

CO₂ IN NORTH SEA STORAGE ANALOGUE

**CO₂ - MINERAL REACTION IN A NATURAL ANALOGUE FOR CO₂ STORAGE-
IMPLICATIONS FOR MODELLING**

MARK WILKINSON¹, R. STUART HASZELDINE¹, ANTHONY E. FALICK²; NICOLAS ODLING¹
SUE STOKER³ & ROBERT GATLIFF³

¹ School of GeoSciences, The University of Edinburgh, Grant Institute, The King's Buildings, West Mains Road, Edinburgh, EH9 3JW

² Scottish Universities Environmental Research Centre, East Kilbride, G75 0QU, Scotland.

³ British Geological Survey, 376 Gilmerton Road, Edinburgh EH17 7QS.

mark.wilkinson@ed.ac.uk

KeyWords: CO₂, storage, mineral reaction, North Sea, Rotliegend

ABSTRACT: Geochemical models of CO₂ injection into reservoir sandstones often predict the growth of minerals that will permanently store the CO₂ in solid form, and injection experiments record significant fluctuations in porewater chemistry on a short time scale. Yet the proportion of CO₂ reaction may be small, even over geological time scales. A southern North Sea (UK) gas accumulation with a high natural CO₂ content (c. 50 %) forms a natural analogue to engineered storage, and provides a calibration point for computer models of CO₂-rock reaction. In the analogue site, the carbonate mineral dawsonite has formed in only trace amounts (0.4 ± 0.3 % solid volume) even after at least 50 Ma. It is calculated that only 2.4 (± 0.9) % of the CO₂ present within the structure is currently locked up as dawsonite, and a similar quantity in solution in the porewaters. Comparison of stable O and C stable isotopes with a neighbouring field with low CO₂ content gas suggests that up to 0.7 (± 2) % solid volume dolomite cement is associated with the CO₂ charge, equivalent to 0 – 25 % of the total CO₂. The remaining 70 - 95 % of the CO₂ is present as a free phase, after tens of millions of years. Consequently, geological storage of anthropogenic CO₂ must rely on physical containment and not mineral sequestration. The Rotliegend Group is still an excellent candidate for a CO₂ storage reservoir, though using physical trapping mechanisms and not chemical ones.

INTRODUCTION

One of the potential mitigation strategies for rising atmospheric CO₂ levels is the storage of large volumes of CO₂ in geological formations (IPCC, 2005). To ensure public support the technology must be shown to be safe, which involves predicting the fate of the CO₂ over thousands of years. Prediction of the fate of the injected CO₂ will rely upon modelling, since neither experiments nor test facilities can be run over the time scales of 1000s of years for which storage must be achieved. Many published geochemical modelling simulations predict that a significant percentage of the injected CO₂ will react with the reservoir rock to form solid minerals, effectively 'sequestering' the CO₂, with no possibility of escape back to the atmosphere (Gunter et al., 2000; Xu et al., 2005; Knauss et al., 2005; White et al., 2005; Zerai et al., 2006). To be of use, the predictions must both identify the correct chemical reactions that will occur and accurately estimate the volume of CO₂ that will be involved in these reactions. Predictions from simulations can be tested by investigation of natural CO₂ occurrences in sandstones or carbonate reservoirs where the CO₂ has been in contact with the host-rock for long periods of time. Here, we describe a natural high-CO₂ gas field from the UK North Sea which still contains potentially reactive K-feldspar. Despite these conditions, only a small proportion of the CO₂ is sequestered as mineral phases. This study provides a useful calibration point for geochemical modelling.

The southern North Sea hosts a large number of natural gas fields. Inspection of UK borehole records shows that CO₂ concentrations are generally low (0.5 to 1.5 mol %). However, in a minority of fields much higher concentrations are encountered, providing both a risk to commercial gas exploration and a natural laboratory to evaluate long-timescale CO₂-rock interaction. In the so-called Fizzy accumulation (Fig. 1), the CO₂ concentration of the reservoir gases is c. 50%, according to analyses performed by Tullow Oil plc. We have studied this reservoir, looking for minerals associated with the present day CO₂ charge that have 'sequestered' CO₂. As a control, we have also studied the geologically similar Orwell Field, which lies some 7 km to the NW of the Fizzy accumulation but in which the gas charge has only a low CO₂ content (< 2 %).

The reservoir within the Fizzy and Orwell accumulations is the early Permian Rotliegend Group, an important gas reservoir in the southern North Sea (Fig. 2). The sediments are predominantly sandstones deposited close to the margins of an inland desert area which covered much of northern Europe, and included large areas of sand dunes that today provide the best reservoirs. The Rotliegend Group is overlain by hundreds of metres of late Permian Zechstein halite evaporates, which provide an excellent seal (Fig 2). The sedimentology, mineralogy, and diagenesis of the Rotliegend Group has been extensively described from other gas fields in the area (see Ziegler, 2006, for a review).

In Fizzy, core samples are available from 2 wells, one well was drilled into the gas zone (UK well 50/26b-6), the other was drilled into the underlying water zone (UK well 50/26-1). The sandstone reservoir is c. 2300m deep, 80 – 100 m thick, and at a present day temperature of 80 – 85 °C. In Orwell, the Rotliegend

Group is at a similar depth, and has a comparable thickness and temperature to Fizzy. The Fizzy accumulation lies close to a regional-scale fault (Fig 3), identified by Tullow Oil plc, and remapped for this study. The tectonic history of the area is relatively complex, with at least 2 episodes of uplift interrupting sedimentation. The Fizzy accumulation, which lies to the east of the fault, has been uplifted by c. 440m since the upper Cretaceous, and by 800 – 1000m since the lower Triassic (Hillis, 1995).

METHODS

All the available conventional core from the Fizzy accumulation and the Orwell field was examined and logged. 40 thin sections were made for conventional petrographic examination, all were stained for feldspars and carbonates. Rock chips and polished thin-sections were studied using an SEM with EDS, back-scatter and CL. Gas and water zones were both studied. Mineral identification was by XRD of whole rock and fine-grain size separates using a Bruker-AXS D8 Advance with 2-theta configuration. Mineral abundances were estimated using the Bruker software package Topaz.

Oxygen and carbon isotopic analyses were performed on 20 whole-rock samples. CO₂ gas for isotopic analysis was extracted from whole-rock powder by overnight reaction with 100% phosphoric acid at 70°C. The evolved carbon dioxide gas was dried, purified before isotopic analysis on a VG-SIRA 10 Mass Spectrometer. Isotopic values are reported relative to V-PDB. A phosphoric acid fractionation factor of 1.01025 (Friedman and O'Neil, 1977) was used to correct the raw values for the $\delta^{18}\text{O}$ composition of the samples. Two samples of produced fluid samples were made available by Tullow Oil, one a gas and the other a water sample with a high gas content. Gas from both samples was cleaned up to remove non-CO₂ components and analysed as above for stable carbon isotope ratios.

