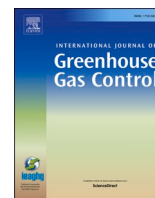






Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggcInteractions of CO₂ with sedimentary blue carbon: the fate of leaked CO₂ from a geological storage siteMalini Kallingal^{a,*} , Tom Kettley^a , Christopher Batchelor-McAuley^b ,
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ARTICLE INFO

Keywords:

Sedimentary blue carbon
Geological carbon storage
Leakage risk
Calcium carbonate
Buffering
Dissolution
Alkalinity
Carbon dioxide

ABSTRACT

One of the main considerations in terms of carbon dioxide removal techniques is the net carbon storage potential, i.e. whether the amount of carbon that can be stored, significantly outweighs the carbon footprint of the process of storage. Here we assess the potential for disruption of blue carbon stored in sediments, and interactions with leaked CO₂ above a sub-seafloor geological storage site. Blue carbon is carbon stored within the ocean which, in this study, is in the form of sedimentary calcium carbonate, or organic carbon. CO₂ injected into sub-sea bed geological storage sites can be effectively trapped and retained. Despite the perceived safety of geological CO₂ storage, it is imperative to thoroughly evaluate and address the risks of carbon loss either through disturbance of sea bed carbon with infrastructure, or through the impacts of potential CO₂ leakage from the storage reservoir. This study aims to quantify the amount of blue carbon, and its different components, which is at risk of loss above a proposed CO₂ reservoir in the North Sea. Second we investigate the impact of CO₂ leakage from the reservoir on sediment-stored blue carbon through laboratory based experiments. The sediments in the North Sea were found to contain minimal organic carbon but a significant variable fraction of biogenic calcite in the form of shells. The leaked CO₂ was found to act as an acid titrating away the CO₃²⁻ ion in seawater to drive undersaturation with respect to calcite until equilibration occurs between the CO₂ stream and the calcite. The study infers that sites abundant in particulate inorganic carbon (PIC) face a heightened risk of blue carbon depletion in the event of leakage, but with considerable potential for re-sequestration of the escaped CO₂ into solution as the HCO₃⁻ ion, as a result of enhanced dissolution of seafloor calcium carbonates and release of buffering alkalinity. This aqueous storage of any released CO₂ will be limited under low rates of release, due to the titration of the carbon dioxide with the alkalinity already present in the sediment pore water. Conversely, at higher release rates the re-sequestration of the escaped CO₂ is controlled by the solubility of the calcium carbonate under near CO₂ saturated conditions, such that the proportion of resequenced CO₂ can be quantified through a thermodynamic framework. Locales rich in particulate organic carbon (POC) tend to exhibit a reduced susceptibility to blue carbon loss, yet have a reduced neutralization potential for CO₂ leakage.

1. Introduction

Carbon capture and storage has become increasingly crucial in the 21st century as the urgency of addressing global warming intensifies (Metz et al., 2005). Geological storage of CO₂ involves capturing carbon dioxide emissions produced from industrial processes or power generation and injecting them into geological formations deep underground. The aim is to remove the released CO₂ from the atmosphere and so limit the global warming impact of this greenhouse gas (Bashir et al., 2024).

Common geological storage sites such as depleted oil and gas fields, deep saline aquifers, and unmineable coal seams provide secure and stable environments where the captured CO₂ can be stored over long periods, minimizing the risk of leakage and ensuring that the greenhouse gas remains trapped underground (Harrison and Falcone, 2014). The process of geological storage plays a pivotal role in the fight against climate change, actively curbing its impact by diminishing the collective carbon footprint resulting from human activities [Locked away- geological carbon storage (Policy Brief, Royal Society)]

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Received 24 June 2024; Received in revised form 9 May 2025; Accepted 9 May 2025

