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Long-term performance of a mudrock seal in natural CO$_2$ storage

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ABSTRACT

The ability of mudrock seals to prevent CO$_2$ leakage is a major concern for geological storage of anthropogenic CO$_2$. The long-term performance of a mudrock seal, which provides a natural analogue, in the North Sea Miller oil field has been evaluated. This mudrock seal is immediately above a natural CO$_2$-rich reservoir. The paper reports the stable isotopes of carbon from carbonate minerals in the mudrock that have precipitated in contact with CO$_2$ during 4 km of burial. A well-defined linear trend of upward-decreasing $\delta^{13}C$ traces the progressive penetration of free-phase CO$_2$ causing dissolution and reprecipitation of carbonate minerals. The CO$_2$ was emplaced ca. 70–80 Ma, and has only penetrated 12 m vertically in this case. The infiltration rate is estimated as $~9.8 \times 10^{-7} \text{g cm}^{-2} \text{yr}^{-1}$. Engineered CO$_2$ storage under this type of mudrock seal will have a considerable safety margin.

INTRODUCTION

For effective storage of industrial CO$_2$, retention times of $~10^4$ yr or greater are required (Lindeberg, 2002). One critical question is whether mudrock seals can remain impermeable to CO$_2$ for such long periods of time. It will not be possible to run pilot schemes or carry out experiments on these time scales, so the gap between current experience (tens of years for storage and enhanced oil recovery, and months for experiments) and the long-term CO$_2$ storage can only be bridged by studying analogues, such as natural CO$_2$ accumulations.

The Miller oil field of the UK North Sea contains an average $~28 \text{ mol}\%$ pristine natural CO$_2$ in oil-associated gas (Baines and Worden, 2004). The Kimmeridge Clay Formation forms a mudrock seal, and has been exposed to the high levels of CO$_2$ on geological time scales. We compare the Kimmeridge Clay Formation seal from the Miller field (well 16/8b-A2) to a similar Kimmeridge Clay Formation sequence from a low-CO$_2$ area $~30 \text{ km}$ to the northeast (well 9/28b-17). The aim of this study is to identify any leakage of CO$_2$ through the seal, and to quantify leakage. To do this, stable isotopes of carbonate minerals precipitated within the mudrock were analyzed. These record the origin of the CO$_2$ source.

The Miller field is located near the western margin of the South Viking Graben (Fig. 1). The reservoir is the Upper Jurassic Brae Formation, which is composed of submarine fan sandstones (Turner et al., 1987), currently buried to $~4 \text{ km}$, which is the maximum burial depth experienced by the reservoir. The present-day reservoir temperature is $~120 \degree \text{C}$ and pressure is $5 \times 10^7 \text{ Pa}$ (Rooksby, 1991). The Kimmeridge Clay Formation, which overlies and underlies the Brae Formation reservoir sandstones, acts as both source rock and seal for the petroleum fields in this region. It consists predominantly of mudrocks, with interbedded thin sands and silt beds (MacKenzie et al., 1987).

The petroleum fields in the Brae-Miller area contain natural CO$_2$, which decreases in concentration eastward from the graben boundary (Fig. 1). The present-day distribution of CO$_2$ suggests upward migration along the boundary fault of the South Viking graben followed by lateral dispersion. The CO$_2$ $\delta^{13}C$ in the Miller field is $~8.2\%e$ (Vienna Pee Dee belemnite, VPDB) (Baines and Worden, 2004), similar to the regional value (James, 1990). It is assumed that the carbon isotopic ratio has remained the same value since the initial charge.

METHODS

For isotopic analysis, mudrock samples were taken from drill core within a $30 \text{ m}$ interval immediately above the reservoir top. Mudrock powder samples were collected from drill at spacing of $~20 \text{ cm}$ adjacent to reservoir top and at progressively wider spacing further up, using an electric drill with a tungsten carbide drill bit. Thin mudrock beds in reservoir section were also sampled. Rock chips of $5–10 \text{ mm}$ diameter were taken, and polished flat for scanning electron microscope (SEM) petrographic analysis with energy dispersive spectrometry (EDS). Two different boreholes were sampled, using identical methods. One from the high-CO$_2$ Miller field (well 16/8b-A2), and a second from an identical geological age and depositional position above the reservoir sandstone, but in a low-CO$_2$ area (well 9/28b-17, henceforth referred to as the control well; Fig. 1). It is assumed that the present-day pattern of CO$_2$ abundance has persisted for geological periods of time. The regional pattern of decreasing CO$_2$ concentrations away from the basin-scale fault suggests a point CO$_2$ conduit.