RESULTS

The cored sections of the Fizzy accumulation and the Orwell field are interpreted as predominantly aeolian dune face sandstone with subordinate interdune facies. The sediments are predominantly coloured grey in both the reservoirs, despite the name of the Rotliegend Group. The bulk composition of the sandstones are summarised in Table 1 and Fig. 4. They majority are sublitharenites according to the classification of Pettijohn et al. (1973). The lithic fragments are a major constituent, and are predominantly quartz-dominated meta-sediments. Muscovite is the only other common mineral within these clasts. There are also fragments of volcanic rocks, some of which have been tentatively identified as trachyte based on microtexture. The majority of the presumed igneous rocks are highly altered and are unidentifiable. There are no intraclasts or clasts of unmetamorphosed sedimentary rock. None of the alkali feldspar is twinned, and is almost unidentifiable without chemical staining, unless it is partly dissolved forming secondary

porosity. There is a complete absence of plagioclase. Kaolin is generally present as discrete grain-sized clusters. There are no organic remains.

Within Fizzy, the abundance of dawsonite is low, with a maximum of 0.8% and means of 0.4 (± 0.3) % for both sampled wells determined by XRD. There is no detectable difference in dawsonite abundance between the gas and water zone wells. Separation of fine grain size fractions ($< 0.1 \mu\text{m}$) by settling resulted in substantially increased concentrations of dawsonite and increased the confidence of the identification (Fig. 5). It has not proved possible to visually identify dawsonite within the Fizzy accumulation sandstones within either thin-sections or rock chips despite extensive use of both light and SEM petrographic techniques. We infer the dawsonite to be clay sized. Neither calcite nor siderite have been identified in the sandstones. There is no dawsonite within the Orwell field, within the resolution of our methods.

Dolomite cement within the Fizzy and Orwell reservoir sandstones has a variable morphology, showing systematic changes with depth, i.e. with distance from the contact with the overlying Zechstein strata. At the top of the cored section the dolomite occurs as grain rimming rhombs with a crystal size that is much smaller than the detrital grain size (Figs. 6A and B). This cement is abundant, such that the majority of the detrital grain surfaces are coated either with individual rhombs or with a grain-coating layer of coalesced rhombs. These petrographical characteristics change gradually downward, with the size of the rhombs increasing and number of rhombs decreasing, until only pore-filling aggregates of dolomite crystals are present (Fig. 6C). These aggregates are substantially larger than the detrital grainsize and enclose detrital grains. Stable isotope data for whole-rock dolomite cement samples from Fizzy and Orwell are in Table 3 and Fig. 7, with regional data for comparison.

The two gas samples from the Fizzy accumulation gave similar results, with $\delta^{13}\text{C}$ of CO_2 of 4.3 and 4.6 ‰ V-PDB.

DISCUSSION

The origin of the CO_2 gas within Fizzy is unknown. The measured carbon isotopic ratios are not diagnostic of any particular process, though they eliminate derivation from organic carbon (Wycherley, et al. 1999). It is tempting to suggest that the high CO_2 -levels within the Fizzy accumulation are related to fluid movement along the regional-scale fault which lies to the west of the structure, but there is no direct evidence for this. However, well 54/1b-6 was drilled into another gas accumulation which lies along the same fault, and this also contained 'material' quantities of CO_2 according to a press release by the drilling company (Serica Energy, 2006). The exact timing of CO_2 charge into the Fizzy accumulation is also unknown, and is not easily resolvable as there are no minerals that definitely grew when the CO_2 arrived for which the isotopic fractionation factors are known. However, the area has been uplifted c. 440 m since the upper Cretaceous

(Hillis, 1995) which would stop thermally-driven CO₂ –generating reactions. Hence it seems likely that the CO₂ charged the reservoir before the inversion and consequently has been in the reservoir, in contact with any reactive minerals, for at least 50 Ma.

In order for the CO₂-charge to be significantly sequestered within a sandstone reservoir, then authigenic carbonate minerals must form. Most deeply buried sandstones contain authigenic carbonates from ‘ordinary’ diagenetic reactions. Consequently, a significant challenge is to identify and quantify those minerals related to the free-phase CO₂. Geochemical modelling in other accumulations suggests that any or all of siderite, calcite, dolomite and dawsonite might form (e.g. Xu et al., 2005; Knauss et al., 2005; White et al., 2005; Zerai et al., 2006). Of these minerals, only dawsonite is distinctively a product of unusually high CO₂ concentrations (e.g. Wopfner and Höcker, 1987, Hellevang et al., 2005; Bénézeth et al., 2007), the other carbonates can be either detrital in origin or form during ‘ordinary’ burial diagenesis.

Dawsonite cement

Dawsonite is known from localities worldwide. A review of classical occurrences at the surface can be found in Wopfner and Höcker (1987), from which it is apparent that dawsonite forms either within alkaline soils (e.g. within the Cretaceous Green River Formation, USA) or during diagenesis or hydrothermal activity associated with high CO₂ concentrations. It has not been previously reported within the southern North Sea, or in the Rotliegend Formation elsewhere. Given that this formation has been intensely studied, the occurrence in the Fizzy accumulation must be extremely unusual if not unique. Even here, dawsonite is present in only low abundances (0.4 ± 0.3 %; Table 1), from which the percentage of CO₂ sequestered in solid form within the dawsonite is calculated using Eqn (1). Values of parameters are given in Table 2.

$$\text{weight \% CO}_2 \text{ dawsonite} = \frac{100 * \rho_{\text{solid rock}} * W_{\text{dawsonite}} * (1 - \phi) * F_{\text{CO}_2, \text{dawsonite}}}{\rho_{\text{solid rock}} * (1 - \phi) * [F_{\text{CO}_2, \text{dawsonite}} + W_{\text{dawsonite}} + F_{\text{CO}_2, \text{dolomite}} * W_{\text{dolomite}}] + \phi * S_g * M_{\text{CO}_2} * \rho_{\text{gas}} + \phi * (1 - S_g) * \text{Sol}_{\text{CO}_2}}$$

$\rho_{\text{solid rock}}$ is the average density of the solid components of the rock, $W_{\text{dawsonite}}$ is the weight fraction of dawsonite determined by XRD (Table 1); ϕ is average rock porosity (Table 1); $F_{\text{CO}_2, \text{dawsonite}}$ is the weight fraction of CO₂ in dawsonite from the chemical formula. S_g is the gas saturation in the reservoir (i.e. volume fraction of porespace filled with gas phase); M_{CO_2} is weight fraction of CO₂ in gas phase, both supplied by Tullow oil; ρ_{gas} is density of the gas phase under reservoir conditions, assumed to be an ideal mix of CO₂ and methane, with CO₂ density from the equation of state by Huang et al., (1985). Sol_{CO_2} is the solubility of CO₂ in the porewaters under reservoir conditions, corrected for a porewater salinity of approximately 9000 ppm NaCl from an analysis supplied by Tullow Oil (Spycher et al., 2003). The solubility is also corrected for the presence of methane using Henry’s Law which is only an approximation at such high gas concentrations. W_{dolomite} is the weight fraction of dolomite that is related to the CO₂ charge (note not total dolomite, see below) and $F_{\text{CO}_2, \text{dolomite}}$ is the weight fraction of CO₂ in dolomite from the

chemical formula. Even the largest reasonable variations in parameters are insufficient to alter the conclusions of the paper. We calculate that 2.4 (± 0.9) mole % of the CO₂ present within the structure is currently locked up as dawsonite, i.e. a small proportion.

