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Geochemical interactions between supercritical CO_2 and the Midale Formation.
V: Experiments investigating reactions of the Midale Vuggy

Reservoir Geosciences Programme
Weyburn Monitoring and Storage Project
Commissioned Report CR/03/334 N

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/03/334N

Geochemical interactions between supercritical CO_2 and the Midale Formation.
V: Experiments investigating reactions of the Midale Vuggy

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Key words

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Foreword

This report is the published product of a study by the British Geological Survey (BGS), and forms part of the international IEA Weyburn Carbon Dioxide (CO_2) Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO_2 in the Midale reservoir at the Weyburn field in southern Saskatchewan, Canada, using methods that include; time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock.

This report provides a description of fluid chemical and mineralogical changes occurring in a series of experiments that have been conducted within the Hydrothermal Laboratory of the British Geological Survey. These experiments were undertaken to identify what geochemical changes would result from the injection of CO_2 into the Midale Vuggy formation. The experiments utilised samples of Midale Vuggy core material from the Weyburn field, synthetic formation water based upon measured well fluid compositions, and either CO_2 or N_2 as a pressurising medium.

Acknowledgements

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The authors would like to thank the European Commission (project number NNE5-2000-00096) and the UK Department of Trade and Industry (contract C/06/00296/00/00) for helping to fund this work.

The authors would also like to thank researchers at the University of Calgary for information on the baseline formation water chemistry of the Weyburn oil field.

Finally, the authors would like to thank staff at Saskatchewan Energy and Mines for their help in the selection of samples of core material from their extensive collection of borehole cores form the Weyburn oil field.

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Summary

This report describes work undertaken at the British Geological Survey (BGS) that forms part of the international IEA Weyburn Carbon Dioxide (CO_2) Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO_2 into the Midale reservoir at the Weyburn oil field in southern Saskatchewan, Canada, using methods that include; time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock. This report aims to provide a description of fluid chemical and mineralogical changes occurring in a series of experiments that have been conducted within the Hydrothermal Laboratory of the British Geological Survey. These experiments were undertaken to identify what geochemical changes would result from the injection of CO_2 into the Midale Vuggy formation. The experiments utilised samples of Midale Vuggy core material from the Weyburn field, synthetic formation water based upon measured well fluid compositions, and either CO_2 or N_2 as a pressurising medium.

The experiments were conducted at 60°C and pressurised to either 150 bar [15 MPa] or 250 bar [25 MPa], using either CO_2 or N_2. Experiment durations ranged from one week to 6 months.

The evolution over time of a selection of solutes was followed. Relative to the N_2 'baseline' experiments, it was found that the impact of CO_2 was to:

- increase the concentrations of Ca, Si and HCO_3^-
- decrease the concentrations of total S and possibly Sr, and pH values
- have little impact on the concentrations of Mg, Mn and Al

It is noted that these fluid chemical changes are not dissimilar to those found in the Midale Marly experiments (Rochelle *et al.*, 2003a)

All monoliths reacted in CO_2-rich synthetic pore waters showed clear evidence of 'tidemarks' on their external surfaces, with the area below the water-CO_2 interface appearing bleached. After 4 weeks of reaction of the monoliths with CO_2, euhedral prismatic gypsum crystals up to 500 µm in length formed below the water line in the CO_2 experiment. By 8 weeks reaction the gypsum crystals were at least 2.5 mm long, and at 17 weeks reaction gypsum crystals up to 500 µm long also developed in the baseline N_2 experiment. In addition, most calcite and anhydrite surfaces below the water line were corroded to a depth of 10-30 µm in both the CO_2 and the baseline N_2 experiments. This porosity was easily distinguishable from the vuggy porosity developed during diagenesis. Scanning electron microscopy also revealed that a fine coating of halite developed above the water-CO_2 interface during the experiment. In the experiments containing crushed Midale Vuggy, euhedral tabular prismatic gypsum crystals up to 1.8 mm long developed after 2 weeks reaction. Only limited evidence for minor corrosion was tentatively observed. After 26 weeks of reaction, the only evidence for dissolution in the <250 µm crushed samples was slightly less 'dust' in the baseline N_2 experiment relative to the CO_2 experiment.

It was noted that the CO_2 experiments give lower S concentrations compared to the N_2 experiments, with S (as SO_4) removed from solution by gypsum precipitation. During the early parts of the experiments at least, this appears to be faster than the rate of SO_4 addition from anhydrite dissolution. Later in the CO_2 experiments steady-state concentrations appear to be reached, and it is likely that saturation with respect to gypsum balances lower S concentrations with higher Ca concentrations.

The changes described above were interpreted as being due to some calcite dissolution (probably more than observed in the Midale Marly experiments), some anhydrite dissolution, a little aluminosilicate mineral dissolution and a fair amount of gypsum precipitation. It is still unclear if there is an overall net increase or decrease in porosity or permeability. However, if significant gypsum precipitation reduced the permeability of the Midale Vuggy unit, then this may be a beneficial reaction in terms of the EOR operation, as it might reduce the potential for the injected CO_2 to ‘under-ride’ the target Marly unit.

1 Introduction

The experiments detailed in this report were undertaken to investigate the impact of CO_2 injection into the Midale Vuggy formation at the Weyburn oil field, Saskatchewan, Canada. The experiments used samples of Midale Vuggy core material (cleaned and prepared), and a synthetic porewater based upon actual measured well fluid compositions. The pressures and temperatures used within the experiments were representative of *in-situ* conditions (60°C, 150 bar [15 MPa]) and those near to injection wells (60°C, 250 bar [25 MPa]). As such, the study aims to replicate as closely as possible, processes occurring in the deep subsurface at Weyburn, including those conditions that will exist even after oil production and CO_2 injection have ceased.

This study follows the procedures outlined in Rochelle *et al.* (2002a), and builds upon some initial scoping test experiments using samples of Midale Marly material (Rochelle *et al.*, 2002b), and other experiments using samples of Midale Marly (Rochelle *et al.*, 2003a) and Midale Evaporite (Rochelle *et al.*, 2003b).

The Midale Vuggy sample used came from well 12-11-6-14 and was selected by staff from BGS and GEUS (Pearce and Springer, 2001) because baseline fluid chemical information was also available from the same well (sample 12-11-6-14 as provided by the University of Calgary [Shevallier, pers. comm.]). The Midale Vuggy sample has the following identifiers:

- BGS12A (GEUS reference number)
- HTL 136 (Hydrothermal Laboratory reference number)
- H638 (BGS Mineralogy and Petrology reference number)

Further details about the Midale Vuggy sample and the baseline fluid chemistry can be found in Rochelle *et al.*, (2002a)

Two main types of experiments were conducted during this study:

- Experiments pressurised with N_2 to provide a baseline ‘non-reacting’ control, which could then be compared to the ‘reactive’ CO_2 experiments. The N_2 experiments could also be compared with data from actual analyses of well fluids – they should be comparable.
- Experiments pressurised with CO_2. These ‘reactive’ experiments were performed to provide information on the chemical and mineralogical changes that might occur during the injection of CO_2 into the Midale Marly formation at the Weyburn oil field.

Three different types of solid material were utilised in both types of experiments outlined above:

- Experiments using ground solid material with ‘fines’ included (<250 μm size fraction). These experiments maximised the reactive surface area, and as such were best able to investigate steady-state conditions within the limited timescale of this study. They had durations of up to 6 months, and a 10:1 fluid:rock ratio. Although suitable for fluid chemical data and XRD mineralogical analyses, the fine-grained nature of the solids made them less suitable for SEM (scanning electron microscope) observations of the reacted products.
- Experiments using ground solid material, but with ‘fines’ removed (250-500 μm size fraction). These experiments had a lower solid surface area to those described above, and hence reacted slower. However, their surface area was measured, and this allowed for rates of element release (i.e. dissolution) to be calculated. They had durations of up to 3 months, and a 10:1 fluid:rock ratio. The absence of fine material also made the solid reaction products more suitable for SEM observations.

- Experiments using ‘monoliths’ of solid material (approximately 1x1x4 cm). These experiments had the lowest solid surface area, and thus the slowest reaction. However, the intact nature of the solid sample allowed for straightforward observations by SEM. The monoliths were arranged so that they straddled the interface between the aqueous phase and the CO_2 phase. By doing this, it was possible to readily identify any difference in overall reactivity within either fluid phase. They had durations of up to 3 months, and a somewhat more variable fluid:rock ratio.

The experimental equipment used in this study was of relatively small volume (<200 ml). Although it was possible to take several samples from each experiment, usually no more than six could be extracted. In order to allow more detailed information to be obtained (i.e. more samples), several similar experiments tended to be run together, and their results combined. Combining results in this way also provided a check on the quality of the data (i.e. the data sets should agree). In this way, confidence in the data was increased. Further details about the set up of the experiments can be found in Rochelle *et al.*, (2002a).

The data presented in Section 2 are derived from solutions sampled at atmospheric pressure, 150 bar [15 MPa], and 250 bar [25 MPa]. The ‘Starting fluid’ and ‘UoC well fluid analysis’ (UoC = University of Calgary) were sampled at atmospheric pressure, and the ‘CO2+fines (25 MPa)’ experimental data were sampled at 250 bar [25 MPa]. All other experimental data were sampled at 150 bar [150 MPa].

Details of all experiments undertaken in this study, their run conditions, and caveats about the use of individual analyses, are given in Appendixes 1 and 2.

2 Results of fluid chemical analysis

In the following sections it should be noted that the value ranges on the axes of the plots have been chosen so that they are exactly the same as in similar reports dealing with studies of Midale Marly and Midale Evaporite (Rochelle *et al.*, 2003a, b). This was undertaken to facilitate comparisons between the different studies/datasets, as was presenting our initial interpretation of the results in ‘bullet point’ format.

2.1 CHLORIDE

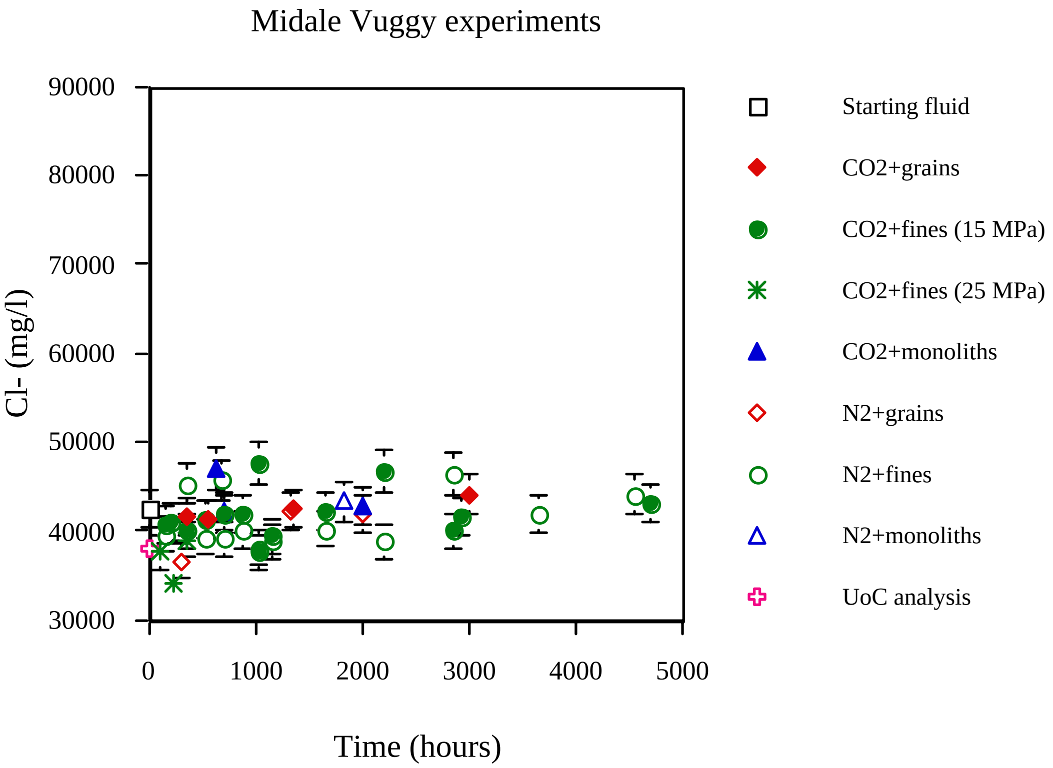


Figure 1 Cl^- concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- The experimental starting fluid composition is slightly higher (by about 12%) than the equivalent well fluid as analysed by the University of Calgary. This is close to the 8% as predicted for making up a charge-balanced synthetic starting solution (Rochelle *et al.*, 2002a).
- There is no apparent difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 does not effect the behaviour of Cl^- in these experiments).
- It is unclear exactly why the 25 MPa data tend to be somewhat below the starting fluid composition, though as there are so few data points it is hard to draw definitive conclusions.

2.2 SODIUM

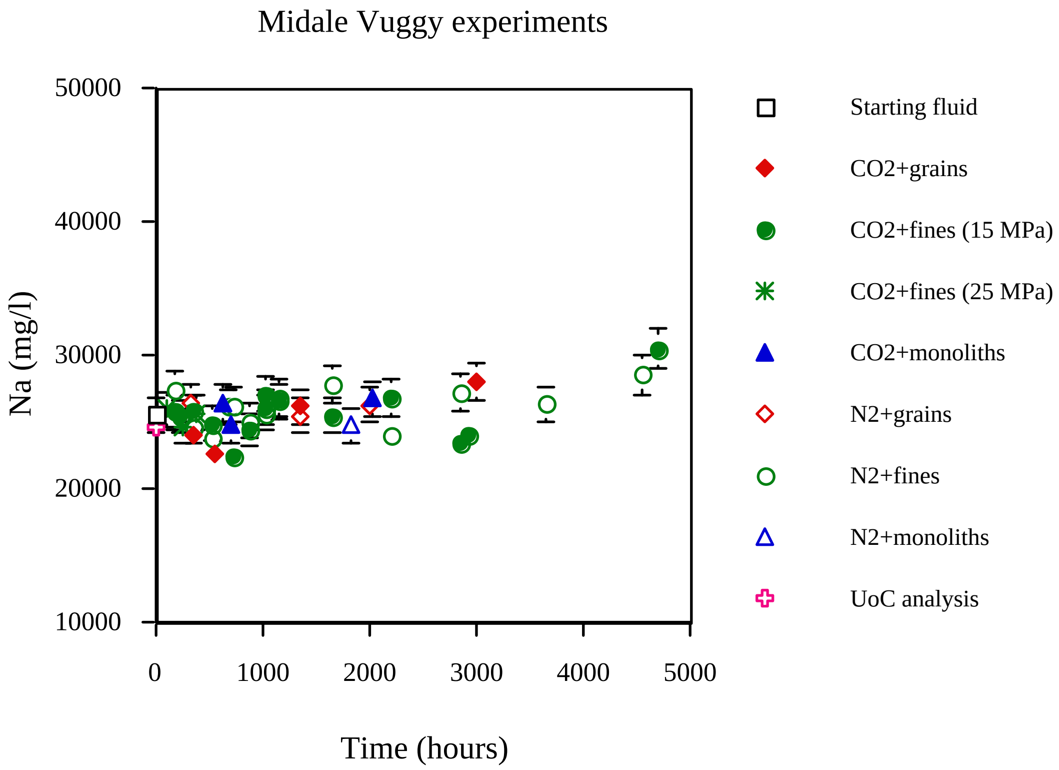


Figure 2 Na concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- There is a good agreement between the experimental starting fluid composition and the equivalent well fluid as analysed by the University of Calgary.
- There is no apparent difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 does not effect the behaviour of Na in these experiments).
- There are generally stable concentrations over time, as would be expected for a relatively non-reacting analyte such as Na, though there *may* be an indication of a very slight increase over time, possibly as a result of water loss through evaporation. However, the two longest timescale samples (from Runs 1077 and 1078) are slightly higher than expected, most likely due to the modified sampling procedure used (see Appendix 1).

