

CO₂-MINERAL REACTION IN A NATURAL ANALOGUE FOR CO₂ STORAGE—IMPLICATIONS FOR MODELING

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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 geochemical 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) despite exposure to high levels of CO₂ for 50 Myr or more. 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 isotopes with a neighboring 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 in reservoirs similar to the Rotliegend Group 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 modeling, since neither experiments nor test facilities can be run over the time scales of thousands of years for which storage must be achieved. Many published geochemical modeling 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 modeling.

The southern North Sea hosts a large number of natural gas fields. CO₂ contents in hydrocarbon gases of the Southern North Sea are generally

low (0.1 to 1.0 mol % in 15 fields; Abbotts 1991). 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 in 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 meters of Late Permian Zechstein halite evaporites, 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 two 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. 2300 m deep, 80–100 m thick, and at a present-day temperature of 80–85

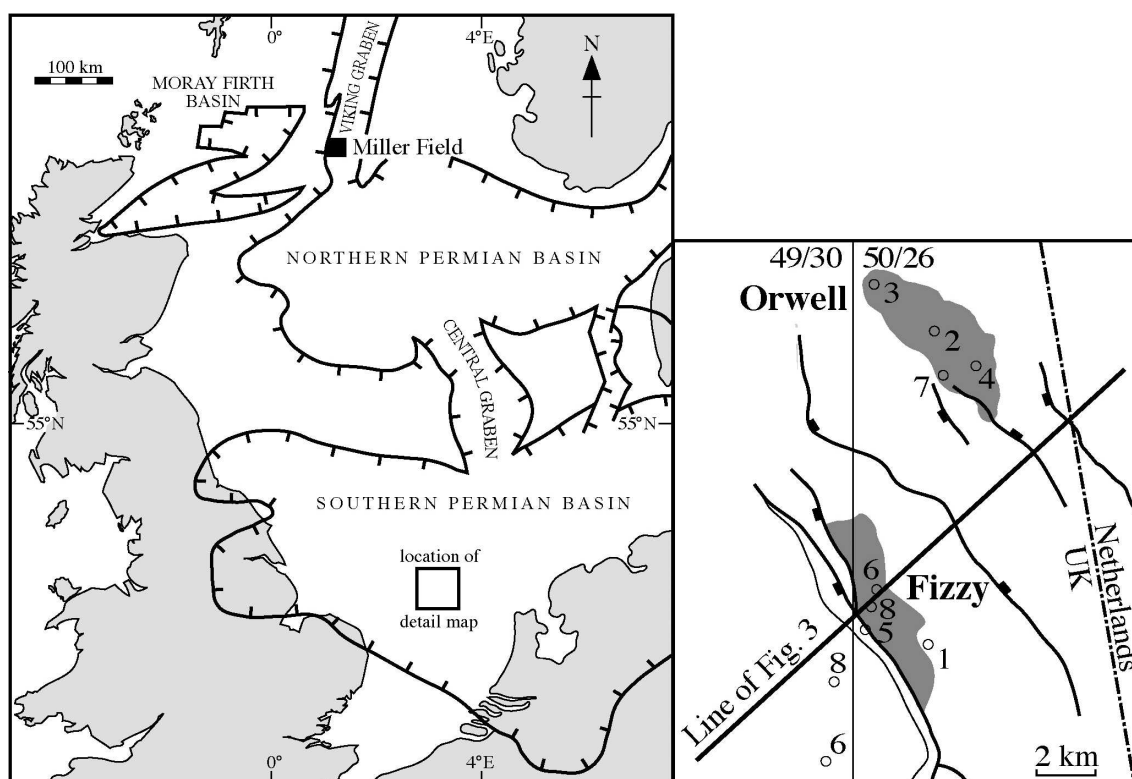


FIG. 1.—Location map for the Fizzy and Orwell gas accumulations in the North Sea. Also shown are the tectonic elements for the Early Permian (Glennie 1998). The enlargement shows parts of UK blocks 49/30 and 50/26 including wells identified by number.

°C. In Orwell, the Rotliegend Group is at a similar depth, and has a thickness and temperature comparable 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 two episodes of uplift interrupting sedimentation. The Fizzy accumulation, which lies to the east of the fault, has been uplifted by c. 440 m since the Late Cretaceous, and by 800–1000 m since the Early Triassic (Hillis 1995).

