the presence of magnetite, iron sulphide greigite, pyrrhotite or pyrite. For the HT susceptibility measurements, the samples were heated in argon.

Low and high -temperature measurements were also examined for the dry well (Figure 5.13). From the given data, low-temperature field curve (FC), zero-field curve (ZFC) parameters are needed for characterizing minerals which are magnetically invisible at room temperature. These background samples would give information on the filling history of a basin or could be used in the calibration of the petroleum systems model in both frontier and mature basins. The Nisku pool, background samples show the suspected presence of paramagnetic pyrite or siderite.

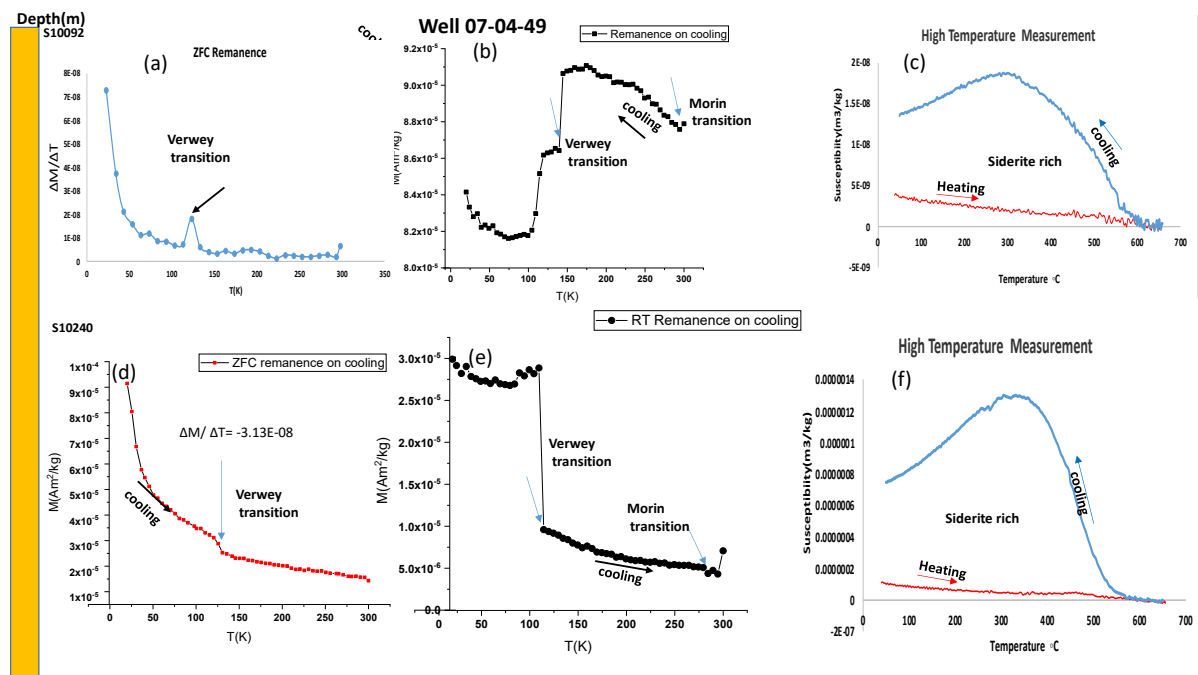


Figure 5.13: LT experiments (cycling cooling, cycling warming, FC and ZFC), HT susceptibility experiments for samples in dry well 07-04-49-25W5. a-c) Results for sample at 10092 m; a) LT experiments suggest the presence of magnetite and hematite, b) Remanence on cooling suggests the presence of magnetite and hematite, c) HT experiment suggests a siderite rich sample. d-f) Results for sample at 10240 m; d) LT experiments suggest the presence of magnetite, e) Remanence on cooling suggests the presence of magnetite and hematite, f) HT experiment suggests a siderite rich sample. For the HT susceptibility measurements, the samples were heated in argon.

From (Figure 5.13) samples S10092 and S10240 from a dry well have low and high-temperature experiments carried out on them with low-temperature crystallographic transition showing the suspected presence of magnetite with Verwey transition ~120K and Morin transition ~260K Figure 5.13 (a-b; d-e) and a siderite rich presence from the high-temperature experiments Figure 5.13 (c and f).

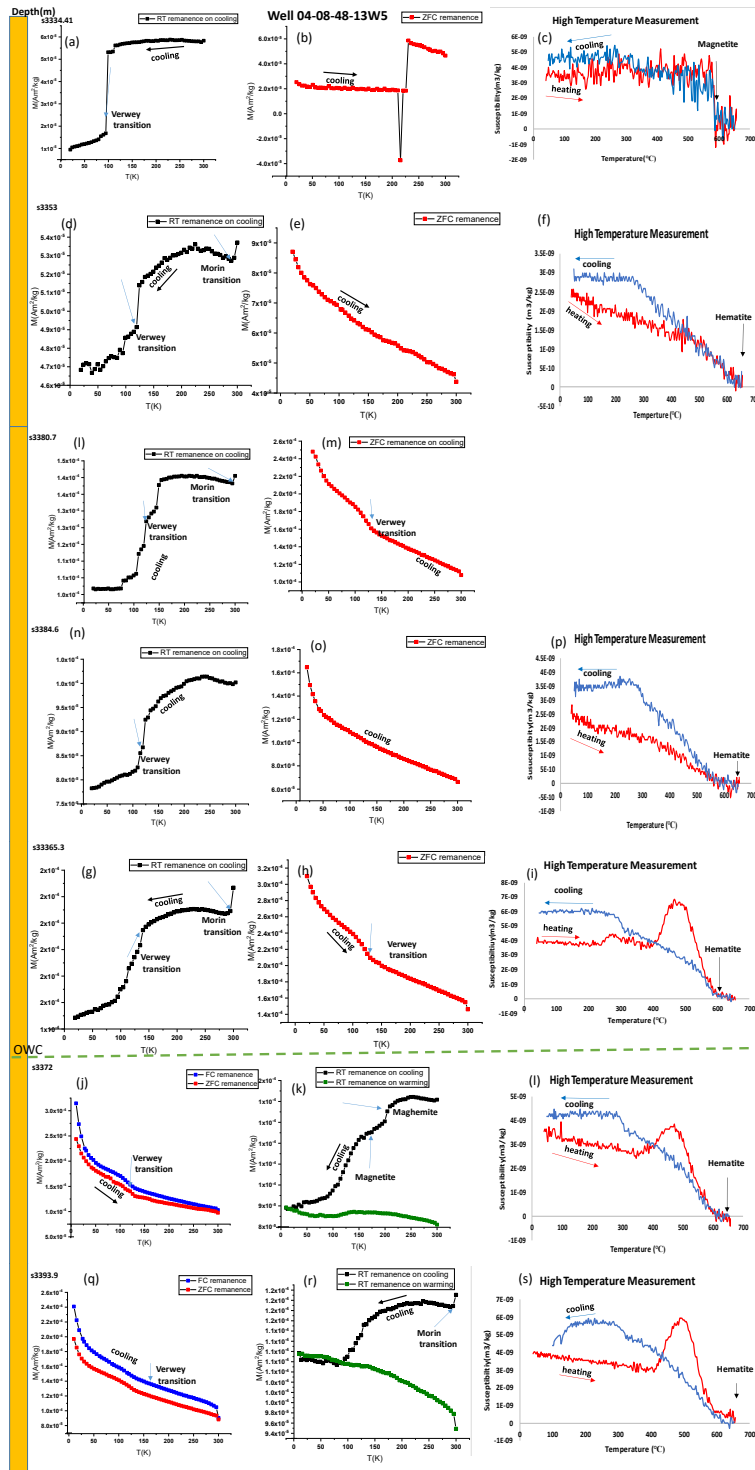


Figure 5.14: LT experiments (cycling cooling, cycling warming, FC and ZFC), HT susceptibility experiments for samples in dry well 04-08-48-13W5. a-c) Results for sample at 3334.41 m; a) LT experiments suggest the presence of magnetite, b) zero-field Remanence on cooling, c) HT experiment suggests the presence of hematite. d-f) Results for sample at 3353 m; d) LT experiments suggest the presence of pyrrhotite, magnetite and hematite, e) zero-field remanence on cooling, f) HT susceptibility experiments suggests the presence of titanohematite and iron sulphide. g-i) Results for sample at 3365.3 m, at OWC; f) LT experiments suggest the presence of magnetite and hematite, g) zero field cooling curve suggests the presence of magnetite, h) HT susceptibility experiment suggest the presence of hematite and iron sulphide. j-l) Results for sample at 3372 m; j) LT experiments suggest the presence of siderite and magnetite, k) remanence on cooling and warming curve suggests the presence of magnetite and maghemite; l) HT susceptibility experiments suggest the presence of hematite and iron sulphide. 33380.7; q) HT susceptibility experiment suggest the presence of hematite and iron sulphide. 33393.9; r) LT experiments suggest the presence of siderite and magnetite, s) remanence on cooling

From Figure 5.14 there is much evidence for the presence of magnetite through the presence of the Verwey transition and hematite through the presence of the Morin transition. Maghemite is also likely to present, as suggested by the hump on heating at ~350 °C (Figure 5.14), and again the presence of hematite is supported by the high Curie temperature ~670 °C. The shape of the high-temperature susceptibility curves also suggest the presence of greigite and pyrite, as high lighted

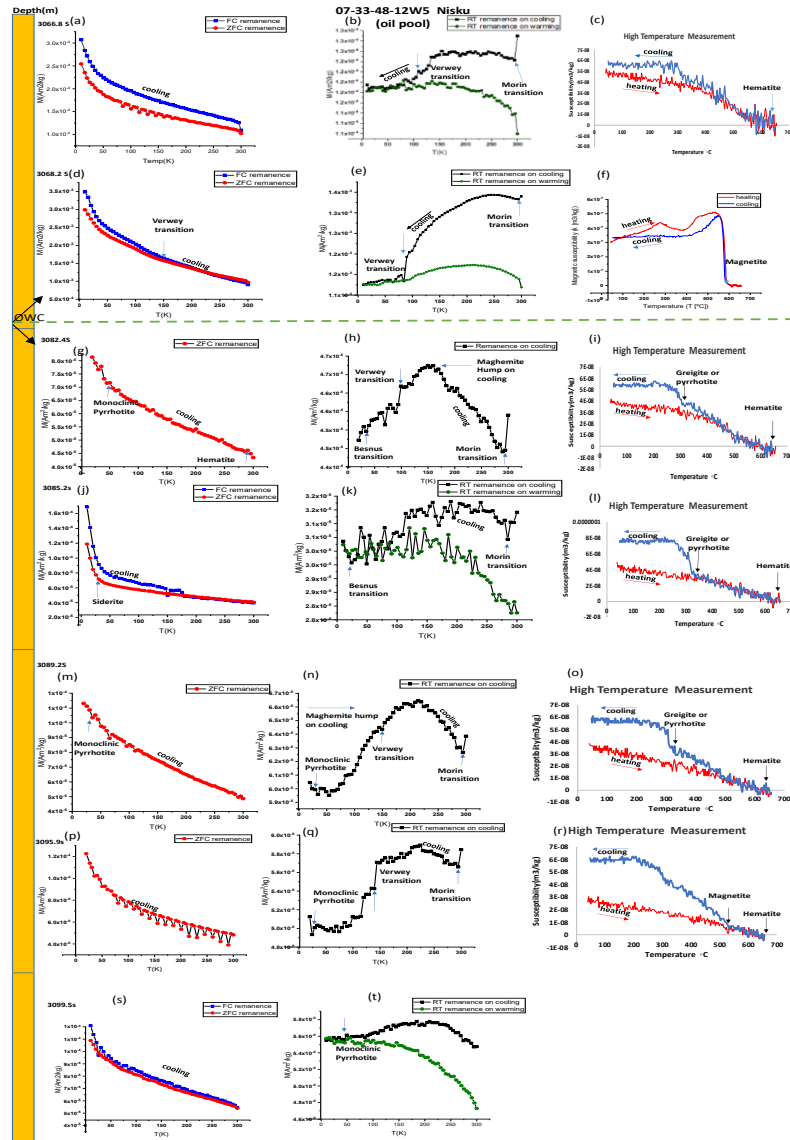


Figure 5.15: LT experiments (cycling cooling, cycling warming, FC and ZFC), HT susceptibility experiments for samples in oil well 07-33-48-12W5. a-c) Results for sample at 3066.8 m; a) LT experiments suggest the presence of magnetite and hematite, b) zero-field Remanence on cooling, c) HT experiment suggests the presence of magnetite and iron sulphide. d-f) Results for the sample at 3068.2 m, at OWC; d) LT experiments suggest the presence of magnetite e) remanence on cooling suggests the presence of magnetite and hematite, f) HT susceptibility experiments suggest the presence of magnetite and iron sulphide. g-i) Results for a sample at 3082.4 m; g) LT experiments suggest the presence of monoclinic pyrrhotite, h) remanence on cooling curve suggests the presence of magnetite, pyrrhotite, maghemite, and hematite, i) HT susceptibility experiment suggest the presence of hematite and iron sulphide greigite or pyrrhotite. j-l) Results for sample at 3085.2 m; j) LT experiments suggest the presence of siderite, k) remanence on cooling, and warming curve suggest the presence of magnetite and pyrrhotite; l) HT susceptibility experiments suggest the presence of hematite and iron sulphide greigite or pyrrhotite. m-o) Results for the sample at 3089.2 m; m) LT experiments suggest the presence of monoclinic pyrrhotite, n) remanence on cooling curve suggests the presence of monoclinic pyrrhotite, magnetite, hematite, and maghemite, o) HT susceptibility experiment suggest the presence of hematite and iron sulphide greigite or pyrrhotite. p-r) Results for sample at 3095.9 m; p) zero-field cooling curve, q) remanence on cooling curve suggesting the presence of magnetite, pyrrhotite and maghemite, r) HT susceptibility experiment suggest the presence of hematite and iron sulphide. s-t) Results for sample at 3099.5 m; s) LT experiments suggest the presence of siderite, t) remanence on cooling and warming suggests the presence of magnetite, titanohematite, or goethite

5.4. Microscopy results

To aid magnetic mineral characterization, which can be non-unique, e.g., it is difficult to magnetically differentiate between pyrrhotite and greigite, I undertook a scanning electron microscope (SEM) imaging of four samples from four (4) wells (Fig.5.16). These samples were chosen because they have both variety combinations of sweet and sour wells. Their respective saturation magnetization from the low-temperature measurements were distinctly clear and also very high. The purpose was to look at iron oxide and sulphide minerals present in the samples to validate the magnetic results. These minerals were identified using EDX; I also analysed the morphology and grain sizes of the iron oxide and sulphide minerals. The abundance of magnetic minerals was $\ll 1\%$, and the initial SEM I carried out without magnetic extraction was unsuccessful, I carried out magnetic extraction. To achieve this, samples were ground to an even grain size, and passed through a Frantz electromagnet magnetic separator four times to increase the relative abundance of magnetic materials following the protocol developed by Chang et al. (2012) Samples were coated in gold for imaging energy dispersive X-ray (EDX) analysis on the Zeiss LEO Gemini 1525 SEM at the Dept. of Materials, Imperial College London. The EDX analysis had a spot size of $\sim 1\text{ }\mu\text{m}$.

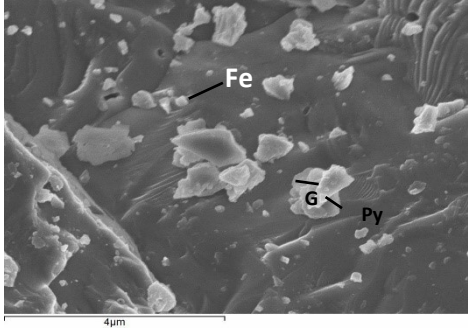
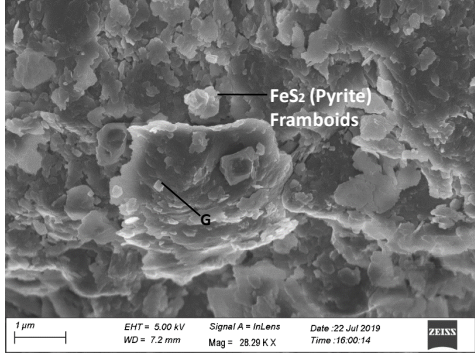
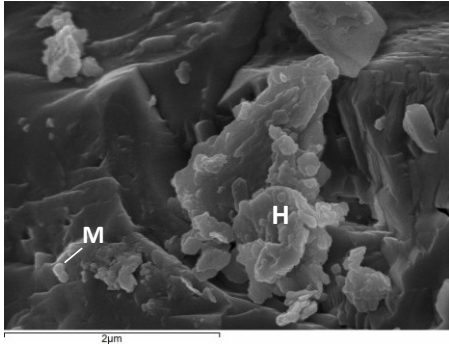
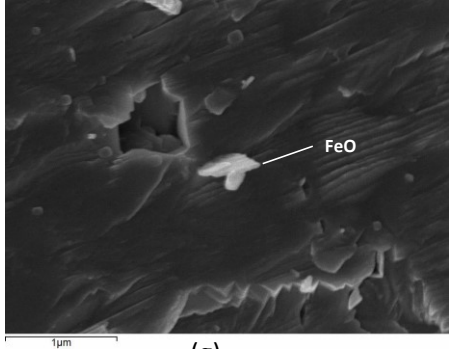
Well 02-12-48-12W5 Sour gas well	(a) 	Sample depth is 3201m	Sample at this depth interval was chosen because it had the highest saturation magnetisation in the well at the contact
Well A2-19-48-12W5 Sour gas well	(b) 	Sample depth is at 3177m	Sample at this depth interval was chosen because it had the highest saturation magnetisation in the well at the contact
Well 04-08-48 Sweet Pool	(c) 	Sample depth is at 3372.6m	Sample at this depth interval was chosen because it had the highest saturation magnetisation in the well
Well 07-33-48 Sweet Pool	(d) 	Sample depth is at 3067.05m	Sample at this depth interval was chosen because it had the highest saturation magnetisation in the well

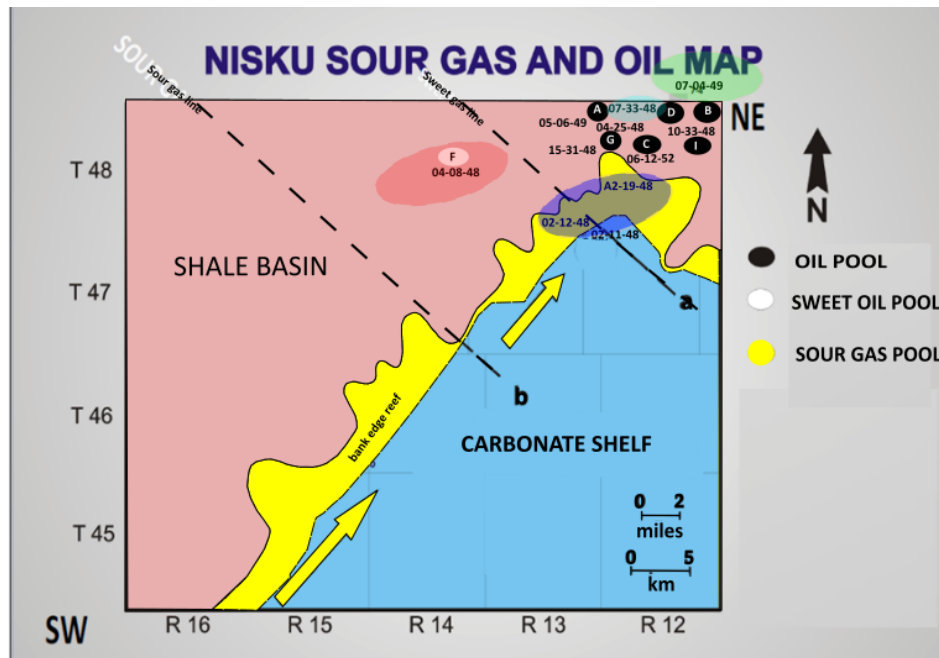
Figure 5.16: SEM images showing the magnetic mineralogy, morphology, and grain size of magnetic minerals from the hydrocarbon contact of the Nisku pools. Sour gas pool 02-12 GWC; a) SEM suggests the presence of iron oxide and sulphide minerals (pyrite and hexagonal pyrrhotite). Sour gas pool A2-19 GWC; b) SEM suggests the presence of iron sulphide mineral (greigite). Oil pool 07-33-48 OWC; c) SEM suggests the presence of iron oxide. Sweet oil and gas pool 04-04-48 OWC; d) SEM suggests the presence of iron oxide minerals. H= Hematite, M= Magnetite, G= Greigite, Py=Pyrrhotite

From the SEM imaging, it was observed that the sweet pool is dominated by the presence of iron oxides. The SEM results also showed that some iron sulphides were found which corresponds with the low-temperature magnetometry results showing some sulphides (pyrite, pyrrhotite, or greigite) and iron oxides (maghemite, magnetite, hematite). The SEM results for Well 02-12-48-12W5 found greigite and hexagonal pyrrhotite (Figure 5.16) confirming the low-temperature magnetometry results of the same well which found pyrrhotite and high-temperature magnetometry results which found greigite (Figure 5.11): the presence of iron sulphides is therefore confirmed. The morphology of the hexagonal pyrrhotite is $<1\mu\text{m}$ in size. The SEM results for Well A2-19 found pyrite fambroids and magnetite confirming low-temperature magnetometry results for samples from the GWC (Figure 5.11) which found pyrrhotite and magnetite. Magnetite was also found from high-temperature magnetometry results along with pyrite. The result from this well suggests the combinative presence of oxides of iron and sulphur, the grain size of the minerals are $<1\mu\text{m}$ nanoparticle grain size around 50 to 100 nm in size (Figure 5.19). Well, 07-33-48 from low-temperature results at the OWC suggesting the presence of iron oxide (magnetite, hematite, maghemite) (Figure 5.15) confirms what the SEM results showing very low oxide of iron composition and no sulphides (Figure 5.16). This could be a result of extremely low sulphur concentration in the pool.

Lastly, SEM results also confirm the presence of very weak iron oxides and sulphides which is shown from the low-temperature results for well 04-04-48 at the OWC (Figure 5.14) suggests the presence of iron oxide (magnetite, maghemite, and hematite) and sulphides of pyrite, its corresponding SEM result confirms the presence of very weak iron oxides and sulphides (Figure 5.16d) judging from the concentration of sulphur in the pools (sweet pool).

5.5. DISCUSSION

In (Table ii), a summary of the main findings is shown. In this table, the magnetic mineralogies found are listed, and conclusions on the magnetic mineralogy of samples from the hydrocarbon contact of the wells are summarized and shown (Figure 5.17). My findings summarize that the pools in the bank edge reef, appears to be dominated by the presence of iron sulphide minerals pyrrhotite and greigite alongside other minerals while the pools in the shale basin up-dip are largely dominated by iron oxide minerals, this change in the mineralogy between wells in the shelf margin and the shale basin is realistic because the migration of H_2S from the deepest part of the build-up SW to NE only affects the wells on the bank edge reef and is not able to permeate into wells in the shale basin up-dip, this I believe is the reason why we do not have a very increased proportion of sulphide minerals for wells in the shale basin NE.



- sour gas pools rich in MD pyrrhotite and greigite, with small proportions of siderite, maghemite, magnetite
- sweet gas pool rich in pseudosingle domain grain magnetite, hematite at OWC with some small maghemite
- dry well rich in siderite, and some negligible hematite & magnetite. grains are multidomain
- oil pool rich in magnetite, pyrrhotite, maghemite, hematite at OWC with pseudosingle domain grains

Figure 5.17: Nisku sour gas pool of the Brazeau study area showing all the wells magnetically examined in this study and the respective magnetic mineralogy predominant in them

Table ii: Summarised findings from measurements carried out on samples from the hydrocarbon contacts of the Nisku pools showing their mineralogy, morphology, grain size, and H₂S concentration. The concentration of H₂S was obtained from Burton (1995)

Pool	Well	Location	Mineralogy at the hydrocarbon fluid contact (OWC and GWC)	SEM of hydrocarbon contact and Morphology	The grain size of minerals	H ₂ S concentration
Gas pool	02-12-48-13w5	Bank edge reef	Iron sulphides (pyrrhotite and greigite appears to be more dominant than the rest) with some negligible trace of Iron oxide (maghemite, magnetite, hematite pyrite and siderite	Hexagonal pyrrhotite and cubic greigite present	0-3 µm	20%
Gas pool	A2-19-12W5	Bank edge reef	Iron sulphide pyrrhotite and greigite appears to be more dominant than in this pool with some trace of iron oxide (maghemite, magnetite, hematite) and pyrite	Cubic greigite with pyrrhotite present	0 to 0.03-0.1 µm	16%
Oil pool	07-33-48-12W5	Shale Basin	Iron oxide (magnetite, hematite, maghemite) is dominant in the pool with some trace of monoclinic pyrrhotite	Iron oxides	0-0.1µm	0.5%
Sweet pool	04-08-13W5	Shale Basin	Iron oxide (magnetite, hematite, maghemite), the sulphide of pyrite	Iron oxides	0-0.1µm	0%
Dry well	07-04-49-25W5	Shale Basin	Siderite is predominant, with some trace of, magnetite, hematite grains		0-0.1µm	0%

Five different kinds of magnetic tests were carried out on samples at the hydrocarbon contacts to characterize their respective magnetic mineralogy and found magnetic enhancement to be greatly enhanced at the gas-water contact of two sour gas wells (02-12-38-12W5 and A2-19-48-13W5) located on the bank edge reef characterized by the presence of ferromagnetic greigite and pyrrhotite. The presence of ferromagnetic minerals in the hydrocarbon contact is the story of this study and how they change under a varying range of temperature and pressure conditions, the grain sizes of these dominant ferromagnetic minerals, and their respective concentration in ppm.

Consider well 02-12-48-13W5, which from room-temperature measurements shows that magnetic enhancement can be found at the GWC (Figure 5.4). The low and high-temperature measurements for this core indicates that this enhancement was due to an increased presence of iron sulphide pyrrhotite and greigite. Paramagnetic pyrite was suspected to be present at room temperature, which upon heating at high temperature began to show the formation of pyrrhotite and greigite with a Curie temperature range of 320°C to 350°C (Figure 5.11). Crystallographic transition further helped to identify the magnetic mineral pyrrhotite which was magnetically invisible at room temperature (Figure 5.11). These findings were supported by SEM observations and analysis (Figure 5.16a), which confirmed the presence of hexagonal pyrrhotite with grain size ranging from 20-100nm from FORC analysis (Figure 5.7) and greigite 0-30 nm from SEM results with its cubic morphology. This predicts some obvious diagenetic inorganic precipitation of SP (0-30 nm) to SD (30 -100 nm) and MD grain with larger grain size >30 nm (Tauxe, 2010) at the hydrocarbon contact as H₂S charged the pool when laterally migrating from the deepest part of the build-up SW to the NE direction, the second-highest peak was not exactly at the hydrocarbon contact, the remagnetization and precipitation from the top of the gas column could be responsible for depositing ferromagnetic minerals above the contact, hence the reason for the spike above the contact (Figure 5.19). Above the contact, the diamagnetic behaviour of the samples is responsible for the low magnetic signals from the room temperature experiments (Figure 5.4), upon carrying out crystallographic transition on these samples, there seem to be a change in mineralogy to pyrrhotite. The presence of pyrrhotite and greigite from the high-temperature experiments and SEM results gives a clue of the possible impact of hydrocarbon migration, the only difference between the mineralogy of the minerals above the contact and at the contact is the grain size. The grain size of the minerals present at the contact is much larger than the minerals above the contact, signifying the precipitation of larger grains minerals (of both authigenic and detrital origin at the hydrocarbon water zone as hydrocarbon invades the pool. (Figure 5.19). Well A2-19-12W5 on the carbonate shelf margin had the GWC to be identified at 3163m from resistivity log, lithological description, and RFT data, and displayed magnetic enhancement from the room temperature measurement results to be paramagnetic pyrite or siderite (Table 5.1) with mineralogy from low and high-

temperature measurements suggesting the presence of iron sulphide (pyrrhotite or greigite) respectively which are magnetically invisible at room temperature. Paramagnetic siderite or pyrite is equally suspected to be present at room temperature from the positive high field slope results (Table 5.1) and SEM microscopy confirming the presence of cubic greigite with fine particle grain size ranging from SP (0-0.03 μm) to SD (0.03-0.1 μm) from FORC measurements (Figure 5.16). The presence of iron sulphide greigite, pyrrhotite and pyrite found in the sour gas pool was as a result of the migration of H_2S from the deepest part of the build-up. H_2S as a by-product of thermochemical sulphate reduction migrates from SW to NE direction, influencing the sulphide minerals formed during migration. The crude formed from thermal maturation for the pools in the reefs found the in the up deep direction, the H_2S from the deepest part of the build-up SW to NE did not influence the wells in the shale basin, maybe due to facies transition between the carbonate shelf margin and the shale basin

5.6. Magnetic Enhancement at Fluid contacts

From the presented results, the room-temperature saturation magnetization measurements (Figure 5.4) and high-field slope results of samples above the contact, at the contact, and below the fluid contact (Table 5.1). Some wells had clear enhancements at the hydrocarbon contact while some did not. The reason could be because of the complex diagenesis in carbonate systems which influences its reservoir heterogeneity and hydrocarbon distribution in the petroleum system. However, the Nisku is a foreland basin, there is also a possibility of having tilted hydrocarbon fluid contacts due to its reservoir heterogeneity as most tilted hydrocarbon contacts usually indicate hydrodynamic activity (i.e. lateral movement of fluid). There is also a likely hood that a paleo-contact must have been identified which was originally horizontal and became tilted over time (Figure 5.4). The sour gas wells located on the bank edge reef in the carbonate shelf margin had distinct gas-water contact (GWC) (Figure 5.2) while the oil pools in the shale basin had dissimilar hydrocarbon contacts (Figure 5.5; Figure 5.6). These pools are in isolated reefs between the carbonate shelf margin and the shale basin.