Dolomite cement

Assessing the quantity of CO₂ sequestered by dolomite cement is more difficult, because the Rotliegend sandstone of the Fizzy and Orwell accumulations contain an early diagenetic dolomite cement that pre-dates the CO₂ charge. The problem then is to distinguish dolomite related to the CO₂-charge from the early diagenetic dolomite. Dolomite cements that are very similar to those from the study sites have been described from the Rotliegend in other southern North Sea gas fields (Sullivan et al., 1990; Purvis, 1992). In these settings the dolomite is thought to be of early diagenetic origin and related to the transgression of the late Permian Zechstein Sea. Purvis (1992) and Sullivan et al. (1990) describe Rotliegend dolomite as being euhedral, micro-rhombic grain rimming cements near the top of the formation, and rare anhedral pore-filling 'micro-concretions' towards the base of the formation. There is a gradual transition between the two morphologies, with dolomite crystal size and separation increasing downwards. This description fits the dolomite within both Fizzy and Orwell very well, except that some of the rare pore-filling cement is euhedral in Fizzy. During TX and SEM examination, we noted no evidence of late-stage rimming cements around grains. A comparison of zonation patterns between the 2 fields using SEM-CL revealed no systematic differences (Fig. 6D). The bright zone that rims the dolomite crystals in Fig. 6D is a ferroan zone. This is developed throughout the region (Purvis, 1992; Sullivan et al., 1990) and is not obviously related to the CO₂ influx into Fizzy.

The quantity of dolomite cement is variable within the Rotliegend fields that have been previously studied, with means within wells varying from 0 – 13 % even within a single sedimentary facies, in this case dune bedded sandstones (Purvis, 1992). The abundance of dolomite within both Fizzy and Orwell falls within this (admittedly rather considerable) range. Given that the regional data are so variable, a simple comparison of dolomite abundance between Fizzy and Orwell would be meaningless, as the assumption that both fields developed the same mean quantity of authigenic dolomite cement prior to the influx of CO₂ into Fizzy is not justifiable. It is apparent that there could be percent levels of late CO₂-charge related dolomite within Fizzy that would not be revealed by simple comparison of the dolomite abundance between Fizzy and Orwell. Although, based on petrography (above), we conclude that the vast majority of dolomite cement in the Fizzy reservoir is of conventional early diagenetic origin, stable isotopic analysis was used to quantify the proportion of late CO₂-related dolomite.

Stable isotope evidence

Stable isotope analysis of dolomites has been used to further quantify the volume of dolomite grown from the present day CO₂ gas charge. Figure 7 shows both data from the Fizzy and Orwell accumulations, and the predicted composition of dolomite in equilibrium with the present-day CO₂ charge at various burial temperatures. Also shown are data from the Rotliegend reservoir sandstone from other gas fields in the area (Purvis 1992; Sullivan et al., 1992). Note that the Fizzy and Orwell data fall within the range of the regional data. The small range of the Fizzy data could be a consequence of the CO₂ charge preventing dolomite growth at higher temperatures. Unfortunately, due to the complex burial and exhumation history of the area, it is not possible to relate the temperature to a time of CO₂-charging.

The dolomite stable isotopic data from the Fizzy and Orwell accumulations are similar, though perhaps not identical. Could this difference be the result of precipitation of extra dolomite associated with the high CO₂-charge in the Fizzy accumulation? Figure 7 shows the calculated compositions of dolomite that would have been in equilibrium with the CO₂ for temperatures in the range of 40 to 80 °C. The oxygen fractionation factor of Fisher and Land (1986) is utilised, but the more recent equation of Vasconcelos et al. (2005) gives very similar results that do not impact on the conclusion of the paper. The carbon fractionation of Deines et al. (1974) for calcite is used in the absence of a specific dolomite equation. The calculations utilise a porewater oxygen isotope ratio from the Leman Field ($\delta^{18}\text{O} = 0.3$ to 0.4 ‰ V-SMOW; Warren and Smalley, 1992) because there is no available data from either Fizzy or Orwell. The geology of the Leman Field is very similar to that of the study area, though the burial history may differ in detail. It is hence reasonable to suppose that the porewater in Fizzy is similar to the Leman Field, and small variations (say ± 2 ‰) will not have a large influence on the conclusions of this paper.

There is a conspicuous lack of any mixing line from the Fizzy field towards the calculated dolomite compositions, however, there is a small difference between the mean $\delta^{13}\text{C}$ value of the dolomite within the 2 fields (Fizzy mean $\delta^{13}\text{C} = -0.7 \pm 0.1$ ‰ PDB; Orwell mean $\delta^{13}\text{C} = -1.3 \pm 0.4$ ‰ PDB). If this difference is due to the presence of dolomite precipitated from the CO₂ charge in the Fizzy accumulation, then 10 (± 30) % of the total dolomite in Fizzy would be related to the CO₂ charge. Scatter within the isotope data preclude a more accurate estimate. This implies sequestration of 0 - 25 of the total CO₂ within the reservoir as dolomite, with petrographic study favouring a low figure within this range, as above.

Combining the CO₂ sequestered within the dawsonite and possibly within the dolomite cements, leads to an estimate that between 0.5 and 30 % of the total CO₂ within the Fizzy accumulation has been sequestered. Even if the porewaters are saturated with CO₂ then only a small proportion (2 - 3%) of the unsequestered CO₂ can be in aqueous solution (as above), so that the vast majority of the CO₂ is present as a free gas (70 - 95 %), mixed with methane and nitrogen. It should also be noted that, even if all the dolomite in Fizzy were the product of the late CO₂ charge (a highly unlikely scenario), that only 44 % of the CO₂ would be sequestered leaving 53 % in the free gas phase. We conclude that this result is a useful calibration point for

geochemical modelling, and that the low proportion of CO₂ present as mineral phases would also apply to the injection of CO₂ for storage purposes in reservoirs similar to the study one.

Mineral dissolution

Injection of CO₂ into the Frio Formation in Texas, USA resulted in rapid changes of porefluid pH which were buffered by the dissolution of carbonate minerals (Kharaka et al., 2006). Examination of the surfaces of authigenic dolomite crystals from the Fizzy reservoir using an SEM reveals no evidence for major dissolution. The crystal surfaces are planar, and lack etch pitting or other irregularities; the crystal edges and corners are sharp (on an SEM scale; Fig. 6A). Sections through dolomite crystals show no textures of late overgrowth enclosing a dissolution surface (Fig. 6D). These observations indicate that significant dissolution has not occurred.

Implications

It has been asserted by several modelling studies that when large volumes of CO₂ are injected into a sandstone reservoir that significant volumes of that CO₂ will be permanently sequestered by mineral reactions. These reactions produce carbonates, including dawsonite, usually at the expense of feldspars (Gunter et al., 2000; Xu et al., 2005; Knauss et al., 2005; White et al., 2005; Zerai et al., 2006). However, our study of a natural high-CO₂ accumulation within the UK North Sea has found only small quantities of dawsonite and other late carbonates linked to CO₂ despite the presence of c. 5 % of detrital K-feldspar within the reservoir. We suggest that the role of mineral reactions in sequestering CO₂ in a solid phase has sometimes been over-estimated.

