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# Geochemical characterisation of gases, fluids and rocks in the Harvey-1 data well

## Final Report to ANLECR&D Project 7-1111-200

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Thanks to Nathan Reid (CSIRO) and an anonymous reviewer for comments on the report.

# Executive summary

The Harvey-1 stratigraphic well, drilled in 2012 as a part of the evaluation of the area in South West Western Australia for a suitable carbon storage site, has undergone a geochemical evaluation. Two gas samples from the potential source of $CO_2$ (CSBP and BOC in Kwinana) that may be piped south for a pilot scale test have been analysed and found to contain almost pure $CO_2$, in excess of 98.3 mol.% with little in the way of organic contaminants. The carbon isotopic composition of this gas is $\delta^{13}C$ -37.6 ± 0.28 ‰, which is quite distinct from other background natural sources of $CO_2$ and might act as a tracer in the future. Oxygen isotope data from the $CO_2$ have been collected to build the database of information that can be used to understand trapping mechanisms and their contribution in the future.

Organic analyses were conducted on a series of core plugs and on some drilling fluids from equivalent depths. Extraction of the core plugs showed that while there was some hydrocarbons present in both the core and drilling fluids, the richest core sample has only a total extractable organic matter content of 304.93 mg/kg rock. The volumes measured were insignificant compared with source rock extracts or amounts seen in sandstone dominated hydrocarbon reservoirs which might contain upwards of 100,000 mg/kg rock. These low volumes indicate that there is no active source rock of quantitative significance in the immediate area of this well and means that there is unlikely to be any form of basin resource conflict in relation to oil or gas finds in the immediate area.

Contamination by the drilling fluid for the organic components was extensive and prevented any general observations being made about the source of the hydrocarbons observed in the cores. Limited vitrinite data collected by the Geological Survey of Western Australia (GSWA) showed that at ~900m in the Harvey-1 well any in situ organic matter would be immature, but by ~2500m any organic matter would be within the oil generation and expulsion window.

A chemical tracer such as fluorescein would have been a beneficial method for back calculating some of that contamination for both the organic geochemical analyses and for reconstructing the fluid salinity in the sole sample collected from the Harvey-1 well (discussed below).

A shallow well adjacent to the Harvey-1 well was used as a water source for drilling Harvey-1. A sample from the slotted interval at 27-35 m BNS (below natural surface) was analysed and compared with regional data. The depth is close to the surfical aquifer/Leederville Formation boundary. It contained TDS (total dissolved solids) values of 458 mg/L and the chemistry of the formation compared broadly with the compositions reported for some wells in the area that intersect the Leederville Formation.

Only one deeper sample was provided from the Harvey-1 well itself. The sample taken was unconfined and pumped to surface by a third party and were supplied later. There was extensive evidence of drilling fluid contamination in the inorganic measurements as well as in the organic materials (as mentioned above). Attempts to reconstruct the chemistry of the fluids were not possible with the information available. The various modelling scenarios used to reconstruct the chemistry suggested that the fluids were affected by either the potential presence of organic acids, partial barite precipitation (from the drilling fluids) and/or enhanced alkalinity due to organic matter decomposition which together have contributed to the difficulty in backing out a true TDS measurement. The uncorrected value of 52,319 mg/L is higher than that calculated from wireline petrophysical log interpretation (40,000 mg/L in the Yalgorup and 30,000 mg/L in the Wonnerup Members). Again the conclusion is that a tracer chemical should be introduced to the drilling fluids for future wells irrespective of the sampling methods used.

Modelling techniques were also employed in an attempt to calculate a corrected formation fluid salinity and composition for the project. Reconstructions using information on the measured composition of the drilling fluids did not facilitate this calculation as the combination of different potential contaminants all together may have contributed to the failure to match the chemistry and levels of contamination.

Mineralogical modelling to determine the chemistry of formation fluids based on the local mineralogy were more successful and provided confidence in using other sample information from the regional data set as input for modelling. Matches between the model and the measured sample were not perfect, however, and this is believed to be due to the poor degree of equilibration of the minerals at lower temperatures.

Initial modelling of $CO_2$ injection into rocks from Harvey-1 showed that only moderate changes may be observed. $CO_2$ is consumed by the conversion of albite and phrengite to dawsonite. K-feldspar is completely converted to muscovite and quartz leaving little capacity for the rock to adsorb $CO_2$, therefore it remains in solution.

The conclusion of the modelling work to date is that much more can be done with the data set in the future when better quality fluid samples can be obtained and analysed to confirm the chemistry of formation fluids for different intervals.

The modelling work was very complementary to the core flood analyses. The report provides one of the most detailed analyses of core flood effluents conducted and demonstrates acid attack on clay minerals. Al is observed to be a key constituent controlling rate steps. At this stage, the single sample tested suggests that both chemical changes and (based on results from Delle Piane et al, 2013) fines mobilisation both have impact on the behaviour of this single rock sample from one facies. Further work on more samples would have to be conducted to confirm the contribution and rates of change to any samples from Harvey-1. Fortunately there are many samples that could be tested in a subsequent project. Significant contamination from the steel rig was also observed, but conducting additional tests in future would enable corrections to be made to report Fe data in the future.

In conclusion, this current geochemical evaluation of the Harvey-1 well has used a combination of standard and novel techniques to show that the geology in this area appears suitable for geological storage of $CO_2$

# Reviewer Comments with Author's Response

**Reviewer Comment 1:**

> "More effort should have been directed to backing out a formation water composition for the major ions (Na, Mg, Ca, Cl, $SO_4$) by using the composition of the mud liquid. Bicarbonate is a problem but since there is calcite in the formation and calcite has rapid kinetics, the formation water could be assumed to be in equilibrium with calcite to calculate a bicarbonate concentration. The analyses of the trace elements of the Harvey 1 sample are useless because of the extent of the drilling mud contamination."

**Author Response:** All best efforts were made but there were too many unknowns as described in the text. The data from the mud tests was not beneficial to conducting the activities suggested above. The team used an equivalent sample that seemed reasonably representative of the 856m sample instead. Lack of deeper samples were out of our control and there was no real sense in trying to predict the composition and concentrations further at this stage with the current set up. New approaches are being evaluated and we would like to submit a proposal that could address some of this. We have made suggestions relating to changes to the drilling program to alleviate future problems.

**Reviewer Comment 2:**

> "The boundary conditions for the modelling were poorly chosen. An adjusted formation water composition from the Harvey-1 well should have been used for the modelling. A kinetic model for the mineral reactions should have been used. The addition of $CO_2$ should have been cut-off when the pressure of $CO_2$ in the formation reached the allowed pressure (i.e. some pressure above hydrostatic but below frac pressure; for example 200 bars), not exceeding frac pressure by running the simulation to 2000 bars $CO_2$ pressure. Any interpretation above the frac pressure is meaningless."

**Author Response:** It is believed that it was not possible to provide an "adjusted formation water composition from the Harvey-1 well for the modelling" as the model equilibrates the solution to the rocks and the chemistry did not match. As for the comment on the addition of $CO_2$, the modelling was revised to the conditions as suggested. This study is preliminary and provides significant learnings for future activity when the next wells are drilled and new formation fluids are received.

**Reviewer Comment 3:**

> "The coreflood design was poor. The design should have been based on geochemical kinetic modelling which would justify doing the coreflood. The coreflood was only two days in length which is too short to see the effects of mineral – fluid reactions. It should have started by injecting a brine representative of the Harvey 1 formation water that was unsaturated with $CO_2$ as a baseline. Instead, only a two component NaCl brine (not a synthetic Harvey-1 formation water) saturated with $CO_2$ was injected. Consequently the effect of the $CO_2$ could not be separated from the effect of the brine. Contamination of the effluent from the stainless steel container was evident. Sampling of the effluent was at STP without regard to the depressurization of the brine from 20 MPa to 0.1 MPa which has likely resulted in precipitation of some of the dissolved constituents such as calcite (e.g. a similar process results in calcite scaling in oil wells due to pressure drop and boiling off of the $CO_2$). This will lead to incorrect water chemistry characterization. No SEM work was done on the core to substantiate any of the mineral reactions which were postulated to occur.

**Author Response:** This project received the fluids from another project (Facies-based rock properties distribution along the Harvey 1 stratigraphic well Project 7-1111-0199) and had no control over the aspects noted in this comment. The work was conducted before we had an opportunity to contribute to the design of any of the core flood experiments. We are in full agreement and believe that addressing this is important in finding out the degree of reactivity of the rocks going forward. This is partially addressed in the revised recommendations. The plan forward would be to submit an EOI describing a new program for the next batch of experiments e.g. brine only start/more representative and SEM work which is stated in the report. We agree that the depressurization will impact on $HCO_3$ measurements etc., but it will not change the calcite measurement as acid was added after collection to dissolve any precipitates in solution. Future experiments may address this issue.

**Reviewer Comment 4:**

> "The discussion of the coreflood effluent analyses was qualitative and the conclusions drawn were not justified since the experimental controls were poor. A number of different conclusions could just as easily be made. The interpretation of the coreflood effluent chemistry has to be history matched with geochemical kinetic computer models and justified with identification of the reactions through SEM observations. This was not done. However, in this case because of the poor experimental controls, such additional work would not be justifiable. It was a leaching experiment with contribution to the chemistry of the effluent from undesired (external) sources."

**Author Response:** We agree with the first comment and believe that we stated this in the report. The comment regarding the leaching experiment – we had proposed that we do these sorts of tests in the program of activities but this was removed from the scope of work at the request of ANLEC R&D.

**Reviewer Comment 5:**

> "In order to show the robustness of the chemical analyses, a charge balance calculation should be shown as one row of the table, and the results discussed (For example, the Cl concentration seems to be low for the 1000 m mud liquid). Also, the relationships between total S & $SO_4$; and total P & $PO_4$ need to be discussed. Are there other S and P species besides $SO_4$ and $PO_4$?"

**Author Response:** No other species are expected. Therefore while it is a simple calculation to convert between the two we felt this added no information and was not relevant to our understanding.

**Reviewer Comment 6:**

> "As stated, the Harvey -1 sample is severely contaminated by the drilling mud. The statement is made that "Efforts were made to use ratios of other cations and anions" to correct the Harvey – 1 analysis but were not successful. I would suggest a fairly simple approach to correct the analyses since it appears that a concentrated KCl drilling mud was used. From table 15, it can be seen that the deep formation waters generally have K concentrations less than 100 mg/l while the dilling mud had K concentrations two orders of magnitude greater. Consequently, most of the K analyzed in the Harvey -1 sample can be attributed to the drilling mud contamination. Average K content of the two drilling mud liquid analyses is 26,900 mg/l while the measured concentration of the Harvey -1 sample is 15,800 suggesting a contamination of approximately 15,800/26,900 of 59%. If you apply this correction, some of the ions will not track across because they probably precipitated out during mixing (e.g. Fe, Ba, Mn) but the corrected values for major cations (e.g. Mg, Ca, and Na) should be good. pH and Al values are never accurate in formation water samples even if they are uncontaminated by drilling mud. Assumptions have to be made for the other ions."

**Author Response:** We appreciate the comments made, and did approach the data in this fashion. However, removing the K and associated Cl did not correct the values for the major cations. There are other issues (as described in the report). We were working on a sample that was less than ideal and look forward to obtaining better samples from the next well.

**Reviewer Comment 7:**

> "The coreflood dynamics were postulated based only on the effluent water chemistry which were quench measurements which would be affected by the boiling off of the $CO_2$ during the pressure reduction from 20MPa (the pressure of the coreflood) to 0.1 MPa (the pressure of the sampling). The consistently high Mn values could only be from the stainless steel containers; and probably the other metals follow suit (i.e. Fe and a lot of the trace metals etc.). The only major cations that could

> be related to mineral reactions in the core would be Ca, Mg and K. Na cannot be used because of its high concentration in the injection fluid. The consistently high Al values is puzzling since gibbsite saturation would be expected to effectively control the Al concentration to low values. It is possible, colloidal Al is being analyzed."

**Author Response:** Yes, these are good comments and we would like to take them forward with future proposed core flood tests.

**Reviewer Comment 8:**

> "The chemical reactions that are controlling the chemistry of the leachate from the coreflood are not adequately discussed. Normally, a simple geochemical analysis would use Saturation Index calculations to back up what was happening. This was not done. This would then be followed by a path type kinetic calculation to history match the water effluent chemistry."

**Author Response:** We agree it is possible to potentially perform these calculations in future.

# 1 Introduction

## 1.1 Geochemical Investigation of the Harvey-1 Well

The Harvey-1 well is part of a systematic investigation to evaluate the viability of the region of investigation for safe and secure carbon dioxide storage for the South West $CO_2$ Geosequestration Hub Flagship Project. A staged approach to collecting information and developing an understanding of the subsurface geochemical regime in the area is a vital scientific contribution towards building the case for a commercial CCS demonstration at the South West $CO_2$ Hub. By researching various geochemical aspects of the subsurface region of interest that are complementary to industry standard characterisation, geological uncertainties regarding the predicted behaviour of $CO_2$ to be stored in the deep geological system will be reduced together with the associated project risks. The information obtained from this study can be incorporated into the static and dynamic models for the area to better characterise the storage capacity, containment security and injectivity of the site.

The geochemical evaluation of the Harvey-1 well has a number of discrete purposes. These include:

- Evaluate the composition of two injectant gases that may be supplied for the small scale demonstration injection in the future (one sample is to be obtained from CSBP prior to BOC clean-up and one sample of gas that BOC puts into the pipeline to Alcoa following clean-up),
- Evaluate the composition of 3 drilling mud samples collected from Harvey-1 drilling operations. The chemistry of the drilling mud will be used to understand degree of contamination by drilling mud of other fluid samples and related data taken in Harvey-1,
- Basin resource management to determine if there is any evidence for in situ or migrated oil through the proposed $CO_2$ storage reservoir or surrounding strata,
- Maximising data acquisition from the Harvey-1 data well (for multiple basin resource purposes) in a geographic region with few well penetrations to date,
- Obtain baseline and regionally significant geochemical data for integration with related current and future studies. This includes an evaluation of the composition of two aquifer water samples collected from Harvey-1 at 856m and a near-by shallow water bore at 27-35m BNS,
- Evaluate the potential for the reservoir, seal and baffles to react or plug on contact with $CO_2$ based on results from coreflood activities in ANLEC Project 7-1111-0199 (Facies-based rock properties distribution along the Harvey 1 stratigraphic well),
- Develop the framework and conduct preliminary reactive transport modelling in preparation for the future wells, reservoir level formation water sample data and small scale injection,
- Provide relevant input to other projects that are being conducted by WA ERA/NGL for WA DMP's South West Hub Project, and,
- Lessons learned for the sample acquisition from drilling in the area.

## 1.2 Harvey-1 well location and South West $CO_2$ Geosequestration Hub Project

The Harvey-1 well, (drilling location 115°46'28.4"E and 32°59'34.2"S) was drilled to provide new data for the South Western Australia $CO_2$ Geosequestration Flagship (South West Hub), a government industry partnership lead by the Western Australian Department of Mines and Petroleum (Table 1). The South West Hub partners are Alcoa Australia, Griffin Energy Developments, Perdaman Chemicals and Fertilsers, Electricity Generation Corporation (Verve) and Premier coal Limited. The South West Hub has a series of gates or phases to move from a trial phase towards commercial scale capture, transport and storage. These phases include the following:

- Preparation phase (2011-2012) – precompetitive data acquisition and analysis to test suitability of the storage interval (the Lesueur Sandstone) in the Southern Perth Basin. The region identified and being actively studied is an area south of Mandurah and north of the Kemerton Industrial Area (Figure 1),
- Enabling Case (2013-2015) – a new pipeline from Kwinana (gas providers CSBP and BOC) to the Lesueur area via Alcoa's Pinjarra and Wagerup alumina refineries (Figure 1). The purpose of the pipeline is to provide $CO_2$ to be sequestered in the highly alkaline bauxite residue,
- Base Case (2015-2017) – commercial scale capture, transport and storage of gas from Perdaman Chemicals and Fertilisers' plant in Collie to the Lesueur site via an additional pipeline, and,
- Extended Case (2018-2023) – additional capture, transport and storage capacity for other industrial sources of $CO_2$ in the Collie and SW region.

Further details can be found in a report by the Western Australian Department of Mines and Petroleum published in May 2012.

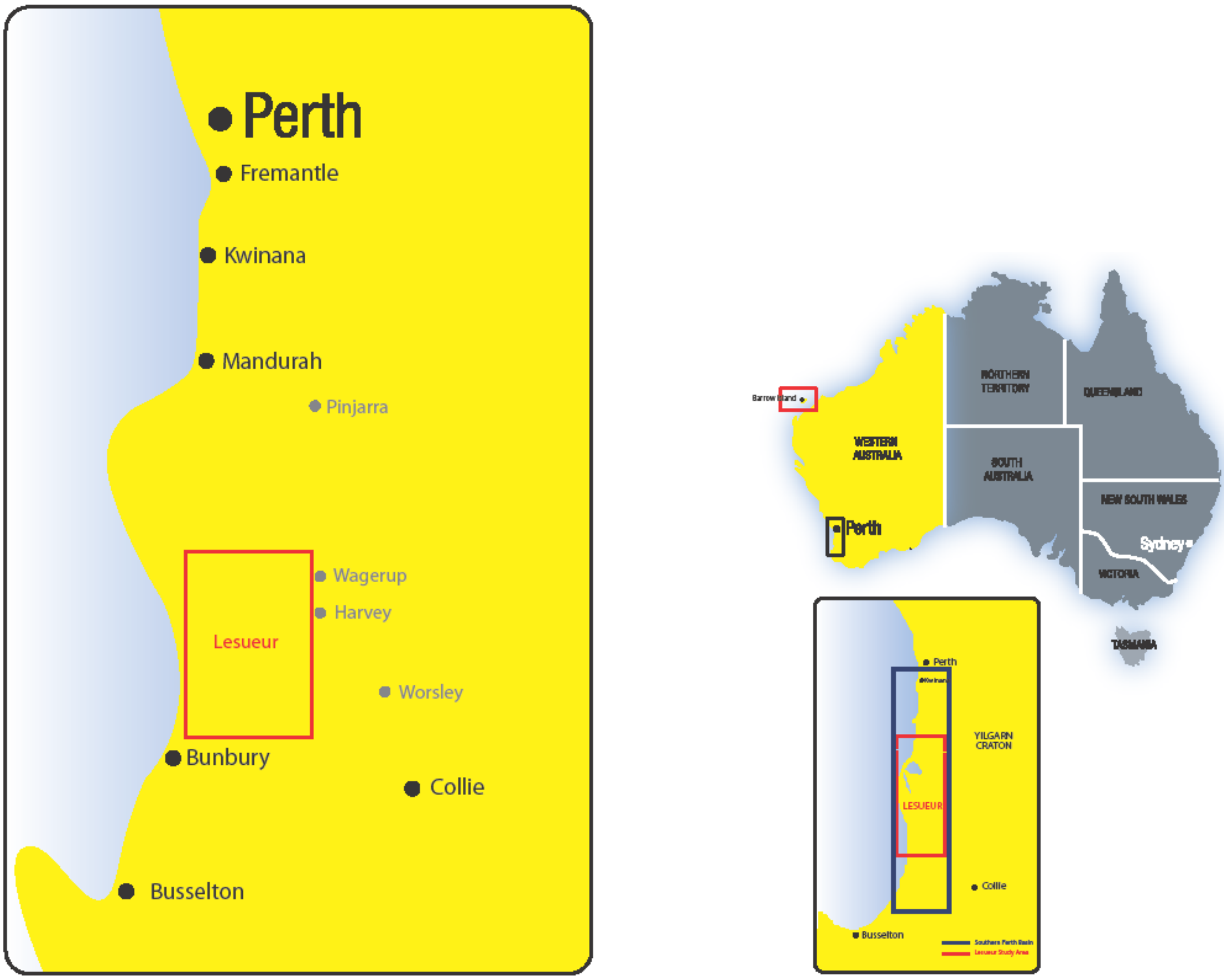


Figure 1 Location Map of the South West Hub Project with location of Harvey-1 well marked. The project location is also shown in context with the rest of Australia (inset) where the location of the Gorgon CCS project is also marked.

The well site, one hundred metres to the north of the Riverdale Road and 500m to the east of State Forest near Harvey, WA was chosen based on previous studies and from the results of a 2D seismic survey conducted by WA DMP and Geoscience Australia in 2011 (Figure 2). The location of the well was chosen so that a 3km vertical well could characterise all of the Triassic aged Lesueur Formation, this formation being the potential target interval for the storage of $CO_2$ for the South West Hub (Figure 3). The nomenclature of the samples reflects the identification code provided by GSWA. Formation names and Formation tops are taken from the post-drilling documents circulated by the GSWA.

**Any reference to sample depth used in this report is based on the indications provided on the casing of the retrieved cores corresponding to measured depth relative to the rotary table (MDRT) provided by GSWA (Table 1).**

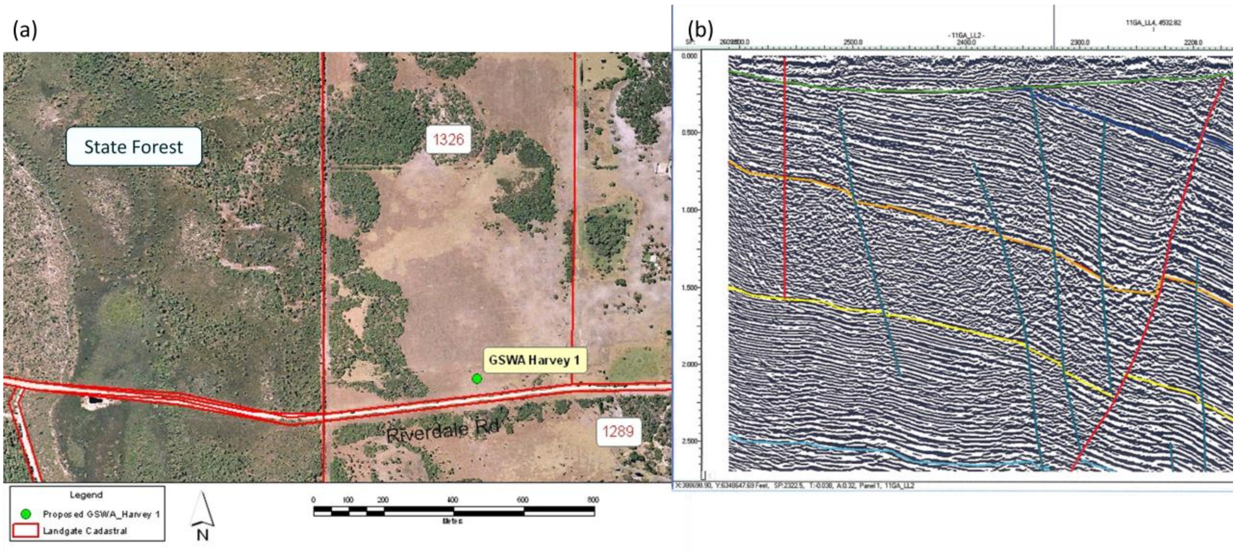


Figure 2 (a) Location of the Harvey-1 well near Harvey, WA. (b) 2D seismic line illustrating 3km depth intersection with base of the Lesueur Formation.

Table 1 Well details for Harvey-1.

| | | | |
|---|---|---|---|
| **Well Data Record** | | | |
| **Well Name:** | GSWA Harvey 1 (2066) | | |
| **Well Classification:** | Stratigraphic | **Spud Date:** | 00:00h 7th February 2012 |
| **TD Date:** | 22:00 h 8th March 2012 | **Rig Release Date:** | 06:30h 26th March 2012 |
| **Final TD mMDRT/mTVDSS** | 2945.0 / 2913.8 | **Total Rig Days** | 48 |
| **Completion Status:** | Plugged & Abandoned | **Permit / License:** | N/A |
| **Surface Coordinates:** | Lat: 32°59' 30.730"S<br>Long: 115°46' 28.093"E | **TD Coordinates:** | Lat: 32°59' 33.730"S<br>Long: 115°46' 26.734"E |
| **Surface Location Coordinates (UTM):** | 385502.044E<br>6348947.564N | **TD Coordinates (UTM):** | 385467.77E<br>6348860.13N |
| **Permanent Datum:** | AHD | **RT to GL:** | 5.38m |
| **Ground Level (GL) to AHD:** | 19.10m | **RT to AHD:** | 24.48m |
| To correct MDRT to TVDSS - take 24.48 m from the MDRT value. | | | |

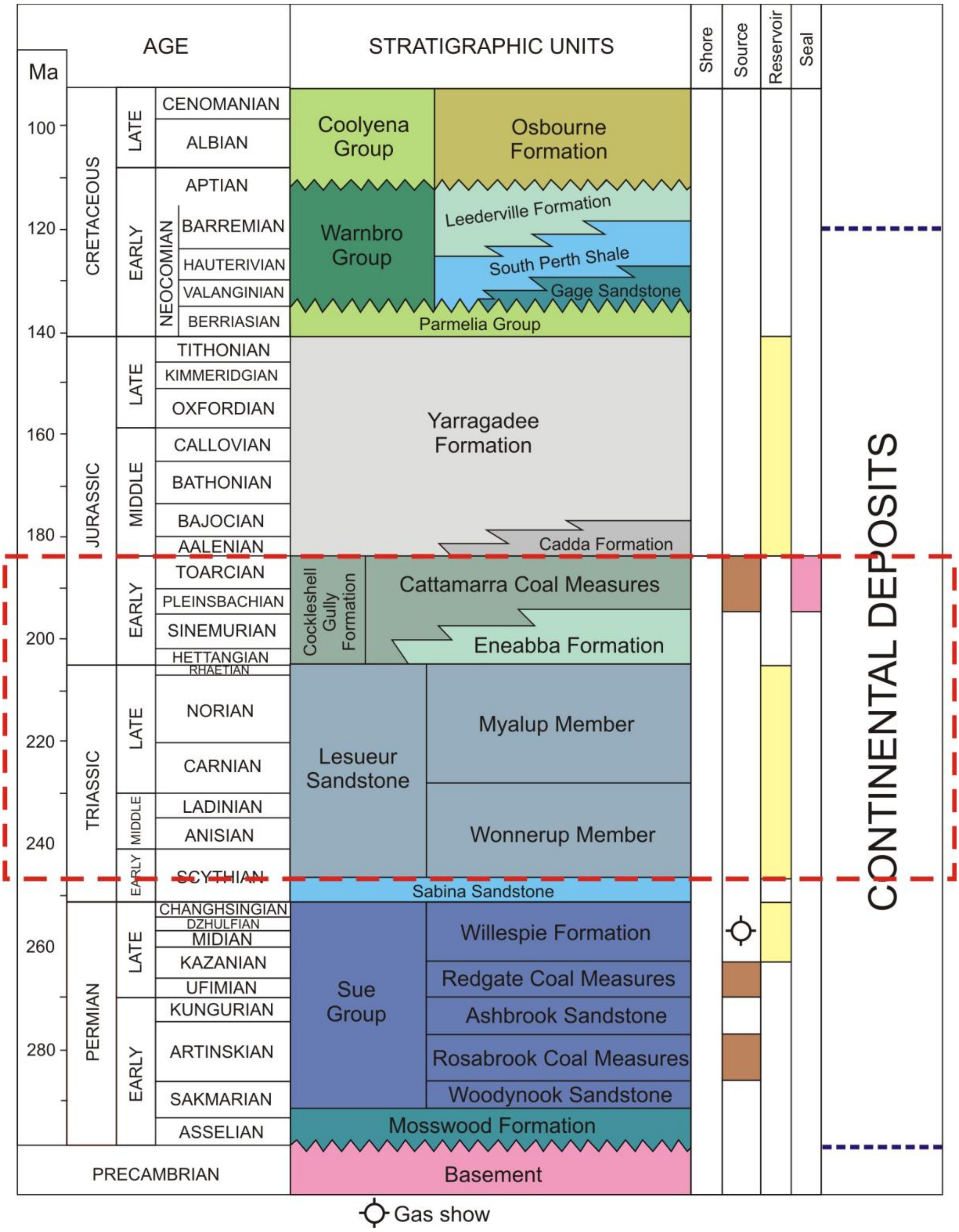


**Figure 3 Stratigraphic column of the Southern Perth Basin, including the key area of interest marked in red of the Triassic aged Lesueur Formation overlain by the Cockleshell Gully Formation. Crostella and Backhouse, 2000.**

## 1.3 Purpose of this study

The Harvey-1 well is the first data well drilled in Western Australia for systematic investigation to evaluate the viability of the region for safe and secure carbon storage. A staged approach to collecting information and developing an understanding of the subsurface geochemical regime in the area is a vital scientific contribution towards building the case for a commercial CCS demonstration at the South West $CO_2$ Hub. By researching various geochemical aspects of the subsurface region of interest that are complementary to industry standard characterisation, geological uncertainties regarding the predicted behaviour of $CO_2$ to be stored in the deep geological system will be reduced together with the associated project risks. The information obtained from this study can be incorporated into the static and dynamic models for the area to better characterise the storage capacity, containment security and injectivity of the site. As stated in Section 1.1 the geochemical evaluation has a number of discrete purposes to obtain data for the region. An analytical program was prepared in order to capture relevant data for the South West Hub project, outlined in Table 2. The report describes the samples taken, methods used to analyse them, results and interpretation of the data in light of the needs for the project.

By conducting a geochemical characterisation of gases, fluids and rocks relating to the Harvey-1 well and the South West Hub project, the activities reported here should be able to provide preliminary information on the following:

- Gas geochemistry of potential feedstock gases (composition and isotopic data),
- Water chemistry data for samples taken in the superficial aquifer and other samples obtained,
- Chemistry of the core materials to show presence or absence of *in situ* or migrated hydrocarbons, and,
- The level of contamination experienced by the fluid and rock samples from drilling muds.

The data acquired can provide the following:

- New information to update basin resources mapping,
- Geological information on the source of any organic matter,
- Potential for geochemical changes to facies or formations during $CO_2$ migration, and,
- Provide baseline geochemical data for the region to be integrated with existing and new well data.

The following sampling program was developed to provide the relevant data for characterising the Harvey-1 well and related samples for the purpose of advancing the activities for the South West Hub project (Table 2).

**Table 2 Completed analytical program.**

| Sample Type | Analytical methods | Objective of analysis |
|---|---|---|
| **Feedstock Gas**(2 samples)<br>CSBP sample<br>BOC sample | Gas composition<br>Stable isotopes (C & H) | Percentage of gaseous components including $CO_2$<br>Carbon isotope composition of $CO_2$ and other hydrocarbon components |
| **Purpose** - to characterize the feedstock gas from CSBP before and after treatment to identify composition and contaminants | | |
| **Harvey-1 formation fluids** (1 sample)<br>Harvey-1 pumped sample from 856m (unconstrained) | Organic extraction of the waters<br>Preliminary hydrocarbon analysis<br>Characterisation of metals<br>pH, Ec, TDS<br>Isotopes | Hydrocarbon components (BTEX, PAH, TPH)<br>Presence of metal types<br>Provenance/age of species |
| **Purpose** - to characterize the groundwater and formation fluids collected in the wells | | |
| **Drilling muds** (multiple samples) | Organic extraction of the muds<br>Preliminary hydrocarbon analysis<br>Characterisation of metals<br>pH, Ec, TDS<br>Isotopes | Hydrocarbon components (BTEX, PAH, TPH)<br>Presence of metal types |
| **Purpose** - to provide information on mud invasion & contamination on the rock and fluid samples | | |
| **Shallow bore fluids** (1 sample)<br>27-35m BNS slots | Organic extraction of the waters<br>Preliminary hydrocarbon analysis<br>Characterisation of metals<br>pH, Ec, TDS<br>Isotopes | Hydrocarbon components (BTEX, PAH, TPH)<br>Presence of metal types<br>Provenance/age of species |
| **Purpose** - to provide information on the shallow aquifer water chemistry, age and quality for comparison with deeper formations and to form baseline data for the region | | |
| **Rock Chemistry** (8 samples) | Organic extraction of the core plugs<br>Preliminary hydrocarbon analysis | Presence/absence of hydrocarbons<br>Limited source/maturity information |
| **Purpose** - to determine presence of hydrocarbons as a part of an active petroleum system<br>**Purpose** - to determine presence of hydrocarbons that could be mobilised by migration of $CO_2$<br>**Purpose** - to provide data for modelling and input to core flood experiments | | |
| **Core Flood Effluent Analysis** (53 samples) | Characterisation of metals<br>pH, Ec, TDS | Measure change in pore fluid chemistry over time during flooding in $CO_2$ saturated brine at representative subsurface conditions. |
| **Purpose** - to analyse effluents from core flood experiments with the same workflow as for the well materials. This information contributes to the reactive modelling preliminary work. | | |

# 2 Organic geochemistry of gas and liquid fractions relating to the South West Hub and Harvey-1

## 2.1 Introduction

In addition to the samples collected from the Harvey-1 well, described in detail below, two samples were collected and analysed from the anticipated gas source at Kwinana (from the CSBP and BOC plants). A number of samples were collected from the Harvey-1 well for organic and inorganic geochemical analysis. Because the methods and interpretation of results are quite different for each of these areas, they have been reported in Section 2 and 3 respectively.

The analyses provide chemical data that can be used to infer geological information about the samples taken or their provenance and the impact of that information on the South West Hub project in the ongoing evaluation of the area as a potential carbon storage site.

## 2.2 Geochemistry of gases from CSBP and BOC

The gas source for the Enabling Case for the South West Hub project is likely to come from the CSBP Fertiliser plant in Kwinana. It is anticipated that of the approximately 350,000 tonnes per annum $CO_2$ produced, 250,000 tonnes will be sequestered at the Alcoa alumina refineries at Pinjarra and Wagerup (Figure 1) by neutralising red mud bauxite residue. The remainder will be piped to a suitable pilot test site in the Lesueur area to conduct a small scale evaluation. Currently the carbon dioxide gas from CSBP is processed at BOC in Kwinana before being supplied to a number of other industries. The processing is primarily to remove organic contaminants to produce Food Grade $CO_2$. Some of this gas output is currently transferred by pipeline 10km to the Alcoa Kwinana plant to be sequestered in the bauxite residue generated at that particular plant.

Understanding the detailed chemistry of the gas supply is important for site characterisation, as various incidental components, which may be regarded as contaminants, can impact in a number of ways; for example non-condensables versus condensables or reactive versus conservative species in terms of chemical reactivity. The presence of certain contaminants may have an impact on:

- Storage capacity – non-condensable gases are less easily compressed, using more pore space. Measuring the amount of non-condensable gases in a gas stream to be sequestered can be used to model the expected storage capacity for a given location. These gases are typically $O_2$, Ar or $N_2$,
- Injectivity – chemical reactions between the in situ rock, formation fluids and introduced contaminants have the potential to result in scaling/fouling of the injector, may result in changes in pH (with impact on rock reactivity) and mineral reactions beyond the injector and mobilisation of cation/anions (Stalker et al., 2011 and references therein), and,
- Containment Security – well bore integrity may be impacted in resultant changes in pH or remobilisation of, or reactions with contaminants and in situ materials. Transport of contaminants as pollutants or tracers is also possible.

A detailed compositional analysis of the CSBP and BOC feedstock gases (hydrocarbons and non-hydrocarbons composition), particulates and metallic species, before and after clean up by BOC was proposed as a part of this study. Subsequently, it was agreed to attempt to obtain a third sample from the pipeline from the Kwinana Alcoa site where red mud neutralisation already occurs.

### 2.2.1 METHODS FOR CHARACTERISING GASES

#### Sampling the Gases

Two visits were made to the BOC Plant in Kwinana to sample the gases. The first was to discuss the needs for samples with the Production Manager. The second was to collect samples for organic geochemical analyses of gases and identify flow rates and information that would be relevant to acquiring any metal species.

During the second visit, Sample G2092 was taken from the inlet side of the plant where CSBP supplies gas as a by-product of its coal to urea production. Sample G2093 was taken from the outlet side of BOC post-processing, where the purpose of the processing is to reduce organic contaminants for sale of $CO_2$ as a food-grade product. An example of the analysis conducted by BOC was provided (not reported here) to the project by way of indication of the purity of the $CO_2$ post-processing. The data provided by BOC did indicate a very pure $CO_2$ stream containing 99.99+ v/v% $CO_2$.

Table 3 Gas samples taken for organic geochemical analysis from Kwinana.

| Sample Name | Location | Sample Type | Description | Analysis conducted on all samples |
|---|---|---|---|---|
| G2092 | BOC, Kwinana | Low pressure Gas sample | Gas taken from the inlet valve from CSBP into BOC prior to processing. | Gas composition ($C_1$-$C_{6+}$, CO, $N_2$)<br>Stable carbon isotopes of $CO_2$<br>Stable oxygen isotopes of $CO_2$ |
| G2093 | BOC, Kwinana | Low pressure Gas sample | Gas taken from the outlet valve after processing at BOC. | |

The sample lines from which the samples were taken flowed at a rate of 4L/minute providing a pressure in the gas cylinder reported as 5-6 inches of water gauge (WG) pressure or approximately 1.2-1.5 kPa. The pressure vessel (150 mL) was attached by stainless steel fittings and both valves on the pressure vessel opened. Around 10-12 volumes of gas, over 30 seconds, was passed through the pressure vessel before the valves were sealed simultaneously.

#### Sampling metals from gases

During the project it was recommended that a third sample be collected, from the Alcoa Kwinana Plant. The gas from BOC is already supplied via a 10km pipeline to be used in the neutralisation of bauxite residue at Kwinana. This pipeline process is analogous to the proposed Enabling Case for the South West Hub where the pipeline is planned to be extended to deliver gas onwards to the Lesueur study area. The main purpose of obtaining a sample from this site was to observe any differences to the volatile or particulate metal species in the gas following the transportation of the $CO_2$ rich gas 10km from BOC. Unfortunately, the metals analysis in the gas samples was not conducted for this project and it was agreed with Alcoa that it was not appropriate, or relevant, to sample at this time.

There are a number of reasons why the gas samples did not undergo metals analysis as originally planned. Finding either a suitable sampling technique or analytical method to conduct the analysis in a meaningful quantifiable manner proved extremely difficult to identify. Preliminary investigations and advice from CSIRO colleagues suggested approaching external suppliers to conduct the analyses.

However, without a suitable sampling method, there was significant concern that taking a standard gas sample into a stainless steel cylinder would not provide an appropriate sample type that would be consistent and representative of the gas stream (volatiles and particulates were very likely to drop out of solution and coat the vessel walls). No supplier could be identified who could conduct these analyses so alternatives were sought.

The second possible method was solely calibrated to measure mercury in different forms in hydrocarbon gas streams. As $CO_2$ is the major component in these gas samples, the method may not have been appropriately calibrated for different media and would have required significant method development and additional costs for few samples.

Finding appropriate methods and suppliers of appropriate services was particularly difficult and extensive consultation took place to identify either. One company had greater experience in sampling from stack and low pressure systems. They visited the site to evaluate the potential for sampling from the inlet and outlets at BOC, and collected the samples for the gaseous components described above. Having obtained the relevant pressure and flow measurements and applying their knowledge of various EPA methods (specifically USEPA Method 29 (Determination of Metals Emissions from Stationary Sources), the contractor calculated a lower detection limit for the metals suite from USEPA Method 29. At 4 litres per minute sampling for 30 minutes, it would be possible to obtain a corrected sample volume of about 0.110 cubic metres of sample gas. The analytical detection limit for the metals trapped in a solution of $HNO_3/H_2O_2$ solution is about 2.5 micrograms. If, in addition an acidified permanganate solution was added to also measure for mercury the ADL is 0.5 micrograms. The method detection limit then becomes 22.7 micrograms per cubic metre for the metals trapped in the $HNO_3/H_2O_2$ solution and 4.5 micrograms per cubic metre of mercury. This was not expected to be sufficient for measurement in a laboratory.

Further issues were encountered in that BOC had identified that the only way to sample gases from the main ports was to bypass their safety controls for a period of time, and this was deemed inappropriate.

Further discussion with staff from CSIRO Energy Technology noted that during their pilot and laboratory testing to quantitate contaminants by EPA and other certified methods, they found that all methods had to be modified and tested before application (Azzi et al., 2010; Thong et al, 2012). They experienced this during testing of emissions from an amine plant and were particular to organic analytical methods. However, analogies again can be drawn with measuring materials in atypical media from that described in an analytical method. Further discussion with a collaborator with this team (Dr. Brendan Halliburton of CSIRO's Division of Energy Technology) suggested that validation would still be required for employing EPA metal methods for measuring contaminants in potential gas streams for CCS and a process of validation in the laboratory would be required.

It was concluded that without further research (including method development and testing) it would not be possible at this time to collect samples that were representative and where relevant uncertainties in measurements had been reduced to a point where data could be reported. It was decided by the project team at this point that measuring the metals species in the gases for this project were not appropriate as the developments required fell out of the scope for the Harvey-1 characterisation at this time and the project was re-scoped accordingly.

## Bulk Gas Compositional Measurements

Two natural gas analysis methods were used to analyse the gases, Method A which is less sensitive at the low end of the scale and Method B which is more sensitive for trace quantities of hydrocarbons. This overcomes issues of dynamic range when trying to measure samples with such varied concentrations.

Method A utilized a bulk compositional analysis conducted on an Agilent 6890N Natural Gas Analyser (NGA) with a thermal conductivity (TCD) detector that has a lower detection limit of approximately 350 ppm. Method B utilised a Varian 490 MicroGC NGA to obtain trace levels of hydrocarbon and other gases. This instrument has a lower detection limit of approximately 10 ppm.

Method A: The full method for the Agilent 6890N NGA is as follows. An aliquot of sample was introduced through the vacuum manifold into a sample loop (0.25 mL) at atmospheric pressure for GC analysis on an Agilent 6890N Natural Gas Analyser, with a thermal conductivity detector (TCD). Four packed columns with Valco valve column switching are used to separate the gases, a 2 foot 12% UCW982 on PAW 80/100 mesh (pre-column), a 15 foot 25% DC200 on Paw 80/100 mesh, a 10 foot HaysepQ 80/100 mesh and a 10 foot Molecular Sieve 13X 45/60 mesh column. The oven was isothermally maintained at 90°C throughout the 20 minute run. The amount of separated gas components was determined against an external standard calibration. The molecular composition of gas components was corrected to air free values, assuming atmospheric ratios for the oxygen+argon/nitrogen peaks. At 90°C, oxygen and argon co-elute on the 13X molecular sieve column.

Method B: Gas samples were collected from stainless steel cylinder via a gas-tight syringe. Samples were injected into the front injection port of the Micro-GC (490) by syringe pump. The Micro-GC is equipped with three different column modules: 10 m Molsieve 5Å column with backflush, a 10 m Pora Plot Q column with backflush and a 10 m CP-Sil-5CB column. Gases were detected using a micro machined thermal conductivity detector for each module; limit of detection is in the order of ~1 ppm. The injector has a built-in 10 uL sample loop and the helium carrier pressure was set to 15psi and the injector temperature was 90°C. The temperature of the Molsieve 5 Å column in channel 1, the Pora Plot Q column in channel 2 and the CP-Sil-5CB column in channel 3 was set to 90°C, 70°C and 60°C respectively.

After being injected into Micro-GC, gases are drawn by a vacuum pump through the sample loop and then the inlet system injects the gas sample from the sample loop into the carrier gas stream. $O_2$/Ar, $N_2$, $CH_4$ are separated on the Molsieve 5Å column. $CO_2$, $C_2H_6$ and $C_3H_8$ are separated on the Pora Plot Q column. $C_4$-$C_5$ hydrocarbon gases are separated on the CP-Sil-5CB column. The backflush feature on the first two columns minimises the impact of potentially damaging gases from reacting with the column media.

### Gas Stable Carbon Isotopic Composition

Stable isotopic analysis of the gases will be used as information for any baseline monitoring studies (as a potential source indicator for $CO_2$).

The carbon isotopic composition of gases in the cylinders was measured by GC-C-IRMS (gas chromatography/combustion/isotope-ratio mass spectrometry). The GC-C-IRMS system consisted of a GC unit (6890N, Agilent Technologies, USA) connected to a GC-C/TC III combustion device coupled via open split to a Delta V Plus mass spectrometer (ThermoFisher Scientific, Germany). The analytes of the GC effluent stream were oxidised to $CO_2$ in the combustion furnace held at 1000 °C on a CuO/Ni/Pt catalyst. $CO_2$ was transferred on-line to the mass spectrometer to determine carbon isotope ratios. A 10 µL of sample gas was injected to the split/splitless inlet system (Agilent Technologies, USA), working in split mode (20:1 ratio). The injector was held at a temperature of 150 °C. The gas components were separated on a fused silica capillary column (PoraPlot Q, 25 m x 0.32 mm ID, Varian). The GC was held isothermally at 40 °C. Helium was the carrier gas, set to a constant flow rate of 1.4 mL/min. All gas samples were measured in duplicate with a standard deviation of ≤0.5 ‰ for the standards and samples. The quality of the carbon isotope measurements was checked regularly by measuring secondary standards of pure $CH_4$ and $CH_4/CO_2$ mixtures with known isotopic composition as determined by inter-comparison on dual bellows inlet mode on a Finnigan MAT 252 against international primary carbonate standards prepared by the phosphoric acid method.