2.3 POTASSIUM

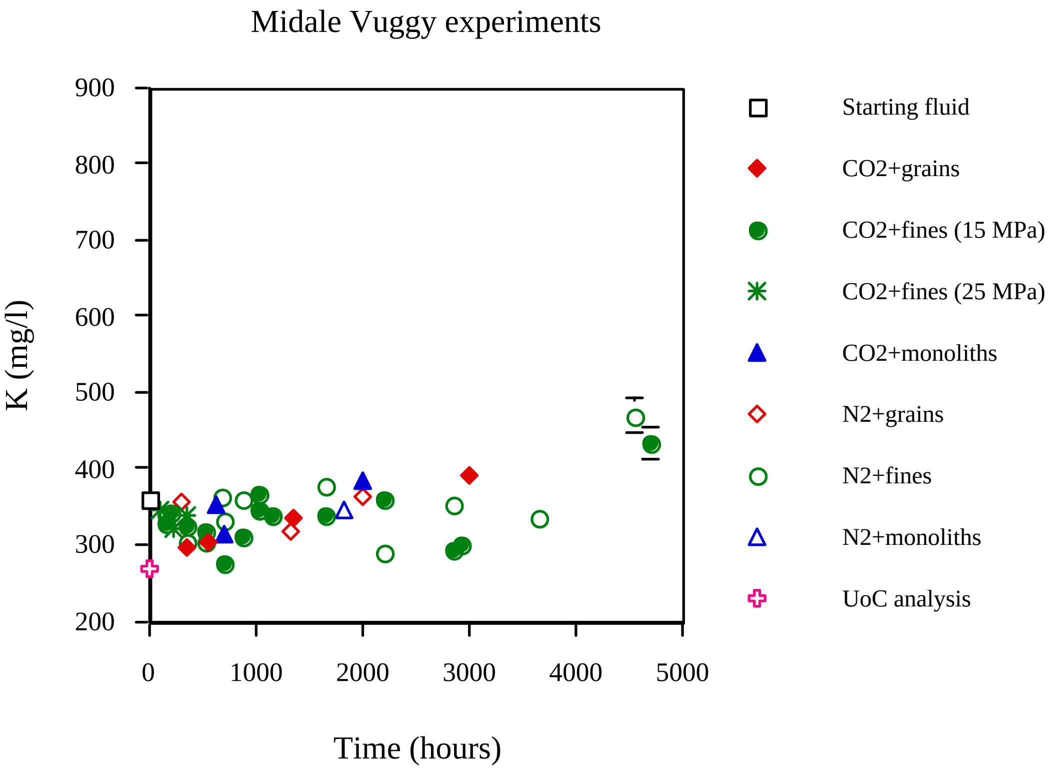


Figure 3 K concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- The experimental starting fluid composition is somewhat higher than the equivalent well fluid as analysed by the University of Calgary. Given that many of the experiments have K concentrations below that of the starting fluid, it is thought that the starting fluid concentration may be somewhat too high, and the value should be treated with caution.
- There is no apparent difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 does not effect the behaviour of K in these experiments).
- There are generally stable concentrations over time, as would be expected for a relatively non-reacting analyte such as K, though there *may* be an indication of a very slight increase over time – possibly as a result of water loss through evaporation as mentioned previously. However, the two longest timescale samples (from Runs 1077 and 1078) are slightly higher than expected, which may also due to the modified sampling procedure used (see Appendix 1).

2.4 CALCIUM

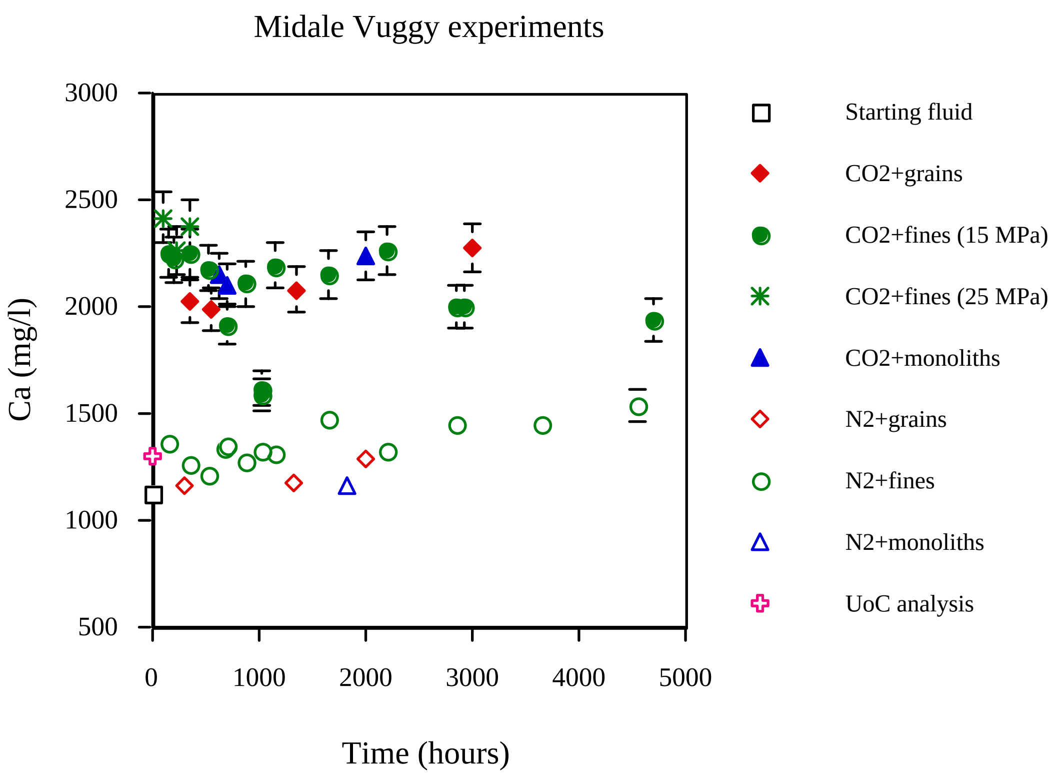


Figure 4 Ca concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- The experimental starting fluid composition is a little lower than the equivalent well fluid as analysed by the University of Calgary.
- There is a large difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 has a marked effect on the behaviour of Ca in these experiments)
- The N_2 experiments rapidly (within about a week) achieve a pseudo steady-state concentration of ~1300 mg/l. Such a constant value tends to suggest that there is good equilibration with a Ca-rich mineral phase (probably calcite, but other possibilities are dolomite and anhydrite). This is similar to the measured well fluid composition – as might be expected in this 'non-reacting' experimental system. However, in detail there *may* also be evidence for a possible slow increase in Ca concentrations over time, though it is hard to be definitive
- Most of the CO_2 experiments appear to be heading towards a steady-state concentration in the order of ~2200 mg/l (though there is some scatter in the data). The move towards a steady-state concentration of ~2200 mg/l tends to suggest that there is rapid and significant dissolution of a Ca-rich mineral phase (probably calcite, but other possibilities are dolomite and anhydrite).
- However, two data points from the CO_2 experiments at approximately 1000 hours are significantly lower than expected, and should be treated as being 'uncertain'. Indeed, there were technical problems during the taking of one of these samples (Run 1101, sample 6 and Run 1120, sample 5) and they could not be done in the usual rapid manner. As a

consequence, it is possible that some re-equilibration (and hence decrease in Ca concentration) may have occurred between depressurisation and sampling. The longest timescale sample (from Run 1077) is slightly higher than expected, most likely due to the modified sampling procedure used (see Appendix 1).

- The 25 MPa CO_2 experiments give very slightly higher concentrations compared to the 15 MPa CO_2 experiments - in the order of 2400 mg/l. These few data suggest that Ca solubility may be elevated slightly in the presence of higher CO_2 pressures.

2.5 MAGNESIUM

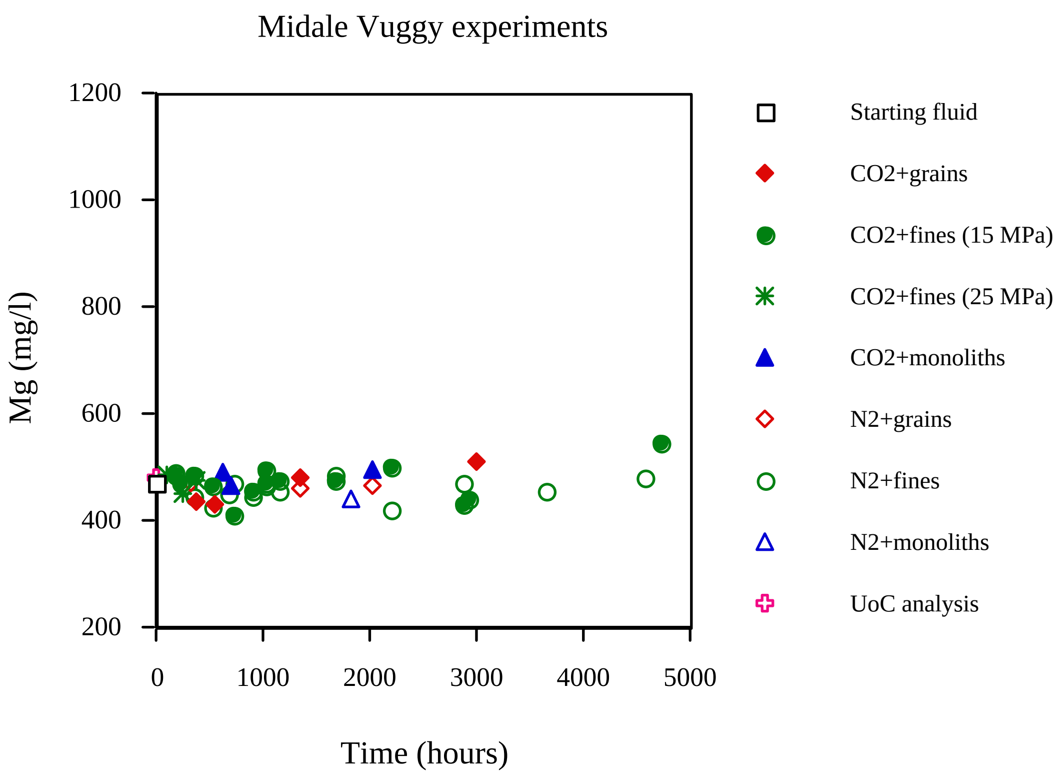


Figure 5 Mg concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- There is a good agreement between the experimental starting fluid composition and the equivalent well fluid as analysed by the University of Calgary.
- There is no apparent difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 does not effect the behaviour of K in these experiments).
- The 15 MPa and 25 MPa CO_2 experiments give very similar results, suggesting that Mg solubility will remain fairly constant even over a wide pressure range.
- However, the longest timescale sample (from Run 1077) is slightly higher than expected, most likely due to the modified sampling procedure used (see Appendix 1).

2.6 STRONTIUM

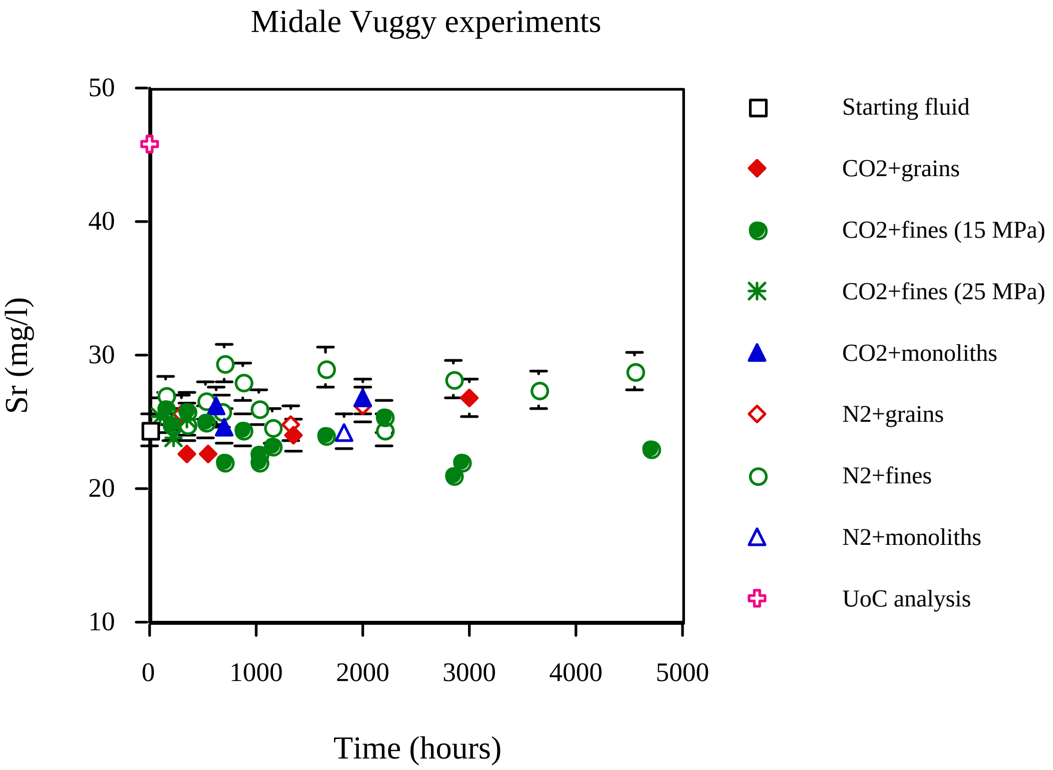


Figure 6 Sr concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- The experimental starting fluid composition is far below the equivalent well fluid as analysed by the University of Calgary. The exact reason for this difference is not clear, and it is of a magnitude greater than that expected for simple analytical/sampling errors. Other possibilities include: some initial precipitation of a Sr phase in the tank holding the stock solution, or confusion between the molecular weights of $SrCl_2$ and $SrCl_2.6H_20$ during solution makeup. Whatever the exact reason for this discrepancy, it appears to make little difference to the experiments, as reaction does not appear to liberate any Sr from the rock.
- There is *possibly* a slight difference between the results of the CO_2 and N_2 experiments, i.e. the presence of CO_2 *may* have a *very slight* impact on the behaviour of Sr in these experiments. In contrast to Ca, the CO_2 experiments *may* have a very slightly lower Sr concentrations compared to the N_2 experiments. For the CO_2 experiments, steady-state concentrations are in the order of 23 mg/l, whereas for the N_2 experiments comparable concentrations appears to be approximately 27 mg/l. However, given the small size of this difference and the scatter in the data, it is hard to be any more definitive about such a small difference.
- Although the 25 MPa CO_2 experiments did not run for very long, they do appear to result in similar steady-state concentrations compared to the 15 MPa experiments, suggesting that Sr solubility will remain fairly constant even over a wide pressure range.