Several parameters may provide misleading model results. Firstly, the sandstone detrital composition is important. In a model of a conceptual sand-shale system, Xu et al. (2005) predicted up to 90 kg/m³ of CO₂ would be trapped in sandstone after 100,000 years, compatible only with the highest possible interpretation of the data from Fizzy. However, in the simulations, cations for the carbonates were primarily supplied by the dissolution of chlorite, haematite and oligoclase (Xu et al., 2005). The Rotliegend reservoir in the Fizzy field lacks significant quantities of any of these minerals – consequently, authigenic carbonates form in only small quantities. Many oilfield reservoir sandstones also lack these minerals, so that CO₂ sequestration will be limited by cation availability. The lack of dawsonite cannot be explained by cation availability – there is a low concentration of sodium in the present-day porewaters in the Fizzy field, where dawsonite is present (2940 ppm from an analysis of produced fluid by Tullow Oil) but much higher concentrations in nearby fields in which dawsonite is absent, sourced by dissolution of halite from the overlying Zechstein evaporates. For example in the Welland Field which lies some 20 km to the west of Fizzy and has very similar geology, porewater concentrations of sodium are around 70,000 ppm (Warren and Smalley, 1994).

There must be other factors that control the growth of dawsonite, including pH and nucleation (Bénézech et al., 2007).

In an example from Utah, USA, White et al. (2005) predicted that, 1500 years after injection started, 70 % of the CO₂ was sequestered. The major cation sources were sourced from the dissolution of albite, anorthite and Na-smectite, with predicted precipitation of dawsonite and calcite. The volumes predicted were high, with 6 volume % dawsonite and 7 % calcite after 950 years, again an order of magnitude more than we observe. The reason for the discrepancy could be the assumption by White et al. (2005) that the majority of the clay in the reservoir sandstone is smectite, a relatively reactive clay mineral. In the North Sea, detrital smectite transforms to relatively unreactive illite with increasing burial depth (Wilkinson et al., 2006), and similar reactions have been described for the Gulf Coast (Hower et al., 1976). Hence the potential for CO₂ sequestration is substantially reduced in deeply buried sands. Another study where sequestration is dependant upon an unusual mineral is that of Gunter et al. (2000). Here, glauconite provided the majority of cations. Modelling the Glauconitic Sandstone of the Alberta Sedimentary Basin, Gunter et al. (1997) predicted that over 90% of CO₂ would be sequestered by reaction with ferro-magnesian minerals over thousands of years. Even then, this high trapping efficiency was dependant upon the CO₂ reacting to completion with all solid silicates, as well as excess CO₂ migrating out of the storage site to find fresh minerals to react with.

Perhaps the only simulations that have volumes of CO₂ sequestered comparable to the preferred lower end of the estimates for the Fizzy example are those in which 'acid gas' is injected, i.e. a mix of CO₂ and either H₂S or SO₂, and the sandstone reservoir contains a small quantity of reactive iron in the form of haematite. Palandri and Kharaka (2005) calculated that 7 g of CO₂ would be sequestered per kg of rock, which would correspond to 0.2 wt % of dawsonite, while Knauss et al. (2005) calculated 0.2 – 0.6 wt % dawsonite equivalent. There is no H₂S present within the Fizzy reservoir gases (according to an analysis provided by Tullow Oil) and presumably no SO₂ due to the generally reducing conditions found in hydrocarbon reservoirs. The mineral assemblage used in the simulations of Knauss et al. (2005) contained only small quantities of feldspar, and only relatively unreactive illite clay. This mineral assemblage yielded the modelling results most similar to the lower end of the estimates from the Fizzy accumulation.

As an alternative explanation of the lack of apparent reaction products from the CO₂ charge in Fizzy, could high porewater salinity reduce the reactivity of CO₂ by limiting dissolution and dissociation to reactive bicarbonate ions? The solubility of CO₂ is depressed by increasing salinity (Spycher and Pruess, 2005) but it is a minor influence compared to temperature and pressure. The fraction of CO₂ in the free gas also influences CO₂ solubility, but assuming that Henry's Law can be used (an approximation only at such high gas concentrations) then again the effect is relatively minor. Using the equations of Speyer and Pruess (2005) it can be calculated that the effect of having only 50 % CO₂ in the gas phase and a porewater salinity

of 9000 ppm (from the single available porewater analysis supplied by Tullow Oil) reduces solubility to 48 % compared to freshwater in contact with a pure CO₂ gas phase. Even using a saline brine (230,000 ppm, the average for published analyses for the Leman Field; Warren and Smalley, 1992) only reduces the solubility to 26 % of the reference case. Detailed geochemical modelling could potentially resolve whether this depression in CO₂ solubility was sufficient to limit dawsonite or other carbonate mineral stability. Hellevang et al. (2005) note that in an engineered storage scenario, dawsonite might form as a temporary phase associated with very high but transient concentrations of CO₂. As the concentration of CO₂ decreases due to dispersion away from the injection site, the dawsonite might be expected to dissolve. This scenario is not applicable to the situation in the Fizzy accumulation, as there is no reason to assume that previous concentrations of CO₂ have been much higher. Indeed, the concentration in the gas phase cannot possibly have been more than twice as high as at the present day.

CONCLUSIONS

- 1) The quantity of CO₂ sequestered as solid minerals within a natural accumulation within the UK North Sea is relatively small, 0.5 – 30 % total CO₂, with the lower end of this range being more probable. This forms a useful calibration point for the modelling of long-term CO₂-rock interaction, on a time-scale which is inaccessible to both laboratory experiments and test-scale sequestration experiments.
- 2) The quantity of CO₂ fixed by mineral formation within a sandstone may be limited by cation availability. Some geochemical simulations optimistically assume that large quantities of reactive minerals will be available, such as chlorite and glauconite. If these are not present in the sandstone, as in many North Sea and Gulf Coast examples, then large volumes of CO₂ cannot be fixed in solid form.
- 3) The Rotliegend sandstones contain c. 5 % K-feldspar, which might be predicted to dissolve and produce kaolin and carbonate minerals at reduced pH levels. However, this mineral has remained stable in the presence of high CO₂ concentrations for geological periods of time, probably in excess of 50 Ma.
- 4) The Rotliegend sandstone still comprises an excellent potential store for anthropogenic CO₂. This formation is extensive, has high permeabilities and porosities and is overlain by a highly effective evaporite seal. However, storage must rely upon physical trapping of the CO₂, i.e. physical trapping, residual saturation trapping and solution trapping, and not upon mineral trapping which will be ineffective on the 'short' timescales for which storage need to be achieved.

ACKNOWLEDGEMENTS

We thank Mark Allen of Tullow Oil for drawing our attention to the Fizzy Accumulation, and for providing useful background information. We are grateful for core samples taken from the BGS corestore in Edinburgh. Western Geco kindly supplied the 3D seismic data from which Fig. 3 was drafted. SS and RL publish with the permission of the Director of BGS, MW is funded by the UK Energy Research Centre, RSH is funded by the Scottish Centre for Carbon Storage. SUERC is funded by NERC and the Scottish Universities

REFERENCES

Bénézech, P., Palmer, D.A., Anovitz, L.M. and Horita, J., 2007, Dawsonite synthesis and reevaluation of its thermodynamic properties from solubility measurements: Implications for mineral trapping of CO₂: *Geochimica Cosmochimica Acta*, v. 71, p. 4438-4455

Deines, P., Langmuir, D., and Harmon, R.S., 1974, Stable carbon isotope ratios and existence of a gas-phase in evolution of carbonate ground waters: *Geochimica et Cosmochimica Acta*, v. 38, p. 1147-1164.