The stable carbon isotope compositions are expressed in parts per thousand (‰) relative to PeeDee Belemnite (PDB), according to the expression:

$$\delta^{13}\text{C ‰} = 1000 \times \frac{({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}} - {}^{13}\text{C}/{}^{12}\text{C}_{\text{reference}})}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{reference}}}$$

### Gas Stable Oxygen Isotopic Composition

A Finnegan MAT 252 Isotope ratio mass spectrometer was used to obtain the stable isotopic oxygen values for the $CO_2$. The low pressure gas was injected and compared with the VSMOW standard and the values expressed in a similar manner to that for the carbon isotopes.

## 2.3 Results from the Feedstock Gases from CSBP and BOC

The results of the organic geochemical analyses of the gases are presented in Table 4 and Table 5.

## Bulk Gas Composition results

Bulk compositional data (Table 4) was measured on two different instruments partly to overcome issues of dynamic range resulting from the very high concentrations of $CO_2$ (using Method A) and very low concentrations of hydrocarbons were measured (Method B). Gas geochemical analyses are commonly reported as normalised percent (mol %). The results show that after the air-free calculation, $CO_2$ makes up 99.79 mol % of the gas from the CSBP inlet and 98.30 mol % of the gas after processing at BOC based on Method A. It is to be noted that the instrument used has a TCD detector which is less sensitive than other methods, and the samples were at a lower pressure than is typically provided for that instrument. However the results agree with data provided by BOC. BOC send samples on a quarterly basis for detailed screening for organic contaminants and report values in excess of 99.99 mol %.

**Table 4 Bulk composition of gases collected at BOC in mole %. Results are provided for two methods (due to the high concentration of $CO_2$ and low concentration of hydrocarbon gases).**

| Sample | $CO_2$ | Methane | Ethane | Propane | Iso-Butane | n-Butane | $O_2$ & Ar | Nitrogen | Total |
|---|---|---|---|---|---|---|---|---|---|
| Molecular Composition - Method A GC-TCD NGA results | | | | | | | | | |
| Normalised percent | | | | | | | | | |
| G2092 BOC inlet from CSBP | 99.36 | | | | | | 0.10 | 0.54 | 100.00 |
| G2093 BOC outlet to Alcoa | 94.95 | | | | | | 0.75 | 4.31 | 100.00 |
| After air-free calculation | | | | | | | | | |
| G2092 BOC inlet from CSBP | 99.79 | | | | | | | 0.21 | 100.00 |
| G2093 BOC outlet to Alcoa | 98.30 | | | | | | | 1.70 | 100.00 |
| | | | | | | | | | |
| Molecular Composition – Method B MicroGC NGA trace components | | | | | | | | | |
| Results in percent (raw) | | | | | | | | | |
| G2092 BOC inlet from CSBP | N/A | 0.020 | 0.0036 | | 0.0020 | | N/A | N/A | |
| G2093 BOC outlet to Alcoa | N/A | 0.001 | 0.0038 | | | | N/A | N/A | |

The measurement of other species (notably hydrocarbon gases) was conducted by Method B. The results show very low levels of methane, ethane and iso-butane (0.020, 0.0036 and 0.0020 mol % respectively) for the gases before processing. After BOC processing, iso-butane is below the limit of detection and methane has substantially reduced to 0.001 mol %. Ethane appears unchanged. The results imply some degree of removal of hydrocarbons, probably the heavier hydrocarbons are the major focus, based on the data that BOC measure to certify their gases (information not presented here).

Over all, the results of both this work and the unpublished BOC analyses suggest that there are few contaminants present that might be volumetrically significant relative to the amount of $CO_2$ that might be injected.

## Gas Stable Isotope composition results

Results of the stable isotopic analysis of the gases (Table 5) are for both carbon and oxygen of $CO_2$. The values for $CO_2$ produced from CSBP are $\delta^{13}C$ -37.6‰ and $\delta^{18}O$ -2.9 ± 0.14‰, while results from the gas post-processing at BOC are $\delta^{13}C$ -37.6 ± 0.28 ‰ and $\delta^{18}O$ -2.15 ± 0.07 ‰. The results suggest that there has been no impact on the carbon isotopes during the processing stage (there is always concern that any process will isotopically fractionate the stable isotopes, e.g., respiration) however there has been a slight change (greater than analytical error) to the oxygen isotopes.

The source material for CSBP to produce urea from coal to produce fertilizer is from the coal excavation at Collie. Collie coal has a sub-bituminous rank and is Permian in age (Crostella and Backhouse, 2000). No information on the carbon isotopes of the source coal were found in the literature, however there is limited data on the carbon isotopes of Permian coals from other parts of Australia. Smith and Pallasser (1996) measured a few samples from the Permian age coals from the Sydney and Bowen basins, which have carbon isotopic compositions that range from $\delta^{13}C$ -21.6 to -26.6 (45 samples analysed) with a mean of $\delta^{13}C$ -22.9 (Figure 4). Based on that information the source material used at CSBP for the production of fertilizer is likely to be similar in isotopic composition to that of Permian coals measured elsewhere in Australia, i.e., ranging from approximately $\delta^{13}C$ -22 to -27‰. Analysis of some of the coal feedstock would be required to confirm this.

**Table 5 Carbon and oxygen isotopes of carbon dioxide from the supply from CSBP (BOC inlet) and BOC outlet to Alcoa.**

| Sample | $\delta^{13}C$ $CO_2$ ‰ VPDB | $\delta^{18}O$ $CO_2$ ‰ VSMOW |
|---|---|---|
| G2092 | -37.6 | -3.0 |
| BOC inlet from CSBP | -37.6 | -2.8 |
| G2093 | -37.4 | -2.2 |
| BOC outlet to Alcoa | -37.8 | -2.1 |

By contrast the measured values of the gas from both the inlet and outlet of the BOC plant have values of $\delta^{13}C$ -37.6 ± 0.14 ‰. This value is at the light end of terrestrial lipids (Figure 4) and may be an indicator of source materials, or it may be fractionation effects resulting from the coal to urea processing. In other locations, such as the gasification plant in North Dakota that supplies the IEA GHG Weyburn-Midale Storage Project, values are $\delta^{13}C$ -20.4‰ (Mayer et al, 2013 and references therein). This is much closer to most organic signatures (Figure 4).

What is of major importance however, is that the carbon isotopic composition in this case is quite different from atmospheric $CO_2$ ($\delta^{13}C$ -7‰) and different too to terrestrial plants and their typical signatures of decomposition are around $\delta^{13}C$ -20 to -25 ‰ (Jenkins et al, 2012 and references therein). This suggests that the carbon isotopic composition will be a useful marker for monitoring and verification onwards as the measured value is quite unique compared with natural sources of $CO_2$ (see Figure 4). Further support from this approach comes from monitoring and verification activities at the IEA-GHG Weyburn-Midale $CO_2$ Monitoring and Storage Project (Mayer et al., 2013) and at the Pembina Cardium $CO_2$ Monitoring Project (Johnson et al 2011a, b). In both cases stable carbon isotopes of $CO_2$ and other species have been measured and monitored using well head samples and compared with the feedstock gas values. The feedstock/injected gas, as mentioned above, has $\delta^{13}C$ values of -20.4‰ which was sufficiently different from median values of the background $CO_2$ ($\delta^{13}C$ -12.7‰) and the $HCO_3^-$ ($\delta^{13}C$ -1.8‰) in the reservoir fluids. The data has been measured from over a 10 year period where the enhanced oil recovery of oil in a dolomitic reservoir has contributed to a CCS test. In this test the $CO_2$ movement from injectors to production wells could be monitored, monitoring of the dissolution of $CO_2$ in reservoir brines and ionic trapping of injected $CO_2$ in conjunction with dissolution of carbonate minerals was observed. The authors concluded that the stable carbon (Mayer et al., 2013) and stable oxygen (Johnson et al., 2011a, b; Johnson and Mayer, 2011) may be used to as an effective tracer tool for ongoing monitoring of the fate of the $CO_2$ in these storage sites at Weyburn-Midale and Pembina. With the unusual values for the carbon isotopes of $CO_2$ in the potential feedstock gases at the South West Hub, this approach could also be used.

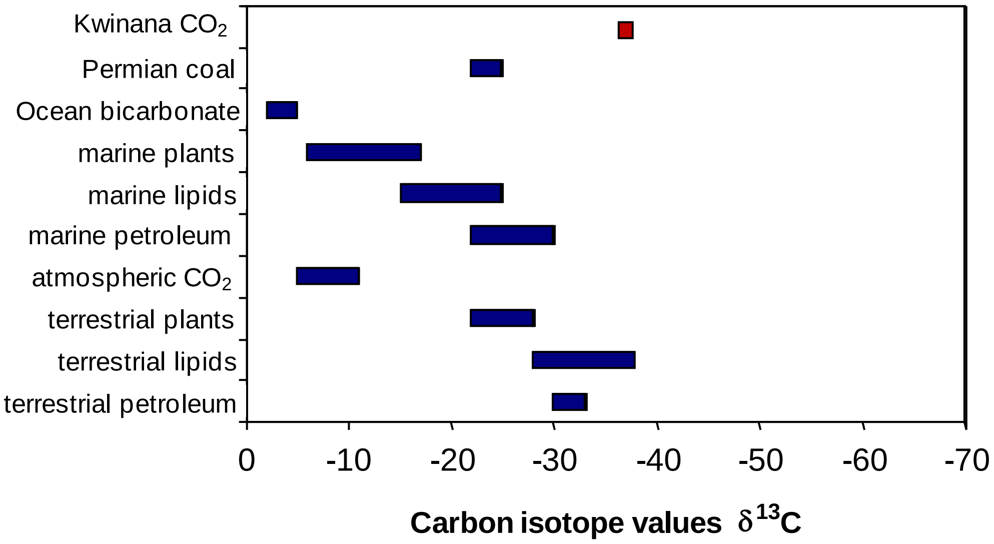


**Figure 4 Illustration of the carbon isotopic composition of the $CO_2$ from BOC to be transported to Alcoa and the test site at the SW Hub (in red). Dark blue bars indicate ranges in carbon isotopes of a variety of materials.**

With a source gas signature from a volcanic or magmatic source, the CO2CRC Otway Project (Stage 1) in Victoria, Australia also was able to use a unique isotopic signature as a tracer for monitoring and verification in some instances. This source gas from Buttress-1, with $\delta^{13}C$ $CO_2$ value of -7‰, is isotopically distinct from any $CO_2$ derived from the maturation of organic matter (with a range of $\delta^{13}C$ -12 to -15‰) as seen in the $CO_2$ from the depleted natural gas field (Naylor Field) storage site (Boreham et al, 2011). This signature is also quite different from surface biological $CO_2$ isotopic signatures which are approximately $\delta^{13}C$ -20‰. However, $\delta^{13}C$ -7‰ is very similar to the atmospheric signature and would prove difficult for atmospheric monitoring. These typical $CO_2$ sources have known ranges of carbon isotopes (Figure4) and can be generally predicted, and this is why the extensive difference of the injected gas ($\delta^{13}C$ -37‰) from CSBP and BOC in Kwinana provides a distinct signature that can be utilised during any pilot testing with this gas as an in situ tracer for the $CO_2$.

Oxygen isotopes are reported in Table 5 . At this point the data are collected as a part of information gathering for future monitoring. Oxygen in $CO_2$ is affected by contact with water and is more of an indicator of temperature. However it can be used in the understanding of water saturation and mineral precipitation during $CO_2$ flood (Johnson et al, 2011a). Therefore these measurements are not discussed further at this time, but will be used in future studies during the pilot injection.

## 2.4 Gas analysis summary

Stable carbon isotopes have unusual values, isotopically depleted in $^{13}C$. With values of $\delta^{13}C$ -37.6 ± 0.28 ‰ post gas processing at BOC, this signature appears quite distinct from other potential sources of $CO_2$ in the atmosphere, plants and photo-respiration so that the $CO_2$ isotopic value might act as a tracer in its own right. Oxygen isotopes of $\delta^{18}O$ -2.15 ± 0.07 ‰ post processing are slightly enriched relative to the gas entering the BOC plant. Oxygen isotopes do not function in the same way as carbon isotopes and can provide other information that may enable calculations to assess the extent of solubility and ionic trapping of injected $CO_2$ together with other measurements typically measured in formation fluids (Johnson et al., 2011a, b; Johnson and Mayer, 2011; Mayer et al., 2013). Thus the carbon and oxygen isotopes of the $CO_2$ anticipated to be used for the first stages of the SW Hub storage test appear to be of significance for the monitoring and verification program in future.

In the case of the early stages of the South West Hub, the use of gases from coal to urea plants typically provides high $CO_2$ purity gases. The compositional data suggest that there are few contaminants in the gas from CSBP and BOC with $CO_2$ in excess of 98.3 mol % post processing, and only minor methane and ethane. As mentioned in Stalker et al., (2009) there is the potential for some contaminants to be used as tracers in the subsurface if they are suitably stable and persistent in the environment. For the current case, there will be limited amounts of any trace contaminants, but this should be evaluated for future $CO_2$ sources.

No metals analyses of the gases were conducted. This was due to a lack of methods for the capturing of representative samples from BOC and some potentially difficult operational issues that would have to be overcome at the BOC Plant. Discussions with a variety of specialists suggested that significant method development would be required to conduct these tests. The benefit of obtaining this data for a typical CCS project would be to characterise any potential contaminants and their overall contribution that might impact on (a) injectivity, (b) reactivity with the storage interval or (c) mobility of some of these components outside of the storage container if leakage were to occur.

Analysis of the coal feedstock for carbon isotopes would be beneficial in the overall audit of carbon sources for the project and provide an understanding of the potential fractionations that might occur during the processing or combustion of the coals as source materials for $CO_2$.

## 2.5 Organic Geochemistry of liquids

## 2.6 Introduction

A preliminary petroleum geochemical evaluation of the Harvey-1 well addresses a number of activities relevant to the South West Hub Project. This includes:

- Determination of presence or absence of free/migrated petroleum in sandy or higher permeability formations, and,
- Determination of volatile components to identify any presence of compounds such as BTEX or other partially soluble organic compounds (contamination, background surface organics etc.) that may need to be identified and quantified for regulatory purposes.

Supercritical $CO_2$ is a known solvent that is used to extract organic compounds, particularly polyaromatic hydrocarbons (PAHs) in the laboratory (Langenfeld et al., 1993; Librando et al., 2004) therefore it is relevant to conduct assessments of the potential to mobilise any hydrocarbon species for subsequent monitoring and verification purposes. This provides some basic baseline information for the potential impact of mobilised hydrocarbons for the general area. The presence of organics in rocks also impacts on wettability and is often considered during core flooding activities (Iglauer, Pers. Comm. 2012). Characterising the presence of hydrocarbon compounds as a part of a detailed coreflood might be important for understanding the behaviour of the different fluids flooding a sample.

In the case of the South West Hub project, the Harvey-1 well is located in the vicinity of the structural high known as the Harvey Ridge. As there is a potential seal present higher up in the geological column there is the possibility that this location could act as a hydrocarbon trap that might be a focus for any mobile hydrocarbons in the area. By evaluating the petroleum hydrocarbon potential of the region from the Harvey-1 well data, the South West Hub project can assess the resource conflict risk with mobile, readily extractable, hydrocarbons that may exist in the interbedded silts and shales.

Eight core samples and three drilling fluid samples were analysed to characterise any hydrocarbons present. None of the water samples were evaluated by this method due to limited supply. It was decided that maximizing the inorganic geochemistry data generated from those fluids was of greater importance. The organic geochemical sampling and analytical methods are described below.

### 2.6.1 METHODS FOR CHARACTERISING LIQUIDS

#### Core Samples

Eight core samples from a range of locations (Table 6), were selected as 'sister' samples to horizontal core plugs taken at these locations based on depth and the facies and rock properties defined in the project *Facies-based rock proprieties distribution along Harvey-1 stratigraphic well* (Delle Piane et al., 2013). Sample nomenclature for the core plugs match those used in Delle Piane et al. (2013), while other samples such as drilling fluids use separate bar coding numbers.

**Table 6 Core samples analysed as a part of this project. All horizontal plugs arrived wrapped in neoprene sleeves (a potential source of contamination). These are sister samples to those described in Delle Piane et al, 2013.**

| Sample Number | Bar Code | Depth (m) | Core tested | Sample Type | Description | Facies Type |
|---|---|---|---|---|---|---|
| **Yalgorup Member** | | | | | | |
| 206611 | W12/010405 | 913.9 | 1 | Horizontal plug | Coarse to very coarse sandstone, less coarse interval | Aii |
| 206629 | W12/010406 | 1289.61 | 2 | Horizontal plug | Oxidised silty shale | G |
| 206630 | W12/010407 | 1289.71 | 2 | Horizontal plug | Fine to medium grained massive sandstone, mottled | D |
| 206631 | W12/010408 | 1299.88 | 2 | Horizontal plug | Mildly oxidised shale | D |
| 206632 | W12/010409 | 1301.73 | 2 | Horizontal plug | mottled sandstone/shale - predominantly shale | D |
| 206633 | W12/010410 | 1305.69 | 2 | Horizontal plug | Yellow-brown oxidised silty shale | D |
| **Wonnerup Member** | | | | | | |
| 206657 | W12/010411 | 1929.45 | 5 | Horizontal plug | weakly laminated coarse sandstone | Aii |
| 206687 | W12/010412 | 2523.37 | 6 | Horizontal plug | Fine to coarse sandstone, cross-bedded, variable clay% | Aii |

Samples from the Delle Piane et al. (2013) study could not be used here due to differences in the requirements for preparation. For example, the core plugs had to be treated with a specified solvent (toluene) to remove all organic contamination for the petrophysical and other tests conducted as a part of the facies analysis investigation. This was done in a batch process that placed a large number of plugs in one vessel for extraction with solvent. In the case of a geochemical analysis, each sample was prepared individually, using a different set of specified solvents) to understand the provenance of any organic matter and how it related to that particular rock type. Other analyses in the Delle Piane et al. (2013) study were destructive and left limited materials for the geochemical analyses.

The facies types described in Table 6 are based on the synthesis as described by Delle Piane et al. (2013). For ease of reference, the key facies types are reproduced here (Figure 5, Figure 6 & Figure 7). The figures show the relative similarities of some facies and differences in others. These factors were taken into consideration by Delle Piane et al. (2013) when choosing appropriate samples for comparison. The facies type descriptions are based on a modified scheme first developed by Miall (1996). This approach was previously applied to a Perth Basin study conducted by Timms et al. (2012). Using this method, Delle Piane et al. (2013) identified nine distinct lithofacies for the Harvey-1 well, which are reproduced below and summarised in Figure 5:

**Ai** – High energy channel fill, commonly cross bedded, gravelly to very coarse sandstone;

**Aii** – High energy fluvial channel barforms, medium to very coarse cross bedded sandstone with significant grain size variation between beds;

**Aiii** – Fluidized fluvial barforms, massive, coarse sandstone;

**B** – Moderate energy fluvial barforms, massive, medium sandstone with flaser cross lamination;

**C** – Moderate to low energy stacked rippleforms, fine to medium cross laminated sandstone, with common organic fragments and flaser-drapes;

**D** – Floodplain palaeosols (often vertisols), fine to medium homogenized sandstone with rootlets, dessication cracks and slickensides;

**E** – Swampy/lagoonal deposits, under waterlogged conditions, muddy bioturbated sandstone with slumps and dewatering structures;

**F** – Crevasse splays and overbank deposits, interbedded silty fine sandstone and siltstone with trough cross lamination;

**G** – Swampy/ overbank deposits, muddy laminated silt with plant fragments and thin laminated fine sandstone.

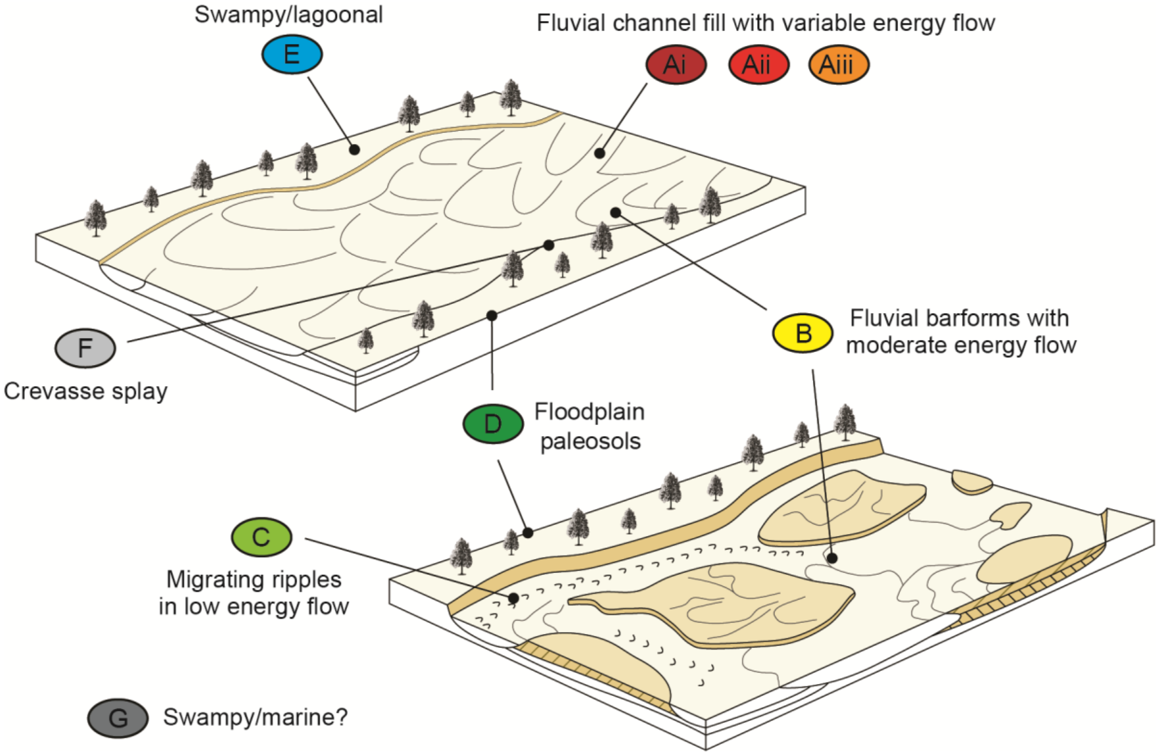


Figure 5 Block diagrams to illustrate the sedimentary depositional environment and architecture of lithofacies Ai-G from Delle Piane et al. (2013). After Miall (1996).

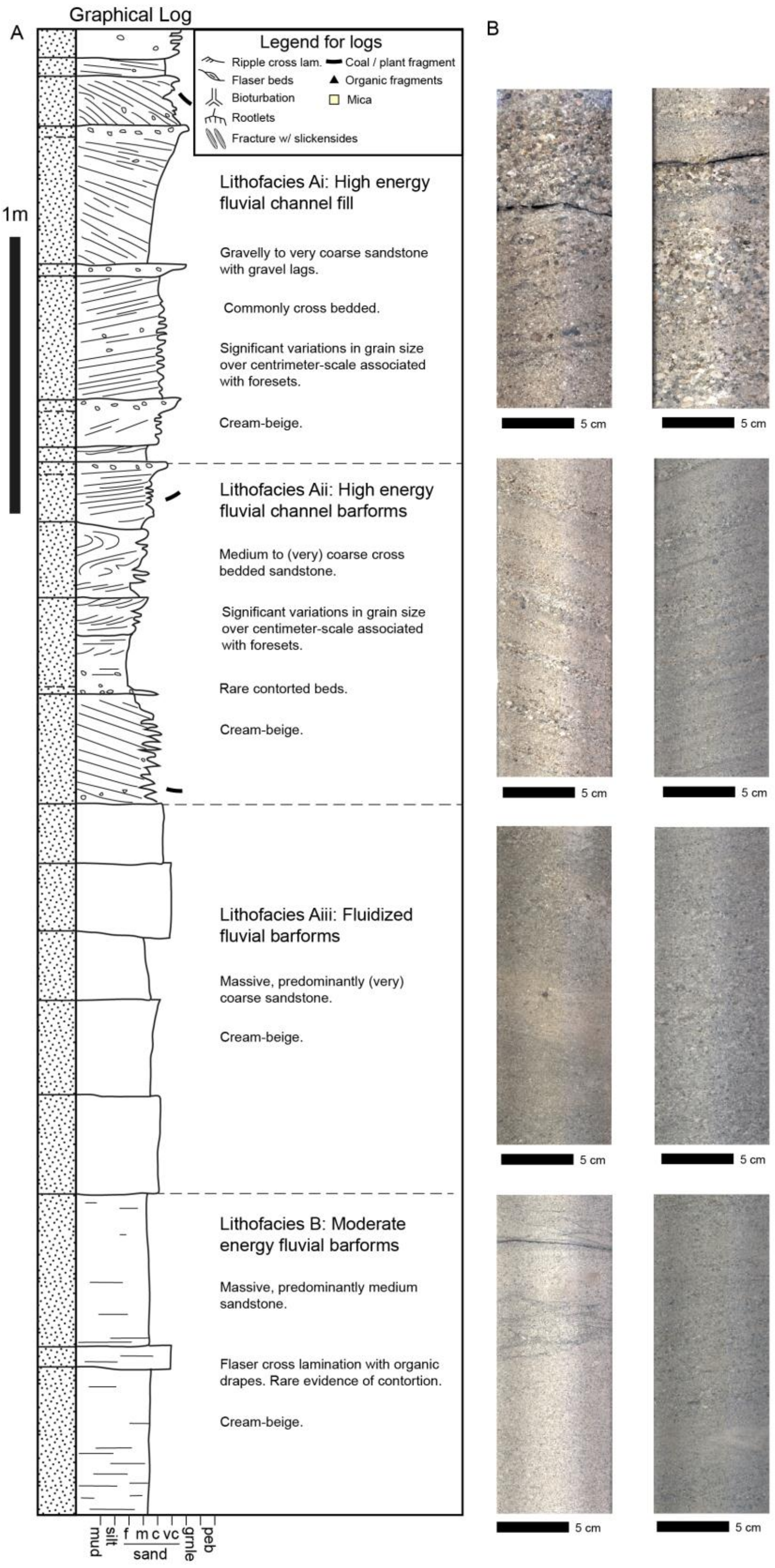


**Figure 6 A summary of the lithofacies scheme developed for the Mesozoic stratigraphy of the central Perth Basin. (A) Graphical sedimentary logs and descriptions. (B) Example core photographs from Harvey-1 for each of the lithofacies examples depicted in the graphical log. Figure courtesy of Delle Piane et al. (2013).**

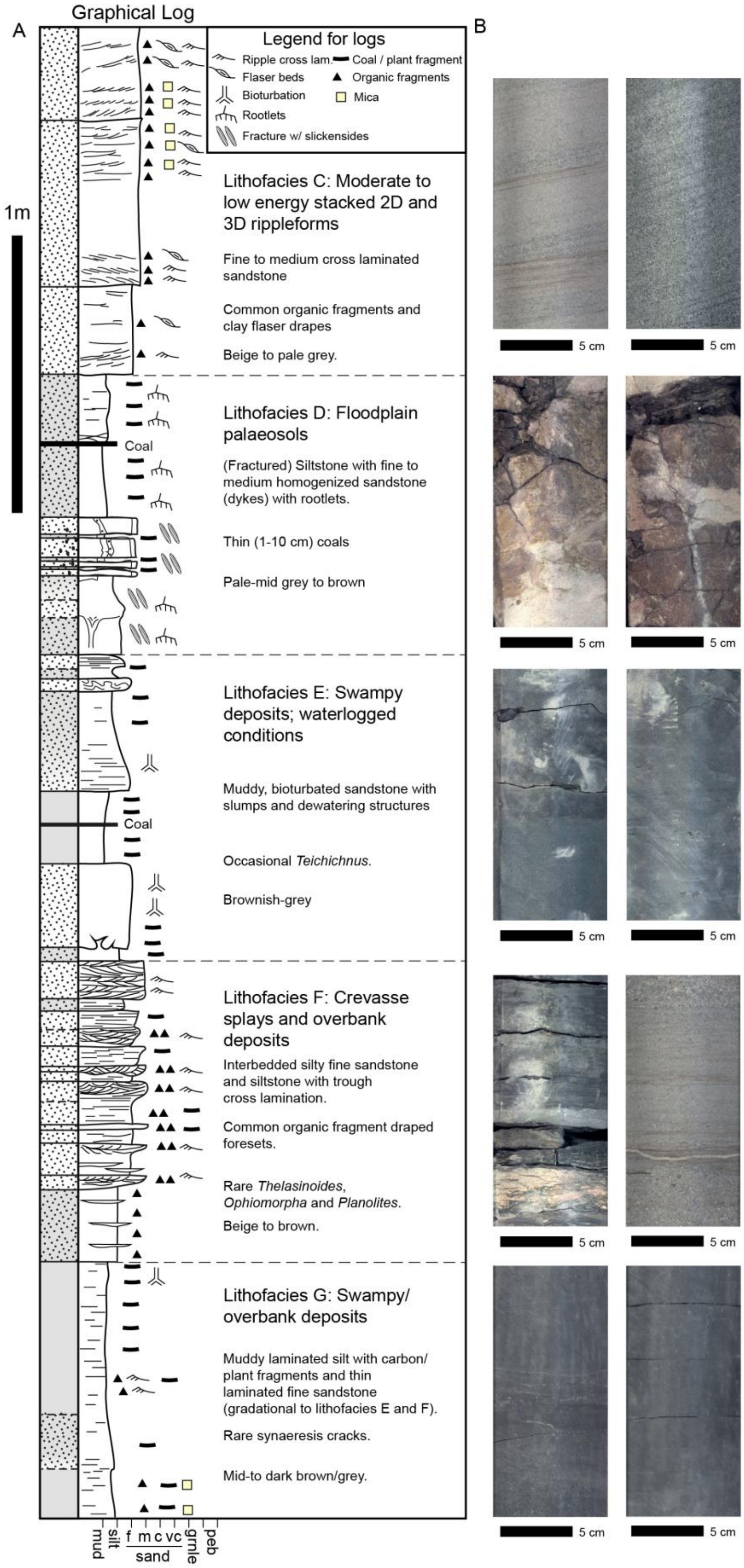


**Figure 7 A summary of the lithofacies scheme developed for the Mesozoic stratigraphy of the central Perth Basin. (A) Graphical sedimentary logs and descriptions. (B) Example core photographs from Harvey-1 for each of the lithofacies examples depicted in the graphical log. Figure courtesy of Delle Piane et al. (2013).**

More Yalgorup Member samples were chosen based on the greater variation in facies in that member. By contrast, the Wonnerup Member is reasonably uniform and dominated by the Aii facies, and all A facies together make up 85% of that facies (Delle Piane et al., 2013).

For the purposes of an organic geochemical evaluation, the important features were the degree of porosity and permeability (i.e., an ability to be able to reservoir fluids) and the amount of organic rich clays that may contribute towards in situ organic matter presence. Determining through extraction the presence, type and volume of hydrocarbons allows for an initial basin resource assessment and an evaluation of the risk for resource conflicts with carbon storage.

## Preparation of Core Samples

Core plugs received from GSWA Core Store (via Geotechical Services Pty Ltd) had only been cut from the well core and were otherwise untreated. The samples were received wrapped in rubber (neoprene) sleeves, which was not anticipated, and can be a potential contamination source. Cores also had been written on with a marker pen for orientation information. The following procedure was used to clean the core and laboratory apparatus used prior to the process of obtaining any extractable organic matter from the core samples.

1. Soxhlet thimbles and cotton wool were extracted overnight in a soxhlet apparatus in a 500 mL mixture of dichloromethane (DCM) and methanol (93:7 v/v).
2. The rubber around the cores was cut and removed and archived. A photograph was taken.
3. The cores (where possible) were brushed hard with a wire brush and cleaned on the surface with DCM. The brush was cleaned with DCM between samples. This removed surface contamination including the blue marker pen, with one exception where the sample 206632 (W12/010409 at 1301.73m) was too friable to be scrubbed (Appendix B ).
4. The cores were placed in the cleaned soxhlet thimble, topped with cleaned cotton wool and placed in the soxhlet apparatus with a 500 mL azeotropic mixture of dichloromethane (DCM) and methanol (93:7 v/v), and 5 anti-bumping granules. The core plugs were extracted for 72 hr.
5. The fluid collected was transferred in its round bottomed flask to a rotary evaporator and the volume of solvent reduced.
6. The reduced fluid was filtered over cleaned cotton wool in a glass pipette to remove any particulates and fibres present in the solution.
7. The fluid and the washings from the round bottomed flask were placed in a cleaned 10 mL glass cylinder and topped up to 10 mL with clean DCM.
8. 1 mL of this extract is transferred to a clean weighed vial and reduced to dryness under nitrogen to give a final weight for the total extract.
9. The remaining 9 mL is further reduced and stored in a 2.5 mL vial for further analysis retaining the more volatile components that are naturally lost during the drying of the 10% sample for weighing.
10. Photographs were take of the cleaned cores, the vial of material extracted and the sleeve (Appendix B ).

The 2.5 mL sample was then submitted for characterisation by Gas Chromatography-Flame Ionisation Detection (GC-FID) and rapid screening Volatile Organic Compound analysis by Gas Chromatography Mass Spectrometry (GCMS).

## Collection and Preparation of Drilling Fluid Samples

The original analytical program proposed the analysis of two drilling fluid (or drilling mud) samples in order to evaluate the degree of contamination the water and core samples may have been exposed to during sample collection. Mud samples from depths closest to some of the core plugs were analysed to evaluate drilling fluid contamination. The samples are collected on site in glass and plastic vessels and were supplied by GSWA.

Due to the low volumes of drilling mud taken in some cases, it was not possible to conduct both organic and inorganic geochemical analyses on the same samples (Figure 8). Care was taken to choose samples that were near the core plugs, the water sample (856m) or other mud samples when it became apparent there was insufficient material (Table 7). As there are both sediment and liquid fractions present in the larger samples. These were filtered and treated separately. The filtrate samples relate to the solids that were extracted, versus the liquid fraction.

The drilling mud samples then underwent extraction to monitor for organic matter contamination in the core plugs.

**Figure 8 Photograph of the first batch of drilling mud samples received from GSWA. Note the differences between the two 900m mud samples provide at the back left of the photograph.**

In the case of the mud sample from 900m, the sample was supplied in two separate containers (Figure 8). They were so visibly different that it was decided to treat them as two discrete samples in order to understand if the visual difference was relevant (Table 7). Two new samples were subsequently obtained for extraction for organic geochemistry, as all materials from the first pair were completely consumed during the analysis.

Extraction of the drilling fluids and water samples for isolation of organic compounds occurs in a similar manner. Rather than washing the solid material with a soxhlet, the fluid is introduced to a separation funnel with a specific solvent mixture (usually the azeotrope of dichloromethane and methanol). The drilling fluids or formation water samples are then washed by agitation in the separation funnel. The funnel is then left so that the water and organic phases separate. The denser organic phase is drained off and the process repeated at least 3 times to recover all the organic compounds. Internal standards are added to facilitate the calculation of recovery rates and compared with the unknowns.

The drilling fluid samples were treated in a similar manner as for the core samples for characterisation by GC-FID and rapid screening Volatile Organic Compound analysis by GCMS.

Table 7 Drilling fluid (mud) samples from the Harvey-1 well. The 900m and 1320m samples were single samples provided in two vessels for analyses.

| Sample Number | Depth (m) | Sample Description | Sample Type |
|---|---|---|---|
| W12/010401 | 900 | Bottle 1 | Sediment & water analysed |
| W12/010402 | 900 | Bottle 2 | Sediment & water analysed |
| W12/010404 | 1320 | Single sample | Water only |

### Total Petroleum Hydrocarbons (GC-FID)

Analysis was conducted by National Measurements Institute (NMI) based on USEPA Method 3510. Extracts are concentrated or diluted to be injected into a GC using a non-polar column (typically a DB-1 or DB-5) to be chromatographically separated and quantified using a flame ionisation detector (FID). The oven temperature is increased over time to aid this process.

### Volatile Organic Compound Analysis by Gas Chromatography/Mass Spectrometry (GC/MS)

Volatile organic compound (VOC) analyses of extracts from the core plug and drilling fluids samples was conducted at NMI. The method measures most volatile compounds that have boiling points below 200°C as per EPA Method 8260C.

The lower limit of quantitation is dependent on the compound investigated, the instrument used and the choice of sample preparation/introduction method into the instrument. They limits are 5ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes and 5 ug/L measured by purge-and-trap. Results are reported below.

## 2.7 Results from the liquid samples extracted from the core and drilling fluids

### Core Samples

The extraction process for the core samples provides data on the amount of total extractible organic matter (EOM) as shown in Table 8. These data are commonly used in the oil and gas industry to give some indication of the presence of economic quantities of hydrocarbons present.
It is clear from the results that there is the presence of organic matter in each of the core samples. This organic matter may come from either;

1. Organic matter residing in shales that were deposited with the sediments, which have subsequently matured to some degree,
2. Organic matter has matured and been expelled, and subsequently migrated from an area of higher maturity into the rocks in these intervals, or,
3. Contamination has occurred from the presence of the drilling fluids.

The greatest amount of extract was in sample 206611 at a depth of 913.94m in the Yalgorup Member (Figure 9). This sample was classified as facies Aii and contained a total of 57.00 mg hydrocarbons (Table 8). Converted to mg/kg rock, this sample contained 304.93 mg/kg hydrocarbon which is low when compared with known source rocks such as North Sea Jurassic source rocks which may contain 16,000 mg/kg organic extract (Weiss et al., 2000). A sandstone such as the Heimdal Formation, Norwegian North Sea, with porosity of 33-35% and about 70% oil saturation may contain up to 100,000 mg/kg hydrocarbons (Ross, 2004), further emphasising the small recoveries of hydrocarbons from the Harvey-1 rocks analysed. The GC-FID chromatogram (Figure 9) shows a presence of *n*-alkanes ranging from approximately $nC_{14}$ to $nC_{34}$ and include isoprenoids (such as pristine and phytane) and other biomarkers seen on top of the hump between $nC_{25}$ to $nC_{30}$. These compounds are typical of organic matter extracts and could be from in situ or migrated hydrocarbons. Sample 206611 from 913.94m and classified as facies Aii is made up of high energy fluvial channel barforms, medium to very coarse cross bedded sandstone with significant grain size variation between beds (Delle Piane et al. 2013), where there is little or no clay or organic rich material which might contribute to the presence of EOM this sample. In other words this is not source rock material. The other seven samples contain an order of magnitude less EOM, but have similar GC-FID chromatogram features to one another (Appendix C).

The GC-FID analyses confirm that there is some contribution from natural organic matter in each of the samples (Appendix C) although it is difficult to quantify due to probable drilling fluid contamination (as discussed below).

Quantifiable components using the Total Petroleum Hydrocarbon (GC-FID) method (Table 11) as well as other components in the core extracts were not identifiable by GC-FID alone. The TPH data show very low levels of *n*-alkanes present, mostly at or below the limits of detection. By contrast, the filtrate part of the drilling muds contain higher quantities of hydrocarbons. The suggestion here is that the EOM contribution is not solely from simple hydrocarbons such as *n*-alkanes and may be from more polar materials that are unresolvable (such as esters which can also be components of drilling muds). Evidence for this can be seen in the chromatograms of the drilling fluid extract from the mud filtrate (Figure 10) where some of the material comes from the unresolved complex mixture which appears under the "hump" of the $nC_{25}$ to $nC_{30}$ alkanes labelled on Figure 9 and is more obvious in the drilling mud chromatogram (Figure 10b). This hump is far larger than for any of the other core extract samples (Appendix C ) and may contribute to the larger EOM.

Porosity and permeability data where available (Table 9) for samples near the same depth intervals shows little in the way of an obvious relationship with the relative amounts of EOM recovered i.e., greater porosity and permeability providing more accommodation space for migrated hydrocarbons. Rather, there may be a potential impact on the amount of drilling fluid invasion.

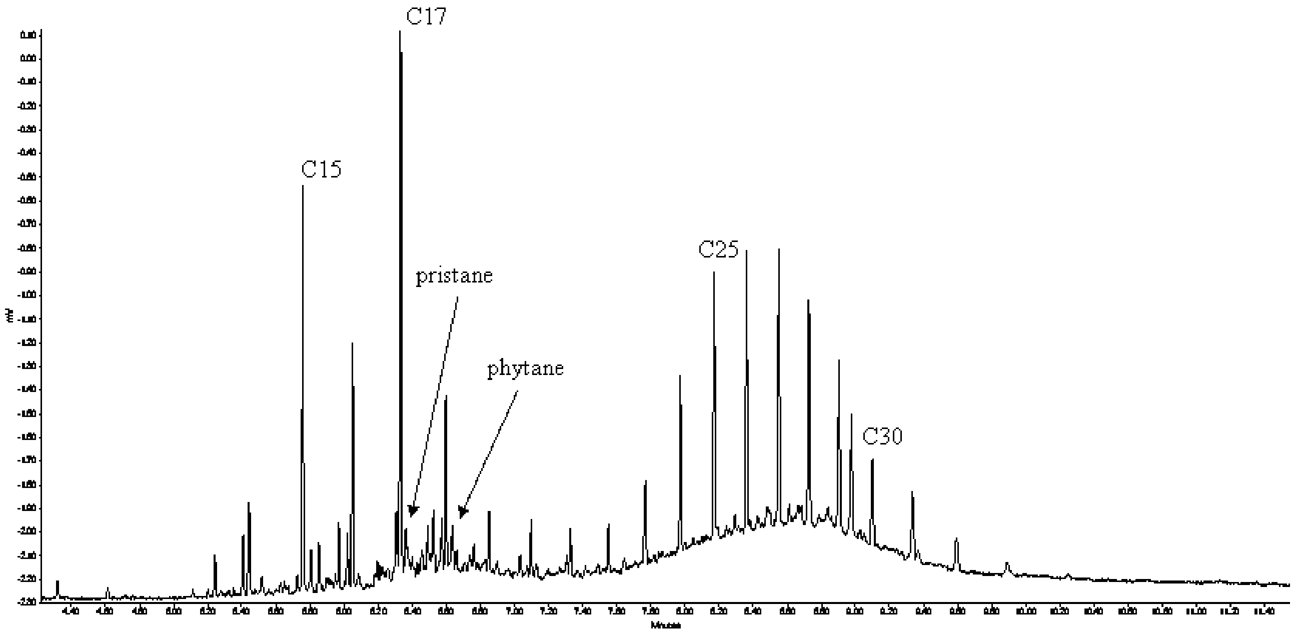
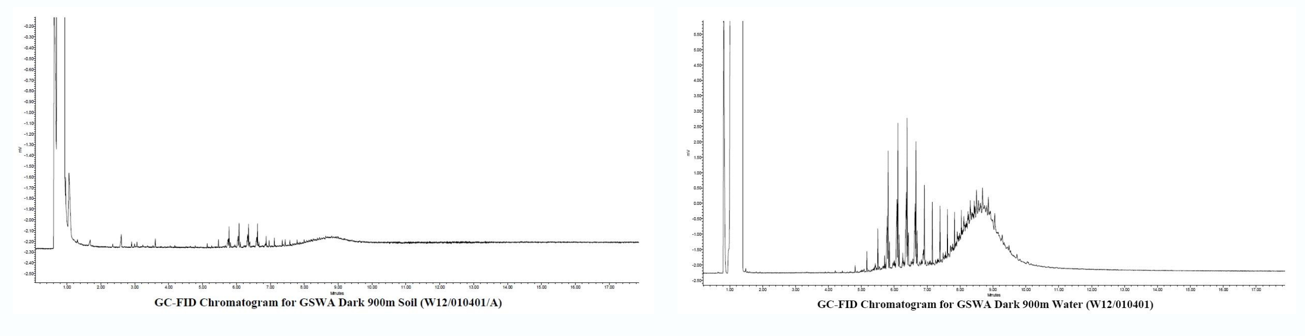


Figure 9 Whole oil GC of extract from sample 206611 (W12/010405) from 913.94m in the Upper Lesueur, Facies Aii.


GC-FID Chromatogram for GSWA Dark 900m Soil (W12/010401/A)

GC-FID Chromatogram for GSWA Dark 900m Water (W12/010401)

**Figure 10 Whole oil GC of extract from drilling mud samples from W12/010402 at 900m with (a) sediment extract (filtrate) and (b) fluid extract (liquid). See Appendix D for a larger scale image of the figures.**

As noted in Delle Piane et al. (2013) significant borehole enlargement and drilling problems may have contributed to variations in drilling mud weights to compensate for the varying stresses. This occurred in particular from depths of around 900m and may have contributed to varying degrees of contamination through the well. Wireline log information (Figure 11) from 900m to around 1400m shows the degree of outbursting that may have contributed to different levels of mud contamination in some samples.

Use of the molecular data for evaluating the source of the EOM in the samples has unfortunately been sufficiently compromised as the compounds from the mud appear to coelute with the pristine, phytane and *n*-alkanes in that region from *n*-$C_{16}$ to *n*-$C_{20}$. No estimates of source of the hydrocarbon or maturity levels can be calculated by standard methods such as measuring the ratio of pristine/phytane or *n*$C_{17}$/pristine or carbon preference index (CPI) to evaluate whether the organic matter seen in the core samples is in situ or migrated.