5.7. Possible causes of magnetic enhancement at the hydrocarbon contact

Some several mechanisms or factors could cause magnetic enhancement at the hydrocarbon contacts. Biodegradation was suspected to be a possible cause of magnetic enhancement at the hydrocarbon contact (Badejo et al., 2020). The reservoir system is too hot and deep for biodegradation to occur.

1). **Diagenetic precipitation:** Another mechanism is that precipitation started from the top of the gas column in the reservoir down to the bottom of the gas column until the spill point was reached and GWC formed as H_2S charged the pool. A schematic showing the

variation of grain sizes of magnetic minerals precipitated due to the diagenetic environment caused by hydrocarbons is shown in Figure 5.18 and Figure 5.19.

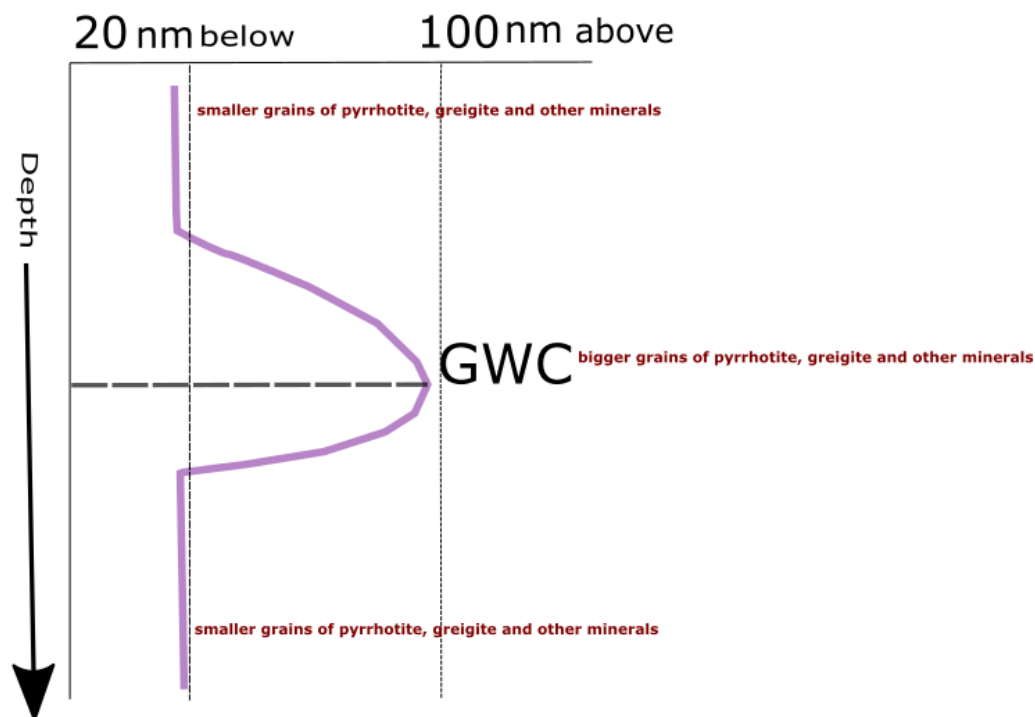


Figure 5.18: A schematic of the authigenic ferromagnetic magnetic mineral grain sizes as a function of depth within the Nisku

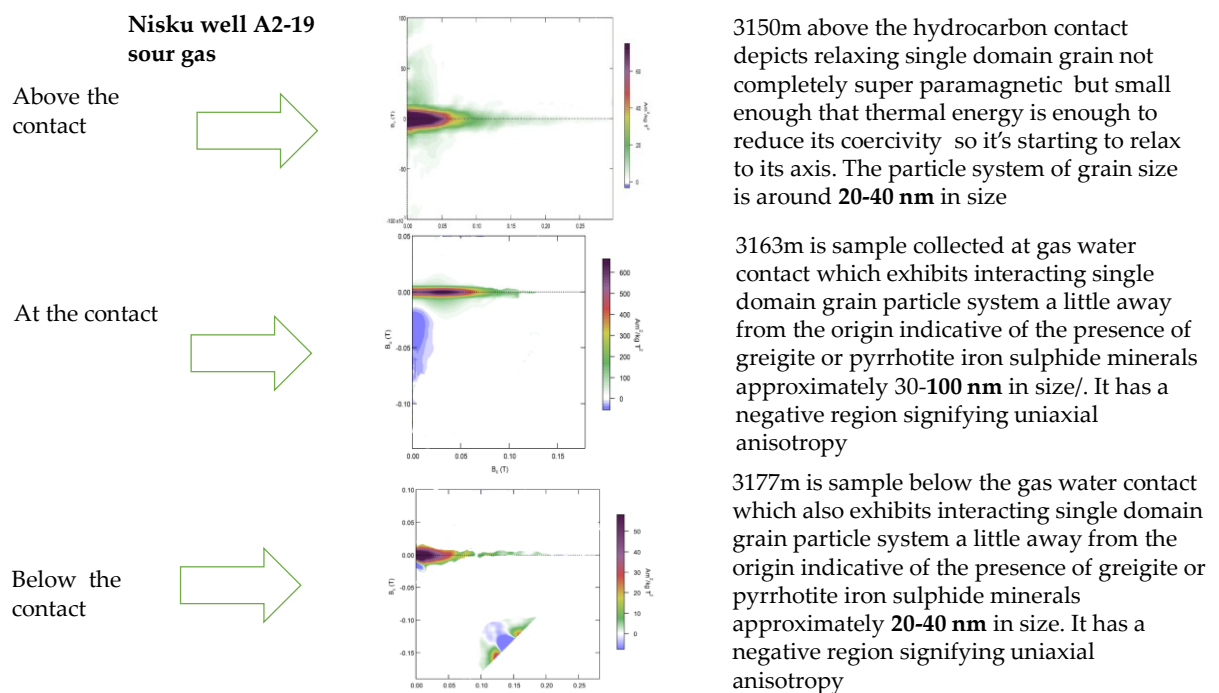
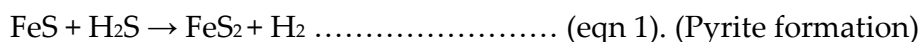


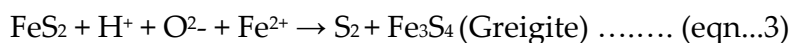
Figure 5.19: mineralogy, grain size description of minerals above the contact, at the contact and below the contact for wells a2-19 sour gas well of the Nisku formation

The H₂S which charged the pool on the carbonate shelf margin is a by-product of thermochemical sulphate reduction (TSR) that took place down-dip in the basin (Machel and Burton 1995). The abundance of sulphur in the pool influenced the geochemical environment giving room for the formation of paramagnetic pyrite which precipitated from the top of the gas column and settled at the gas-water transition zone (Machel and Burton 1995). When the weakly magnetic minerals react with iron minerals and hydrocarbon-rich water, it further contributes to the authigenic growth of greigite and pyrrhotite at greater depth, as the iron from the detrital minerals dissipates upon dissolution when the water zone was reached, reacting with H₂S and leading to inorganic diagenetic precipitation, causing an enhancement of magnetic signals at the GWC. Iron sulphides react with H₂S in the pool to form pyrite (eqn 1), but at greater depth, pyrite undergoes desulphidation to form pyrrhotite (Roberts et al., 2018).



When water reacts with pyrite, pyrrhotite, and greigite is formed in the presence of hydrogen sulphide gas (Burtler et al., 2014, Roberts et al., 2018).

2). Pyrite dissolution: The H⁺ and O²⁻ in water reacts with ferric iron and with pyrite resulting in the dissolution of pyrite to form elemental sulphur and other sulphide minerals (Lan and Butler 2014). The positive high field slope from room temperature results predicts the presence of pyrite (Figure 5.2). All the samples measured for the dry well (Well 07-04-09-12W5) had a positive high field slope. This mechanism is responsible for the yellowish colour observed during geological observation of the Nisku core samples (Machel and Burton 1995). This colouration was found around the gas water transition depth interval for Well 02-12 and A2-19 which are said to be hydrologically contagious (Machel and Burton, 2003), as they are laterally located at the bank edge reef. Increased sulphur in the system aids further precipitation of pyrite, but when sulphur supply is reduced, it further aids the precipitation of pyrite precursor greigite in the presence of ferric iron.

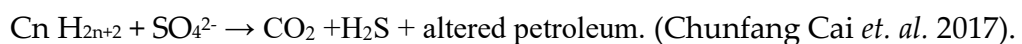


3). Pyrite oxidation: This did not occur in the subsurface, but instead when the cores are exposed to the atmosphere. Pyrite is the most stable magnetic mineral in the universe (Egon et al 2017; Emerson et al., 2019), however, pyrite can still undergo oxidation when exposed to air. The oxidation of pyrite and other factors affecting the kinetics of oxidation (O_2 , Fe^{3+} , temperature, pH, Eh) can cause the enhancement of magnetic signals when exposed to the air. The chemical oxidation of pyrite involves surface interaction with dissolved O_2 , Fe^{3+} , and other mineral catalysts. The presence of atmospheric oxygen aids oxidation of pyrite to produce one mole of Fe^{2+} , two moles of SO_4^{2-} and two moles of H^+ for every mole of pyrite oxidized (Nordstrom, 1982).

Wells 02-12 and A2-19 had clear enhancement at the gas-water contact. (Figure 5.2). The other two oil wells located in the shale basin in the up-dip direction which are wells

07-33-48-12W5 and 04-08-13W5 (Figure 5.5; Figure 5.6) also had their oil-water contacts determined from resistivity logs, lithological description, but did not have magnetic enhancement at these depth intervals but had magnetic anomalies in other depth intervals within the pools when room temperature measurements were carried out on them. Their mineralogical composition had the presence of iron sulphides (monoclinic pyrrhotite, greigite) from low and high-temperature measurements, and SEM also confirmed the presence of iron sulphides cubic greigite and pyrrhotite.

(4) Thermochemical Sulphate reduction: This is a process whereby aqueous sulphate and petroleum compounds react at a temperature higher than $120^\circ C$ (Chunfang Cai *et. al.* 2017).



This occurs in the subsurface, at great depths. During Thermochemical Sulphate reduction, some of the sulphur vapour is released which then increases the iron to sulphur ratio in pyrrhotite ($Fe:S$). The impact of sulphur or H_2S charge into sour gas pools and the invasion of hydrocarbon support precipitation of new magnetic minerals in the pools aiding possible magnetic enhancement (Roberts et al., 2018). For the pools up-dip, there was no H_2S charge as they are pools in the isolated reefs in the shale basin, they are the sweet pools. The facies transition between the carbonate shelf margin and the shale basin area did not favour the migration of H_2S into the pools up-dip to possibly displace the oil or causing charge that will support the diagenetic growth of new authigenic mineral pyrite up-dip (Machel and Burton 1995; Burton et al., 2003).

The high field slope results show that magnetic minerals (pyrite) is suspected to be present. Large high field results are indicative of the presence of paramagnetic magnetic

minerals signaling no presence of ferromagnetic components (*sensu lato*). The result of the Nisku at room temperature indicates the dominance of the diamagnetic component from the negative field slope results (Table 5.1).

From my observation, the room temperature results from the Nisku study area high field susceptibility results predict the dominance of diamagnetic minerals (CaCO_3) and the very negligible presence of paramagnetic minerals (pyrite, siderite). The low temperature and high-temperature results predict the strong presence of ferromagnetic minerals, which is where the bone of contention in this research is focused as their magnetic behaviours helps characterizes the mechanism of increased magnetic enhancement at the hydrocarbon contacts. These paramagnetic minerals (pyrite) detected at room temperature diagenetically alter to ferromagnetic pyrrhotite and greigite at high-temperature conditions as seen in (Figure 5.11; Figure 5.12; Figure 5.13; Figure 5.14; Figure 5.15) when heated in the presence of argon by desulphidation reaction. Pyrite could also have been formed at high temperatures from the dissolution of magnetite earlier formed from oxidation. The pyrite when heated in argon forms magnetite (Hu et al., 2006), this newly formed magnetite reacts with sulphur atoms released from the pyrite lattice and converts it to pyrrhotite at a higher temperature (Hu et al., 2006).

The domination of diamagnetic versus paramagnetic and ferrimagnetic components is responsible for the cyclic trend in susceptibility records, whereby higher values correspond to a higher percentage of paramagnetic mainly (iron-rich clay minerals, i.e. illite, chlorite, and pyrite) and a small amount of ferrimagnetic magnetite, while lower susceptibility values relate to an absence of paramagnetic and ferromagnetic minerals.

Total magnetization is a combination of ferromagnetic, paramagnetic, and diamagnetic component which could be estimated to be equal to the percentage (%) of the Ferromagnetic components (magnetite, greigite, pyrrhotite) + the percentage (%) of the paramagnetic components (clay minerals illite + chlorite+ paramagnetic pyrite, siderite + the percentage(%) of the diamagnetic components (biogenic CaCO_3 + Quartz) (Chang et al., 2014). Either through qualitative or quantitative analysis of the samples from the Nisku pool, high field slope approximately has the highest percentage of the minerals appearing to be diamagnetic (CaCO_3), followed by the paramagnetic components with very negligible ferrimagnetic composition. Table 5.1 shows that the magnetic properties of the minerals from the Nisku are diamagnetic (Calcium carbonate) which is highly repulsive in magnetic behaviour. This explains the reason for the weak magnetic signals seen from the magnetic measurements. Carbonates are known to exhibit weak magnetic behaviours because of this. Another key factor to note is the sulphur concentration in the pool enhances the paramagnetic behaviours in the samples, e.g. pyrite and siderite (Robert et al., 2018). These paramagnetic behaviours, further exhibit ferrimagnetic properties when heated, in the presence of argon, A typical case study is the formation of pyrrhotite when pyrite undergoes desulphidation and oxidation, in the presence of oxygen to form magnetite, further dissolution of magnetite leads to the formation of

pyrite. When the pyrite becomes too saturated and there is no more supply of sulphur during desulphidation, ferrimagnetic greigite is formed (Robert et al., 2015; Robert et al., 2018).

For the ferromagnetic minerals which are the bone of contention of this study, it can be observed that the grain size of magnetic minerals at the hydrocarbon contact appears to be much larger than the grain sizes of the ferromagnetic minerals above and below the hydrocarbon contacts. (Figure 5.18) as a result of these diagenetic conditions and processes aiding magnetic mineral precipitation. Also, the estimated concentration of the minerals at the contact, above the contact and below the contact is expressed in ppm calculated from their respective saturation magnetization values and sample mass (Figure 5.20) The concentration of the magnetic minerals above the contact is more, from this estimation and can be assumed to diagenetically settle below the water transition zone and increase in concentration.

		Conc (ppm)	Conc (ppm)	Conc (ppm)	Grain size (nm)
	Sample	greigite	pyrrhotite	magnetite	
Above hydrocarbon contact	3150	7.27E-05	9.09E-05	1.98E-05	20-40
At hydrocarbon contact	3163	1.77E-03	0.002210811	0.000480611	30-100
Below hydrocarbon contact	3177	5.46E-04	6.83E-04	1.48E-04	20-40

Figure 5.20: The concentration of magnetic minerals above, at and below the contact for Well A2-19 of the Nisku sour gas pool.

5.8 Conclusion

Increased magnetic enhancement of measured magnetic susceptibility, saturation magnetization, and remanent saturation magnetization was observed at the GWC in the Nisku sour gas pools (Figure 5.4). FORC analysis showed these peaks to be due to an increased proportion of single domain, greigite, and pyrrhotite at the hydrocarbon contacts. (Figure 5.9; Figure 5.5; Figure 5.18) with their grain sizes at the hydrocarbon contact appearing to be larger than they are above and below the contact. The quantitative analysis further showed how the concentration of the minerals in ppm appears to be stronger at the contact. SEM imaging also confirmed the presence of iron sulphide pyrrhotite and greigite. The Invasion and charge of H₂S which is a by-product of TSR in the pool, coupled with hydrocarbon invasion, and migration from the source rock to the reservoir rock, these minerals had the possible ability to transport through the pore throat of the rocks as their grain sizes are very small than the pore size of these rocks and some subtle diagenetic changes resulted in the growth of these new minerals.

In principle, the presence of H₂S should aid the precipitation of pyrite thermodynamically (Machel and Burton 1993) which would, in turn, make the samples in the sour gas pool to be magnetically weak. Low sulphur concentration in the pools could have aided the growth of the authigenic greigite. This observation could be used for the effective

identification of both the GWC, OWC and GOC when conventional methods are not dependable. This process is equally very cost-effective to carry out. Given that most of the magnetic minerals would remain in the host rock after hydrocarbon invasion or leakage, this technique has the prospect to identify paleo hydrocarbon contacts; which could either be flat or tilted because of structure. Identification of paleo-hydrocarbon contacts can provide information on the filling history of a series of fields within a basin which can help in calibrating petroleum systems models. Contrary to (Badejo et al.,2020) prediction of biodegradation as a possible cause of magnetic enhancement in the pool, the Nisku formation has its fluid contact identified at a much greater depth of about 3000m unlike the North Sea which has its fluid contact detected at shallow depth 1000m, the API gravity is also very higher for the Nisku. This rule out the possibility of biodegradation as being one of the causes of this increased anomaly at hydrocarbon contact of the sour gas pools of the Nisku. This observation was also seen for just two wells on the bank edge reef and not all the wells where hydrocarbon fluid contact was identified which could be found on the isolated reefs in the shale basin. These wells on the isolated reefs are not connected in any way unlike wells on the central North Sea, located on the same hydrocarbon migration pathway. This, therefore, leaves these magnetic enhancements to be study area-specific i.e. carbonate vs clastics. The complexity of the carbonate system could limit the universality of this study of magnetic signal enhancement at the hydrocarbon contacts. Of all the mechanisms proposed to be the cause of this enhancement, diagenetic precipitation is my preferred option. This observation could be of great importance to the oil industry as the presence of paleo- hydrocarbon fluid contacts can be identified by carrying out quick magnetic susceptibility measurements on whole core samples from dry wells and it would give information on the filling history of a basin or could be used in the calibration of petroleum systems model in both frontier and mature basins and that this method can importantly be used on core samples from hydrocarbon wells where conventional methods failed to identify the GOC or OWC. It is also very important to note that some of the spikes in the well have the possibility of being paleo-contacts even though these spikes could not be seen in current day hydrocarbon contact as observed for wells on the carbonate shelf margin up-dip. The method is therefore viable and would enable universal applicability when adopted.

Chapter 6

6.1 CONCLUSION, RECOMMENDATION, FUTURE WORK

6.1.1 Magnetisation

Combining, low temperature, room temperature, high-temperature magnetic measurement on hydrocarbon impregnated samples of the Devonian Nisku formation of the west Canada sedimentary basin, a unique relationship between hydrocarbon and magnetisation has been established for the very first time on a carbonate formation. With increased magnetic anomalies discovered at the hydrocarbon contact (Table ii). Microscopy also helped to further identify the grain size of the mineralogy at the contact (Figure 5.16).

After carrying out these series of magnetic measurements at the hydrocarbon contacts, it is found that the presence of iron-sulphide ferromagnetic minerals greigite and pyrrhotite are present at the hydrocarbon contact in dominant proportion alongside other magnetic minerals as seen from the FORC diagram (Figure 5.18, Figure 5.19, Figure 5.20). The dominance of iron sulphide minerals is responsible for the magnetic anomalies found at the hydrocarbon contacts (Figure 5.18, Figure 5.19 and Figure 5.20). The grain sizes of these ferromagnetic minerals are much larger at the contact, i.e., > 100 nm than they appear above and below the hydrocarbon contacts as shown in the FORC diagram (Figure 5.19). The formation and growth of these magnetic minerals are linked to inorganic precipitation at the contact, where the presence of sulphur-rich hydrocarbons mix with water, from large iron sulphide particles. Distal from the contact, smaller ferromagnetic nanoparticles, i.e., < 100 nm, are dominant. These smaller minerals may have precipitated in presence of hydrocarbons or have migrated with the hydrocarbons. Biodegradation is ruled out as the Nisku is too deep and hot for microorganisms.

Some wells appear to have had increased magnetic anomalies not exactly at the present-day hydrocarbon contact, but some meters, i.e., > 10 m, distant the present-day hydrocarbon contact. These intervals were suspected to be paleo-contacts from lithological studies; the magnetic anomaly observed for well 02-12 at depth 3201m, (Figure 5.4) Machel and Burton 1995), is suggested to be a palaeo-contact. It is suggested that magnetic anomalies seen in other wells are also palaeo-contacts (Figure 5.5; Figure 5.6). This hypothesis needs to be verified with magnetic measurements as part of future work to see if this is obtainable on other carbonate fields.

Besides, Basin modelling should be added to the magnetic studies as this helps to test for scenarios that ascertain the structural evolution of basins, and gives a better understanding of the complex geological history of the basin telling a more realistic and coherent story with regards to hydrocarbon migration. The ability to test these scenarios would help conceptualize migration.

Further lithological studies should be carried out on other carbonate wells to identify where dolomitization starts to form, as dolomites form at the beginning of the water leg in the reservoir of the Nisku. The depth interval where saddle dolomite starts to form is likely the paleo-contact (Machel and Burton 1995; 2003).

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Appendices

Appendix 1: Thin section: Recall from the beginning of the study, where the emphasis is being made on the combination of Geochemistry and magnetics of the Nisku formation. The thin section results are some of Professor Hans Machel's geochemical findings on the samples of the Nisku which I've examined magnetically. I asked for his express permission to add this to my thesis, which he obliged me. The photomicrograph scale of the measurement ranged from the scale of 0.3 to 1.5 mm in **size**.

Appendix 2: Well log interpretation

2.1 Lithology logs

2.2 pressure data

Appendix 3: Magnetic experiments of sedimentary rocks

3.1 Hysteresis FORC, low temperature, susceptibility vs temperature

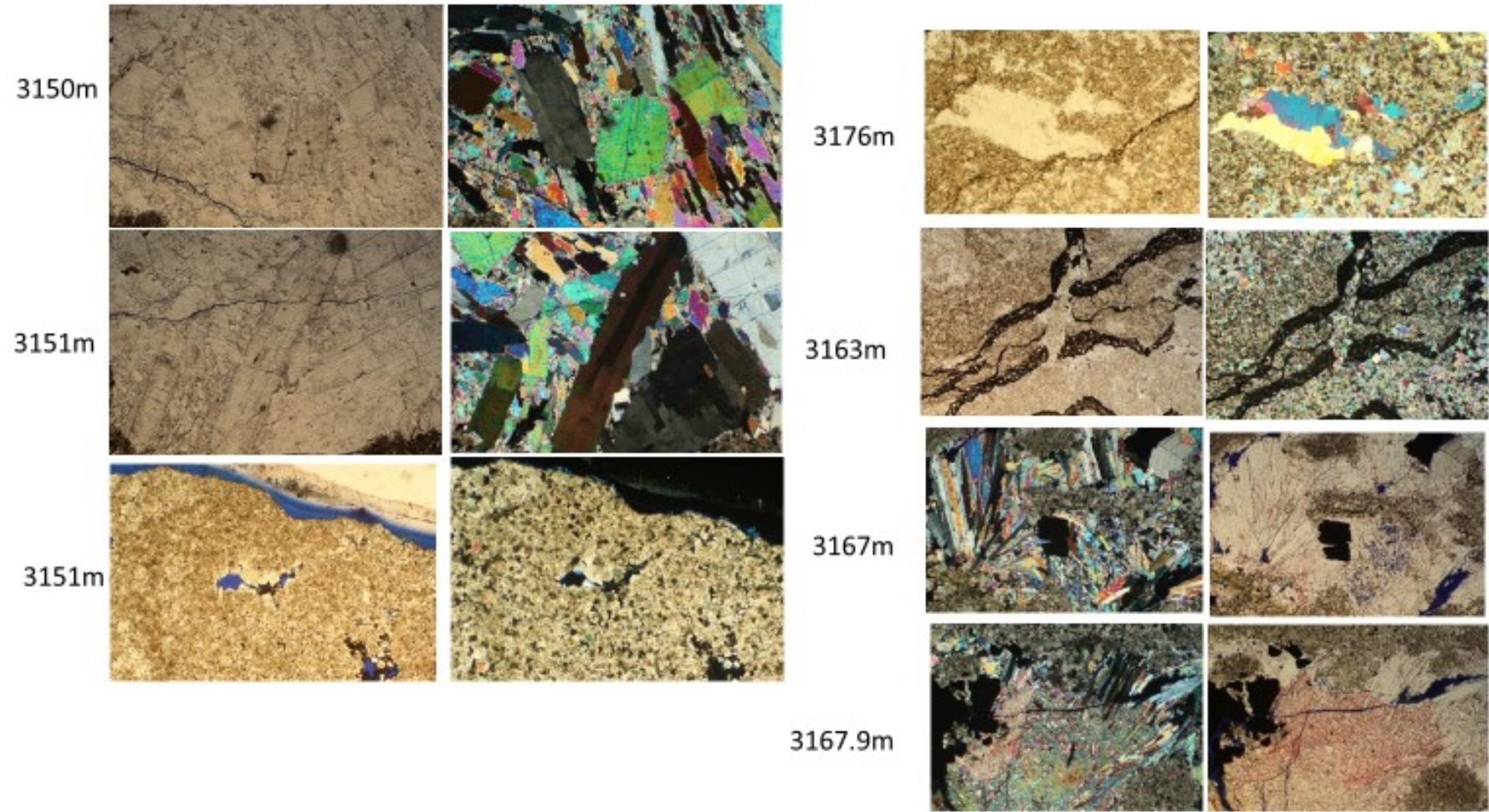
Appendix 4: Hysteresis

4.1 Measured hysteresis parameters for all wells

Appendix 1

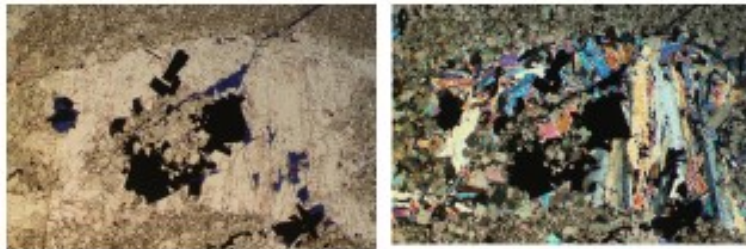
1.1 Thin section

Nisku Wells
Well A2-19

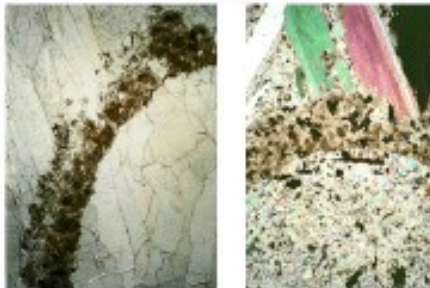
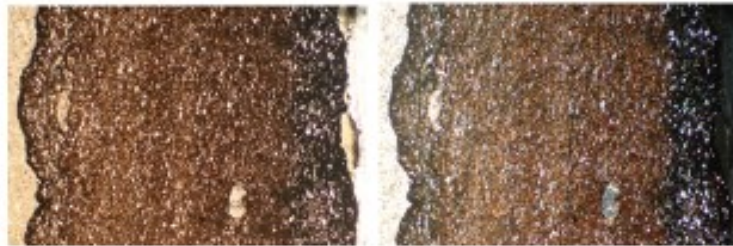