2.7 BARIUM

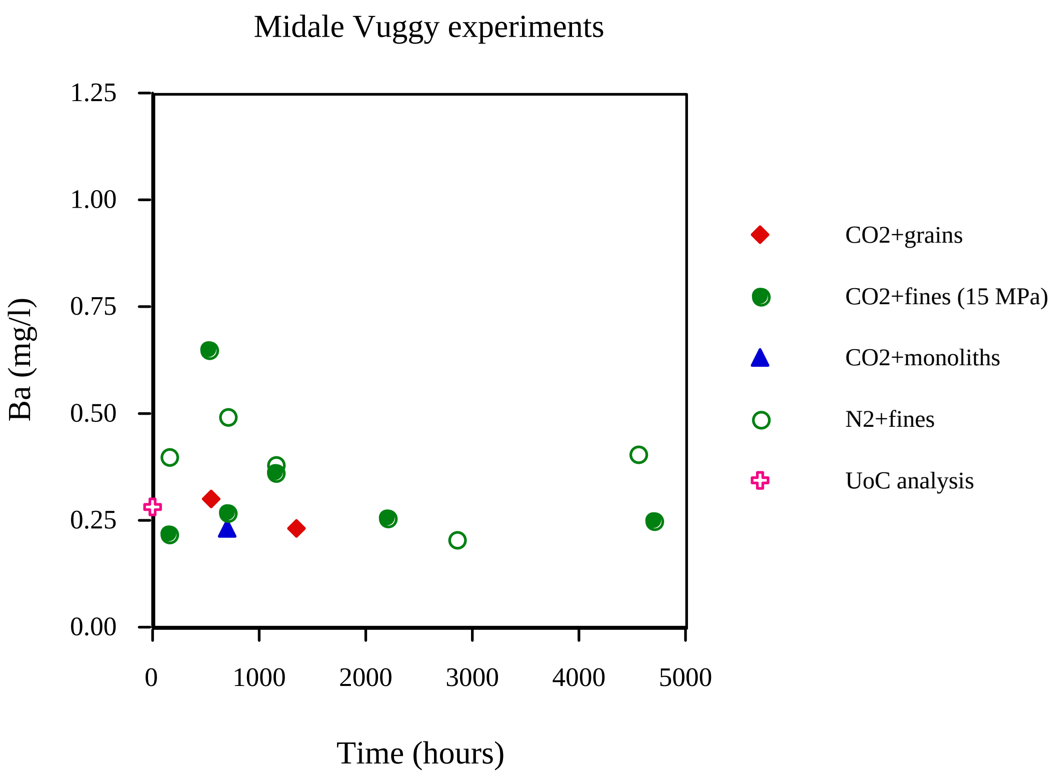


Figure 7 Ba concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- No Ba was found in the starting fluid.
- There are generally similar results between CO_2 and N_2 experiments (i.e. the presence of CO_2 appears to have no effect the behaviour of Ba in these experiments).
- There are some scatter in the data, with no real trends in concentration over time.

2.8 MANGANESE

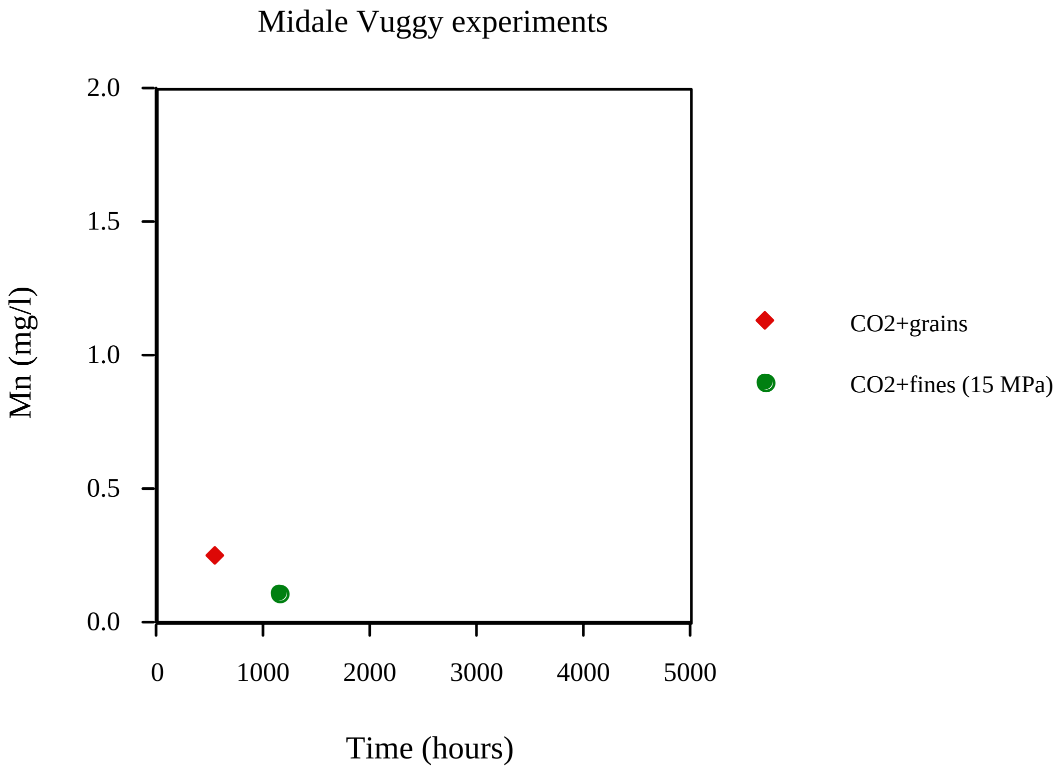


Figure 8 Mn concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- No Mn was found in the starting fluid or in the equivalent well fluid composition analysed by the University of Calgary.
- Only two samples gave results above detection limits. It is unclear whether these represent contamination, or a general lack of Mn in the Midale Vuggy samples.
- That the two data points both come from CO_2 experiments, *may* indicate a higher reactivity of the Midale Vuggy to CO_2-rich solutions, or a higher solubility of Mn in them. However, it should be noted that all of the data points plotted in Figure 8 are not far above the analytical detection limit, and thus have increased uncertainty associated with their exact concentration.

2.9 IRON

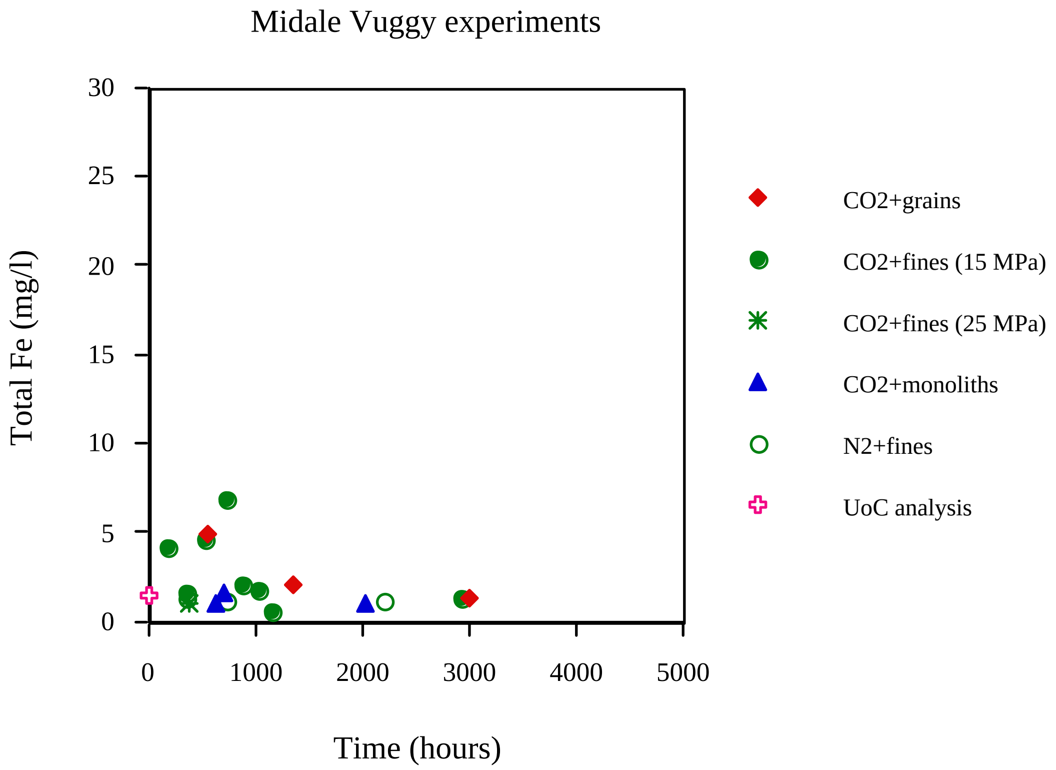


Figure 9 Fe concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- No Fe was found in the starting fluid.
- There is some scatter in the data, but no real trends in concentration over time.
- Although there are generally similar results between CO_2 and N_2 experiments, many more CO_2 data lie above the detection limit. This *may* indicate that the presence of CO_2 has a positive impact on dissolved Fe concentrations. However, it is hard to be definitive about this, as data points are relatively few, and concentration differences relatively small.
- Although there is very limited data from the 25 MPa CO_2 experiments, they do appear to result in similar steady-state concentrations to the 15 MPa experiments, suggesting that Fe solubility *may* remain fairly constant even over a wide pressure range.

2.10 SILICON

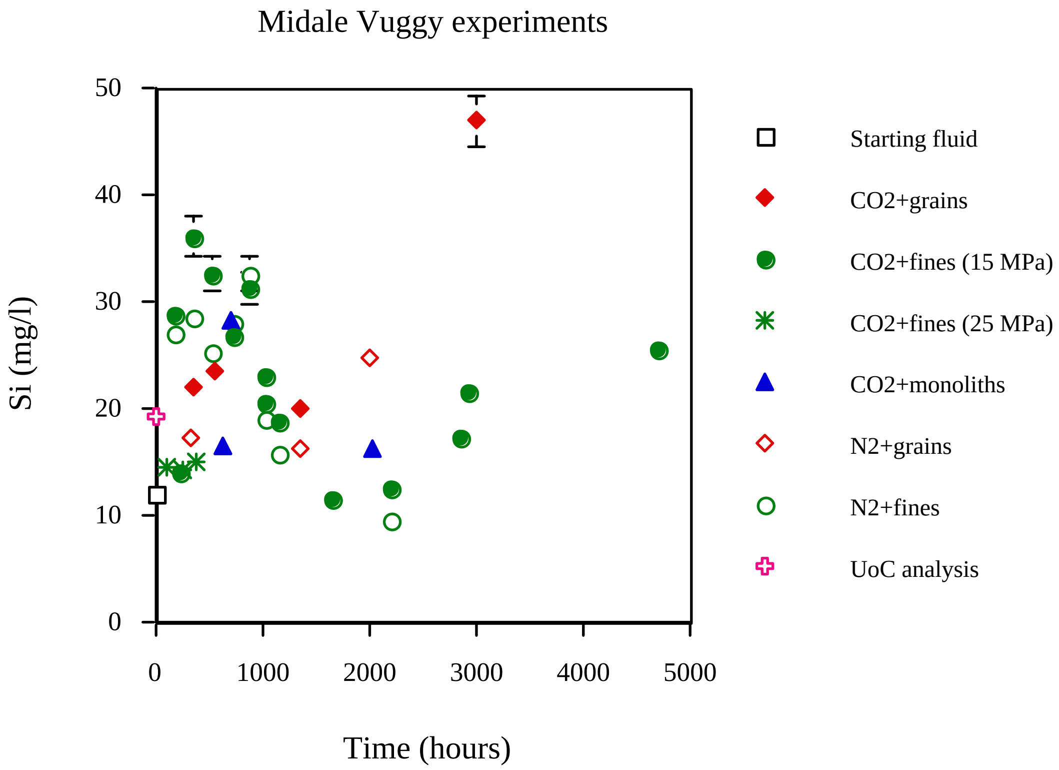


Figure 10 Si concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- The experimental starting fluid composition is somewhat lower than the equivalent well fluid as analysed by the University of Calgary.
- There are generally similar results between CO_2 and N_2 experiments (i.e. the presence of CO_2 appears to have no effect the behaviour of Si in these experiments).
- It is possible that there *might* be an indication of initial increases in Si concentrations followed by later decreases. However, given the degree of scatter in the data, it is hard to make out any real trends in concentration over time.
- Data from the 25 MPa CO_2 experiments are broadly similar to data from the 15 MPa CO_2 experiments. However, as the 25 MPa data are very few, it is hard to be more definitive about the relationship between CO_2 pressure and Si concentrations.