Table 8 Organic matter extracted from core samples.

| Sample Number | Bar Code | Depth (m) | Formation | Facies | Total extract (mg) | Extract Yield ppm = mg extract/Kg core |
|---|---|---|---|---|---|---|
| **206611** | W12/0104 05 | 913.94 | Yalgorup | Aii | 57.00 | 304.93 |
| **206629** | W12/0104 06 | 1289.66 | Yalgorup | G | 12.20 | 46.60 |
| **206630** | W12/0104 07 | 1289.78 | Yalgorup | D | 5.80 | 23.02 |
| **206631** | W12/0104 08 | 1299.88 | Yalgorup | D | 4.60 | 33.20 |
| **206632** | W12/0104 09 | 1301.73 | Yalgorup | D | 10.20 | 54.34 |
| **206633** | W12/0104 10 | 1305.75 | Yalgorup | D | 15.10 | 58.93 |
| **206657** | W12/0104 11 | 1929.46 | Wonnerup | Aii | 8.00 | 33.82 |
| **206687** | W12/0104 12 | 2523.4 | Wonnerup | Aii | 5.60 | 20.47 |

Table 9 Porosity and permeability measurements for samples close to those measured for geochemical analyses.

| Sample Number | Depth (m) | Formation | Facies | Porosity % @ 800 psi* | Permeability mD @ 800 psi* |
|---|---|---|---|---|---|
| **206609** | 911.53 | Yalgorup | Aii | 25.66 | Nd |
| **206616** | 920.56 | Yalgorup | C | 19.33 | 5.15 |
| **206628** | 1273.89 | Yalgorup | B | 15.01 | 0.72 |
| **206635** | 1323.93 | Yalgorup | Ai | 18.50 | 12.40 |
| **206660** | 1935.50 | Wonnerup | Aii | 16.33 | 122.38 |
| **206688** | 2525.83 | Wonnerup | Aii | 12.33 | 5.32 |

* Data provided by Geotechnical Services Pty Ltd (in Delle Piane et al. 2013)

An alternative method for estimating organic matter maturity is by using vitrinite reflectance data. Only two values were measured (data provided by GSWA) due to the dearth of organic matter observed in the samples (Table 10). The $R_o$ value at 916.42m of 0.36-0.38% indicates a very low thermal maturity, below the threshold for liquid hydrocarbon generation. This sample is close to that of the sample with the highest occurring EOM (sample 206611 at 913.90m) so it would suggest that any of the organic material in that sample is not indigenous to the Aii facies. The deeper sample from 2514.45m contained no vitrinite and instead a series of other measurements were used to calculate a vitrinite reflectance equivalent (Rv equivalent) value of 0.7-0.8% which is in the middle of the oil generating window. As the Wonnerup is made up of 85% Ai, Aii and Aiii facies (i.e., sandy units), there is likely to be an absence of sufficient organic matter to permit hydrocarbon generation at these depths.

Based on the low yields of hydrocarbons and levels of contamination seen in both the extracts from the cores and drilling fluids, CSIRO and ANLECR&D agreed not to proceed with further testing at this time.

Table 10 Vitrinite reflectance measurements (GSWA supplied).

| Sample number | Depth m | Rv Max | Range | SD | N | Rv random | Rv equivalent | Nearest samples collected by Delle Piane et al. (2013) |
|---|---|---|---|---|---|---|---|---|
| L6616 | 916.42 | 0.4 | 0.31-0.46 | 0.031 | 25 | 0.36-0.38 | | 206612 @ 915.46m (B/C) |
| L6617 | 2514.45 | 1.52 | 1.02-1.98 | 0.291 | 15 | | 0.7-0.8 | 206683 @ 2516.00m (Aii) |

Screening of volatile organic compounds (VOC) as shown in Table 12 has been conducted partly for baseline monitoring as it is an important measurement of water quality in drinking water supply. While normally measured from water bores and point-source release sites, there is an increasing move towards monitoring from aquifers themselves (Zogorski et al, 2006). VOCs were detected in the majority of the aquifers monitored in that report, so it is useful to do an assessment of any samples to see potential contributions at this early stage, and be aware of any species that could be mobilised by $CO_2$ in the future. The core extracts were analysed for VOC components (Table 12), and showed that there was some presence of these materials. However they do not appear to have been sourced from the drilling fluids as contaminants.

Results for the drilling fluids (both the extracted mud filtrates and the liquid fractions) generally fit with an estimated value of < 0.001 mg/L calculated based on the fact that the measured result was greater than the method detection limit, but lower than the limit of quantitation as defined by the detailed methods used by NMI. Thus most of the compounds measured were detected but below the < 0.001 mg/L value, and therefore not a major contributor to the presence of VOCs in the core extracts.

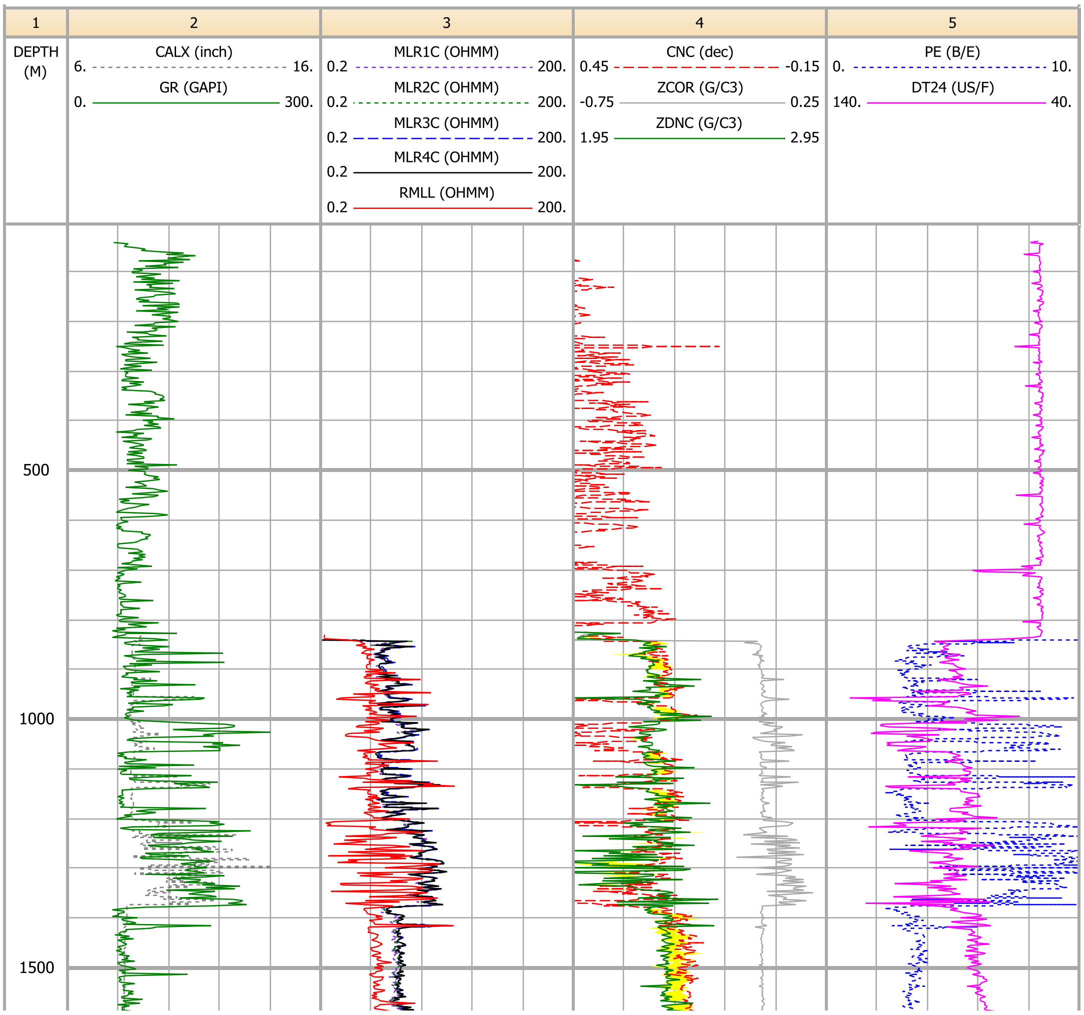


**Figure 11 Log data showing the borehole size enlargement from just over 900m to approximately the top of the Wonnerup Member at 1380m. Modified from Delle Piane et al. (2013).**

Table 11 Total Petroleum Hydrocarbons (GC-FID) in mg/L.

| Compound | 206611 913_94m 010405 : Core Aii | 206629 1289_66m 010406 : Core G | 206630 1289_78m 010407 : Core D | 206631 1299_88m 010408 : Core D | 206632 1301_73m 010409 : Core D | 206633 1305_75m 010410 : Core D | 206657 1929_46m 010411 : Core Aii | 206687 2523_4m 010412 : Core Aii | 900m 010401 Mud Liquid | 900m 010402 : Mud Liquid | 1320m 010404 : Mud Liquid |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sediment/Core Samples** | | | | | | | | | | | |
| Benzo(a)anthracene | nd | nd | nd | nd | nd | nd | nd | nd | 0.01 | | |
| Benzo(a)pyrene | nd | nd | nd | nd | nd | nd | nd | nd | 0.01 | | |
| Dichloromethane | nd | nd | nd | nd | nd | nd | nd | nd | 55 | 30 | |
| 2-Butanone(MEK) | nd | nd | nd | nd | nd | nd | nd | nd | | | 0.5 |
| 3+4-Methylphenol | nd | nd | nd | nd | nd | nd | nd | nd | 0.25 | | 0.11 |
| 4-Methyl-2-pentanone(MIBK) | nd | nd | nd | nd | nd | nd | nd | nd | 0.086 | 0.062 | 0.02 |
| **Total_TPH** | **4.6** | **0.71** | **0.65** | **2.0** | **1.23** | **1.0** | **1.3** | **0.58** | **8.5** | **15** | **5.6** |
| TPH_$C_6$-$C_9$ | | | | | | | | | 0.062 | 0.14 | |
| TPH_$C_{10}$-$C_{14}$ | | | | | | | | | 0.1 | 0.17 | 0.038 |
| TPH_$C_{15}$-$C_{28}$ | 2.7 | 0.71 | 0.65 | 1.3 | 0.65 | 1.0 | 1.3 | 0.58 | 5.3 | 9.2 | 3.1 |
| TPH_$C_{29}$-$C_{36}$ | 1.9 | | | 0.7 | 0.58 | | | | 3.2 | 5.9 | 2.5 |

nd = below limits of detection

**Table 12 VOC (by GCMS) Results for Extracts in mg/L.**

| Compound | 206611<br>913_94m<br>010405 :<br>Core Aii | 206629<br>1289_66m<br>010406 :<br>Core G | 206630<br>1289_78m<br>010407 :<br>Core D | 206631<br>1299_88m<br>010408 :<br>Core D | 206632<br>1301_73m<br>010409 :<br>Core D | 206633<br>1305_75m<br>010410 :<br>Core D | 206657<br>1929_46m<br>010411 :<br>Core Aii | 206687<br>2523_4m<br>010412 :<br>Core Aii |
|---|---|---|---|---|---|---|---|---|
| 1-Methylnaphthalene | 0.0232 | 0.0754 | 0.0425 | 0.054 | 0.0333 | 0.0432 | 0.0156 | 0.0211 |
| 2-Fluorobiphenyl | | | | | | | | |
| 2-Methylnaphthalene | 0.0401 | 0.1018 | 0.0672 | 0.098 | 0.0423 | 0.0708 | 0.0331 | 0.0431 |
| Acenaphthene | 0.0068 | 0.0167 | 0.0086 | 0.0084 | 0.0065 | 0.0118 | 0.0038 | 0.0063 |
| Acenaphthylene | 0.0074 | 0.0134 | 0.0068 | 0.004 | 0.0042 | 0.0079 | | |
| Anthracene | 0.0038 | 0.0025 | | | | | | |
| Benzo(a)anthracene | 0.0017 | | | 0.0012 | 0.0015 | | | 0.0011 |
| Benzo(a)pyrene | | 0.0016 | | | | | 0.0064 | 0.0035 |
| Benzo(b)fluoranthene | 0.0025 | 0.0019 | 0.0013 | 0.0015 | 0.0019 | 0.0019 | 0.0017 | 0.0015 |
| Benzo(ghi)perylene | 0.0209 | 0.0014 | | | 0.0013 | | 0.0013 | |
| Benzo(k)fluoranthene | 0.0024 | | | | | 0.0024 | | |
| Biphenyl | 0.0346 | 0.0578 | 0.0361 | 0.0418 | 0.0359 | 0.0508 | 0.0241 | 0.0254 |
| Chrysene | 0.002 | 0.0011 | | 0.0013 | 0.0013 | | 0.0011 | |
| Dibenz(ah)anthracene | | | | | | 0.0011 | 0.0011 | |
| Dibenzothiophene | | 0.0118 | 0.0068 | 0.0059 | 0.0065 | 0.01 | 0.0039 | 0.0058 |
| Fluoranthene | 0.055 | 0.0297 | 0.0178 | 0.0114 | 0.0228 | 0.0227 | 0.0117 | 0.0124 |
| Fluorene | 0.0372 | 0.063 | 0.0016 | 0.0346 | 0.0016 | | | |
| Indeno(1,2,3,c,d)pyrene | | | | | | | | |
| Naphthalene | 0.0441 | 0.1285 | 0.0922 | 0.1132 | 0.0569 | 0.0998 | 0.0382 | 0.0526 |
| Phenanthrene | 0.0918 | 0.1197 | 0.079 | 0.055 | 0.0687 | 0.0928 | 0.0418 | 0.0595 |
| Pyrene | 0.0896 | 0.0566 | 0.0314 | 0.0204 | 0.0273 | 0.0395 | 0.0178 | 0.0262 |

## 2.8 Summary of organic liquids investigation

While organic matter was detected in the eight core plugs tested, the contamination from the drilling fluids is significant and prevents detailed evaluation of the GC-FID chromatogram data. Total petroleum hydrocarbon (TPH) analysis of the cores show very low abundance of naturally occurring hydrocarbons to be present further confirming previous interpretations that there is little in the way of petroleum prospects in the immediate area. Samples 206629 and 206630 were within 12 cm of one another, there were no striking similarities between the extractable organic matter composition. In the absence of more detailed analyses, it is difficult to say whether this is due to the fact that the different facies types may have different in situ organic matter components.

Analysis of drilling fluids to quantify the extent of contamination was not successful. This is in part due to the limited types of analyses conducted on the extractable organic matter from the cores and drilling fluids (limited sensitivity or ability to identify suitable components). Addition of a drilling fluid tracer such as fluorescein would have aided in the estimation of the extent of drilling fluid contamination and its impact on any hydrocarbons present. This too would aid in the reconstruction of any formation waters for salinity data and is strongly recommended in future wells. This has been used to good effect in the past at the CO2CRC Otway Site in Victoria and been adequate for back calculating the fluid compositions (D. Kirste, Pers. Comm.). An attempt was also made to correct the salinity through detailed analysis of the drilling fluids by inorganic geochemical methods, discussed in the next section.

The very limited vitrinite reflectance data suggests that by 2500m the well is in the oil generating window, but shallower, at the 900m interval, any organic matter in any shaly materials will be immature with respect to oil generation and expulsion.

GCMS analysis to characterise biomarkers in the core samples would potentially address the contamination issue and allow for an evaluation of the following;

1. Maturity of the organic compounds (i.e., are they in keeping with the perceived depth that the sediments reached or have they migrated in from elsewhere?),
2. Source of the organic compounds (i.e., are they from a marine, terrestrial, lacustrine, oxic, clastic starved etc source).

Much of that information may not as yet be of benefit to an overview of Harvey-1 for CCS purposes, but may aid in the understanding of the burial history in the region and complement the vitrinite reflectance data and basin modelling thus becoming part of future study for WA DMP or GSWA. The low yields in extractable organic matter from the core samples determined that a detailed study with respect to basin resource management was not relevant as the yields suggest an absence of an active economic petroleum system in the vicinity of the well. As the well is located near the structural high of the Harvey Ridge (and therefore a likely migration pathway), the absence of significant quantities of hydrocarbon here suggests a general absence of hydrocarbons. Furthermore, it suggests that there is little or no organic source rocks in the oil or gas window, which to an extent is confirmed by the large amounts of sandy facies absent of vitrinite seen in this well.

# 3 Inorganic Geochemistry

## 3.1 Background

Four MDT (modular dynamic testing) samples representing the main geological formations were planned to be collected during drilling, to provide information on the water chemistry across the four formations, which could then be used as an input to geological modelling. However, the MDT tool became stuck during sampling and pressurised samples could not be collected. At this point a recovery process to fish the tool out of the well commenced. After 5 days the costs for the drill rig and fishing were beginning to out-weighed the costs of the tool and the recovery process abandoned. At this point GSWA and consultants agreed to cease any further attempts to recover the tool. Instead, the drilling company obtained one water sample from the Yalgorup Member at 856 m by pumping fluids to surface (sampling method described below). The Yalgorup Member extends from 704-1380m. This sample is from the uppermost part of the Yalgorup and may represent the formation water between the Yalgorup intraformational seals and the overlying basal Eneabba Formation (possible seal). This sample is not from the intended depth of storage and it is not certain that this represents the formation water of the planned storage reservoir. It was the only sample available to the project from the Harvey-1 well. The sample was supplied to us afterwards and we were only then notified of the issues described above. No further sampling of fluids can be done in this well due to the blockage and it has subsequently been plugged and abandoned.

A separate shallow water supply well was drilled adjacent to the location of the Harvey-1 well. This well provided information about the local shallow aquifer water for baseline monitoring. The sample is from the superficial shallow aquifer that is recharged by percolating rainfall. The sample is from an interval of 27-36m BNS below the surface. The deepest point of the screened bore hole terminates at an interface between coarse sand and dark grey clay that possibly represents the top of the Leederville Formation.

The results of the analyses provide data for shallow background monitoring and one interval of the Yalgorup Member, which were combined with existing groundwater data from the Binningup and Harvey borehole lines published by Deeney (1989a and 1988b). Analyses conducted on these samples included:

- Element analysis (~60), total dissolved solids, pH, EC, Eh, density and alkalinity, to characterise the chemical composition of the groundwater.
- Element analysis and alkalinity to characterisation of fluids to determine the chemical changes that might occur as these fluids are mobilised with or without $CO_2$ (core flood experiment).
- Isotope ($^{14}C$, $SF_6$) analysis of waters to integrate with any regional groundwater data which is publicly available for the South Perth Basin and as a part of the Resource Management for Carbon Storage Project (ANLEC Project 3-0510-0057).

Methods for sampling and analysis are provided below.

As with the previous section investigating the organic geochemistry of the core plugs taken, drilling fluid samples have also been taken and characterised for inorganic geochemistry in an attempt to work out the extent of contamination. These are not the same samples as were characterised for organic geochemistry, but are similar in depth and time of extraction.

### Deep Formation Sampling 856m Yalgorup Member

The sample zone is believed to be at the base of the casing point into the open hole at 856m. An RCI (Reservoir Characterisation Instrument) was used collect the sample. First the internal plumbing lines from the sampling probe to the tanks were filled with distilled water to reduce drilling mud contamination. The added volumes of distilled water were 40.5cc to the 10L tank and 7.3cc to the second 4L tank in addition to the sampled fluids. The sample was collected in two plastic drums and not treated or preserved prior to transportation by road to Perth for analysis. The water sample was delivered to ARRC and was not chilled.

### Shallow Sampling

Staff from CSIRO (Ryan Noble) and DoW (Geoff Sadgrove) visited the Harvey-1 well site on 20/4/2012 to collect a sample from the adjacent shallow bore. The well is slotted at 27-36m BNS. Approximately three bore volumes were pumped out using a Grundfos submersible pump, and conductivity, Eh, dissolved $O_2$ and pH monitored through a flow-through-cell until these water parameters were stable - indicating a freshly recharging sample. Samples were collected, filtered on site and acidified if necessary (for cation analyses). Isotope samples were also collected without exposure of the water to the surface atmosphere. The following samples were collected:

2* 1L in brown glass

2* 120mL in glass

3* 5 L in HDPE plastic

2* 250mL in HDPE filtered (1 for anions) and filtered and acidified (cations)

1* 125 mL for alkalinity titration

All samples were stored at 4°C during transportation and storage prior to analysis.

### Drilling Mud Samples

Material from 1000m and 1896m was available for sampling (Table 13). There were not sufficient materials from existing samples that had been tested for organic contaminants to also perform inorganic geochemical tests. Drilling mud samples were collected in glass and plastic vessels (Figure 8) and were obtained from the GSWA Core Store with permission. These samples were separated into their constituent sediment and liquid samples, as they had separated out in the vessels. Both fractions were analysed to assist interpretation of the drilling fluid contamination for the 856m unconstrained sample.

**Table 13 Samples taken from Harvey-1 and the adjacent to Harvey-1 water bore, including drilling fluids analysed in this project.**

| Sample Name | Bar Code | Depth (m) | Sample Type | Description |
|---|---|---|---|---|
| **Water Samples** | | | | |
| Harvey Shallow Water Well | W12/007168 | 27-35* | Ground Water | Pumped to surface. Clear, with no sediment present. |
| Harvey-1 | W12/007169 | 856 | Formation Water | Unconfined sample pumped to surface. |
| **Drilling Fluid Samples** | | | | |
| Drilling mud | W12/014442 | 1000 | Drilling fluid | Filtrate particles and liquid component<br>Dark water with settled dark mud.<br>Water and sediment analysed separately. |
| Drilling mud | W12/014443 | 1896 | Drilling fluid | Filtrate particles and liquid component<br>Dark water with settled beige mud.<br>Water and sediment analysed separately. |

*mBNS

## 3.1.1 METHODS FOR ANALYSIS

### Trace Metals in Water

NATA methods (NT2.47, NT2.44 and NT2.51) have been used by the National Measurement Institute (NMI) for analysis of saline or fresh water, influent, effluent and waste water. The limit of reporting is 0.1 to 10 µg/L, depending on the matrix material or element measured.

Solid samples were digested in aqua regia acid prior to analysis. The water samples were analysed directly with dilutions incorporated as necessary. ICPMS and ICPAES were used for the analysis of approximately 60 elements. Blanks, sample spikes, laboratory control samples and duplicates re introduced for each batch.

### DOC, TOC, DIC and TIC

Dissolved organic carbon (DOC), total organic carbon (TOC), dissolved inorganic carbon (DIC) and total inorganic carbon (TIC) in water were measured by a NATA accredited method WL240 by NMI. The limit of detection is 1 mg/L. The preferred sample collection is in an amber glass bottle with no headspace and kept at 4°C. This was not done for the 856m sample, as the team were not on site for its collection. Samples were filtered and acidified later in the CSIRO laboratories.

### Alkalinity, Bicarbonate, Carbonate and Hydroxide Titration

Alkalinity (commonly comprising $HCO_3^-$, $CO_3^{2-}$, or even $OH^-$ in alkaline solutions) was measured using the NATA certified method WL122 by NMI. The method has limits of reporting down to 1 mg/L as $CaCO_3$ in water, or 5 mg/kg as leachable $CaCO_3$ in soil (or equivalent solids).

Soil samples, and the drilling fluid filtrates, were pre-treated by extracting with water (1:5 soil:water) for 2 hours and reported as leached alkalinity. Alkalinity for the shallow monitoring sample was measured 24 hrs after collection using the standard method above. Equivalent measurements were not made on the deep sample.

### Common Anions in Water and Soil

Common anions include the following:

- In water and soil - bromide, chloride, nitrate, nitrite and sulphate
- Other anions in water – iodide, perchlorate, thiocyanate and thiosulphate

These were analysed using Method WL119 by NMI using ion chromatography. Most, but not all the anions are NATA accredited measurements. The water samples were filtered and injected into an ion chromatograph and compared with known analytical standards. The soil samples were pre-extracted with water as described for the alkalinity tests and the leachate measured.

### Ammonia, Phosphate, Total Oxidised Nitrogen, Total Nitrogen, Total Phosphate and Silicate

The following: Ammonia ($NH_3$), Phosphate ($PO_4$), Total Oxidised Nitrogen (TON), Total Nitrogen (TN), Total Phosphate (TP) and silicate ($SiO_2$) were measured by a NATA accredited method WL239 by NMI. Methods vary slightly for each of the species, but were conducted by an auto analyser.

## 3.2 Results of inorganic geochemistry of the water samples

Results for the shallow bore, the single sample in the Harvey-1 well and a series of drilling mud samples are presented in Table 14. Each sample was, where possible, measured by the same methods for the same materials. The purpose of analysing the drilling mud fluids was to provide some information on the potential contamination levels of the fluid samples in the absence of any tracer to back-calculate drilling mud contamination. The information was used in the modelling section of the work to attempt to address this issue.

**Table 14 Selected Anion, Cation and Fundamental Measurements on Waters and Drilling Fluids to Compare Contaminants.**

| Species | Shallow Bore 27-35m BNS | Harvey-1 856m | 1000m W12/014442 Mud Liquid | 1896m W12/014443 Mud Liquid | 1000m W12/014442 Mud Filtrate | 1896m W12/014443 Mud Filtrate |
|---|---|---|---|---|---|---|
| Al mg/L | 0.007 | 0.007 | 1.1 | 1.2 | 1890 | 2110 |
| Ba mg/L | 0.064 | 0.28 | 7.8 | 53 | 2510 | 4610 |
| Ca mg/L | 98 | 1130 | 350 | 420 | 4750 | 18900 |
| Fe mg/L | 1.5 | 1.2 | 17 | 260 | 6170 | 6710 |
| Mg mg/L | 11 | 510 | 45 | 96 | 400 | 660 |
| Mn mg/L | 0.065 | 5.2 | 36 | 150 | 150 | 570 |
| P mg/L | 0.093 | 5.8 | 5.1 | 12 | 130 | 80 |
| **K mg/L** | **5.4** | **15800** | **29900** | **23900** | **39700** | **19300** |
| Rb mg/L | 0.011 | 2.1 | 5.7 | 3.4 | 11 | 6.6 |
| Si mg/L | 8.1 | 10 | 12 | 15 | 510 | 400 |
| Na mg/L | 75 | 8850 | 1720 | 3010 | 2640 | 2650 |
| Sr mg/L | 0.51 | 20 | 5 | 20 | 200 | 170 |
| S mg/L | 0.53 | 630 | 290 | 30 | 3780 | 1890 |
| $HCO_3$ mg/L | 317 | 671 | | | | |
| **Cl mg/L** | **110** | **24000** | **3000** | **23600** | | |
| DOC mg/L | 16 | 590 | 3400 | 5100 | | |
| $NO_3$ mg/L | 0.25 | 0.031 | 0.34 | 0.075 | | |
| $PO_4$ mg/L | 0.028 | 0.006 | 400 | | | |
| $SO_4$ mg/L | 2.5 | 1700 | | | | |
| Cl mg/kg | | | | | 65000 | 8000 |
| **TDS ppm** | **458** | **52319** | **>135000** | **>120000** | | |
| **Alkalinity*** | **260** | **550** | **2000** | **3200** | **4000** | **2800** |
| **pH** | **7.24** | | | | | |
| **EC µS/cm** | **940** | | | | | |
| **T°C** | **18.5** | | | | | |
| **Eh mV** | **199** | | | | | |
| **DO %** | **5.5** | | | | | |

Note – sample from 856m was collected by pumping to surface from just below the casing point.

*$CaCO_3$ equivalent in mg/L

## Deep Formation Sampling

The sample taken from the Harvey-1 well at 856m in the Yalgorup Member has a total dissolved solids (TDS) value of 52,300 mg/L. Calculated values for the wireline logging (Figure 12) reported in Delle Piane et al., (2013) are 40,000 mg/L NaCl equivalent for the Yalgorup Member and 30,000 mg/L NaCl equivalent for the Wonnerup Member. The variation between the values from the sample measurement and the wireline calculation – a measure of resistivity may be the result of drilling fluid contamination and drilling mud invasion. However, more importantly the calculated TDS is a direct measurement, the wireline is an estimate. The wireline calculates a TDS from theoretical relationship between resistivity and TDS. This relationship is influenced by the bivalent to monovalent cation composition influencing the resistivity. The correction factor is between 0.5-0.7 and this can explain the difference between the estimated wireline result and the measured TDS.

The results show that both the aqueous and solid fractions of the drilling fluids contain significantly higher quantities of major cations and anions than the groundwater sample. For example, the TDS of the aqueous sample (W12/14443) from 1896m is greater than 120,000 mg/L. Some species, notably K and Cl (constituents of KCl based drilling fluids) can have a major influence on TDS values shown by a comparison between the 856m Yalgorup sample (15,800 mg/L) and the mud aqueous samples (23,900 to 29,900 mg/L) or solid filtrate residue (19,300 to 39,700 mg/kg).

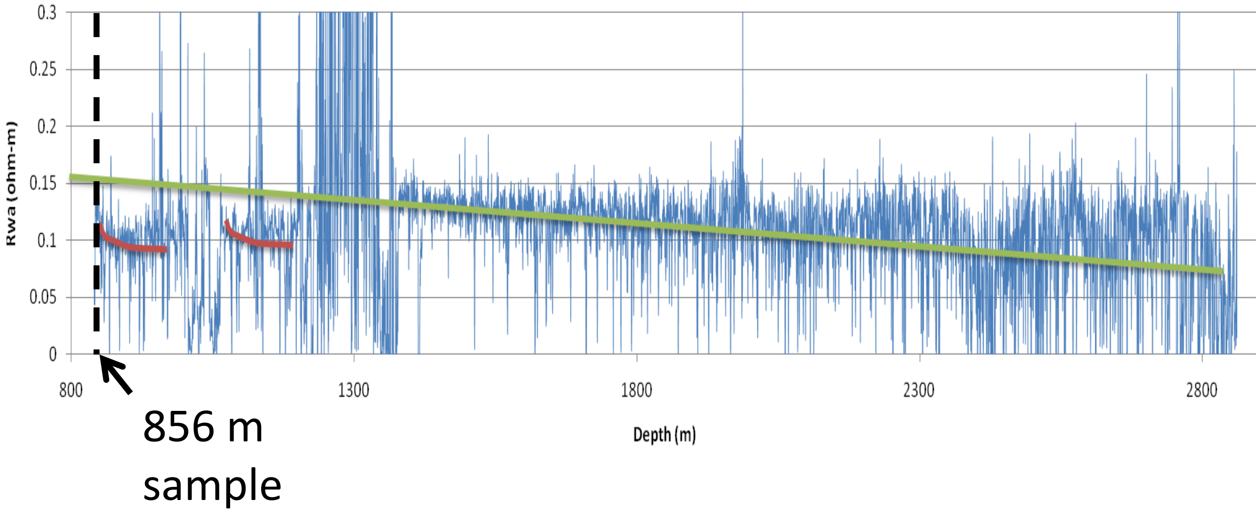


**Figure 12 Pore water resistivity for the Lesueur Sandstone. Green line shows the general salinity trend with depth for Wonnerup Member. From Delle Piane et al. (2103).**

Extensive contamination is also indicated by a comparison of the results from the Harvey-1 sample with regional samples from similar depths reported by Deeney (1989a; 1989b) for a series of research wells drilled to the north and south of the township of Harvey, known as the Binningup and Harvey lines (Figure 13). The Harvey Line, drilled between 1982 and 1985, is made up of eight wells drilled at four sites to depths ranging from 48 to 588n BNS (below natural surface) and were extensively tested at a number of screened intervals (Deeney, 1989b). The Binningup Line is similar, with drilling occurring in 1984 and has six wells at four sites with a similar testing regime (Deeney, 1989a). In both studies, wells are located in an east-west direction from the Darling Fault towards the ocean. If comparisons were to be made between the Harvey-1 sample from 856m in the Yalgorup Member with the four deepest samples from the Binningup and Harvey Line water bores, i.e., BPL1A3 from 633m BNS, HL1B3 from 588m BNS, HL2A3 from 792m BNS and HL3A3 from 574m BNS, each in the Cockleshell Gully Formation, the ranges in major element chemistry are similar (Table 16). Calcium data suggest that the Harvey-1 sample from 856m, with 1130 mg/L dissolved Ca, fits in with broad measurements in the area where regional values for the Cockleshell Gully Formation (as reported by Deeney, 1989a and 1989b) range from 556 to 3180 mg/L. This pattern is repeated for Mg and Na. Potassium and Cl results are significantly different from Harvey-1 856m with concentrations of 15,800 and 24,000 mg/L, respectively for K and Cl, versus a range for these four deep samples from the Harvey and Binningup Lines ranging from 34 to 241 mg/L for K and 11,900 to 19,100 mg/L for Cl (K shown in Figure 14).

The Cockleshell Gully Formation is Lower Jurassic in age and hosts the Cattamarra and Eneabba members. The basal Eneabba seal unit is above the Triassic Yalgorup Member samples with the MDT water sample. We are effectively comparing regional groundwater from just above the sealing unit with the Harvey-1 MDT sample just below the seal formation. The comparison was made to assess if the regional samples could be used despite the host formation differences and primarily because there is significant KCl contamination with the MDT sample taken. This presence of drilling fluid contamination was also observed in the organic geochemical analysis discussed earlier. The clear influence of this contamination is represented by the arrow in Figure 14.

Efforts were made to use ratios of other cations and anions to approximate the expected concentrations of the Harvey-1 water sample, but the results were not representative or useful. For modelling purposes reported in the next chapter we used averages of the deeper regional samples from the Binningup and Harvey Line water bores as a starting point – even though the relatively minor differences did not significantly influence the modelling results.

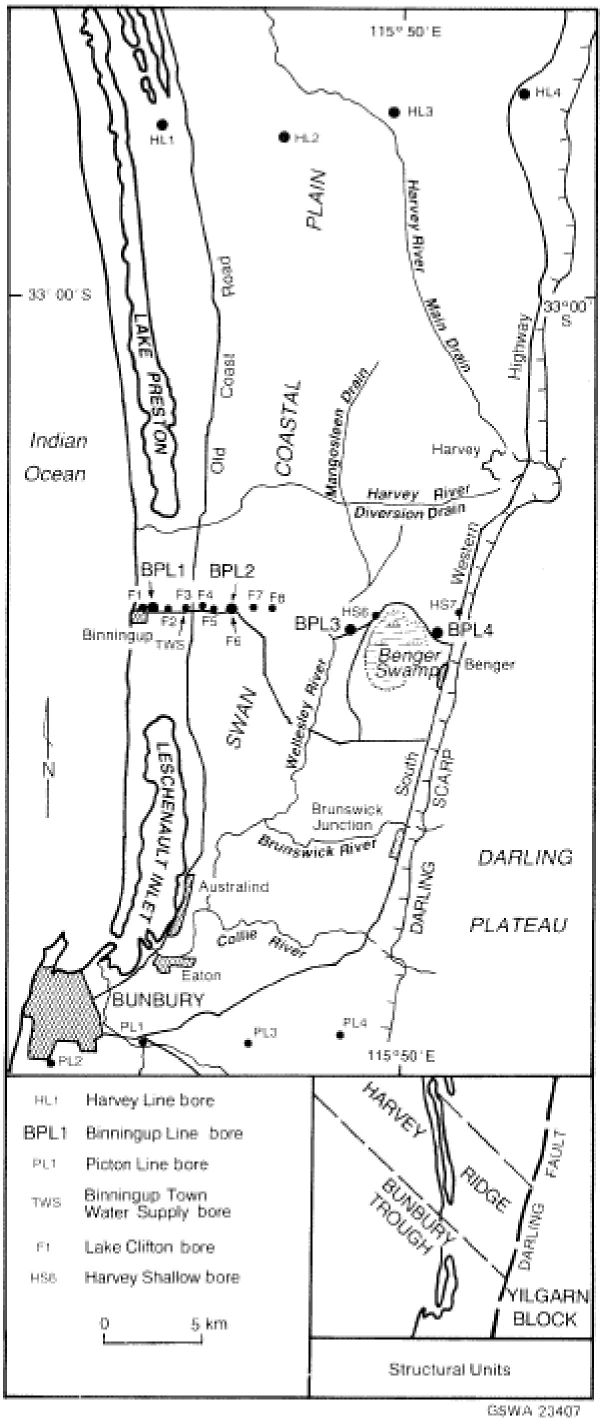


**Figure 13 Location map of the Harvey and Binningup Line water bores. From Deeney, 1989a.**

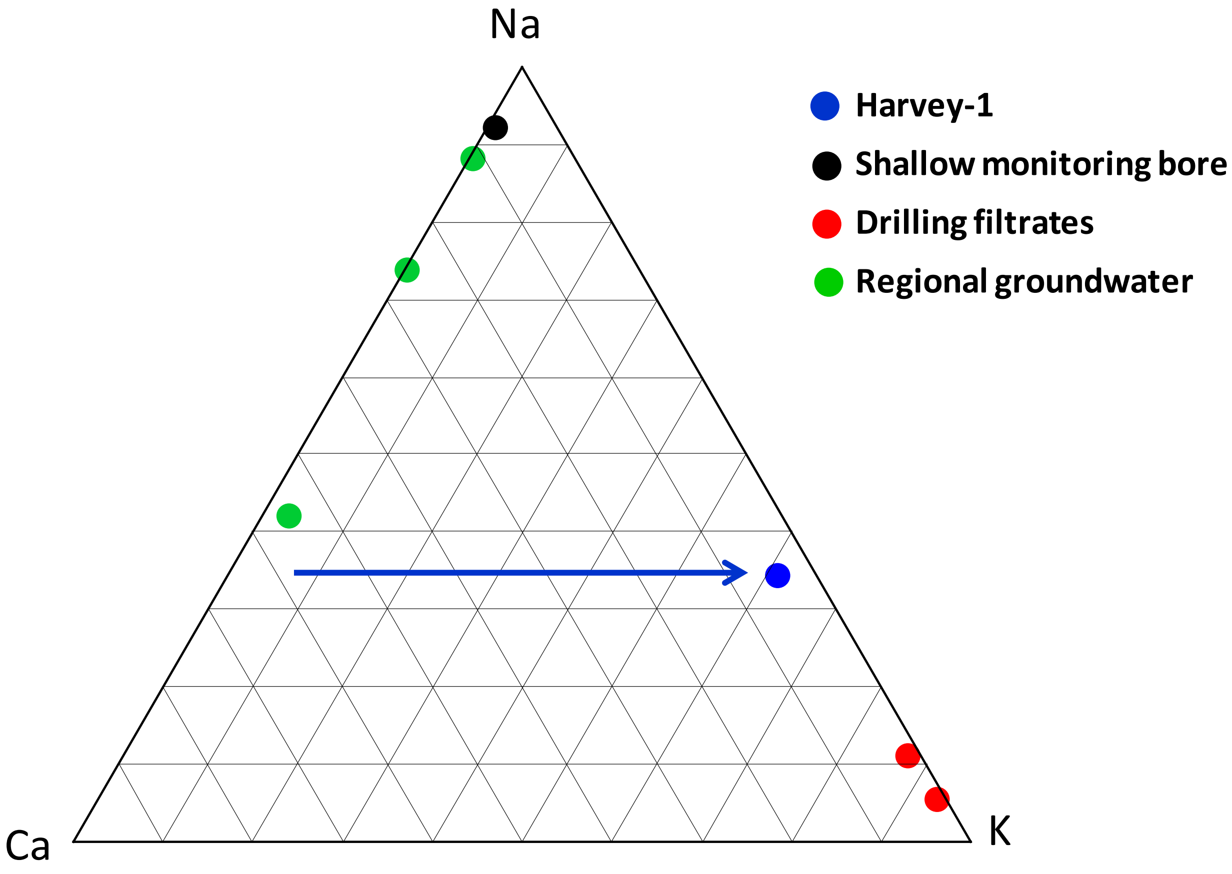


Figure 14. Ternary diagram of major cation water chemistry in the Harvey-1 (blue), shallow monitoring bore (black), regional representative samples from the Binningup and Harvey Line water bores (green) and the drilling mud filtrates (red). The arrows represent the influence of contamination of Harvey 1 from the more representative regional sample groundwater chemistry.

## Shallow Sample from 27-35m BNS Leederville Formation

This sample is not impacted by drilling fluids and is representative of water from the zone sampled. The TDS value for this sample was 458 ppm with neutral pH and was typical of shallow surficial aquifers in the Perth Basin. The water is regularly used for agriculture and is of reasonable drinking water quality. The low TDS and full characterisation of this sample allows for effective future monitoring of changes. A second shallow sample could not be obtained from the Harvey-1 well as the deeper well was immediately plugged and abandoned on completion of all drilling activities as scheduled.

Some specialised analyses were conducted on the shallow water bore and single sample from Harvey-1, to build on information for the Southern Perth Basin area and specifically around the general region of the Lesueur site. These analyses were conducted at the CSIRO Land and Water Laboratories or sub-contracted to third parties where relevant. Unexpectedly, the shallow site has an older age than the deeper sample according to $C^{14}$ dating (Table 14). Some upwelling of the underlying Leederville aquifer may have influenced this result, but given the low TDS it seems that the sample is mostly surficial water and should be sampled and analysed separately again to check this result. Another explanation for the unexpected age of the deeper samples is potential contamination from drilling lubricants that contain modern carbon polymers. This will result in a dilution of the $C^{14}$ age signature of the deeper sample. The inverted age profile of the water implies the region may be a discharge site, however there is no evidence of this. Analytically the samples may have been mixed up or another undetermined error. The only reasonable course of action is to repeat the sampling and analysis in the future with more duplicates. The C14 age signature for the shallow groundwater is a little older than other estimates from the Swan Coastal Plain for the superficial aquifer. Turner et al. (2008) observed C14 ages of modern to ~3000 years, with deeper formations in the Margaret River area up to 28,000 years old. In the study by Turner et al. (2008) The expected decrease in $^{14}$C activities due to radioactive decay was observed in all cases where multi-level samples were obtained, however, this was not observed here. The age of 8000 years measured in the shallow well indicates recharge into this zone is at least three times slower than anticipated.

Table 15 Additional analytical results for water samples.

| Species | Shallow Bore 27-35m BNS | Harvey-1 856m |
|---|---:|---:|
| $C^{14}$ Age (Years) | 7740 | 3005 |
| $\delta^{14}$ C | -618.6 | -312.1 |
| Percent Modern Carbon (%) | 38.147 | 68.794 |
| $SF_6$ Calculated Partial Pressure (pptv) | 0.19 | |
| $SF_6$ Concentration in Water (FemtoMol/kg) | 0.05 | |
| $SF_6$ Piston Flow Model Recharge Age (Years) | 42.9 | |
| $SF_6$ Piston Flow Model Recharge Year (as stated) | 1969.5 | |
| $SF_6$ Calculated Partial Pressure (pptv) | 0.42 | |
| $SF_6$ Concentration in Water (FemtoMol/kg) | 0.11 | |
| $SF_6$ Piston Flow Model Recharge Age (Years) | 35.9 | |
| $SF_6$ Piston Flow Model Recharge Year (as stated) | 1976.5 | |

Table 16 Data from the shallow monitoring bore and the Harvey-1 and regional groundwater data from Deeney (1989a, b). Missing data was not reported by Deeney (1989a and 1989b).

| Species | Shallow Bore | Harvey-1 | BPL1A1 | BPL1A2 | BPL1A3 | BPL2A1 | BPL2A2 | BPL3A1 | BPL4A2 | HL1B1 | HL1B2 | HL1B3 | HL2A1 | HL2A2 | HL2A3 | HL3A1 | HL3A2 | HL3A3 | HL4A1 | HL4B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Depth** | **27-35m bns** | **856m** | 108m bns | 347m bns | 633m bns | 71m bns | 274m bns | 120m bns | 260m bns | 123m bns | 285m bns | 588m bns | 111m bns | 330m bns | 792m bns | 66m bns | 247m bns | 574m bns | 282m bns | 48m bns |
| **Formation** | S/LV | Yalgorup | LV | CG | CG | LV | CG | LV | CG | LV | CG | CG | LV | CG | CG | LV | CG | CG | LV | CG |
| **Al mg/L** | 0.0067 | 0.0065 | | | | | | | | | | | | | | | | | | |
| **Ba mg/L** | 0.064 | 0.28 | | | | | | | | | | | | | | | | | | |
| **Ca mg/L** | 98 | 1130 | 80 | 14 | 557 | 100 | 18 | 149 | 2010 | 187 | 51 | 556 | 68 | 59 | 1230 | 50 | 648 | 3180 | 127 | 35 |
| **Fe mg/L** | 1.5 | 1.2 | | | | | | | | | | | | | | | | | | |
| **Mg mg/L** | 11 | 510 | 64 | 8 | 316 | 34 | 9 | 123 | 365 | 81 | 32 | 723 | 45 | 32 | 692 | 47 | 12 | 205 | 25 | 24 |
| **Mn mg/L** | 0.065 | 5.2 | | | | | | | | | | | | | | | | | | |
| **P mg/L** | 0.093 | 5.8 | | | | | | | | | | | | | | | | | | |
| **K mg/L** | 5.4 | 15800 | 37 | 14 | 73 | 8 | 24 | 40 | 76 | 13 | 26 | 241 | 16 | 26 | 44 | 19 | 50 | 34 | 8 | 14 |
| **Rb mg/L** | 0.011 | 2.1 | | | | | | | | | | | | | | | | | | |
| **Si mg/L** | 8.1 | 10 | | | | | | | | | | | | | | | | | | |
| **$SiO_2$ mg/L** | | | 22 | 14 | 14 | 21 | 9 | 11 | 11 | 18 | 12 | 2 | 13 | 13 | 9 | 13 | 16 | 15 | 14 | 8 |
| **Na mg/L** | 75 | 8850 | 135 | 964 | 7500 | 165 | 1760 | 2160 | 7560 | 590 | 763 | 10200 | 394 | 1240 | 9560 | 461 | 3840 | 9070 | 1700 | 565 |
| **Sr mg/L** | 0.51 | 20 | | | | | | | | | | | | | | | | | | |
| **S mg/L** | 0.53 | 630 | | | | | | | | | | | | | | | | | | |
| **$HCO_3$ mg/L** | 317.2 | 671 | 131 | 406 | 189 | 235 | 204 | 159 | 82 | 253 | 332 | 140 | 220 | 265 | 125 | 275 | 119 | 40 | 125 | 207 |
| **Cl mg/L** | 110 | 24000 | 429 | 1060 | 11900 | 320 | 2420 | 3560 | 15600 | 1220 | 90 | 17800 | 679 | 1840 | 18100 | 749 | 6710 | 19100 | 2740 | 880 |
| **F mg/L** | | | | | | | | | | 0.2 | | | | | | | | | | |
| **DOC mg/L** | 16 | 590 | | | | | | | | | | | | | | | | | | |
| **$NO_3$ mg/L** | 0.25 | 0.031 | <1 | <1 | <1 | <1 | <1 | 6 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 1 | <1 | <1 | <1 | <1 |
| **$PO_4$ mg/L** | 0.028 | 0.006 | | | | | | | | | | | | | | | | | | |
| **$SO_4$ mg/L** | 2.5 | 1700 | 9 | 150 | 1800 | 24 | 289 | 342 | 462 | 116 | 125 | 918 | 55 | 203 | 1610 | 83 | 418 | 910 | 109 | 60 |
| **TDS calc** | 458 | 52319 | 890 | 2510 | 22300 | 850 | 4690 | 6510 | 26100 | 2360 | 2270 | 30500 | 1390 | 3550 | 31400 | 1560 | 11700 | 32500 | 4790 | 1690 |
| **pH** | 7.24 | | 8.6 | 8.9 | 7.9 | 8.6 | 8.6 | 8.5 | 7.6 | 8.5 | 8.3 | 8.0 | 8.4 | 8.1 | 7.8 | 8.5 | 7.3 | 7.2 | 7.7 | 7.6 |
| **EC µS/cm** | 940 | | 175 | 428 | 3230 | 158 | 824 | 1100 | 3890 | 439 | 418 | 4650 | 271 | 644 | 4500 | 290 | 1900 | 4330 | 859 | 318 |
| **T °C** | 18.5 | | | | | | | | | | | | | | | | | | | |
| **Eh mV** | 199 | | | | | | | | | | | | | | | | | | | |
| **DO %** | **5.5** | | | | | | | | | | | | | | | | | | | |

Abbreviations; S = superficial; LV = Leederville Formation; CG = Cockleshell Gully Formation. bns = below natural surface.
For the full suite of data see Deeney (1989a; 1989b).