Well A2-19

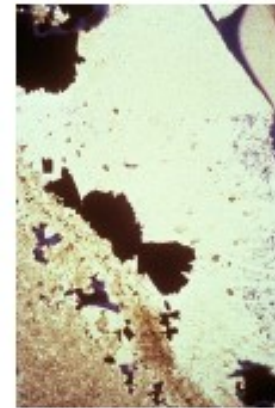
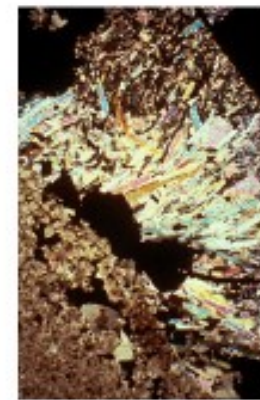
3167.9m



3173.1m



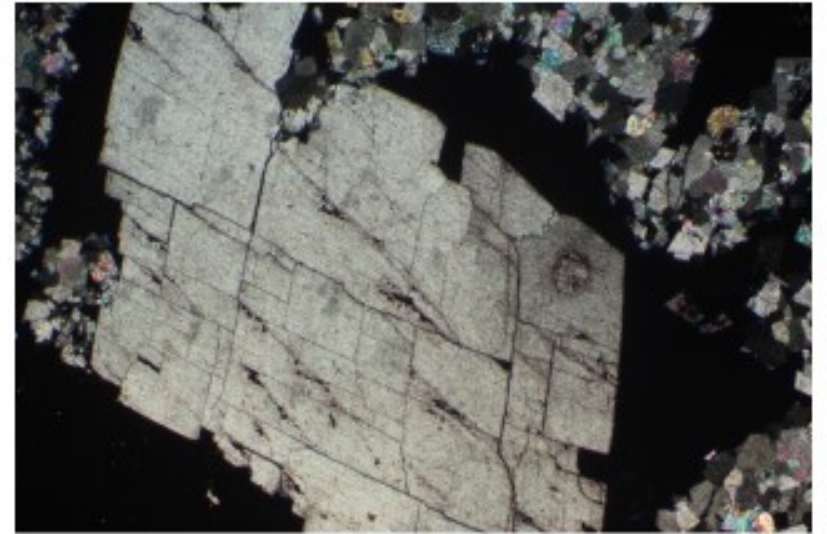
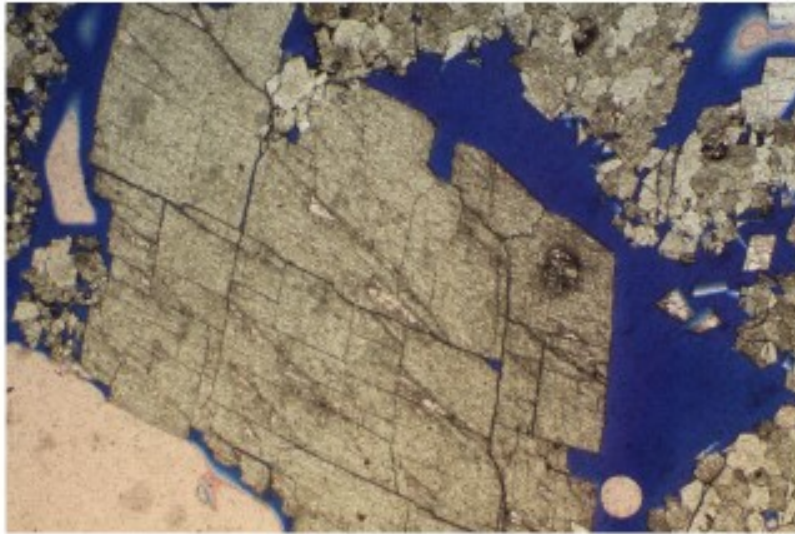
Corrotopic anhydrite



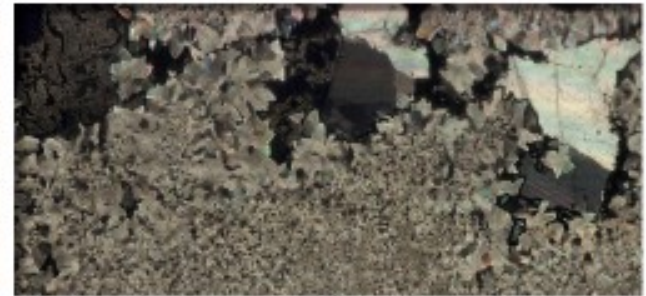
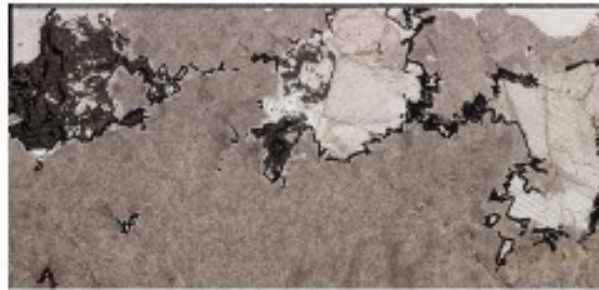
Pyrite replacing anhydrite

Well 02-12

3232m



Well 02-14

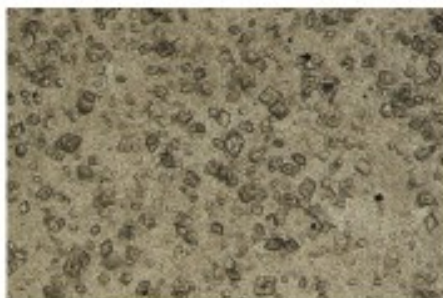


03-15

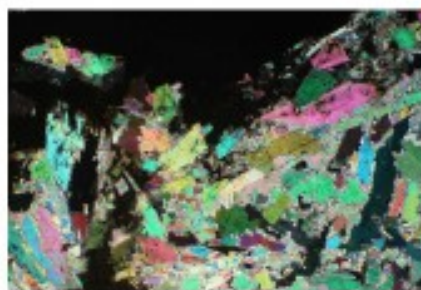
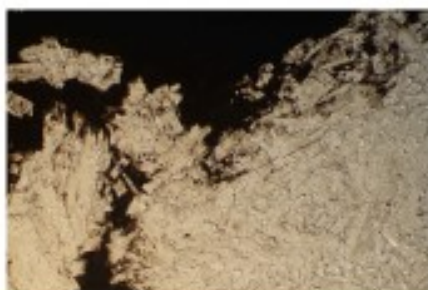
4438.32m



4438.10m

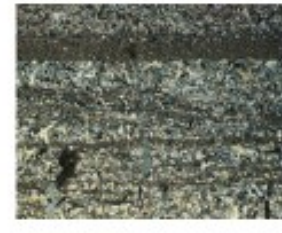
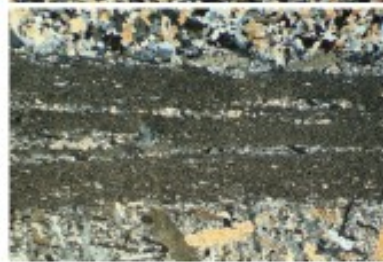
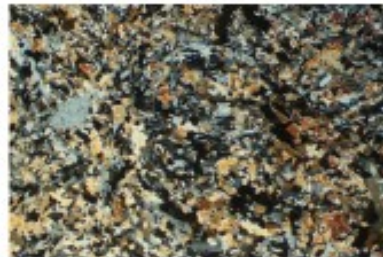


4464.32m



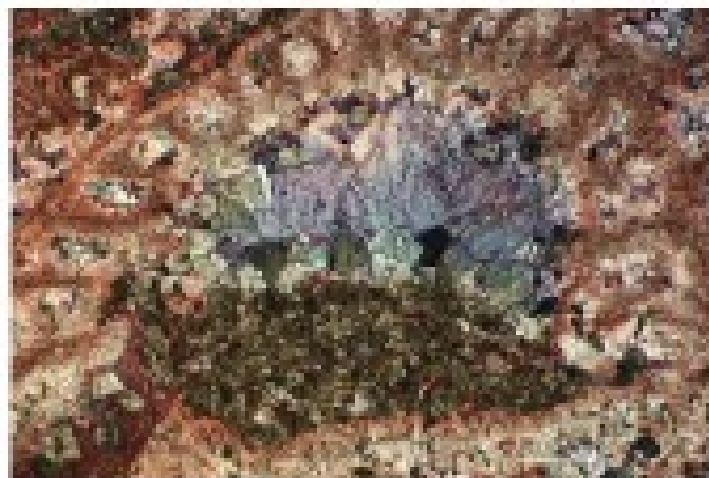
04-08-37-22W4

5388.32 m



Well 06-12 Bigoray

2401.6m



Appendix 2

2.1 Synthetics used for interpretation

The synthesis was generated from Integrated petrophysics (IP) from neutron porosity, gamma-ray, density and wireline logs.

The raw data of the logs were gotten from the core research center in Calgary in LAS format, I used integrated petrophysics (IP) to plot them out, and the output is the resultant logs below. The Nisku wells do not have easy resistivity logs like the ones on the Central North Sea (CNS) where the OWC was easily written for everyone to see, to tackle this challenge, I requested the raw log files for the wells I used. The raw data of the logs were gotten from the core research centre in Calgary in LAS format, I then learnt myself how to use integrated petrophysics (IP) to plot them out, the output are the resultant logs below, logs are my work, I did not lift them from anywhere. Unfortunately, the Core research center Calgary (CRC) did not have LAS format for all the wells I requested neither did they have easy resistivity logs

RESULTS WELL 02-12-48 sour gas well

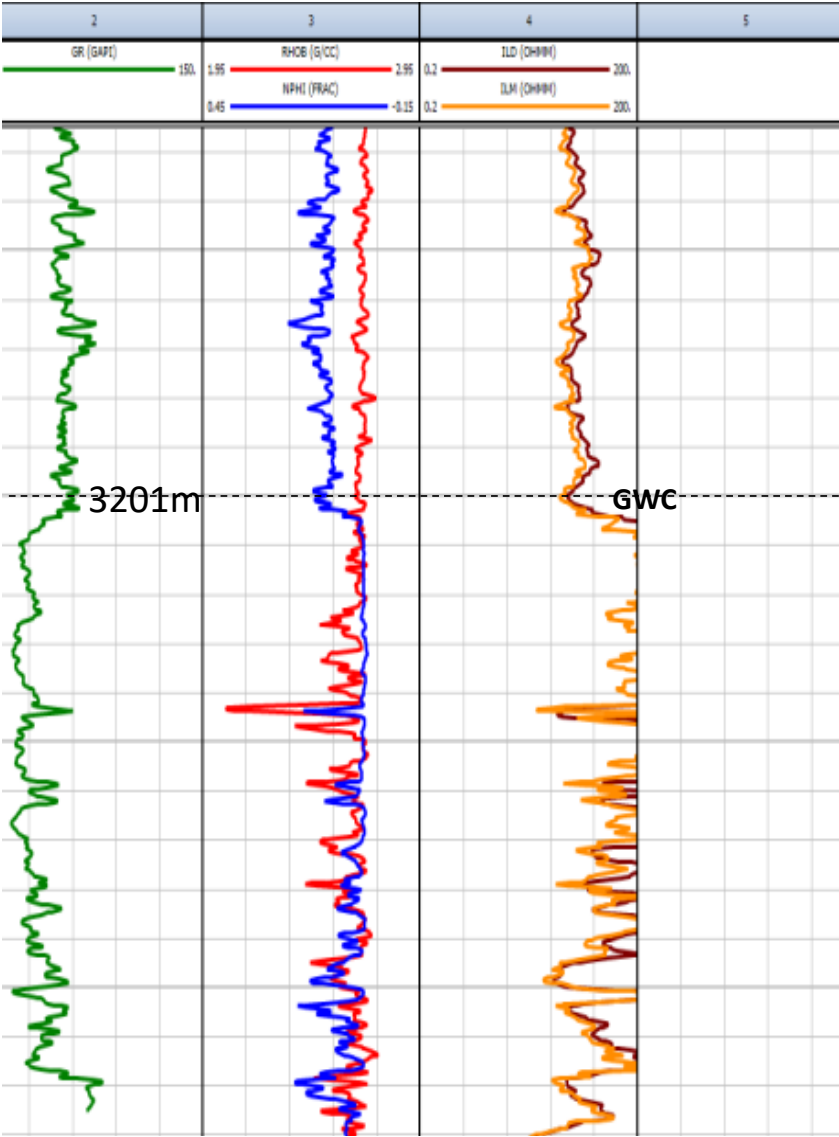


Figure 5: composite log for Well Location 02-12-48-13W5 of the Devonian Nisku formation

RESULTS WELL 04-08-48 sweet gas well

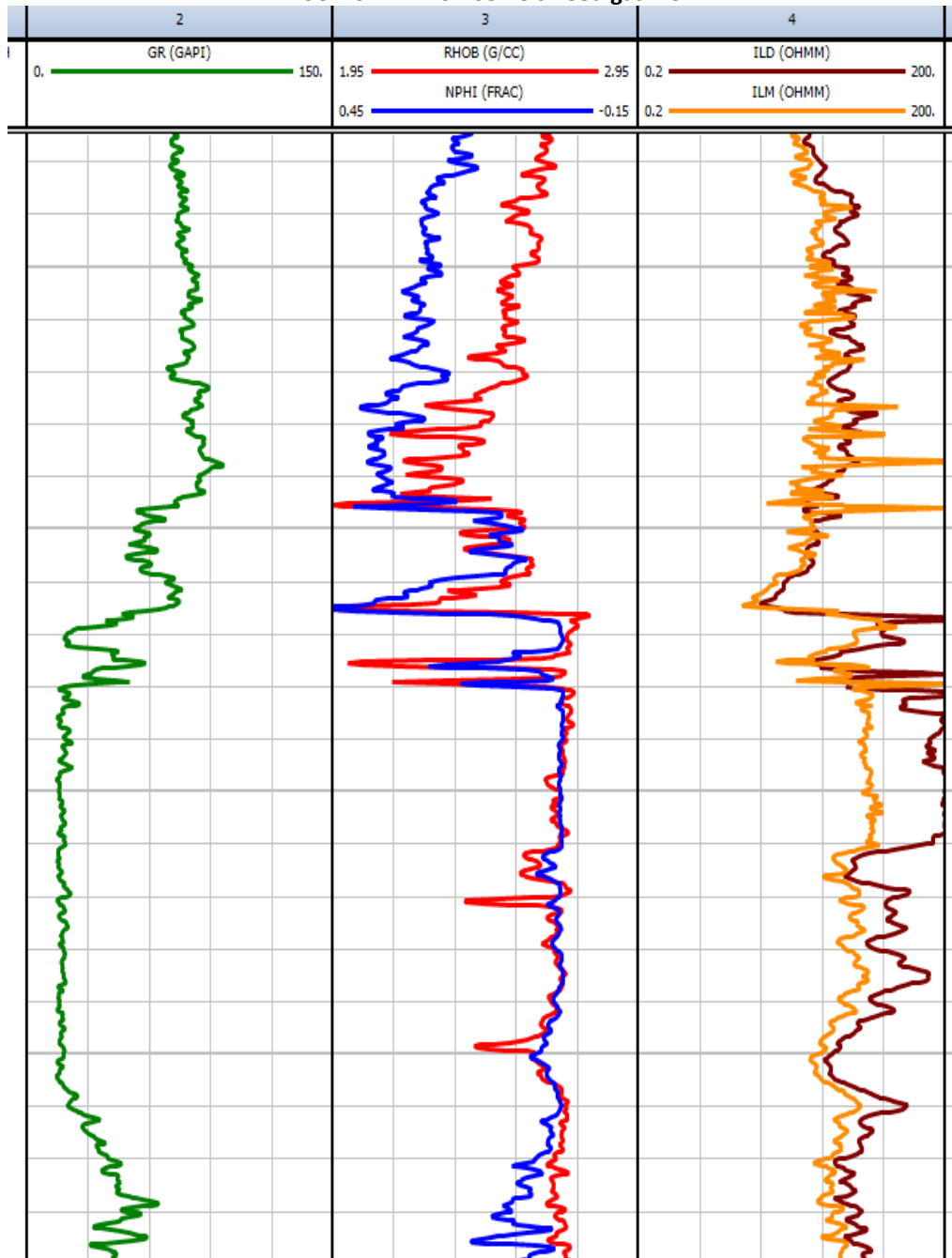


Figure 6: composite log for Well Location 02-12-48-13W5 of the Devonian Nisku formation

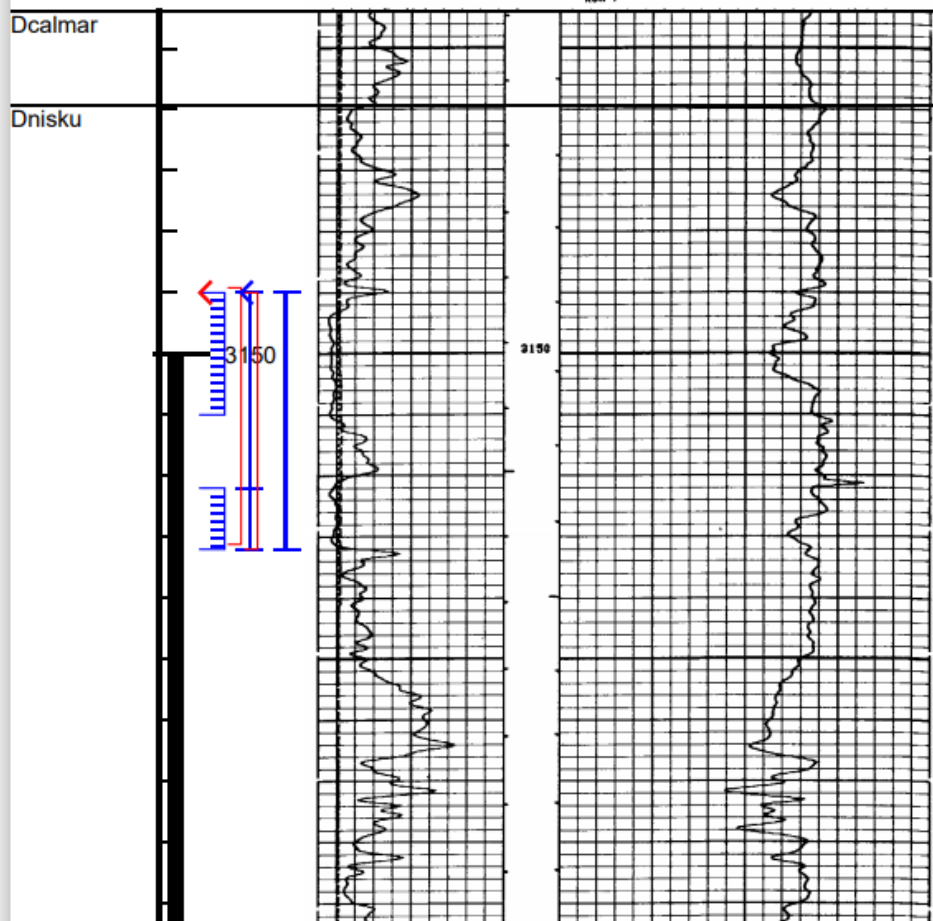
102/02-19-048-12W5/00

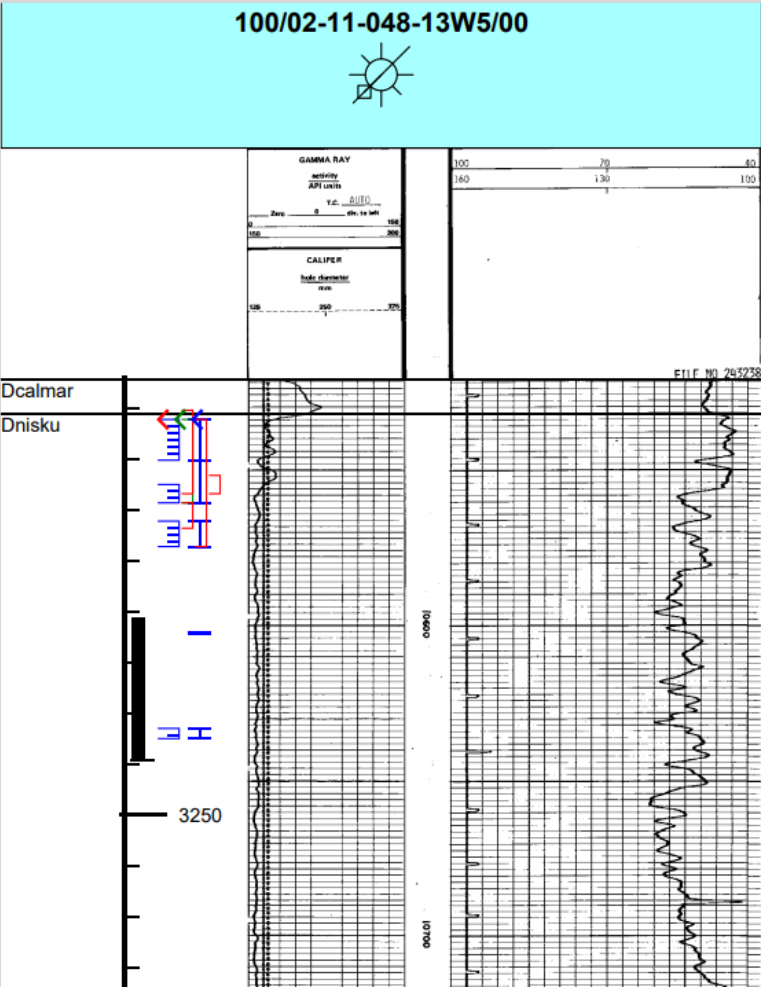


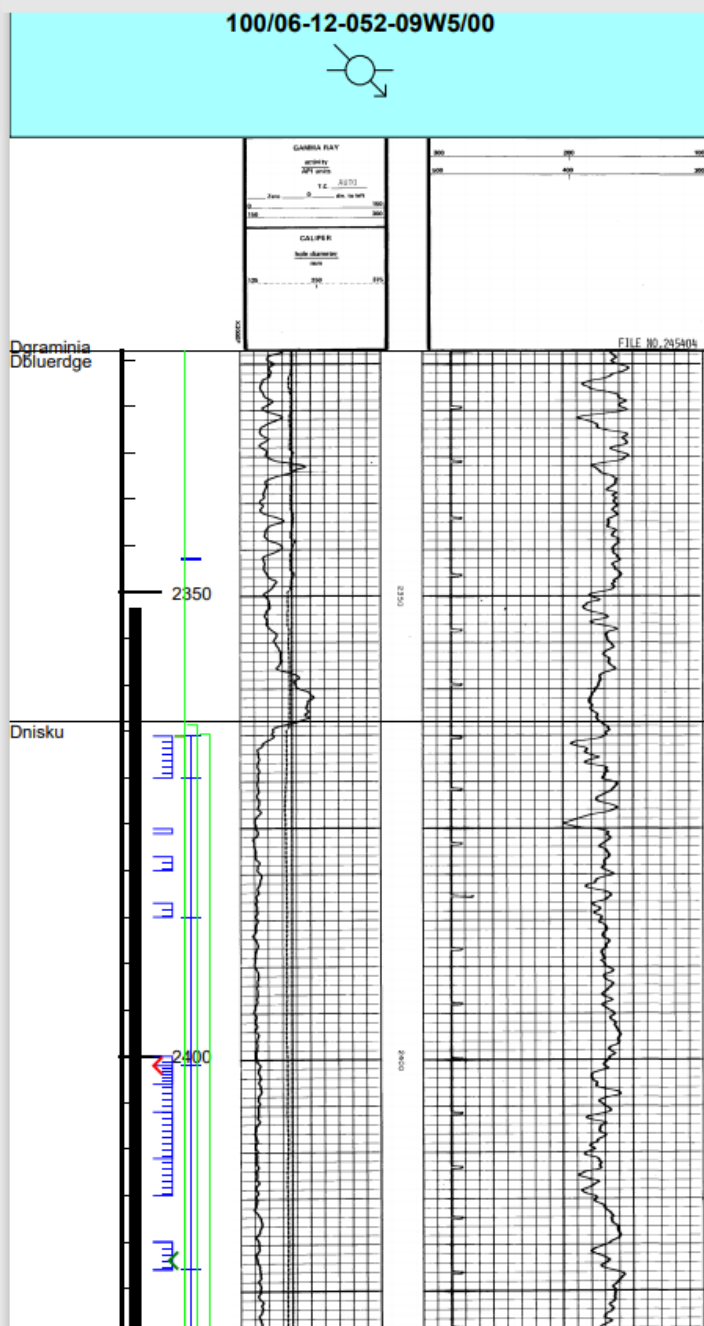
GAMMA RAY		DEPTH meters	INTERVAL TRANSIT TIME $\mu\text{s}/\text{m}$	
activity API units	Ta: AUTO		500	100
0	0	0	500	100
100	0	100	500	500

CALIPER	
hole diameter mm	mm
125	125
125	125

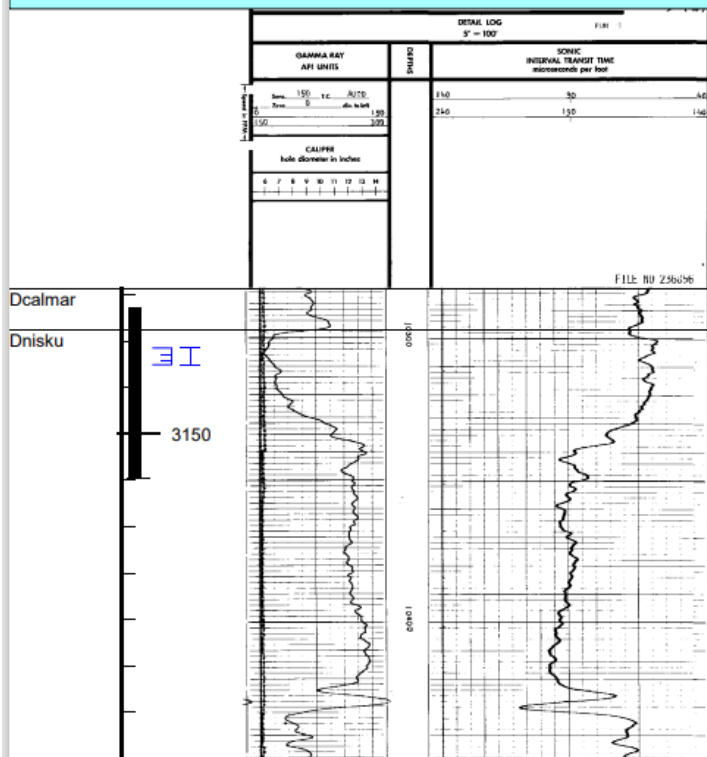
Run 1





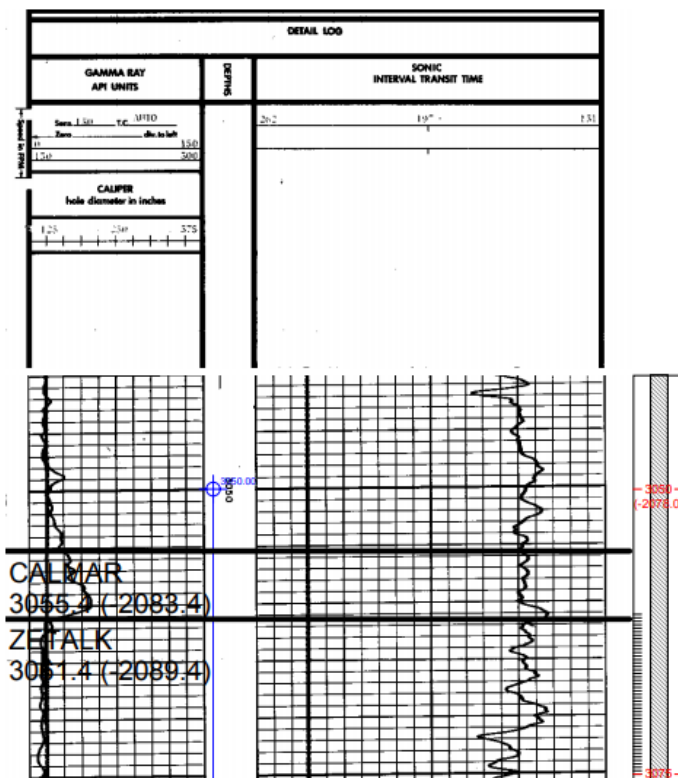


100/04-25-048-13W5/00



00/05-06-049-12W5/0

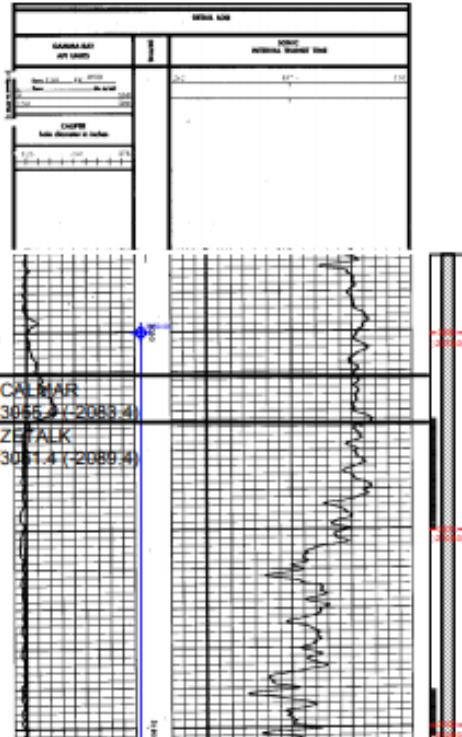
KB: 972.0 m RR: 1978-07-22
TD: 3206.5 m FormTD: IRETON
Mode: Flow Fluid: Oil
PC NORCENPL BRAZR 5-6-49-