2.11 ALUMINIUM

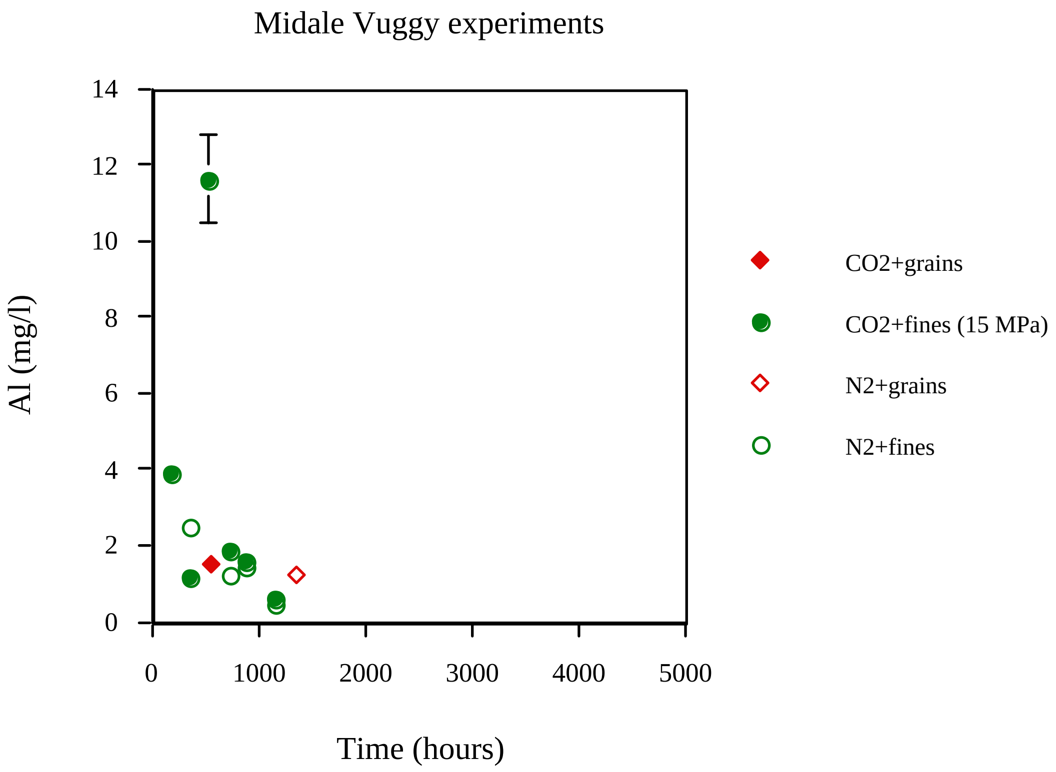


Figure 11 Al concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- No Al found in the starting fluid or the well fluid as analysed by the University of Calgary.
- There is significant scatter in the data. The higher values (>2 mg/l) are thought to be erroneous, resulting from possible contamination. Note that the remaining values are not far above the analytical detection limit (results for experiments not shown were below that limit).
- Although it is hard to be definitive as the data points are few, there appears to be generally similar results between CO_2 and N_2 experiments (i.e. Al-controlling reaction apparently not greatly effected by CO_2).

2.12 BICARBONATE

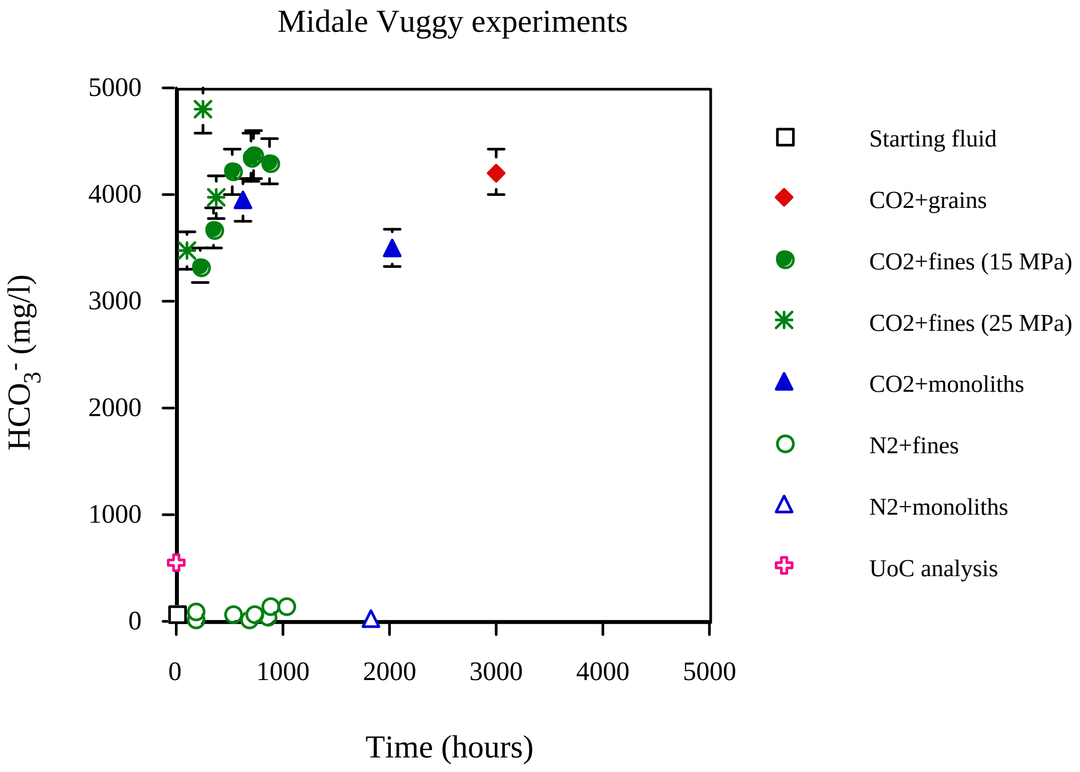


Figure 12 Bicarbonate concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- The well fluid datum as analysed by the University of Calgary is somewhat higher than the starting fluid. This may reflect a naturally higher alkalinity within the Midale formation compared to the synthetic experimental porewater.
- There is a large difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 has a marked effect on the behaviour of bicarbonate in these experiments).
- There is evidence for a very rapid increase in bicarbonate in the 15 MPa CO_2 experiments. The data obtained do not appear to resolve an exact steady state concentration, though it would appear to be in excess of ~4000 mg/l. Although most of this rapid increase occurred with a week, reaction appears to have been still occurring up to 700 hours.
- The 15 MPa and 25 MPa CO_2 experiments give broadly similar results, though it appears that bicarbonate concentrations in the 25 MPa experiment are heading to slightly higher steady-state concentrations – possibly in excess of ~5000 mg/l.
- The N_2 experiments have bicarbonate concentrations of <100 mg/l or even below detection. The concentrations measured are noticeably lower than the well fluid analysis by the University of Calgary.
- Note that bicarbonate analytical data from the *first* few experiments were not thought highly reliable (for the CO_2 experiments at least). Later data were obtained on solutions analysed within 30 minutes of sampling and are considered more reliable.

2.13 SULPHUR

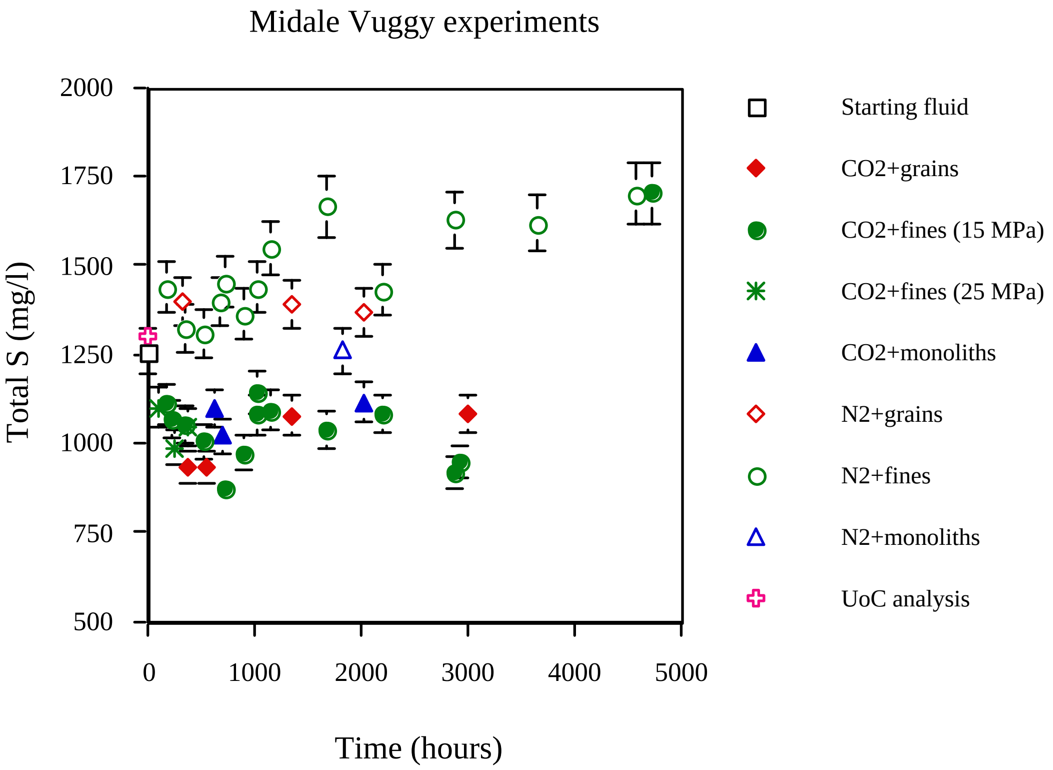


Figure 13 S concentrations (mg/l) over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- Total S as analysed by ICP is plotted instead of SO_4 from ion chromatography (IC), together with SO_4 data from the University converted to total S. This was because the IC sample had to be diluted by a huge amount (500x or 1000x). Such a dilution can lead to large uncertainties, and the ICP data were thought to be more consistent.
- There is a good agreement between the experimental starting fluid composition and the equivalent well fluid as analysed by the University of Calgary.
- There is a large difference between the results of the CO_2 and N_2 experiments (i.e. the presence of CO_2 has a marked effect on the behaviour of dissolved S in these experiments).
- The CO_2 experiments show a relatively rapid initial decrease in S concentrations, followed by an attainment of steady-state concentrations in the order of approximately 1000 mg/l. This reflects precipitation of a secondary S-rich phase such as gypsum (see Figures 26-28. Note that the longest timescale data point (Run 1077, sample 6) appears to be unduly high and is considered highly ‘uncertain’.
- The 15 MPa and 25 MPa CO_2 experiments give broadly similar results, suggesting that S solubility remains fairly constant even over a wide pressure range.
- Although there is some scatter in the data, the N_2 experiments show a slow increase in S concentrations, followed by an attainment of steady-state concentrations in the order of approximately 1700 mg/l. This may reflect equilibration with a secondary S-rich phase such as gypsum.

2.14 pH

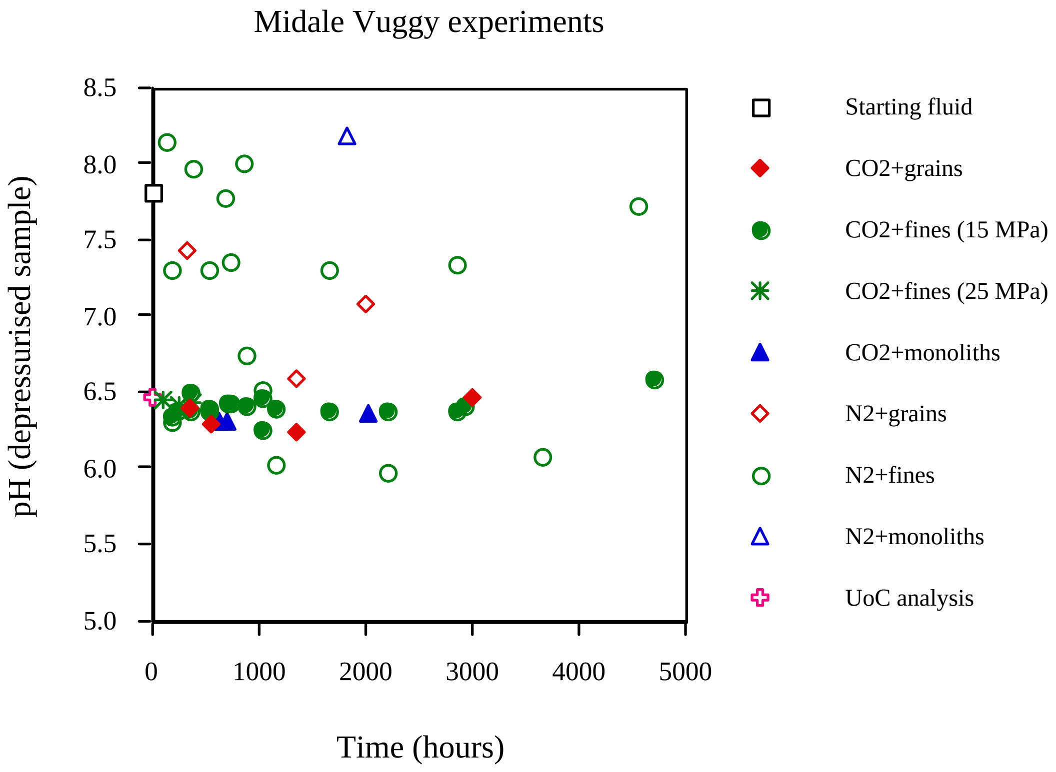


Figure 14 pH variation over time in the Midale Vuggy batch experiments.

An initial interpretation of the fluid chemical data is as follows:

- NOTE; the pH measured on <u>depressurised</u> solutions at room temperature (as opposed to 150 or 250 bar and 60°C).
- The experimental starting fluid composition is more alkaline compared to the equivalent well fluid as analysed by the University of Calgary. This may reflect the presence of trace organic acids in the actual well fluids. However, the pH of the fluid would have rapidly changed once in the experiments, as it would be buffered by the presence of CO_2 and/or Midale rocks.
- The CO_2 experiments have a generally lower pH compared to N_2 experiments (i.e. the presence of CO_2 has a noticeable effect in these experiments). The pH values are also less scattered (buffered better), with most values lying within ±0.2 units of 6.4.
- The 15 MPa and 25 MPa CO_2 experiments give very similar results, though this may just represent re-equilibration to 1 atmospheric pressure in both cases.
- The N_2 experiments appear to have generally higher pH values and are give more scattered data, with most values lying within ±0.5 units of 7.5. It was noticed that when taking the pH readings immediately after sampling, those from the N_2 experiments tended to increase slowly (by up to 1 unit) over 30-60 minutes. By comparison, those from the CO_2 experiments were relatively stable. This may represent a difference in buffering between the two sets of experiments. No explanation can be found for the pH values of approximately 6, and these appear to be unexpectedly low. Consideration of the data in Appendix 2 shows that some the N_2 experiments (and in particular Runs 1078 and 1102)

produced consecutive samples having very different pH values - varying by up to nearly 2 units. Such values were checked more than once. That otherwise similar samples should produce such a range in pH values is unexpected.

3 Results of mineralogical analysis

3.1 STARTING MATERIAL

The Mississippian Midale Beds form a cycle from the Frobisher Evaporite to the lower deeper water limestones of the Midale Vuggy, through an upward-shallowing sequence of dolomitic mudstones (the Midale Marly) to the supratidal evaporites (the Midale Evaporite). The Midale Vuggy consists largely of vuggy limestone, packstones and wackestones (Wegelin, 1987) deposited in shoal and intershoal environments.

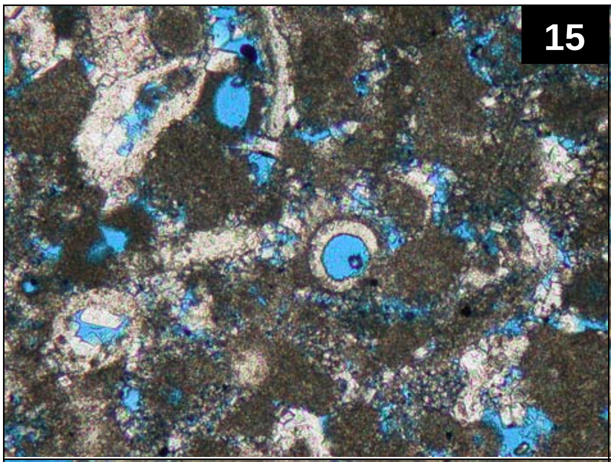
The samples used for these experiments were collected by GEUS and BGS and shipped to GEUS during the summer of 2001 (refer to Pearce and Springer (2001) which also summarises the sampling approach). On arrival at GEUS, core-plugs were taken and cold-flush cleaned at room temperature using methanol and toluene as the miscible cleaning liquids. Finally they were soxhlet cleaned for 24 hours in methylene chloride (BP ~45°C) to remove all traces of hydrocarbons. To prepare the sample for the various experiments, a series of monolithic blocks approximately 5.5x2x2 cm were cut from the sample. The remaining material was crushed in small batches and sieved to produce 250-500 µm and <250 µm fractions.