## 3.3 Summary

The deeper groundwater aquifer was not adequately characterised due to drilling mud contamination. As will be discussed in the next chapter, it was not possible to correct for this. Trace element data may not be influenced greatly, but this cannot be assessed from the variability in major elements particularly K and Cl from the drilling muds. Selected regional samples from Deeney (1989a and 1989b) are more usable than the contaminated sample, and have been used as a starting point for modelling the geochemical influence of $CO_2$ injection. Given the groundwater in the lower aquifers was similar in salinity levels and most likely major element chemistry we calibrated the model against the regional data from the upper part of the strata. Regardless, the $CO_2$ injection creates a major change in this chemistry meaning you could start with almost any Perth regional groundwater chemistry and achieve the same result. Once the model was produced reasonable starting solution we then applied this to the deeper strata where no reliable groundwater data exists.

Again, it must be strongly noted that a tracer would have been invaluable in making some attempt to reconstruct the deeper water sample from the Yalgorup Member.

# 4 Modelling of Potential Reactivity

## 4.1 Background

Data from other projects, including Project 7-1111-0199, Delle Piane et al. (2103) and Deeney (1989a, b), were used to build preliminary models to evaluate the reactive processes that might occur in the Upper Lesueur Formation on contact with $CO_2$. The aim of this research was to get an indication of liberated species for monitoring and to determine future research directions or knowledge gaps for geochemical modelling of CCS at Harvey. A preliminary static model allows a better assessment of rock reactivity and the behaviour of the $CO_2$, demonstrates the kinetic issues in comparison to the core flood experiments (next Chapter) and should contribute to a future reactive transport model.

Preliminary modelling has previously been used to assess the impact of supercritical $CO_2$, subcritical $CO_2$ and changes in pH in the geological formations of interest. Early development of the model parameters and preliminary modelling will provide a valuable framework to input new data from the upcoming wells and prepare for future activities within the South West $CO_2$ Hub drilling program and research framework.

## 4.2 Solution Interaction Modelling

### 4.2.1 DRILL MUD CHEMISTRY

Even using the chemistry and weights of the fractions, it was not possible to adequately get a mass balance from the drilling muds to the original groundwater samples at the Harvey-1 well. The data shows the 1000m and 1896m muds samples are very different (Table 17). There was no way to use the aqueous and sediment data to give similar original mud chemistries at the two depths.

Table 17 Results for groundwater and sediment fractions of the drilling mud, with summarised regional representative groundwater samples (from Deeney, 1989a and 1989b).

| Species | Harvey-1 856m | Aqueous Mud$^1$ Filtrate 1000m | Aqueous Mud$^2$ Filtrate 1896m | Sediment Mud$^1$ Filtrate 1000m | Sediment Mud$^2$ Filtrate 1896m | BPL1A3 633m bns | HL2A3 792m bns | HL3A3 574m bns | HL2A3 |
|---|---|---|---|---|---|---|---|---|---|
| Al mg/L | 0.0065 | 1.1 | 1.2 | 1890 | 2110 | | | | |
| Ba mg/L | 0.28 | 7.8 | 53 | 2510 | 4610 | | | | |
| Ca mg/L | 1130 | 350 | 420 | 4750 | 18900 | 557 | 1230 | 3180 | |
| Fe mg/L | 1.2 | 17 | 260 | 6170 | 6710 | | | | |
| Mg mg/L | 510 | 45 | 96 | 400 | 660 | 316 | 692 | 205 | |
| Mn mg/L | 5.2 | 36 | 150 | 150 | 570 | | | | |
| P mg/L | 5.8 | 5.1 | 12 | 130 | 80 | | | | |
| **K mg/L** | **15800** | **29900** | **23900** | **39700** | **19300** | **73** | **44** | **34** | |
| Rb mg/L | 2.1 | 5.7 | 3.4 | 11 | 6.6 | | | | |
| Si mg/L | 10 | 12 | 15 | 510 | 400 | | | | |
| Na mg/L | 8850 | 1720 | 3010 | 2640 | 2650 | 7500 | 9560 | 9070 | |
| Sr mg/L | 20 | 5 | 20 | 200 | 170 | | | | |
| S mg/L | 630 | | | 3780 | 1890 | | | | |
| **Cl mg/L** | **24000** | **30000** | **23600** | | | **11900** | **18100** | **19100** | |
| DOC mg/L | 590 | 3400 | 5100 | | | | | | |
| $NO_3$ mg/L | 0.031 | | | <1 | <1 | <1 | <1 | <1 | |
| $PO_4$ mg/L | 0.006 | | | <0.5 | <0.5 | | | | |
| $SO_4$ mg/L | 1700 | 400 | | 340 | <25 | 1800 | 1610 | 910 | |
| $Cl^-$ mg/kg | | 65000 | 8000 | | | | | | |
| **TDS calc** | **52319** | **>135000** | **>120000** | | | **22300** | **31400** | **32500** | |
| **Alkalinity as $HCO_3$ (mg/L)** | **550** | **2000** | **3200** | **4000** | **2800** | **189** | **125** | **40** | |
| **pH** | | | | | | 7.9 | 7.8 | 7.2 | |
| **EC μS/cm** | | | | | | 32300 | 45000 | 43300 | |

Bns = below natural surface

## “Correcting” the 856m sample

Due to contamination of the groundwater from the drilling mud and the varied data on this mud material, it has not proved possible to obtain the “true” groundwater chemistry of sample 856m. Initially we thought we would be able to generate an approximate mass balance from the drilling mud samples and the 856m MDT sample, but the errors and issues with back-calculating prevented iteration back to a “correct” chemistry. One illustration is shown below (Figure 15). The ion balance of any solution should be 0 (i.e., cation charge = anion charge). The calculated ion balance for 856m sample is 0.11, which would be considered too high for normal quality control. This is possibly due to a number of potential effects, including organic acids, partial barite precipitation, and/or enhanced alkalinity due to organic matter decomposition. When correcting by subtracting a fixed component of KCl from the 1000m mud solution, back towards a K concentration less than 100 mg/L (denoted by the direction of the arrow), ion balance error increases dramatically, demonstrating the method is dramatically increasing error in prediction of solution composition.

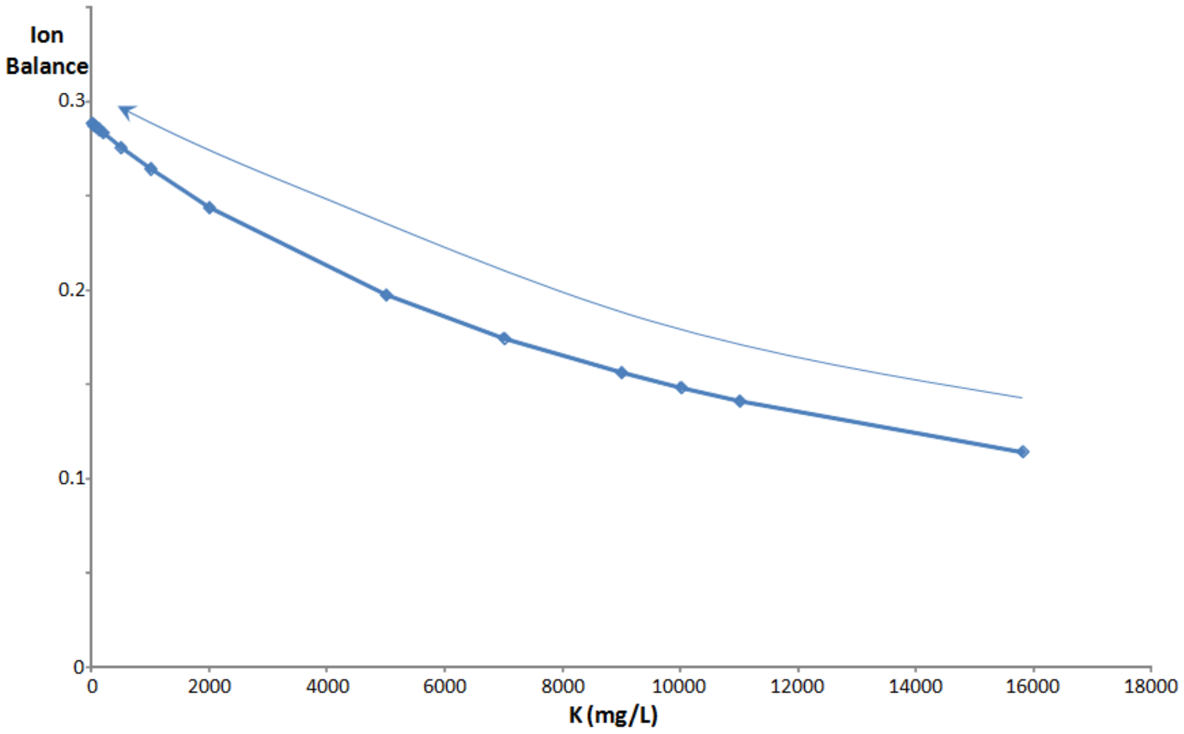


Figure 15: Theoretical adjustment of the K levels in drilling solution back to a more representative level and how the ionic balance is influenced. To be effective it should approach 0.

For the test modelling a regional groundwater sample was used for the solid-solution interaction modelling (HL2A3; Table 17). While imperfect, this was deemed to be a significantly better option than a severely flawed “estimated” bore chemistry and, as will be discussed, will have little influence on the final results of the modelling.

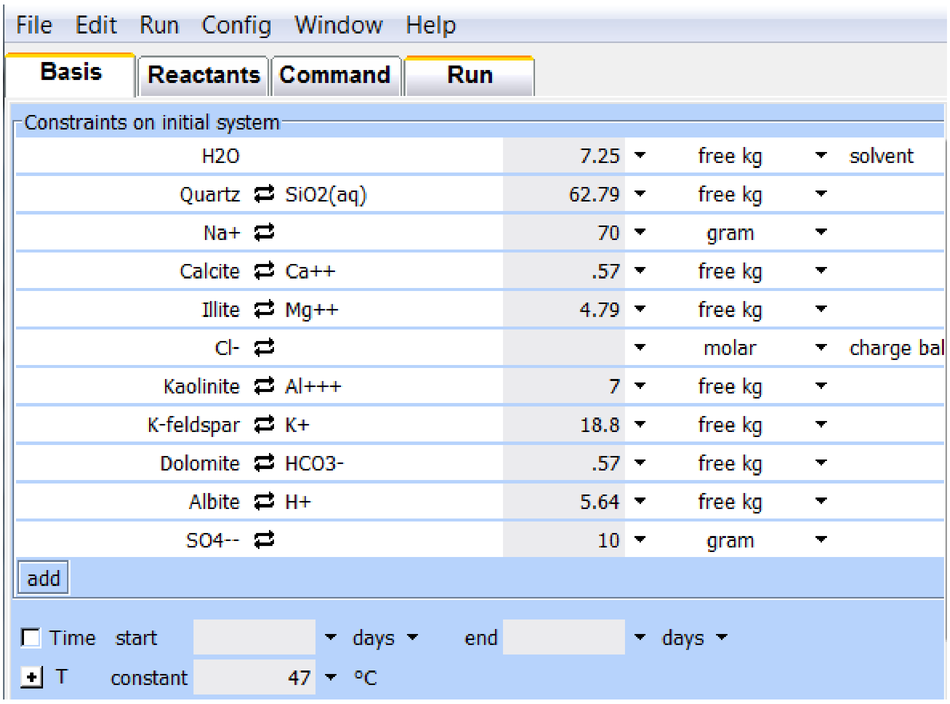
### 4.2.2 MODELLING FACIES / WATER INTERACTION

A generalised Yalgorup facies was used to model water equilibration. Using the results from Delle Piane et al. (2103) the commonly occurring minerals and the percentage composition that were measured by XRD were averaged (Table 18).

**Table 18 Yalgorup solid phase parameters initially tested using the average values from Delle Piane et al. (2013).**

| Parameter | Average or estimated value |
|---|---|
| Porosity | 0.238 |
| Effective porosity % volume | 16 |
| Permeability mD | 13 |
| Est Temp C | 46 |
| Est Pressure Mpa | 8.4 |
| Quartz weight % | 62.8 |
| Plagioclase (albite) weight % | 5.6 |
| K-feldspar weight % | 18.8 |
| Calcite weight % | 0.3 |
| High-Mg calcite weight % | 0.5 |
| Dolomite weight % | 0.4 |
| Ankerite weight % | 0.1 |
| Kaolin weight % | 7.0 |
| Berthierine weight % | 0.1 |
| Illite/muscovite weight % | 2.6 |
| Smectite weight % | 1.9 |
| Mixed Illite-smectite weight % | 0.4 |

A slightly simpler mineral assemblage was required to be used as the larger number of minerals violated the phase rule for mineral equilibration, with minor phases high Mg calcite, ankerite, berthierine, combined with the higher concentration of similar minerals. Dissolved Na and $SO_4$ were added to simulate the pore solution.  Other critical parameters were a porosity of 16% and temperature of 47°C. Modelling was done using React (Geochemist's Workbench Version 8.0; Figure 16). This mixture was equilibrated, with resultant mineral (Table 19) and solution (Table 20) properties.



Constraints on initial system

| | | | |
|---|---|---|---|
| H2O | 7.25 | free kg | solvent |
| Quartz ⇄ SiO2(aq) | 62.79 | free kg | |
| Na+ ⇄ | 70 | gram | |
| Calcite ⇄ Ca++ | .57 | free kg | |
| Illite ⇄ Mg++ | 4.79 | free kg | |
| Cl- ⇄ | | molar | charge bal |
| Kaolinite ⇄ Al+++ | 7 | free kg | |
| K-feldspar ⇄ K+ | 18.8 | free kg | |
| Dolomite ⇄ HCO3- | .57 | free kg | |
| Albite ⇄ H+ | 5.64 | free kg | |
| SO4-- ⇄ | 10 | gram | |

☐ Time start days end days

T constant 47 °C

Figure 16 Screen shot of modelling parameters.

Table 19 Equilibrated model properties.

| Mineral | Input | Initial Equilibration |
|---|---|---|
| Albite | 5.64 | 4.79 |
| Calcite | 0.57 | 0.88 |
| Dolomite | 0.57 | 0.28 |
| K-Feldspar | 18.8 | 8.62 |
| Illite | 4.79 | - |
| Kaolinite | 7 | - |
| Muscovite | - | 15.72 |
| Phengite | - | 1.90 |
| Quartz | 62.79 | 67.81 |

Modelled equilibration converted illite and kaolinite to less hydrous forms (muscovite and phengite), with partial conversion of K-Feldspar to muscovite. With this mineral conversion are changes in the modelled groundwater composition. The HL2A3 measured groundwater composition (Table 20) was close but did not exactly match the modelling of the solution equilibrated with the Input mineralogy, nor with the properly equilibrated mineral assemblage. This is consistent with the poor degree of thermodynamic equilibration at these low temperatures. The most noted departure from measured and modelled concentrations is for Mg, which is almost 200 times lower in the modelled groundwater, indicating that in the natural condition the groundwaters are not properly equilibrating with dolomite.

Table 20 Initial Solution equilibration, compared with results from HL2A3.

| Parameter | Input | Initial Equilibration | HL2A3 |
|---|---|---|---|
| pH | 7.44 | 7.64 | 7.8 |
| Na | 9387 | 18457 | 9560 |
| Ca | 8440 | 129 | 1230 |
| Mg | 290 | 4 | 692 |
| K | 36 | 70 | 44 |
| Cl | 29296 | 27739 | 18100 |
| SO4 | 1341 | 1270 | 1610 |
| HCO3 | 5.7 | 155 | 125 |
| Si | 5.0 | 5.4 | nd |

### 4.2.3 MODELLED INJECTION OF $CO_2$

In this initial modelling, $CO_2$ was injected up to 4% (by weight) of the original rock mass, reaching approximately 350 atm $CO_2$ pressure (Figure 17). The $CO_2$ caused significant changes in mineral and fluid compositions. At the early stages (first 10%), there are only moderate solution changes as $CO_2$ is dominantly consumed by the conversion of albite and phengite to dawsonite ($NaAlCO_3(OH)_2$). Once this is complete, the major reaction is the acid-consuming conversion of K-Feldspar to muscovite and quartz (Figure 18). Quartz varies from 67.5 to 73% (not shown).

After the complete formation of dawsonite, there is little capacity for the rock to adsorb $CO_2$ and it remains in solution (Figure 19). The formation of dawsonite is consistent with coal seam gas observations where dawsonite is precipitated in fractures (Golab et al. 2006).

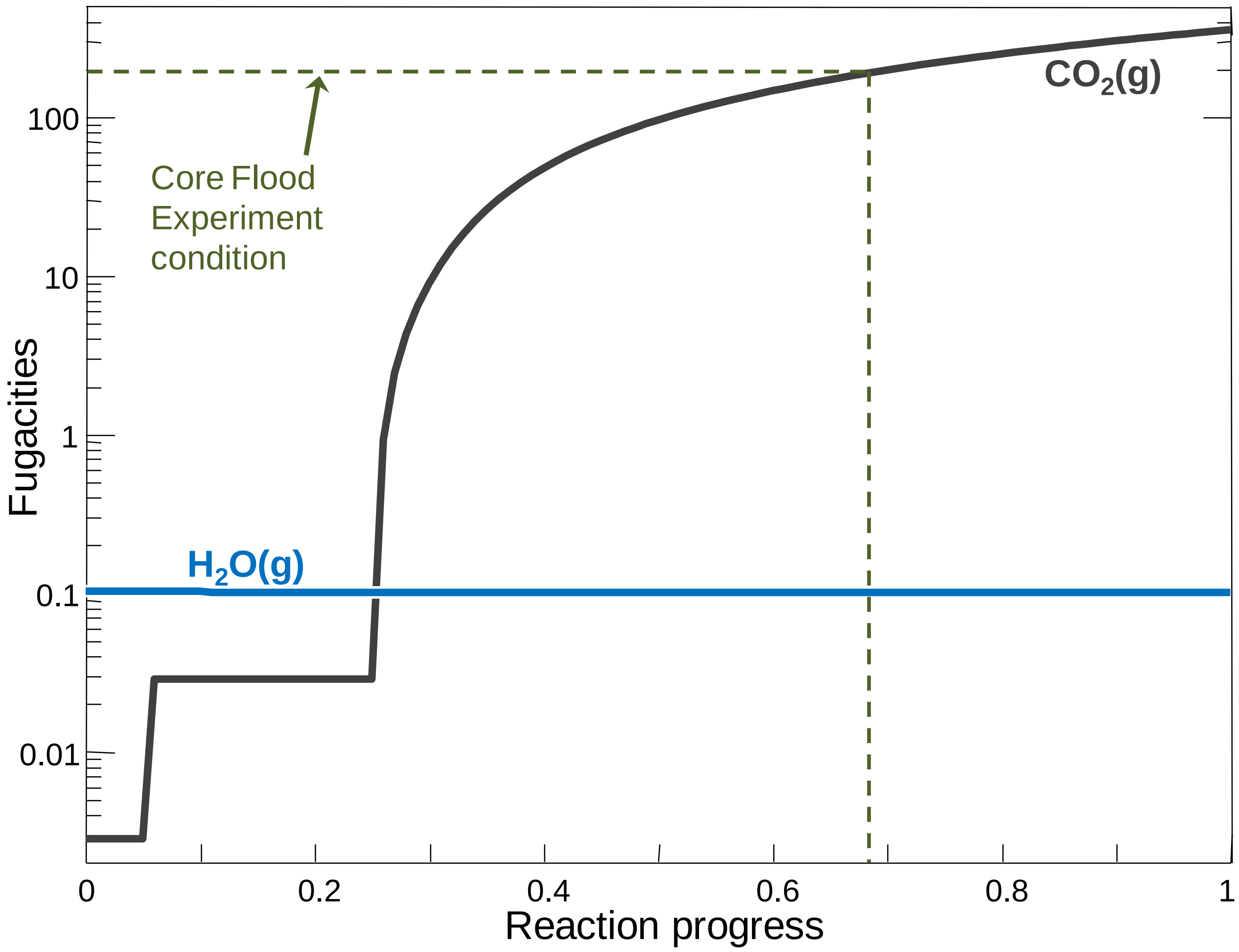


Figure 17: $CO_2$ fugacity increasing as the reaction progresses. Dashed line represents the approximate conditions for the core flooding experiment.

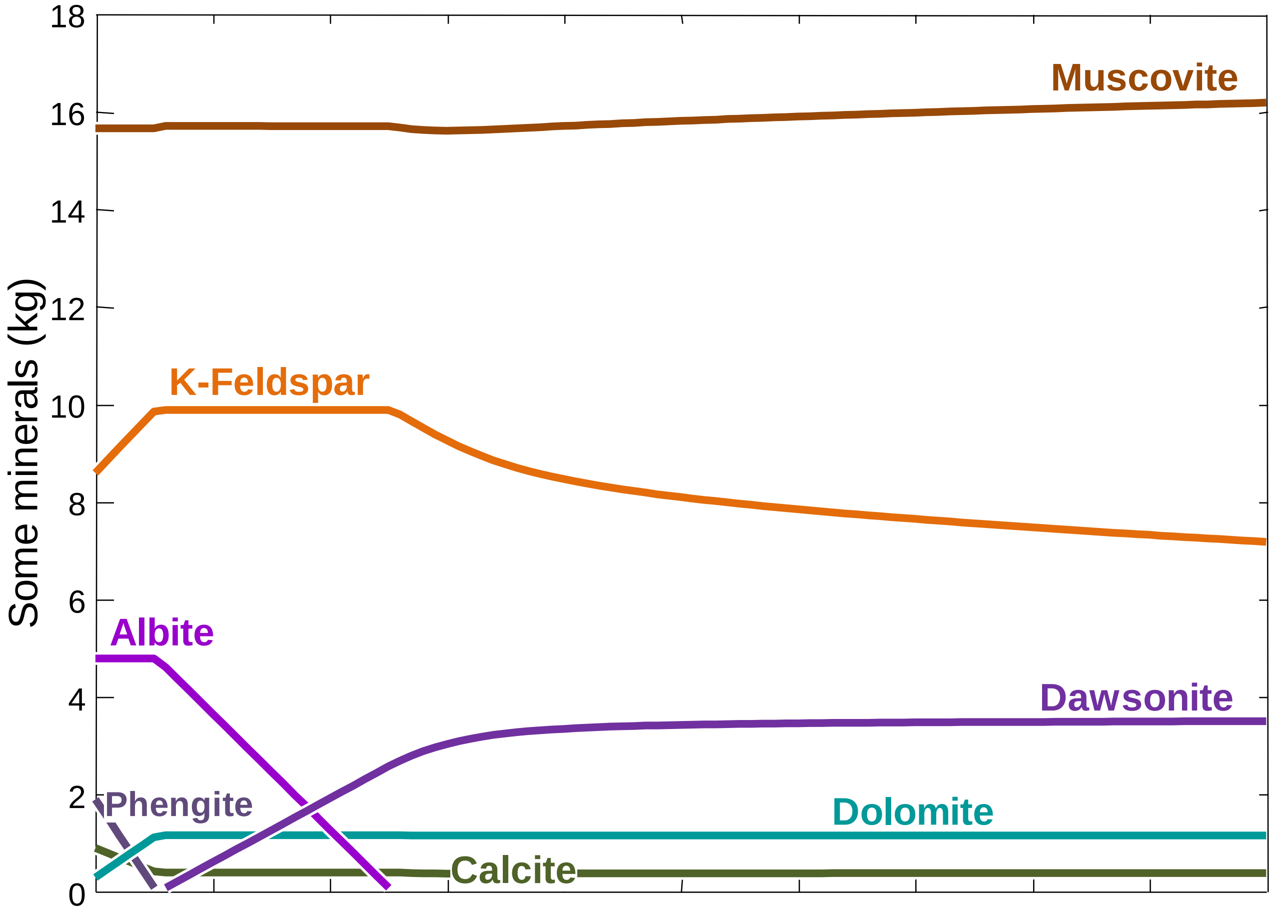


**Figure 18 Reaction modelling progress showing the consumption of feldspar and the precipitation of dawsonite as $CO_2$ is added to the Yalgorup rock mass.**

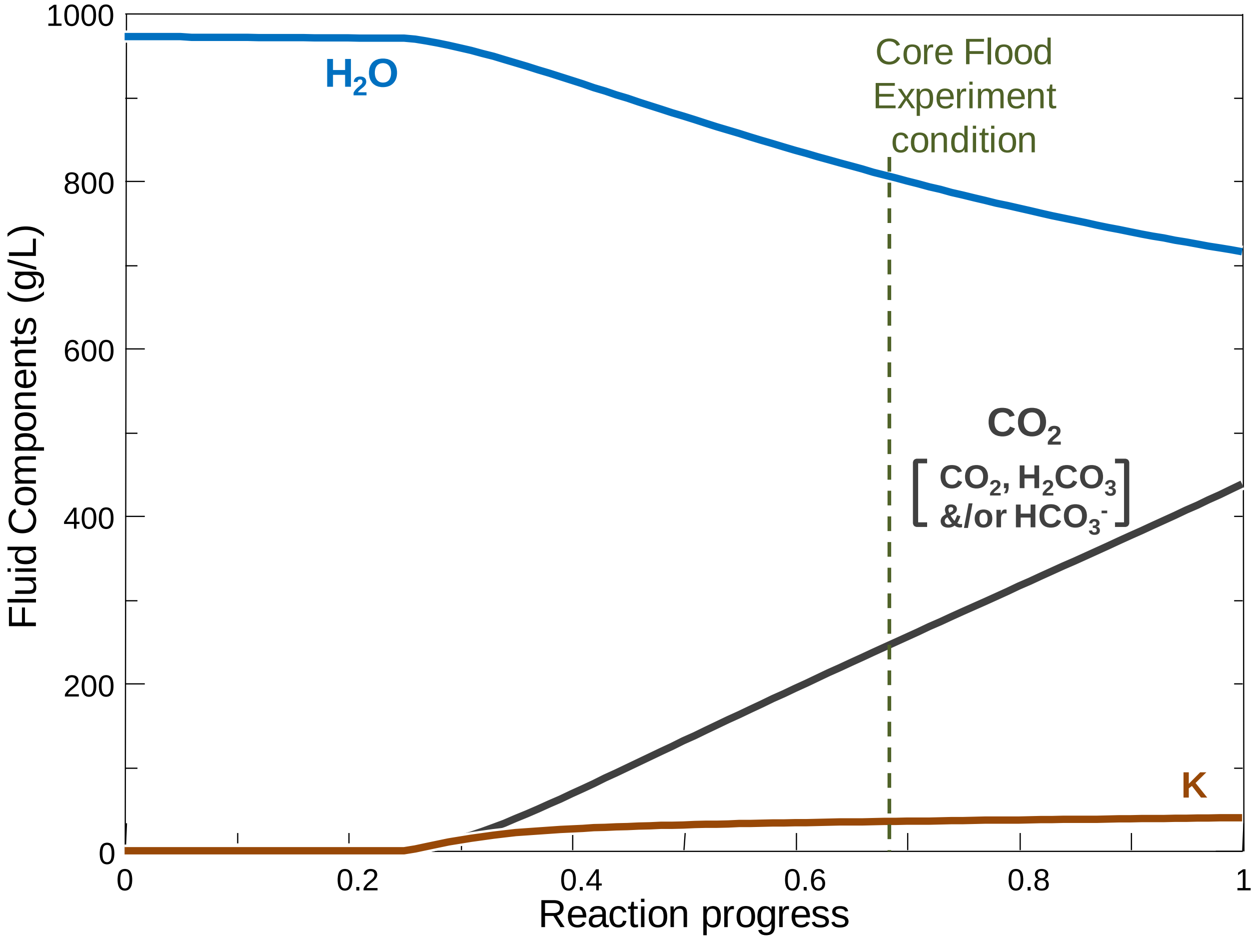


Figure 19 Reaction modelling showing the inability to consume $CO_2$, with $HCO_3$ (carbonic acid from $CO_2$) remaining in solution and ultimately becoming the main fluid constituent. Green dashed line represents the approximate conditions for the core flooding experiment.

This simulation was conducted so as to reach a $CO_2$ pressure between the expected hydrostatic head (200 bars) and fracture pressure (500 bars) at 2000m depth (Figure 17). Relating this to core flood experiments (following chapter) reveals modelled gas fugacity to be greater, with the experiments only achieving conditions of about 67% of the reaction progress in this model.

The water component is diluted as the $CO_2$ increases (Figure 20). As $CO_2$ is hydrolysed

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

this produces acid, resulting in the above-mentioned breakdown of K-Feldspar, and decrease in pH (Figure 21).

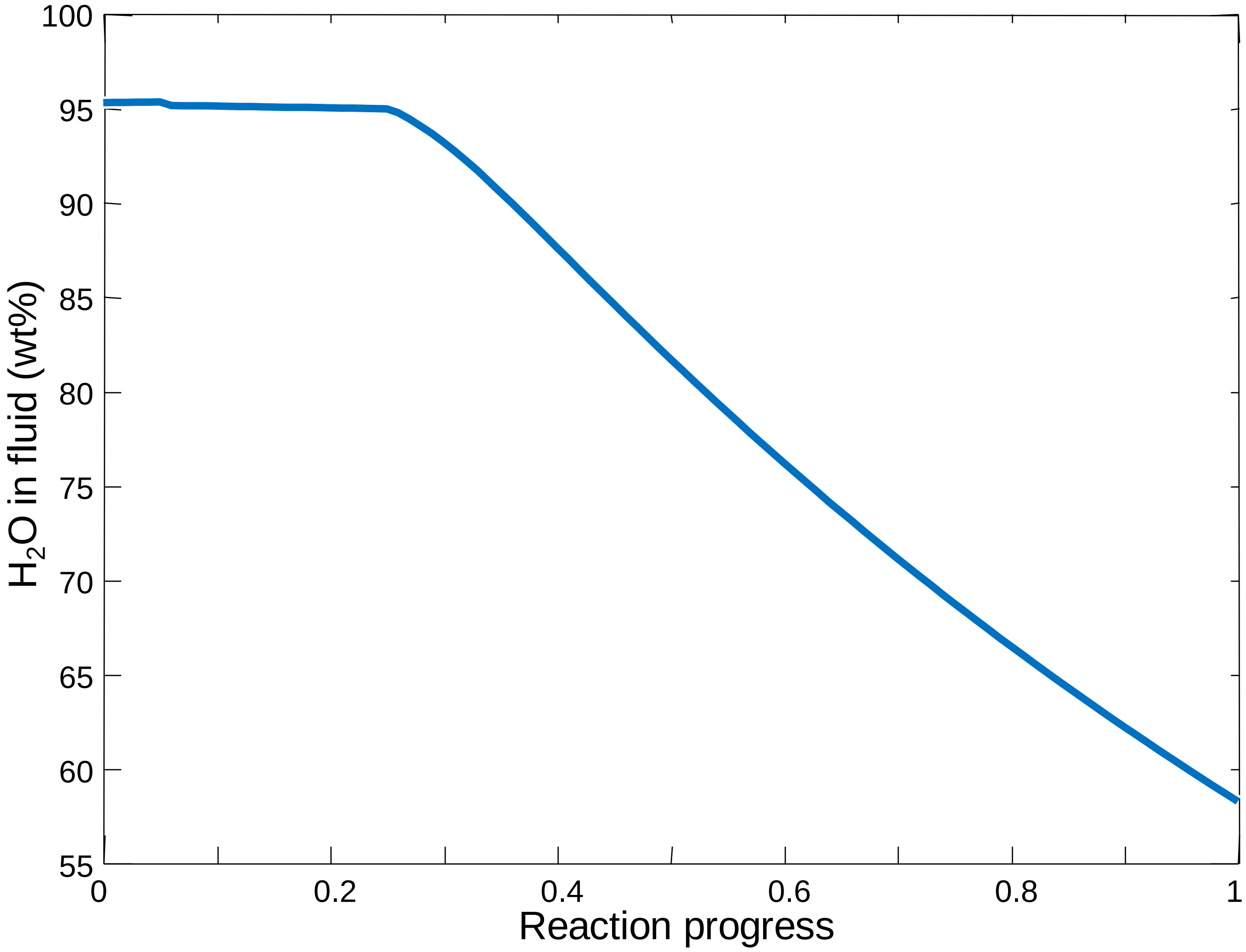


**Figure 20 Reduction of water proportion in the fluid due to dilution, hydrolysation of carbon dioxide, and formation of hydrous minerals such as muscovite.**

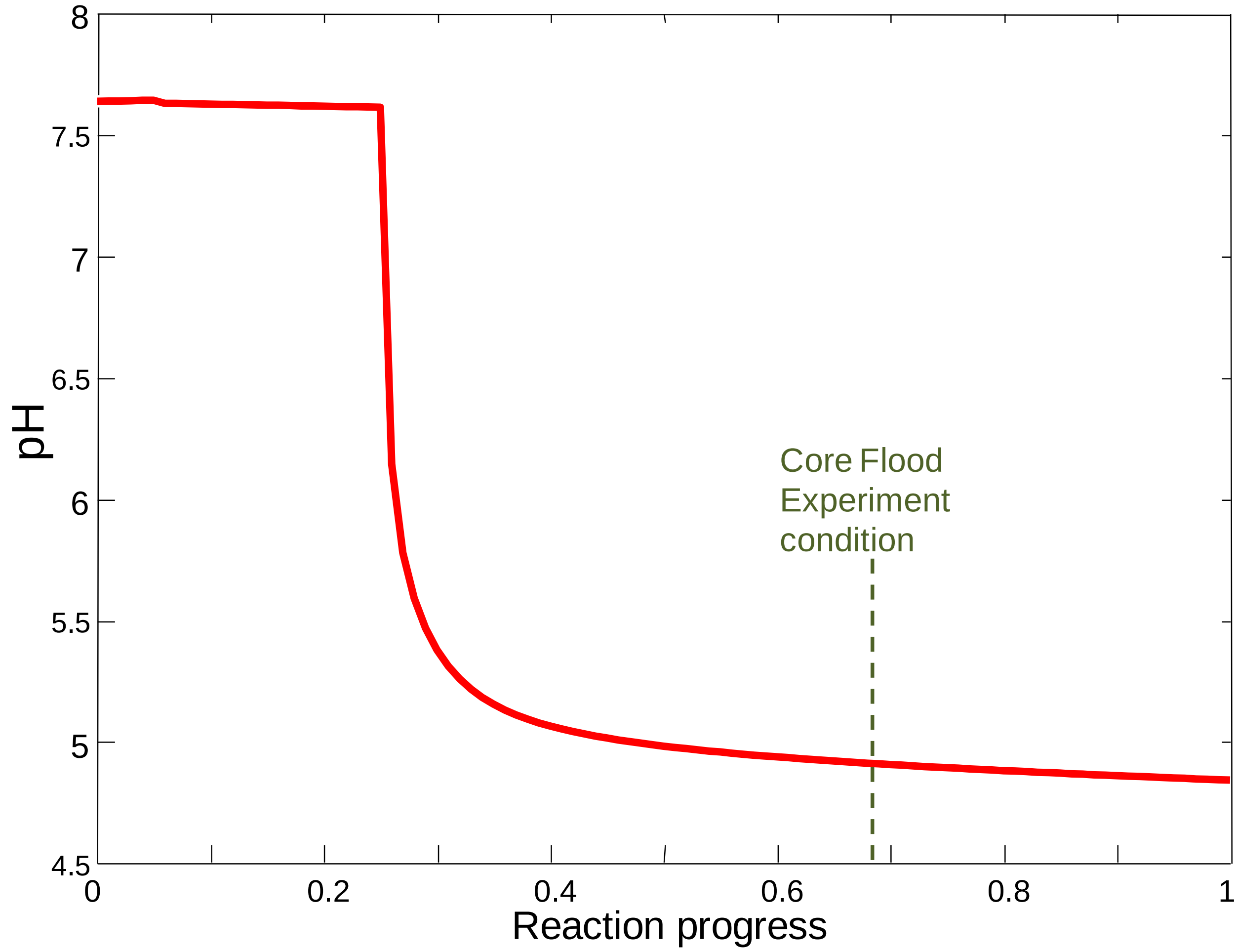


**Figure 21 Production of carbonic acid and loss of neutralising capacity in the rock results in reduced pH conditions.**

For monitoring purposes and follow up with resulting core flood experiments the most significant change in metal concentrations is the release of K from feldspar breakdown, eventually leading to [K] approaching 40 g/L (40,000 mg/L, Figure 22). The core flood experiments in the next chapter do not match the modelled changes in chemistry, as discussed in the following chapter.

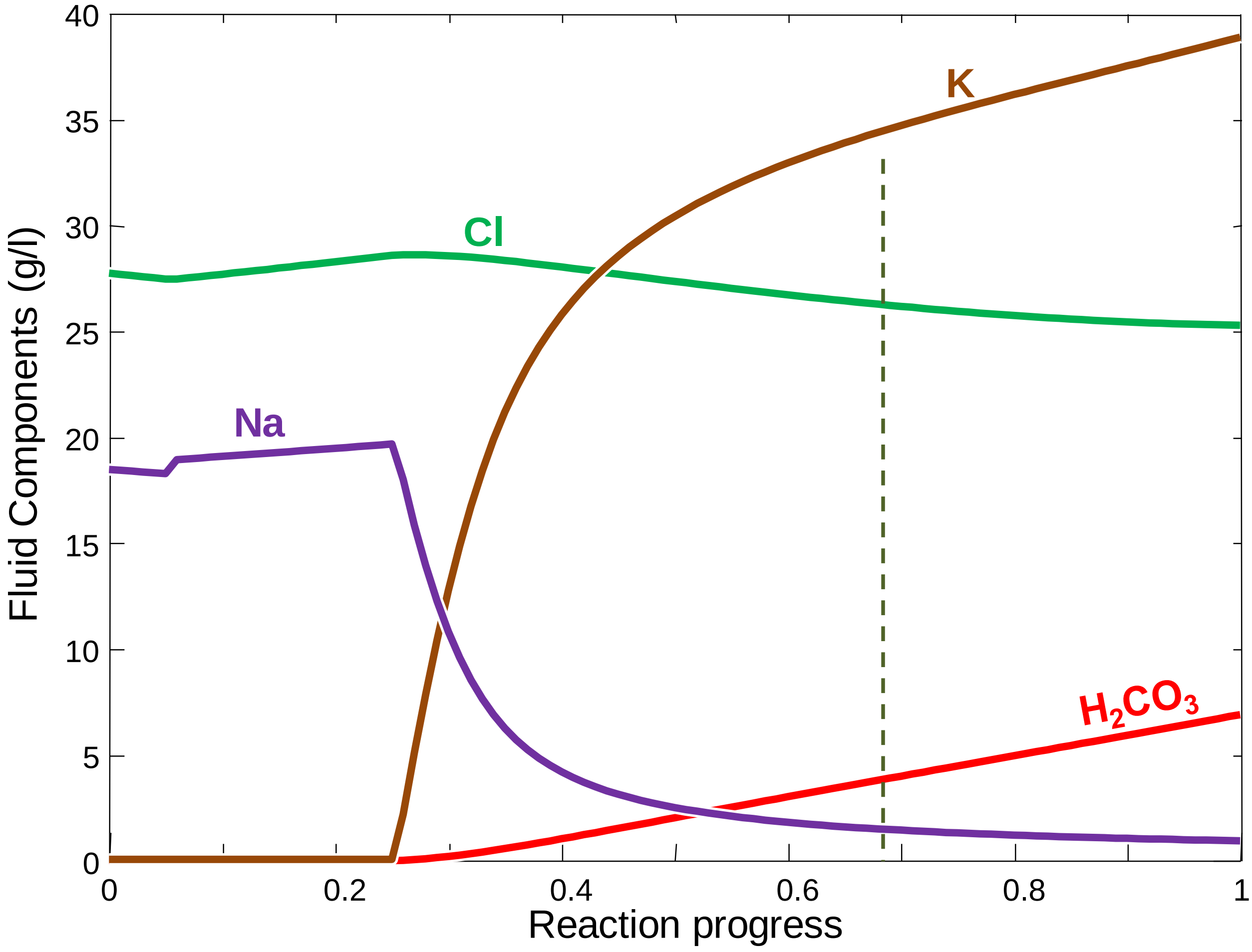


Figure 22 Major cations and anions released into solution from the simulated injection of $CO_2$ into the Yalgorup rocks. Green dashed line represents the approximate conditions for the core flooding experiment.

Increases in concentration of elements such as Cl are related to the decrease in the water content. Dissolved Na significantly decreases to < 150 mg/L, due to incorporation in dawsonite. Once dissolved $CO_2$ increases, Ca and Mg increase to > 500 and > 25 mg/L, respectively (Figure 23).