00/05-06-049-12W5/0

KB: 972.0 m
TD: 3206.5 m
Mode: Flow
PC NORCEMPL BRAZR 5-6-49-

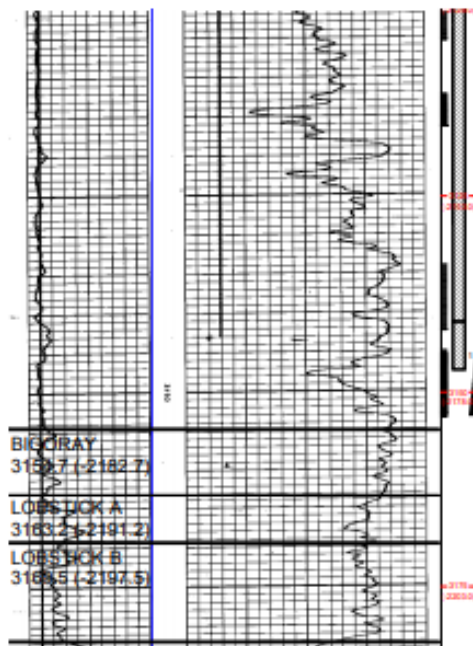
R/E: 1978-07-22
FormID: WETON
Fluid: Oil



C:\CCCLM-1\Borehole\LOCALS-ST\LOCALS\BLOGS_000
Projection: North, Fixed spacing: 1.00 m

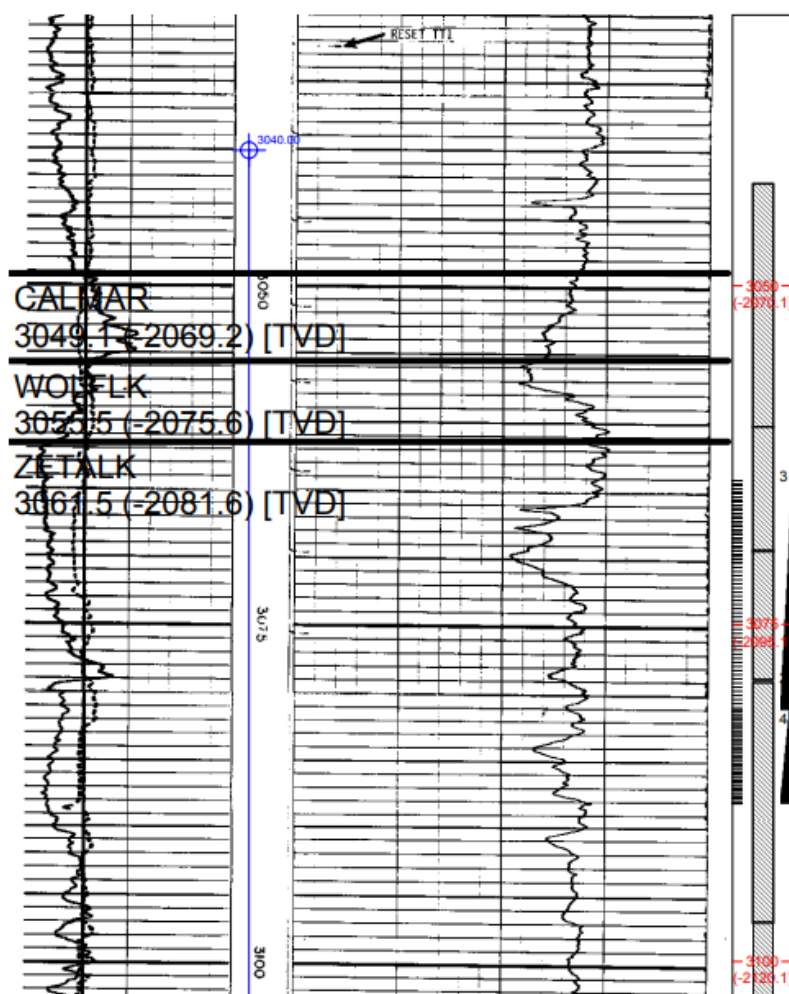
Page 1 of 2 (Row 1 Col A)

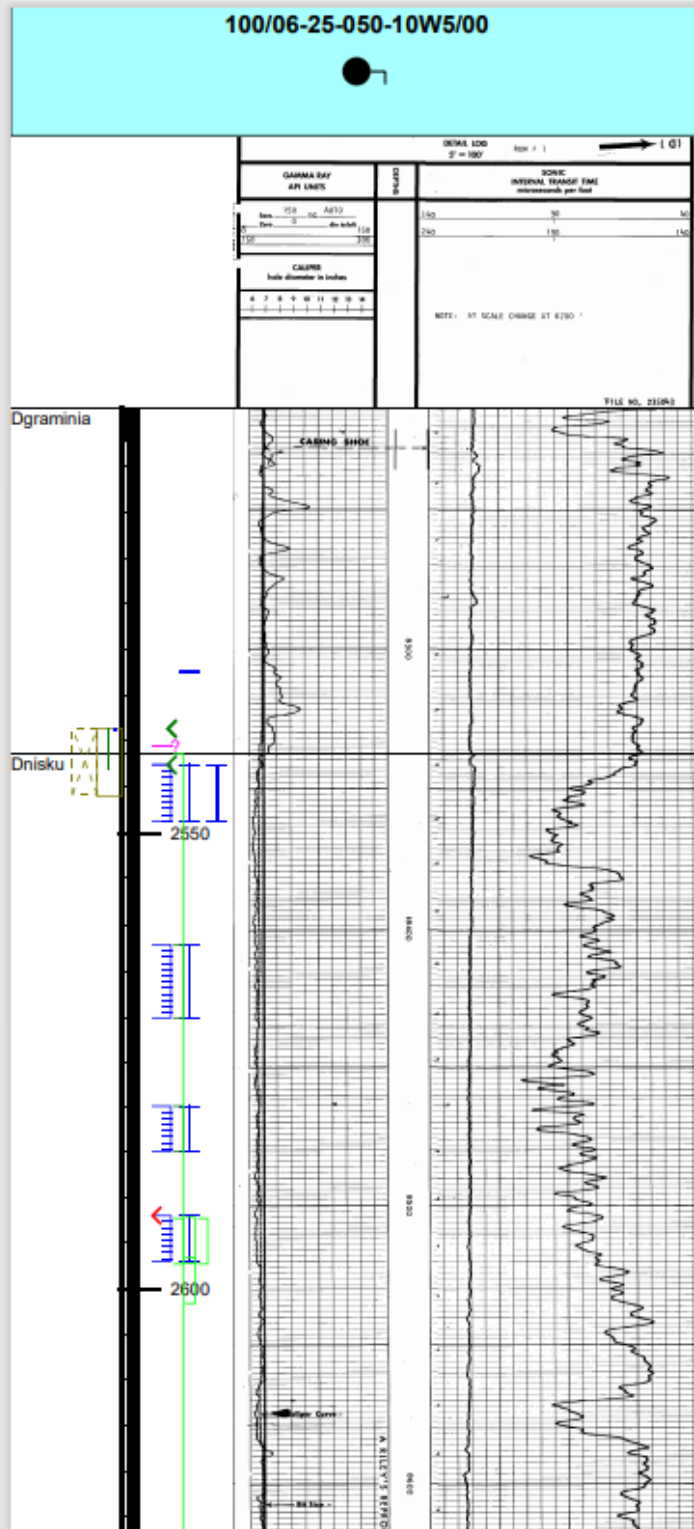
[BoreLog Viewer, v6.3.2.0] Dec 10, 2003 12:08:44



00/05-34-048-12W5/0

KB: 979.9 m RR: 1979-08-23
TD: 3177.5 m [TVD] FormTD: IRETON
Mode: Flow Fluid: Oil
PC BRAZR 5-34-48-12

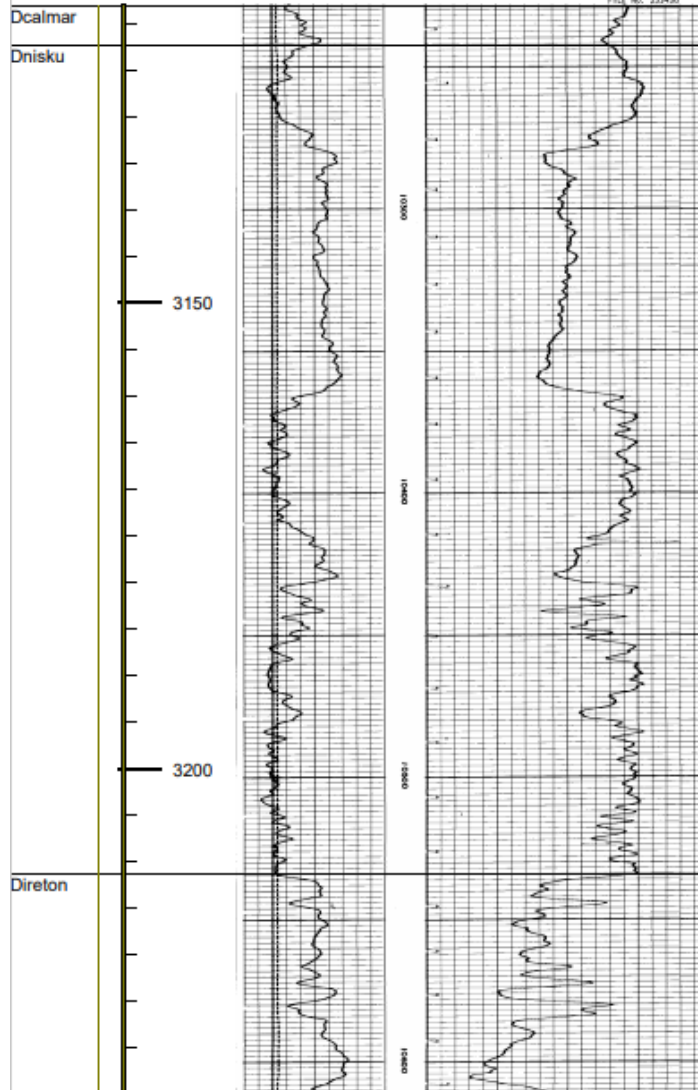




100/06-30-048-12W5/00

NITRA LOG
1" = 100'

(V)



100/07-04-049-12W5/00

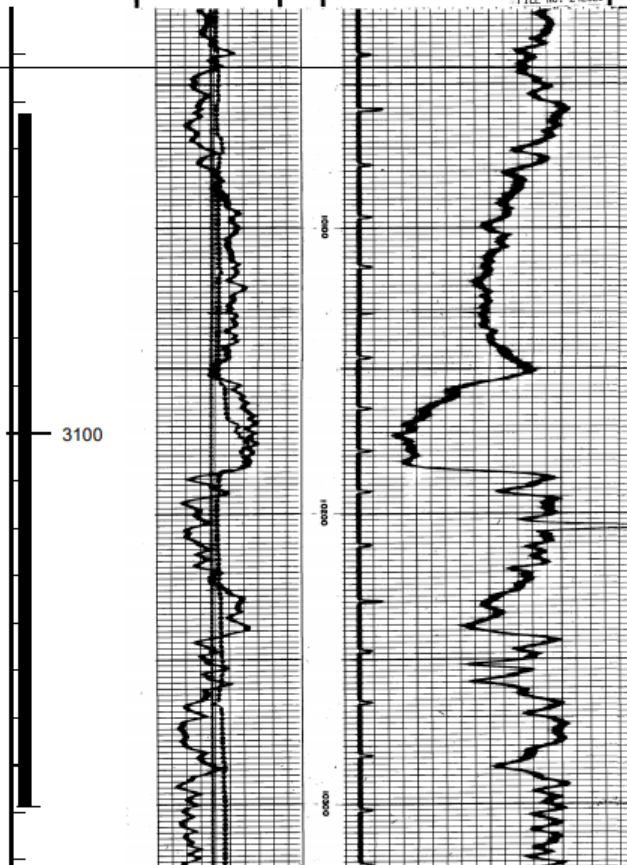


DETAIL LOG 5' = 100'	
GAMMA RAY API UNITS	SONIC INTERVAL TRANSIT TIME microseconds per foot
Scale 100 TC AUTO	110 90 60
Zero 0 div to left	150 150 150
10 100	
CALIPER hole diameter in inches	
4 7 8 9 10 11 12 13 14	

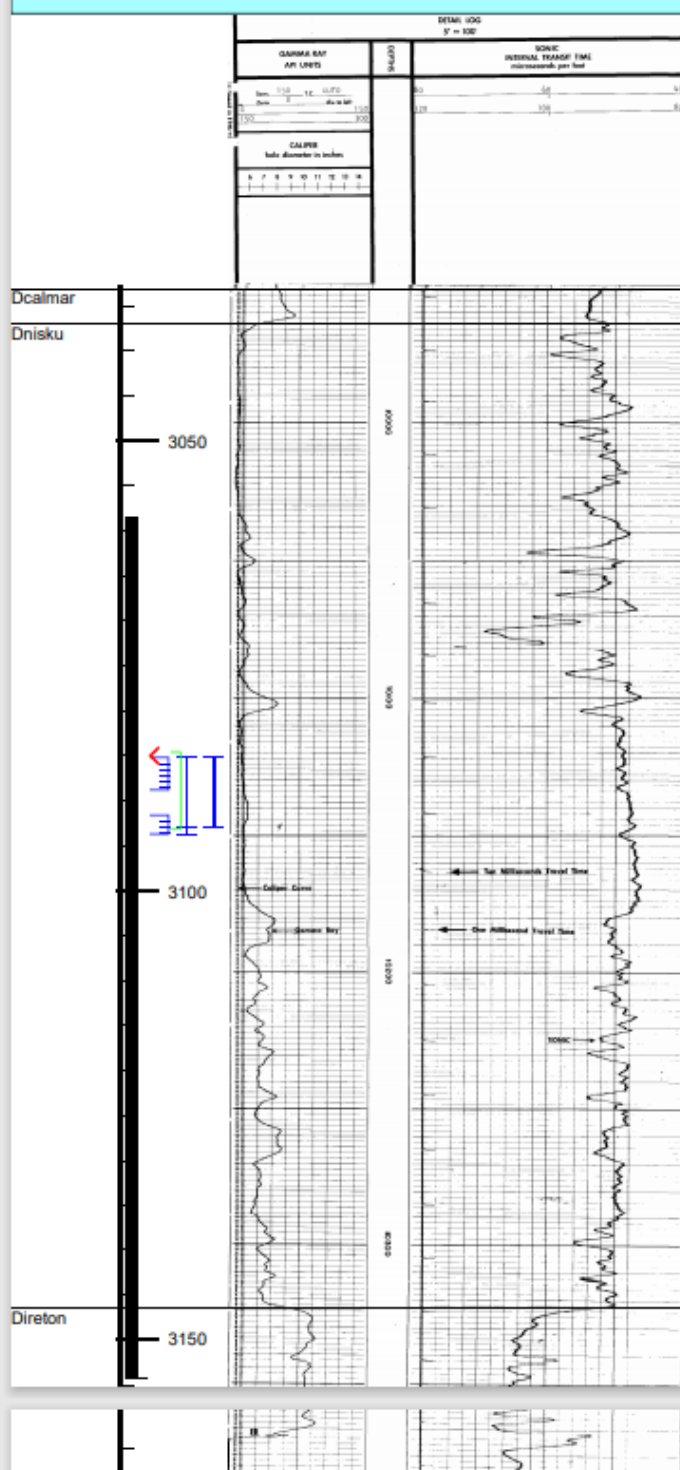
FILE NO. 242023

Dcalmar

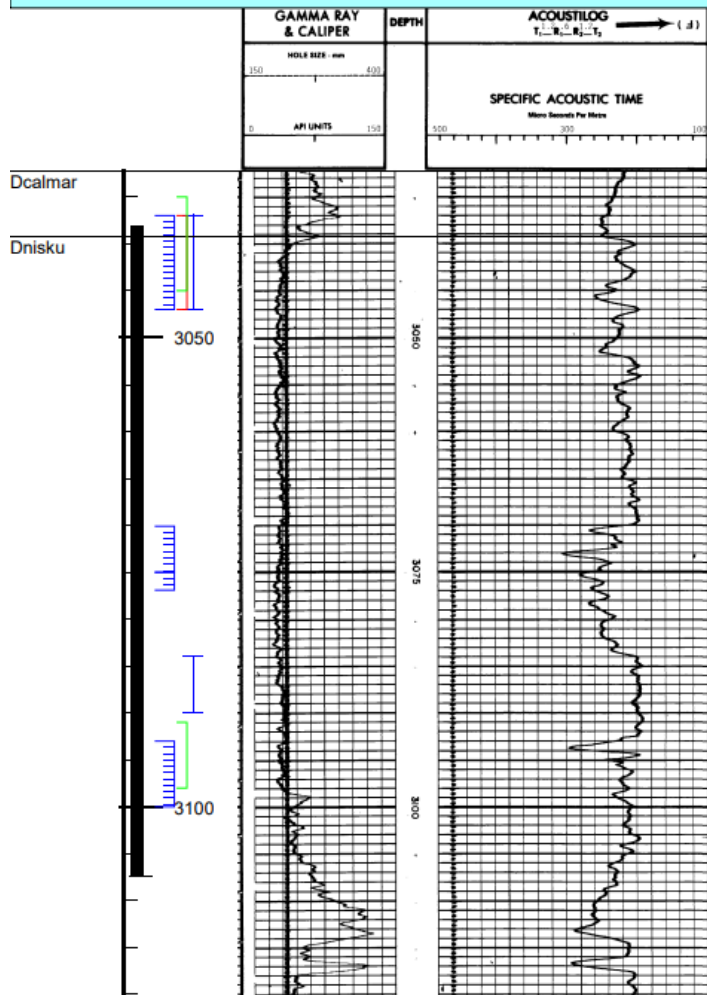
Dnisku



100/07-33-048-12W5/00



100/10-33-048-12W5/00



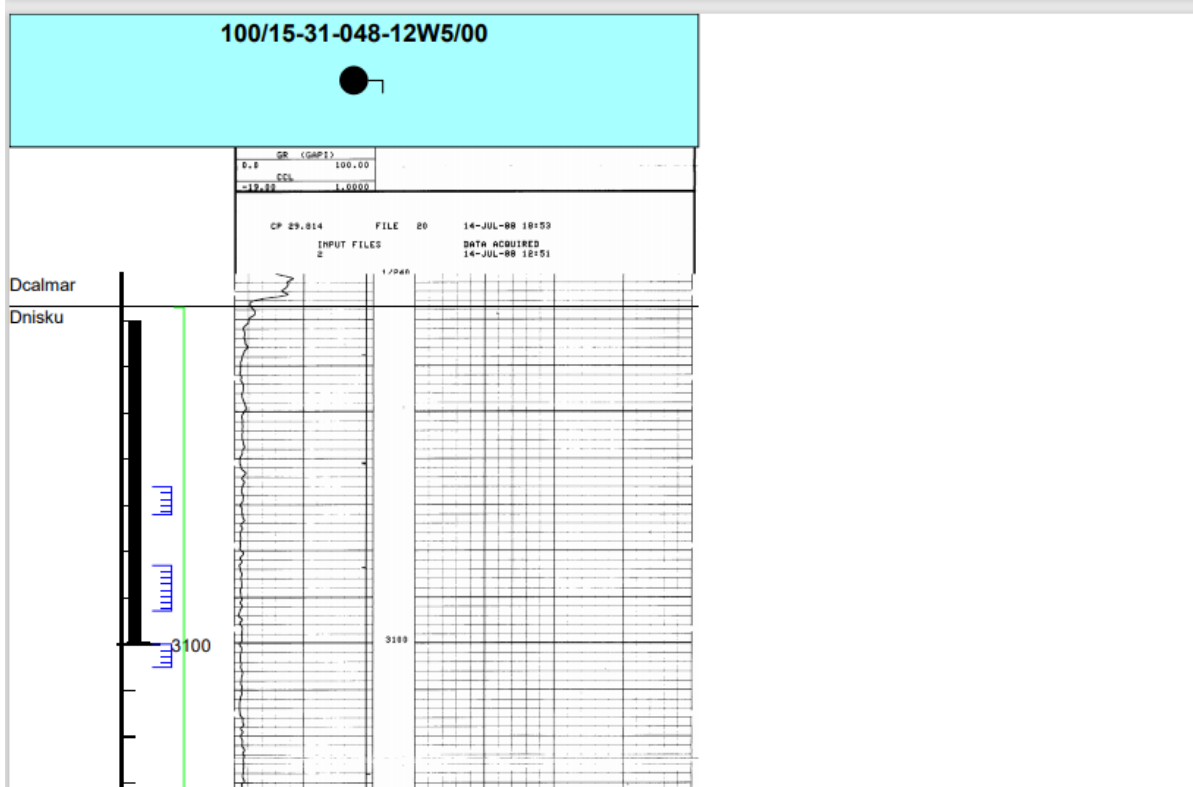
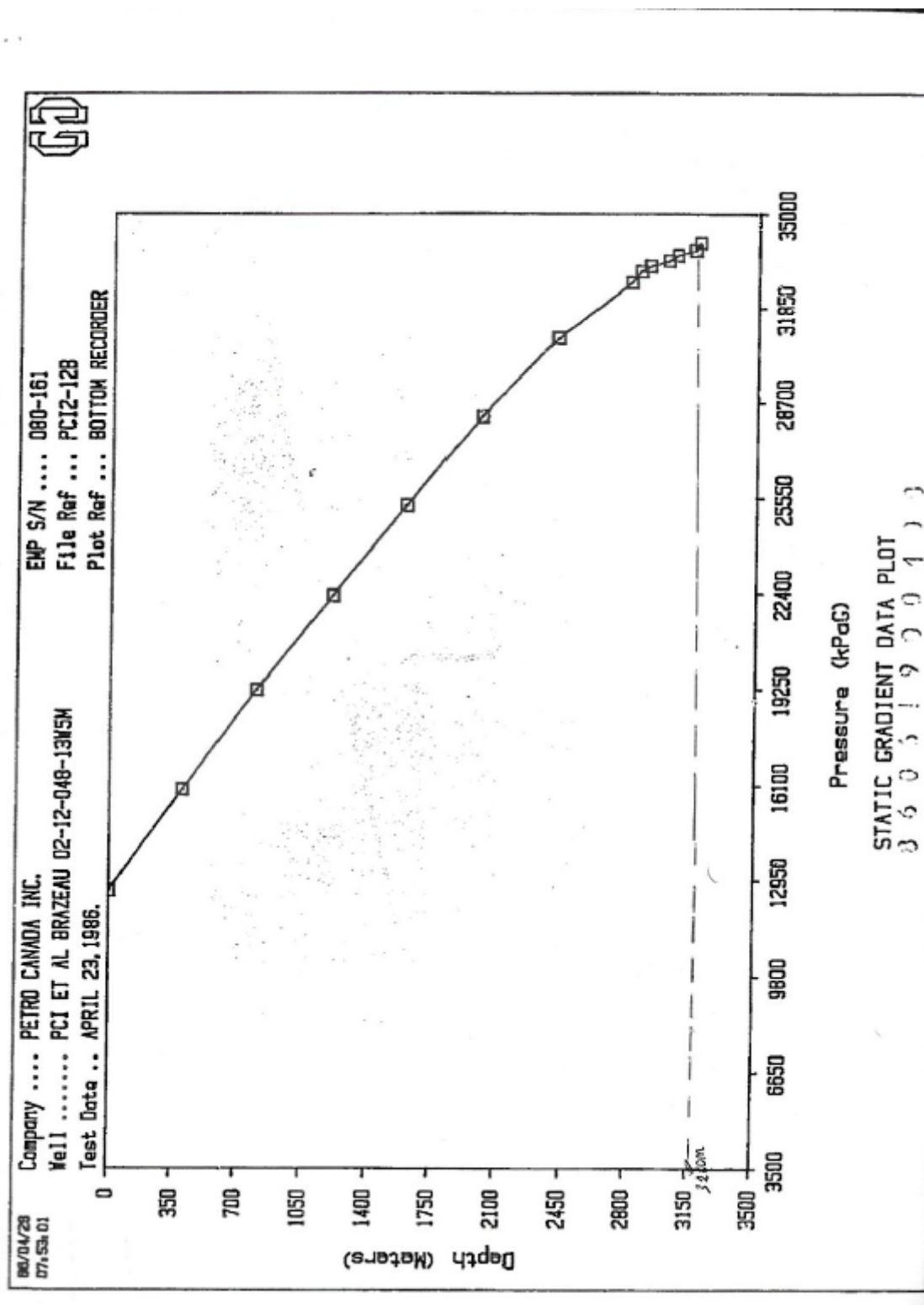


Table iii: Figure showing examined wells and the depth interval where samples were collected from

Well location	Depth interval where sampling was collected from (m)
02-12-48-13W5	3180-3255
02-A219-13W5	3150-3177
04-08-13W5	3334-3394
07-33-48-12W5	3067-3100
06-25-50-12W5	2528-2563
07-04-49-13W5	3076-3121
15-31-48-12W5	3072-3080
05-06-49-12W5	3074-3109
02-11-48-13W5	3236-3244
10-33-48-12W5	3038-3093
04-25-48-13W5	3077-3136
06-12-52-9W5	2352-2389

2.2 Pressure data was used in conjunction with lithology logs to identify hydrocarbon contacts. Pressure data were available for four (4) wells in the Nisku, the depth interval where pressure-depth interval breaks are regarded as the pressure gradient, and the break is identified at the hydrocarbon contacts.