METHODS

All of the available conventional core from the Fizzy accumulation and the Orwell field was examined and logged. Two wells from the Fizzy accumulation have 86 m of core in total (UK well numbers 50/26-1 and 50/26b-6), and two wells from Orwell have 83 m (UK well numbers 50/26a-2 and 50/26a-7). Forty 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, both gas and water zones were studied. Mineral identification was aided by XRD analyses of 10 whole-rock samples from Fizzy, and 10 from Orwell. Separates of clay-grain-size were prepared from a subset of these, those with the most prominent whole-rock dawsonite peaks. A Bruker-AXS D8 Advance with 2-theta configuration was used. 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, and 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 analyzed as above for stable carbon isotope ratios.

RESULTS

The cored sections of the Fizzy accumulation and the Orwell field are interpreted as predominantly eolian dune-face sandstone with subordinate interdune facies. The sediments are predominantly colored gray in both the reservoirs, despite the name of the Rotliegend Group. The composition of the sandstones is given in Table 1 and Figure 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 metasediments. 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. The alkali feldspar is untwinned, and is difficult to identify without chemical staining unless partial dissolution has taken place. There is a complete absence of plagioclase. Kaolin is generally present as discrete grain-size clusters. There are no organic remains.

In Fizzy, the abundance of dawsonite is low, with a maximum of 0.8% and means of 0.4 (\pm 0.3)% for both sampled wells determined by XRD. There is no detectable difference in dawsonite abundance between the gas and water zone wells (Table 1). Separation of fine grain-size fractions (< 0.1 μm) by settling resulted in substantially increased concentrations