Available online 19 May 2025

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Among geological formations suitable for CO₂ geological storage, offshore sediments emerge as one of the most voluminous options, offering significant potential for carbon sequestration. The capacity is estimated at >70 Gtonnes in the UK offshore realm, since the sediment reservoirs potentially offer large storage capacities and, compared to other methods, may have less immediate impact on terrestrial ecosystems (Holloway and Savage, 1993). Seafloor sediments contain a vast quantity of already stored carbon in the form of sedimentary blue carbon. The term “sedimentary blue carbon” denotes the carbon sequestered within coastal and marine sedimentary settings, predominantly comprised of organic matter and inorganic carbonate originating from marine flora and fauna (Fest et al., 2022; Graves et al., 2022). Blue carbon refers to the significant reservoirs of carbon already stored in, for example, coastal ecosystems like mangroves, salt marshes, and sea grasses. The capacity of these marine sediments to store CO₂ may be disturbed by two actions (Atwood et al., 2020). First, the deployment of infrastructure may destroy sedimentary blue carbon. It has been shown that trawling of the seafloor for fishing by re-suspending sediments can result in net loss of sedimentary blue carbon (Atwood et al., 2024; Pusceddu et al., 2014). Second, although small, and mitigated against by careful choice of storage site, there is a risk of leakage of materials from the geological store site including CO₂ dissolved in brines, which may disturb sedimentary blue carbon, depending on the form of carbon within the sediments (Birkholzer et al., 2011; Reguera et al., 2013). Such a release of CO₂ from any storage site, through local acidification, has the potential to detrimentally affect organic carbon degradation (Rastelli et al., 2016) or to lead to mineral dissolution (Lichtschlag et al., 2021) and/or toxic metal release (Wunsch et al., 2014; Kirsch et al., 2014; Ardelan et al., 2009) within sea-floor sediments above a storage site. Leakage is known to be a risk from storage sites as pockmarks. As an example, in reports from the Norwegian Petroleum Directorate a major leakage accident was revealed at the Tordis oil field of the Tampen area with the detection of a sinkhole of 30–40 m wide and 7 m deep in the seabed (Eidvin, 2009).

The potential for leakage of CO₂ exists primarily through faults, fractures, or poorly sealed wells, which could compromise the integrity of the storage system and lead to environmental risk including the disruption of sea-bed sedimentary carbon stores above the storage site. Assuming well-regulated storage in regions with moderate well densities, it is likely that leakage can be minimised to 0.0008 % per year, with over 98 % of the injected CO₂ retained in the subsurface over 10,000 years (Alcalde et al., 2018). Seismic activity, whether natural or induced, can alter the subsurface geological structures, potentially

creating new fractures or reactivating existing faults that can serve as conduits for CO₂ to escape from the storage reservoir (Kano et al., 2010). The intense pressure changes and ground movements associated with seismic events can compromise the integrity of the caprock, the primary barrier that prevents CO₂ from migrating upward. Additionally, seismic events can damage wellbore integrity, including both injection and abandoned wells, making them potential pathways for CO₂ leakage. For example, a study highlighted that fault reactivation during CO₂ injection can alter the permeability of fault zones, although predicting the extent of permeability changes is challenging. This research indicates that while seismic events might not always create continuous leakage pathways, they can still significantly affect the leakage rate depending on the stress and strain conditions of the faults involved (Rinaldi et al., 2014). Whether significant reactivation of faults, occurs, or act as routes for CO₂ leakage is highly regionally variable depending on the characteristics of the reservoir and the geometry of the faults (Mortazavi and Maratov, 2024; Vilarrasa et al., 2017; Glubokovskikh et al., 2022).

It is important to assess the impact of CO₂ leakage from these storage reservoirs on the quota of blue carbon present in the sediment above them. If there were a leakage from geological carbon storage (GCS) reservoirs, the loss of CO₂ could further feedback onto additional loss of sedimentary blue carbon (Fig. 1).

Based on in-situ experimentation, it has been suggested that mineral dissolution could re-sequester some proportion of leaked CO₂ (Lichtschlag et al., 2021) but there have not been extensive assessments of how that CO₂ re-sequestration depends on the sediment composition, nor on the leakage rate. The assessment of the effect of leakage on sedimentary blue carbon has not been extensively studied, and the North Sea merits detailed investigation due to its aptitude to contain multiple CO₂ storage sites. The aim of this study was two-fold: 1) to assess the amount of carbon at risk of loss through leakage or disturbance at sample sites in a selected GCS reservoir in North Sea and 2) to study the chemical dynamics of a CO₂ plume and its interactions with components of the carbon stored in sediments through a simplified gas bubbling experiment.