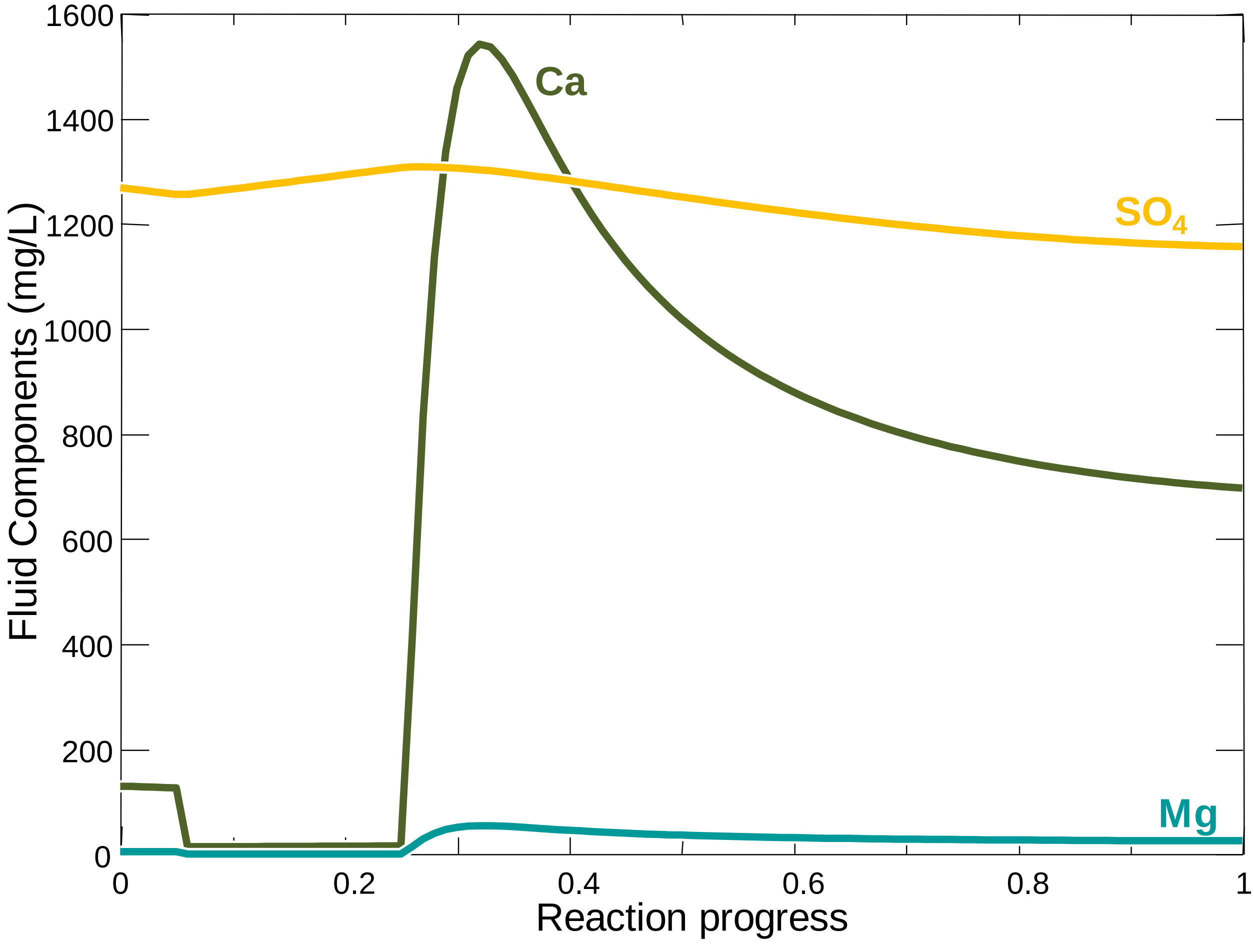


Figure 23 Other cations and anions released into solution from the simulated injection of $CO_2$ into the Yalgorup rocks.

## 4.3 Summary

The chemical modelling is useful in delineating the potential reactions and the influences these will have on the formation mineralogy and the groundwater chemistry. As will be discussed below, they are also useful in understanding the results from the core flooding experiment. In particular, the rocks theoretically have some capacity to maintain circum-neutral conditions, until all albite is converted to dawsonite, with removal of dissolved Na. Once this stage is reached, pH drops to about 5, and $CO_2$ fugacity increases dramatically. However, pH is maintained above 4.5 by the acid-consuming conversion of feldspar to muscovite and quartz, with major release of K.

The emulation of these systems could be improved by better solution and mineral information, and by moving from static to reaction-path modelling. However, it is important to note that kinetic barriers at this relatively low temperature, and other effects such as inability of fluids to migrate into the mineral mass from the pore space, could strongly reduce the degree of reaction in the real world, and the speed of these effects. These modelling results should be seen as an indication only and need to be tested by laboratory and field tests.

# 5 Core Flooding Analysis

## 5.1 Introduction

A core flood experiment was conducted on samples from the Harvey-1 well (Delle Piane et al., 2013) to obtain data on relative permeability under in situ conditions, measure potential supercritical $CO_2$ residual trapping potential and to evaluate any differences in the porosity and permeability of samples pre- and post $CO_2$ core flooding. One experiment was conducted in which the core flood effluents were collected in order to evaluate potential chemical reactions between the injected fluids and the host rock materials under in situ conditions, but over a short (days) period of time. This type of analysis has not been previously conducted in the Curtin University core flood experimental setup, but has potential to tie into the previous modelling and provide initial kinetic information to augment the previous chapter's modelling. Core flood effluents were provided to evaluate the samples geochemically and infer what processes might have taken place during the flooding. This provides further insights into the potential for chemical reactions during storage at the South West Hub site. There is limited material in the literature describing detailed geochemical analyses of core flood effluents. See Saeedi (2012) for a fuller review of this statement.

### Sample Description

Sample 206660H from 1935m depth is a laminated coarse to very coarse sandstone classified as facies Aii, and representative of the Wonnerup Member. It is dominated by quartz, K-feldspar, kaolinite and ankerite (Table 21). Porosity and permeability values before flooding were representative of many of the samples measured in the Wonnerup Member in Delle Piane et al. (2013; Table 22).

**Table 21 Percentage composition of observed X-ray diffraction mineralogy for 206660H. From Delle Piane et al. (2013).**

| Sample | Depth (m) | Quartz | K-feldspar | Kaolinite | Ankerite |
|---|---|---|---|---|---|
| 206660 | 1935.5 | 77 | 12 | 7 | 4 |

Samples were prepared and analysed by Geotechnical Services PTY LTD.

**Table 22 Porosity and permeability values for 206660H. From Delle Piane et al. (2013). Data in grey from Geotech, data in italics from CSIRO.**

| Sample | Z (m) | ϕ(%) 800 PSI | Kl(mD) 800 PSI | ϕ (%) 4300 PSI | Kl (mD) 4300 PSI | Hg-ϕ (%) | ϕ (%) 500 PSI | ϕ (%) 2000 PSI | ϕ (%) 5000 PSI | Kl (md) 500 PSI | Kl (md) 2000 PSI | Kl (md) 5000 PSI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 206660 | 1935.5 | 16.33 | 122.38 | 15.97 | 111.49 | 16.38 | *16.02* | *15.64* | *15.52* | *138.25* | *131.12* | *128.21* |

Tabulated porosity and permeability values measured on samples from Harvey-1. Z= depth, f = porosity; kl = permeability; Hg-f = porosity from mercury injection experiments.

## Methods

### Experimental Conditions for Core Flooding

In situ reservoir parameters used for the flooding of sample 206660H were based on the depth and wireline data. The experimental conditions were as follows;

- Pore pressure, MPa = 19.39
- Overburden pressure, MPa = 43.78
- Reservoir temperature, °C = 61.2
- Formation water salinity, ppm NaCL = 30,000
- The solubility of $CO_2$ in brine at these conditions is calculated to be 1.097 mol/kg of water

As the wireline data suggested values of 30,000 (Wonnerup) to 40,000 mg/L (Yalgorup), a synthetic brine of 30,000 mg/L NaCl was used for the core flood experiment as reported in Delle Piane et al, (2013). The lower salinity was preferred as it has a less impact on the metal parts of the core flood equipment.

The flooding was conducted using the high pressure-high temperature three-phase steady-state core-flooding apparatus located within the Department of Petroleum Engineering at Curtin University. Full descriptions of the rig and the preparation and flooding methods are given in Delle Piane et al. (2013). The core size was 7.52 cm long with a diameter of 3.76 cm. Details of the brine saturation and full parameters are documented by Saeedi (2012). In brief, these fluids included $CO_2$-saturated brine (i.e. brine saturated with $CO_2$ at the in situ reservoir P–T conditions) and water-saturated $CO_2$ (i.e. supercritical $CO_2$ saturated with water vapour). The $CO_2$ gas used was of a bottled high-purity grade (99.99%) carbon dioxide. The brine was prepared in the lab using demineralised water and appropriate amounts of analytical grade (99.95%) sodium chloride (NaCl) (Saeedi, 2012).

For this particular experiment, rather than the flood effluents being directed to a separator, the produced brines were collected in small volumes of approximately 10mL in plastic vials. The 53 samples were capped and stored in a refrigerator before undergoing a series of analyses. The flow and $CO_2$ conditions were varied during the experiment; Table 23 gives an indication of the flow rates and fluids injected as each sample was taken.

**Table 23 Fluid samples taken from the core flooding of 206660H from the Wonnerup Member. Note major experimental conditional changes highlighted in the grey coloured rows and colours are representative of background plots for later figures in this chapter.**

| Conditions | Sample name | Sample time | Flow Rate | Fluid injected |
|---|---|---|---|---|
| **$CO_2$ saturated brine** | 1-1, 1-2, 1-3 | 6/11/12 | 50cc/hr | $CO_2$ saturated brine |
| | 1-4, 1-5, 1-6 | 6/11/12 | 100cc/hr | $CO_2$ saturated brine |
| | 1-7, 1-8, 1-9 | 6/11/12 | 150cc/hr | $CO_2$ saturated brine |
| | 1-10 to 1-32 | 6/11/12 | 50cc/hr | $CO_2$ saturated brine |
| **Sample saturated with carbonated brine overnight** | | | | |
| **$CO_2$ saturated brine** | 1-40 to 1-49 | 7/11/12 | 50cc/hr | $CO_2$ saturated brine |
| **$CO_2$ injection** | | | | |
| **$CO_2$ injection** | 2-1, 2-2 | 7/11/12 | 50cc/hr | $CO_2$ |
| **Brine injection after $CO_2$ injection** | | | | |
| **$CO_2$ saturated brine** | 3-1 to 3-10 | 7/11/12 | 50cc/hr | $CO_2$ saturated brine |

The flooding test was conducted over a two day period. The first 31 samples were obtained during flooding at a series of different rates during the first day, before being sealed in the $CO_2$ saturated brine overnight. On restarting flow the next day, a further 10 samples were collected before an injection of supercritical $CO_2$ only was pushed into the core and two samples taken. A final flush with $CO_2$ saturated brine was conducted and ten more samples were collected (Table 23). The volume of the samples was approximately 10mL making a number of specific analyses problematic as normally 50 -100mL would be required. Since the brine was saturated with $CO_2$ at 19.39 MPa, a lot of this $CO_2$ escaped during the sample collection. This affects the pH measurements, can cause precipitation and also affect the alkalinity. The influence of precipitation was reversed with the addition of acid to the samples to re-solubilise any precipitates for analysis. However, the change in pH and alkalinity could not be adjusted and was used only as a guide of changing conditions. The alkalinity concentrations in the samples were low and near detection limits.

Following the core flooding, the same core was used to obtain measurements of residual saturation and relative permeability (Delle Piane et al., 2013).

## 5.2 Laboratory analyses

A set volume of 2mL was diluted to 25 mL and titrated for $HCO_3^-$ with a known concentration of acid (e.g. 0.01 M HCl) to an endpoint of pH = 4.3 at CSIRO Laboratories in Kensington, WA. The solution was not under pressure. Major anions (Cl, $SO_4$, Br, F and $NO_3$) were analysed following filtration by Ion Chromatography (IC) at CESRE Laboratories in Kensington, WA. The IC equipment used was a Metrohm modular IC using an acid re-generated suppressor, MetroSep A Supp150 column, a carbonate/bicarbonate eluent (32 mM $Na_2CO_3$ and 10 mM $NaHCO_3$) and a conductivity detector. A sample split was sent to CSIRO Land and Water Laboratory in Adelaide for analysis of major and trace elements. This remaining sample was acidified and filtered. Elements Al, B, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, S, Si, Sr and Zn) were analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) at CSIRO in Adelaide. Trace elements (Ag, As, Ba, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Th, U, V, W, Y, Yb, Zn and Zr) were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at CSIRO in Adelaide. Detection limits for ICP analyses are affected by salinity, with more saline samples having higher detection limits due to increased dilution requirements.

## 5.3 Results of the analysis of core flood effluents

Selected results are tabulated and presented in Table 24 and Table 25. This data is also graphically presented in Figure 24 to Figure 30, with colour change in the background used to represent the different stages of flooding experienced by sample 206660H.

The use of the 30,000 mg/L NaCl imparts a consistently high concentration of Na and Cl (Table 24 and Figure 24). The minor variation may partially represent analytical error. However, the similar temporal patterns in the variation of Na and Cl, even though they are analysed by differing methods, suggests fluid effects having a measurable effect on salt content. Another possibility is evaporation effects during sampling as $CO_2$ boils off as pressure is reduced and sampling water is removed with it. The high salinity of the solutions does raise detection limits for other elements due to the required dilution for analysis in the ICPOES and ICPMS, although the ICPMS trace element data were not significantly impacted (Appendix E ).

**Table 24 Important major element data and pH in the core flood eluent. Lines indicate important changes in experimental conditions.**

| Sample ID | Flow Rate | pH | Ca mg/L | K mg/L | Mg mg/L | Na mg/L | Al mg/L | Fe mg/L | Mn mg/L | Cl mg/L | Si mg/L | Rb µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-2 | 50cc/hr | 3.76 | 5.6 | 8.3 | 8.78 | 10700 | <2.5 | 64.6 | 50 | 16896 | <5 | 62 |
| 1-3 | 50cc/hr | 4.84 | 5.5 | 8.1 | 7.61 | 11600 | <2.5 | 75.8 | 46.5 | 18345 | <5 | 72 |
| 1-4 | 100cc/hr | 4.87 | <5 | 7.3 | 5.34 | 10800 | <2.5 | 65.4 | 38.4 | 17194 | <5 | 66 |
| 1-5 | 100cc/hr | 2.91 | <5 | 7.6 | <5 | 12200 | <2.5 | 65.1 | 38.6 | 21740 | <5 | 62 |
| 1-6 | 100cc/hr | 4.45 | <5 | 6.8 | <5 | 11500 | <2.5 | 67.3 | 37.4 | 17964 | <5 | 56 |
| 1-7 | 150cc/hr | 4.43 | <5 | 7.0 | <5 | 11600 | <2.5 | 56.6 | 37.6 | 18211 | <5 | 58 |
| 1-8 | 150cc/hr | 2.3 | 5.3 | 6.2 | <5 | 11600 | <2.5 | 49.7 | 36.9 | 18699 | <5 | 54 |
| 1-9 | 150cc/hr | 4.26 | <5 | 6.4 | <5 | 12100 | <2.5 | 47.1 | 38.8 | 18992 | <5 | 54 |
| 1-10 | 50cc/hr | 4.42 | <5 | 5.9 | <5 | 11700 | <2.5 | 48.6 | 37.9 | 18040 | <5 | 51 |
| 1-11 | 50cc/hr | 4.51 | <5 | 6.8 | <5 | 11000 | <2.5 | 47.8 | 41.5 | 17245 | <5 | 49 |
| 1-12 | 50cc/hr | 4.61 | <5 | 7.0 | <5 | 11600 | <2.5 | 61.9 | 48.9 | 18585 | <5 | 54 |
| 1-13 | 50cc/hr | 4.66 | <5 | 7.3 | <5 | 11500 | <2.5 | 57.4 | 46.5 | 18528 | <5 | 55 |
| 1-14 | 50cc/hr | 4.81 | <5 | 7.2 | <5 | 11700 | <2.5 | 59.2 | 46.5 | 18682 | <5 | 57 |
| 1-15 | 50cc/hr | 4.67 | <5 | 6.9 | <5 | 11600 | <2.5 | 58.8 | 45.6 | 18480 | <5 | 51 |
| 1-16 | 50cc/hr | 4.7 | <5 | 6.7 | <5 | 11200 | <2.5 | 78.4 | 45.3 | 18777 | <5 | 50 |
| 1-17 | 50cc/hr | 4.7 | <5 | 7.1 | <5 | 11700 | <2.5 | 58.2 | 46.2 | 18820 | <5 | 49 |
| 1-18 | 50cc/hr | 4.68 | <5 | 6.8 | <5 | 11500 | <2.5 | 60.6 | 45.5 | 18746 | <5 | 50 |
| 1-19 | 50cc/hr | 4.63 | <5 | 6.7 | <5 | 11300 | <2.5 | 60.9 | 44.9 | 17813 | <5 | 51 |
| 1-20 | 50cc/hr | 4.68 | 5.5 | <5 | <5 | 12000 | 3.0 | 62.1 | 48.8 | 18613 | <5 | 46 |
| 1-21 | 50cc/hr | 4.79 | <5 | <5 | <5 | 12200 | 2.8 | 57.5 | 48.9 | 19314 | <5 | 47 |
| 1-22 | 50cc/hr | 3.06 | <5 | <5 | <5 | 12400 | 3.1 | 57.7 | 49.7 | 19685 | <5 | 44 |
| 1-23 | 50cc/hr | 4.56 | <5 | <5 | <5 | 11700 | 4.8 | 73.3 | 48.6 | 17174 | <5 | 43 |
| 1-24 | 50cc/hr | 4.69 | <5 | <5 | <5 | 12300 | 3.3 | 56 | 50.1 | 18789 | <5 | 43 |
| 1-25 | 50cc/hr | 4.67 | <5 | <5 | <5 | 12200 | 3.3 | 54.4 | 49.9 | 19417 | <5 | 42 |
| 1-26 | 50cc/hr | 4.59 | <5 | <5 | <5 | 12000 | 3.3 | 53.3 | 49 | 18654 | <5 | 38 |
| 1-27 | 50cc/hr | 4.52 | <5 | <5 | <5 | 11900 | 3.9 | 57 | 48.9 | 18876 | <5 | 43 |
| 1-28 | 50cc/hr | 4.59 | <5 | <5 | <5 | 12700 | 3.7 | 55.7 | 51.6 | 19081 | <5 | 41 |
| 1-29 | 50cc/hr | 4.52 | <5 | <5 | <5 | 11900 | 3.7 | 52.1 | 49.7 | 19408 | <5 | 36 |
| 1-30 | 50cc/hr | 4.58 | <5 | <5 | <5 | 11900 | 3.9 | 53 | 48.7 | 18262 | <5 | 36 |
| 1-31 | 50cc/hr | 4.51 | <5 | <5 | <5 | 13200 | 4.5 | 55.1 | 53.8 | 19858 | <5 | 41 |
| 1-32 | 50cc/hr | 4.45 | <5 | <5 | <5 | 11900 | 5.3 | 57.6 | 48.8 | 17811 | <5 | 35 |
| 1-40 | 50cc/hr | 4.32 | 5.0 | 6.1 | <5 | 11700 | 4.2 | 69.6 | 54 | 17641 | <5 | 28 |
| 1-41 | 50cc/hr | 3.89 | 10.1 | 7.5 | 12 | 11800 | <2.5 | 136 | 86.7 | 18787 | <5 | 39 |
| 1-42 | 50cc/hr | 3.96 | 6.8 | 5.3 | 7.0 | 11900 | 1.9 | 128 | 56.2 | 17812 | <5 | 36 |
| 1-43 | 50cc/hr | 3.79 | <5 | <5 | <5 | 12200 | 3 | 92.3 | 48 | 17626 | <5 | 36 |
| 1-44 | 50cc/hr | 4.48 | <5 | <5 | <5 | 11700 | 3.4 | 80.8 | 47.5 | 18001 | <5 | 34 |
| 1-45 | 50cc/hr | 3.43 | <5 | <5 | <5 | 11700 | 3.5 | 56.9 | 49.7 | 18042 | <5 | 33 |
| 1-46 | 50cc/hr | 4.45 | <5 | <5 | <5 | 11800 | 3.9 | 52.5 | 51.6 | 18086 | <5 | 29 |
| 1-47 | 50cc/hr | 4.4 | <5 | <5 | <5 | 11900 | 4.4 | 51 | 53.3 | 20086 | <5 | 33 |
| 1-48 | 50cc/hr | 3.43 | <5 | <5 | <5 | 11800 | 4.5 | 51.1 | 53.3 | 18271 | <5 | 31 |
| 1-49 | 50cc/hr | 4.36 | <5 | <5 | <5 | 11900 | 5.0 | 52.9 | 53.1 | 18096 | <5 | 30 |

Table 23 (continued). Important major element data and pH in the core flood eluent. Lines indicate important changes in experimental conditions.

| Sample ID | Flow Rate | pH | Ca mg/L | K mg/L | Mg mg/L | Na mg/L | Al mg/L | Fe mg/L | Mn mg/L | Cl mg/L | Si mg/L | Rb µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-1 | 50cc/hr | 4.44 | <5 | <5 | <5 | 11800 | 4.7 | 48.2 | 53.8 | 17640 | <5 | 28 |
| 2-2 | 50cc/hr | 4.4 | <5 | <5 | <5 | 11300 | 3.5 | 63.6 | 59.7 | 17817 | <5 | 30 |
| 3-1 | 50cc/hr | 4.55 | <5 | <5 | <5 | 11600 | 4.5 | 53.1 | 51.9 | 18134 | <5 | 39 |
| 3-2 | 50cc/hr | 5.15 | <5 | <5 | <5 | 11800 | 4.9 | 48.3 | 54 | 19091 | 9.43 | 51 |
| 3-3 | 50cc/hr | 4.2 | <5 | <5 | <5 | 11700 | 5.0 | 43 | 55 | 17592 | 5.35 | 49 |
| 3-4 | 50cc/hr | 4.25 | <5 | <5 | <5 | 11700 | 5.4 | 45.8 | 54.1 | 20781 | <5 | 41 |
| 3-5 | 50cc/hr | 4.41 | <5 | <5 | <5 | 11700 | 5.4 | 43 | 54.2 | 18476 | <5 | 36 |
| 3-6 | 50cc/hr | 4.43 | <5 | <5 | <5 | 12300 | 5.6 | 44 | 55.9 | 18586 | <5 | 33 |
| 3-7 | 50cc/hr | 4.48 | <5 | <5 | <5 | 12000 | 5.8 | 44.4 | 54 | 18439 | <5 | 29 |
| 3-8 | 50cc/hr | 4.04 | <5 | <5 | <5 | 12000 | 5.7 | 43.6 | 52.3 | 18054 | <5 | 32 |
| 3-9 | 50cc/hr | 4.49 | <5 | <5 | <5 | 11800 | 6.0 | 42.4 | 51.8 | 18179 | <5 | 32 |
| 3-10 | 50cc/hr | 3.28 | <5 | <5 | <5 | 11900 | 6.1 | 42.3 | 51.1 | 19159 | <5 | 31 |

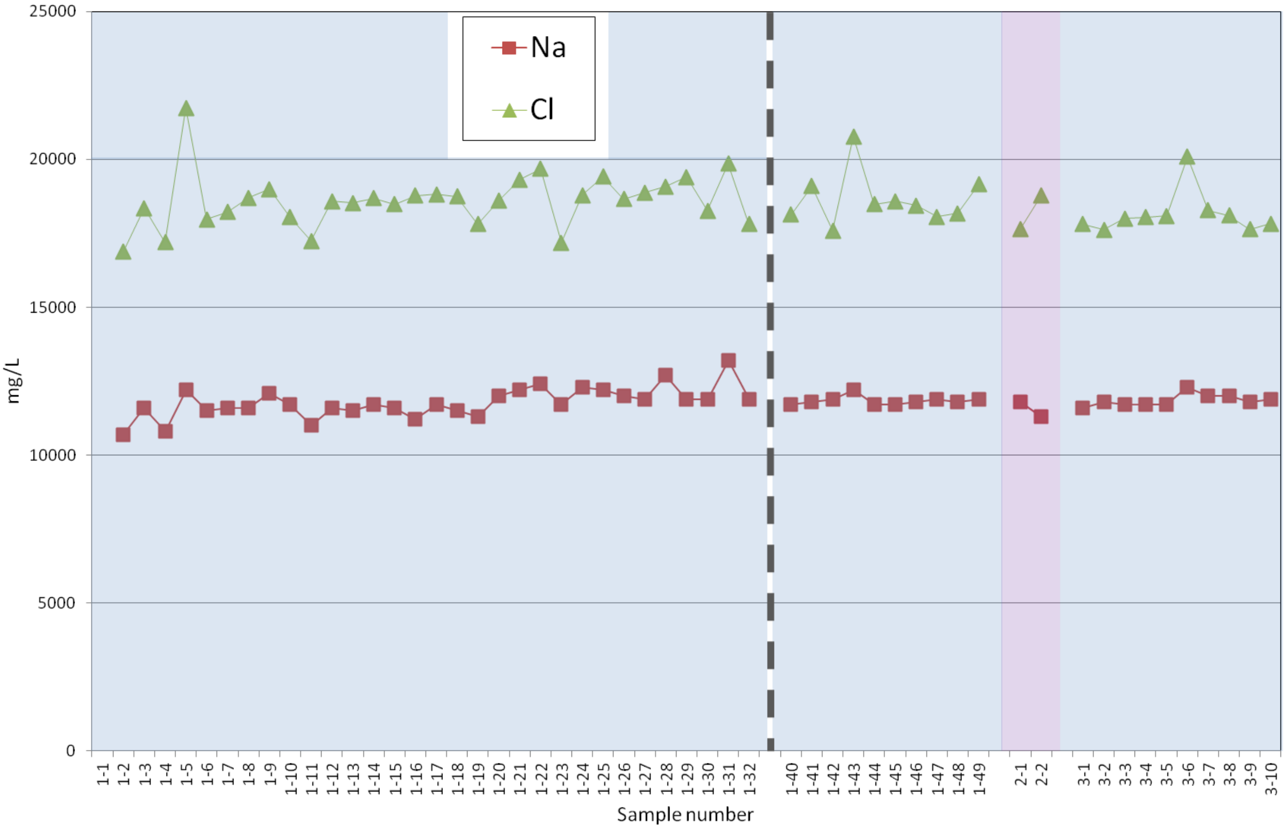


Figure 24 Sodium and Cl (mg/L) eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection.

**Table 25 Important minor element data in the core flood eluent. Lines indicate important changes in experimental conditions.**

| Sample ID | Flow Rate (cc/hr) | Co µg/L | Cr µg/L | Cu µg/L | Mo µg/L | Ni µg/L | Sr µg/L | V µg/L | Y µg/L | Zn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-2 | 50 | 1058 | 290 | 170 | 6 | 4928 | 39 | 18 | 7 | 8130 |
| 1-3 | 50 | 944 | 460 | 210 | 6 | 4928 | 36 | 21 | 10 | 7580 |
| 1-4 | 100 | 600 | 490 | 160 | 6 | 3936 | 21 | 18 | 10 | 5530 |
| 1-5 | 100 | 396 | 570 | 150 | 2 | 3380 | 14 | 14 | 11 | 3980 |
| 1-6 | 100 | 319 | 680 | 170 | 2 | 2920 | 12 | 12 | 12 | 3660 |
| 1-7 | 150 | 272 | 730 | 180 | 4 | 2660 | 12 | 12 | 12 | 3050 |
| 1-8 | 150 | 203 | 780 | 190 | 2 | 2340 | 10 | 12 | 11 | 2430 |
| 1-9 | 150 | 179 | 780 | 190 | 2 | 2170 | 8 | 11 | 10 | 2080 |
| 1-10 | 50 | 167 | 900 | 200 | 3 | 2070 | 9 | 12 | 11 | 2060 |
| 1-11 | 50 | 173 | 700 | 140 | 3 | 1880 | 9 | 7 | 9 | 1930 |
| 1-12 | 50 | 210 | 620 | 140 | 4 | 1960 | 12 | 14 | 10 | 2340 |
| 1-13 | 50 | 209 | 580 | 120 | 3 | 2120 | 10 | 11 | 10 | 2040 |
| 1-14 | 50 | 196 | 620 | 120 | 4 | 2320 | 11 | 13 | 10 | 2010 |
| 1-15 | 50 | 162 | 590 | 110 | 4 | 2140 | 10 | 12 | 9 | 1730 |
| 1-16 | 50 | 158 | 570 | 150 | 6 | 2280 | 10 | 12 | 12 | 2120 |
| 1-17 | 50 | 138 | 660 | 110 | 8 | 2100 | 10 | 13 | 9 | 1580 |
| 1-18 | 50 | 133 | 740 | 120 | 5 | 2140 | 10 | 14 | 10 | 1670 |
| 1-19 | 50 | 129 | 830 | 120 | 6 | 2160 | 10 | 14 | 10 | 1670 |
| 1-20 | 50 | 109 | 700 | 100 | 5 | 1900 | 9 | 13 | 9 | 1400 |
| 1-21 | 50 | 107 | 710 | 100 | 5 | 1920 | 9 | 13 | 9 | 1350 |
| 1-22 | 50 | 96 | 730 | 110 | 84 | 1800 | 8 | 11 | 8 | 1260 |
| 1-23 | 50 | 95 | 1050 | 120 | 478 | 1920 | 10 | 8 | 11 | 1600 |
| 1-24 | 50 | 85 | 740 | 110 | 7 | 1696 | 8 | 10 | 8 | 1190 |
| 1-25 | 50 | 80 | 740 | 80 | 5 | 1656 | 7 | 6 | 8 | 1120 |
| 1-26 | 50 | 70 | 680 | 80 | 5 | 1480 | 6 | 5 | 7 | 1010 |
| 1-27 | 50 | 82 | 900 | 100 | 9 | 1776 | 8 | 7 | 9 | 1250 |
| 1-28 | 50 | 72 | 810 | 90 | 11 | 1608 | 7 | 5 | 7 | 1080 |
| 1-29 | 50 | 63 | 770 | 80 | 7 | 1456 | 6 | 5 | 7 | 980 |
| 1-30 | 50 | 59 | 800 | 80 | 7 | 1416 | 6 | 5 | 7 | 970 |
| 1-31 | 50 | 66 | 890 | 90 | 8 | 1576 | 7 | 6 | 7 | 1060 |
| 1-32 | 50 | 56 | 910 | 80 | 7 | 1384 | 6 | 5 | 7 | 1020 |
| 1-40 | 50 | 60 | 830 | 60 | 5 | 1032 | 4 | 5 | 6 | 670 |
| 1-41 | 50 | 52 | 620 | 200 | 689 | 1184 | 12 | 5 | 8 | 1140 |
| 1-42 | 50 | 41 | 840 | 140 | 8 | 1296 | 5 | 5 | 8 | 940 |
| 1-43 | 50 | 34 | 910 | 130 | 7 | 1256 | 5 | 5 | 8 | 830 |
| 1-44 | 50 | 31 | 890 | 90 | 6 | 1176 | 4 | 5 | 7 | 790 |
| 1-45 | 50 | 31 | 990 | 90 | 7 | 1192 | 4 | 5 | 7 | 750 |
| 1-46 | 50 | 27 | 830 | 80 | 6 | 1056 | 4 | 4 | 6 | 700 |
| 1-47 | 50 | 31 | 980 | 120 | 9 | 1224 | 4 | 5 | 7 | 800 |
| 1-48 | 50 | 29 | 950 | 70 | 8 | 1160 | 4 | 5 | 6 | 770 |
| 1-49 | 50 | 29 | 980 | 70 | 9 | 1176 | 4 | 5 | 6 | 760 |

Table 24 (continued). Important minor element data in the core flood eluent. Lines indicate important changes in experimental conditions.

| Sample ID | Flow Rate (cc/hr) | Co µg/L | Cr µg/L | Cu µg/L | Mo µg/L | Ni µg/L | Sr µg/L | V µg/L | Y µg/L | Zn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|
| 2-1 | 50 | 27 | 920 | 70 | 8 | 1088 | 4 | 4 | 5 | 700 |
| 2-2 | 50 | 29 | 990 | 80 | 11 | 1184 | 4 | 5 | 5 | 770 |
| 3-1 | 50 | 115 | 1230 | 460 | 30 | 2070 | 24 | 10 | 9 | 2100 |
| 3-2 | 50 | 328 | 300 | 50 | 14 | 1980 | 44 | 4 | 7 | 3840 |
| 3-3 | 50 | 213 | 920 | 80 | 8 | 2380 | 28 | 4 | 10 | 3330 |
| 3-4 | 50 | 121 | 1620 | 40 | 6 | 2840 | 14 | 6 | 10 | 2030 |
| 3-5 | 50 | 79 | 1370 | 40 | 5 | 2250 | 10 | 4 | 10 | 1580 |
| 3-6 | 50 | 54 | 1050 | 40 | 4 | 1608 | 6 | 4 | 8 | 1090 |
| 3-7 | 50 | 38 | 870 | 40 | 4 | 1208 | 4 | 4 | 7 | 890 |
| 3-8 | 50 | 38 | 960 | 60 | 4 | 1248 | 4 | 4 | 8 | 890 |
| 3-9 | 50 | 37 | 960 | 60 | 5 | 1264 | 5 | 5 | 8 | 910 |
| 3-10 | 50 | 35 | 1040 | 70 | 6 | 1208 | 5 | 5 | 8 | 780 |

Figure 24 through to Figure 30 show the elements mobilised from sample 206660H facies Aii over the range of flooding conditions used. The pH was measured using samples at least partially equilibrated with the atmosphere, so can only be an approximate measure. The first eluent was measured at pH > 6 (Figure 25). As the plug pore volume is calculated to be 13.0 $cm^3$, then this first 10 mL eluent is presumably water within the pore space before the $CO_2$ fluid moves completely through the rock plug. Sample 1-1 was lost prior to geochemical analysis. After this first eluent, the measured pH stabilises at an upper level of approximately 4.5. The $CO_2$ brine injected in this experiment represents a very small amount of $CO_2$, relative to the quantities modelled in the previous chapter. Thus, if the $CO_2$ brine was totally equilibrated with the rock during the core flooding, pH should remain neutral, due to dawsonite formation:

$$NaAlSi_3O_8 + H_2CO_3 \rightleftharpoons NaAlCO_3(OH)_2 + 3SiO_2$$

(Albite) (Dawsonite) (Quartz)

Dawsonite is the major reaction in the modelling that maintains a near neutral pH. After dawsonite is consumed the pH becomes much more acidic. This indicates that the $CO_2$ brine reactions with the rock is incomplete, due to various kinetic constraints. After the overnight “soak” of the sample in $CO_2$ saturated brine, the second eluent had the highest measured pH (except for the very first eluent). This suggests that longer retention times appear to be resulting in greater chemical reactions between rock and solution. The measured pH was determined after atmospheric equilibration and is only an indicator i.e. there may be significant variation in the measurements and these are only qualitative.

In the case of Al and Si there is a significant lag between the flooding initiation and dissolved concentrations above detection (Figure 25). This increase in Al concentrations does not appear related to the change in flow rates (Table 24). The Al concentration drops to below detection limits after the overnight “soak” of the sample in $CO_2$ saturated brine, but reappears with similar concentrations, dipping at the point of $CO_2$ injection and then steadily climbs after the $CO_2$ injection. This drop should be considered in terms of mineral transformations occurring when the system is allowed a longer time period for equilibration.

Silica is detected in solution in only two samples (1-41 to 1-42) after the overnight “soak” of the sample in $CO_2$ saturated brine, increasing to more than double other concentrations, and is close to quartz saturation. Silica changes can be related to many reactions and conditions, however in this experiment we believe the silica is likely a result of increased acid attack on the rock minerals , the destruction of clays and the formation of dawsonite – this reflects the modelling reactions in the previous chapter as the formation of dawsonite will remove Al, Na and $CO_2$ from solution. Silica will be released from the clays that provide the Al. This is the rate limiting element as Na and $CO_2$ are abundant and small decrease in these compounds will not be detected. However, a loss of Al and a slight increase of Si does represent this reaction and is detected in the core flood eluent (Figure 25). The presence of Si is not detected after this time.

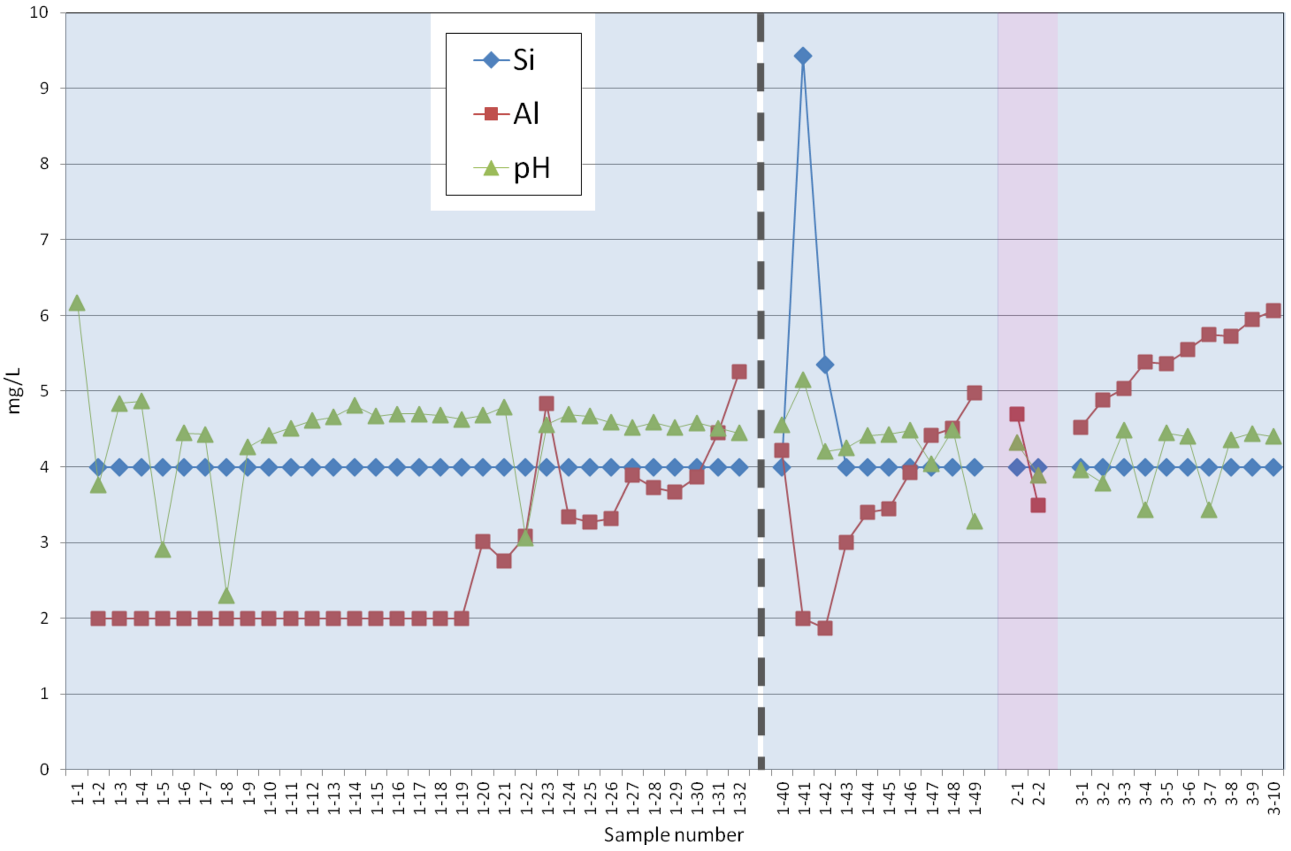


**Figure 25 Aluminium and Si (mg/L) with pH eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection. Values below detection are plotted at 80% of the detection limit.**

A plot of Ca, K and Mg shows some K measured at the very beginning of flooding which drops slightly until there are no measured concentrations above the detection limits (Figure 26). Samples 1-40 to 1-42 (after the overnight soak) show K is briefly detected at similar concentrations to that seen in the first sample. This also represents the destruction of clay minerals as occurs with Si indicating a small quantity of dawsonite is precipitated. By contrast, the amounts of Ca and Mg drop very soon after the commencement of flooding. There are periodic spikes in the Ca concentration in the first day, but it is generally below the limits of detection (Figure 26). Mg is detected on the first day at the start of flooding but is not observed until after the overnight soak period. This Ca and Mg may well represent dissolution of any dolomite and/or calcite that is accessible to the solution:

$$MgCa(CO3)_2 + 2H_2CO_3 \rightleftharpoons Mg^{2+} + Ca^{2+} + 2HCO_3^-$$

Calcium, K and Mg all appear in samples 1-40 to 1-42 (i.e., the first three samples after the overnight “soak”) before falling below the limits of detection.

**Table 26 Composition ranges for 316L stainless steel (%) used in the core flood experiment (from http://www.azom.com/article.aspx?ArticleID=2382).**

| Steel type | | C | Mn | Si | P | S | Cr | Mo | Ni | N |
|---|---|---|---|---|---|---|---|---|---|---|
| 316L | Min | - | - | - | - | - | 16.0 | 2.00 | 10.0 | - |
| | Max | 0.03 | 2.0 | 0.75 | 0.045 | 0.03 | 18.0 | 3.00 | 14.0 | 0.10 |

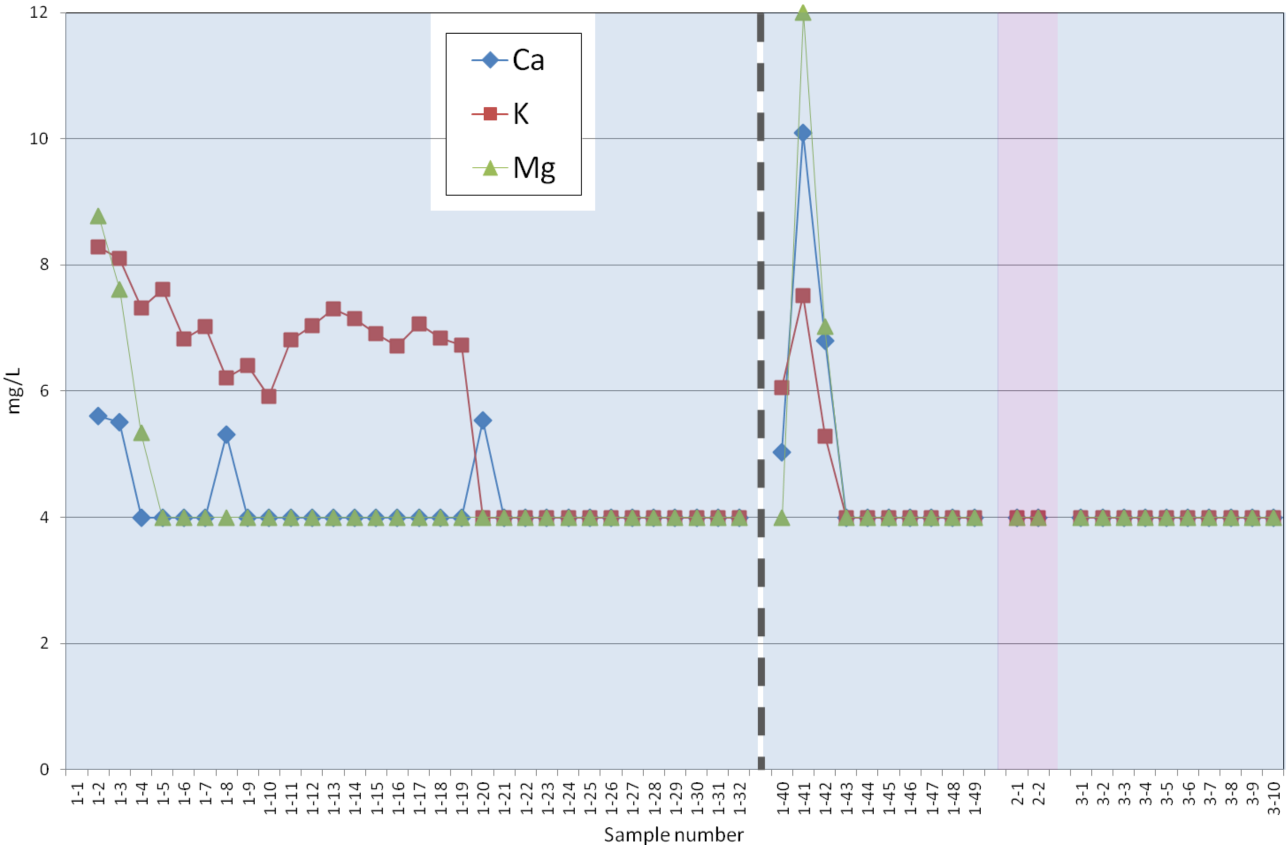


**Figure 26 Calcium, K and Mg (mg/L) eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection. Values below detection are plotted at 80% of the detection limit.**

Other elements are present and more easily detected concentrations in the core flood effluents. Figure 27 shows the presence of Fe, Mn and Rb. Dissolved Rb commonly correlates with K, and for this experiment shows very similar behaviour to K (as expected), although the effect is smoother as there are less detection issues.

Iron and Mn are present in greater and steadier concentrations. Both the high values and the steady background is of concern as these elements tend to concentrate in different phases and should show more variable behaviour. It is feasible that a significant amount of the Fe, Mn (Figure 27) and metals such as Ni, Zn and Cr (Figure 28), which all have high and relatively stable background eluent concentration are sourced from the corrosion of the SS 316L stainless steel tubing used to pump the fluids under pressure and temperature. The composition of the stainless steel is shown in Table 26 and this is similar to the composition of the eluted metals. However the ratios are significantly different, but this could reflect non-congruent dissolution of the metal. The chamber containing the rock plug is comprised of Hastelloy, which is primarily composed of Ni, Cr, Fe and Mo. Dissolved Cr (Figure 28) behaves differently from other elements, as its concentration slowly rises then stabilises, and it dips down immediately after the overnight soak. Chromium is known to protect stainless steel by migrating to the surface and forming a thin film of $Cr_2O_3$. This compound is soluble below pH 4, possibly explaining this behaviour. Molybdenum is another major constituent of the steel (Table 26), and dissolved Mo (Figure 29), behaves differently from any other element analysed, with very significant spikes in the middle of the day 1 flooding and during the $CO_2$ injection. It is not clear why Mo should behave so differently, but it made be due to specific differences in how Mo is dissolved out of steel.