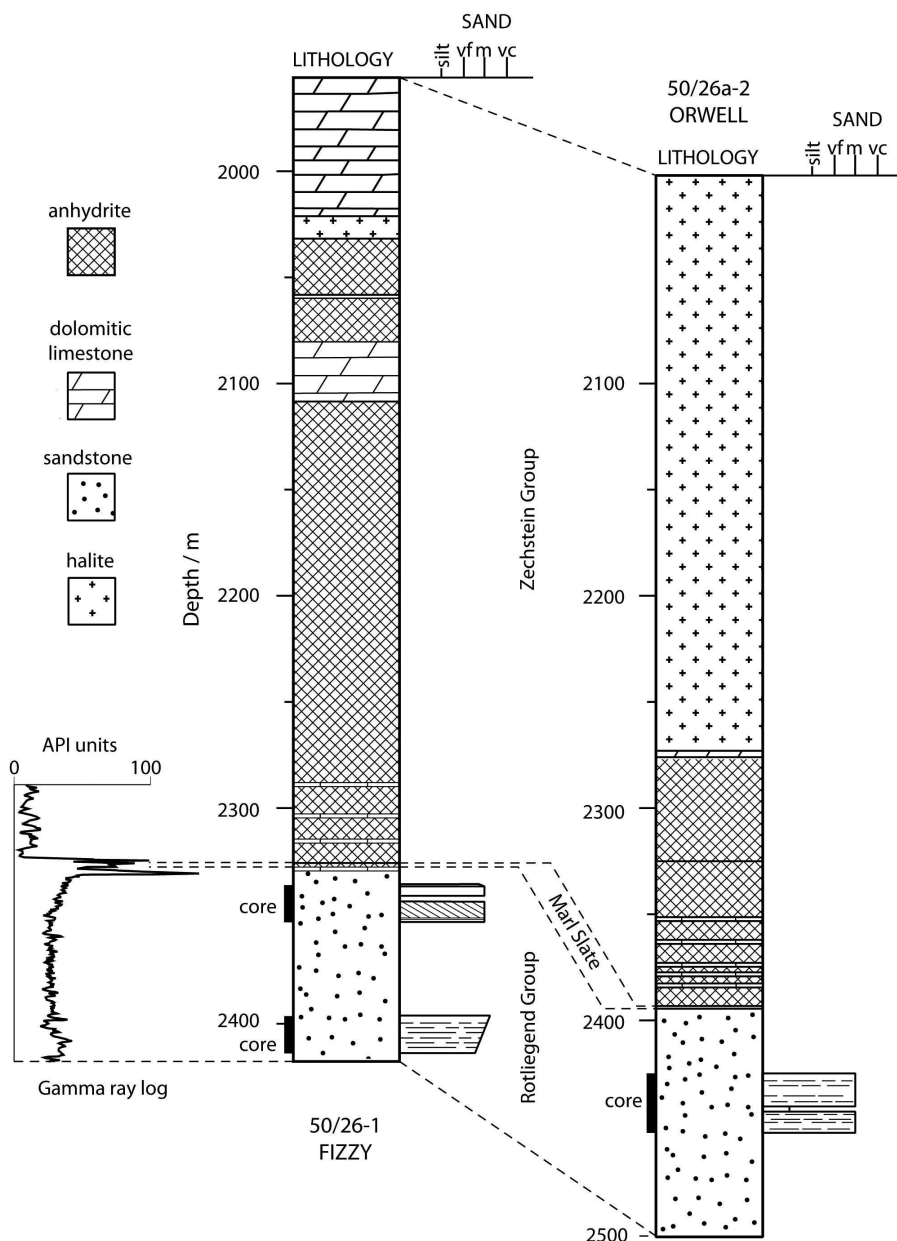


FIG. 2.—Stratigraphic log of reservoir and seal of the Fizzy accumulation and the Orwell field, drawn from composite logs released by the UK Government. Grain sizes are shown only for cored sections (shown as black bars) which are deemed to be representative of the uncored sections as illustrated by the gamma ray log.

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 in either thin sections or rock chips despite extensive use of both light and SEM petrographic techniques. We infer the dawsonite to be clay sized. No other carbonates have been identified in the sandstones, though siderite and magnesite have been reported in other Rotliegend sandstones from the Southern North Sea (Purvis 1992; Zeigler 2006). There is no dawsonite in the available samples of Rotliegend of the Orwell field, within the resolution of our methods.

Dolomite cement in 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 (Fig. 6A, 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 grain size 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 in Fizzy is unknown. It is tempting to suggest that the high CO_2 levels in the Fizzy accumulation are related to fluid movement up the regional-scale fault which lies to the west of the

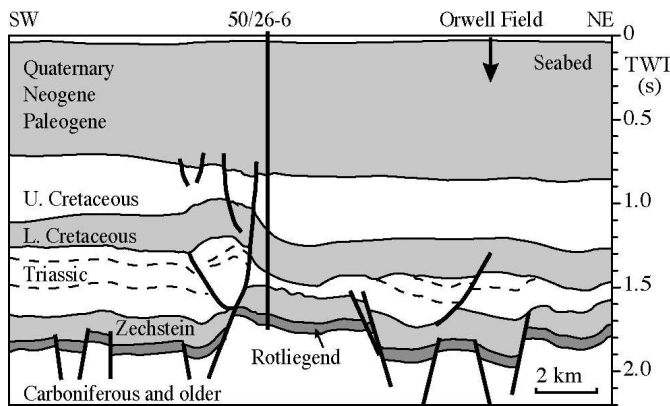


FIG. 3.— Cross section through the Fizzy accumulation. For location see Figure 1. Drawn from seismic; note that the section is not depth-converted so that the vertical axis is two-way travel time.

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 CO₂ according to a press release by the drilling company (Serica Energy 2006). It is hence assumed that the CO₂ is derived from below the Rotliegend reservoir, and is not the product of relatively shallow, biogenic reactions. Note that the carbon isotope ratio of the CO₂ is within the range that biogenic reactions could produce, but the ratio is not diagnostic of a particular process and would have to be a mixing of the result of two or more metabolic processes (Wycherley et al. 1999). Assuming a deep source, there are two most likely origins: thermal alteration of sediments or mantle degassing (Wycherley