Fisher, R.S. and Land, L.S., 1986, Diagenetic history of Eocene Wilcox Sandstones, south-central Texas: *Geochimica et Cosmochimica Acta*, v. 50, p. 551-561.

Friedman, I. and O'Neil, J.R., 1977, Compilation of stable isotope fractionation factors of geochemical interest, in Fleischer, M., ed., *Data of Geochemistry* (6th edition): USGS Professional Paper, v. 440-KK.

Glennie, K.W. and Buller, A.T., 1983, The Permian Weissliegendes of NW Europe: the partial deformation of aeolian dune sands caused by the Zechstein transgression: *Sedimentary Geology*, v. 35, p. 43-81.

Gunter, W.D. Perkins, E.H., Hutcheon, I., 2000, Aquifer disposal of acid gases: modelling of water-rock reactions for trapping of acid wastes: *Applied Geochemistry*, v. 15, p. 1085-1095.

Gunter, W. D., Wiwchar, B., and Perkins, E. H., 1997, Aquifer disposal of CO₂-rich greenhouse gases: extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling: *Mineralogy and Petrology*, v. 59, p. 121-140.

Hellevang, H., Aagaard, P., Oelkers, E.H., and Kvamme, B., 2005, Can dawsonite permanently trap CO₂?: *Environmental science & technology* v. 39, p. 8281-8287.

Hillis, R.R., 1995, Quantification of Tertiary exhumation in the United Kingdom southern North Sea using sonic velocity data: *AAPG Bulletin* v. 79, p. 130-152.

Hower, J., Eslinger, E.V., Hower, M.E., and Perry, E.A., 1976, Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence: Geological Society of America Bulletin, v. 87, p. 725-737.

Huang, F., Li, M., Lee, L., and Starling, K., 1985, An accurate equation of state for carbon dioxide: Journal of Chemical Engineering of Japan, v. 18, p. XX

IPCC, 2005, IPCC Special report on Carbon Capture and Storage, prepared by working group III of the Intergovernmental Panel on Climate Change: Cambridge University Press, Cambridge, UK and New York, USA, 442 pp.

Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G., and Freifeld, B.M., 2006, Gas-water-rock interactions in Frio Formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins: Geology, v. 34, p. 577-580.

Knauss, K.G., Johnson, J.W. & Steefel C.I., 2005, Evaluation of the impact of CO₂, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO₂: Chemical Geology, v. 217, p. 339-350.

Palandri, J.L., & Kharaka, Y. K., 2005, Ferric iron-bearing sediments as a mineral trap for CO₂ sequestration: Iron reduction using sulfur-bearing waste gas: Chemical Geology, v. 217, p. 351- 364.

Pettijohn, F.J., Potter, P.E. and Siever, R., 1973, Sand and Sandstones. Springer-Verlag, Berlin, 617pp.

Purvis, K. 1992. Lower Permian Rotliegend Sandstones, Southern North-Sea - A case-study of sandstone diagenesis in evaporite-associated sequences: Sedimentary Geology, v. 77, p. 155-171.

Serica Energy, 2006, Serica Energy plc Tests Gas in two UK North Sea Exploration Wells: <http://www.serica-energy.com/pages/np/index.asp?NPID=75>, accessed December 2006, currently unavailable.

Spycher N., Pruess, K., and Ennis-King J., 2003, CO₂-H₂O mixtures in the geological sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100 degrees C and up to 600 bar: Geochimica et Cosmochimica Acta, v. 67, p. 3015-3031.

- Spycher, N. and Pruess, K., 2005, CO₂ - H₂O mixtures in the geological sequestration of CO₂. II. Partitioning in chloride brines at 12–100°C and up to 600 bar: *Geochimica et Cosmochimica Acta*, 69, 3309–3320.
- Sullivan, M., R.S. Haszeldine and A.E. Fallick, 1990, Linear coupling of carbon and strontium isotopes in Rotliegend Sandstone, North Sea: evidence for cross-formational fluid flow: *Geology*, v. 18, p. 1215 – 1218.
- Vasconcelos, C., McKenzie, J.A., Warthmann, R., Bernasconi, S., 2005. Calibration of the δ¹⁸O paleothermometer for dolomite precipitated in microbial cultures and natural environments. *Geology* 33, 317–320.
- Warren, E.A. and Smalley, P.C., 1992, North Sea formation Water Atlas: Geological Society Memoir 15, London. p. 208.
- White, S.P., Allis, R.G., Moore, J., Chidsey, T., Morgan, C., Gwynn, W. & Adams, M., 2005, Simulation of reactive transport of injected CO₂ on the Colorado Plateau, Utah: *Chemical Geology*, v. 217, p. 387-405.
- Wilkinson, M., Haszeldine, R.S. & E. Fallick, A.E., 2006, Jurassic and Cretaceous clays of the northern and central North Sea hydrocarbon reservoirs reviewed: *Clay Minerals*, v. 41, p. 151-186.
- Wopfner, H. & Höcker, C.F.W., 1987, The Permian Groedan Sandstone between Bozen and Meran (northern Italy), a habit of dawsonite and nordstrandite: *Neus Jahrbuch für Paläont. Mh.* v. 3, p. 161 – 176.
- Wycherley, H., Fleet, A., and Shaw, H., 1999, Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins: *Marine and Petroleum Geology* 16, 489-494.
- Xu, T, Apps, J. A. and Pruess, K., 2005, Mineral sequestration of carbon dioxide in a sandstone-shale system: *Chemical Geology*, v. 217, p. 295-318.
- Zerai B., Saylor, B.Z. and Matisoff, G., 2006, Computer simulation of CO₂ trapped through mineral precipitation in the Rose Run Sandstone, Ohio: *Applied Geochemistry*, v. 21, p. 223-240.
- Ziegler, K., 2006, Clay minerals of the Permian Rotliegend Group in the North Sea and adjacent areas: *Clay Minerals*, v. 41, p. 355-393.

FIGURE CAPTIONS:

Fig. 1 – Location map for the Fizzy and Orwell gas accumulations within the North Sea. Also shown are the tectonic elements for the Lower Permian (Glennie, 1998). The enlargement shows parts of UK blocks 49/30 and 50/26 including wells identified by number.

Fig. 2 – Stratigraphic log of reservoir and seal of the Fizzy accumulation and the Orwell field, drawn from composite logs released by the UK Government. Grain sizes are shown only for cored sections (shown as black bars).