Oxygen and carbon isotopic analyses were performed on both sample suites at Scottish Universities Environmental Research Centre, Scotland. Isotopes were measured from whole-rock samples. Carbon and oxygen isotope ratios of carbonate were determined using conventional procedures. The CO$_2$ gas for isotopic analysis was extracted from whole-rock powder by overnight reaction with 103% phosphoric acid at $70 \degree \text{C}$. The
evolved carbon dioxide gas was dried and purified before isotopic analysis on an Analytical Precision AP 2003 mass spectrometer. Isotopic values are reported as δ‰ values relative to VPDB. Precision and accuracy are better than ±0.2‰ at 1σ. The fractionation factors between free-phase CO₂ and calcite used here are from Deines et al. (1974).

Carbonate mineral abundance was determined by measuring total inorganic carbon using a CM 5012 CO₂ coulometer supplied by UIC Coulometrics Inc. Approximately 80 mg of powder for each sample was acidified with two molar perchloric acid. The evolved CO₂ was extracted from solution and transferred to the detector.

RESULTS

A strong correlation of δ¹³C versus depth was revealed in well 16/8b-A2 of the Miller field. Figure 2A shows that δ¹³C of whole-rock carbonates linearly decreases upward from −0.77‰ to −7.4‰ VPDB over a vertical interval of ~12 m in the seal immediately above reservoir (Fig. 2A; GSA Data Repository Table DR1¹). The correlation coefficient (R²) between δ¹³C and depth is 0.90, such that the linear correlation is strong for any reasonable degree of significance. Above this 12 m zone, δ¹³C data are scattered randomly, with an average of −5.3‰ VPDB. Carbon isotopes of mudstone within the reservoir are at the high δ¹³C end of the linear trend, ranging from −0.65‰ to −4.6‰ VPDB. No such linear correlation exists in the control well (R² is only 0.18 in the same interval; Fig. 3A). Oxygen isotopes show a weak correlation with depth in the 12 m zone of the Miller well (R² = 0.31; Fig. 2B), and no correlation can be seen in the control well (R² = 0.15; Fig. 3B).

In the 12 m interval above the reservoir in the Miller well, carbonate abundance in mudrock displays a general upward increase from 0.17 to 3.08 wt% (Fig. 2C; Table DR2). Data above the interval show a random distribution with overall higher values. EDS analysis of polished samples on an SEM shows that the predominant carbonate mineral is calcite (>90%), with small amounts of dolomite and ankerite, and no detectable siderite (Fig. 4). The carbonate minerals are often seen growing in secondary pores, indicating late growth periods (Fig. 4).

DISCUSSION

Stratigraphic correlations of carbonate isotopes have been observed elsewhere and have been interpreted to be controlled by volcanism (Weisett and Erba, 2004), by changes in paleoclimate during deposition (Schmid et al., 2006), by diagenesis related to oil filling (Wilkinson et al., 2004), and by pore-water stratification (Macaulay et al., 1992). We argue that the δ¹³C isotopic trend observed in the Miller well resulted from a diagenetic event and not from depositional processes. The 12-m-thick interval in the Miller well immediately overlying the reservoir is referred to as the anomalous zone.

In the Miller well, unlike in the Corrib field where δ¹³C was interpreted to be controlled by changes in paleoclimate (Schmid et al., 2006), no systematic lithologic variations are observed in the drill cores and the wireline logs throughout the anomalous zone (Fig. 2D), as would be expected if a change in environment had occurred during deposition. In addition, a linear isotopic trend does not exist, or is not well developed, in the low-CO₂ control well located in a similar geological setting, as would be expected for a regional change in paleoenvironment. Petrographic examination shows that the carbonates often infill secondary pores related to mineral dissolution and/or intergrow with diagenetic minerals such as kaolin, indicating a late diagenetic origin (Fig. 4). These observations strongly suggest that the isotopic trend is not a result of depositional or early diagenetic processes. Both oil filling and pore-water layering are reported to result in oxygen isotope variation, not carbon (Wilkinson et al., 2004; Macaulay et al., 1992). It is hence argued that the anomalous zone is related to the CO₂ accumulation in the underlying reservoir.