et al. 1999). There is no recent igneous activity in the area, but it is not possible to eliminate mantle sources, perhaps associated with inversion which began in the Late Cretaceous (Hillis 1995). If the CO₂ is derived by the thermal alteration of sediments, then the source sediment is unidentified. The measured carbon isotopic ratios of the CO₂ apparently eliminates derivation from the abundant coal in the underlying Carboniferous Coal Measures (Wycherley et al. 1999), leaving a limestone as the possible source. Given that the area has been uplifted c. 440 m since the Late Cretaceous (Hillis 1995) and has consequently cooled, thermally driven CO₂-generating reactions would be expected to substantially slow or stop. It seems probable that the CO₂, if thermally derived, predates the inversion. Hence, regardless of the source of the CO₂, it can be argued that the CO₂ charged the reservoir before or during the inversion, and consequently has been in the reservoir, in contact with any reactive minerals, for at least 50 Myr. This is the only estimate of the timing of CO₂ charge into the Fizzy accumulation, insomuch as there are no minerals that definitely grew when the CO₂ arrived for which the isotopic fractionation factors are known.

In order for the CO₂ charge to be significantly sequestered within a sandstone reservoir, 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 modeling 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.

TABLE 1.— Composition of Rotliegend sandstone from Fizzy accumulation and Orwell fields, point-count data. Dawsonite determined by XRD.

Field	Well	Depth / m	Fluid Zone	Rock Frag-ments	Quartz	K-feld-spar	Plagio-clase	Micas	FOG	QOG	Dolo-mite	Clay (Not Kaolin)	Kao-lin	Gypsum And Anhydrite	Dawsonite	Porosity
Fizzy	50/26-1	2338.4	water	51	12	7	0	0	0	1	14	0	3	0	0.6	12
Fizzy	50/26-1	2343.9	water	46	14	8	0	0	0	5	14	0	5	0	0.2	7
Fizzy	50/26-1	2354.8	water	54	18	5	0	0	0	2	6	0	3	0	0.3	12
Fizzy	50/26-1	2350.9	water	51	19	6	0	0	0	2	8	2	1	0	0.3	9
Fizzy	50/26-1	2402.9	water	59	16	2	0	0	0	1	5	2	1	0	0.5	14
Fizzy	50/26b-6	2292.6	gas	56	27	2	0	0	0	0	5	1	1	0	0.7	7
Fizzy	50/26b-6	2299.1	gas	47	14	10	0	0	0	2	7	0	2	4	0.8	13
Fizzy	50/26b-6	2305.1	gas	50	14	6	0	0	0	1	10	0	3	2	0.1	13
Fizzy	50/26b-6	2311.3	gas	57	17	5	0	0	0	2	2	0	4	3	0.5	9
Fizzy	50/26b-6	2316.3	gas	60	19	3	0	0	0	2	1	0	2	2	0.1	10
Orwell	50/26a-7	2333.7	unknown	42	11	19	0	0	0	1	11	0	0	5	Below detection	10
Orwell	50/26a-7	2342.7	unknown	37	11	22	0	0	0	0	14	0	1	3	Below detection	13
Orwell	50/26a-7	2352.4	unknown	43	12	12	0	0	0	2	10	0	6	3	Below detection	10
Orwell	50/26a-7	2363.7	unknown	40	13	17	0	0	0	0	11	0	4	1	Below detection	11
Orwell	50/26a-7	2376.3	unknown	37	14	18	0	0	0	0	9	1	5	7	Below detection	7
Orwell	50/26a-2	2425.9	unknown	46	8	11	0	0	0	0	11	0	6	15	Below detection	3
Orwell	50/26a-2	2428.6	unknown	47	11	11	0	0	0	0	8	0	7	4	Below detection	11
Orwell	50/26a-2	2432.3	unknown	40	10	10	0	0	0	0	11	0	12	5	Below detection	10
Orwell	50/26a-2	2440.5	unknown	42	11	8	0	0	0	0	23	0	3	11	Below detection	0
Orwell	50/26a-2	2447.5	unknown	42	8	7	0	0	0	0	12	0	8	13	Below detection	7