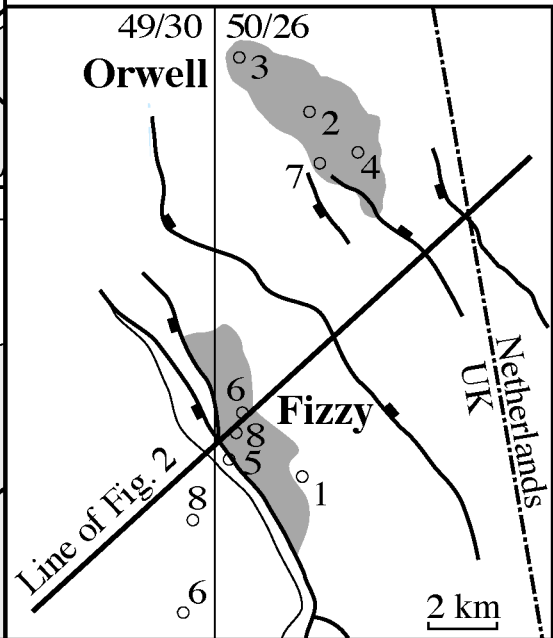
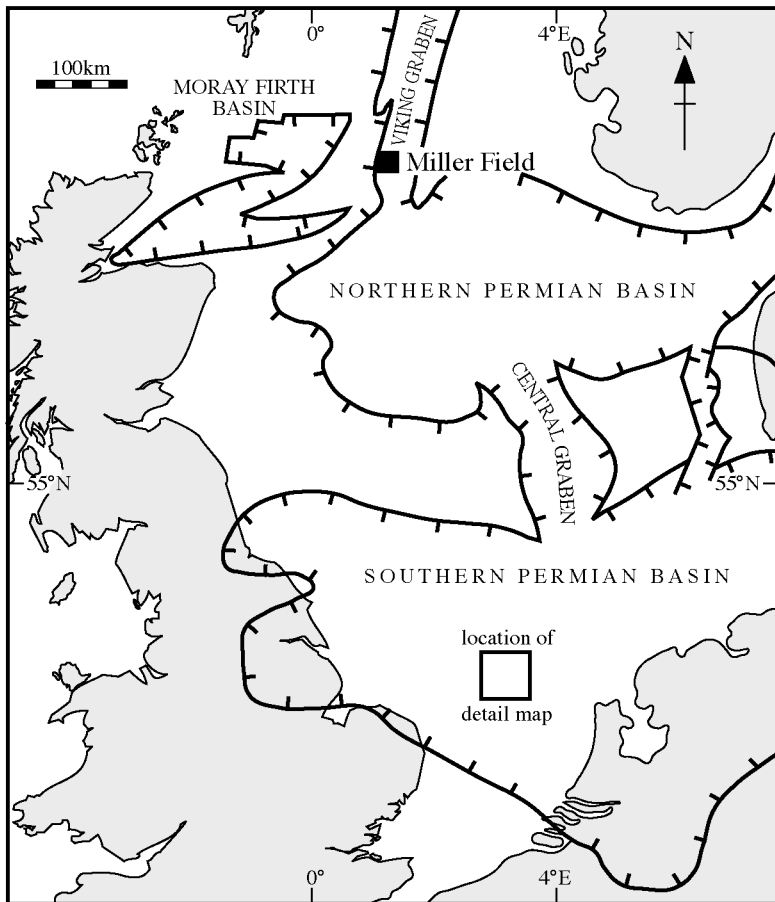
Fig. 3 – X section through the Fizzy accumulation. For location see Fig. 1. Drawn from seismic, note that the section is not depth-converted so that the y-axis is two-way travel time.

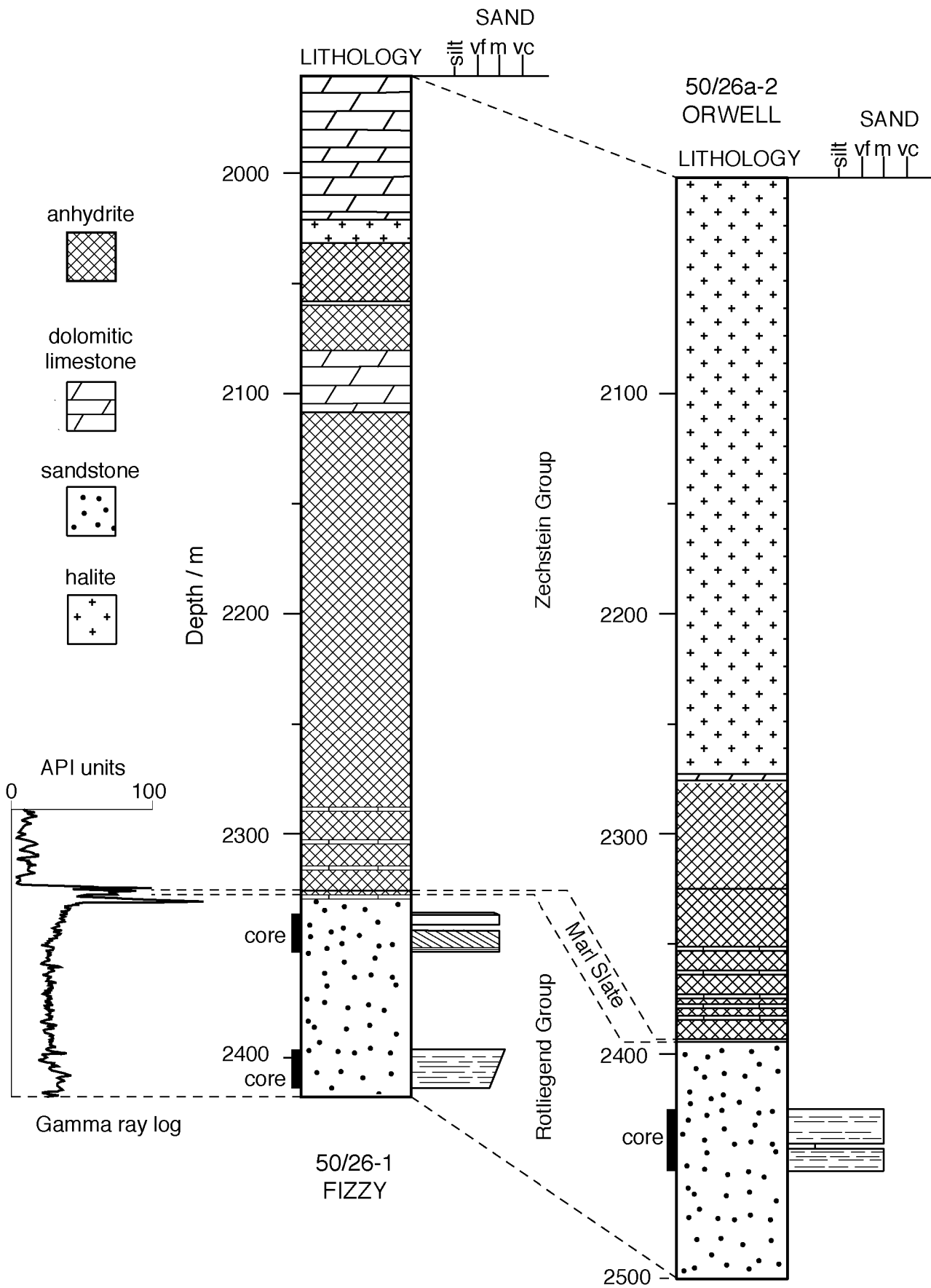
Fig. 4 – Petrographic composition of sandstones within Fizzy accumulation from point count data.

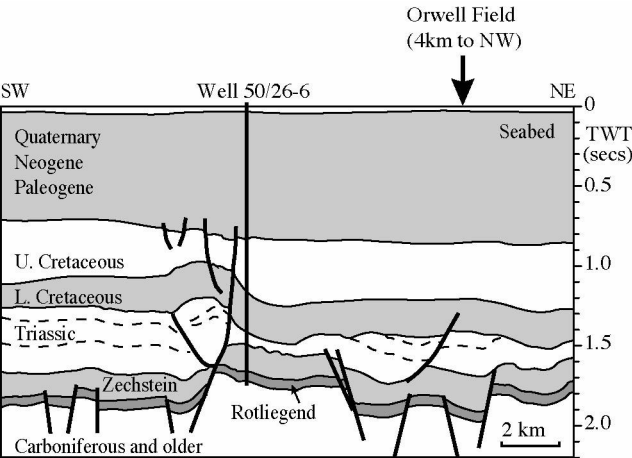
Fig. 5 – XRD trace of clay-sized fraction (< 2 μm equivalent spherical diameter) showing the 110 dawsonite peak. Cu $K\alpha$ radiation.