How did the influx of CO₂ into the reservoir change the isotope ratios from those in the unaltered zone to those of the anomalous zone within the seal? One mechanism for resetting isotopes is to simply overwhelm the original isotopic ratios by the precipitation of large volumes of new carbonate. However, the abundance of carbonate within the anomalous zone (average 1.5%) is, at least in part, lower than the overlying unaltered zone (average 2.0%). Carbonate inorganic carbon is in equilibrium with the wet CO₂. With the CO₂ accumulation in the underlying reservoir, the δ¹³C of the carbonate will be changed by dissolution and/or incorporation into the carbonate mineral. Because CO₂ is not a mineral phase, it cannot be preserved in the fossil record. The δ¹³C signal needs to be reset to reflect the CO₂ accumulation in the underlying reservoir. One mechanism to reset the carbonate δ¹³C is by exhumation and burial of the carbonate rock. This mechanism will also change the δ¹⁸O signal of the carbonate. The δ¹³C and δ¹⁸O values of the carbonate in the Miller well are lower than those in the unaltered zone, indicating that the δ¹³C signal has been reset to reflect the CO₂ accumulation in the underlying reservoir. The δ¹⁸O signal of the carbonate in the Miller well is also lower than those in the unaltered zone, indicating that the δ¹⁸O signal has been reset to reflect the CO₂ accumulation in the underlying reservoir. The low δ¹³C and δ¹⁸O values of the carbonate in the Miller well are consistent with the CO₂ accumulation in the underlying reservoir. The δ¹³C and δ¹⁸O values of the carbonate in the Miller well are consistent with the CO₂ accumulation in the underlying reservoir. The δ¹³C and δ¹⁸O values of the carbonate in the Miller well are consistent with the CO₂ accumulation in the underlying reservoir.

GSA Data Repository item 2009009, isotope data tables and modeling details, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

![Diagram](Image)

Figure 2. A: δ¹³C‰ versus depth of carbonates in whole-rock mudrock samples, well 16/8b-A2, Miller field. Carbon isotope ratio varies linearly with depth in the anomalous zone. This is interpreted as dissolution of original carbonates, followed by regrowth incorporating signatures of infiltrated CO₂. Projection of modeled results (oblique dashed line) shows good match to data. VPDB—Vienna Pee Dee belemnite; TVDSS—true vertical depth subsea. B: δ¹⁸O‰ versus depth of carbonates in the same samples, showing poor correlation between isotope and depth. However, general lower δ¹⁸O‰ values in anomalous zone indicate later formation. C: Carbonate abundance in the mudstone generally increases upward within anomalous zone and scatters randomly above. D: Gamma ray, density, neutron, and sonic logs show no systematic variations through anomalous zone to suggest lithologic transitions. High values in resistivity logs (rightmost) in anomalous zone indicate infiltrated CO₂ replacing pore water.
zone (0.50%–2.8%; average 1.7%) and is certainly not significantly higher (Fig. 2C). This disproves the “overwhelming” hypothesis, which would inevitably result in an increase in carbonate abundance. Another hypothesis would be mixing of two end members with different isotopic composition. While it has not proved possible to produce quantitative abundances of the different carbonate minerals with depth, or to analyze individual carbonate grains due to their very small size, it is clear from SEM studies that calcite is always the predominant carbonate phase present (Fig. 4). Several two end-member mixing models were constructed as part of this study, but no model considered could explain the observed data while using geologically feasible end members. Note that the δ13C trend extends well beyond the data range of the overlying zone and there is an abrupt change across the upper boundary of the anomalous zone. This also argues against a smooth transition or mixing between two carbon domains. Hence, the conventional model of two carbonate end-member mixing is dismissed in this case.

If the anomalous zone is related to the upward infiltration of CO2 from the underlying reservoir, then the top of the zone represents the limit of vertical CO2 penetration. In the anomalous zone, dissolution of pre-existing carbonate should have preceded the growth of the present-day carbonates containing a partial signature from the penetrating CO2, so that the scattered isotopes preserved in the overlying unaltered section were eliminated. This dissolution can be attributed to the initial acidifying effects of the CO2 infiltration. The overall quantity of carbonates precipitated is similar to those dissolved, suggesting approximate cation conservation.

A model is hence proposed for the equilibrium formation of the present-day carbonates in the anomalous zone, involving mixing of three carbon sources in varying proportions as a function of distance from the CO2-rich reservoir (Fig. 5). Simpler, two-component mixing was considered, but none adequately reproduced the measured data when justifiable components were used. In the model, the carbonates in the anomalous zone precipitated from mixing of three sources, after total dissolution of the original carbonates. The first carbon source is hence the dissolved original carbonates, with an average δ13C = −5.3‰ VPDB. The proportion of total C from this source is assumed to be constant through the zone (20% of total C; 0.005 g C/cm3 of whole rock). Both δ13C and abundance of source 1 are taken from the averages of the carbonates above the anomalous zone. The second C source is the CO2 infiltrating into the seal from the reservoir (δ13C = −8.2‰ VPDB, assumed constant through time), which triggered the dissolution of the pre-existing carbonates. The proportion of total C contributed by this source decreases linearly from 80% at the bottom to 46% at the top of the anomalous zone (0.02–0.01125 g C/cm3 of whole rock; gas saturation of 50%–90%). The third source is from thermal decarboxylation of organic matter (δ13C = −20‰ VPDB) (Irwin et al., 1977), the proportion of which increases from zero to 36% (0–0.00875 g C/cm3) from the bottom to top of the anomalous zone. This represents the increasing rate of decarboxylation as burial temperature progressively increases. Mixing of carbon sources 2 and 3 in linearly varying proportions, and source 1 as a constant proportion, would produce carbonates with linearly varying isotopic compositions.