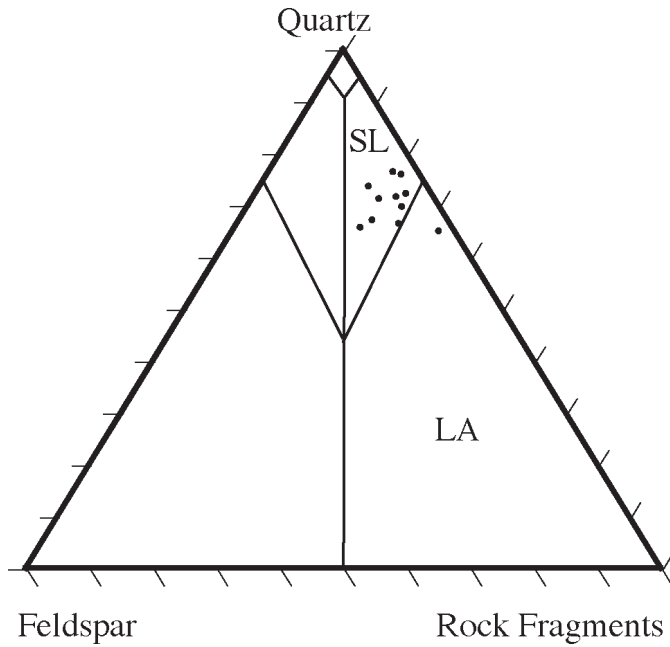


FIG. 4.—Petrographic composition of sandstones within Fizzy accumulation from point count-data. LA = litharenite; SA = sublitharenite.

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 in alkaline soils (e.g., within the Eocene Green River Formation, USA) or during diagenesis or hydrothermal activity associated with high CO₂ concentrations. It has not been previously reported in 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, certainly in sufficient quantities for detection by XRD. 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 Equation 1. Values of parameters are given in Table 2.

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

$\rho_{\text{solid rock}}$ 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 pore space 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

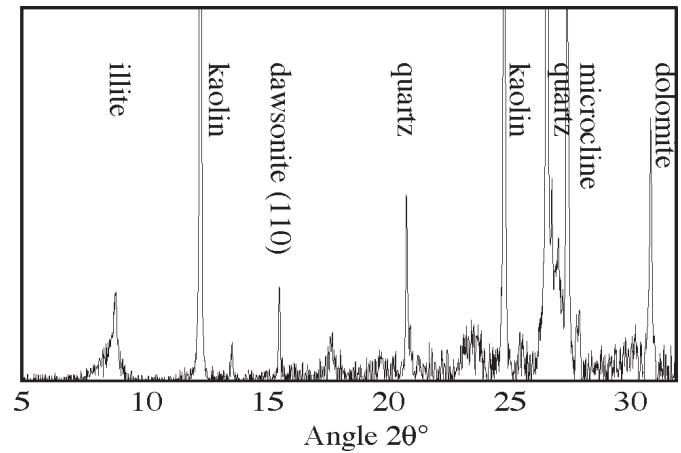


FIG. 5.—XRD trace of clay-size fraction (< 2 μm equivalent spherical diameter) showing the 110 dawsonite peak. Cu K α radiation.

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 predates the CO₂ charge. There is no petrographic evidence of a late dolomite cement; however, the problem is still 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 in 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 two fields using SEM-CL revealed no systematic differences (Fig. 6D). The bright zone that rims the dolomite crystals in Figure 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 in the Rotliegend fields that have been previously studied, with means in wells varying from 0 to 13% even within a single sedimentary facies, in this case dune-bedded sandstones (Purvis 1992). The abundance of dolomite in 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, inasmuch 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