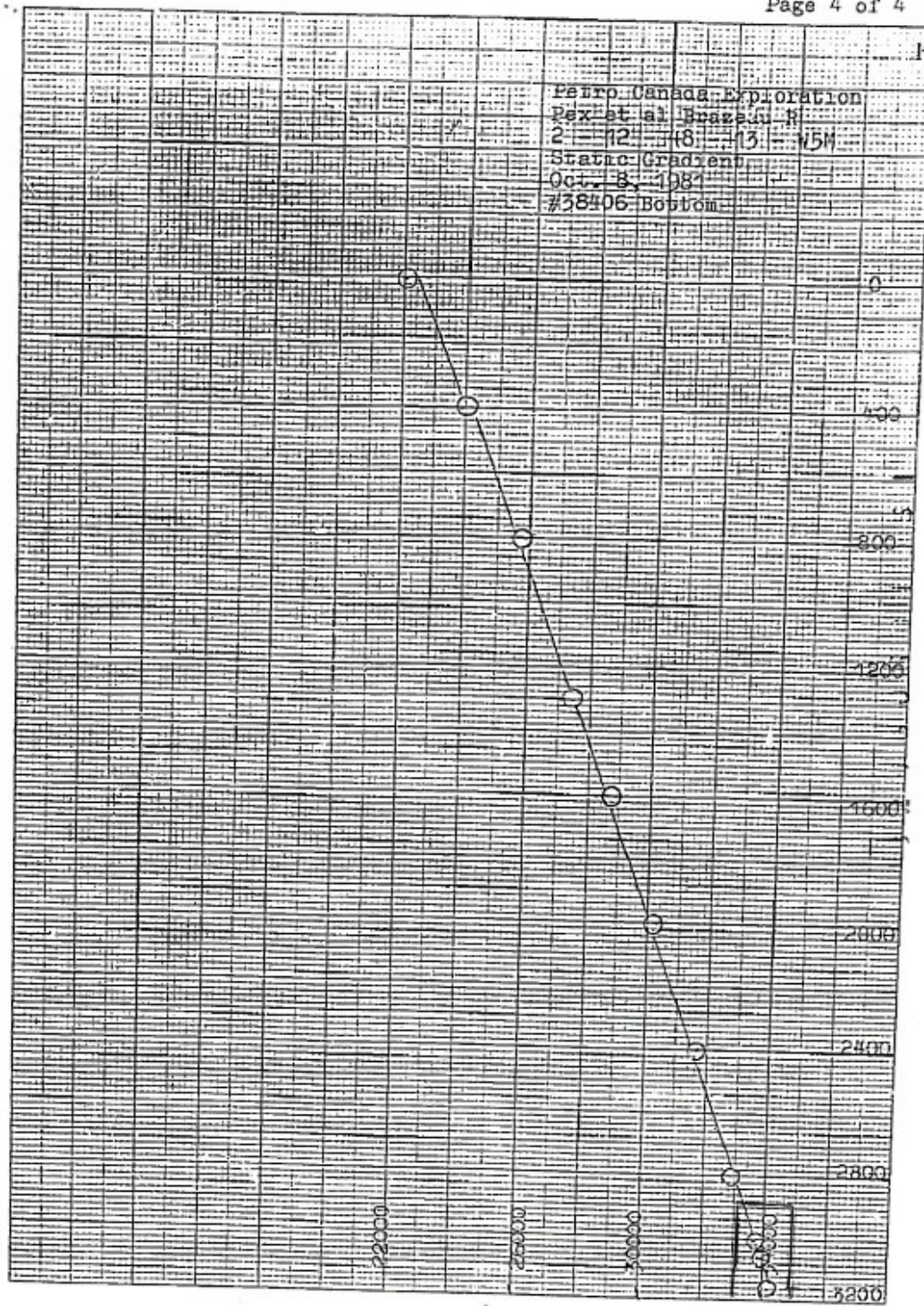
The pressure data was gotten from the Core research centre in Calgary and was sent electronically. Unfortunately, the research center in Calgary did not have pressure data information for the other wells as they were really old wells



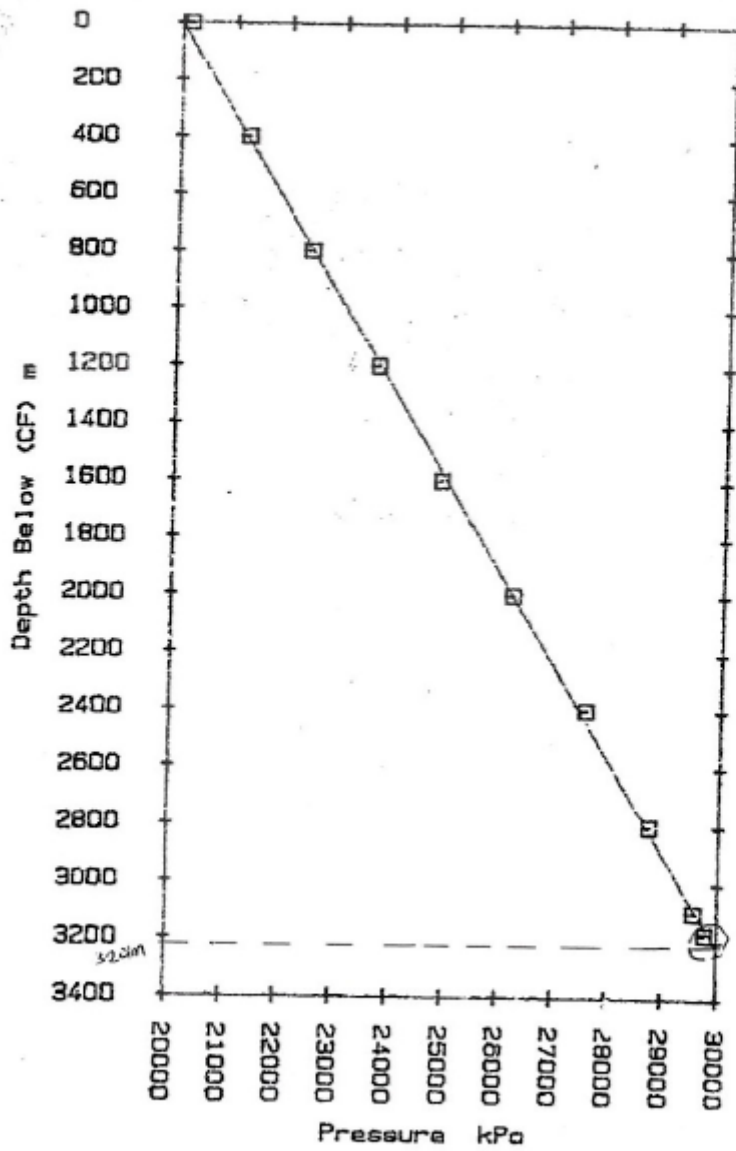
46 1242

K-E 25 X 25 TO THE INCHES 7.4 10 INCHES
REPTED & CORRECTED

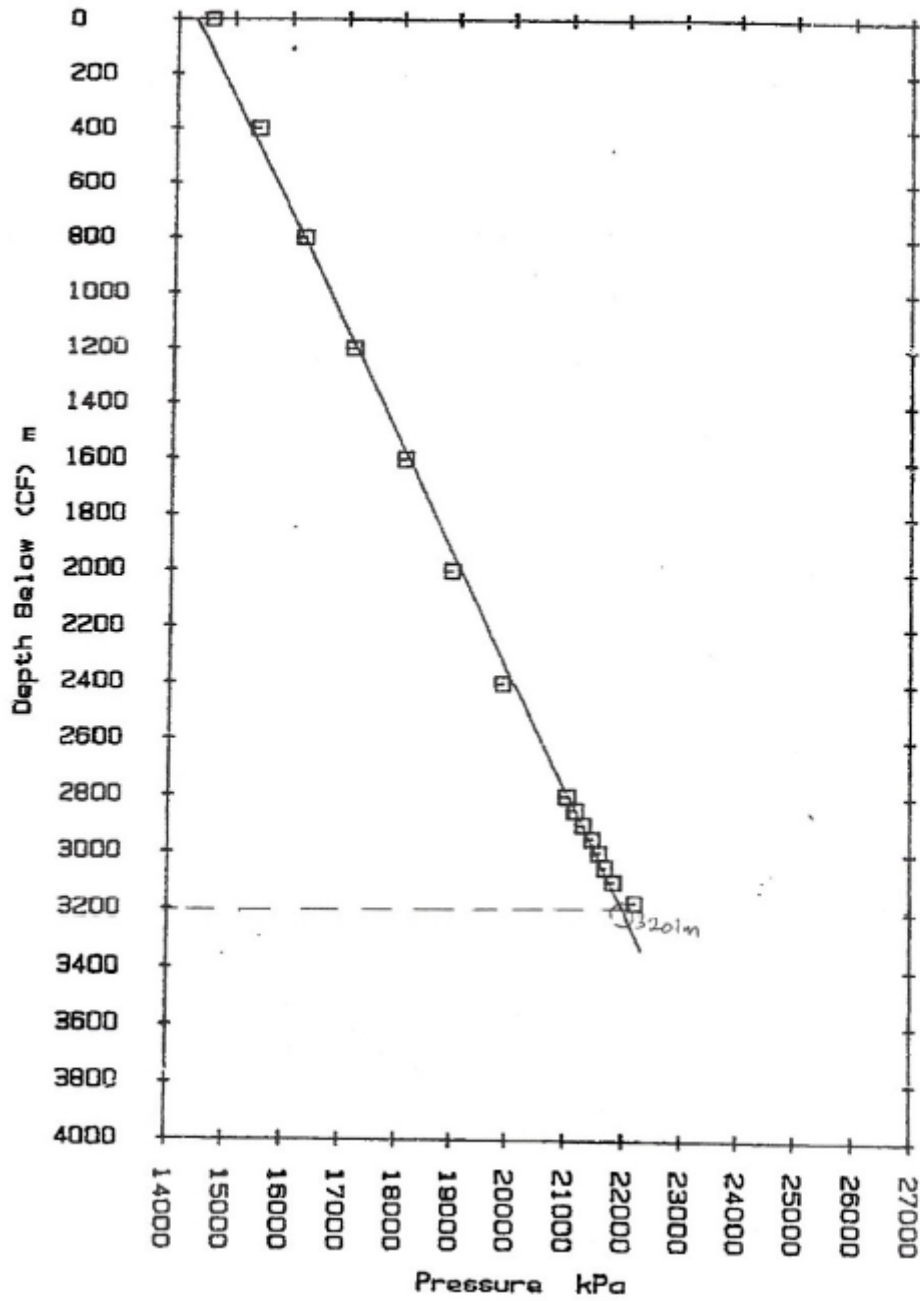
kPa



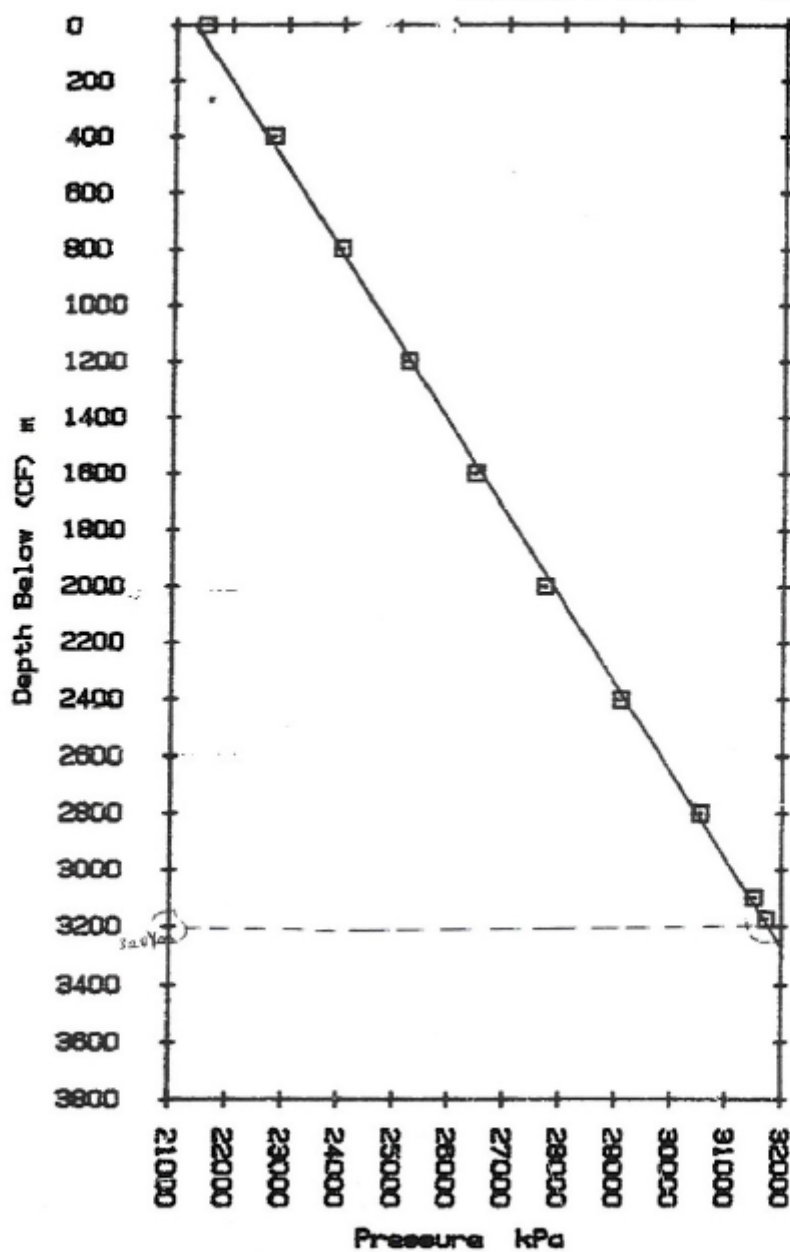
PETRO CANADA EXPLORATION LTD.
PCI ET AL BRAZEAU R
LOCATION 2-12-49-13W5
Element # 16991 861209



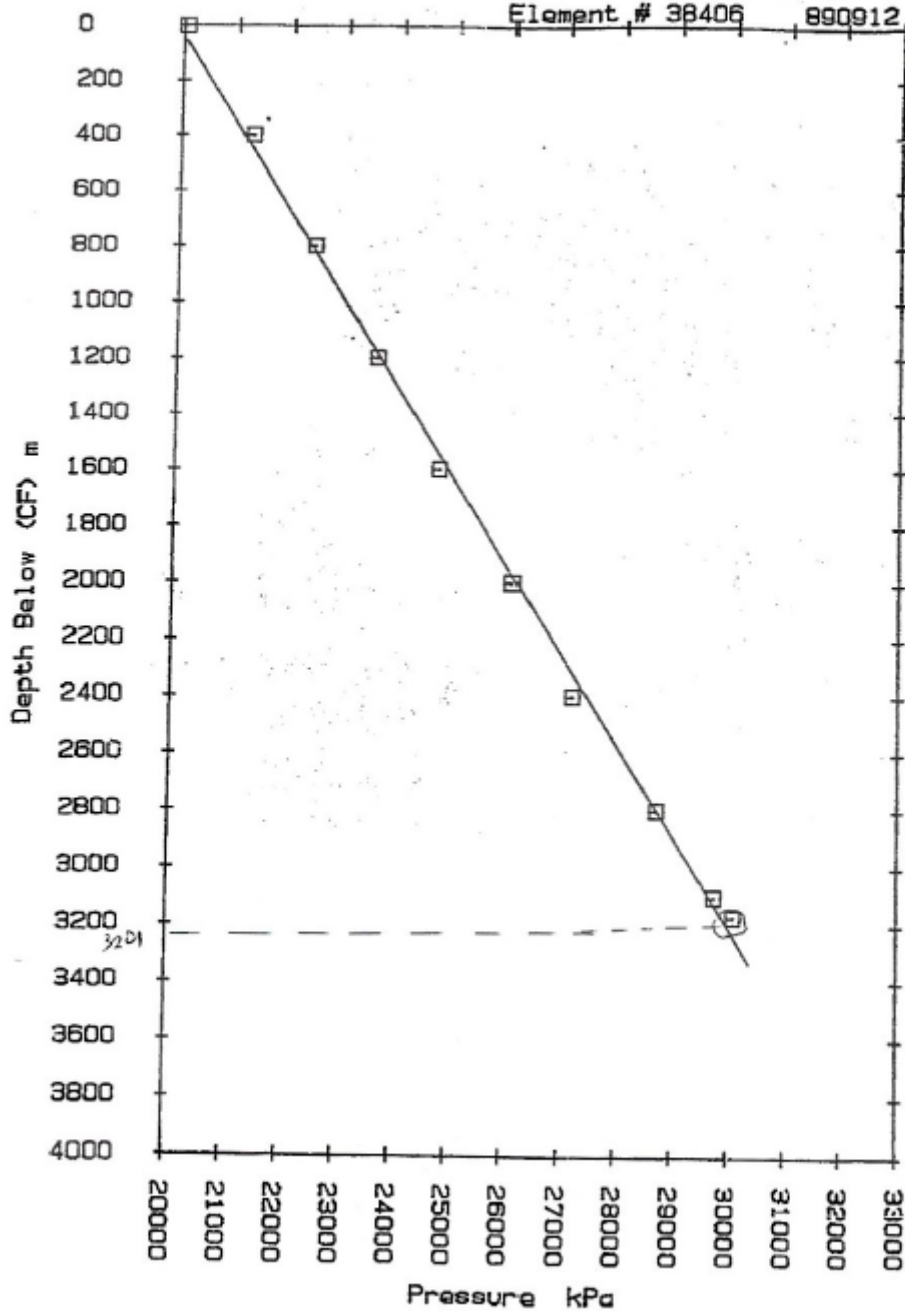
PETRO CANADA EXPLORATION
PCI ET AL BRAZEAU
LOCATION 2-12-48-13W5
Element # 17002 860626



PETRO CANADA EXPLORATION LTD.
 PCI ET AL BRAZEAU R
 LOCATION 2-12-48-13W5
 Element # 38407 880403



PETRO CANADA INC.
PCI ET AL BRAZEAU RIVER
LOCATION 2-12-48-13W5
Element # 38406 890912



PETRO CANADA EXPLORATION LTD.

LOCATION 4-8-48-13W5

Element # 18991 860923

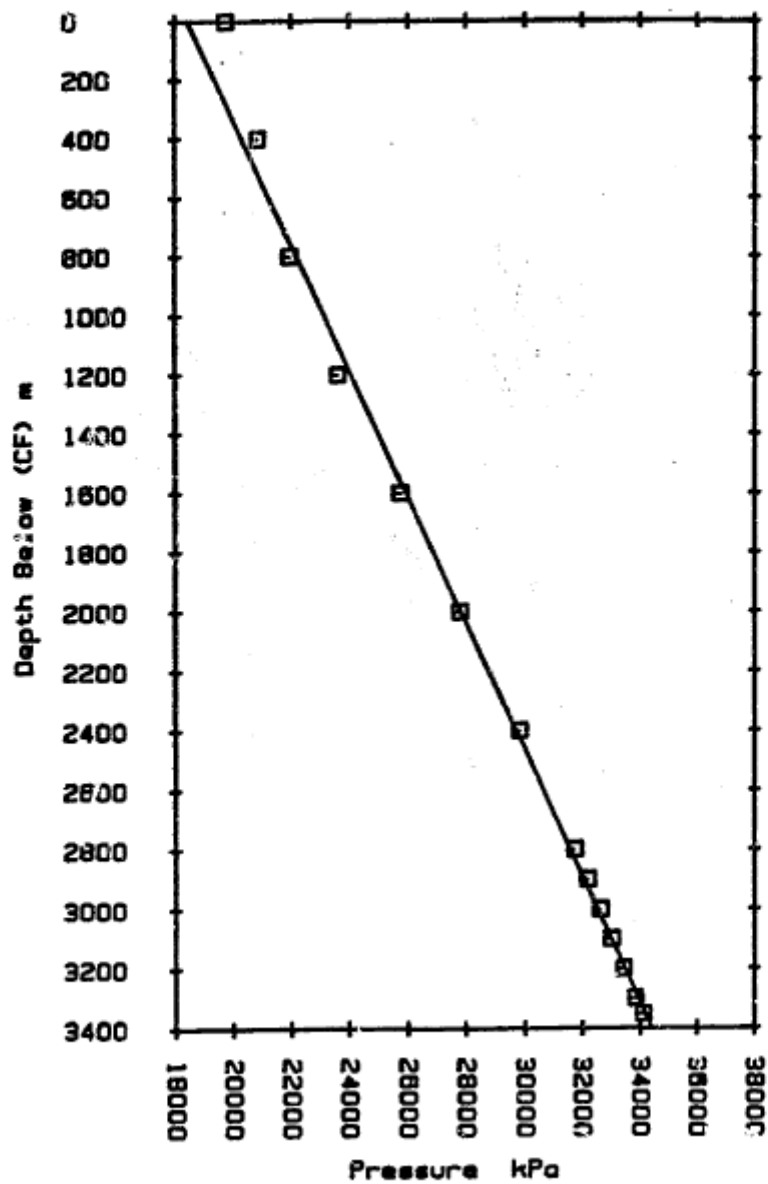
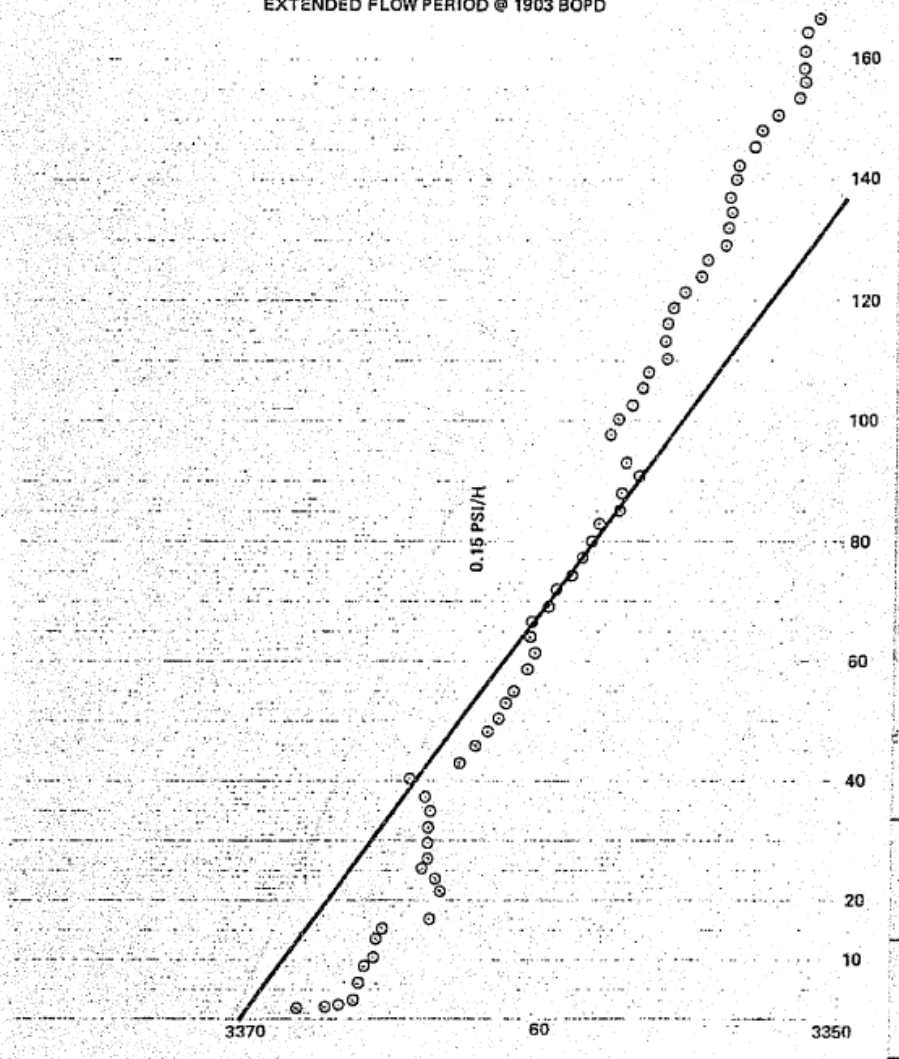


FIGURE 2C
 CHEVRON PEMBINA 6-25-50-10 W5M
 RESERVOIR DRAWDOWN DURING 168 HOUR
 EXTENDED FLOW PERIOD @ 1903 BOPD



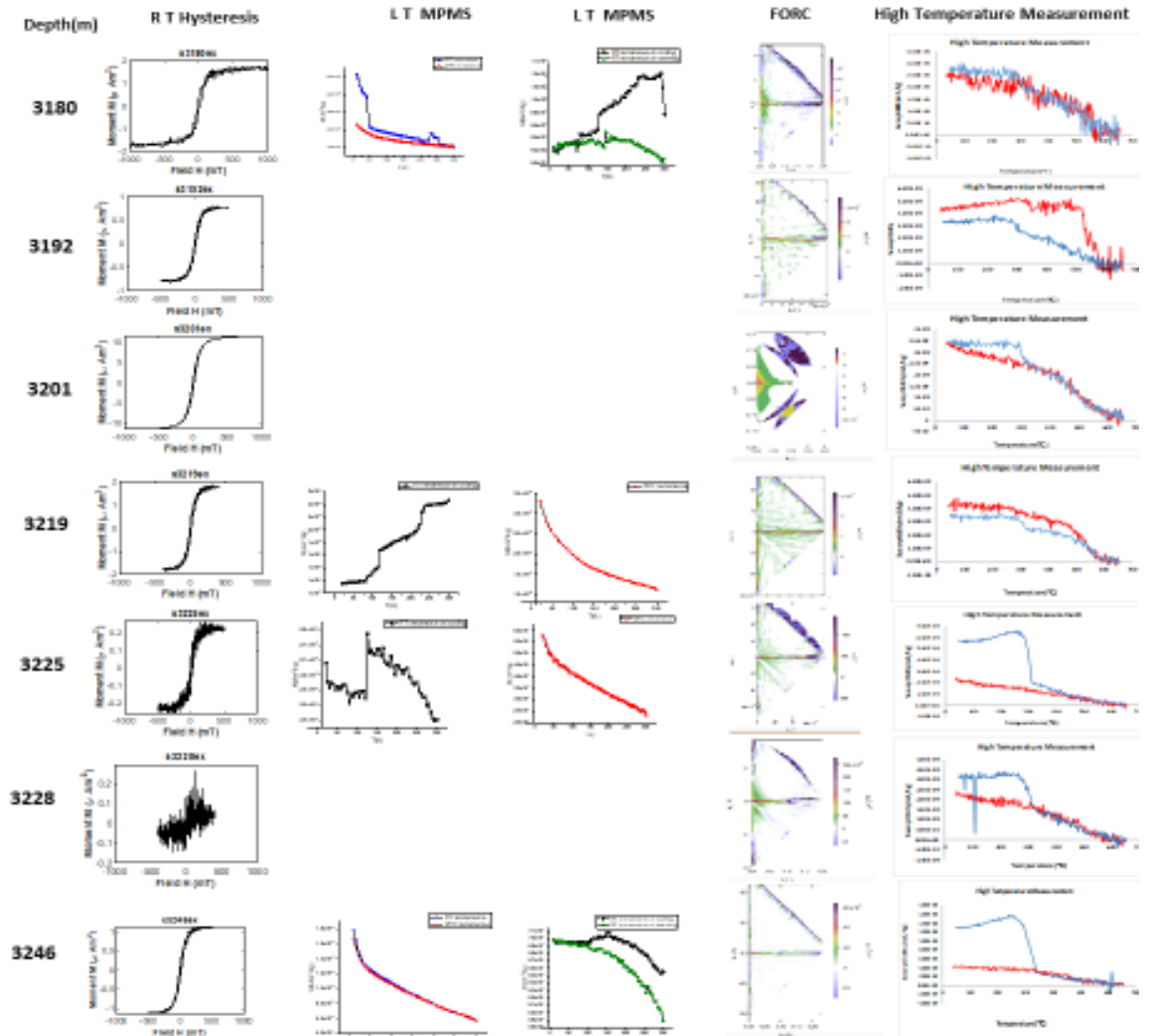
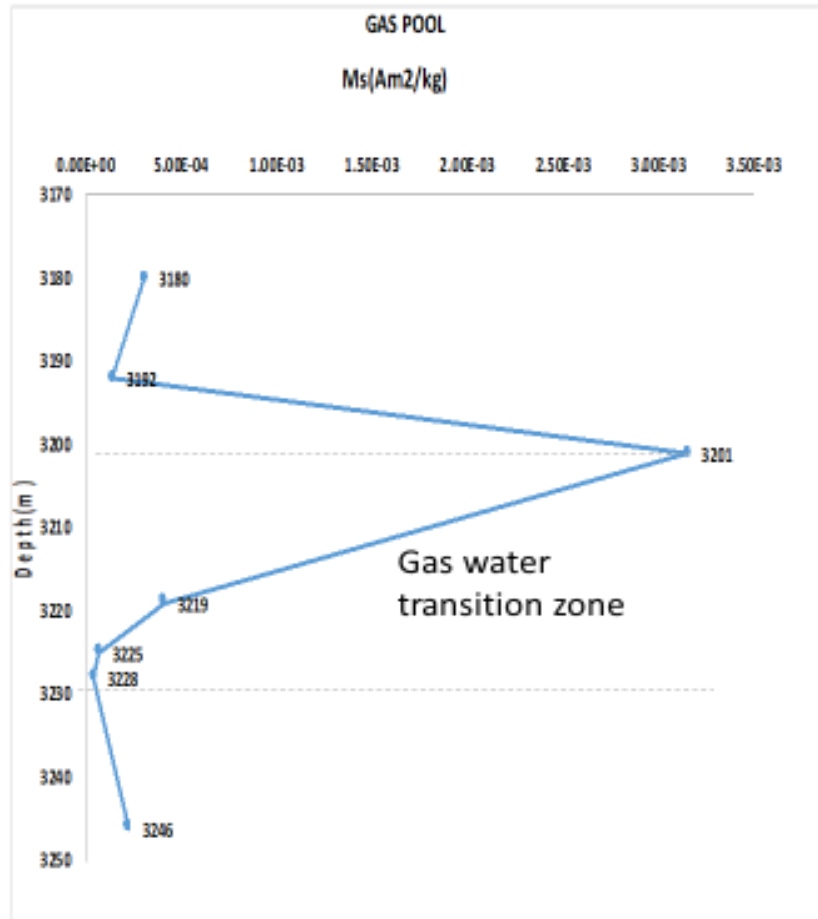
Appendix 3