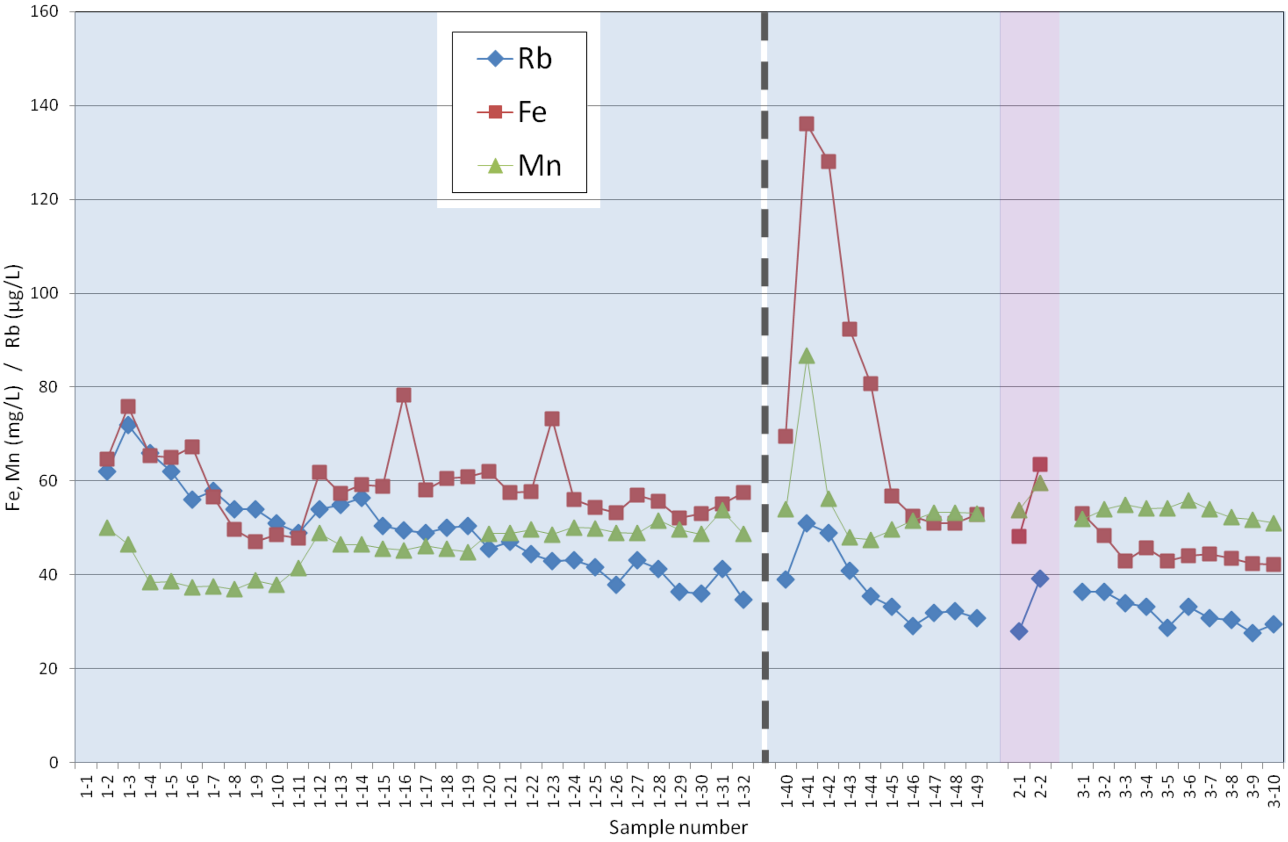


**Figure 27 Iron and Mn (mg/L) and Rb (µg/L) eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection.**

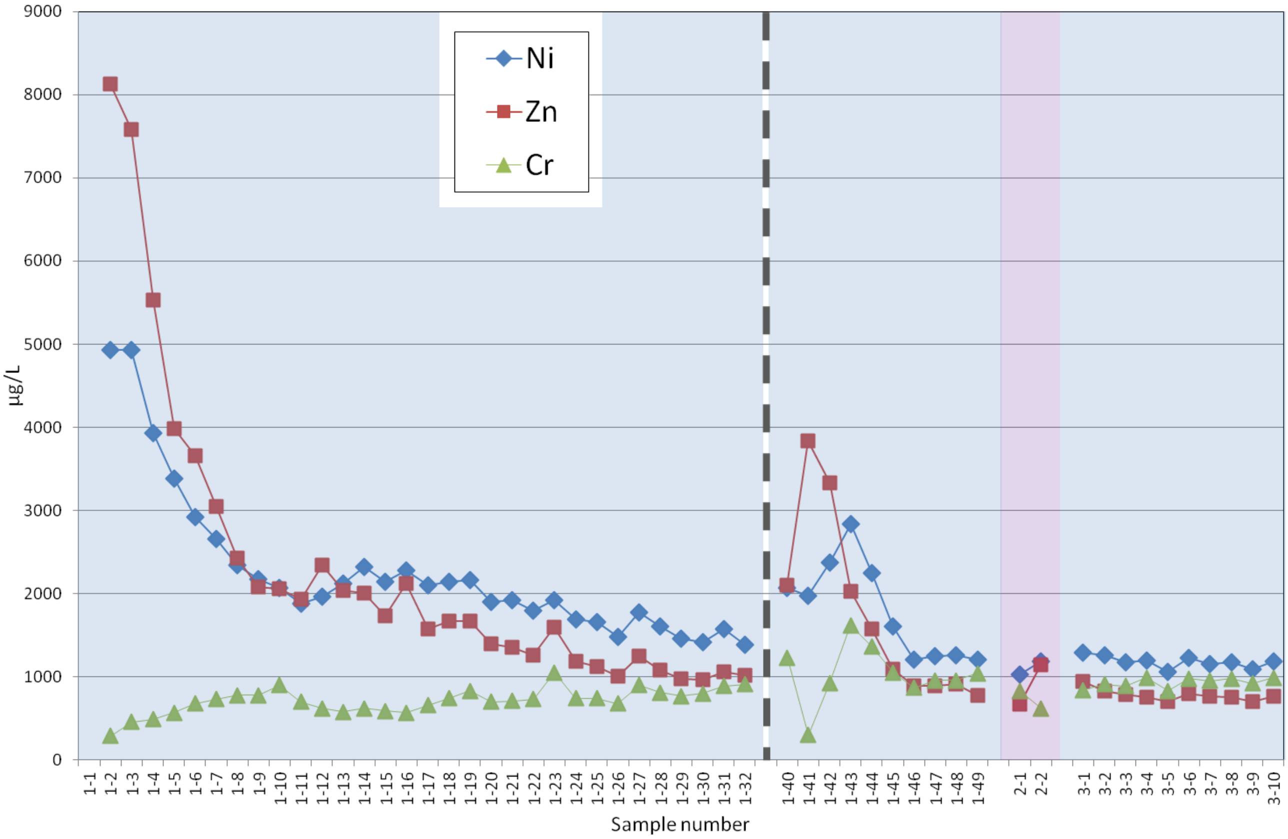


**Figure 28 Nickel, Zn and Cr (µg/L) eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection.**

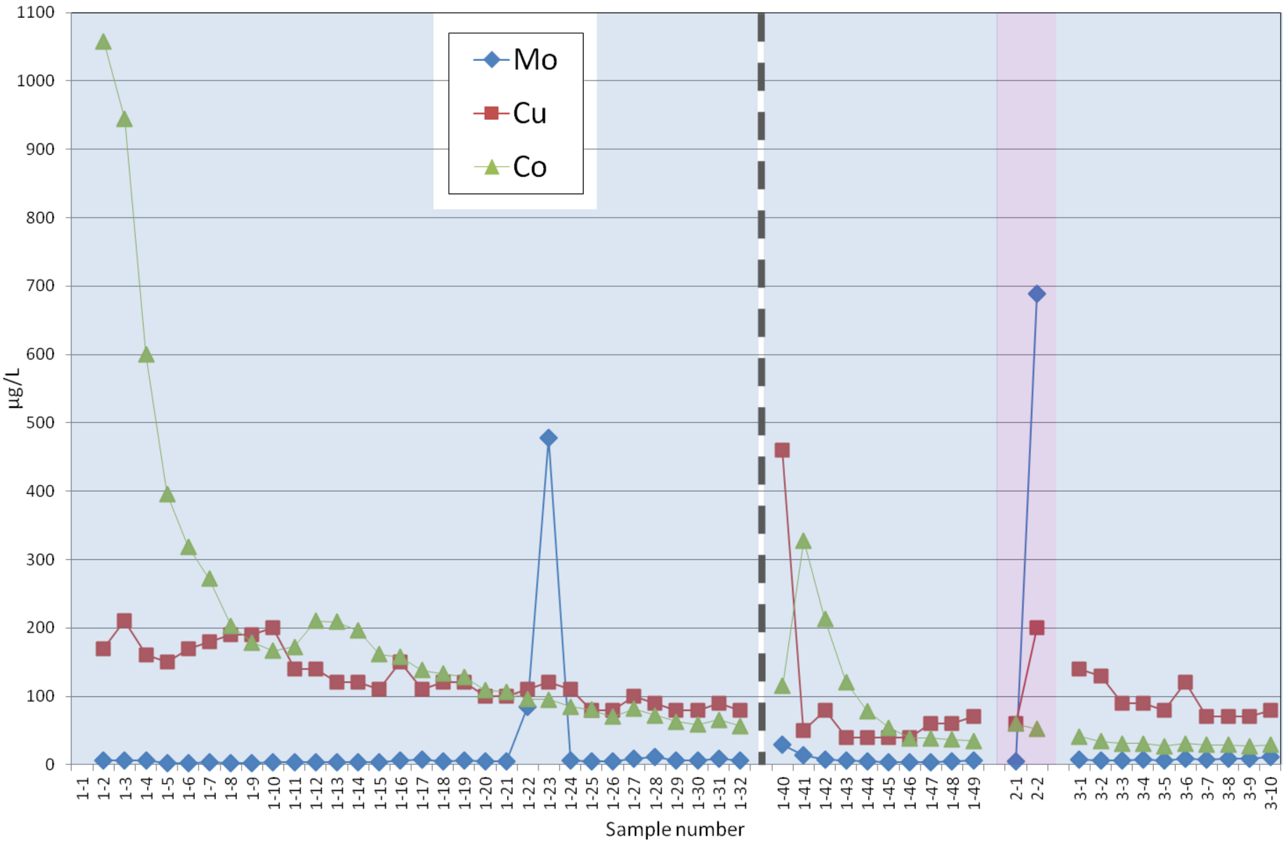


**Figure 29 Molybdenum, Cu and Co (µg/L) eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection.**

Although we will describe below effects that we think are due to brine interactions with the rock plug, it should be acknowledged that there is presently doubt over which behaviours of these various metals could potentially be partially due to corrosion effects. One way of compensating for this potential "contamination" of Fe and other elements would be to conduct a "blank" run with no rock and another with an inert quartz-rich sandstone (e.g., the Berea) and a suitable synthetic brine. This could determine the impact of the experimental setup in the presence of $CO_2$ saturated brine or with a $CO_2$ injection, to allow for a sensitivity analysis and/or a back calculation of any additional metals from corroding tubing.

Iron in particular, and also Mn, Zn and other metals, do show a major peak (over double for Fe) immediately after the overnight soak (Figure 27). This could indicate dissolution of Fe-bearing phases being greater for longer incubation periods.

Dissolved Co showed significant variation during the run, and decreased to very low values by the end of the experiment, consistent with there being low levels of corrosion "contamination; and it may show the best indication of how metal are being leached out of the rock. There were very high dissolved values for the initial eluents, consistent with the $CO_2$ brine attacking any Mn and amorphous Fe phases and releasing Co. It showed minor increase at 1-12, possibly indicating more dissolution as the brine pushed further into the rock matrix. Dissolved Co then decreased, with a moderate peak after overnight soaking and a minor peak with the $CO_2$ injection.

Most other trace and transition metals were below detection. Dissolved Sr (Figure 30) showed behaviour similar to Mg and Ca, and elements such as Y and V showed minor concentrations that tended to decrease during the experiment, possibly due to release from Fe-, clay- or resistate-minerals. Thus, V is uniformly low but above the limits of detection (Figure 30). Yttrium (Figure 30) shows again the impact of the initial flooding, spiking in concentrations following the overnight soak and at the time of the $CO_2$ injection. Results reported in Delle Piane et al. (2013) for sample 206660H (porosity was 15.56%) postulated a reduction in permeability due to fines migration, based on XRD analysis and the presence of 7% kaolinite (Table 21). Also noted in Delle Piane et al. (2013) is the observation that supercritical $CO_2$ saturation is very high and may be caused by blockage or plugging of the pre-throats by kaolinite or other fines migration. Fines migration refers to clays or other minerals such as quartz, feldspars, carbonates or salts in these core flood studies (Saeedi, 2012). This process can be exaggerated by the addition of multiphase flow particularly with the addition of $CO_2$ where mineral dissolution can accelerate dislodgement of particles and increase formation damage in the subsurface.

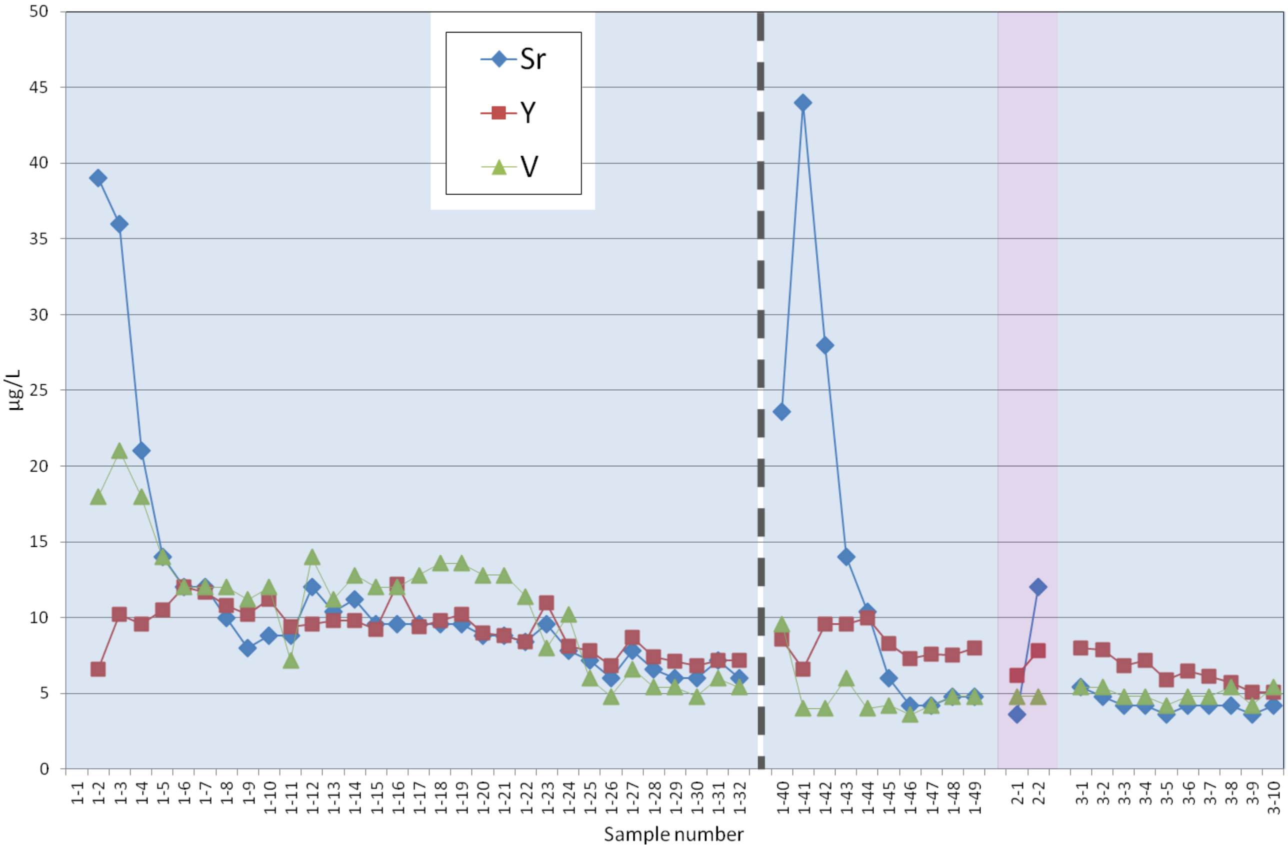


**Figure 30 Strontium, Y and V (µg/L) eluted over the course of the flooding test. The dashed line represents the overnight saturation and the pink zone shows the $CO_2$ injection.**

The core flood effluent chemistry indicates the fine clays are attacked and dissolved in part to form dawsonite. The limits of this reaction may be linked to pore blockage observed in the other studies, but modelling in the previous chapter shows that the rock in the core flood is not close to equilibrium. Kinetic factors are substantial and it may not be possible to thermodynamically simulate this experiment fully. An example of the kinetic effects can be seen in the effects of hydrothermal fluids that went through Archaean rocks, possibly for many years. The alteration from the fluids is around the veins and has not affected the entire rock providing a real world demonstration of the influence of kinetics in these modelled reactions (S. Barnes *pers. comm.*).

A literature review (Saeedi, 2012) has indicated limited data on detailed geochemical analyses of core flood effluents has been conducted. Geochemical information from core floods provides some indication of the contribution of mineral dissolution or precipitation versus fines migration on porosity and permeability of an interval. Furthermore, it may provide information on the potential for remobilisation of various inorganic species. Previous work by Ross et al., (1982) is one of the few examples of a suite of geochemical analyses being conducted on core flood effluents. As the total volume of fluids recovered from the flooding of sample 206660H was of the order of 500-1000mL the comparison with results in Figure 31 is not the same in terms of volume or the timing of sampling. However, as with many of the elements measured in this work, there is a peak early in the flooding with carbonated brine where there are higher concentrations of Ca and Mg, which decrease over time. In the experiments reported here, there are more steps that repeat this pattern particularly after the overnight soak period and again with some elements after a small $CO_2$ flood (Table 24). Other core flood experiments reviewed in Saeedi (2012 and references therein) indicate that permeability may increase, or decrease depending on a number of factors, including the pressure of the experiments and the ratio of dissolution to fines migration, depending on the type of samples used.

Using this one case, it can be seen that there is a degree of reactivity of the Wonnerup Aii facies. However, further flooding and geochemical characterisation would greatly improve the current knowledge on the behaviour of the likely storage reservoir and the range of reactivity across the same facies at different depths and temperatures. This would help in the understanding of the extent to which diagenesis has already impacted on rock reactivity with reservoir temperature.

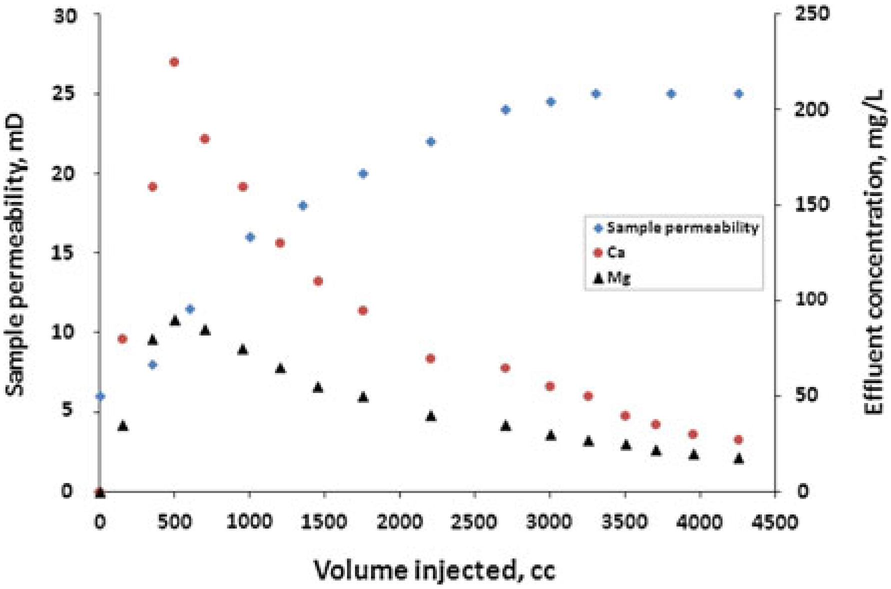


**Figure 31 Relationship between permeability, core flood injection volumes and concentration of elements recovered from a core flood test of a Rotliegende calcareous sandstone sample in carbonated brine (2,000 psi and 80°C). From Ross et al. 1982. Figure reproduced from Saeedi (2012).**

The suitability of water samples available to conduct a detailed characterisation of the Harvey-1 well, the use of a synthetic brine and the quantitative measurements made for the core flood test can begin to inform the South West Hub of likely reactions in the formation. With more analyses, the work could provide sufficient data to develop a potential model for likely behaviour in some of the major facies. The Harvey-1 and regional groundwater will enable a much more representative fluid to be used in future core flooding experiments. This coupled with better blank and analytical controls on the eluents and more detailed mineral analysis (SEM in conjunction with XRD) will provide a much fuller assessment of potential reactions and mineral transformations expected with super critical $CO_2$ injection.

Other key considerations for future experiments would be to get an initial pH as the solution is collected and since Al seems important we can get significantly improved, lower detection limits for the analysis of Al. This will assist modelling of clay mineral transformations. The use of SEM analysis of mineral grains and trace element mapping pre and post experiment will greatly improve the value of core flood experiments, providing a geochemical context to support the physical rock property changes associated with $CO_2$ injection.

## 5.4 Summary

The core flooding of sample 206660H from the Aii facies of the Wonnerup Member at 1935.5m has produced sufficient core flood effluent for geochemical characterisation of 53 samples. While the samples were only 10mL, we were sufficiently able to characterise the elemental composition of the eluent and measure the pH. Results showed that there was some dissolution of minerals and supported the modelling with the potential precipitation of dawsonite observed in the decrease of Al and increase of Si following the longest period of rock-water interaction (overnight “soak”). Many elements, such as Ni, Zn, Cr, Mo, Cu and V were mobilised, but this is possibly due at least partially to corrosion of the stainless steel.

There are few examples of such detailed analyses of core flood effluents in the literature (see Saeedi, 2012 for a fuller review). Improved core flood experimental setup with blanks, lower detection limits of key elements, rapid pH testing of the eluent, SEM mineralogical characterisation and more representative fluid composition (adding other anions and cations, not just NaCl) there is significant opportunity to improve our understanding of the geochemical changes of the host rocks when subject to $CO_2$ injection. These improvements will provide a sufficient data set to draw conclusions on the rates of dissolution for the South West Hub or other localities to better understand the long term injectivity of the storage intervals at this or other sites.

# 6 Conclusions, Recommendations and Lessons Learned

The geochemical analysis of gases from Kwinana and rock, drilling fluid and water samples from the Harvey-1 stratigraphic well have yielded abundant information to be integrated with the South West $CO_2$ Geosequestration Project.

## Gases

Gas analyses have shown that the gas from CSBP in Kwinana is a fairly pure $CO_2$ stream containing 98.3 mol. % $CO_2$ with a carbon isotopic composition of $\delta^{13}C$ -37.6 ± 0.28 ‰. This isotopic signature is quite unique relative to background signals from the atmosphere or organic matter decomposition, and could act as a useful tracer. Analysis of feedstock coal to understand the primary carbon isotopic signature of the coal used at CSBP would be of value to understand the origin of the $\delta^{13}C$ value of the $CO_2$ from CSBP and whether there is significant fractionation occurring during the coal to urea processing. This would aid in understanding likely variation in that specific signature in an ongoing evaluation of the carbon isotopic composition of the gas being a suitable tracer for a pilot scale test.

Oxygen isotopes of $CO_2$ were also measured by way of baseline information and were found to have values of $\delta^{18}O$ -2.15 ± 0.07 ‰. The oxygen data are more prone to changes on contact with water and can be used in later estimates on trapping mechanisms based on work described in Johnson et al, (2011a).

While there was a significant effort to identify sampling and analysis methods for determining the metals composition of the gases, this was not executed. At no point were we satisfied that methods could be applied without significant development and testing in the lab and in the field to obtain relevant, reportable numbers.

**Recommendations**:

- analyse feedstock coal for $d^{13}C$ data to build up the mass balance for the use of the $CO_2$ injectant gas as a natural tracer, and,
- with the new NGL equipment it is possible to evaluate new methods for measuring metal contents in gases.

## Organic Liquids in Cores

Extraction of eight core samples through the well yielded amounts of hydrocarbons. The richest sample, 206611 with an extractable organic matter content of 304.93 mg/kg rock resided in a Aii Facies sample from 913.45 m horizontal core plug. This amount of organic matter was still significantly lower than any seen in hydrocarbon-rich systems that might be regarded as economic oil prospects. For example, the sandstone rich Heimdal Formation in Norway, with an average porosity of around 33% and 70% oil saturation might contain around 100,000 mg/kg rock extractable organic matter (Ross, 2004). The remaining samples measured had an order of magnitude lower extractable organic matter than sample 206611. This suggests that no local source rocks are in the area. Delle Piane's et al., (2013) description of the rock facies confirms this locally.

Any attempts to understand the provenance of the small amounts of organic matter extracted were rendered impossible by the extensive drilling mud contamination. The materials present in the drilling fluids coeluted with the relevant compounds that would typically be used in a GC-FID evaluation of *n*-alkanes and isoprenoids to understand source or maturity of the hydrocarbons in an attempt to understand if the organic matter was from a marine, lacustrine or terrestrial source, or if it was from in situ generation or migrated from elsewhere. GSWA provided two vitrinite reflectance data points which showed that at about 900m the samples (particularly sample 206611 at 913.45m) would have had a vitrinite reflectance value of about 0.3% or immature with respect to oil generation. By 2500m the calculated value for vitrinite reflectance of 0.8% indicates that rocks in that interval would have sufficient maturity to generate and expel oil if organic carbon was present.

**Recommendation**:

- The addition of a drilling fluid tracer would have aided in our understanding of the extent of drilling fluid contamination in the core plugs and extracts, as well as for reconstructing any salinity measurements in formation fluids collected. This is not without precedent, and has occurred at the CO2CRC Otway Project during drilling of wells CRC-1 and -2, as well as being used in other examples, such as the drilling of Precambrian rocks for analysis to confirm early life biomarkers.

While it would have be useful to conduct GCMS analyses on the biomarker signature of the extracts to overcome the presence of contamination to aid in the understanding of the source and maturity of the extractable organic matter from these cores, it was decided that it was not appropriate based on the low volumes of material extracted, nor was there any guarantee that the contamination may not have continued to impact on the interpretation of some of the biomarkers.

**Recommendation**: Conduct a full suite of organic geochemical analysis (to evaluate organic matter provenance).

Not all of the facies types were sampled and cored for the geochemistry project. The shale-rich facies were collected and preserved under oil which would have potentially contributed to a different degree of contamination. This would require testing before considering any evaluation of preserved shales in the future.

**Recommendation**: Evaluate sampling protocol for shale intervals (preserved in oil) to see if the shale samples can be investigated. Presence of oil impacts on geochemical analysis. Core plugs were not taken due to the poor consolidation of the samples, however these could be investigated further.

## Inorganic geochemistry of the shallow bore and deep water sample from Harvey-1

The single deep sample (from 856m in the Yalgorup Member) was found to be heavily contaminated by drilling fluids. Preliminary comparisons were made with the Cockleshell Gully Formation data from Deeney (1989a and 1989b) and showed that it was not exceptional even though it was from below the Eneabba seal in the Yalgorup Member. This could indicate that there is no hydraulic or geochemical gradient between the two, however, it is more likely the various deeper aquifers have saline groundwater of a roughly similar level, even though they are not of similar genesis and connectivity. The variability with the contamination of the MDT makes further comparison not feasible. This new groundwater data from the MDT is more detailed with about 60 elements measured. This information will contribute towards future measurements in other deeper and shallower wells in the area to provide some very general baseline data and provide a more representative synthetic brine for future coreflood analyses. The results compare reasonably well with the wireline data, but contamination again has been a major influence on the results. The TDS value for this sample was 52,319 ppm but could not be recalculated to remove the drilling fluid contamination.

**Recommendation**:

- As the sample was provided to us at a date well past the recommended holding period for water analyses, this indicates a need to include the researchers during the drilling and sample collection phase. This is further confirmed by our collection of the shallow water sample that was well preserved.

## Modelling data

Attempts at correcting the TDS and other salinity data for the deep 856 m Harvey-1 sample from the Yalgorup Member proved to be too difficult and a match could not be achieved. This was due to potential for the presence of organic acids, partial barite precipitation and/or enhanced alkalinity due to organic matter decomposition. Instead it was preferred to use some of the regional data (Deeney, 1989a and 1989b) as a proxy for the ongoing modelling activities.

Information on the mineralogy of samples from Delle Piane et al. (2013) was used to develop parameters for use in modelling simple mineral assemblages. Geochemist's Workbench software was used to perform calculations. Modelled equilibrations for a number of minerals showed that it was possible to broadly compare the calculations with the regional groundwater data, however, a lack of a perfect match was suggested to be more a reflection of the poor degree of thermodynamic equilibration at lower temperatures.

In the initial modelling, at the early stages of $CO_2$ injection, only moderate changes are observed where $CO_2$ is consumed by the conversion of albite and phrengite to dawsonite. After this is complete, K-feldspar is converted to muscovite and quartz. After the complete formation of dawsonite, there remains little capacity for the rock to adsorb $CO_2$ and it remains in solution.

Coreflood conditions have been transposed on to the models in this section to illustrate the conditions modelled. Comparisons between the modelled data and the corefloods do not show a good match for reasons described below.

**Recommendation**:

- While the initial models are a sensible commencement of work for this site, much more needs to be done. This will require new data, for example SEM mineral mapping and more detailed mineralogical understanding. However, lack of water chemistry data from deeper intervals limit immediate activities to continue.

## Core flood results

Geochemical characterisation of the metal species during the flooding of one core sample from the Wonnerup Member has proved a valuable means of identifying the extent to which a core sample might be reactive in the presence of $CO_2$. Detailed evaluations of this type are rarely conducted on this scale (Saeedi, 2012). The data measured were able to be reviewed in the light of the modelling of mineral behaviour conducted for other samples mentioned above. A pattern was observed where it appears that the coreflood observations, identified that removal of Al and Si could be reflective of the destruction of clays and the formation of other minerals such as dawsonite. Silica could be released from clays under acid attack Loss of K soon after flooding commences is also an indicator of clay mineral destruction.

Presence of Fe and other metals indicate evidence of corrosion of the SS 316 tubing in the core flooding rig. This suggests that further work should include the running of suitable "blank" experiments, allowing back calculation of the corrosion contaminants in the future.

While there is evidence to suggest that some of the porosity and permeability changes in the flooded rock samples is due to fines migration, there is evidence in the geochemistry of the core flood effluents to suggest that the $CO_2$ has dissolved clays. Kinetic effects may impact the extent to which some of the reactions proceed.

This first detailed characterisation of a coreflood effluent where up to 60 elements can be characterised has demonstrated that the combined experimental core flood, modelling and geochemical analyses can provide a powerful tool in estimating aspects of injectivity and trapping in the future.

**Recommendation**:

- Improvements can be made based on changing the brine chemistry to reduce the impacts of the concentration effects in the effluents for obtaining better quality data (as discussed) and the use of blanks and spikes to quantify other aspects of the core flooding tests. Improved characterisation of the samples (SEM rather than XRD) would also aid in both the calculations and modelling of any dissolution, precipitation or remobilisation of minerals in the future.
- Analysis of all of the major facies identified would also be a sensible minimum requirement and comparisons with equivalent facies in Pinjarra-1, a well to the north with very similar facies

distributions, however, Pinjarra-1 has undergone significant diagenetic alteration not seen at Harvey-1.

There is no evidence from the geochemical analyses to suggest that the South West $CO_2$ Geosequestration Hub Project should not proceed.

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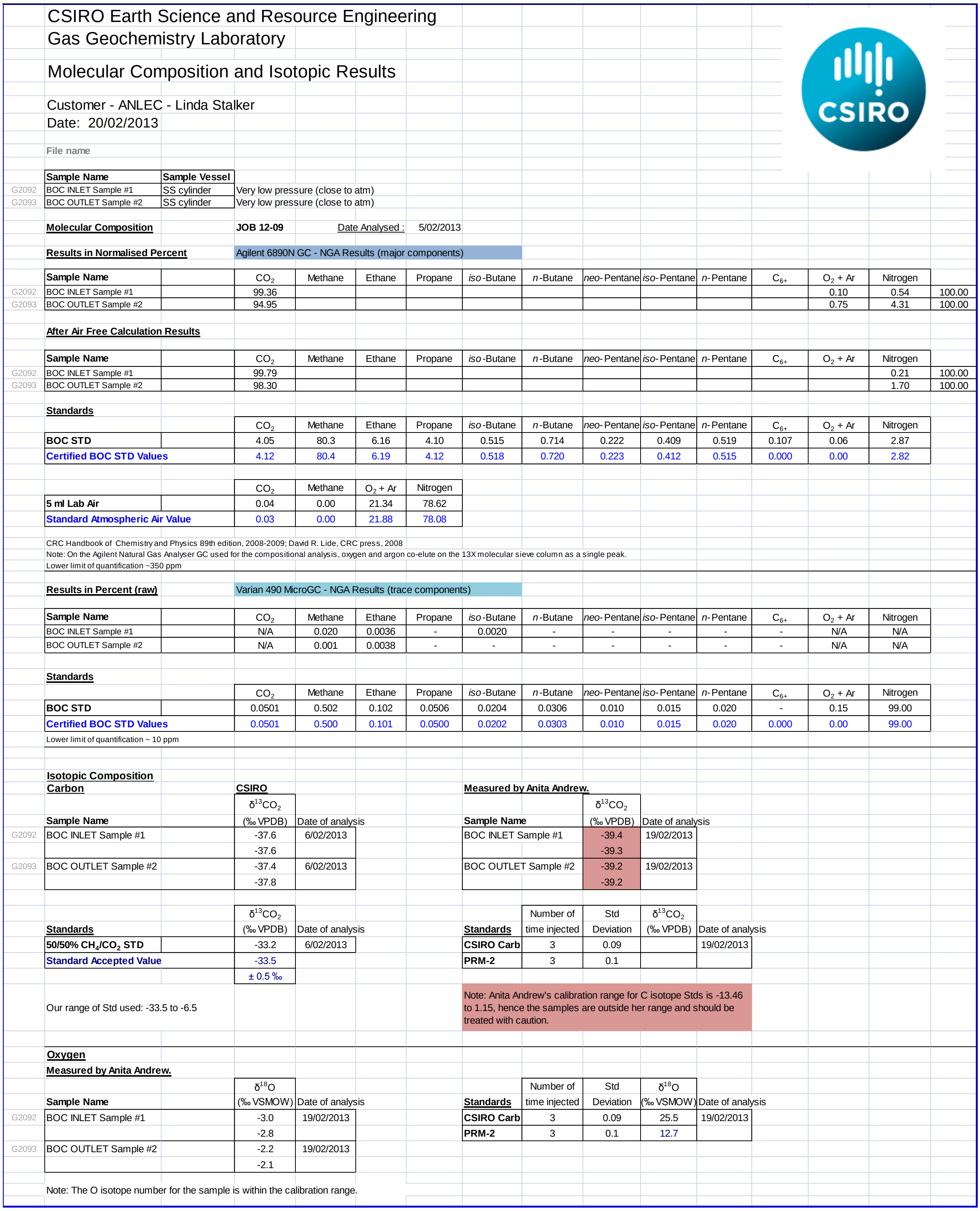
# Appendix A Results in Full for Organic Geochemical Analysis of Gas Samples

Organic Geochemistry of Gas Samples from CSBP and BOC



CSIRO Earth Science and Resource Engineering
Gas Geochemistry Laboratory

Molecular Composition and Isotopic Results

Customer - ANLEC - Linda Stalker
Date: 20/02/2013

File name

| | Sample Name | Sample Vessel | |
|---|---|---|---|
| G2092 | BOC INLET Sample #1 | SS cylinder | Very low pressure (close to atm) |
| G2093 | BOC OUTLET Sample #2 | SS cylinder | Very low pressure (close to atm) |

**Molecular Composition** **JOB 12-09** Date Analysed : 5/02/2013

**Results in Normalised Percent** Agilent 6890N GC - NGA Results (major components)

| | Sample Name | $CO_2$ | Methane | Ethane | Propane | *iso*-Butane | *n*-Butane | *neo*-Pentane | *iso*-Pentane | *n*-Pentane | $C_{6+}$ | $O_2$ + Ar | Nitrogen | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| G2092 | BOC INLET Sample #1 | 99.36 | | | | | | | | | | 0.10 | 0.54 | 100.00 |
| G2093 | BOC OUTLET Sample #2 | 94.95 | | | | | | | | | | 0.75 | 4.31 | 100.00 |

**After Air Free Calculation Results**

| | Sample Name | $CO_2$ | Methane | Ethane | Propane | *iso*-Butane | *n*-Butane | *neo*-Pentane | *iso*-Pentane | *n*-Pentane | $C_{6+}$ | $O_2$ + Ar | Nitrogen | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| G2092 | BOC INLET Sample #1 | 99.79 | | | | | | | | | | | 0.21 | 100.00 |
| G2093 | BOC OUTLET Sample #2 | 98.30 | | | | | | | | | | | 1.70 | 100.00 |

**Standards**

| | $CO_2$ | Methane | Ethane | Propane | *iso*-Butane | *n*-Butane | *neo*-Pentane | *iso*-Pentane | *n*-Pentane | $C_{6+}$ | $O_2$ + Ar | Nitrogen |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **BOC STD** | 4.05 | 80.3 | 6.16 | 4.10 | 0.515 | 0.714 | 0.222 | 0.409 | 0.519 | 0.107 | 0.06 | 2.87 |
| **Certified BOC STD Values** | 4.12 | 80.4 | 6.19 | 4.12 | 0.518 | 0.720 | 0.223 | 0.412 | 0.515 | 0.000 | 0.00 | 2.82 |

| | $CO_2$ | Methane | $O_2$ + Ar | Nitrogen |
|---|---|---|---|---|
| **5 ml Lab Air** | 0.04 | 0.00 | 21.34 | 78.62 |
| **Standard Atmospheric Air Value** | 0.03 | 0.00 | 21.88 | 78.08 |

CRC Handbook of Chemistry and Physics 89th edition, 2008-2009; David R. Lide, CRC press, 2008
Note: On the Agilent Natural Gas Analyser GC used for the compositional analysis, oxygen and argon co-elute on the 13X molecular sieve column as a single peak.
Lower limit of quantification ~350 ppm

**Results in Percent (raw)** Varian 490 MicroGC - NGA Results (trace components)

| Sample Name | $CO_2$ | Methane | Ethane | Propane | *iso*-Butane | *n*-Butane | *neo*-Pentane | *iso*-Pentane | *n*-Pentane | $C_{6+}$ | $O_2$ + Ar | Nitrogen |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BOC INLET Sample #1 | N/A | 0.020 | 0.0036 | - | 0.0020 | - | - | - | - | - | N/A | N/A |
| BOC OUTLET Sample #2 | N/A | 0.001 | 0.0038 | - | - | - | - | - | - | - | N/A | N/A |

**Standards**

| | $CO_2$ | Methane | Ethane | Propane | *iso*-Butane | *n*-Butane | *neo*-Pentane | *iso*-Pentane | *n*-Pentane | $C_{6+}$ | $O_2$ + Ar | Nitrogen |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **BOC STD** | 0.0501 | 0.502 | 0.102 | 0.0506 | 0.0204 | 0.0306 | 0.010 | 0.015 | 0.020 | - | 0.15 | 99.00 |
| **Certified BOC STD Values** | 0.0501 | 0.500 | 0.101 | 0.0500 | 0.0202 | 0.0303 | 0.010 | 0.015 | 0.020 | 0.000 | 0.00 | 99.00 |

Lower limit of quantification ~ 10 ppm

**Isotopic Composition**
**Carbon**

**CSIRO**

| | Sample Name | $\delta^{13}CO_2$ (‰ VPDB) | Date of analysis |
|---|---|---|---|
| G2092 | BOC INLET Sample #1 | -37.6 | 6/02/2013 |
| | | -37.6 | |
| G2093 | BOC OUTLET Sample #2 | -37.4 | 6/02/2013 |
| | | -37.8 | |

**Measured by Anita Andrew.**

| Sample Name | $\delta^{13}CO_2$ (‰ VPDB) | Date of analysis |
|---|---|---|
| BOC INLET Sample #1 | -39.4 | 19/02/2013 |
| | -39.3 | |
| BOC OUTLET Sample #2 | -39.2 | 19/02/2013 |
| | -39.2 | |

| **Standards** | $\delta^{13}CO_2$ (‰ VPDB) | Date of analysis |
|---|---|---|
| **50/50% $CH_4/CO_2$ STD** | -33.2 | 6/02/2013 |
| **Standard Accepted Value** | -33.5 | |
| | ± 0.5 ‰ | |

| **Standards** | Number of time injected | Std Deviation | $\delta^{13}CO_2$ (‰ VPDB) | Date of analysis |
|---|---|---|---|---|
| **CSIRO Carb** | 3 | 0.09 | | 19/02/2013 |
| **PRM-2** | 3 | 0.1 | | |

Our range of Std used: -33.5 to -6.5

Note: Anita Andrew's calibration range for C isotope Stds is -13.46 to 1.15, hence the samples are outside her range and should be treated with caution.

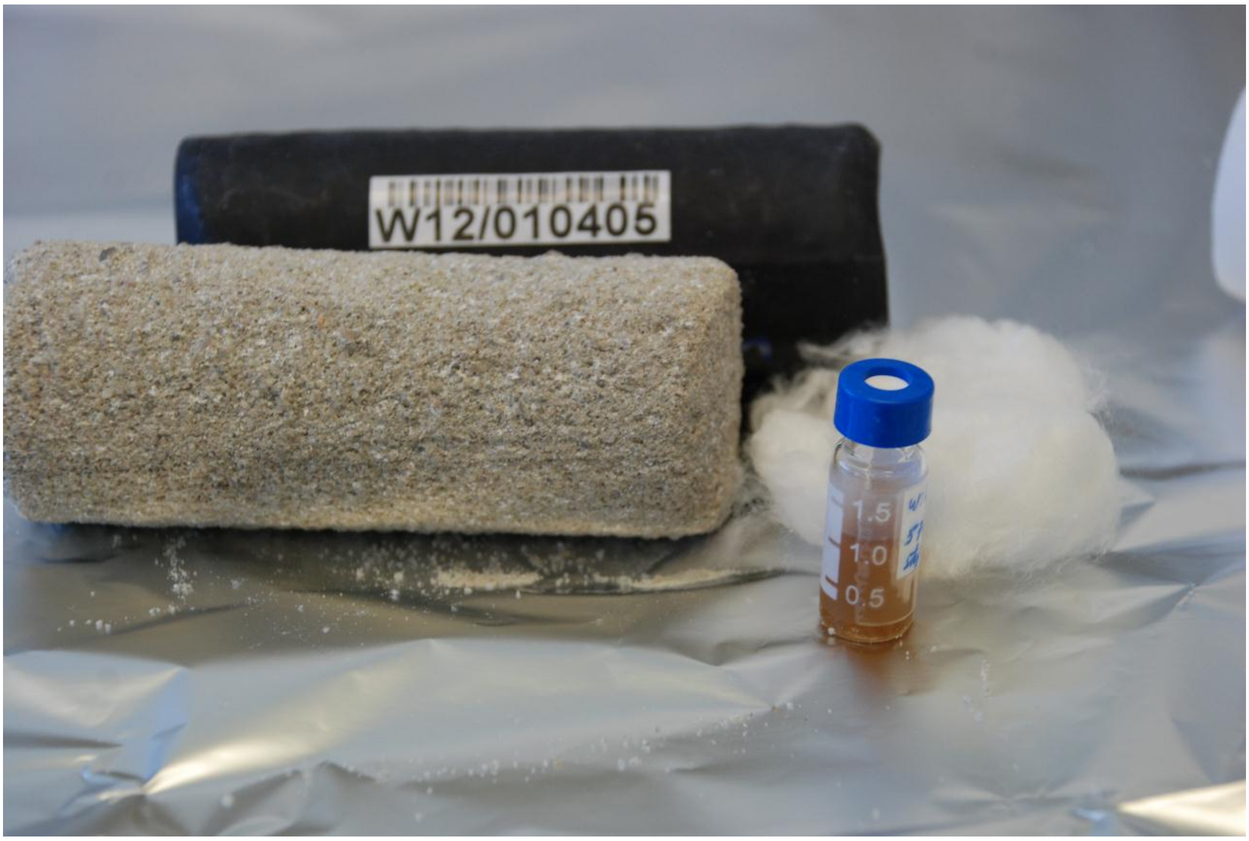
**Oxygen**
**Measured by Anita Andrew.**

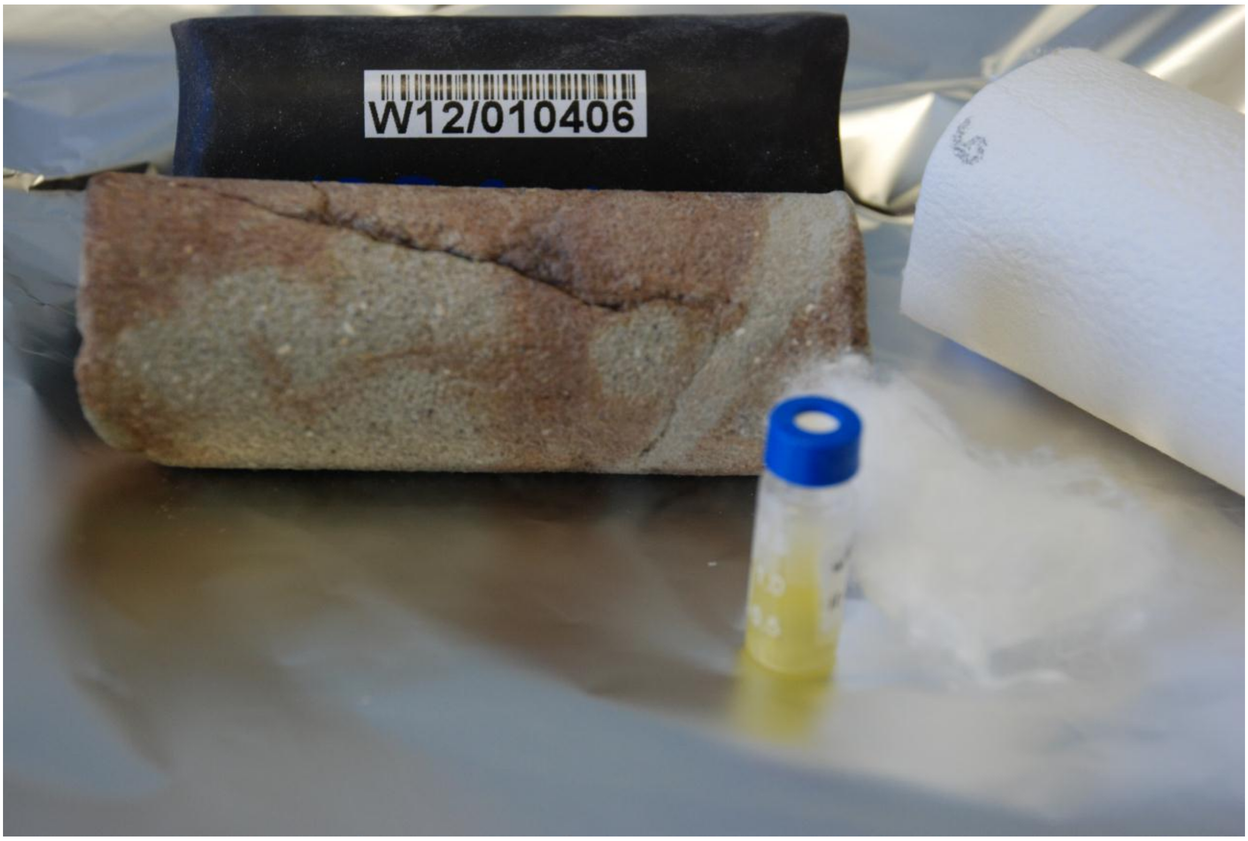
| | Sample Name | $\delta^{18}O$ (‰ VSMOW) | Date of analysis |
|---|---|---|---|
| G2092 | BOC INLET Sample #1 | -3.0 | 19/02/2013 |
| | | -2.8 | |
| G2093 | BOC OUTLET Sample #2 | -2.2 | 19/02/2013 |
| | | -2.1 | |

| **Standards** | Number of time injected | Std Deviation | $\delta^{18}O$ (‰ VSMOW) | Date of analysis |
|---|---|---|---|---|
| **CSIRO Carb** | 3 | 0.09 | 25.5 | 19/02/2013 |
| **PRM-2** | 3 | 0.1 | 12.7 | |

Note: The O isotope number for the sample is within the calibration range.