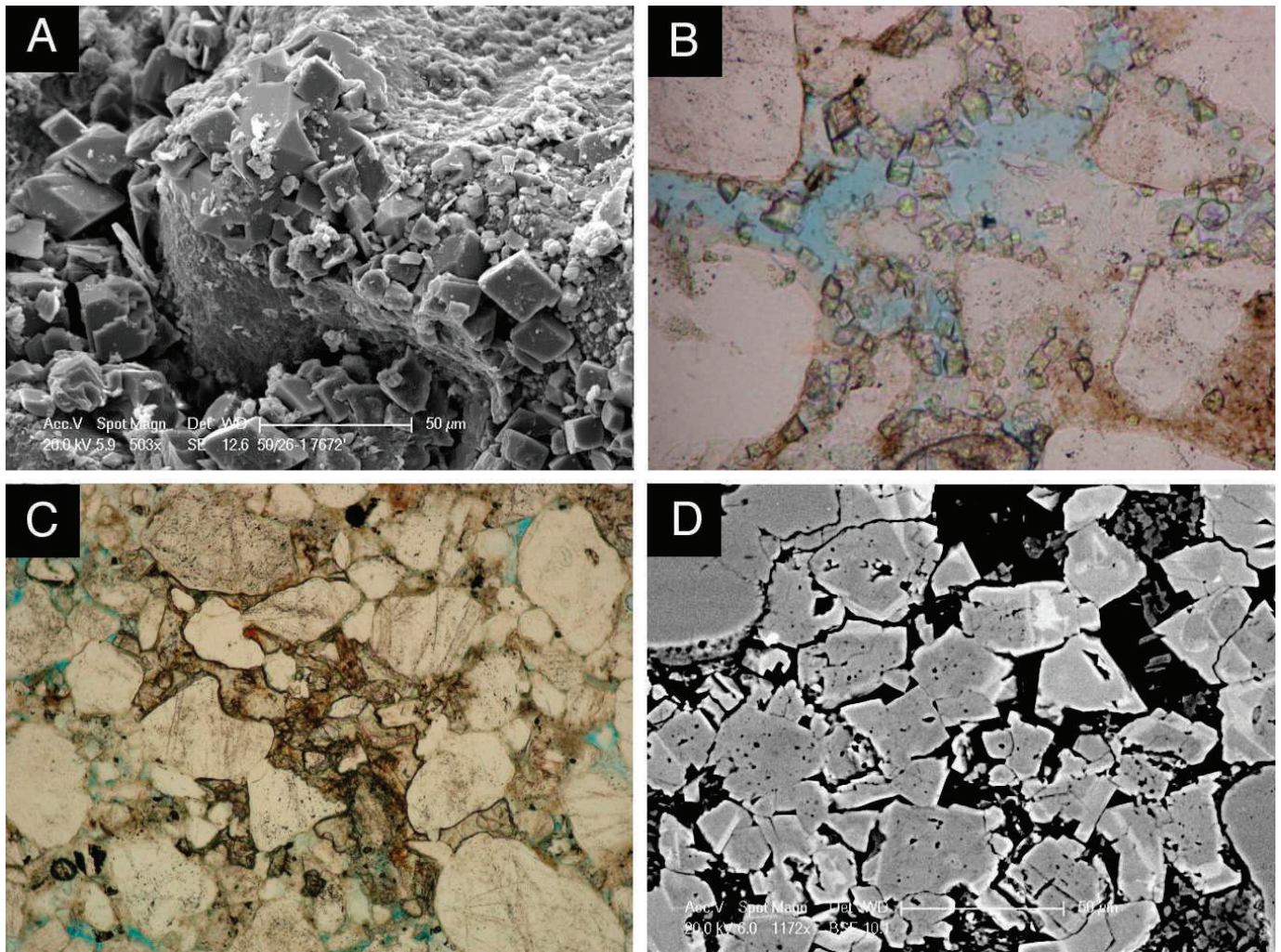


FIG. 6.—A) Pore-lining dolomite cement typical of the upper parts of the Rotliegend section. B) Thin-section view of the pore-lining cement. FOV = 2.5 mm. C) Dolomite mini-concretion from the lower part of the Rotliegend section. FOV = 2.5 mm. D) SEM-CL image of dolomite from the Orwell Field, which is very similar to that in the Fizzy accumulation. FOV = 190 microns.

that there could be percent levels of late CO₂ charge-related dolomite in 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-isotope analysis was used to quantify the proportion of late CO₂-related dolomite.