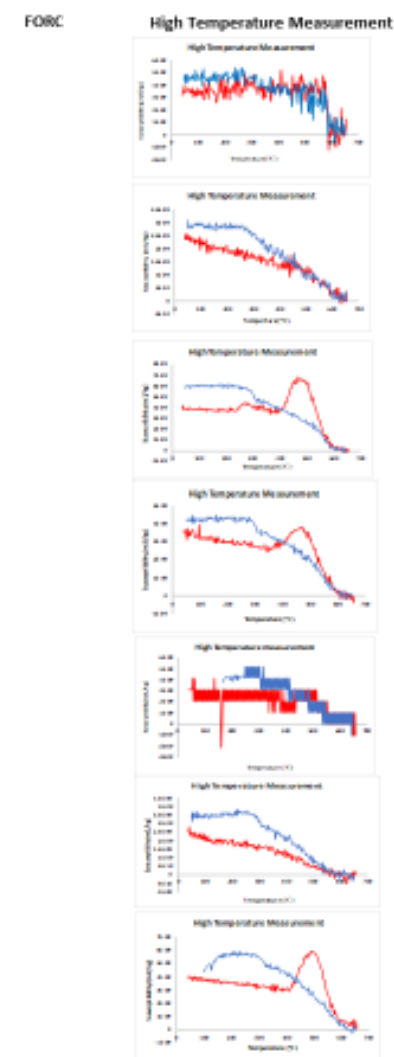
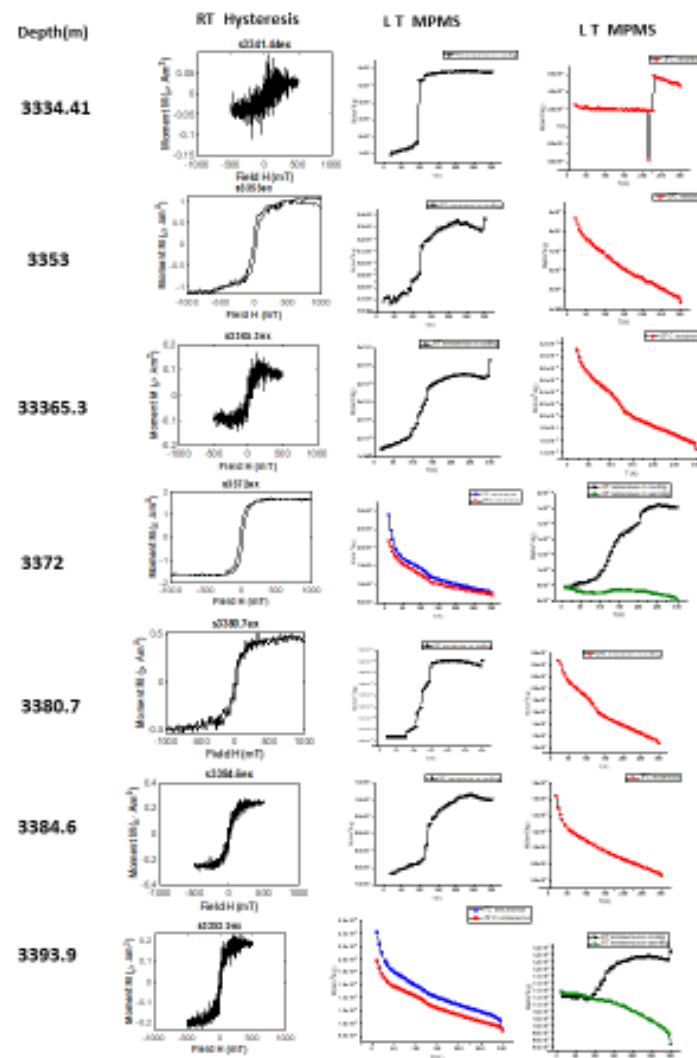
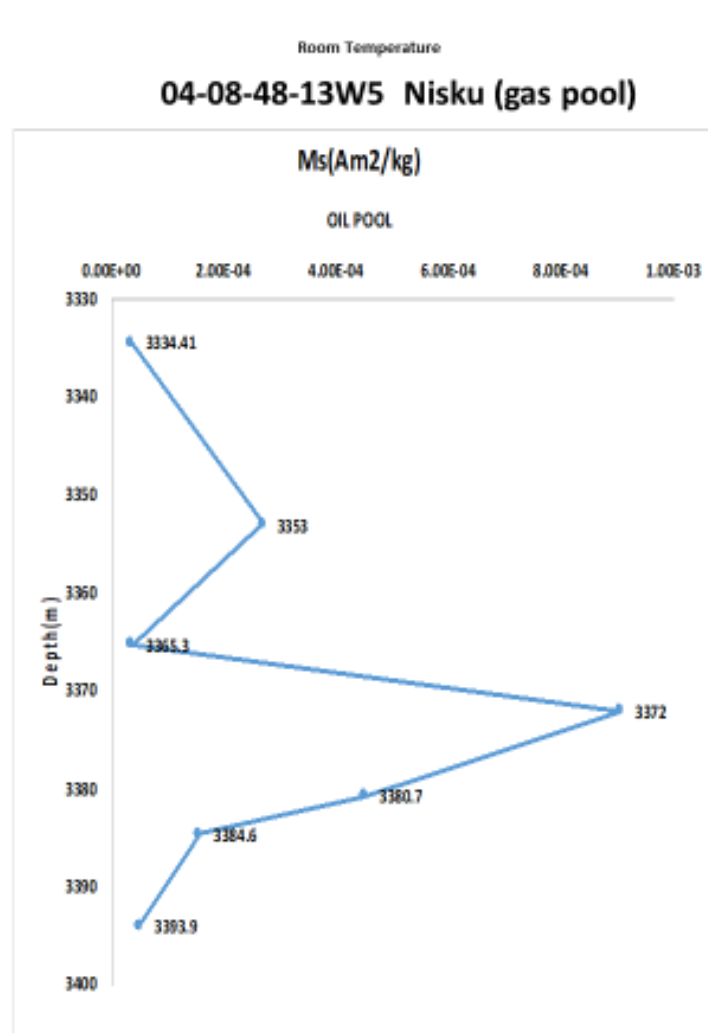
3.1 Hysteresis, FORC, Low temperature, magnetic Susceptibility vs Temperature

Well 02-12-48-13W5

Nisku

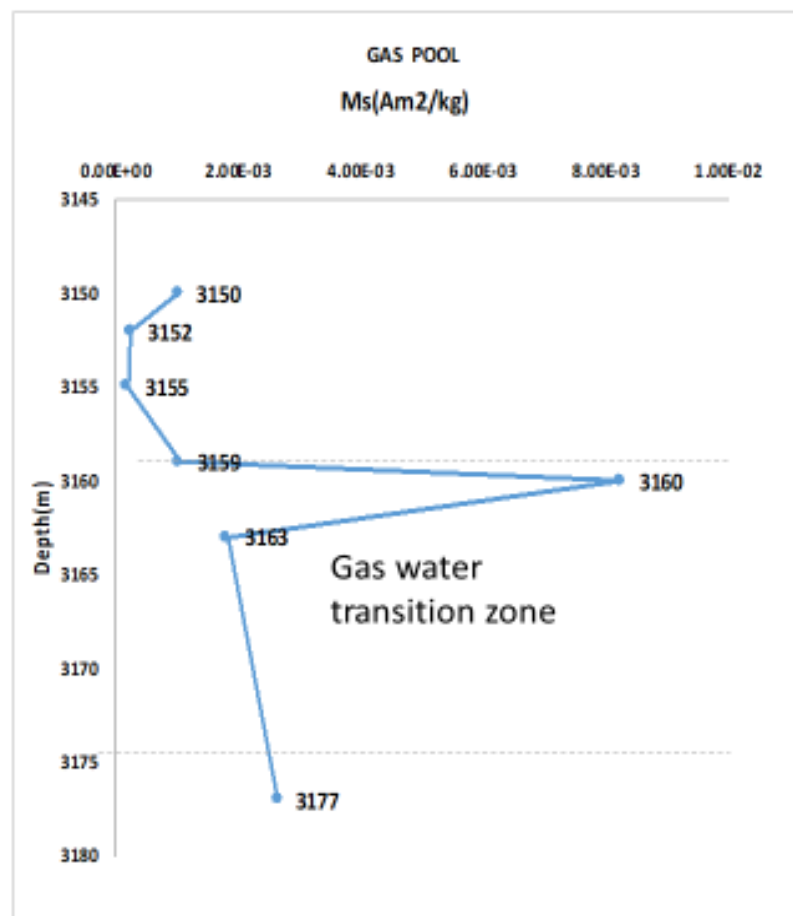
Room Temperature



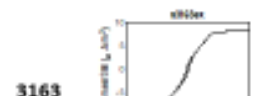
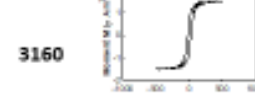
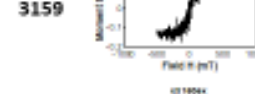
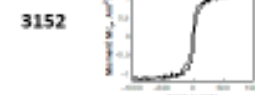
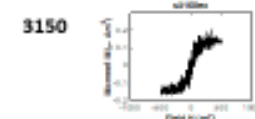


A2-19-12W5 Nisku

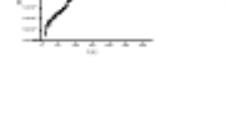
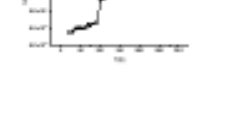
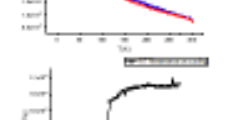
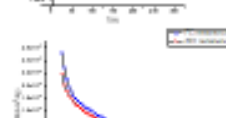
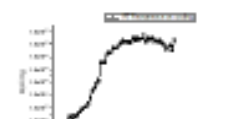
Room Temperature



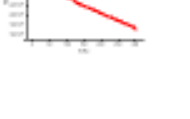
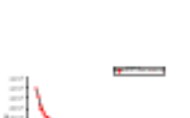
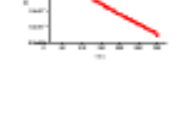
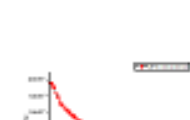
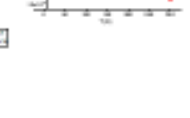
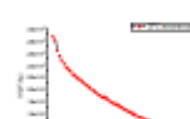
Depth(m) RT Hysteresis



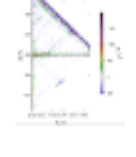
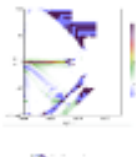
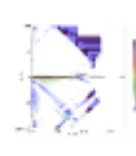
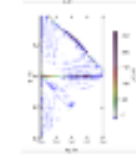
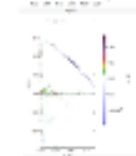
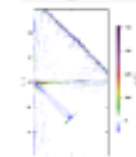
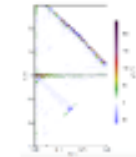
LT MPMS



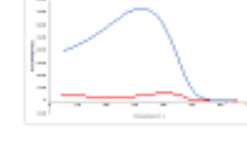
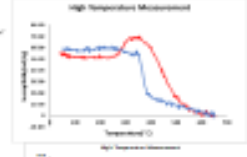
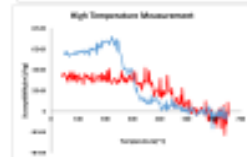
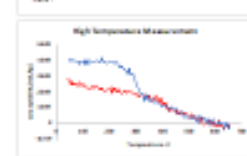
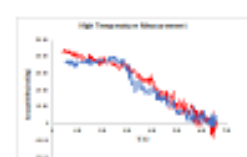
LT MPMS



FORC

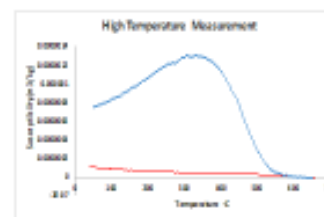
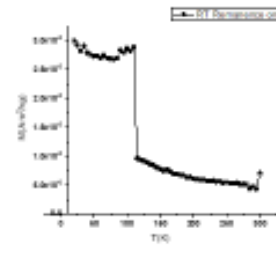
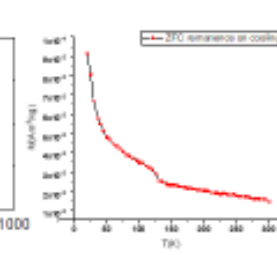
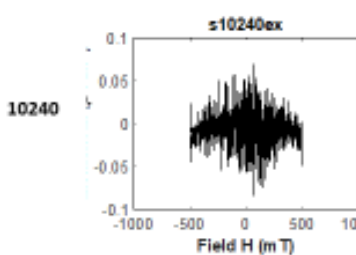
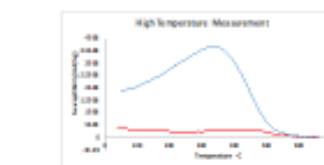
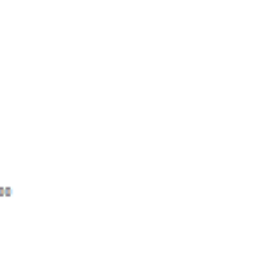
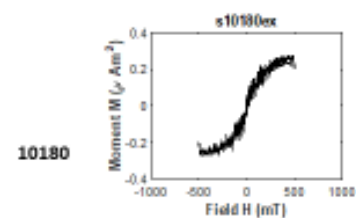
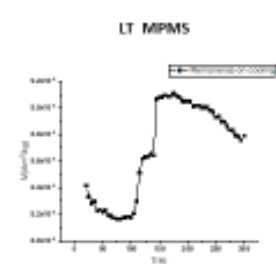
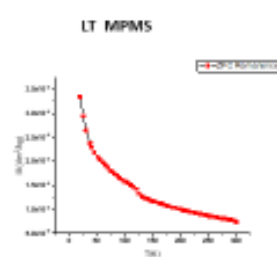
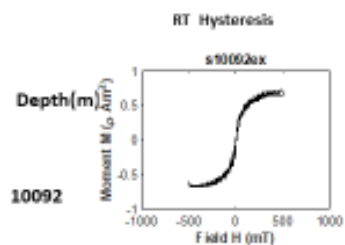
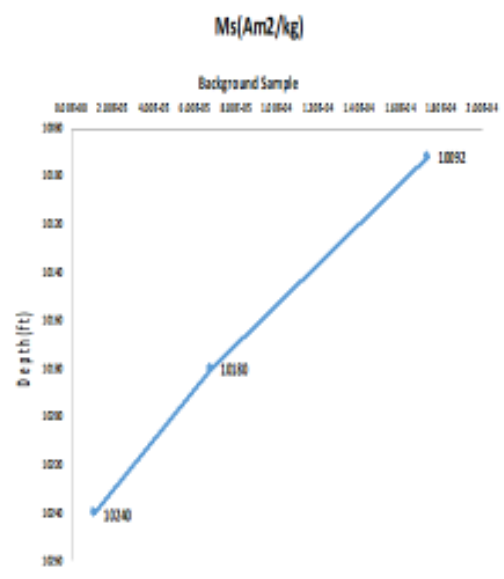


High Temperature Measurement



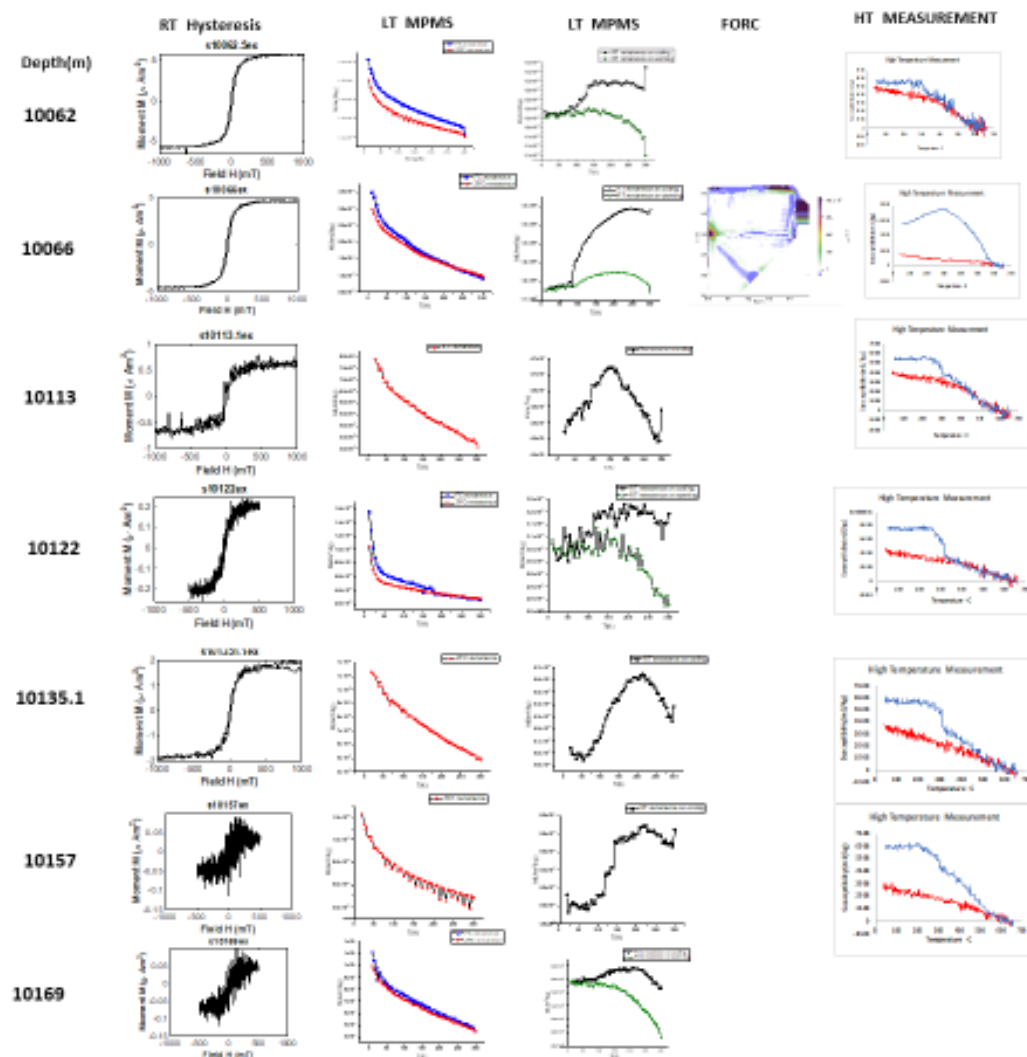
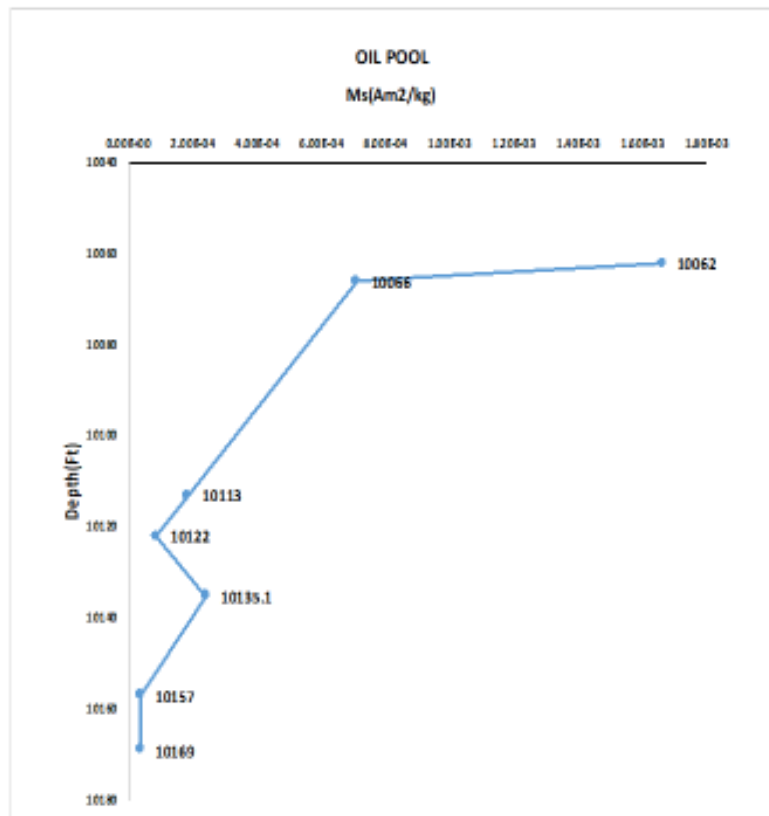
07-04-49-25W5 Nisku (background sample)

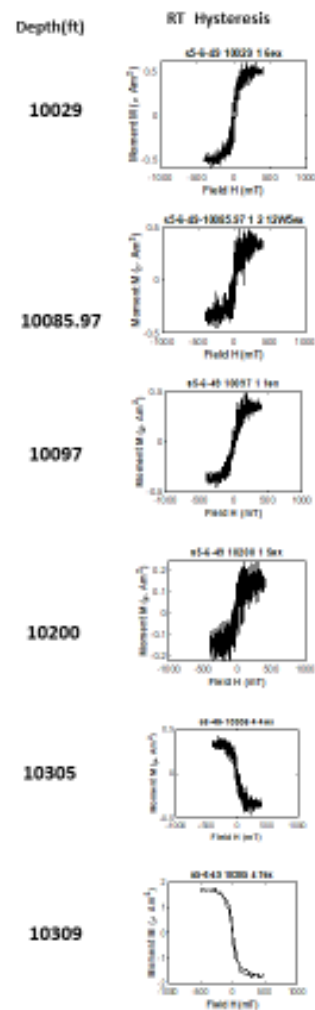
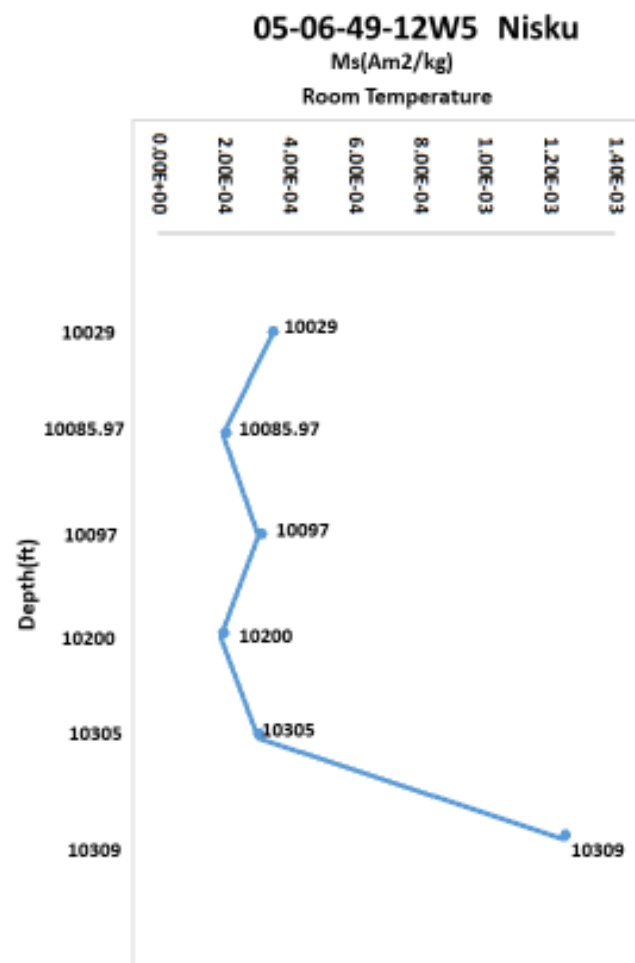
Room Temperature



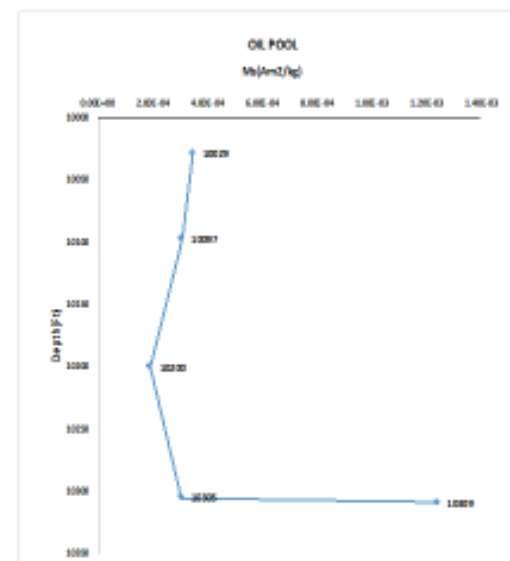
07-33-48-12W5 Nisku (oil pool)

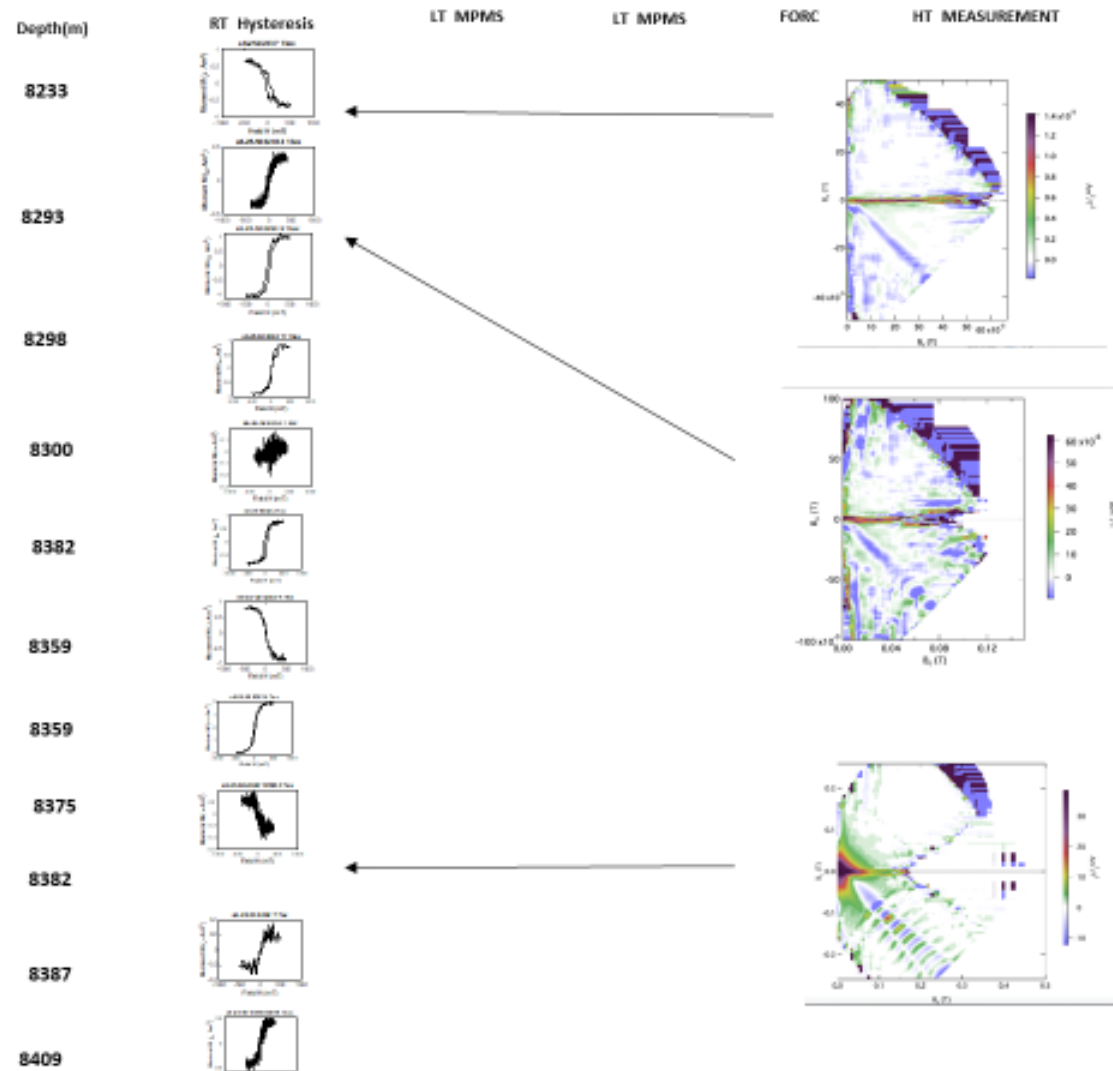
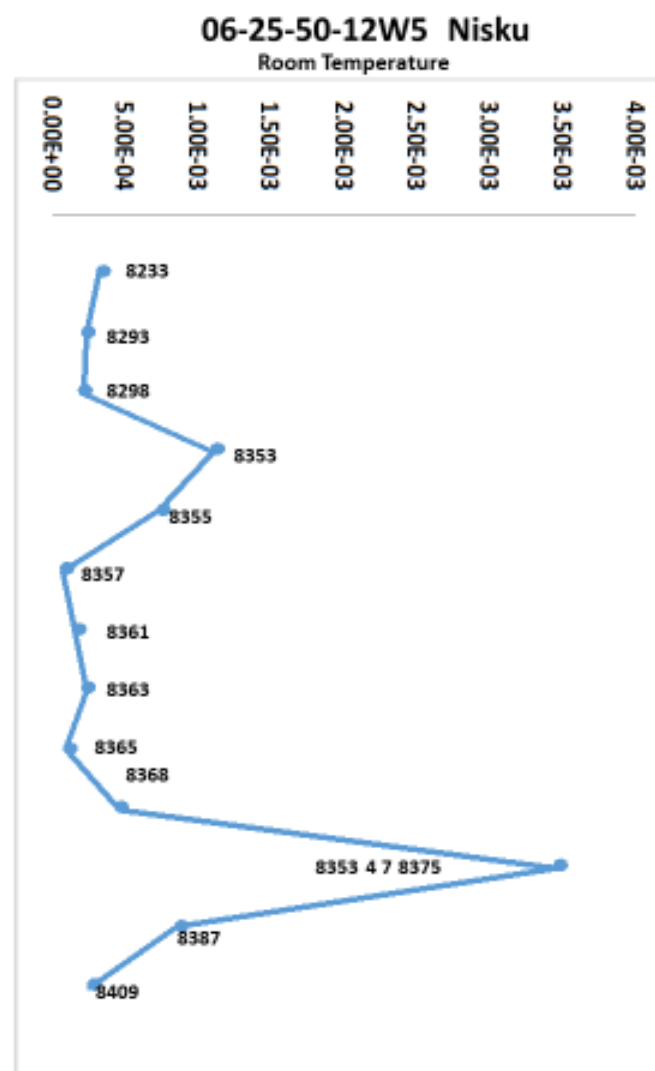
Room Temperature