2. Methods

Our approach combines two distinct methodologies for the assessment of sedimentary blue carbon at risk of disturbance, and experimental investigation of the stability of blue carbon in response to leakage of CO₂.

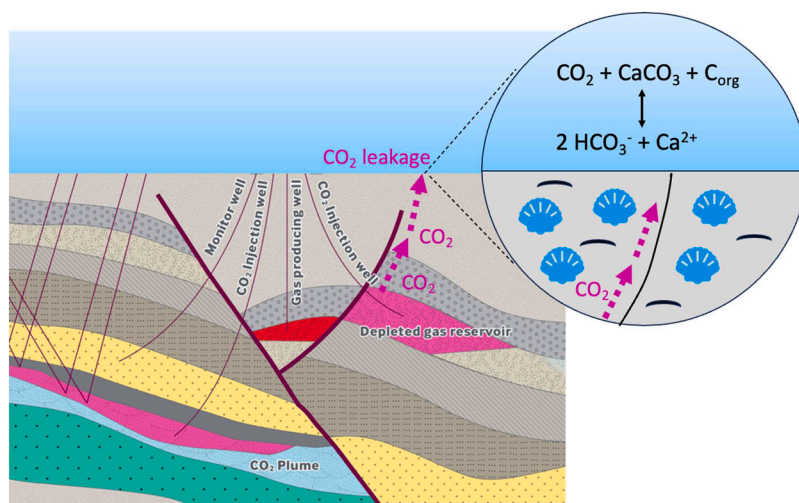


Fig. 1. Schematic depicting the risk of CO₂ leakage from a subsea carbon storage reservoir, along pre-existing or reinvigorated faults, towards the seafloor with potential for interaction with sedimentary blue carbon (CaCO₃: calcium carbonate biominerals in blue), and particulate organic carbon (POC, in black)) as magnified in the circular inset. Figure adapted from the RPS group (<https://www.rpsgroup.com/sectors/energy-consultants/storage/carbon-capture-and-storage-ccs/>).

2.1. Study area

Surface sediment samples were collected from the British Geological Survey (BGS) sample repository representing a range of locations across the sea floor above a proposed geological CO₂ storage site called “Endurance” in the North Sea. The reservoir is a saline aquifer located 60 miles away from Flamborough Head, which is approximately 22 km long, 8 km wide covering an area of 140 km² constituting the UK North Sea blocks 42/25 and 43/21 (Gluyas and Bagudu, 2020). The proposed injection volume slated for the first trial at Endurance stands at 100Mt of CO₂ constituting approximately 3–4 % of the reservoir’s theoretical maximum capacity. This would set the maximum capacity at approximately 2.5 to 3.3 Gt of CO₂, equivalent to around 26 billion barrels. The current maximum storage capacity for the Endurance site is around 450 Mt of CO₂ (Offshore Environmental Statement for the Northern Endurance Partnership, BP report, 2023). Fig. 2 represents the map of North Sea with Endurance site with samples collected from different locations.

2.2. Estimation of total sedimentary blue carbon stock at risk of loss

The grab samples ranged from grit to sandy/clay sediments but notably contained cm-scale white calcium carbonate shells ranging from mm scale fragments to entire cm-scale shells. The samples were ground to a powder in a mortar before analysis. A subsample of 1–2 mg was taken for elemental analysis. It should be noted that some inhomogeneity across the sediment sample may remain due to the size of the shell fragments. The surficial carbon stocks of TC (Total Carbon), PIC (Particulate Inorganic Carbon) and POC (Particulate Organic Carbon) were measured for the samples collected from the Endurance site. For this, determination of carbon content percentages was performed using Thermo Fisher EA Isolink CN elemental analyser. The samples were acid treated with 10 % HCl to remove the CaCO₃ contents. These samples were dried at 70 °C in order to remove excess acid and water and perform the elemental analysis to quantify the POC. The PIC was calculated from the difference in total carbon (TC) and POC values.