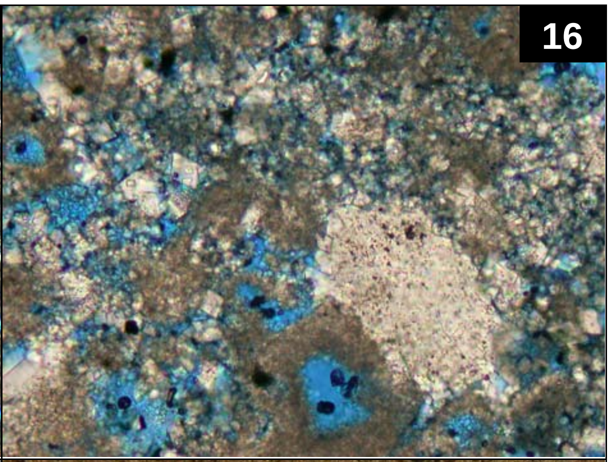
Three samples of Midale Vuggy (V2) have been examined by optical microscopy and X-ray diffraction: two from a shoal environment (sample H337 from well 14-1-6-14W2 [4751.50 ft depth] and sample H341 from well 12-11-6-14W2 [4681.00 ft depth]) and one sample from an intershoal environment (sample H333 from well 14-13-6-14W2 [4652.00 ft depth]). The Midale Vuggy from the shoal facies is a bioclastic wacke-grainstone comprising granular micritic reworked clasts (Figure 15) that have been cemented by further micrite. The micritic matrix is partially dolomitised (Table 1, Figure 16). Fringes of clear, sub-euhedral to euhedral, equant calcite microspar (Figure 17) cement the reworked micritic grains and early dolomite. The microspar lines open voids and sheltered porosity. Bioclasts include bivalves, echinoderms, possible bryozoa, and possible gastropod and algal fragments, all of which have been replaced by neomorphosing drusy calcite microspar. Later, coarse, euhedral, dolomite and poikilotopic anhydrite infill some open voids (Figure 18).

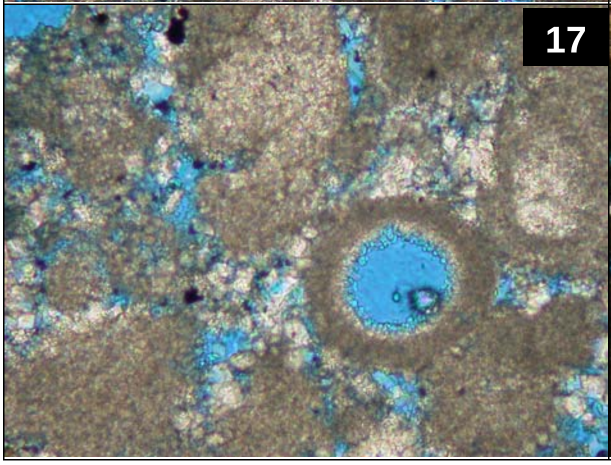
In contrast to the shoal areas, the intershoal Midale Vuggy sample contains no bioclastic material and consists of a micritic wackestone. This micrite has again been partially dolomitised though not to the same extent as the shoal limestones. In addition to the dolomitisation, porosity is enhanced by matrix dissolution to provide common oversized secondary voids. These are subsequently lined by calcite microspar. As seen in the shoal limestones, poikilotopic anhydrite reduced porosity by infilling some of the largest voids, although this has been corroded in some areas.

The Midale Vuggy sample used in these experiments was taken from well 12-11-6-14W2 at a depth of 1426.85 m (4681.25 ft) (for a review of previous mineralogical analyses and more details of the sample selection process, the reader is referred to Pearce and Springer (2001) and references therein). The Midale Vuggy is a crypto-crystalline to micro-crystalline, thin bedded, slightly argillaceous, recrystallised mudstone-wackestone with intergranular, intragranular, moldic and vuggy porosity.

The surface area of a 250-500 µm ‘fine free’ fraction of Midale Vuggy was measured using N_2 BET. It had a surface area of 0.22 m^2g^{-1}.







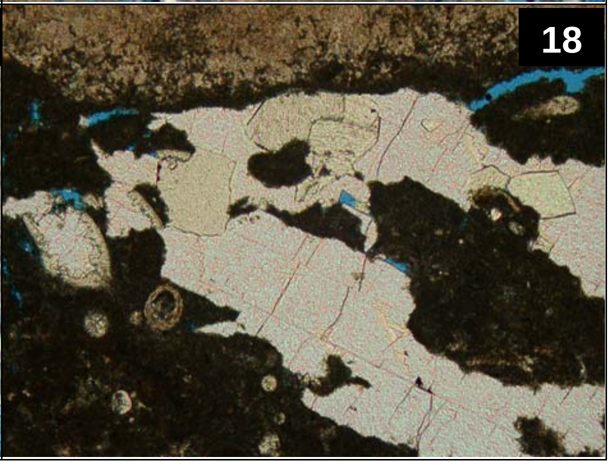


Figure 15 Typical view of bioclastic wacke-grainstone with abundant coarse, well connected intergranular, sheltered and moldic porosity indicated by blue-dyed resin impregnation. Width of field of view is 0.88 mm. (BGS sample identification = H337, image identification = Dscn0449, well = 14-1-6-14W2, sample depth = 4751.50 ft).

Figure 16 Micritic matrix partially dolomitised. Width of field of view is 0.44 mm. (BGS sample identification = H337, image identification = Dscn0456, well = 14-1-6-14W2, sample depth = 4751.50 ft).

Figure 17 Close-up of Figure 15, showing development of calcite microspar fringing open porosity. Width of field of view is 0.44 mm. (BGS sample identification = H337, image identification = Dscn0447, well = 14-1-6-14W2, sample depth = 4751.50 ft).

Figure 18 Open voids lined by calcite spar and subsequently infilled by coarse, poikilotopic anhydrite. Width of field of view is 1.75 mm. (BGS sample identification = H341, image identification = Dscn0433, well = 12-11-6-14W2, sample depth = 4681.00 ft).

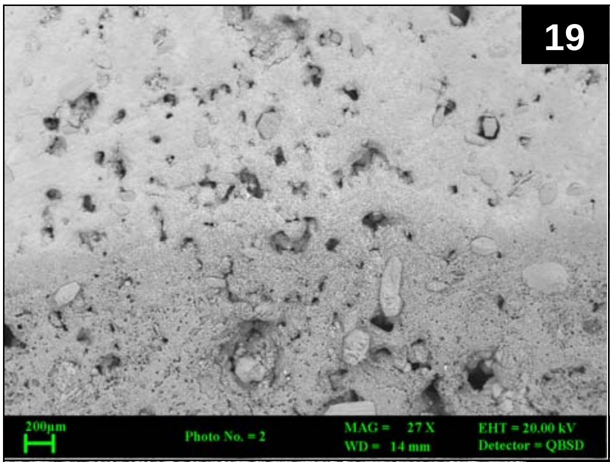
Table 1 X-ray diffraction mineralogical analyses of selected Midale Vuggy (V2) samples.

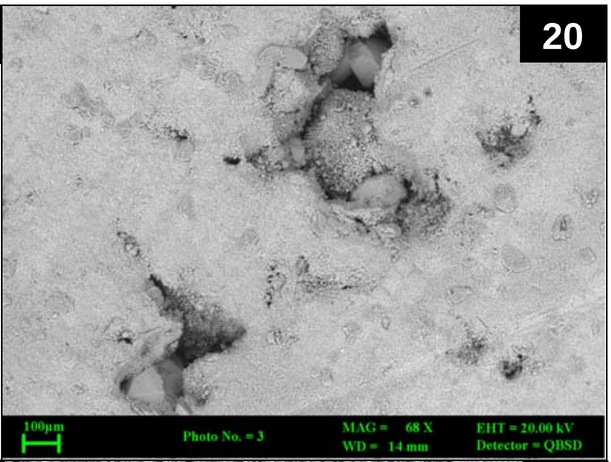
Well no.	Depth (ft)	Stratigraphic Group	GEUS Plug no.	BGS lab code	Description	Whole-rock XRD				
						dolomite	calcite	quartz	anhydrite	'mica'
14-13-6-14W2	4652.5	Midale Vuggy, V2	BGS4	H333	weakly laminated, light grey, fine to medium grained carbonate with conspicuous porosity	?tr	mj	tr	mi	?tr
14-1-6-14W2	4751.5	Midale Vuggy, V2	BGS8	H337	light grey carbonate	mi	mj	tr	-	-
12-11-6-14W2	4681.0	Midale Vuggy, V2	BGS12	H341	light grey, fine to medium grained carbonate with conspicuous porosity	tr	mj	tr	-	?tr

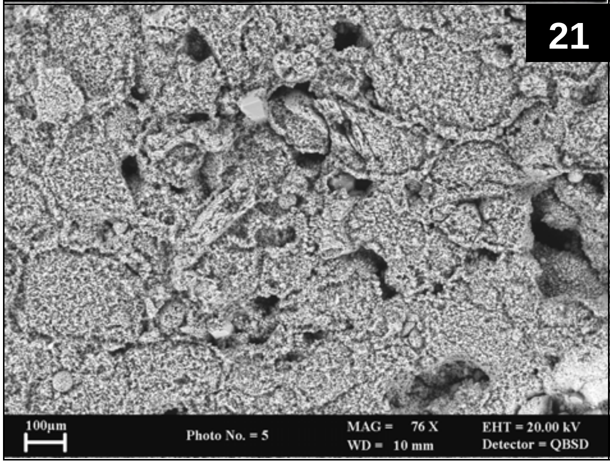
mj = major; mi = minor; tr = trace; '-' = not detected
'mica' = undifferentiated mica species

Table 2 Experimental run products analysed in this study.

Lithology	Starting sample	HTL Code	MPL Code	Expt.	Run Code	Description	Duration
Midale Vuggy	BGS12A	HTL136	J859S1	CO2	1095	Monolith block	4 weeks
Midale Vuggy	BGS12A	HTL136	J861S1	CO_2	1103	Monolith	8 weeks
Midale Vuggy	BGS12A	HTL136	J879S1	CO_2	1094	Monolith	17 weeks
Midale Vuggy	BGS12A	HTL136	J880S1	N_2	1117	Monolith	17 weeks
Midale Vuggy	BGS12A	HTL136	H638S1	n/a	n/a	250-500 µm	Starting material
Midale Vuggy	BGS12A	HTL136	H638S4	CO_2	1086	Experimental apparatus surface	2 weeks
Midale Vuggy	BGS12A	HTL136	H638S5	CO_2	1086	Experimental apparatus surface	2 weeks
Midale Vuggy	BGS12A	HTL136	H638S3	CO_2	1086	250-500 µm	2 weeks
Midale Vuggy	BGS12A	HTL136	J877S1	CO_2	1098	250-500 µm	12 weeks
Midale Vuggy	BGS12A	HTL136	J878S1	N_2	1099	250-500 µm	12 weeks
Midale Vuggy	BGS12A	HTL136	J873S1	CO_2	1101	<250 µm	6 weeks
Midale Vuggy	BGS12A	HTL136	J874S1	N_2	1102	<250 µm	6 weeks
Midale Vuggy	BGS12A	HTL136	J875S1	CO_2	1077	<250 µm	26 weeks
Midale Vuggy	BGS12A	HTL136	J876S1	N_2	1078	<250 µm	26 weeks







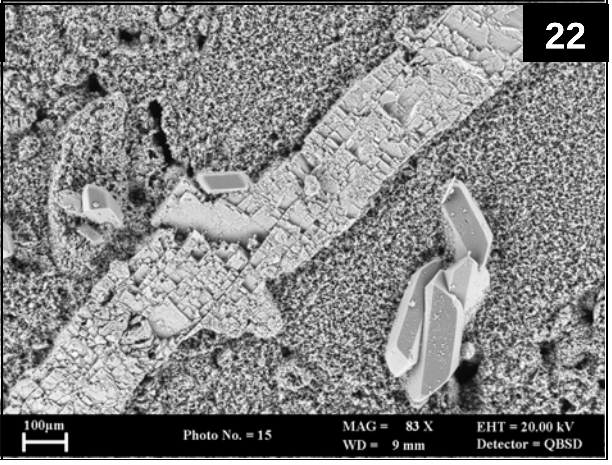


Figure 19 View of Midale Vuggy monolith surface showing the boundary between the lower submerged etched surface with secondary gypsum and upper uncorroded surface. Note that the large vugs seen across the whole surface are secondary dissolution features formed during diagenesis. (Run 1103, CO_2 experiment, 8 weeks duration, image = J861S101.tif).

Figure 20 Typical view of Midale Vuggy monolith surface above the water line with pre-existing secondary voids and the smooth, sawn surface, for comparison with Figures 21 and 22. (Run 1103, CO_2 experiment, 8 weeks duration, image = J861S103.tif).

Figure 21 Corroded Midale Vuggy monolith surface below the waterline showing extensive dissolution after 4 weeks reaction, for comparison with Figures 20 and 22. (Run 1095, CO_2 experiment, 4 weeks duration, image = J859S106.tif).

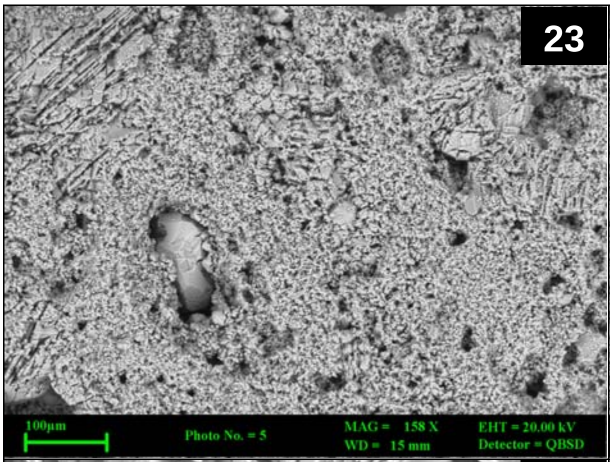
Figure 22 Corroded Midale Vuggy monolith surface below the waterline showing increased dissolution after 8 weeks compared to that after 4 weeks, for comparison with Figures 20 and 21. Note that calcite spar remains uncorroded. (Run 1103, CO_2 experiment, 8 weeks duration, image = J861S105).