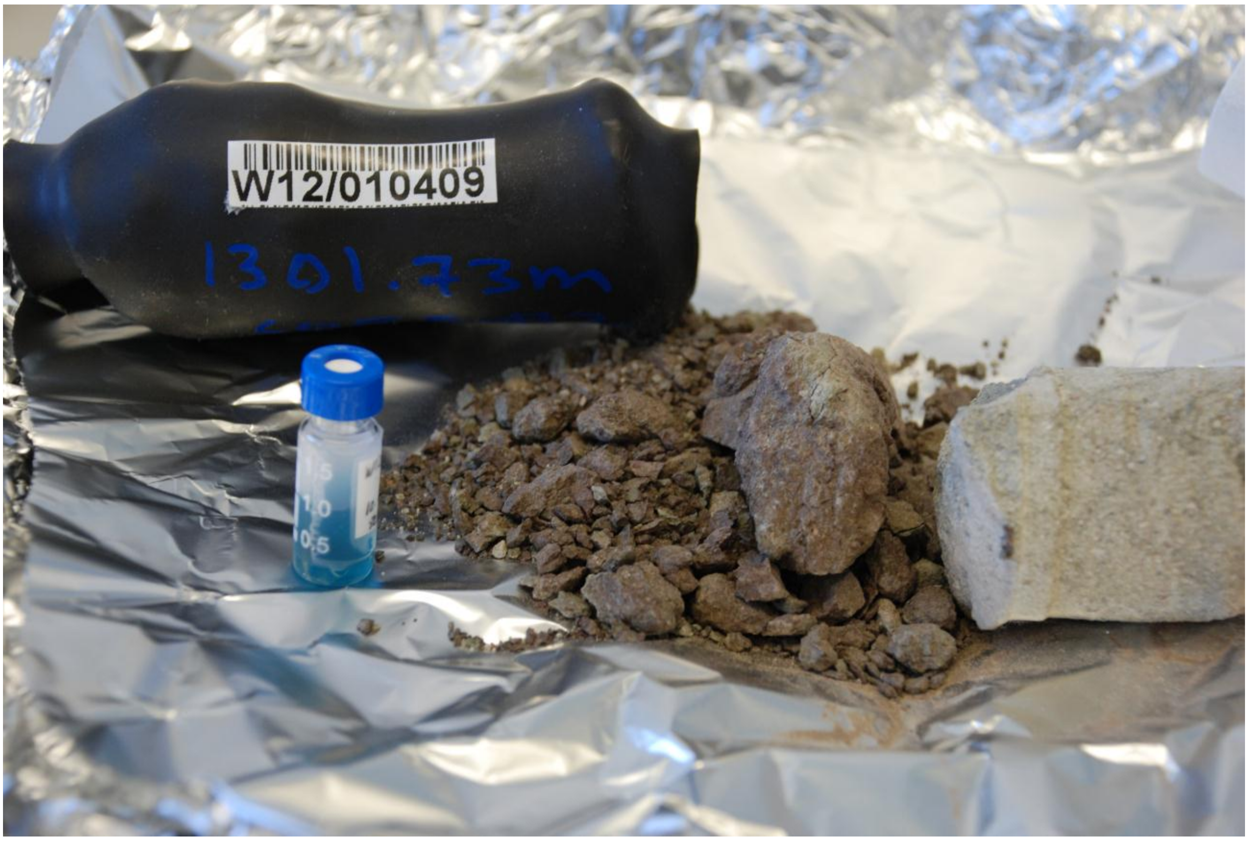
# Appendix B Images of Cores, Extracts and Sleeves

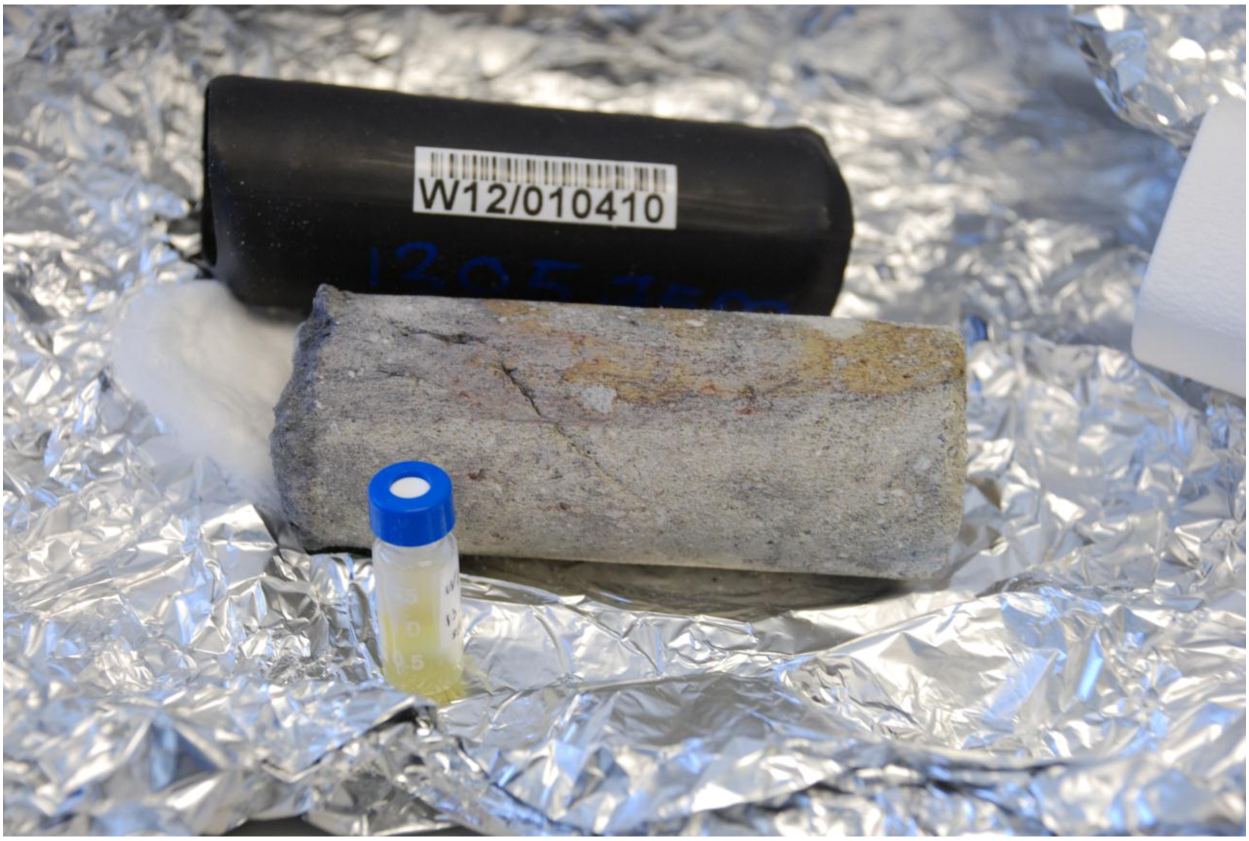


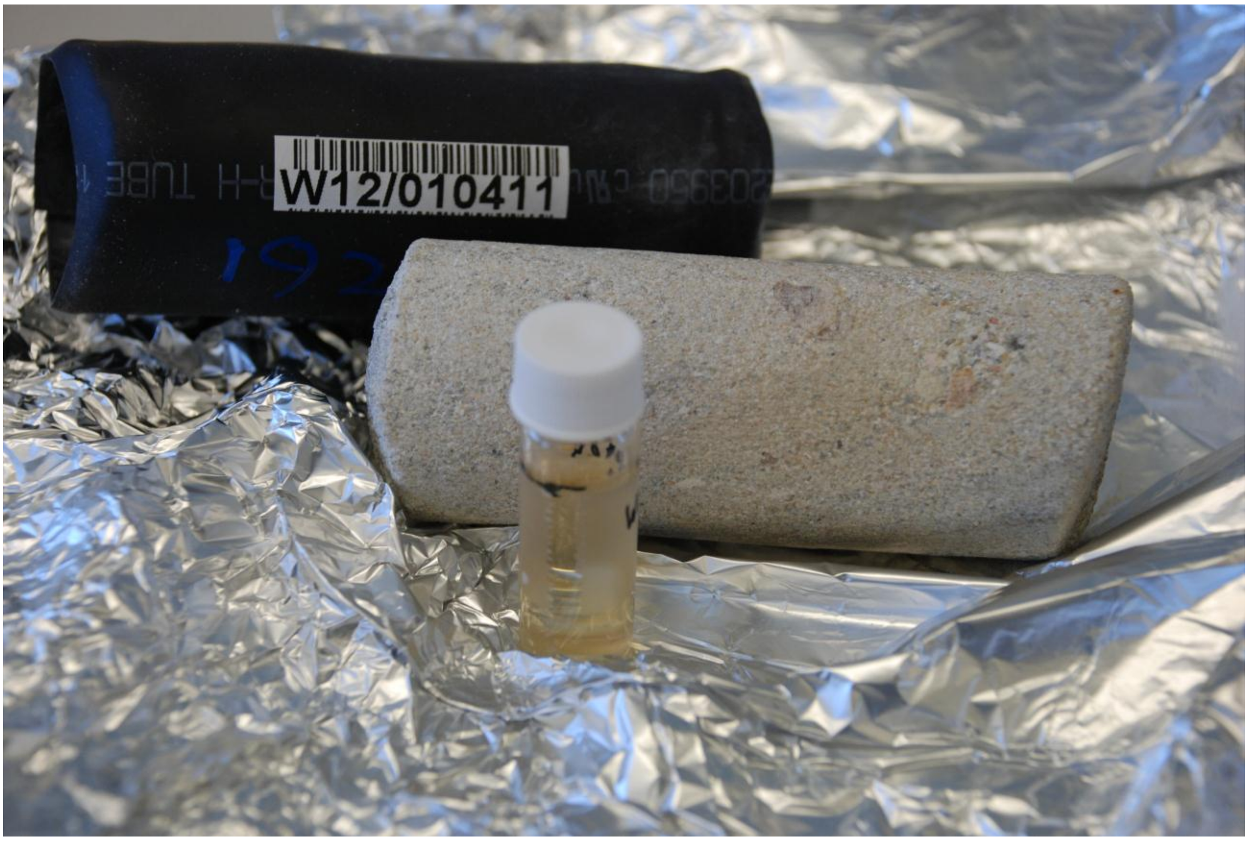



W12/010407


W12/010408

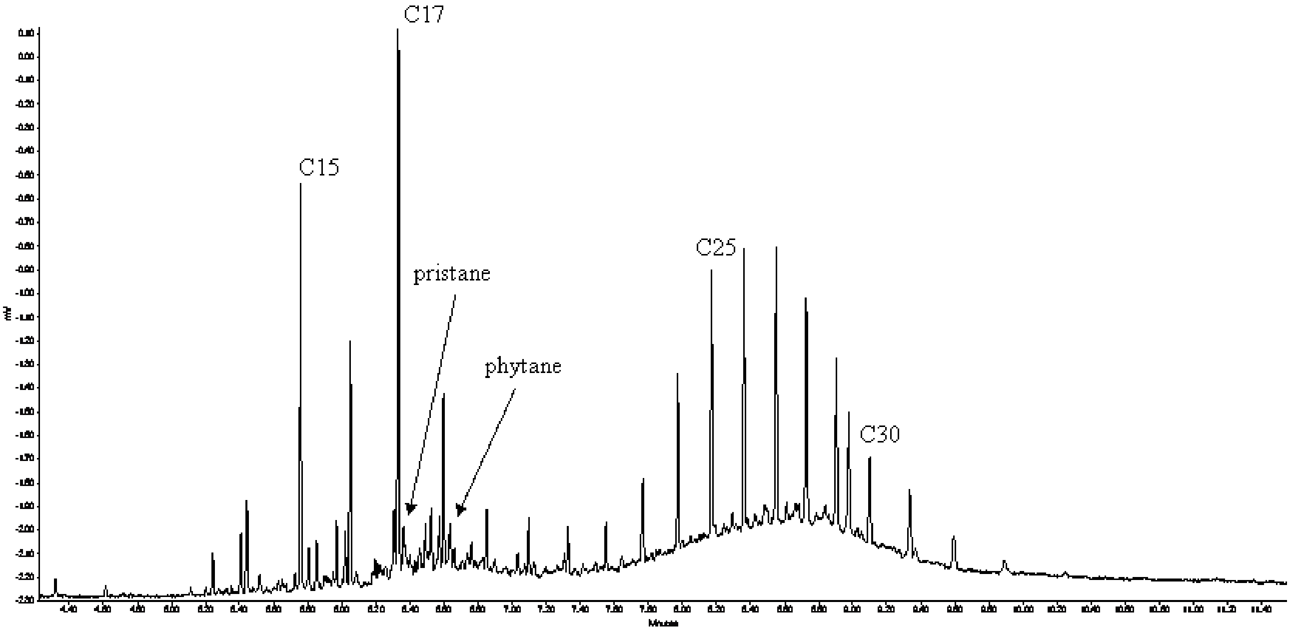

W12/010409
1301.73m


W12/010410

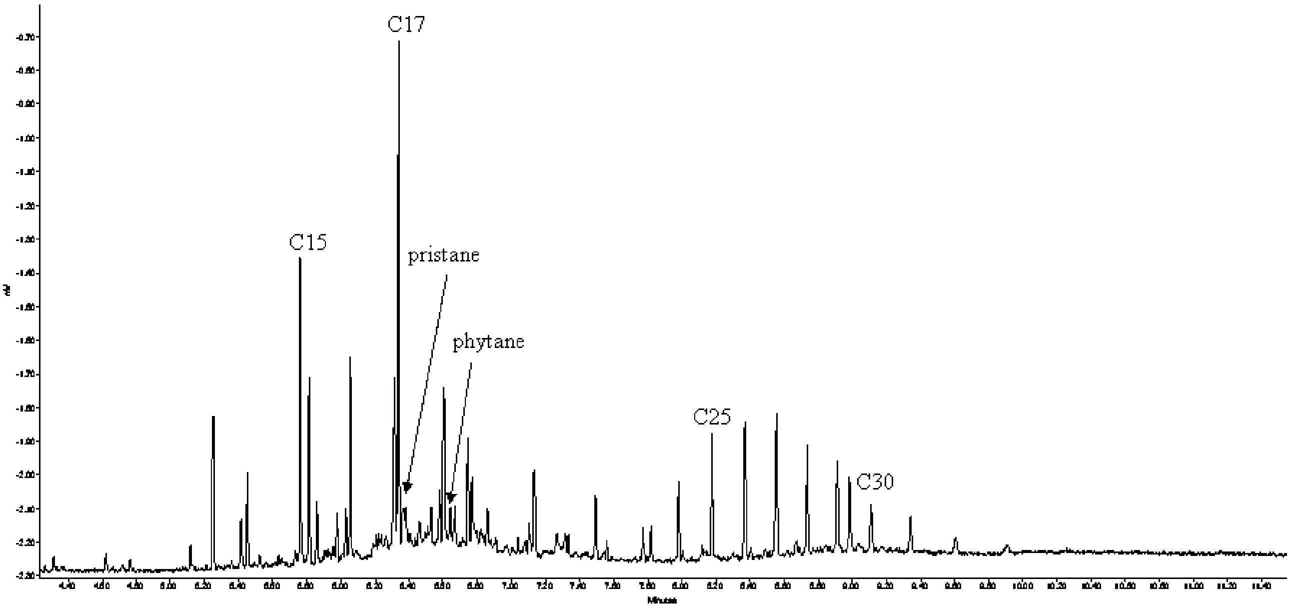

W12/010411


W12/010412
12
W12/
12

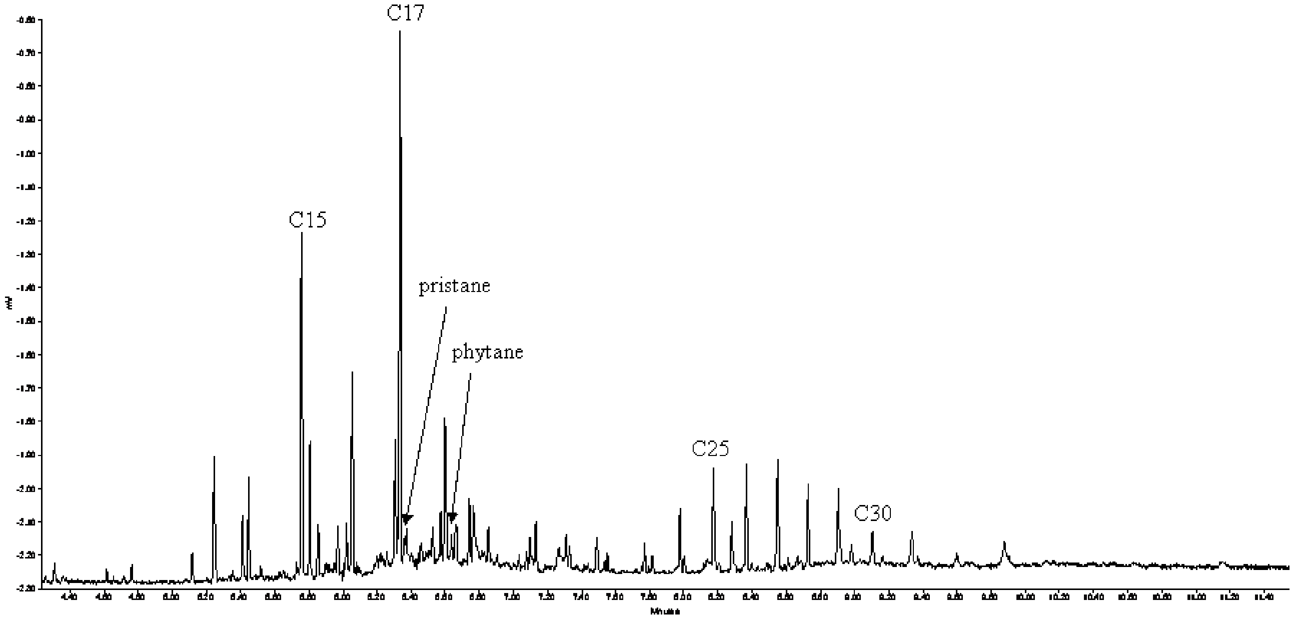
# Appendix C GC-FID Chromatograms of Core Extracts from the Selected Cores



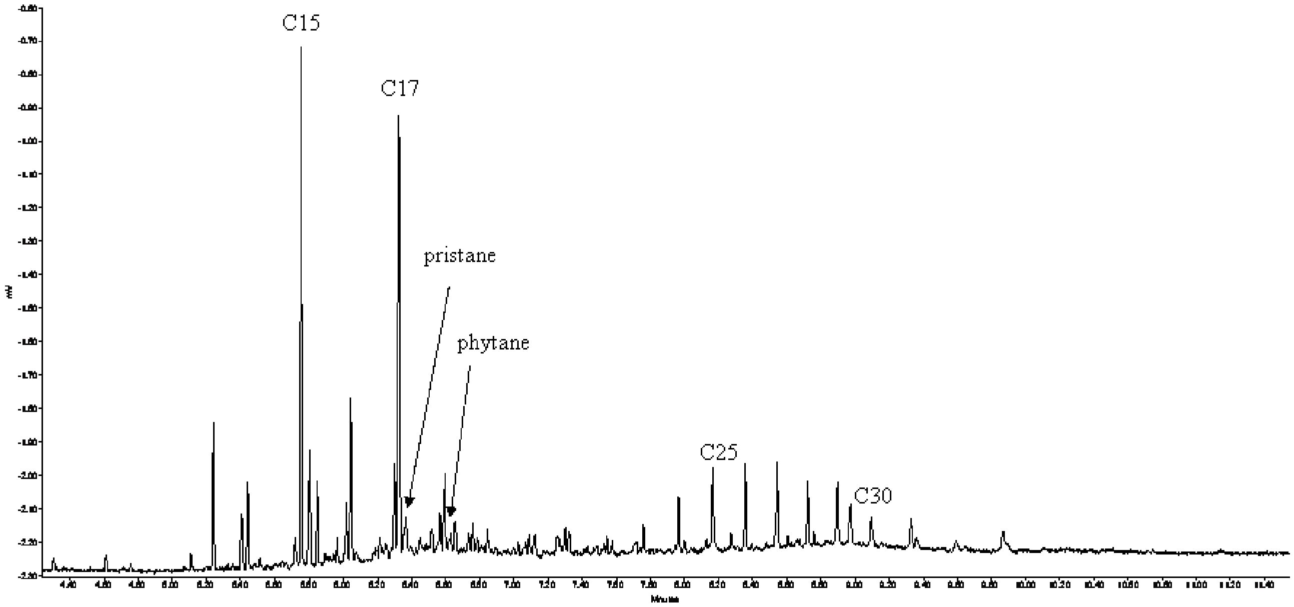
Whole oil GC of extract from sample W12/010405 from 913.94m in the Upper Lesueur, Facies Aii.



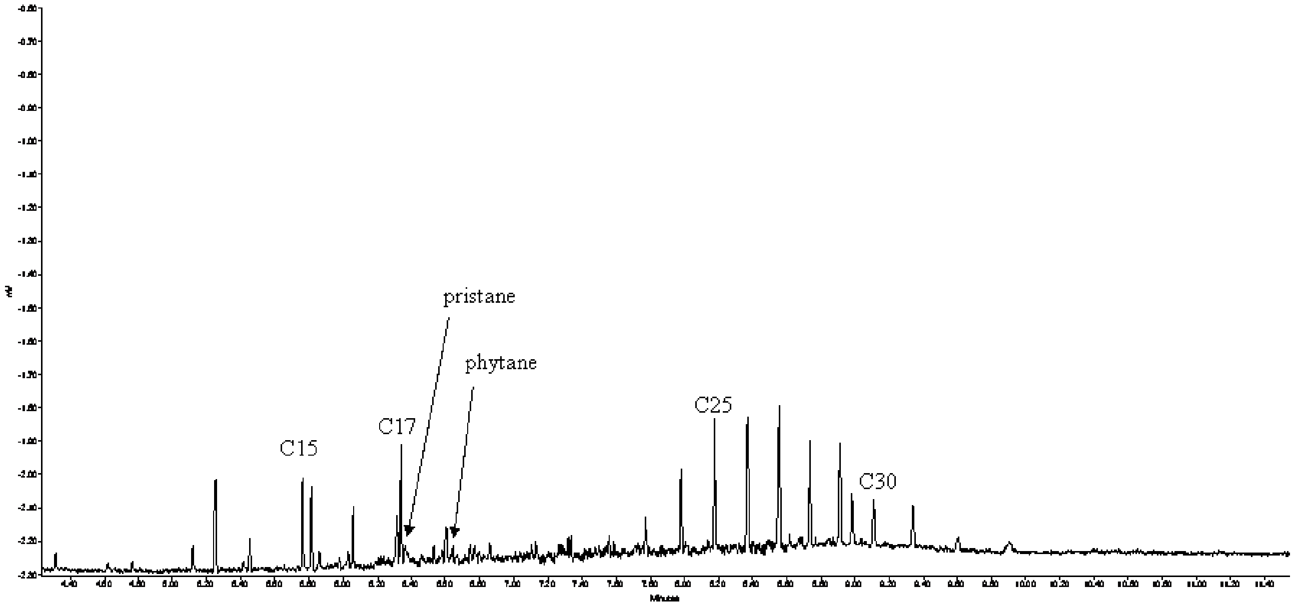
Whole oil GC of extract from sample W12/010406 from 1289.66m in the Upper Lesueur, Facies G.



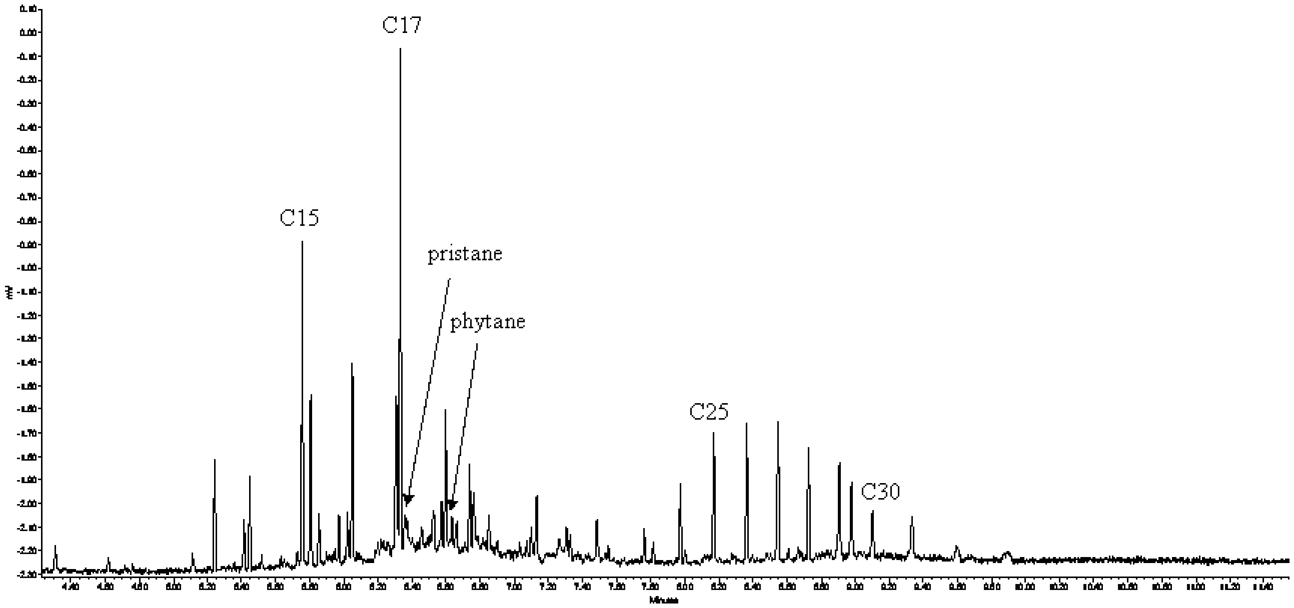
Whole oil GC of extract from sample W12/010407 from 1289.78m in the Upper Lesueur, Facies D.



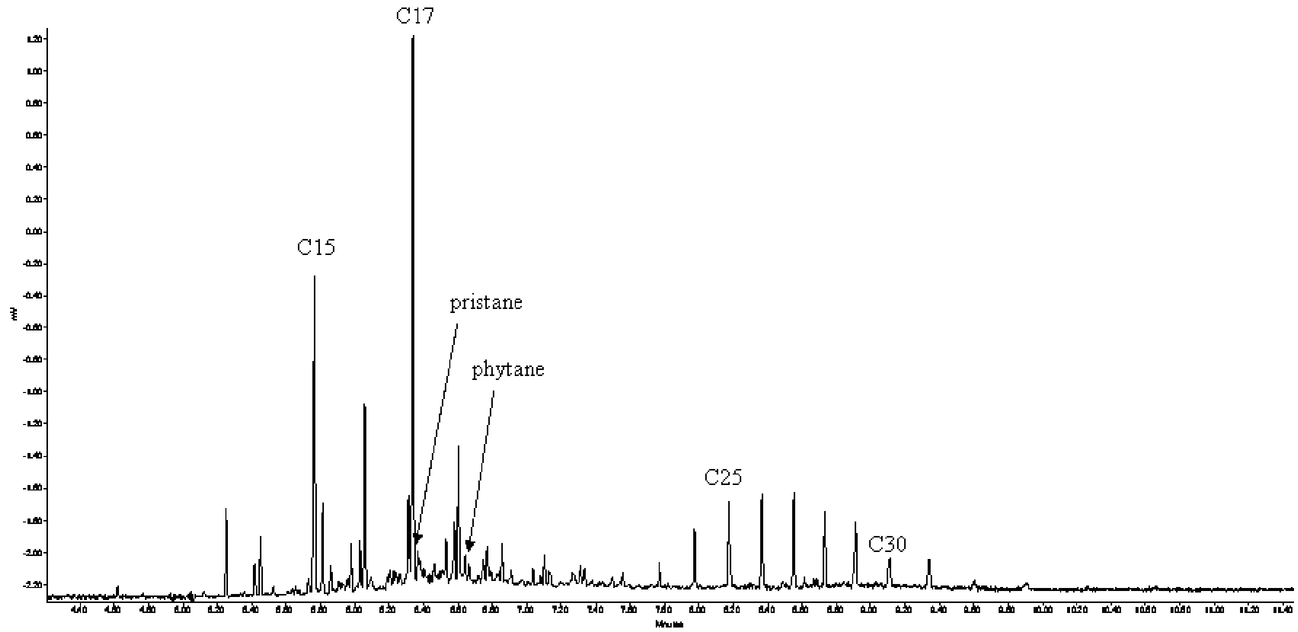
Whole oil GC of extract from sample W12/010408 from 1299.88m in the Upper Lesueur, Facies D.



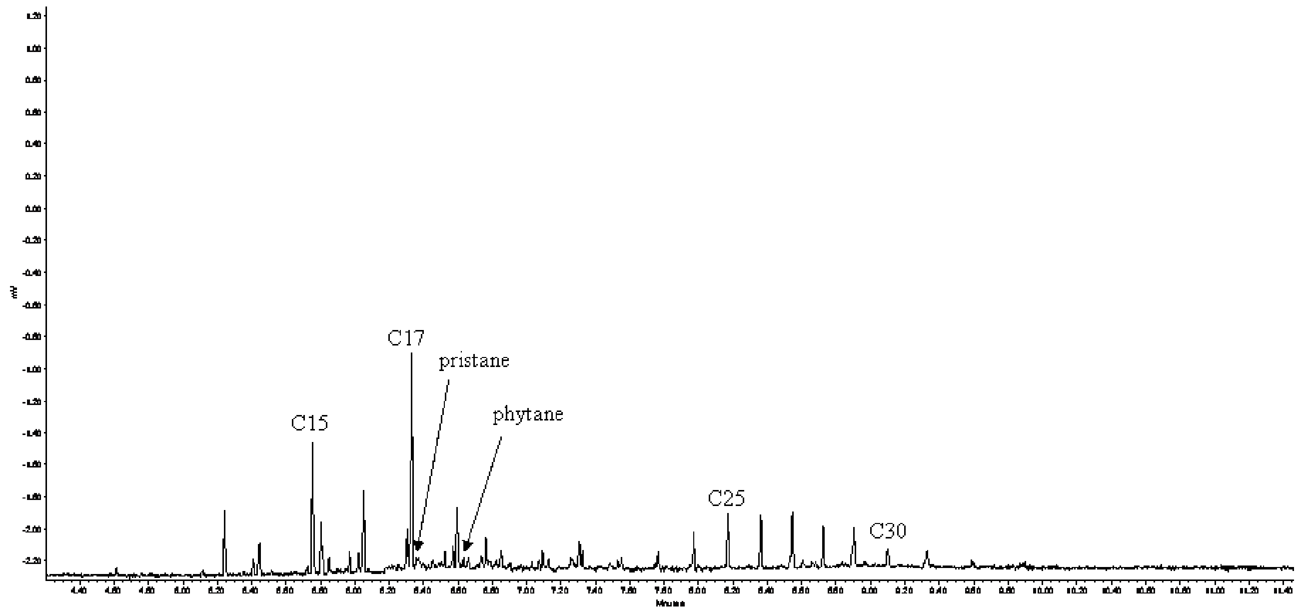
Whole oil GC of extract from sample W12/010409 from 1301.73m in the Upper Lesueur, Facies D.



Whole oil GC of extract from sample W12/010410 from 1305.75m in the Upper Lesueur, Facies D.

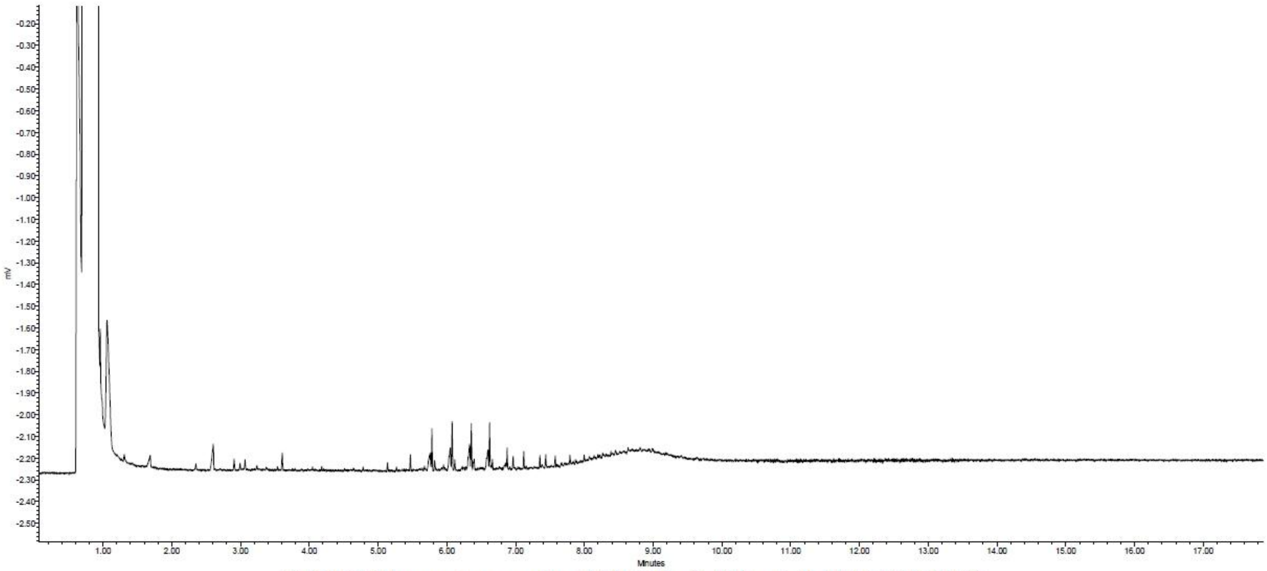


Whole oil GC of extract from sample W12/010411 from 1929.46m in the Lower Lesueur, Facies Aii.



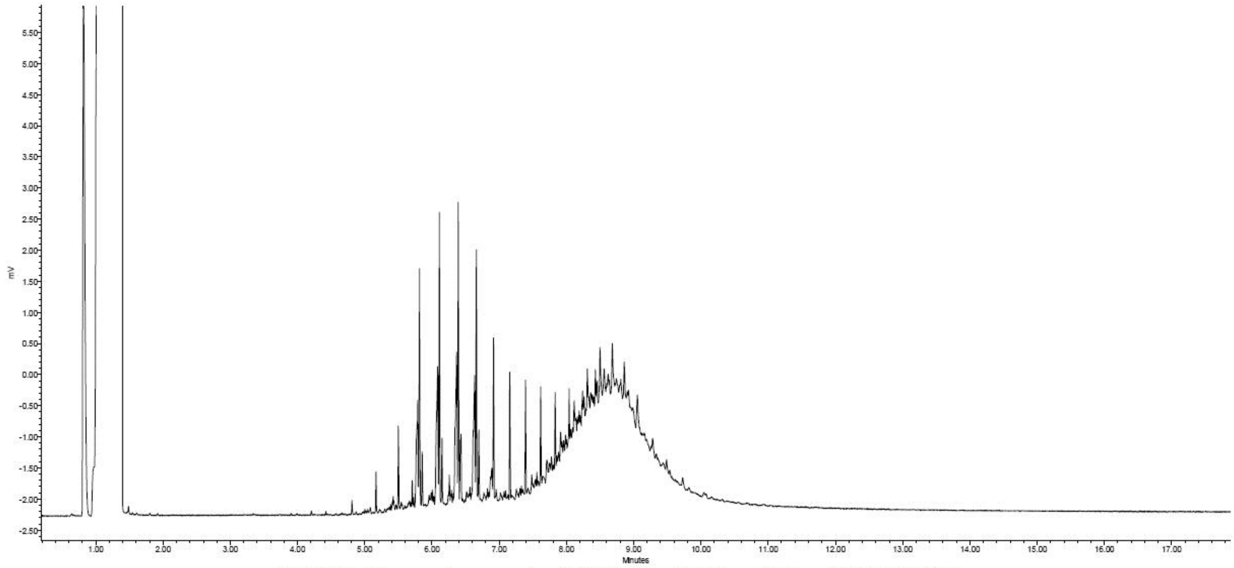
Whole oil GC of extract from sample W12/010412 from 2523.4m in the Lower Lesueur, Facies Aii.

# Appendix D GC-FID Chromatograms of Drilling Fluid Extracts



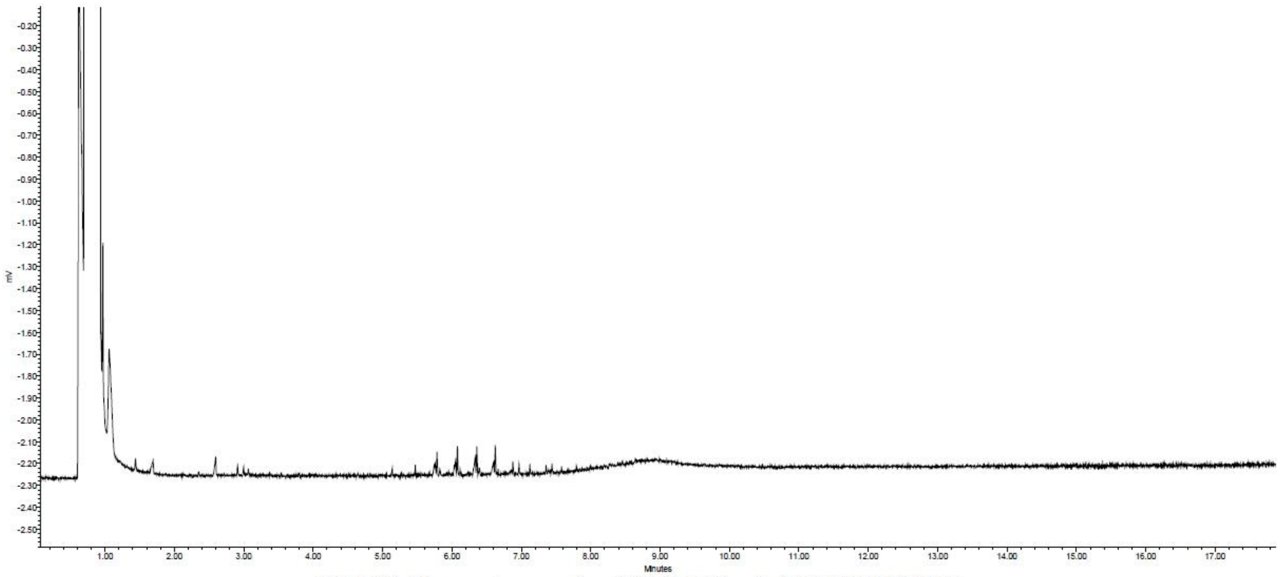
GC-FID Chromatogram for GSWA Dark 900m Soil (W12/010401/A)

Whole oil GC of extract from drilling mud samples from W12/010402 at 900m sediment extract.



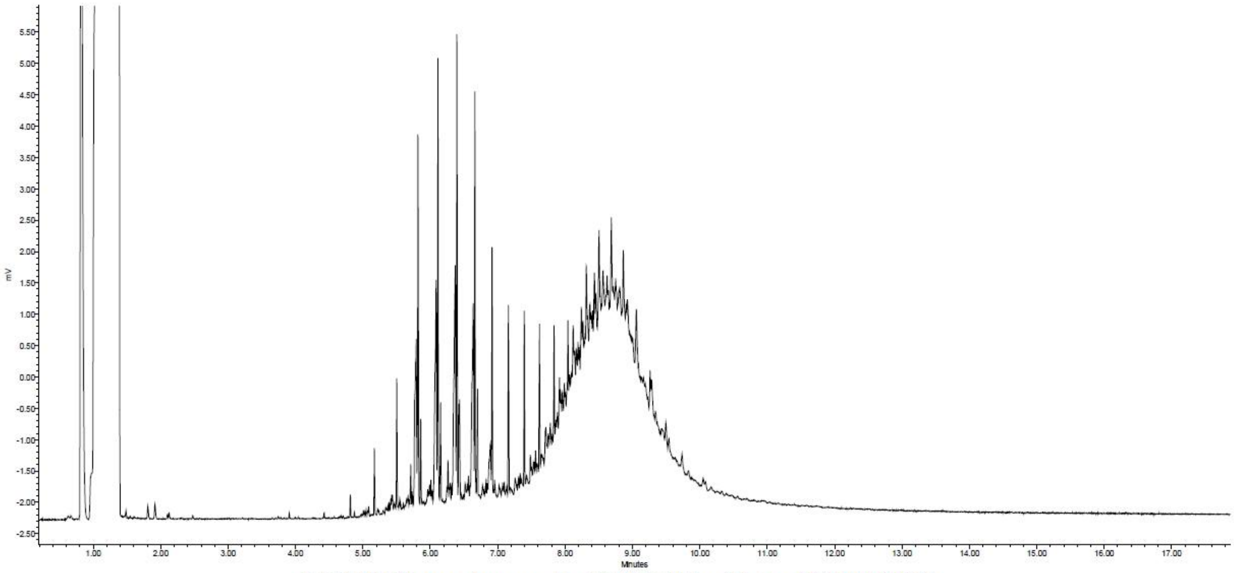
GC-FID Chromatogram for GSWA Dark 900m Water (W12/010401)

Whole oil GC of extract from drilling mud samples from W12/010402 at 900m fluid extract.