The timing of CO2 charge into the reservoir can be estimated from the C isotope ratios of mudstone in the reservoir section, assuming the carbonates have been reset by the charge. The higher δ13C values in the reservoir,
ranging from −0.65‰ to −1.6‰ VPDB, are in equilibrium with the reservoir CO₂ (δ13C = −8.2‰ VPDB) at −60–70 °C. This suggests that the CO₂ charged ca. 70–80 Ma, according to the burial curve of the Miller field (Marchand et al., 2001). The carbonate at the bottom of the anomalous zone (δ13C = −0.77‰ to −1.7‰ VPDB) is also in equilibrium with the CO₂ at similar temperatures. It is hence deduced that CO₂ penetrated into the seal and caused carbonate isotopic resetting immediately after its emplacement.

Therefore, precipitation of the present-day carbonate initiated at 70 °C in the reservoir mudrock and at the bottom of the anomalous zone; precipitation was progressive and the precipitation front moved steadily upward, to reach ~12 m above the reservoir top at the present-day reservoir temperature of 120 °C. Due to change in depositional rate, burial temperature increased faster from 70 to 40 Ma (1.17 °C/m.y.) than from 40 Ma to present-day (0.38 °C/m.y.) (Marchand et al., 2001), which explains the slightly concave shape of the observed isotopic trend. This model provides a good match to the measured data (Figs. 2A and DR1; Table DR3). Above the anomalous zone, the carbonates remain unaltered.

Based on this model, the CO₂ infiltration rate is estimated as an average of 9.8 × 10⁻²g cm⁻² yr⁻¹ over 70 m.y.

Note that the abundance of the infiltrating CO₂ infiltrating (0.02–0.01125 g/cm³) requires the presence of free-phase CO₂ within the anomalous zone. A model that utilized only dissolved CO₂ in pore water would require ≥80% porosity in the mudstone to produce such an isotopic trend, because of the low solubility of CO₂ in water under the field conditions (<5 wt%) (Enick and Klara, 1990; Kohl and Nielsen, 1997). The presence of free-phase CO₂ within the anomalous zone (gas saturation 50%–90%) is supported by the high resistivity in the zone (see the rightmost log in Fig. 2D). Free-phase CO₂ is more resistive than aqueous pore fluid, so its presence in pore space raises the overall resistivity of the rock.

The anomalous zone in the Miller well does not display a strong correlation of δ18O versus depth (Fig. 2B). This probably reflects the rock and water-dominated nature of the chemical system in the mudrock, such that oxygen of the diffused CO₂ was only a minor component and did not dominate the isotope ratio. The wide range of observed δ18O values may reflect influence of local minerals. If the isotopic composition of the pore water within inhomogeneous mudrocks is controlled by the minerals that bound the pore space, any carbonate precipitated within the pore space would be locally controlled, resulting in heterogeneous δ18O values as observed. The suggested temperatures of carbonate precipitation coincide with the smectite to illite transformation in the North Sea (Wilkinson et al., 2006), such that pore-water oxygen ratios could be partly controlled by local smectite abundance and reactivity.

CONCLUSIONS
Carbonate minerals in the mudrock seal, immediately overlying the CO₂-rich reservoir of the Miller oil field, show a linear trend of carbon isotopic ratios versus depth through ~12 m of section. Such a trend is absent in a control well where CO₂ is not abundant. It is suggested that this trend is due to the infiltration of free-phase CO₂ from the underlying reservoir, causing the dissolution of pre-existing authigenic carbonate minerals, and then reprecipitation incorporating small quantities of infiltrating CO₂.

The 8°C values in the reservoir and the bottom of the seal have recorded the earliest CO₂ influx, giving an estimate of first CO₂ charge and infiltration ca. 70–80 Ma. The amount of CO₂ infiltrated into the seal must be limited, and this CO₂ has penetrated only 12 m above the reservoir. The infiltration rate is estimated to average 9.8 × 10⁻²g cm⁻² yr⁻¹ during 70 m.y. It is suggested that the Kimmeridge Clay Formation mudrock at 4 km depth, a widespread seal in the North Sea, would be a robust seal for storage of anthropogenic CO₂, as the natural system appears to have retained a CO₂ accumulation for far longer than is required for engineered storage.

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REFERENCES CITED


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