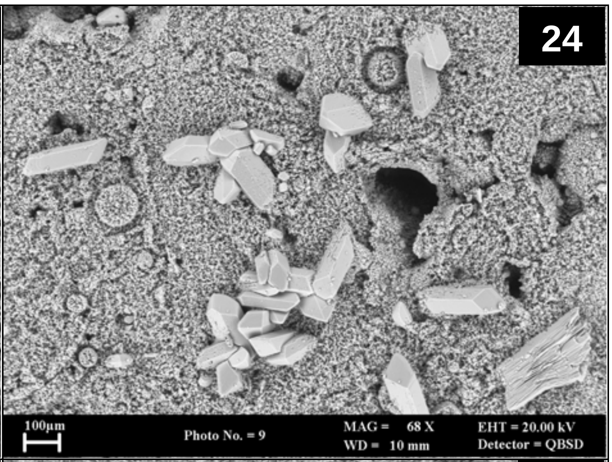
3.2 REACTION PRODUCTS

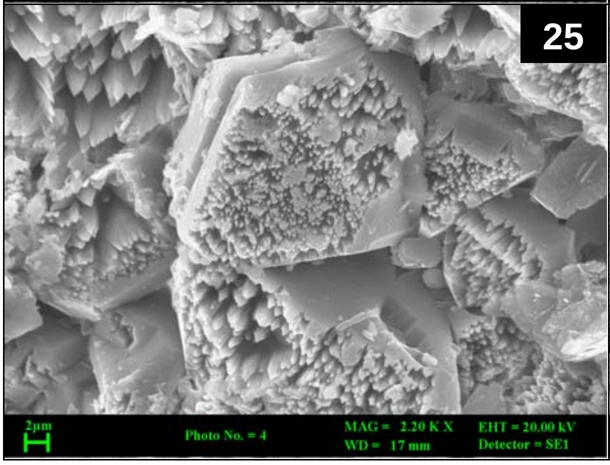
The experimental run products examined are listed in Table 2.

3.2.1 Monoliths

After 4 weeks reaction with CO_2, the lower portion of the monolith block was slightly bleached and encrusted with gypsum crystals (Figure 19). In contrast, the surfaces above the water level remained unreacted (Figure 20). When examined by SEM, the submerged surface is significantly etched to a depth of around 10-30 µm (Figure 21). The corrosion caused by reaction with the CO_2-saturated porewater can be easily differentiated from pre-existing







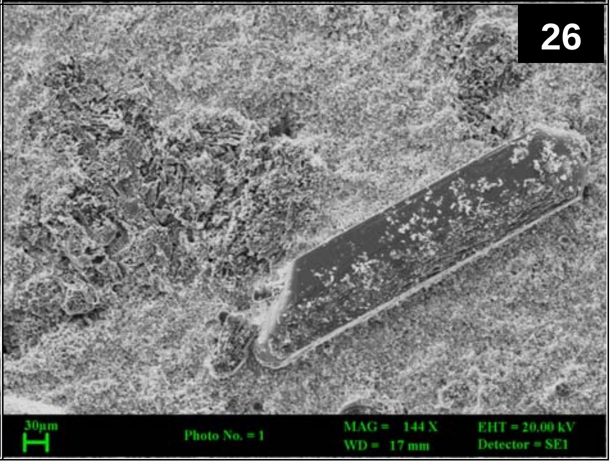


Figure 23 Clusters of twinned, euhedral, tabular gypsum crystals encrusting monolith surfaces below the waterline. Note the corroded echinoderms in this area. (Run 1095, CO_2 experiment, 4 weeks duration, image = J859S109.tif).

Figure 24 A corroded anhydrite veinlet and secondary twinned gypsum crystals. (Run 1095, CO_2 experiment, 4 weeks duration, image = J859S115.tif).

Figure 25 Corroded calcite microspar from a Midale Vuggy monolith. (Run 1117, N_2 experiment, 17 weeks duration, image = J880S104.tif).

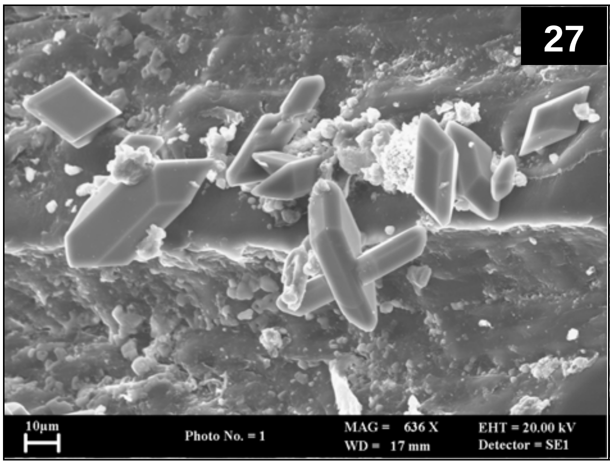
Figure 26 A tabular gypsum crystal, partially coated in halite. Note corrosion of monolith surface. (Run 1117, N_2 experiment, 17 weeks duration, image = J880S101.tif).

secondary voids developed during diagenesis. In addition to calcite, a thin hairline veinlet mineralised by anhydrite is also corroded in the CO_2-saturated fluid (Figure 22).

After 8 weeks of reaction, the degree of corrosion increased only slightly (Figure 23). This supports the fluid chemistry data that indicates rapid dissolution in the first few weeks before trending towards steady state conditions. Dissolution occurred preferentially in the finer-grained micritic matrix and bioclasts, while the coarser calcite spar that partially infills some voids remains uncorroded (Figures 22 and 24).

Euhedral, elongate to tabular gypsum crystals develop up to 3 mm long, after 4 weeks of reaction (Figure 24). These do not appear to grow significantly larger during the further 8 or 17 weeks of reaction.

After 17 weeks, a halite crust obscured much of the surface above the waterline and was also developed to a more limited extent below the waterline. It is thought that this represents *in-situ* precipitation that occurred during the experiments and is not an artefact of subsequent



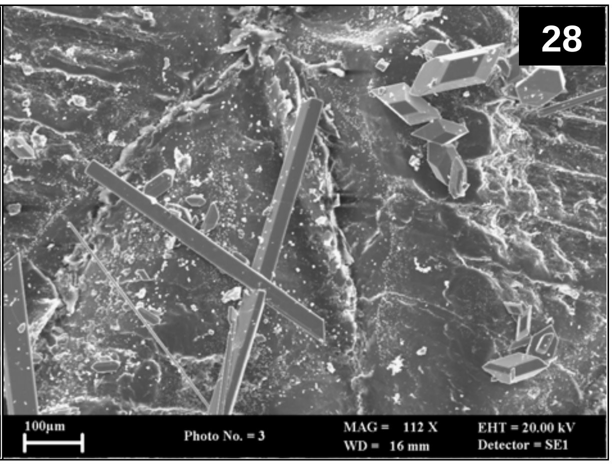


Figure 27 Euhedral tabular gypsum crystals, some twinned, developing on experimental surfaces during reaction with 250-500 µm crushed Vuggy limestone grains. (Run 1086, CO_2 experiment, 2 weeks duration, image = H638S401.tif).

Figure 28 Euhedral tabular and bladed gypsum crystals, some twinned, developing on experimental surfaces during reaction with 250-500 µm crushed Vuggy limestone grains. (Run 1086, CO_2 experiment, 2 weeks duration, image = H638S403.tif).

sample drying, since it can be differentiated from larger ‘hopper’ crystals that are more likely to have formed during sample drying.

Dissolution also occurred in the N_2-baseline experiments and the corrosion was relatively extensive below the waterline (Figure 25). Gypsum crystals also developed, up to approximately 500 µm in length (Figure 26) in contrast to the 2-3 mm scale crystals developed in the CO_2-reacted monoliths.

3.2.2 Granular material

The degree of dissolution is significantly reduced in the experiments containing crushed Midale Vuggy limestone. As with the monoliths, the microspar remains fresh throughout. After 26 weeks of reaction, the only (very tentative) evidence for dissolution in the <250 µm crushed samples was slightly less ‘dust’ in the N_2 experiment relative to the CO_2 experiment. Euhedral tabular prismatic gypsum crystals up to 1.8 mm long developed after 2 weeks reaction. These crystals developed on the experimental surfaces (Figures 27 and 28).

4 Conclusions

An experimental study has been undertaken to react CO_2 with samples of the Midale Vuggy and a synthetic formation water. These were reacted at 60°C and at 150 bar [15 MPa] (representative of *in-situ* conditions), and also at 250 bar [25 MPa] (possible conditions at the bottom of injection wells). Similar, non-reacting experiments pressurised with N_2 were also undertaken. Experiment durations ranged from one week to 6 months. The aim of this study was to provide a description and quantification of important fluid-mineral reactions.

The evolution over time of a selection of solutes was followed. Relative to the N_2 'baseline' experiments, it was found that the impact of CO_2 was to:

- increase the concentrations of Ca, Si and HCO_3^-
- decrease the concentrations of total S and possibly Sr, and pH values
- have little impact on the concentrations of Mg, Mn and Al

It is noted that these fluid chemical changes are not dissimilar to those found in the Midale Marly experiments.

All monoliths reacted in CO_2-rich synthetic pore waters showed clear evidence of 'tidemarks' on their external surfaces, with the area below the water-CO_2 interface appearing bleached. After 4 weeks of reaction of the monoliths with CO_2, euhedral prismatic gypsum crystals up to 500 µm in length formed below the water line in the CO_2 experiment. By 8 weeks reaction the gypsum crystals were at least 2.5 mm long, and at 17 weeks reaction gypsum crystals up to 500 µm long also developed in the baseline N_2 experiment. In addition, most calcite and anhydrite surfaces below the water line were corroded to a depth of 10-30 µm in both the CO_2 and the baseline N_2 experiments. This porosity was easily distinguishable from the vuggy porosity developed during diagenesis. Scanning electron microscopy also revealed that a fine coating of halite developed above the water-CO_2 interface during the experiment.

In the experiments containing crushed Midale Vuggy, euhedral tabular prismatic gypsum crystals up to 1.8 mm long developed after 2 weeks reaction. Only limited evidence for minor corrosion was tentatively observed. After 26 weeks of reaction, the only evidence for dissolution in the <250 µm crushed samples was slightly less 'dust' in the baseline N_2 experiment relative to the CO_2 experiment.

It was noted that the CO_2 experiments give lower S concentrations compared to the N_2 experiments. It is possible that S (as SO_4) is being removed from solution by gypsum precipitation. During the early parts of the experiments at least, this appears to be faster than the rate of SO_4 addition from anhydrite dissolution. Later in the CO_2 experiments steady-state concentrations appear to be reached, and it is likely that saturation with respect to gypsum balances lower S concentrations with higher Ca concentrations.

The changes described above were interpreted as probably being due to some calcite dissolution (probably more than observed in the Midale Marly experiments), some anhydrite dissolution, a little aluminosilicate mineral dissolution, and a fair amount of gypsum precipitation.

Overall therefore, the Midale Vuggy material showed the greatest potential for both dissolution and secondary mineral precipitation. It is unclear at the moment whether these would lead to an overall net increase or decrease in porosity or permeability. However, if significant gypsum precipitation reduced the permeability of the Midale Vuggy unit, then this may be a beneficial reaction in terms of the EOR operation, as it might reduce the potential for the injected CO_2 to 'under-ride' the target Marly unit.

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Appendix 1

Uncertainty and data screening

It is to be expected in any large experimental study, that there will be some (hopefully few) ‘unusual’ and unexplainable data points. The aim of this section is to identify how these might arise and how they were dealt with in this study.

Prior to identifying specific areas of uncertainty, it is worth making a few general comments on how the data were used. During data interpretation, most emphasis was placed on *trends* in the data rather than on individual data points – one particular sample may have been contaminated, or a datum might be in error. As a consequence, a higher degree of certainty in the data can be obtained by concentrating on several consistent data points, which may even come from several experiments. This is very important when assessing the degree of confidence in the data.

There are various reasons why some experimental data may seem at odds with most of the rest of a dataset. These can include: poor experimental set-up and running, sample contamination, unexpected experimental failure, and misreadings of analytical information. All the experiments reported here were set up using the same procedures, and these are outlined in Rochelle et al. (2002a). They were also set up in the same way as experiments using samples of Midale Marly (Rochelle *et al.*, 2003a) and Midale Evaporite (Rochelle *et al.*, 2003b). This should have provided some consistency in technique.

Once running, most of the experiments remained stable, though a few experienced pressure variations. These were caused by factors such as power cuts and seal failures. As several experiments (usually 4, but up to 8) were linked together at a time, sudden pressure loss in one invariably caused pressure loss in the rest. By and large however, these were transitory compared to the lifetime of the experiments, and so had minimal overall impact. Most of the sudden pressure decreases were caused by O-ring failures, usually by extrusion but sometimes by simple shearing. High-pressure syringe pumps running in ‘constant pressure’ mode compensated for slow leaks in CO_2. A regulated N_2 cylinder provided a similar function for the N_2 experiments. Regular checks on these helped identify potential slow leaks. Although slow leakage of CO_2 or N_2 was not itself a problem, it also removed water vapour. This is more important, as a significant amount of water can be lost from an experiment over several weeks. The effect of this would be to increase the concentration of solutes (i.e. increases the salinity), in extreme cases potentially to the point of rendering the data from that experiment as too uncertain to use.

Another source of possible artefacts in the data is sampling. By and large, this was done relatively rapidly by extracting a small sample, and cooling and depressurising it. This was then subject to appropriate sample preservation (see Rochelle *et al.*, 2002a). However, occasionally samples had to be taken after the whole of the reaction vessel had been depressurised, and sometimes also partly cooled (e.g. because the sample valve had become blocked, or because of O-ring failure). This delay in sampling may have allowed the solution to partially equilibrate with the new pressure and temperature conditions, and hence might have caused some chemical changes.

Although all samples were analysed in line with BGS quality assurance (QA) procedures, it is worth commenting on the samples. For IC and ICP analysis (most of the anions and all the cations), samples were grouped together and were analysed in several batches throughout the experimental programme. Internal standards were run during all batches of analyses to ensure that different batches of analyses were comparable. Some batches of samples presented no great difficulties and gave good charge-balances (e.g. LIMS numbers 10526-****, see Appendix 2). Other samples however, had to be re-analysed several times until a consistent set of data was achieved. Instrument instability may have been a reason for some of the inconsistencies. Some unexpected charge imbalances might also have been a function of exactly where a set of analyses lay within the QA-defined bounds (e.g. an overly positive charge imbalance would result if a set of cation analyses lying at the *upper* bound of the acceptable QA range were combined with a set of anion analyses at the *lower* bound of the acceptable QA range). Whatever the exact reason for the problems encountered, significant effort was expended to ensure that there was good confidence in the analytical data and that they were of the highest quality.

Analysis of 'unstable' parameters (e.g. pH and bicarbonate) was carried out immediately after sampling. It is noted however, that some early high bicarbonate samples were not analysed soon enough after sampling (and hence gave lower than expected results). Later analyses of high bicarbonate samples (and all those data points plotted in this completed report) were carried out within 30 minutes of sampling.