Fig. 6 – A: Pore-lining dolomite cement typical of the upper parts of the Rotliegend section. B: Thin-section view of the pore-lining cement. FOV = 2.5 mm. C: Dolomite mini-concretion from the lower part of the Rotliegend section. FOV = 2.5 mm. D: SEM-CL image of dolomite from the Orwell Field, which is very similar to that within the Fizzy accumulation.

Fig. 7 – Stable C and O isotope data for dolomites from the Fizzy and Orwell gas accumulations. Also shown are regional data from the Rotliegend sandstone, and the calculated compositions of dolomite precipitated from the CO_2 -charge for 40 – 80 °C. Note the lack of real data lying on or close to the calculated compositions, and the similarity between the Fizzy data and the regional data.







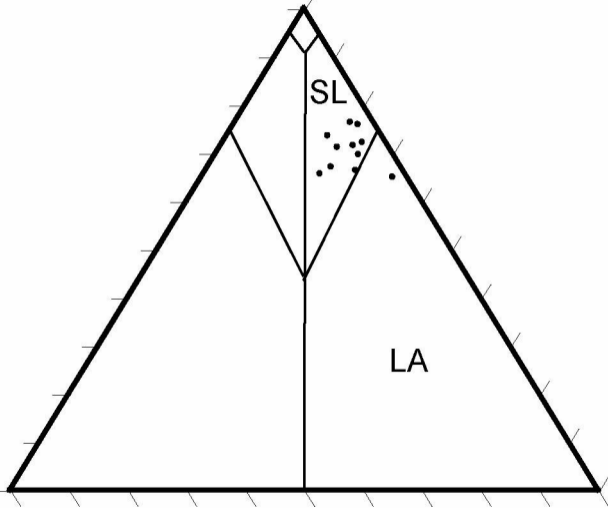
Quartz

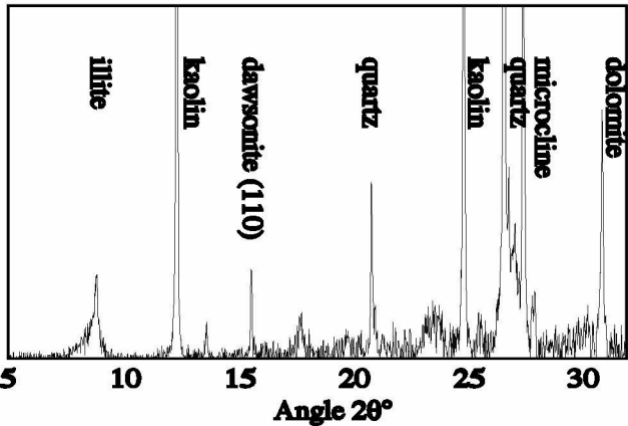
SL

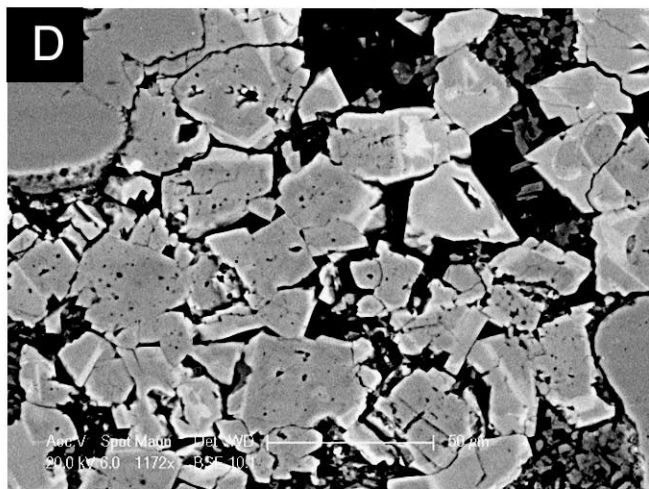
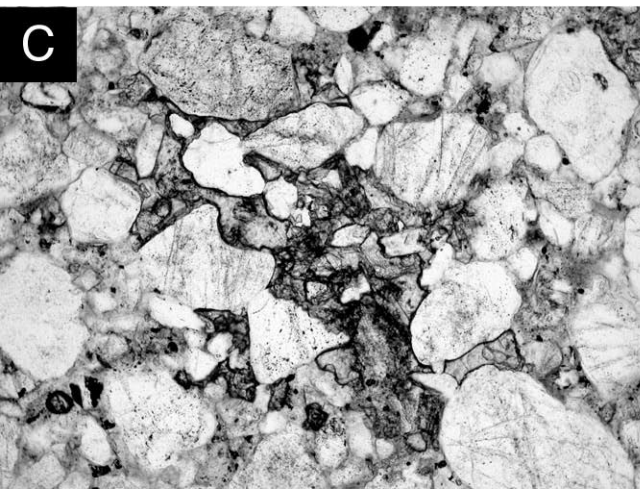
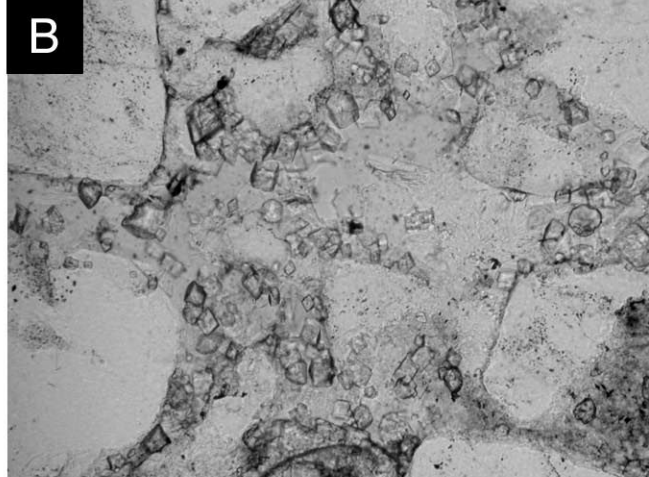
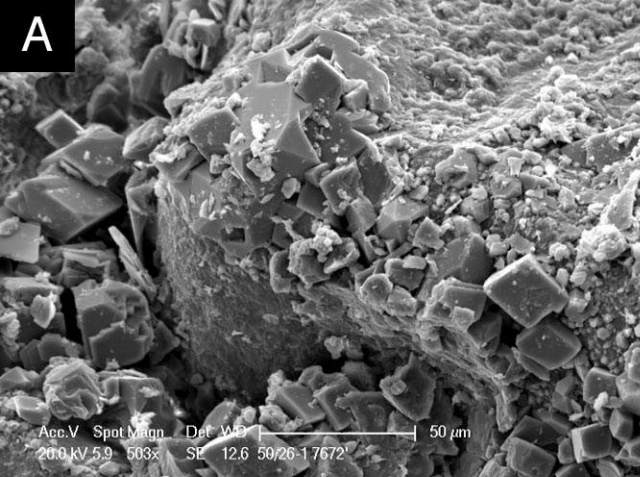
LA