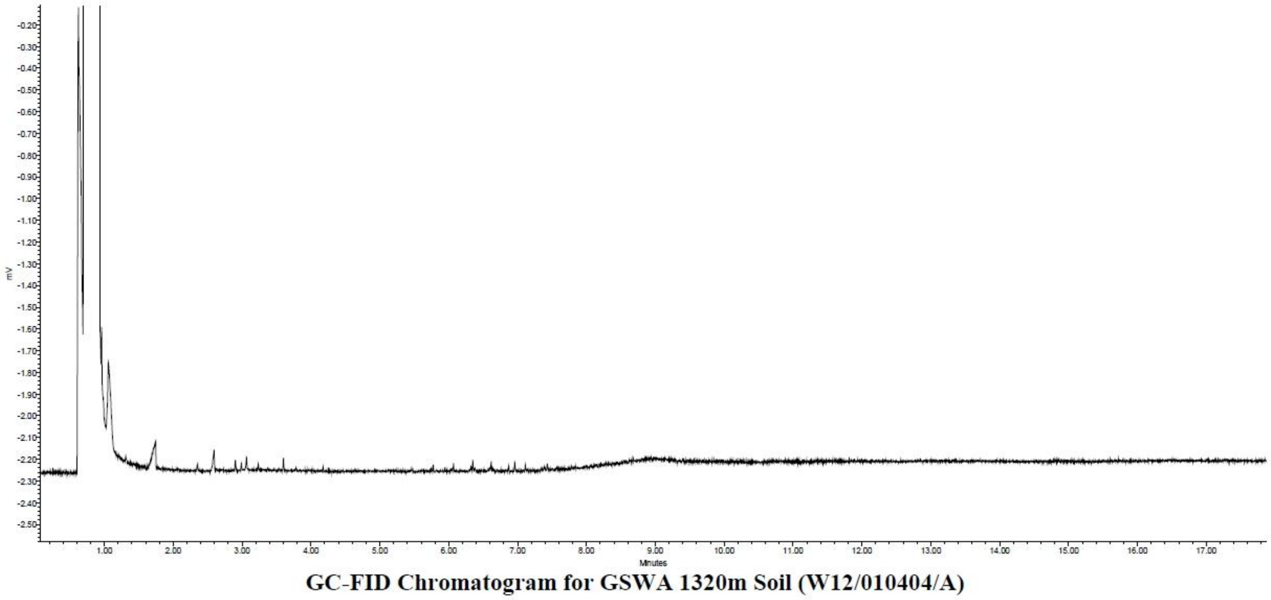
**GC-FID Chromatogram for GSWA 900m Soil (W12/010402/A)**

Whole oil GC of extract from drilling mud samples from W12/010402 at 900m sediment extract.

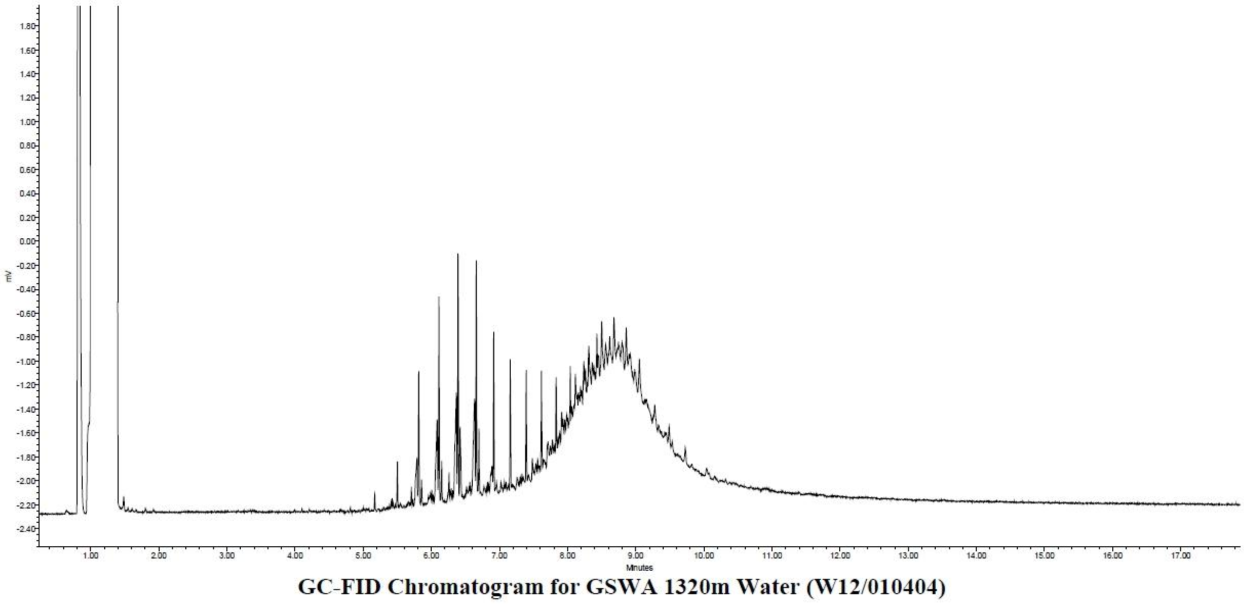


**GC-FID Chromatogram for GSWA 900m Water (W12/010402)**

Whole oil GC of extract from drilling mud samples from W12/010402 at 900m fluid extract. Two bottles containing drilling fluid from the same depth interval were provided but were markedly different and therefore processed as two separate samples.



Whole oil GC of extract from drilling mud samples from 1320m sediment extract.



Whole oil GC of extract from drilling mud samples from 1320m fluid extract.

# Appendix E Selected Tabulated Data from Core Flooding of sample 206660H

Table 27 All ICPOES for elements that were measured at some point during the complete core flooding experimental test. Also measured but with values below limits of detection for ICPOES were S, As,, B, Cd, Co, Cr, Cu, Mo, P, Sb, Se and Sr.

| Sample ID | Flow Rate | Ca mg/L | K mg/L | Mg mg/L | Na mg/L | Al mg/L | Fe mg/L | Mn mg/L | Ni mg/L | Pb mg/L | Si mg/L | Zn mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CO_2$ saturated brine | | | | | | | | | | | | |
| 1-2 | 50cc/hr | 5.6 | 8.28 | 8.78 | 10700 | | 64.6 | 50 | 5.22 | 3.49 | | 8.98 |
| 1-3 | 50cc/hr | 5.51 | 8.11 | 7.61 | 11600 | | 75.8 | 46.5 | 4.68 | 3.94 | | 7.53 |
| 1-4 | 100cc/hr | | 7.32 | 5.34 | 10800 | | 65.4 | 38.4 | 3.82 | 3.12 | | 5.54 |
| 1-5 | 100cc/hr | | 7.61 | | 12200 | | 65.1 | 38.6 | 3.62 | 2.92 | | 4.49 |
| 1-6 | 100cc/hr | | 6.83 | | 11500 | | 67.3 | 37.4 | 3.21 | 2.81 | | 4.07 |
| 1-7 | 150cc/hr | | 7.03 | | 11600 | | 56.6 | 37.6 | 2.67 | | | 3.16 |
| 1-8 | 150cc/hr | 5.31 | 6.21 | | 11600 | | 49.7 | 36.9 | | | | 2.54 |
| 1-9 | 150cc/hr | | 6.41 | | 12100 | | 47.1 | 38.8 | | | | |
| 1-10 | 50cc/hr | | 5.92 | | 11700 | | 48.6 | 37.9 | | | | |
| 1-11 | 50cc/hr | | 6.81 | | 11000 | | 47.8 | 41.5 | | | | |
| 1-12 | 50cc/hr | | 7.04 | | 11600 | | 61.9 | 48.9 | | | | |
| 1-13 | 50cc/hr | | 7.31 | | 11500 | | 57.4 | 46.5 | | | | |
| 1-14 | 50cc/hr | | 7.15 | | 11700 | | 59.2 | 46.5 | | | | |
| 1-15 | 50cc/hr | | 6.91 | | 11600 | | 58.8 | 45.6 | | | | |
| 1-16 | 50cc/hr | | 6.72 | | 11200 | | 78.4 | 45.3 | | | | |
| 1-17 | 50cc/hr | | 7.07 | | 11700 | | 58.2 | 46.2 | | | | |
| 1-18 | 50cc/hr | | 6.84 | | 11500 | | 60.6 | 45.5 | | | | |
| 1-19 | 50cc/hr | | 6.73 | | 11300 | | 60.9 | 44.9 | | | | |
| 1-20 | 50cc/hr | 5.53 | | | 12000 | 3.01 | 62.1 | 48.8 | | | | |
| 1-21 | 50cc/hr | | | | 12200 | 2.76 | 57.5 | 48.9 | | | | |
| 1-22 | 50cc/hr | | | | 12400 | 3.08 | 57.7 | 49.7 | | | | |
| 1-23 | 50cc/hr | | | | 11700 | 4.84 | 73.3 | 48.6 | | | | |
| 1-24 | 50cc/hr | | | | 12300 | 3.34 | 56 | 50.1 | | | | |
| 1-25 | 50cc/hr | | | | 12200 | 3.27 | 54.4 | 49.9 | | | | |
| 1-26 | 50cc/hr | | | | 12000 | 3.32 | 53.3 | 49 | | | | |
| 1-27 | 50cc/hr | | | | 11900 | 3.89 | 57 | 48.9 | | | | |
| 1-28 | 50cc/hr | | | | 12700 | 3.72 | 55.7 | 51.6 | | | | |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-29 | 50cc/hr | | | | 11900 | 3.67 | 52.1 | 49.7 | | | | |
| 1-30 | 50cc/hr | | | | 11900 | 3.87 | 53 | 48.7 | | | | |
| 1-31 | 50cc/hr | | | | 13200 | 4.45 | 55.1 | 53.8 | | | | |
| 1-32 | 50cc/hr | | | | 11900 | 5.26 | 57.6 | 48.8 | | | | |
| **Sample saturated with $CO_2$ saturated brine overnight** | | | | | | | | | | | | |
| 1-40 | 50cc/hr | 5.03 | 6.06 | | 11700 | 4.22 | 69.6 | 54 | | | | |
| 1-41 | 50cc/hr | 10.1 | 7.52 | 12 | 11800 | -2.5 | 136 | 86.7 | | | 9.43 | 4.67 |
| 1-42 | 50cc/hr | 6.8 | 5.28 | 7.02 | 11900 | 1.87 | 128 | 56.2 | | | 5.35 | 3.51 |
| 1-43 | 50cc/hr | | | | 12200 | 3 | 92.3 | 48 | 3.08 | | | |
| 1-44 | 50cc/hr | | | | 11700 | 3.4 | 80.8 | 47.5 | | | | |
| 1-45 | 50cc/hr | | | | 11700 | 3.45 | 56.9 | 49.7 | | | | |
| 1-46 | 50cc/hr | | | | 11800 | 3.93 | 52.5 | 51.6 | | | | |
| 1-47 | 50cc/hr | | | | 11900 | 4.41 | 51 | 53.3 | | | | |
| 1-48 | 50cc/hr | | | | 11800 | 4.51 | 51.1 | 53.3 | | | | |
| 1-49 | 50cc/hr | | | | 11900 | 4.98 | 52.9 | 53.1 | | | | |
| **$CO_2$ injection** | | | | | | | | | | | | |
| 2-1 | 50cc/hr | | | | 11800 | 4.7 | 48.2 | 53.8 | | | | |
| 2-2 | 50cc/hr | | | | 11300 | 3.49 | 63.6 | 59.7 | | | | |
| **Sample saturated with $CO_2$ saturated brine after $CO_2$ injection** | | | | | | | | | | | | |
| 3-1 | 50cc/hr | | | | 11600 | 4.52 | 53.1 | 51.9 | | | | |
| 3-2 | 50cc/hr | | | | 11800 | 4.88 | 48.3 | 54 | | | | |
| 3-3 | 50cc/hr | | | | 11700 | 5.03 | 43 | 55 | | | | |
| 3-4 | 50cc/hr | | | | 11700 | 5.39 | 45.8 | 54.1 | | | | |
| 3-5 | 50cc/hr | | | | 11700 | 5.36 | 43 | 54.2 | | | | |
| 3-6 | 50cc/hr | | | | 12300 | 5.55 | 44 | 55.9 | | | | |
| 3-7 | 50cc/hr | | | | 12000 | 5.75 | 44.4 | 54 | | | | |
| 3-8 | 50cc/hr | | | | 12000 | 5.72 | 43.6 | 52.3 | | | | |
| 3-9 | 50cc/hr | | | | 11800 | 5.95 | 42.4 | 51.8 | | | | |
| 3-10 | 50cc/hr | | | | 11900 | 6.06 | 42.3 | 51.1 | | | | |

**Table 28 ICPMS results of the core flood effluents measured in μg/L for samples that had any values above the detection limits (continues over the next series of tables).**

| Sample ID | Flow Rate | Ag μg/L | As μg/L | Ba μg/L | Cd μg/L | Ce μg/L | Co μg/L | Cr μg/L | Cu μg/L | Dy μg/L | Er μg/L | Eu μg/L | Ga μg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$CO_2$ saturated brine** | | | | | | | | | | | | | |
| 1-2 | 50cc/hr | | | 406 | 9 | 1.2 | 1058 | 290 | 170 | | | | |
| 1-3 | 50cc/hr | | 9 | 328 | 12 | 2.4 | 944 | 460 | 210 | 3 | | 2 | |
| 1-4 | 100cc/hr | | | 200 | 6 | 2.4 | 600 | 490 | 160 | 3 | | 1 | 1 |
| 1-5 | 100cc/hr | | 5 | 132 | 4 | 2.1 | 396 | 570 | 150 | 2 | | 1.0 | |
| 1-6 | 100cc/hr | | 5 | 106 | 2 | 2.1 | 319 | 680 | 170 | 2 | | 1.0 | |
| 1-7 | 150cc/hr | 2 | 5 | 85 | 2 | 2.4 | 272 | 730 | 180 | 4 | | 1.0 | 0.5 |
| 1-8 | 150cc/hr | | 5 | 63 | 4 | 2.1 | 203 | 780 | 190 | 2 | | 1.0 | 0.5 |
| 1-9 | 150cc/hr | 2 | 6 | 54.0 | 1.6 | 2.0 | 179.0 | 780 | 190 | 2.4 | 1.2 | 0.9 | 0.9 |
| 1-10 | 50cc/hr | 2 | 6 | 49.5 | 2.4 | 2.2 | 166.5 | 900 | 200 | 2.4 | 1.2 | 0.9 | 0.6 |
| 1-11 | 50cc/hr | 1 | 6 | 50.0 | 2.4 | 2.0 | 172.5 | 700 | 140 | 2.4 | 1.4 | 0.9 | 0.6 |
| 1-12 | 50cc/hr | | 5 | 56 | 4 | 2.1 | 210 | 620 | 140 | 2 | | 1.0 | 0.5 |
| 1-13 | 50cc/hr | 1 | 4 | 54.0 | 2.4 | 1.8 | 209.0 | 580 | 120 | 2.4 | 1.3 | 0.9 | 0.9 |
| 1-14 | 50cc/hr | 1 | 6 | 52.0 | 2.4 | 2.0 | 196.0 | 620 | 120 | 3.2 | 1.2 | 0.9 | 0.6 |
| 1-15 | 50cc/hr | | 4 | 45.0 | 2.4 | 1.6 | 161.5 | 590 | 110 | 2.4 | 1.2 | 0.6 | 0.9 |
| 1-16 | 50cc/hr | 1 | 6 | 49.5 | 2.4 | 2.4 | 157.5 | 570 | 150 | 3.2 | 1.6 | 0.9 | 0.9 |
| 1-17 | 50cc/hr | 1 | 6 | 41.0 | 2.4 | 1.8 | 138.0 | 660 | 110 | 2.4 | 1.5 | 0.9 | 0.9 |
| 1-18 | 50cc/hr | 1 | 6 | 41.5 | 1.6 | 2.0 | 133.0 | 740 | 120 | 3.2 | 1.5 | 0.9 | 0.9 |
| 1-19 | 50cc/hr | 1 | 6 | 41.5 | 2.4 | 2.0 | 128.5 | 830 | 120 | 3.2 | 1.7 | 1.2 | 1.2 |
| 1-20 | 50cc/hr | | 4 | 36.5 | 2.4 | 1.8 | 109.0 | 700 | 100 | 2.4 | 1.5 | 0.9 | 0.9 |
| 1-21 | 50cc/hr | 1 | 6 | 36.5 | 2.4 | 1.8 | 106.5 | 710 | 100 | 2.4 | 1.5 | 0.9 | 0.9 |
| 1-22 | 50cc/hr | 0.9 | 6 | 34.0 | 2.4 | 1.8 | 95.6 | 730 | 110 | 3.0 | 1.3 | 0.8 | 0.8 |
| 1-23 | 50cc/hr | 1 | 6 | 38.5 | 3.2 | 2.2 | 95.0 | 1050 | 120 | 3.2 | 1.8 | 1.2 | 0.6 |
| 1-24 | 50cc/hr | 1.1 | 4 | 31.6 | 1.8 | 1.7 | 85.2 | 740 | 110 | 2.4 | 1.3 | 1.0 | 0.8 |
| 1-25 | 50cc/hr | 1.2 | 4 | 30.8 | 2.4 | 1.7 | 80.4 | 740 | 80 | 2.4 | 1.4 | 1.0 | 0.6 |
| 1-26 | 50cc/hr | 1.0 | 4 | 27.2 | 1.8 | 1.6 | 70.0 | 680 | 80 | 2.4 | 1.4 | 1.0 | 0.6 |
| 1-27 | 50cc/hr | 1.1 | 8 | 33.6 | 3.0 | 2.1 | 81.6 | 900 | 100 | 3.0 | 1.5 | 1.2 | 0.8 |
| 1-28 | 50cc/hr | 1.0 | 4 | 29.2 | 1.8 | 1.7 | 72.0 | 810 | 90 | 2.4 | 1.3 | 1.0 | 0.6 |
| 1-29 | 50cc/hr | 1.0 | 4 | 26.0 | 1.8 | 1.6 | 63.2 | 770 | 80 | 2.4 | 1.3 | 1.0 | 0.8 |
| 1-30 | 50cc/hr | 0.8 | 4 | 25.2 | 1.8 | 1.5 | 58.8 | 800 | 80 | 2.4 | 1.3 | 0.8 | 0.6 |
| 1-31 | 50cc/hr | 1.2 | 4 | 28.4 | 2.4 | 1.7 | 65.6 | 890 | 90 | 3.0 | 1.5 | 1.0 | 0.8 |
| 1-32 | 50cc/hr | 1.0 | 4 | 24.8 | 1.8 | 1.6 | 56.4 | 910 | 80 | 3.0 | 1.5 | 1.0 | 0.8 |
| **Sample saturated with $CO_2$ saturated brine overnight** | | | | | | | | | | | | | |
| 1-40 | 50cc/hr | 2 | 6 | 80.0 | 3.2 | 2.0 | 115.0 | 1230 | 460 | 3.2 | 1.9 | 0.9 | 0.9 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-41 | 50cc/hr | | 5 | 130 | 10 | 1.2 | 328 | 300 | 50 | 2 | | 1.0 | 1.5 |
| 1-42 | 50cc/hr | | 5 | 84 | 6 | 1.5 | 213 | 920 | 80 | 4 | 2 | 1.5 | 1.0 |
| 1-43 | 50cc/hr | | 5 | 46 | 4 | 1.5 | 121 | 1620 | 40 | 4 | 2 | 1.5 | 0.5 |
| 1-44 | 50cc/hr | | 6 | 37.0 | 2.4 | 1.4 | 78.5 | 1370 | 40 | 3.2 | 1.7 | 0.9 | 0.9 |
| 1-45 | 50cc/hr | 0.8 | 4 | 25.6 | 1.8 | 1.2 | 54.0 | 1050 | 40 | 3.0 | 1.5 | 1.0 | 0.8 |
| 1-46 | 50cc/hr | | 4 | 20.4 | 1.2 | 1.1 | 38.4 | 870 | 40 | 2.4 | 1.3 | 0.8 | 0.6 |
| 1-47 | 50cc/hr | 0.8 | 4 | 20.4 | 1.8 | 1.3 | 38.4 | 960 | 60 | 2.4 | 1.5 | 0.8 | 0.6 |
| 1-48 | 50cc/hr | 0.8 | 4 | 20.0 | 1.8 | 1.4 | 36.8 | 960 | 60 | 2.4 | 1.4 | 1.0 | 0.6 |
| 1-49 | 50cc/hr | 1.0 | 4 | 18.4 | 1.8 | 1.6 | 34.8 | 1040 | 70 | 3.0 | 1.4 | 1.0 | 0.8 |
| **$CO_2$ injection** | | | | | | | | | | | | | |
| 2-1 | 50cc/hr | | 4 | 15.2 | 1.8 | 1.2 | 59.6 | 830 | 60 | 2.4 | 1.4 | 0.8 | 0.6 |
| 2-2 | 50cc/hr | 1.5 | 4 | 25.6 | 4.8 | 1.3 | 52.0 | 620 | 200 | 2.4 | 1.4 | 0.8 | 1.0 |
| **Sample saturated with $CO_2$ saturated brine after $CO_2$ injection** | | | | | | | | | | | | | |
| 3-1 | 50cc/hr | 1.5 | 4 | 20.0 | 3.0 | 1.5 | 41.2 | 840 | 140 | 3.0 | 1.6 | 1.2 | 0.6 |
| 3-2 | 50cc/hr | 1.2 | 4 | 18.4 | 1.8 | 1.6 | 34.4 | 910 | 130 | 3.0 | 1.7 | 1.2 | 0.8 |
| 3-3 | 50cc/hr | 1.1 | 4 | 18.4 | 1.8 | 1.5 | 31.2 | 890 | 90 | 3.0 | 1.4 | 1.0 | 0.8 |
| 3-4 | 50cc/hr | 1.1 | 4 | 18.0 | 1.8 | 1.5 | 30.8 | 990 | 90 | 3.0 | 1.6 | 1.2 | 0.8 |
| 3-5 | 50cc/hr | 1.0 | 4 | 15.6 | 1.2 | 1.3 | 26.8 | 830 | 80 | 2.4 | 1.5 | 1.0 | 0.6 |
| 3-6 | 50cc/hr | 1.0 | 4 | 18.0 | 1.2 | 1.4 | 30.8 | 980 | 120 | 3.0 | 1.4 | 1.0 | 0.8 |
| 3-7 | 50cc/hr | 1.1 | 4 | 17.6 | 1.8 | 1.3 | 29.2 | 950 | 70 | 2.4 | 1.3 | 1.0 | 0.6 |
| 3-8 | 50cc/hr | 0.8 | 4 | 17.2 | 1.8 | 1.4 | 28.8 | 980 | 70 | 2.4 | 1.3 | 1.0 | 0.8 |
| 3-9 | 50cc/hr | 0.9 | 4 | 15.6 | 1.2 | 1.2 | 26.8 | 920 | 70 | 2.4 | 1.2 | 0.8 | 0.8 |
| 3-10 | 50cc/hr | 1.1 | 4 | 16.0 | 1.2 | 1.3 | 29.2 | 990 | 80 | 2.4 | 1.3 | 1.0 | 0.8 |

| Sample ID | Flow Rate | Gd µg/L | Ho µg/L | Hf µg/L | In µg/L | La µg/L | Li µg/L | Lu µg/L | Mo µg/L | Nd µg/L | Ni µg/L | Pb µg/L | Pr µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$CO_2$ saturated brine** | | | | | | | | | | | | | |
| 1-2 | 50cc/hr | | | | 3 | | 240 | | 6 | | 4928 | 3084 | |
| 1-3 | 50cc/hr | 4 | 0.7 | | 4 | 0.8 | 280 | 1 | 6 | 8 | 4928 | 3672 | 0.7 |
| 1-4 | 100cc/hr | 4 | | | 4 | 0.8 | 220 | 1 | 6 | 8 | 3936 | 2896 | 0.7 |
| 1-5 | 100cc/hr | 4 | 0.4 | | 4.0 | 0.8 | 150 | | 2 | 4 | 3380 | 2508 | 0.4 |
| 1-6 | 100cc/hr | 4 | 0.4 | | 4.5 | 0.8 | 140 | | 2 | 4 | 2920 | 2422 | 0.8 |
| 1-7 | 150cc/hr | 4 | 0.8 | | 4.5 | 0.8 | 150 | 0.5 | 4 | 4 | 2660 | 2088 | 0.8 |
| 1-8 | 150cc/hr | 4 | 0.4 | | 4.0 | 0.8 | 130 | | 2 | 4 | 2340 | 1710 | 0.8 |
| 1-9 | 150cc/hr | 3 | 0.4 | | 3.6 | 0.6 | 105 | 0.3 | 2.4 | 4 | 2170 | 1492 | 0.6 |
| 1-10 | 50cc/hr | 3 | 0.4 | | 3.6 | 0.6 | 100 | 0.3 | 3.2 | 4 | 2070 | 1464 | 0.6 |
| 1-11 | 50cc/hr | 3 | 0.6 | 0.8 | 3.3 | 0.6 | 85 | 0.3 | 3.2 | 4 | 1880 | 1210 | 0.6 |
| 1-12 | 50cc/hr | 4 | 0.4 | | 3.0 | 0.8 | 110 | 0.5 | 4 | 4 | 1960 | 1222 | 0.4 |
| 1-13 | 50cc/hr | 3 | 0.4 | | 3.0 | 0.6 | 115 | 0.3 | 3.2 | 4 | 2120 | 1089 | 0.6 |
| 1-14 | 50cc/hr | 3 | 0.4 | | 3.0 | 0.6 | 110 | 0.3 | 4.0 | 4 | 2320 | 1045 | 0.6 |
| 1-15 | 50cc/hr | 3 | 0.4 | | 2.7 | 0.4 | 90 | 0.3 | 4.0 | 4 | 2140 | 898 | 0.6 |
| 1-16 | 50cc/hr | 4 | 0.6 | | 3.6 | 0.6 | 95 | 0.6 | 5.6 | 5 | 2280 | 1053 | 0.6 |
| 1-17 | 50cc/hr | 3 | 0.6 | 0.8 | 2.7 | 0.6 | 95 | 0.3 | 8.0 | 4 | 2100 | 781 | 0.6 |
| 1-18 | 50cc/hr | 3 | 0.6 | 0.8 | 2.7 | 0.6 | 100 | 0.6 | 4.8 | 5 | 2140 | 788 | 0.6 |
| 1-19 | 50cc/hr | 4 | 0.6 | 0.8 | 3.0 | 0.6 | 105 | 0.6 | 5.6 | 5 | 2160 | 758 | 0.8 |
| 1-20 | 50cc/hr | 3 | 0.6 | | 2.1 | 0.6 | 90 | 0.3 | 4.8 | 4 | 1900 | 645 | 0.6 |
| 1-21 | 50cc/hr | 3 | 0.6 | | 2.1 | 0.6 | 75 | 0.3 | 4.8 | 4 | 1920 | 625 | 0.6 |
| 1-22 | 50cc/hr | 3.5 | 0.5 | 0.6 | 2.2 | 0.6 | 80 | 0.4 | 84.0 | 4.0 | 1800 | 562.4 | 0.5 |
| 1-23 | 50cc/hr | 4 | 0.6 | 0.8 | 2.7 | 0.6 | 80 | 0.6 | 477.6 | 6 | 1920 | 687 | 0.8 |
| 1-24 | 50cc/hr | 3.2 | 0.5 | 0.6 | 2.0 | 0.4 | 84 | 0.4 | 6.6 | 4.0 | 1696 | 489.6 | 0.6 |
| 1-25 | 50cc/hr | 3.1 | 0.5 | | 1.8 | 0.4 | 88 | 0.4 | 5.4 | 4.0 | 1656 | 446.4 | 0.6 |
| 1-26 | 50cc/hr | 2.7 | 0.4 | 0.6 | 1.6 | 0.4 | 76 | 0.4 | 5.4 | 3.2 | 1480 | 394.4 | 0.5 |
| 1-27 | 50cc/hr | 3.4 | 0.6 | 1.2 | 2.2 | 0.6 | 88 | 0.4 | 9.0 | 4.8 | 1776 | 454.4 | 0.6 |
| 1-28 | 50cc/hr | 3.3 | 0.5 | 0.6 | 1.8 | 0.4 | 84 | 0.4 | 10.8 | 4.8 | 1608 | 399.2 | 0.6 |
| 1-29 | 50cc/hr | 3.3 | 0.5 | 0.6 | 1.6 | 0.4 | 80 | 0.4 | 6.6 | 4.0 | 1456 | 338.4 | 0.5 |
| 1-30 | 50cc/hr | 3.0 | 0.5 | 0.6 | 1.4 | 0.6 | 76 | 0.6 | 6.6 | 4.0 | 1416 | 312.8 | 0.6 |
| 1-31 | 50cc/hr | 2.9 | 0.5 | 1.2 | 1.6 | 0.4 | 84 | 0.6 | 8.4 | 4.8 | 1576 | 333.6 | 0.5 |
| 1-32 | 50cc/hr | 3.2 | 0.5 | 0.6 | 1.6 | 0.4 | 72 | 0.4 | 6.6 | 4.0 | 1384 | 312.0 | 0.6 |
| **Sample saturated with $CO_2$ saturated brine overnight** | | | | | | | | | | | | | |
| 1-40 | 50cc/hr | 4 | 0.6 | 0.8 | 2.4 | 0.6 | 105 | 0.6 | 29.6 | 5 | 2070 | 223 | 0.6 |
| 1-41 | 50cc/hr | 3 | 0.4 | | 1.0 | 0.8 | 130 | 1.0 | 14 | 4 | 1980 | 238 | 0.8 |
| 1-42 | 50cc/hr | 4 | 0.8 | | 1.5 | 0.8 | 140 | 1.0 | 8 | 6 | 2380 | 438 | 0.8 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-43 | 50cc/hr | 5 | 0.8 | | 2.0 | 0.8 | 150 | 1.0 | 6 | 6 | 2840 | 458 | 0.8 |
| 1-44 | 50cc/hr | 4 | 0.6 | | 1.8 | 0.6 | 110 | 0.6 | 4.8 | 4 | 2250 | 431 | 0.6 |
| 1-45 | 50cc/hr | 3.3 | 0.5 | 0.6 | 1.4 | 0.4 | 80 | 0.4 | 4.2 | 4.0 | 1608 | 347.2 | 0.5 |
| 1-46 | 50cc/hr | 2.8 | 0.4 | 0.6 | 1.4 | 0.4 | 68 | 0.4 | 3.6 | 4.0 | 1208 | 282.4 | 0.4 |
| 1-47 | 50cc/hr | 3.2 | 0.6 | 0.6 | 1.4 | 0.4 | 64 | 0.4 | 4.2 | 4.0 | 1248 | 271.2 | 0.6 |
| 1-48 | 50cc/hr | 3.2 | 0.5 | 0.6 | 1.4 | 0.4 | 72 | 0.4 | 4.8 | 4.0 | 1264 | 248.8 | 0.5 |
| 1-49 | 50cc/hr | 3.4 | 0.5 | 0.6 | 1.4 | 0.4 | 72 | 0.4 | 6.0 | 4.0 | 1208 | 250.4 | 0.6 |
| **$CO_2$ injection** | | | | | | | | | | | | | |
| 2-1 | 50cc/hr | 2.6 | 0.5 | 0.6 | 1.0 | 0.4 | 68 | 0.4 | 4.8 | 3.2 | 1032 | 195.2 | 0.5 |
| 2-2 | 50cc/hr | 3.5 | 0.6 | 1.2 | 1.6 | 0.6 | 84 | 0.6 | 688.8 | 4.0 | 1184 | 288.8 | 0.5 |
| **Sample saturated with $CO_2$ saturated brine after $CO_2$ injection** | | | | | | | | | | | | | |
| 3-1 | 50cc/hr | 3.7 | 0.6 | 1.2 | 1.8 | 0.4 | 84 | 0.4 | 7.8 | 4.0 | 1296 | 283.2 | 0.6 |
| 3-2 | 50cc/hr | 3.7 | 0.6 | 1.2 | 1.6 | 0.6 | 76 | 0.4 | 6.6 | 4.8 | 1256 | 268.8 | 0.6 |
| 3-3 | 50cc/hr | 3.4 | 0.6 | 0.6 | 1.2 | 0.4 | 72 | 0.4 | 6.0 | 4.0 | 1176 | 227.2 | 0.5 |
| 3-4 | 50cc/hr | 3.9 | 0.5 | 0.6 | 1.4 | 0.4 | 68 | 0.4 | 7.2 | 4.0 | 1192 | 230.4 | 0.6 |
| 3-5 | 50cc/hr | 3.0 | 0.5 | 1.2 | 1.0 | 0.4 | 68 | 0.4 | 6.0 | 3.2 | 1056 | 176.0 | 0.5 |
| 3-6 | 50cc/hr | 3.4 | 0.5 | 0.6 | 1.2 | 0.4 | 76 | 0.4 | 9.0 | 4.0 | 1224 | 184.0 | 0.6 |
| 3-7 | 50cc/hr | 3.2 | 0.5 | 1.2 | 1.2 | 0.6 | 72 | 0.4 | 7.8 | 4.0 | 1160 | 169.6 | 0.6 |
| 3-8 | 50cc/hr | 3.2 | 0.5 | 1.2 | 1.0 | 0.4 | 76 | 0.4 | 9.0 | 3.2 | 1176 | 156.8 | 0.5 |
| 3-9 | 50cc/hr | 2.9 | 0.5 | 1.2 | 1.0 | 0.4 | 68 | 0.4 | 8.4 | 3.2 | 1088 | 139.2 | 0.6 |
| 3-10 | 50cc/hr | 3.0 | 0.5 | 1.2 | 1.0 | 0.4 | 72 | 0.4 | 10.8 | 3.2 | 1184 | 138.4 | 0.5 |

| | | Rb | Sb | Se | Sm | Sr | Tb | Th | Tm | U | V | W | Y | Yb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$CO_2$ saturated brine** | | | | | | | | | | | | | | | |
| 1-2 | 50cc/hr | 62 | 2 | 7 | | 39 | | | | 10 | 18 | 18 | 6.6 | | 8130 |
| 1-3 | 50cc/hr | 72 | 4 | 14 | 5 | 36 | 1.2 | 1 | -0.8 | 14 | 21 | 24 | 10.2 | | 7580 |
| 1-4 | 100cc/hr | 66 | 2 | 14 | | 21 | 0.6 | -1 | -0.8 | 11 | 18 | 18 | 9.6 | | 5530 |
| 1-5 | 100cc/hr | 62 | 1 | 12 | | 14 | 0.6 | -0.5 | -0.4 | 9.5 | 14 | 10 | 10.5 | | 3980 |
| 1-6 | 100cc/hr | 56 | 1 | 16 | | 12 | 0.6 | -0.5 | -0.4 | 9.0 | 12 | 8 | 12.0 | | 3660 |
| 1-7 | 150cc/hr | 58 | 2 | 36 | 3 | 12 | 0.6 | -0.5 | -0.4 | 8.0 | 12 | 10 | 11.7 | | 3050 |
| 1-8 | 150cc/hr | 54 | 1 | 36 | | 10 | 0.6 | -0.5 | -0.4 | 7.0 | 12 | 10 | 10.8 | | 2430 |
| 1-9 | 150cc/hr | 54.0 | 1.0 | 40 | 2 | 8.0 | 0.4 | -0.3 | -0.2 | 6.3 | 11.2 | 4.8 | 10.2 | | 2080 |
| 1-10 | 50cc/hr | 51.0 | 1.5 | 34 | 3 | 8.8 | 0.4 | -0.3 | 0.3 | 6.6 | 12.0 | 5.6 | 11.2 | | 2060 |
| 1-11 | 50cc/hr | 49.0 | 1.0 | 26 | 3 | 8.8 | 0.6 | -0.3 | 0.3 | 5.4 | 7.2 | 4.0 | 9.4 | | 1930 |
| 1-12 | 50cc/hr | 54 | 1 | 32 | | 12 | 0.6 | -0.5 | -0.4 | 5.5 | 14 | 10 | 9.6 | | 2340 |
| 1-13 | 50cc/hr | 55.0 | 1.0 | 20 | 3 | 10.4 | 0.6 | -0.3 | -0.2 | 5.1 | 11.2 | 1.6 | 9.8 | | 2040 |
| 1-14 | 50cc/hr | 56.5 | 1.0 | 34 | 3 | 11.2 | 0.6 | 0.3 | 0.2 | 5.4 | 12.8 | 1.6 | 9.8 | | 2010 |
| 1-15 | 50cc/hr | 50.5 | 1.0 | 40 | 2 | 9.6 | 0.4 | -0.3 | 0.3 | 4.8 | 12.0 | 1.6 | 9.2 | | 1730 |
| 1-16 | 50cc/hr | 49.5 | 1.5 | 38 | 3 | 9.6 | 0.6 | 0.3 | 0.2 | 5.4 | 12.0 | 1.6 | 12.2 | | 2120 |
| 1-17 | 50cc/hr | 49.0 | 1.5 | 36 | 3 | 9.6 | 0.6 | 0.3 | 0.3 | 4.5 | 12.8 | 2.4 | 9.4 | | 1580 |
| 1-18 | 50cc/hr | 50.0 | 1.5 | 40 | 3 | 9.6 | 0.6 | 0.3 | 0.3 | 4.2 | 13.6 | 2.4 | 9.8 | | 1670 |
| 1-19 | 50cc/hr | 50.5 | 1.5 | 40 | 3 | 9.6 | 0.6 | 0.6 | 0.3 | 4.5 | 13.6 | 2.4 | 10.2 | | 1670 |
| 1-20 | 50cc/hr | 45.5 | 1.0 | 32 | 3 | 8.8 | 0.6 | 0.3 | 0.3 | 3.9 | 12.8 | 2.4 | 9.0 | | 1400 |
| 1-21 | 50cc/hr | 47.0 | 1.5 | 34 | 3 | 8.8 | 0.6 | 0.3 | 0.3 | 3.9 | 12.8 | 2.4 | 8.8 | | 1350 |
| 1-22 | 50cc/hr | 44.4 | 1.2 | 31 | 3 | 8.4 | 0.6 | 0.2 | 0.2 | 3.4 | 11.4 | 1.8 | 8.4 | 1 | 1260 |
| 1-23 | 50cc/hr | 43.0 | 1.5 | 26 | 4 | 9.6 | 0.6 | 0.3 | 0.4 | 4.2 | 8.0 | 2.4 | 11.0 | | 1600 |
| 1-24 | 50cc/hr | 43.2 | 1.2 | 31 | 3 | 7.8 | 0.5 | 0.4 | 0.3 | 3.0 | 10.2 | 1.8 | 8.1 | 1 | 1190 |
| 1-25 | 50cc/hr | 41.6 | 1.2 | 14 | 2 | 7.2 | 0.5 | 0.4 | 0.3 | 2.8 | 6.0 | 1.8 | 7.8 | 1 | 1120 |
| 1-26 | 50cc/hr | 38.0 | 1.2 | 21 | 2 | 6.0 | 0.5 | 0.4 | 0.3 | 2.6 | 4.8 | 1.8 | 6.8 | 1 | 1010 |
| 1-27 | 50cc/hr | 43.2 | 1.6 | 33 | 4 | 7.8 | 0.6 | 0.4 | 0.3 | 3.0 | 6.6 | 1.8 | 8.7 | 1 | 1250 |
| 1-28 | 50cc/hr | 41.2 | 1.2 | 30 | 3 | 6.6 | 0.6 | 0.2 | 0.3 | 2.6 | 5.4 | 1.8 | 7.4 | 1 | 1080 |
| 1-29 | 50cc/hr | 36.4 | 1.6 | 33 | 3 | 6.0 | 0.5 | 0.4 | 0.3 | 2.4 | 5.4 | 1.8 | 7.1 | 1 | 980 |
| 1-30 | 50cc/hr | 36.0 | 1.2 | 31 | 3 | 6.0 | 0.6 | 0.4 | 0.3 | 2.2 | 4.8 | 1.8 | 6.8 | 1 | 970 |
| 1-31 | 50cc/hr | 41.2 | 1.6 | 35 | 3 | 7.2 | 0.5 | 0.4 | 0.3 | 2.4 | 6.0 | 1.2 | 7.2 | 2 | 1060 |
| 1-32 | 50cc/hr | 34.8 | 1.2 | 30 | 3 | 6.0 | 0.5 | 0.2 | 0.3 | 2.4 | 5.4 | 1.8 | 7.2 | 1 | 1020 |
| **Sample saturated with $CO_2$ saturated brine overnight** | | | | | | | | | | | | | | | |
| 1-40 | 50cc/hr | 39.0 | 4.0 | 26 | 4 | 23.6 | 0.6 | 0.6 | 0.4 | 2.7 | 9.6 | 2.4 | 8.6 | | 2100 |
| 1-41 | 50cc/hr | 51 | 3 | 24 | 3 | 44 | 0.6 | 0.5 | 0.4 | 3.0 | 4 | 4 | 6.6 | | 3840 |
| 1-42 | 50cc/hr | 49 | 3 | 20 | 3 | 28 | 0.9 | 0.5 | 0.6 | 4.5 | 4 | 4 | 9.6 | | 3330 |
| 1-43 | 50cc/hr | 41 | 2 | 24 | 6 | 14 | 0.9 | 1.0 | 0.5 | 4.0 | 6 | 4 | 9.6 | | 2030 |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-44 | 50cc/hr | 35.5 | 1.5 | 14 | 3 | 10.4 | 0.6 | 0.3 | 0.3 | 3.0 | 4.0 | 2.4 | 10.0 |  | 1580 |
| 1-45 | 50cc/hr | 33.2 | 1.2 | 18 | 3 | 6.0 | 0.6 | 0.4 | 0.3 | 2.6 | 4.2 | 1.8 | 8.3 | 1 | 1090 |
| 1-46 | 50cc/hr | 29.2 | 1.2 | 18 | 2 | 4.2 | 0.5 | 0.2 | 0.2 | 2.2 | 3.6 | 1.2 | 7.3 | 1 | 890 |
| 1-47 | 50cc/hr | 32.0 | 1.2 | 21 | 3 | 4.2 | 0.5 | 0.2 | 0.3 | 2.0 | 4.2 | 1.8 | 7.6 | 1 | 890 |
| 1-48 | 50cc/hr | 32.4 | 1.2 | 19 | 3 | 4.8 | 0.5 | 0.4 | 0.3 | 1.8 | 4.8 | 1.8 | 7.5 | 1 | 910 |
| 1-49 | 50cc/hr | 30.8 | 1.2 | 22 | 3 | 4.8 | 0.5 | 0.4 | 0.3 | 2.0 | 4.8 | 1.8 | 8.0 | 1 | 780 |
| **$CO_2$ injection** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 2-1 | 50cc/hr | 28.0 | 1.2 | 27 | 2 | 3.6 | 0.5 | 0.4 | 0.3 | 1.6 | 4.8 | 1.8 | 6.2 | 1 | 670 |
| 2-2 | 50cc/hr | 39.2 | 1.2 | 30 | 3 | 12.0 | 0.6 | 0.4 | 0.4 | 2.4 | 4.8 | 1.8 | 7.8 | 2 | 1140 |
| **Sample saturated with $CO_2$ saturated brine after $CO_2$ injection** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 3-1 | 50cc/hr | 36.4 | 1.2 | 30 | 3 | 5.4 | 0.6 | 0.4 | 0.3 | 2.2 | 5.4 | 1.8 | 8.0 | 2 | 940 |
| 3-2 | 50cc/hr | 36.4 | 1.6 | 31 | 4 | 4.8 | 0.6 | 0.4 | 0.3 | 2.2 | 5.4 | 1.8 | 7.9 | 2 | 830 |
| 3-3 | 50cc/hr | 34.0 | 1.2 | 19 | 3 | 4.2 | 0.6 | 0.4 | 0.3 | 1.8 | 4.8 | 1.8 | 6.8 | 1 | 790 |
| 3-4 | 50cc/hr | 33.2 | 1.2 | 24 | 3 | 4.2 | 0.6 | 0.4 | 0.3 | 1.8 | 4.8 | 1.8 | 7.2 | 2 | 750 |
| 3-5 | 50cc/hr | 28.8 | 1.2 | 23 | 3 | 3.6 | 0.5 | 0.4 | 0.3 | 1.4 | 4.2 | 1.8 | 5.9 | 1 | 700 |
| 3-6 | 50cc/hr | 33.2 | 1.2 | 26 | 3 | 4.2 | 0.6 | 0.4 | 0.2 | 1.6 | 4.8 | 1.8 | 6.5 | 1 | 800 |
| 3-7 | 50cc/hr | 30.8 | 1.6 | 27 | 3 | 4.2 | 0.5 | 0.4 | 0.3 | 1.4 | 4.8 | 1.8 | 6.1 | 2 | 770 |
| 3-8 | 50cc/hr | 30.4 | 1.2 | 25 | 2 | 4.2 | 0.5 | 0.4 | 0.3 | 1.4 | 5.4 | 1.8 | 5.7 | 1 | 760 |
| 3-9 | 50cc/hr | 27.6 | 1.2 | 24 | 3 | 3.6 | 0.5 | 0.4 | 0.3 | 1.2 | 4.2 | 1.8 | 5.1 | 1 | 700 |
| 3-10 | 50cc/hr | 29.6 | 1.6 | 25 | 3 | 4.2 | 0.5 | 0.4 | 0.3 | 1.2 | 5.4 | 1.8 | 5.1 | 1 | 770 |

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