Error bars of ±5% are used in most of the figures in this report. Although some of the analytical uncertainty will be less than this, a ±5% uncertainty was used as this should encompass most of the likely errors (i.e. from sample handling as well as analysis). However, the Al and Mn data are special cases, as they were very close to the detection limit. These data have been plotted with ±10% error bars, though uncertainty may actually be higher than this at the lowermost concentrations plotted. For pH measurements an error of ±0.1 units has been used.

Initial attempts to identify obviously problematic data from the Midale Vuggy experiments involved studying the results of relatively non-reactive analytes such as Cl^- and Na. These might normally be expected to remain unchanged throughout each experiment. In general, Cl^- concentrations remain fairly consistent over time (Figure A1). However, in detail, there *may* be a very slow increase over time, possibly caused by slow loss of water vapour from the experiments (removed with any escaping CO_2 or N_2).

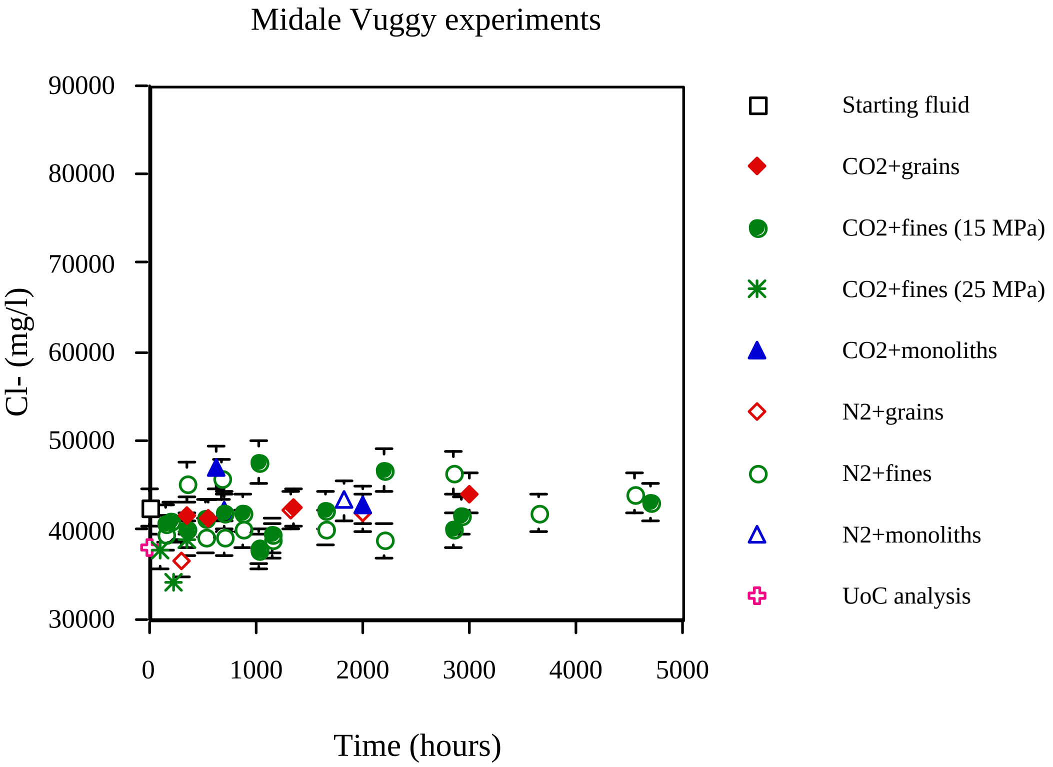

Figure A1 Results of Cl^- analyses (mg/l) from the Midale Vuggy batch experiments.

A similar process was used for Na, and all the available data are plotted in Figure A2. Most data have fairly consistent concentrations, although there *may* be a very slow increase over time, possibly due to slow loss of water vapour. However, the two longest timescale samples (from Runs 1077 and 1078) have slightly higher Na concentrations than might be expected (especially that from Run 1077 ['CO2+fines' experiment]). These samples were taken using a non-standard procedure, which was necessary because of sampling difficulties. As a consequence, these data (especially that from Run 1077) should be treated with caution, though their data have been plotted in this report.

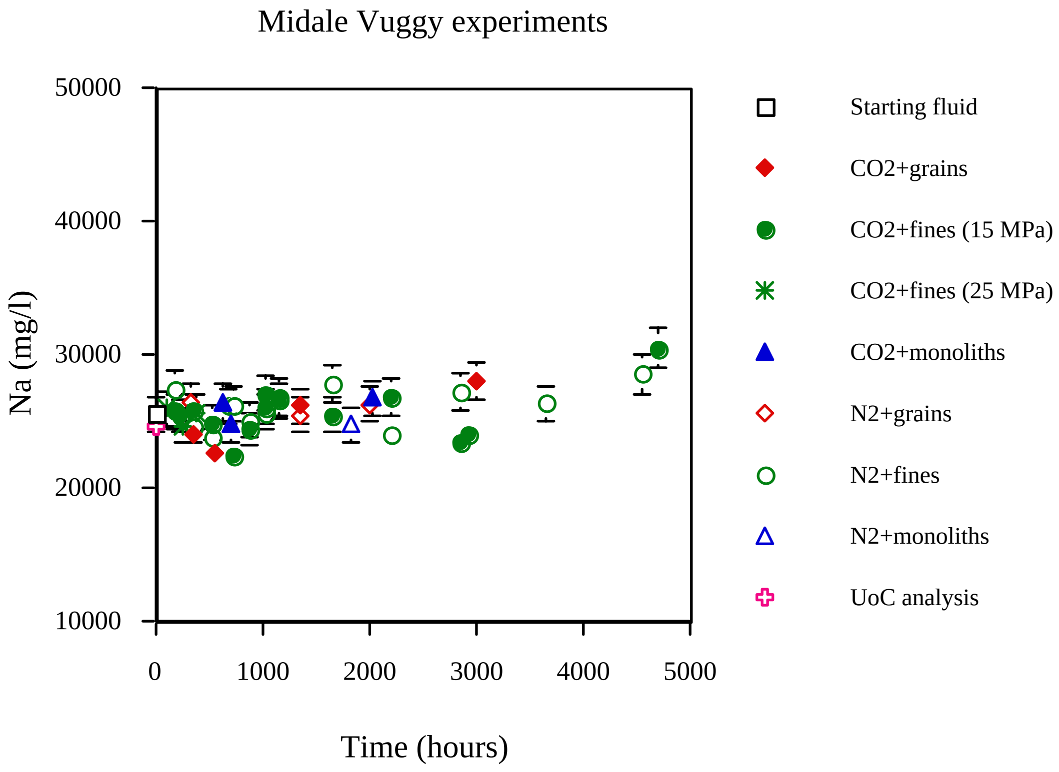

Figure A2 Results of Na analyses (mg/l) from the Midale Vuggy batch experiments.

Appendix 2

Formatted analytical data for the Midale Vuggy experiments.

Note that data in brackets () are identified as ‘suspect’ in some way, and may well have not been used in some of the figures in this report.

ID number	Gas	State	Pressure (MPa)	Temp. (°C)	Run no.	On	Off	Elapse time (h)	Solid used (g)	Solution used (g)
BGS12A	-				12-11-6-14 (initial analysis)			0	-	-
(HTL 136)	-				12-11-6-14 (repeat analysis)			0	-	-
(Vuggy)										
	CO2	250-500µm	15	60	1086	31/03/2003 16:00	15/04/2003 14:40	358.7	4.9996	49.9993
	CO2	250-500µm	15	60	1093	30/04/2003 23:20	23/05/2003 23:30	552.2	4.9996	49.9998
	CO2	250-500µm	15	60	1081	28/03/2003 10:30	23/05/2003 11:15	1344.8	5.0008	49.9997
	CO2	250-500µm	15	60	1098	08/05/2003 14:30	10/09/2003 13:30	2999.0	4.9997	49.9997
	N2	250-500µm	15	60	1082	28/03/2003 12:15	10/04/2003 14:00	313.8	4.9997	49.9992
	N2	250-500µm	15	60	1080	28/03/2003 10:45	23/05/2003 10:25	1343.7	5.0008	49.9993
	N2	250-500µm	15	60	1099	08/05/2003 15:15	31/07/2003 10:40	2011.4	4.9996	50.0003
	CO2	<250 µm	15	60	1101/1	14/05/2003 14:45	21/05/2003 11:25	164.7	8.0004	80.000
	CO2	<250 µm	15	60	1101/2	14/05/2003 14:45	29/05/2003 09:45	355.0	*	*
	CO2	<250 µm	15	60	1101/3	14/05/2003 14:45	05/06/2003 15:00	528.2	*	*
	CO2	<250 µm	15	60	1101/4	14/05/2003 14:45	13/06/2003 11:00	716.3	*	*
	CO2	<250 µm	15	60	1101/5	14/05/2003 14:45	20/06/2003 11:05	884.3	*	*
	CO2	<250 µm	15	60	1101/6	14/05/2003 14:45	26/06/2003 14:10	1031.4	*	*
	CO2	<250 µm	15	60	1077/1	12/12/2002 12:00	29/01/2003 12:00	1152.0	6.0001	60.0108
	CO2	<250 µm	15	60	1077/2	12/12/2002 12:00	19/02/2003 15:50	1659.8	*	*
	CO2	<250 µm	15	60	1077/3	12/12/2002 12:00	14/03/2003 09:30	2205.5	*	*
	CO2	<250 µm	15	60	1077/4	12/12/2002 12:00	10/04/2003 17:15	2861.3	*	*
	CO2	<250 µm	15	60	1077/5	12/12/2002 12:00	13/04/2003 11:00	2927.0	*	*
	CO2	<250 µm	15	60	1077/6	12/12/2002 12:00	26/06/2003 15:45	4707.8	*	*
	CO2	<250 µm	15	60	1120/1	01/07/2003 11:35	10/07/2003 13:55	218.3	5.001	50.000
	CO2	<250 µm	15	60	1120/2	01/07/2003 11:35	15/07/2003 14:25	338.8	*	*
	CO2	<250 µm	15	60	1120/3	01/07/2003 11:35	23/07/2003 13:25	529.8	*	*
	CO2	<250 µm	15	60	1120/4	01/07/2003 11:35	30/07/2003 10:00	694.4	*	*
	CO2	<250 µm	15	60	1120/5	01/07/2003 11:35	13/08/2003 11:30	1031.9	*	*
	N2	<250 µm	15	60	1102/1	14/05/2003 14:30	21/05/2003 12:00	165.5	8.0003	80.000
	N2	<250 µm	15	60	1102/2	14/05/2003 14:30	29/05/2003 10:15	355.8	*	*
	N2	<250 µm	15	60	1102/3	14/05/2003 14:30	05/06/2003 14:25	527.9	*	*
	N2	<250 µm	15	60	1102/4	14/05/2003 14:30	13/06/2003 10:25	715.9	*	*
	N2	<250 µm	15	60	1102/5	14/05/2003 14:30	20/06/2003 11:40	885.2	*	*
	N2	<250 µm	15	60	1102/6	14/05/2003 14:30	26/06/2003 11:20	1028.8	*	*
	N2	<250 µm	15	60	1078/1	12/12/2002 13:00	29/01/2003 12:30	1151.5	6.0002	60.0002
	N2	<250 µm	15	60	1078/2	12/12/2002 13:00	19/02/2003 15:30	1658.5	*	*
	N2	<250 µm	15	60	1078/3	12/12/2002 13:00	14/03/2003 09:50	2204.8	*	*
	N2	<250 µm	15	60	1078/4	12/12/2002 13:00	10/04/2003 16:40	2859.7	*	*
	N2	<250 µm	15	60	1078/5	12/12/2002 13:00	13/05/2003 12:00	3647.0	*	*
	N2	<250 µm	15	60	1078/6	12/12/2002 13:00	20/06/2003 16:00	4563.0	*	*
	N2	<250 µm	15	60	1124/1	06/08/2003 09:00	11/08/2003 13:55	124.9	8.001	79.999
	N2	<250 µm	15	60	1124/2	06/08/2003 09:00	13/08/2003 13:50	172.8	*	*
	N2	<250 µm	15	60	1124/3	06/08/2003 09:00	22/08/2003 11:30	386.5	*	*
	N2	<250 µm	15	60	1124/4	06/08/2003 09:00	03/09/2003 11:20	674.3	*	*
	N2	<250 µm	15	60	1124/5	06/08/2003 09:00	10/09/2003 11:55	842.9	*	*
	CO2	<250 µm	25	60	1119/1	30/06/2003 12:00	04/07/2003 13:05	97.1	50.000	5.001
	CO2	<250 µm	25	60	1119/2	30/06/2003 12:00	10/07/2003 16:05	244.1	*	*
	CO2	<250 µm	25	60	1119/3	30/06/2003 12:00	15/07/2003 16:00	364.0	*	*
	CO2	Monolith	15	60	1095	07/05/2003 14:30	05/06/2003 16:10	697.7	13.6157	36.6596
	CO2	Monolith	15	60	1094	07/05/2003 14:30	30/07/2003 15:00	2016.5	15.3435	31.2918
	CO2	Monolith	15	60	1103	20/06/2003 14:50	16/07/2003 10:55	620.1	14.4267	30.4375
	N2	Monolith	15	60	1117	26/06/2003 16:50	10/09/2003 13:10	1820.3	13.7040	31.452

n/d = not determined
n/s = no sample
( ) = uncertain data
< = value less than detection limit
* = experiment should have maintained the original solid mass, but the amount of solution decreased as samples were withdrawn