Stable-Isotope Evidence

Stable-isotope analysis of dolomites was 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. 1990). 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-isotope 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 utilized, but the more recent equation of Vasconcelos et al. (2005) gives very similar results that do not affect 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 utilize 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 are 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 that in 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 two

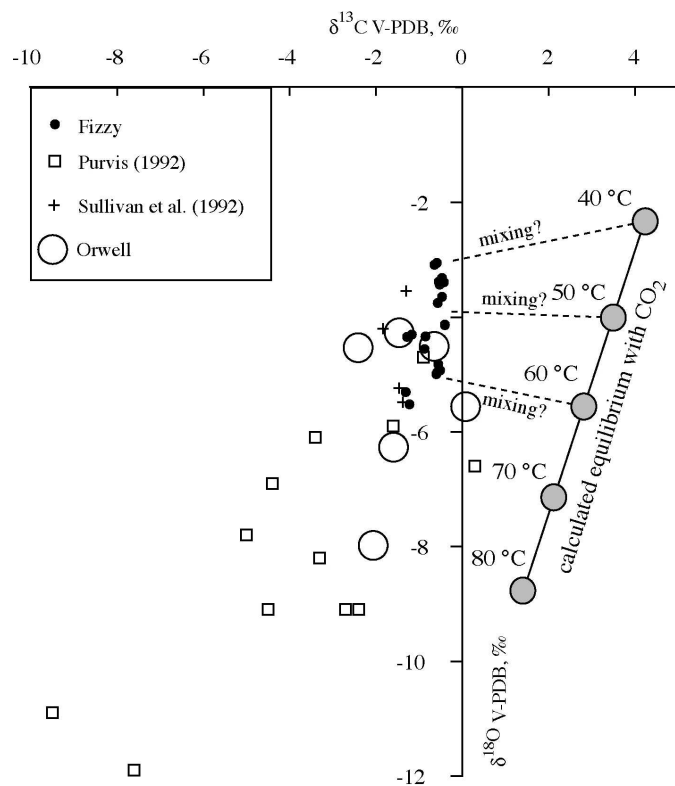


FIG. 7.—Stable C and O isotope data for dolomites from the Fizzy and Orwell gas accumulations. Also shown are regional data from the Rotliegend sandstone, and the calculated compositions of dolomite precipitated from the CO₂ charge for 40–80°C. Note the lack of real data lying on or close to the calculated compositions, and the similarity between the Fizzy data and the regional data.

fields (Fizzy mean $\delta^{13}\text{C} = -0.7 \pm 0.1$ ‰ V-PDB; Orwell mean $\delta^{13}\text{C} = -1.3 \pm 0.4$ ‰ V-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 in 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 favoring a low figure within this range, as above.

Combining the CO₂ sequestered in the dawsonite and possibly in the dolomite cements leads to an estimate that between 0.5 and 30% of the total CO₂ in 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 greater part 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), 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 modeling, 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, U.S.A., 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 modeling studies that when large volumes of CO₂ are injected into a sandstone reservoir, 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 in 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 in the reservoir. We suggest that the role of mineral reactions in sequestering CO₂ in a solid phase has sometimes been overestimated.

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 supplied mainly by the dissolution of chlorite, hematite, and oligoclase (Xu et al. 2005). The Rotliegend reservoir in the Fizzy field lacks significant quantities of any of these minerals, or of other potentially reactive phases such as volcanic rock fragments—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. However, the lack of dawsonite cannot be readily 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

TABLE 2.—Parameters used in calculation of CO₂ distribution.

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 \pm 0.3 %	Table 1
Rock porosity (Φ)	22.3 \pm 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 Pruess (2005)
Weight fraction dolomite in solid rock related to late CO ₂ charge (W_{dolomite})	0.7 \pm 0.2 %	See text
Weight fraction CO ₂ in dolomite ($F_{\text{CO}_2, \text{ dolomite}}$)	0.48	From chemical formula

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?	$\delta^{13}\text{C}$, ‰ V-PDB	$\delta^{18}\text{O}$, ‰ V-PDB
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

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), for which more research is clearly required.

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 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 most 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 dependent upon an unusual mineral is that of Gunter et al. (2000). Here, glauconite provided most of cations. Modeling the Glauconitic Sandstone of the Alberta Sedimentary Basin, Gunter et al. (1997) predicted that over 90% of CO₂ would be sequestered by reaction with ferromagnesian minerals over thousands of years. Even then, this high trapping efficiency was dependent 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 with which to react.

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 hematite. 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 in 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 modeling 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 (only an approximation at such high gas concentrations) then again the effect is relatively minor. Using the equations of Spycher 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 modeling 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,

in that 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 in the natural Fizzy 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 modeling 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 Myr.
- (4) The Rotliegend sandstone is still 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.

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