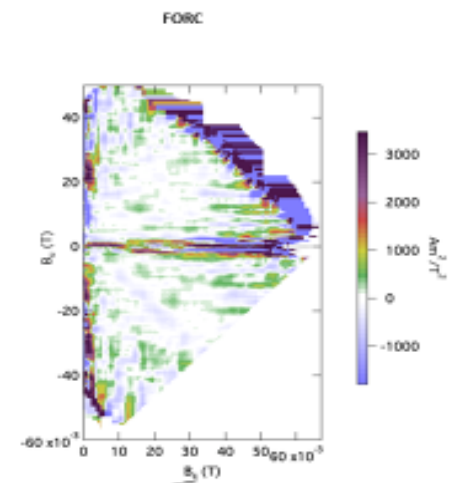
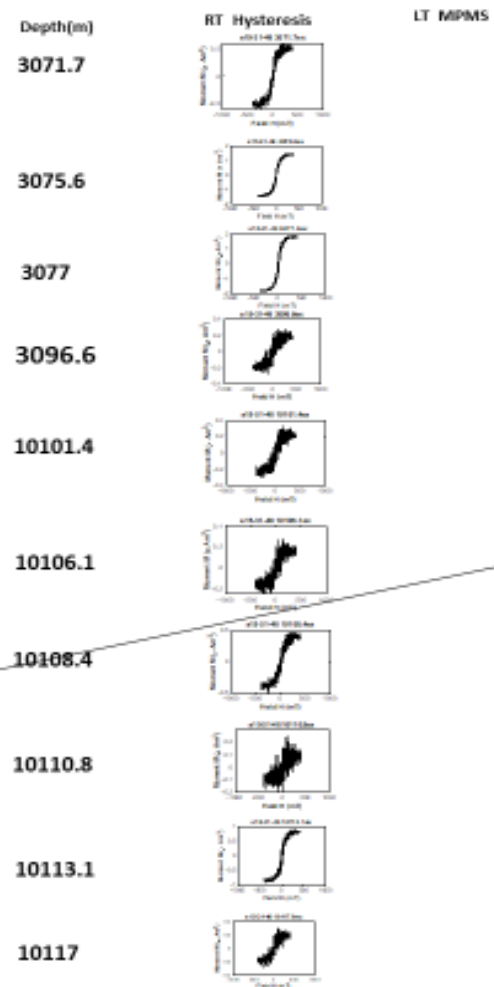
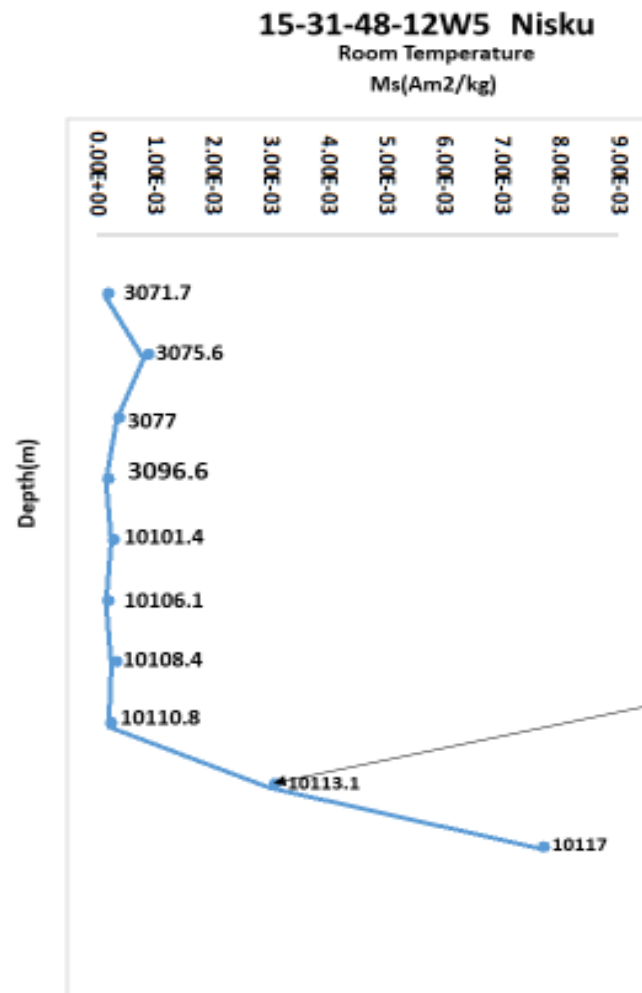


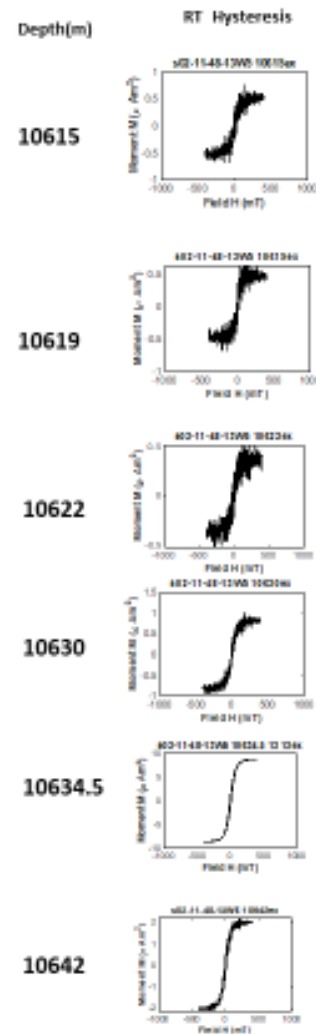
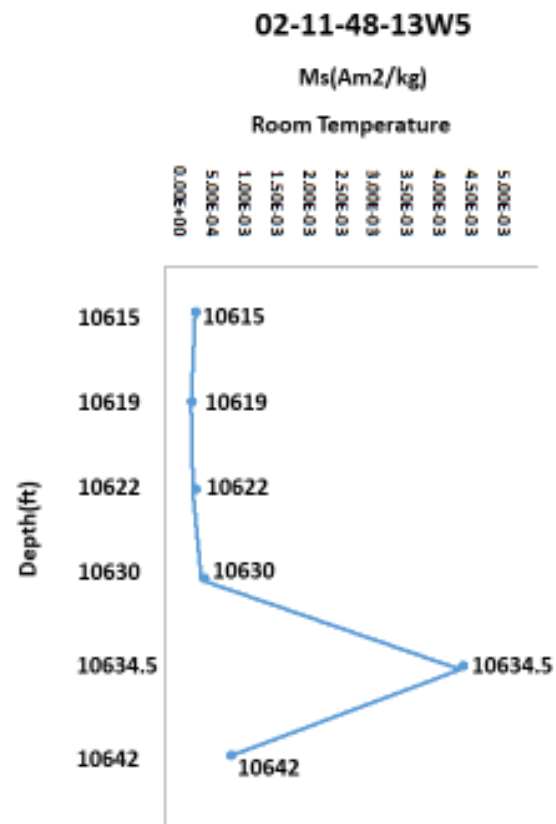


LT MPMS LT MPMS FORC HT MEASUREMENT









Paramagnetic behaviour

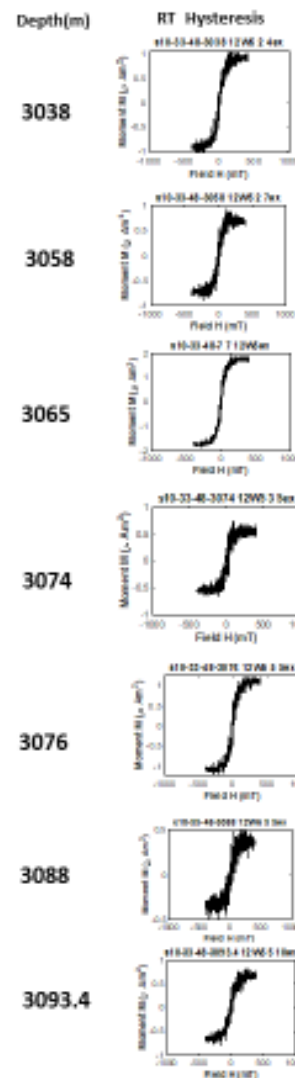
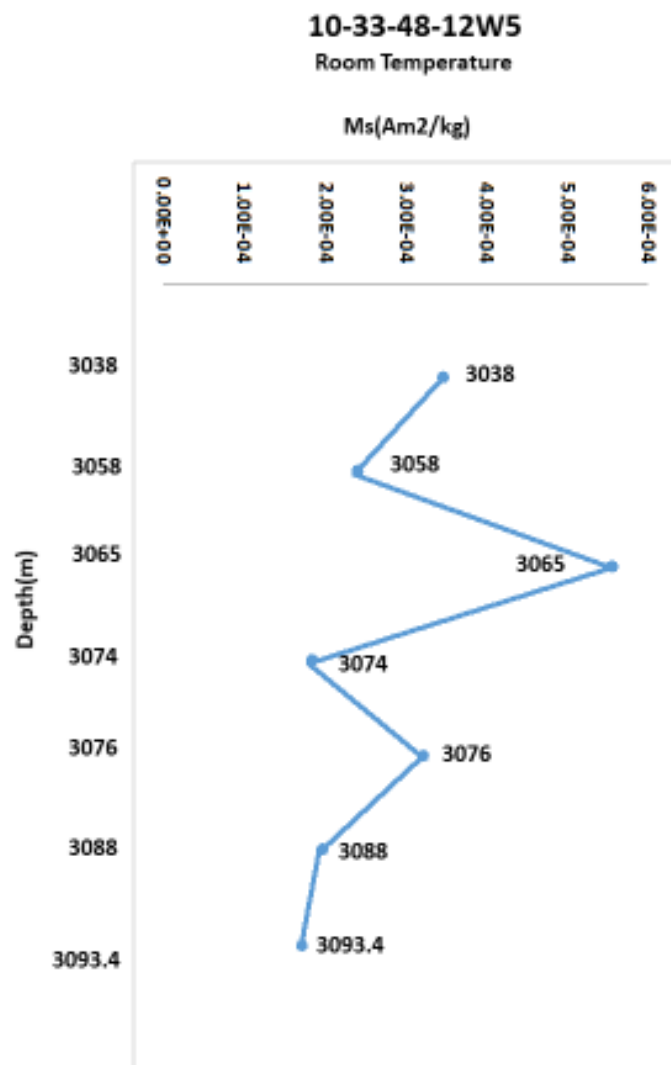
Paramagnetic behaviour

Paramagnetic behaviour

Paramagnetic behaviour

Paramagnetic behaviour

Paramagnetic behaviour



Paramagnetic behaviour

Paramagnetic behaviour

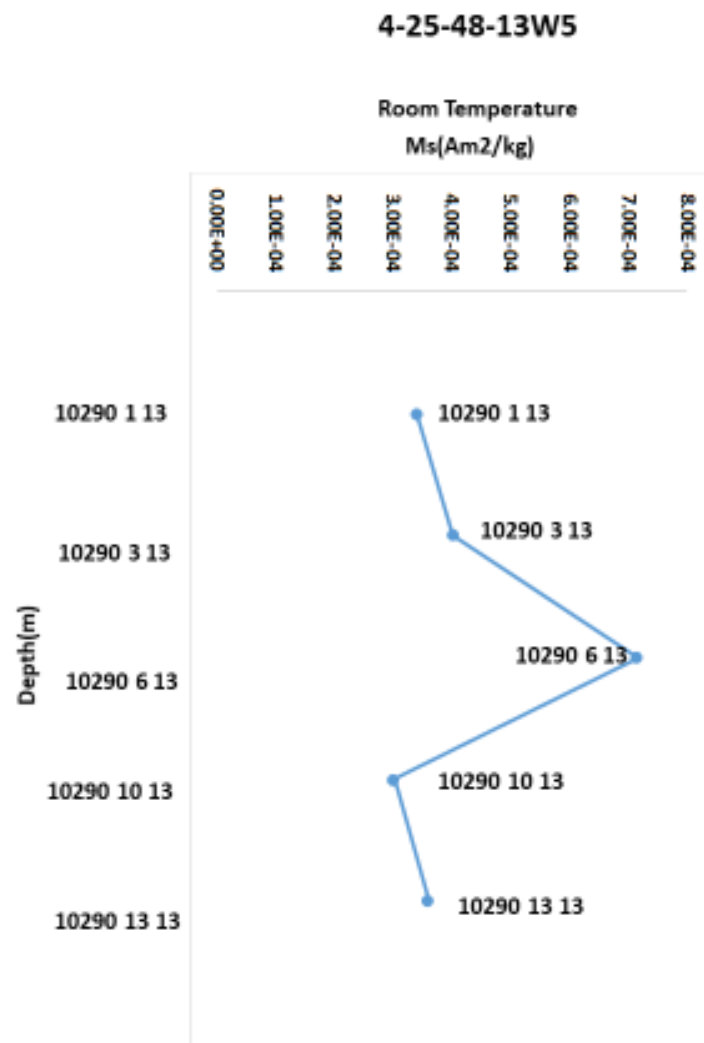
Paramagnetic behaviour

Paramagnetic behaviour

Paramagnetic behaviour

Paramagnetic behaviour

Paramagnetic behaviour



Depth(m)

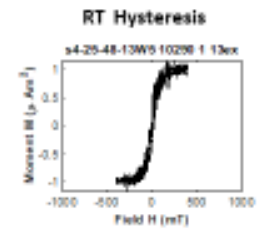
10290 1 13

10290 3 13

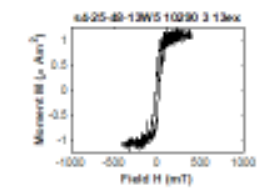
10290 6 13

10290 10 13

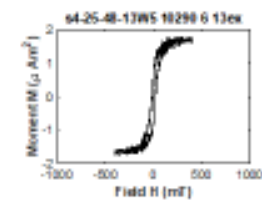
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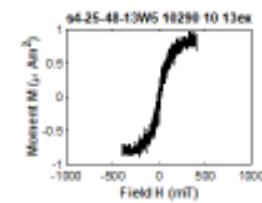
Paramagnetic behaviour



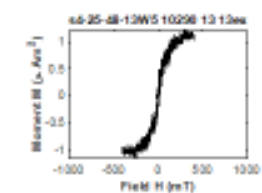
Paramagnetic behaviour



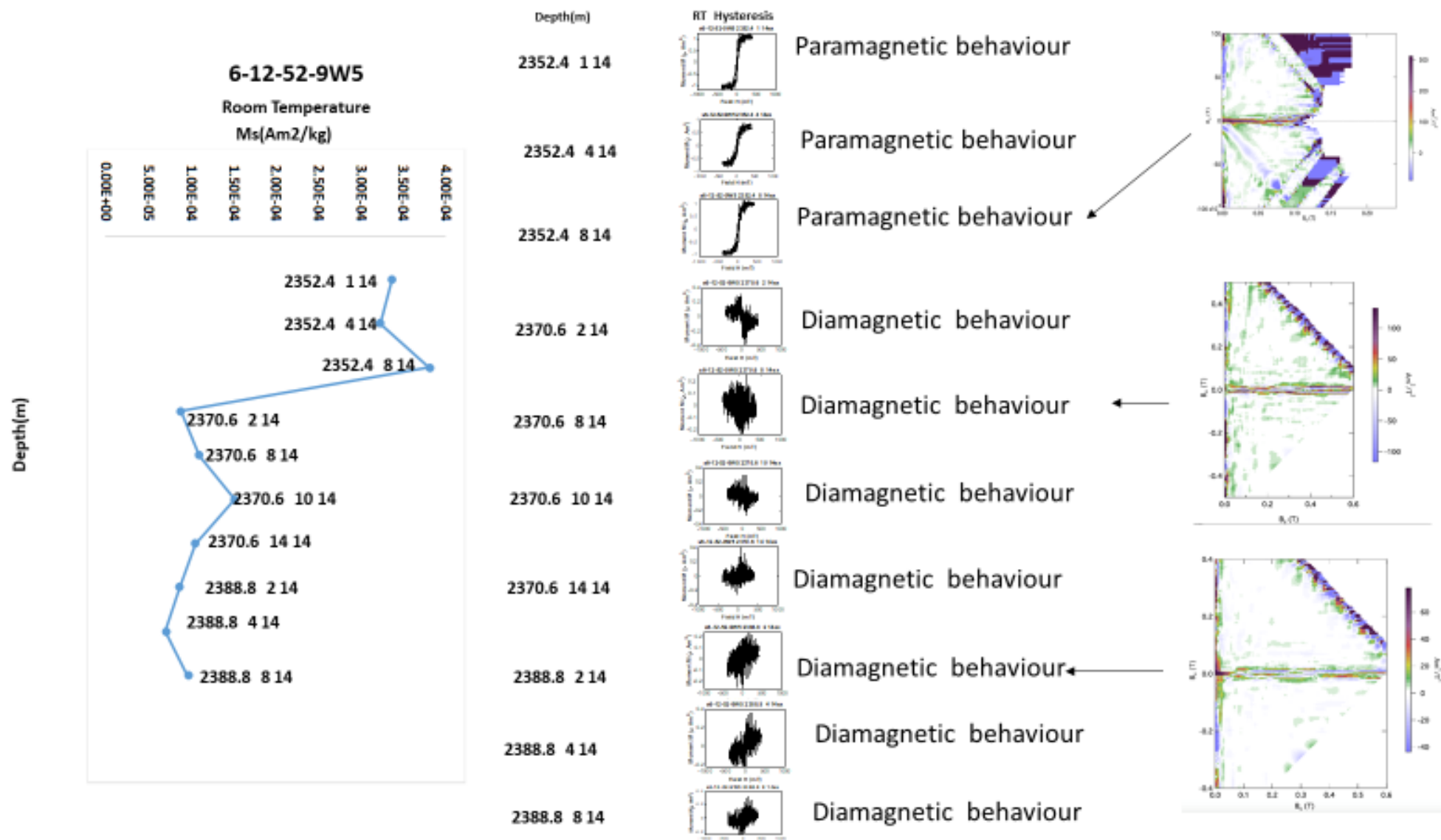
Paramagnetic behaviour



Paramagnetic behaviour

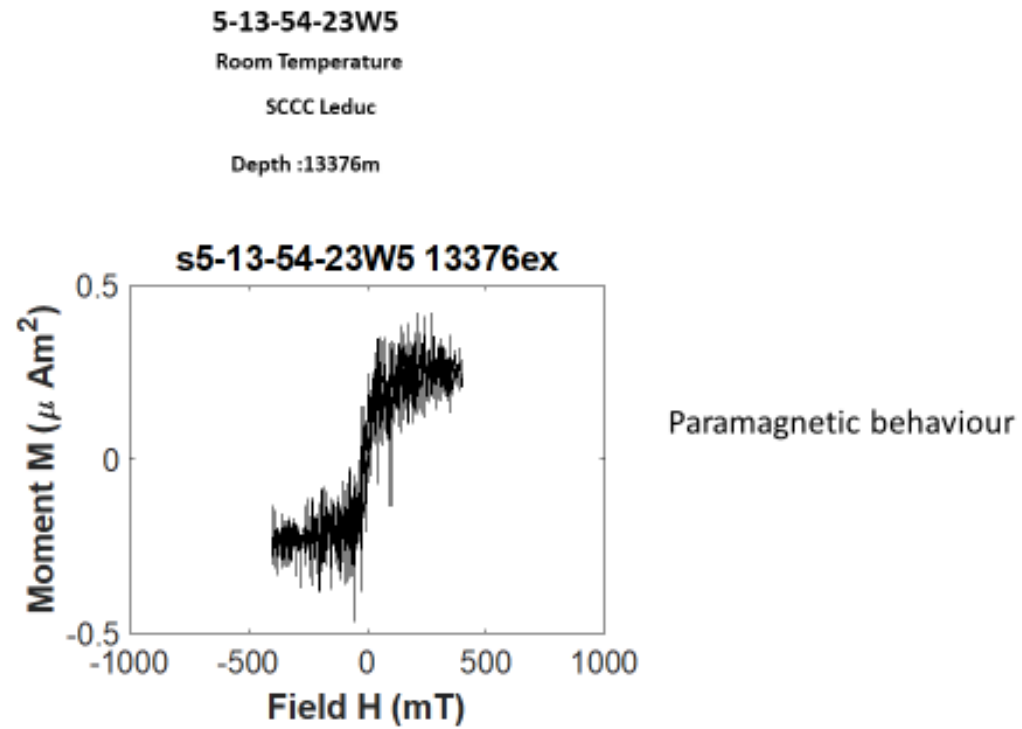


Paramagnetic behaviour



Appendix 4

4.1 Hysteresis

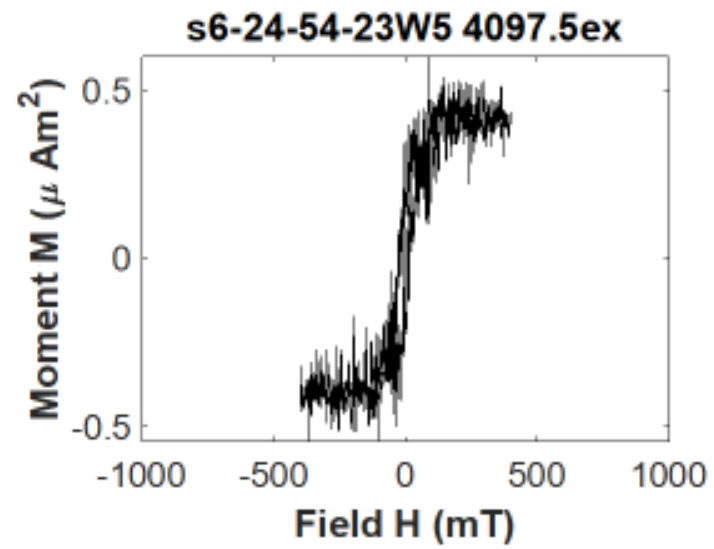


6-24-54-23W5

Room Temperature

SCCC Leduc

Depth :4097.5m



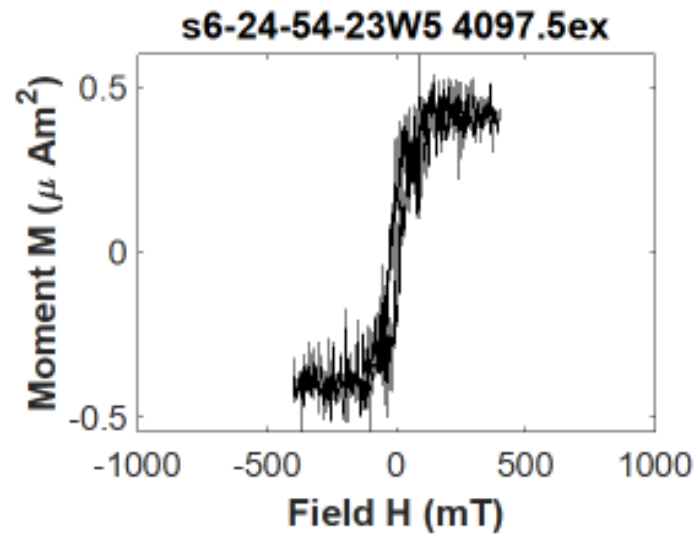
Paramagnetic behaviour

6-24-54-23W5

Room Temperature

SCCC Leduc

Depth :4097.5m



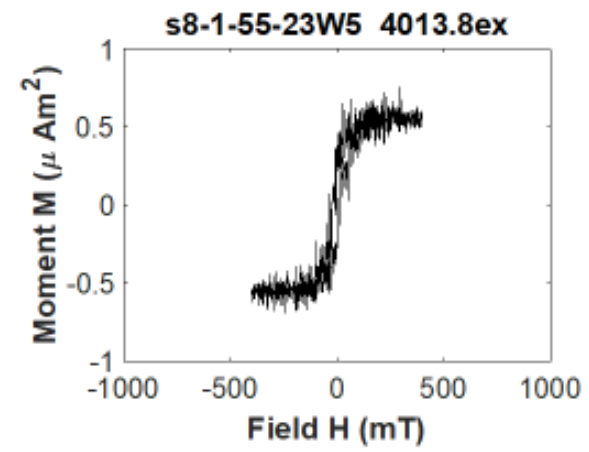
Paramagnetic behaviour

8-1-55-23W5

Room Temperature

SCCC Leduc

Depth :4097.5m



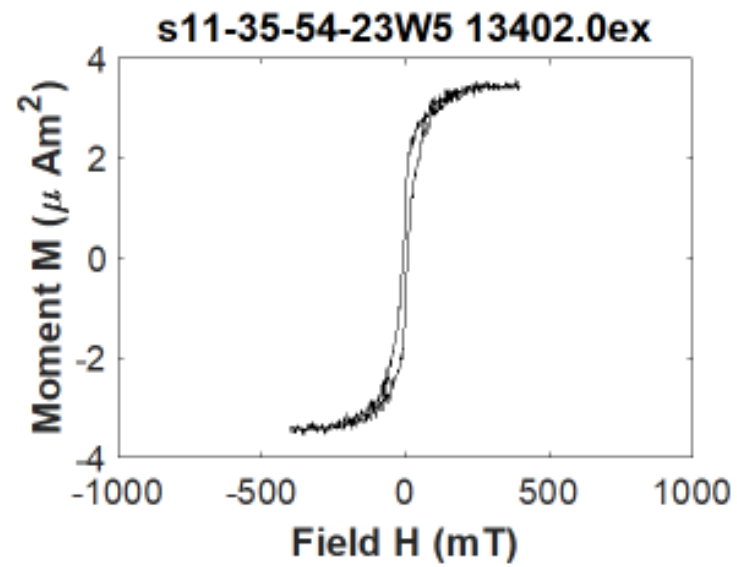
Paramagnetic behaviour

11-35-54-23W5

Room Temperature

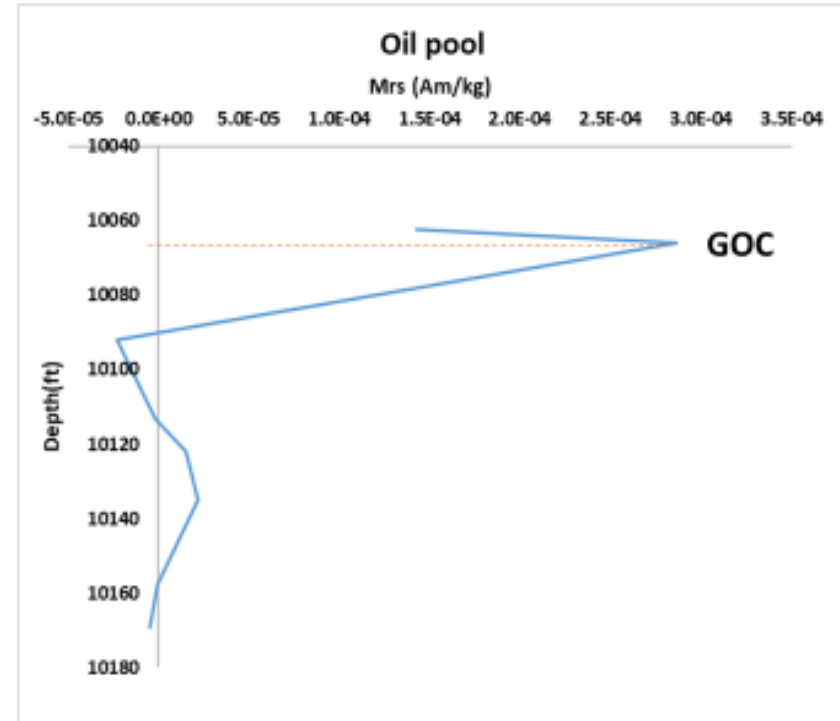
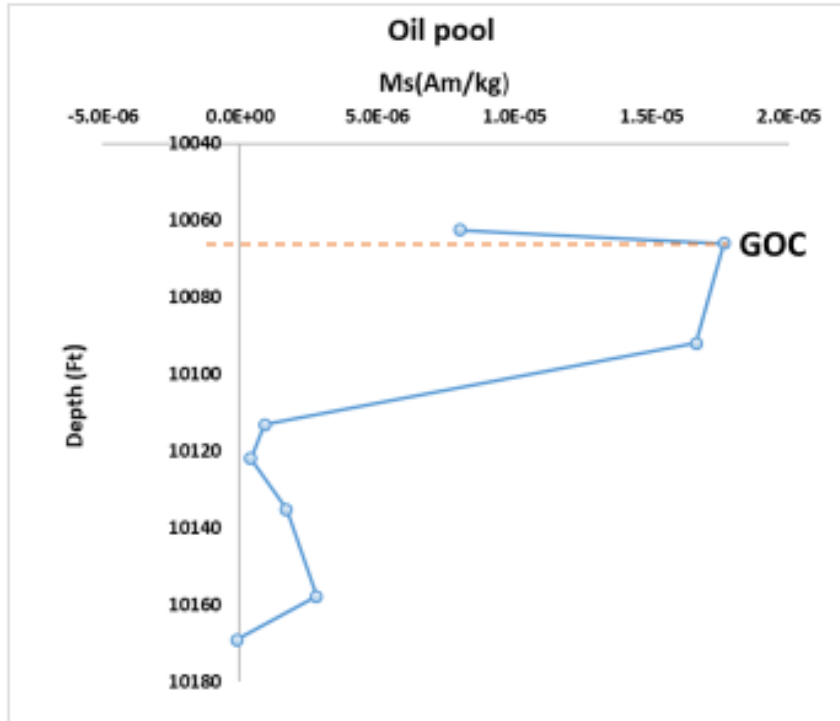
SCCC Leduc