Comments	LIMS code	pH	Ca2+ mg l-1	Mg2+ mg l-1	Na+ mg l-1	K+ mg l-1	HCO3- (old) mg l-1	HCO3- (new) mg l-1
	10583-0024	7.32	(828)	(315)	(18736)	(233)	(254)	n/d
	10762-0037	7.81	1123	467	25453	358	n/d	74
2mm crystals seen on dip tube assembly	10583-0020	6.39	2023	434	23812	295	(3710)	n/d
	10624-0005	6.29	1977	426	22509	303	(795)	n/d
	10624-0002	6.24	2073	476	26019	336	(804)	n/d
	10680-0001	6.46	2264	510	27918	391	n/d	4197
	10762-0035	7.42	1156	468	26297	355	n/d	<44
	10624-0001	6.58	1171	457	25359	319	51.0	n/d
Alkaline sample taken using 2M NaOH. Seemed to work very well. Very small crystals in solid - too small to retrieve	10680-0002	7.07	1279	465	26142	363	n/d	n/d
	10624-0018	6.34	2240	481	25617	329	(505)	n/d
	10624-0019	6.50	2243	484	25654	325	(504)	n/d
	10624-0020	6.38	2173	465	24773	316	(874)	n/d
	10624-0021	6.43	1912	409	22217	275	(849)	4359
	10624-0022	6.41	2101	454	24219	309	(818)	4297
pH taken after depressurisation	10650-0002	(6.26)	(1583)	470	25959	347	n/d	(2017)
	10526-0033	6.39	2187	472	26472	338	(3047)	n/d
	10762-0041	6.37	2144	472	25334	339	n/d	(488)
	10762-0042	6.37	2256	497	26724	361	n/d	(432)
	10583-0013	6.38	1991	428	23284	292	(3534)	n/d
	10624-0007	6.41	1992	437	23968	299	(582)	n/d
pH taken after depressurisation	10624-0008	(6.58)	(1931)	541	(30325)	(433)	(220)	(1497)
Bicarbonate/pH re-analysis run	10650-0016	6.37	2214	470	25307	342	n/d	3321
	n/s	6.37	n/s	n/s	n/s	n/s	n/d	3674
	n/s	6.39	n/s	n/s	n/s	n/s	n/d	4208
	n/s	6.42	n/s	n/s	n/s	n/s	n/d	4341
	10680-0004	6.46	(1610)	491	26962	366	n/d	n/d
pH 6.31 LOW??	10624-0023	6.31	1358	489	27269	338	95.0	n/d
	10624-0024	6.50	1261	442	24598	304	<88.0	n/d
Unusally high pH	10624-0025	7.31	1204	423	23694	304	73.0	n/d
Unusally high pH	10624-0026	7.35	1339	470	26146	333	73.0	<220
	10624-0027	6.74	1265	443	24970	358	70.0	134
	10650-0003	6.52	1322	463	25540	347	n/d	133
	10526-0034	6.03	1303	453	26705	337	<176	n/d
Unusally high pH	10762-0043	7.30	1465	485	27713	377	n/d	<176
	10583-0015	5.98	1325	418	23870	289	<176	n/d
Unusally high pH	10762-0044	7.34	1444	470	27081	354	n/d	<176
	10624-0009	6.07	1440	454	26234	334	<88.0	n/d
pH taken after depressurisation	10624-0010	(7.73)	1528	477	(28413)	(469)	n/d	<88.0
Bicarbonate/pH re-analysis run	n/s	8.15	n/s	n/s	n/s	n/s	n/d	<88.0
	n/s	7.31	n/s	n/s	n/s	n/s	n/d	23.8
	n/s	7.96	n/s	n/s	n/s	n/s	n/d	<22.0
	10680-0006	7.77	1327	450	26033	362	n/d	24.4
	n/s	8.00	n/s	n/s	n/s	n/s	n/d	27.2
	10650-0013	6.44	2412	483	25867	345	n/d	3461
	10650-0014	6.41	2252	447	24456	322	n/d	4792
	10650-0015	6.42	2371	475	25554	337	n/d	3966
Part in water bleached, 4mm crystals seen	10624-0015	6.30	2095	464	24611	313	(797)	n/d
Part in water bleached, 2mm crystals seen	10650-0001	6.35	2231	495	26635	383	n/d	3500
Part in water bleached, 5mm bladed crystals seen	10650-0004	6.31	2141	489	26291	354	n/d	3946
	10680-0003	8.17	1158	437	24611	346	n/d	24.3

Cl- mg l-1	SO42- mg l-1	NO3- mg l-1	Cation Total meq l-1	Anion Total meq l-1	Balance %	Br- mg l-1	NO2- mg l-1	HPO42- mg l-1	F- mg l-1	TOC mg l-1	TIC mg l-1	Total P mg l-1	Total S mg l-1
(39909)	(3329)	(<15.0)	(889)	(1199)	(-14.9)	(<15.0)	(<10.0)	(<50.0)	(<5.0)	(<48.0)	(53.3)	(<1.0)	(901)
42416	3489	12.9	1211	1271	-2.39	<10.0	<5.0	<50.0	<5.0	n/d	n/d	<1.0	1257
41538	2555	47.4	1181	1287	-4.30	<30.0	<20.0	<100	<10.0	<48.0	904	<1.0	932
41364	2446	<20.0	1121	1231	-4.65	<20.0	<10.0	<100	<10.0	n/d	n/d	2.42	929
42366	2568	<20.0	1284	1262	0.86	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1077
44014	2602	<30.0	1380	1296	3.15	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1082
36573	3100	224	1250	1128	5.11	<10.0	<5.0	<50.0	539	n/d	n/d	<1.0	1395
42202	3390	<20.0	1208	1262	-2.19	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1387
41776	3356	<30.0	1249	1248	0.03	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1367
40718	2554	<20.0	1275	1210	2.61	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1110
39978	2360	<20.0	1277	1185	3.72	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1054
41332	2466	<20.0	1233	1233	0.01	<20.0	<10.0	<100	26.3	n/d	n/d	16.6	1004
41826	2486	<20.0	1103	1249	-6.19	<20.0	<10.0	<100	65.2	n/d	n/d	3.24	869
41910	2490	<20.0	1204	1253	-1.98	<20.0	<10.0	<100	101	n/d	n/d	<2.0	970
37510	2400	<30.0	1256	1108	6.27	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1141
39326	2448	<80.0	1309	1210	3.91	<60.0	<20.0	n/d	<100	<48.0	533	<0.50	1092
42163	2589	210	1257	1255	0.07	<20.0	<10.0	<100	13.8	n/d	n/d	<1.0	1037
46717	2806	236	1326	1391	-2.39	<20.0	<10.0	<100	65.4	n/d	n/d	<1.0	1083
39990	2532	140	1155	1241	-3.57	<15.0	<10.0	<50.0	<5.0	63.4	916	<1.0	917
41630	2116	<20.0	1186	1228	-1.73	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	946
43024	3194	<20.0	1472	1284	6.81	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	(1701)
40888	2484	<30.0	1259	1205	2.20	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1066
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
47440	2914	<30.0	1303	1399	-3.54	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1078
39600	3170	<20.0	1303	1186	4.71	<20.0	<10.0	<100	27.3	n/d	n/d	<2.0	1435
45296	3716	39.6	1178	1356	-7.03	<20.0	<10.0	<100	<10.0	n/d	n/d	4.35	1320
39292	3202	<20.0	1134	1176	-1.83	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1306
39042	3186	<20.0	1252	1169	3.44	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1452
40060	3262	<20.0	1196	1201	-0.21	<20.0	<10.0	<100	28.4	n/d	n/d	<2.0	1362
38012	3138	<30.0	1225	1141	3.53	<30.0	<20.0	<100	63.4	n/d	n/d	<1.0	1437
38831	3418	<80.0	1273	1166.59	4.37	<60.0	<20.0	n/d	<100	<48.0	<24.0	<0.50	1547
40125	3680	64.3	1329	1210	4.70	<20.0	<10.0	<100	<10.0	n/d	n/d	<1.0	1663
38703	3947	<15.0	1147	1173.99	-1.17	<15.0	<10.0	<50.0	<5.0	<48.0	<24.0	3.99	1429
46408	4337	188	1298	1403	-3.88	<20.0	<10.0	<100	13.2	n/d	n/d	<1.0	1626
41920	3828	<20.0	1260	1262	-0.11	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1616
44016	3526	<20.0	1364	1315	1.83	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1699
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
45670	3824	<30.0	1245	1368	-4.69	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1397
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
37562	2368	<30.0	1295	1109	7.73	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1099
34194	2048	<30.0	1222	1009	9.56	<30.0	<20.0	<100	25.2	n/d	n/d	<1.0	987
38874	2276	<30.0	1278	1145	5.50	<30.0	<20.0	<100	18.7	n/d	n/d	<1.0	1045
42232	2536	<20.0	1222	1257	-1.42	<20.0	<10.0	<100	<10.0	n/d	n/d	<2.0	1019
42826	2572	<30.0	1321	1262	2.30	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1115
46872	2664	<30.0	1300	1378	-2.88	<30.0	<20.0	<100	<10.0	n/d	n/d	<1.0	1097
43236	3459	<30.0	1174	1293	-4.85	<30.0	<20.0	<100	30.0	n/d	n/d	<1.0	1260

Si mg l-1	SiO2 mg l-1	Ba mg l-1	Sr mg l-1	Mn mg l-1	Total Fe mg l-1	Al mg l-1	Co mg l-1	Ni mg l-1	Cu mg l-1	Zn mg l-1	Cr mg l-1	Mo mg l-1	Cd mg l-1
(13.0)	(27.8)	(<0.20)	(16.9)	(<0.20)	(<1.0)	(<1.0)	(<0.20)	(<0.10)	(<0.20)	(<0.50)	(<0.20)	(<1.50)	(<0.20)
11.9	25.4	<0.20	24.3	<0.20	<1.0	<1.0	<0.20	<0.10	1.07	<0.50	<0.20	<1.50	<0.20
21.8	46.7	<0.20	22.5	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
23.4	50.1	0.296	22.5	0.246	4.92	1.48	<0.20	<0.20	1.84	0.700	<0.20	<1.50	<0.20
19.9	42.6	0.228	24.0	<0.20	2.01	<1.0	<0.20	<0.20	2.39	<0.50	<0.20	<1.50	<0.20
(46.8)	100	<0.20	26.7	<0.20	1.21	<1.0	<0.20	0.120	<0.20	<0.50	<0.20	<1.50	<0.20
17.2	36.9	<0.20	25.6	<0.20	<1.0	<1.0	<0.20	<0.10	0.509	<0.50	<0.20	<1.50	<0.20
16.1	34.5	<0.20	24.8	<0.20	<1.0	1.20	<0.20	<0.20	1.35	<0.50	<0.20	<1.50	<0.20
24.7	52.8	<0.20	26.2	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
28.7	61.4	0.215	25.9	<0.20	4.13	(3.86)	<0.20	<0.20	2.69	0.649	<0.20	<1.50	<0.20
36.0	77.0	<0.20	25.8	<0.20	1.52	1.18	<0.20	<0.20	1.80	<0.50	<0.20	<1.50	<0.20
32.5	69.5	0.645	24.9	<0.20	4.61	(11.6)	<0.20	<0.20	3.05	0.662	<0.20	<1.50	<0.20
26.6	57.0	0.265	22.0	<0.20	6.90	1.84	<0.20	<0.20	2.23	<0.50	<0.20	<1.50	<0.20
31.1	66.6	<0.20	24.3	<0.20	2.07	1.60	<0.20	<0.20	2.06	<0.50	<0.20	<1.50	<0.20
20.5	43.8	<0.20	22.6	<0.20	1.73	<1.0	<0.20	0.838	<0.20	<0.50	<0.20	<1.50	<0.20
18.6	39.7	0.360	23.2	0.108	0.592	0.572	<0.10	0.094	0.476	<0.25	<0.10	<0.75	<0.10
11.5	24.7	<0.20	23.9	<0.20	<1.0	<1.0	<0.20	<0.10	0.987	<0.50	<0.20	<1.50	<0.20
12.3	26.4	0.252	25.3	<0.20	<1.0	<1.0	<0.20	<0.10	0.494	<0.50	<0.20	<1.50	<0.20
17.2	36.7	<0.20	21.0	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
21.5	46.0	<0.20	21.9	<0.20	1.25	<1.0	<0.20	<0.20	1.28	<0.50	<0.20	<1.50	<0.20
25.5	54.6	0.245	23.0	<0.20	<1.0	<1.0	<0.20	<0.20	<1.0	<0.50	<0.20	<1.50	<0.20
14.0	29.9	<0.20	24.7	<0.20	<1.0	<1.0	<0.20	0.415	<0.20	<0.50	<0.20	<1.50	<0.20
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
22.9	48.9	<0.20	22.0	<0.20	<1.0	<1.0	<0.20	0.206	<0.20	<0.50	<0.20	<1.50	<0.20
27.0	57.7	0.395	26.9	<0.20	<1.0	<1.0	<0.20	<0.20	<1.0	<0.50	<0.20	<1.50	<0.20
28.3	60.5	<0.20	24.7	<0.20	1.34	(2.51)	<0.20	<0.20	3.07	<0.50	<0.20	<1.50	<0.20
25.1	53.7	<0.20	26.5	<0.20	<1.0	<1.0	<0.20	<0.20	1.33	<0.50	<0.20	<1.50	<0.20
27.8	59.4	0.49	29.3	<0.20	1.12	1.21	<0.20	<0.20	1.45	0.964	<0.20	<1.50	<0.20
32.4	69.4	<0.20	28.0	<0.20	<1.0	1.42	<0.20	<0.20	2.68	0.552	<0.20	<1.50	<0.20
18.9	40.4	<0.20	26.0	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
15.6	33.3	0.378	24.6	<0.10	<0.50	0.488	<0.10	<0.050	0.959	<0.25	<0.10	<0.75	<0.10
<7.50	<16.0	<0.20	29.0	<0.20	<1.0	<1.0	<0.20	<0.10	0.481	<0.50	<0.20	<1.50	0.201
9.35	20.0	<0.20	24.3	<0.20	1.11	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
<7.50	<16.0	0.206	28.1	<0.20	<1.0	<1.0	<0.20	<0.10	0.611	<0.50	<0.20	<1.50	<0.20
<7.50	<16.0	<0.20	27.3	<0.20	<1.0	<1.0	<0.20	<0.20	1.27	<0.50	<0.20	<1.50	<0.20
<7.50	<16.0	0.406	28.7	<0.20	<1.0	<1.0	<0.20	<0.20	1.00	0.604	<0.20	<1.50	<0.20
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
<7.50	<16.0	<0.20	25.7	<0.20	<1.0	<1.0	<0.20	<0.10	0.235	<0.50	<0.20	<1.50	<0.20
n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s	n/s
14.5	30.9	<0.20	25.4	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
14.2	30.3	<0.20	23.8	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
14.9	31.8	<0.20	25.1	<0.20	1.04	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
28.1	60.1	0.228	24.6	<0.20	1.56	<1.0	<0.20	<0.20	1.59	<0.50	<0.20	<1.50	<0.20
16.2	34.7	<0.20	26.8	<0.20	1.05	<1.0	<0.20	0.116	0.219	<0.50	<0.20	<1.50	<0.20
16.4	35.0	<0.20	26.1	<0.20	1.05	<1.0	<0.20	0.230	0.204	<0.50	<0.20	<1.50	<0.20
<7.50	<16.0	<0.20	24.2	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20

Pb mg l-1	V mg l-1	Li mg l-1	B mg l-1	As mg l-1	Se mg l-1
(<0.50)	(<1.0)	(<2.5)	(<2.5)	(<1.5)	(<1.5)
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<2.50	<1.50	<5.0
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<2.50	<1.50	<5.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.25	<0.50	<1.25	<1.25	<0.75	<0.75
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s
<0.50	<1.0	<2.50	<2.50	<1.50	<5.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.25	<0.50	<1.25	<1.25	1.27	<0.75
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s
n/s	n/s	n/s	n/s	n/s	n/s
<0.50	<1.0	<2.50	<2.50	<1.50	<5.0
n/s	n/s	n/s	n/s	n/s	n/s
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<6.0	<1.50	<2.0
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<1.50
<0.50	<1.0	<2.50	<2.50	<1.50	<5.0