Feldspar

Rock Fragments







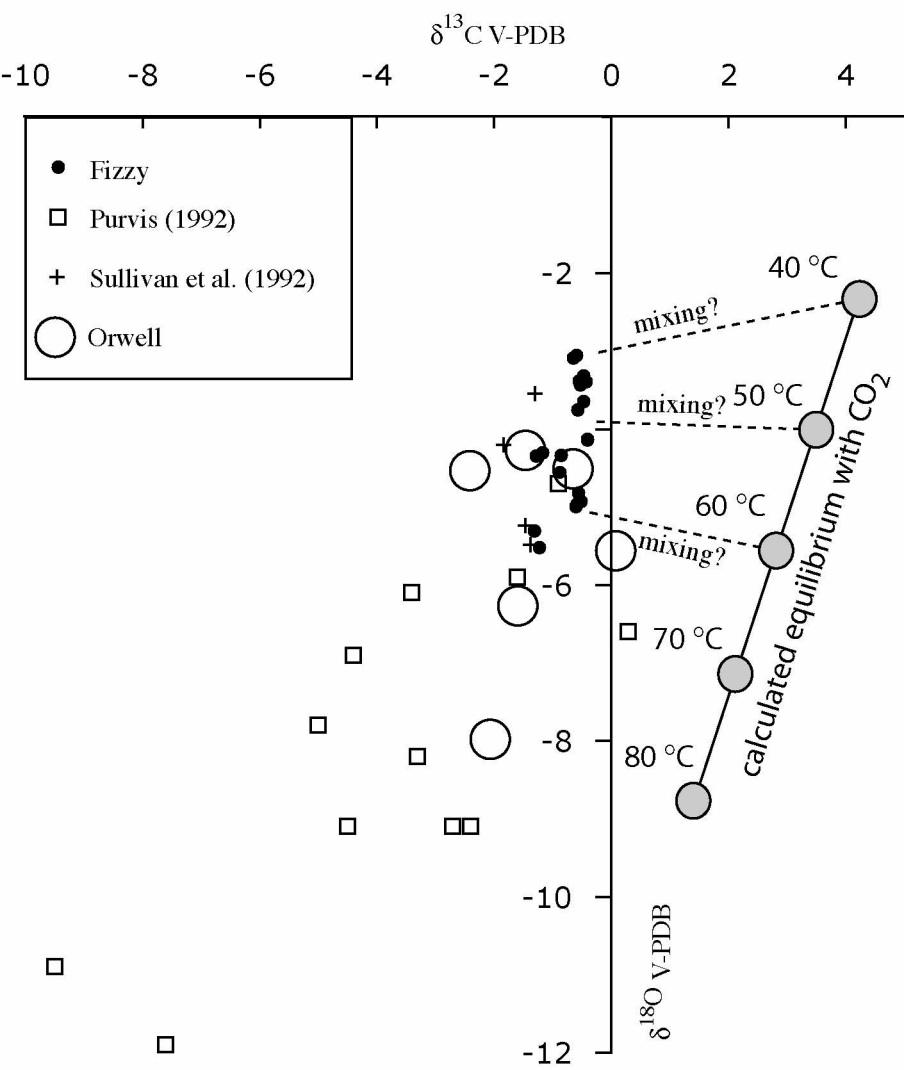


Table 1 – Average composition of Rotliegend sandstone from Fizzy accumulation and Orwell fields, point count data with total solids = 100% and porosity as % whole rock, 1 standard error in brackets. Dawsonite determined by XRD.

	Fizzy accumulation	Orwell field
quartz	61 (3)	47 (1)
rock fragments	19 (1)	12 (1)
K-feldspar	6 (1)	12 (1)
plagioclase	0	0
muscovite	trace	0
feldspar overgrowth	trace	0
quartz overgrowth	2 (1)	0.3 (0.2)
dolomite	7 (2)	12 (1)
clay (excluding kaolin)	0.5 (0.3)	0.2 (0.1)
kaolin	2 (0.5)	6 (1)
gypsum and anhydrite	2 (1)	7 (1)
dawsonite	0.4 (0.3)	0
porosity	12 (1)	7 (1)

Table 2 – Parameters used in CO₂ distribution calculation

Parameter	Value	Source
density solid rock ($\rho_{\text{solid rock}}$)	790 kg / m ³	
weight fraction dawsonite in solid rock ($W_{\text{dawsonite}}$)	0.4 ± 0.3 %	Table 1
rock porosity (ϕ)	22.3 ± 0.3 %	Tullow Oil, unpublished data
weight fraction CO ₂ in dawsonite ($F_{\text{CO}_2, \text{dawsonite}}$)	0.31	from chemical formula
gas saturation in porespace (S_g)	0.68	Tullow Oil, unpublished data
weight fraction of CO ₂ in gas phase (X_{CO_2})	0.48	Tullow Oil, unpublished data
density CO ₂ in reservoir (ρ_{gas})	790 kg / m ³	Huang et al. (1985)
solubility of CO ₂ in the porewaters under reservoir conditions (M_{CO_2})	25.4 kg / m ³	Spycher and Preuss (2005)
weight fraction dolomite in solid rock related to late CO ₂ charge (W_{dolomite})	0.7 ± 0.2 %	See text
weight fraction CO ₂ in dolomite ($F_{\text{CO}_2, \text{dolomite}}$)	0.48	from chemical formula

Wilkinson et al. Table 3

Stable C and O isotopes of authigenic dolomite, Fizzy accumulation (wells 50/26-1 and 50/26b-6) and Orwell Field (wells 50/26a-7 and 50/26a-2).

Well, drillers depth (m)	gas or water?	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
50/26-1, 2338.4	water	-0.5	-4.9
50/26-1, 2338.4	water	-0.6	-5.0
50/26-1, 2343.9	water	-0.9	-4.3
50/26-1, 2343.9	water	-0.9	-4.6
50/26-1. 2354.8	water	-0.5	-3.4
50/26-1. 2354.8	water	-0.5	-3.4
50/26-1. 2350.9	water	-0.6	-3.0
50/26-1. 2350.9	water	-0.7	-3.1
50/26-1. 2402.9	water	-0.5	-3.6
50/26-1. 2402.9	water	-0.6	-3.7
50/26b-6. 2292.6	gas	-0.6	-4.8
50/26b-6. 2292.6	gas	-0.6	-5.0
50/26b-6. 2299.1	gas	-0.4	-4.1
50/26b-6. 2299.1	gas	-0.4	-4.1
50/26b-6. 2305.1	gas	-0.5	-3.3
50/26b-6. 2305.1	gas	-0.4	-3.4
50/26b-6. 2311.3	gas	-1.2	-5.5
50/26b-6. 2311.3	gas	-1.3	-5.3
50/26b-6. 2316.3	gas	-1.2	-4.3
50/26b-6. 2316.3	gas	-1.3	-4.3
50/26a-7, 2333.7	NA	-2.4	-4.4
50/26a-7, 2342.7	NA	-1.5	-4.1
50/26a-2, 2425.9	NA	-0.1	-4.6
50/26a-2, 2428.6	NA	-2.1	-7.6
50/26a-2, 2432.3	NA	-0.7	-4.3
50/26a-2, 2447.5	NA	-1.6	-6.0
50/26a-2, 2440.5	NA	0.1	-5.3