Depth :13402.0m

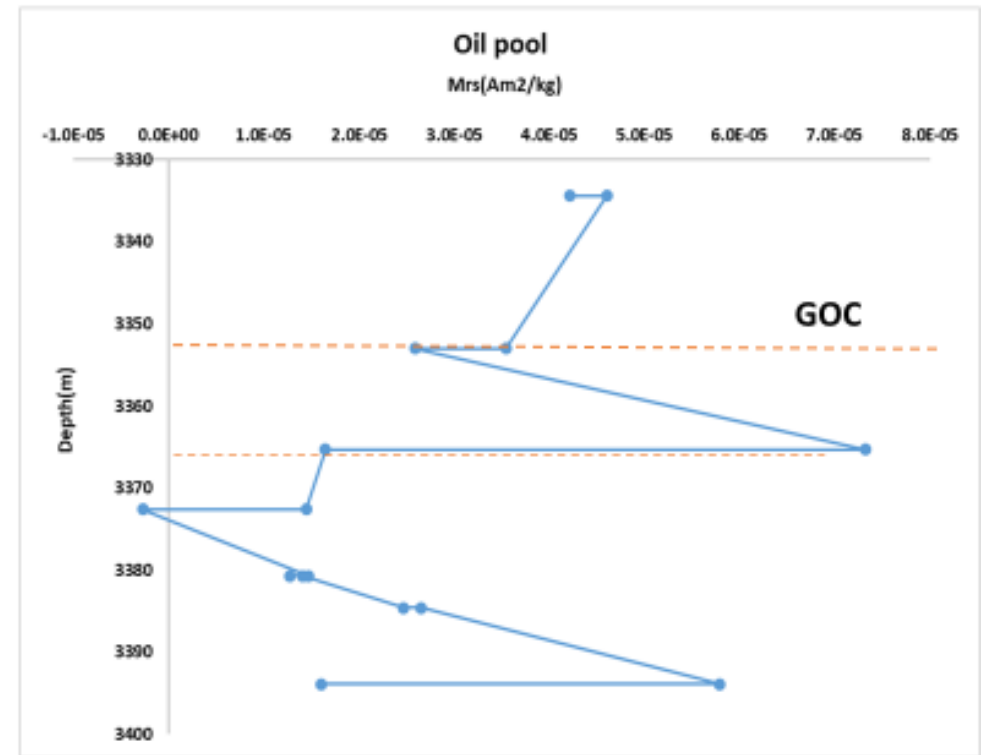
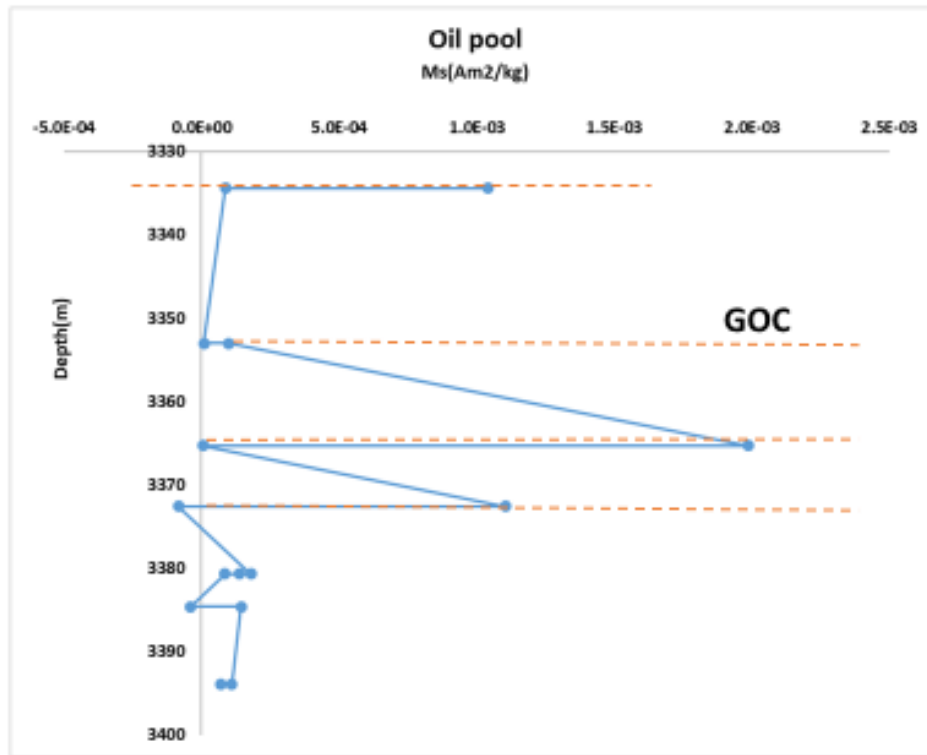


Paramagnetic behaviour

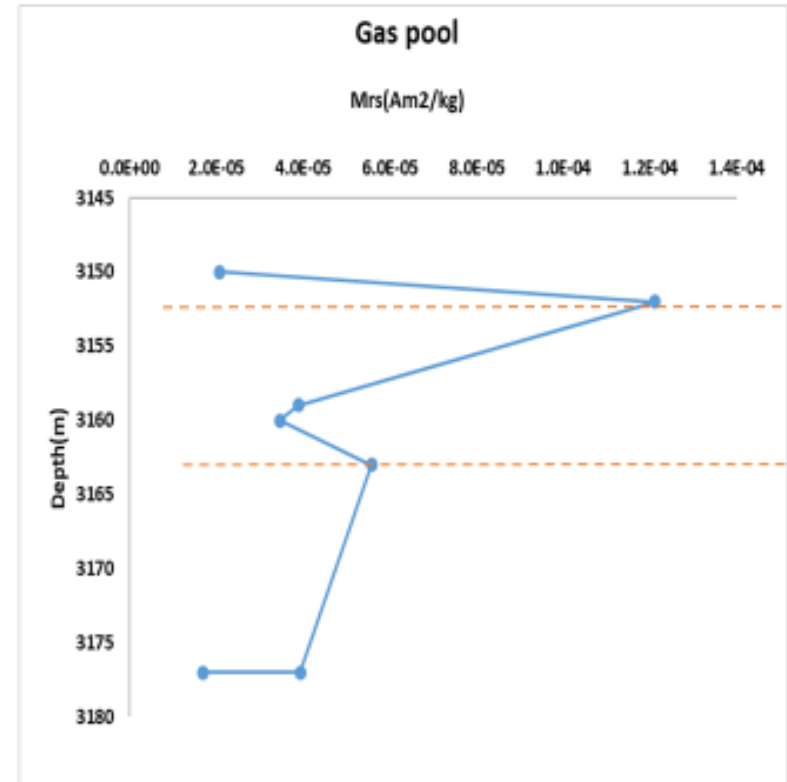
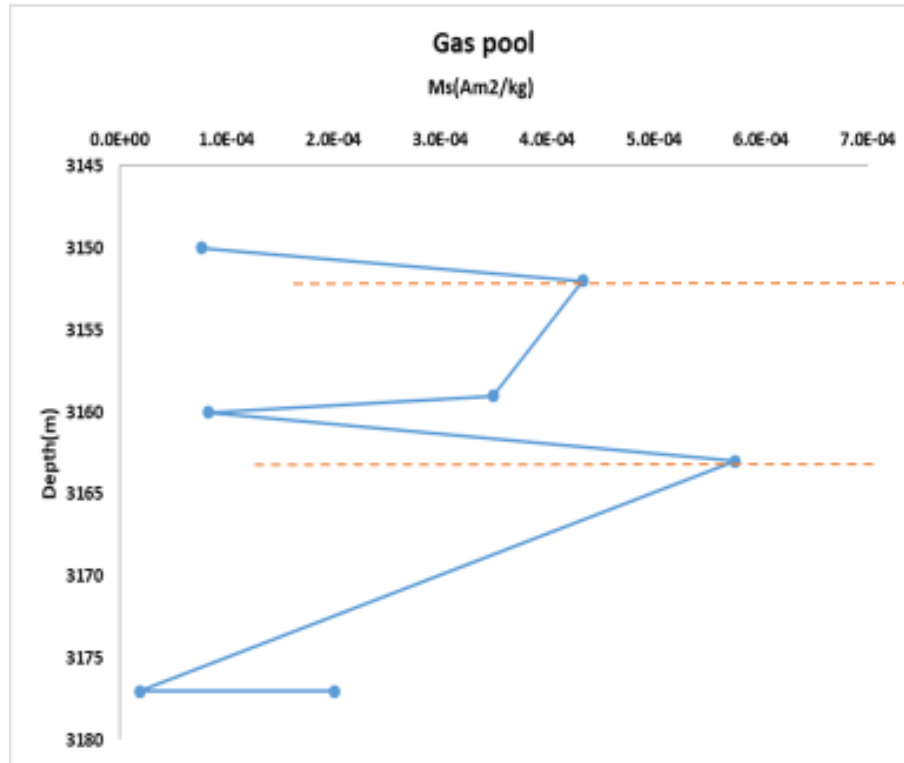
7-33-48-12W5



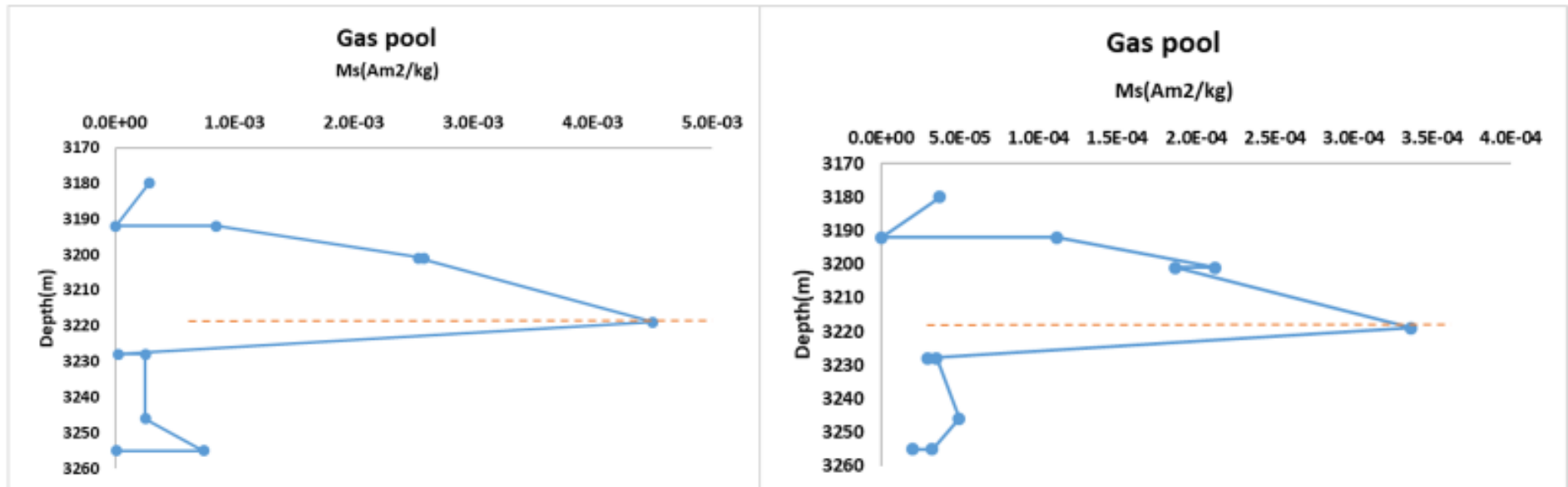
04-08-13-W5



A2-19-12-W5



02-12-48-13-W5



Saturation magnetization, coercivity for measured rock samples.

Sample name	Ms	Mrs	Mrs/Ms	Hc(mT)	Grain size	Well name	Well type
2-12-48-13W5 3210 3 7ex	6.94E-07	1.08E-07	0.16	9.70	Pseudo single domain	well 02-12-48	sour gas Well
02-12-3210-5-7ex	2.99E-06	3.85E-07	0.13	5.73	Pseudo single domain	well 02-12-48	sour gas Well
02-12-3210-7-7ex	1.72E-05	1.74E-06	0.10	5.70	Pseudo single domain	well 02-12-48	sour gas Well
02-12-3210ex	1.61E-06	2.93E-07	0.18	8.71	Pseudo single domain	well 02-12-48	sour gas Well
02-12-3219-1-7ex	1.64E-06	2.64E-07	0.16	6.73	Pseudo single domain	well 02-12-48	sour gas Well
02-12-3219-3-7ex	1.84E-06	2.56E-07	0.14	7.77	Pseudo single domain	well 02-12-48	sour gas Well
02-12-3219-5-7ex	1.90E-07	2.24E-09	0.01	75.36	Multi domain	well 02-12-48	sour gas Well
02-12-3228-3-7ex	2.05E-07	2.16E-08	0.11	127.79	Pseudo single domain	well 02-12-48	sour gas Well
3180ex	1.82E-06	2.03E-07	0.11	5.07	Pseudo single domain	well 02-12-48	sour gas Well
3192ex	8.08E-07	9.10E-08	0.11	8.30	Pseudo single domain	well 02-12-48	sour gas Well
3201ex	1.14E-05	9.24E-07	0.08	7.58	Multi domain	well 02-12-48	sour gas Well
3219ex	1.84E-06	2.56E-07	0.14	7.77	Pseudo single domain	well 02-12-48	sour gas Well
3225ex	2.60E-07	5.37E-08	0.21	9.05	Pseudo single domain	well 02-12-48	sour gas Well
3228ex	2.05E-07	2.16E-08	0.11	127.79	Pseudo single domain	well 02-12-48	sour gas Well
8223.4-13ex	9.31E-07	4.30E-07	0.46	16.68	Single domain	Well 06-25-50-12W5	oil pool
8233.10-13ex	8.35E-07	2.65E-07	0.32	12.82	Pseudo single domain	Well 06-25-50-12W5	oil pool
8233ex	4.53E-07	5.98E-08	0.13	15.43	Pseudo single domain	Well 06-25-50-12W5	oil pool
8293ex	3.78E-07	3.32E-08	0.09	17.29	Multi domain	Well 06-25-50-12W5	oil pool
8409.4-13ex	4.91E-07	8.30E-08	0.17	11.09	Pseudo single domain	Well 06-25-50-12W5	oil pool
8409ex	1.79E-07	4.29E-08	0.24	125.58	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50 8233 7 13ex	3.79E-07	5.74E-08	0.15	21.60	Pseudo single domain	Well 06-25-50-12W5	oil pool
A2-19-3163ex	2.22E-06	9.84E-07	0.44	17.73	Pseudo single domain	Well A2-19	sour gas Well
A2-19ex	3.91E-07	6.41E-08	0.16	5.80	Pseudo single domain	Well A2-19	sour gas Well
3246ex	1.14E-06	1.37E-07	0.12	6.84	Pseudo single domain	Well A2-19	sour gas Well
3150ex	1.92E-07	7.25E-09	0.04	18.03	Multi domain	Well A2-19	sour gas Well
3152ex	1.16E-06	2.62E-07	0.23	10.11	Pseudo single domain	Well A2-19	sour gas Well
3153ex	1.32E-07	8.44E-09	0.06	28.36	Multi domain	Well A2-19	sour gas Well
3155ex	3.91E-07	6.41E-08	0.16	5.80	Pseudo single domain	Well A2-19	sour gas Well
3159ex	1.92E-07	3.80E-08	0.20	13.18	Pseudo single domain	Well A2-19	sour gas Well
3160ex	1.51E-06	6.63E-07	0.44	20.85	Pseudo single domain	Well A2-19	sour gas Well
3163ex	8.15E-06	7.29E-07	0.09	12.62	Multi domain	Well A2-19	sour gas Well
3177ex	4.94E-07	3.97E-08	0.08	3.43	Multi domain	Well A2-19	sour gas Well
3341.44ex	1.03E-07	4.94E-09	0.05	126.69	Multi domain	Well 04-08-48-13W5	sweet gas pool
3353ex	1.15E-06	2.91E-07	0.25	15.14	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
3365.3ex	1.58E-07	5.27E-08	0.33	24.98	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
3372.6ex	3.99E-06	5.56E-07	0.14	27.62	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
3377ex	1.72E-06	5.22E-07	0.30	12.63	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
3380.6ex	5.24E-07	7.96E-08	0.15	10.07	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
3384.6ex	2.83E-07	4.03E-08	0.14	10.31	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
3393.9ex	2.34E-07	3.83E-08	0.16	11.35	Pseudo single domain	Well 04-08-48-13W5	sweet gas pool
10092ex	7.11E-07	5.01E-08	0.07	1.96	Multi domain	Well 07-04-49-25W5	Dry well
10180ex	2.77E-07	1.74E-08	0.06	15.54	Multi domain	Well 07-04-49-25W5	Dry well
10240ex	7.69E-08	6.72E-09	0.09	210.33	Multi domain	Well 07-04-49-25W5	Dry well
10062.5ex	6.22E-06	8.42E-07	0.14	10.13	Pseudo single domain	Well 07-33-48-12W5	oil pool
10066ex	4.77E-06	7.33E-07	0.15	7.59	Pseudo single domain	Well 07-33-48-12W5	oil pool
10113.1ex	8.00E-07	3.56E-08	0.04	17.53	Multi domain	Well 07-33-48-12W5	oil pool
10120ex	2.16E-07	5.49E-08	0.25	42.73	Pseudo single domain	Well 07-33-48-12W5	oil pool
10122ex	2.52E-07	2.19E-08	0.09	11.49	Multi domain	Well 07-33-48-12W5	oil pool
10157ex	1.03E-07	1.16E-08	0.11	78.80	Pseudo single domain	Well 07-33-48-12W5	oil pool
10169ex	1.11E-07	9.87E-09	0.09	89.47	Multi domain	Well 07-33-48-12W5	oil pool
101351.1ex	1.99E-06	2.60E-07	0.13	5.07	Pseudo single domain	Well 07-33-48-12W5	oil pool
6-25-50 8353 7 7ex	1.91E-07	4.61E-08	0.24	148.01	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-8382 2 7ex	8.31E-07	2.86E-07	0.34	17.49	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50 8293 9 13ex	1.14E-06	3.15E-07	0.28	18.25	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50 8293 11 13ex	9.25E-07	1.59E-07	0.17	1.36	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50-10W5 8353 1 7ex	4.36E-07	1.35E-07	0.31	37.83	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50-10W5 8409 9 13ex	5.41E-07	9.16E-08	0.17	28.28	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50-8382 10W5 4 7ex	4.12E-07	7.23E-08	0.18	26.94	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50-8382 4 7ex	9.02E-07	6.23E-08	0.07	21.51	Multi domain	Well 06-25-50-12W5	oil pool
6-25-50-8382 7 7ex	3.39E-07	7.89E-10	0.00	26.38	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50 8293 4 13ex	4.21E-07	6.99E-08	0.17	19.01	Pseudo single domain	Well 06-25-50-12W5	oil pool
6-25-50 8353 4 7ex	1.95E-06	3.78E-07	0.19	1.86	Pseudo single domain	Well 06-25-50-12W5	oil pool
15-31-48 10108.4ex	4.95E-07	8.90E-08	0.18	13.58	Pseudo single domain	Well 15-31-48-12W5	oil pool
15-31-48 10110.8ex	2.24E-07	9.16E-09	0.04	73.77	Multi domain	Well 15-31-48-12W5	oil pool
15-31-48 10113.1ex	9.16E-07	1.88E-07	0.21	11.83	Pseudo single domain	Well 15-31-48-12W5	oil pool
15-31-48 10117.9ex	2.93E-07	4.90E-08	0.17	39.17	Pseudo single domain	Well 15-31-48-12W5	oil pool
15-31-48 3071.7ex	6.05E-07	4.46E-08	0.07	8.41	Multi domain	Well 15-31-48-12W5	oil pool
15-31-48 3075.6ex	1.51E-06	2.26E-07	0.15	9.83	Pseudo single domain	Well 15-31-48-12W5	oil pool
15-31-48 3077.0ex	1.88E-06	3.40E-07	0.18	9.29	Pseudo single domain	Well 15-31-48-12W5	oil pool
15-31-48 3096.6ex	2.77E-07	2.61E-08	0.09	40.87	Multi domain	Well 15-31-48-12W5	oil pool
15-31-48 10101.4ex	3.21E-07	2.26E-08	0.07	25.98	Multi domain	Well 15-31-48-12W5	oil pool
15-31-48 10106.1ex	2.64E-07	1.69E-08	0.06	36.01	Multi domain	Well 15-31-48-12W5	oil pool
5-6-49-10085.97 1 2 12W5ex	4.76E-07	1.58E-07	0.33	27.70	Pseudo single domain	Well 05-06-49-12W5	oil pool
5-6-49-10305 4 4ex	4.38E-07	2.82E-08	0.06	10.39	Multi domain	Well 05-06-49-12W5	oil pool
5-6-49 10305 4 7ex	1.79E-06	9.05E-08	0.05	21.44	Multi domain	Well 05-06-49-12W5	oil pool
5-6-49 10029 1 6ex	6.09E-07	1.17E-07	0.19	19.13	Pseudo single domain	Well 05-06-49-12W5	oil pool
5-6-49 10097 1 1ex	4.78E-07	2.63E-08	0.06	10.75	Multi domain	Well 05-06-49-12W5	oil pool
5-6-49 10200 1 5ex	2.37E-07	1.33E-08	0.06	34.94	Multi domain	Well 05-06-49-12W5	oil pool
02-11-48-13W5 10615ex	7.21E-07	1.91E-07	0.27	14.46	Pseudo single domain	Well 02-11-48-13W5	sour gas Well
02-11-48-13W5 10619ex	6.57E-07	1.36E-07	0.21	14.50	Pseudo single domain	Well 02-11-48-13W5	sour gas Well
02-11-48-13W5 10622ex	5.21E-07	4.60E-08	0.09	10.99	Multi domain	Well 02-11-48-13W5	sour gas Well
02-11-48-13W5 10630ex	9.78E-07	1.39E-07	0.14	5.87	Pseudo single domain	Well 02-11-48-13W5	sour gas Well
02-11-48-13W5 10634.5 13 13ex	8.72E-06	8.70E-07	0.10	5.82	Pseudo single domain	Well 02-11-48-13W5	sour gas Well
02-11-48-13W5 10642ex	2.15E-06	2.81E-07	0.13	9.87	Pseudo single domain	Well 02-11-48-13W5	sour gas Well
10-33-48-7 7 12W5ex	1.92E-06	3.51E-07	0.18	6.78	Pseudo single domain	Well 10-33-48-12W5	oil pool
10-33-48-3038 12W5 2 4ex	1.04E-06	1.35E-07	0.13	13.29	Pseudo single domain	Well 10-33-48-12W5	oil pool
10-33-48-3058 12W5 2 7ex	9.19E-07	2.10E-07	0.23	13.62	Pseudo single domain	Well 10-33-48-12W5	oil pool
6-25-50-10W5 8354 13 13ex	4.59E-07	7.22E-08	0.16	25.73	Pseudo single domain	Well 06-25-50-12W5	oil pool
10-33-48-3074 12W5 3 5ex	7.01E-07	1.42E-07	0.20	15.81	Pseudo single domain	Well 10-33-48-12W5	oil pool
10-33-48-3076 12W5 5 5ex	1.24E-06	2.57E-07	0.21	12.29	Pseudo single domain	Well 10-33-48-12W5	oil pool
10-33-48-3088 12W5 3 3ex	4.99E-07	2.01E-08	0.04	16.66	Multi domain	Well 10-33-48-12W5	oil pool
10-33-48-3093.4 12W5 5 10ex	8.15E-07	9.83E-08	0.12	7.87	Pseudo single domain	Well 10-33-48-12W5	oil pool
4-25-48-13W5 10290 3 13ex	1.25E-06	4.55E-07	0.36	16.84	Pseudo single domain	Well 04-25-48-13W5	oil pool
4-25-48-13W5 10290 1 13ex	1.20E-06	1.32E-07	0.11	7.57	Pseudo single domain	Well 04-25-48-13W5	oil pool
4-25-48-13W5 10290 1 13ex	1.17E-06	2.44E-07	0.21	12.47	Pseudo single domain	Well 04-25-48-13W5	oil pool
4-25-48-13W5 10290 6 13ex	1.77E-06	6.48E-07	0.37	13.81	Pseudo single domain	Well 04-25-48-13W5	oil pool
4-25-48-13W5 10290 10 13ex	9.38E-07	1.30E-07	0.14	8.80	Pseudo single domain	Well 04-25-48-13W5	oil pool
6-12-52-9W5 2352.4 4 14ex	8.43E-07	1.76E-07	0.21	12.81	Pseudo single domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2352.4 1 14ex	1.22E-06	4.33E-07	0.36	14.35	Pseudo single domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2352.4 8 14ex	1.11E-06	2.95E-07	0.27	10.86	Pseudo single domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2370.6 2 14ex	3.47E-07	5.44E-09	0.02	141.60	Multi domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2370.6 8 14ex	2.46E-07	2.04E-08	0.08	169.91	Multi domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2370.6 10 14ex	2.83E-07	1.82E-08	0.06	170.74	Multi domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2370.6 14 14ex	3.29E-07	4.88E-08	0.15	209.79	Pseudo single domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2388.8 2 14ex	2.55E-07	4.45E-09	0.02	145.26	Multi domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2388.8 4 14ex	2.94E-07	1.41E-07	0.48	122.49	Pseudo single domain	Well 06-12-52-9W5	oil pool
6-12-52-9W5 2388.8 8 14ex	2.85E-07	2.71E-08	0.10	166.41	Pseudo single domain	Well 06-12-52-9W5	oil pool
6-24-54-23W5 4097.5ex	5.72E-07	2.00E-07	0.35	15.33	Pseudo single domain	Well 06-24-54-23W5	SCCC
5-13-54-23W5 13376ex	4.46E-07	9.73E-08	0.22	29.04	Pseudo single domain	Well 05-13-54-23W5	SCCC
8-1-55-23W5 4013.8ex	7.25E-07	2.40E-07	0.33	13.62	Pseudo single domain	Well 08-1-55-23W5	SCCC
11-35-54-23W5 13402.0ex	3.55E-06	9.31E-07	0.26	6.83	Pseudo single domain	Well 11-35-54-23W5	SCCC
15-33-48-3089.0ex	5.90E-07	1.22E-07	0.21	28.69	Pseudo single domain	Well 15-33-48	SCCC
15-33-48-3090.2ex	6.19E-07	1.03E-07	0.17	16.74	Pseudo single domain	Well 15-33-48	SCCC