2.3. Laboratory experiments to assess risk of blue carbon loss from sediments through CO₂ leakage

In our calculations of sedimentary blue carbon at risk of loss below, we have assumed all processes will destroy all blue carbon regardless of whether in the form of PIC or POC. Here we investigate which components of the sedimentary carbon store are most at risk of loss in order to refine our estimates of carbon. This experiment was set up to study the dynamics of a CO₂ plume interacting with carbon in the sediments. A vertical column made of polymethyl methacrylate having a length of 40 cm and a diameter of 2 cm was used for the CO₂ bubbling experiment represented in Fig. 3. We chose 5 grab samples at random for the bubbling experiments given that the relative invariance in carbon content in the sediment across the area (see Table 1; mean TC = 1 %, stdev = 1.3 %). Sediments were roughly crushed to break up the shells but not homogenised in the same way as the sediments for analysis above, to preserve the “natural state” of sediments at the Endurance site for the experiment. As a result there is some variation in the PIC and POC contents measured in this experiment compared to the fully crushed subsamples in the previous section. These sediments were filled to a length of 10 cm in the bottom of the column and sea water was filled above the sediments. Upon resuspension, it is likely that the dense calcium carbonate sank to the base of the column accounting for the consistently higher PIC contents at the base compared to the top of the sediment. There were two ports for sampling, one in the top and one in the bottom layer. The pH of the sea water was measured by the pH meter attached in a port at the top of the column. The port in the bottom of the column was to purge CO₂ and the flow was regulated by using a flow meter. The outgassing CO₂ was carried out through another port at the top of the column to the CO₂ analyser.

A CO₂ flow of 40ml/min was passed through the sediments for 6 h each day for 5 days, which represented close to the minimum flow rate which allowed observable bubbling and a measurable flow rate in this experimental set-up. 0.3–0.4 g subsamples were collected from the top and bottom layers of the sediments each day after bubbling for TOC, PIC and POC measurements. The change in pH was monitored from the start

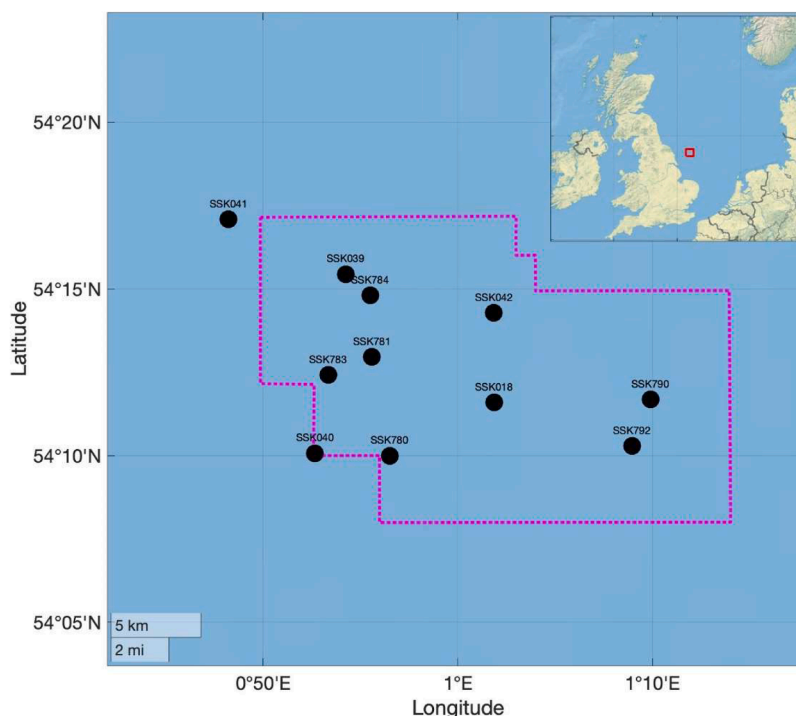


Fig. 2. Map of North Sea with the Endurance site containing samples collected from different locations.

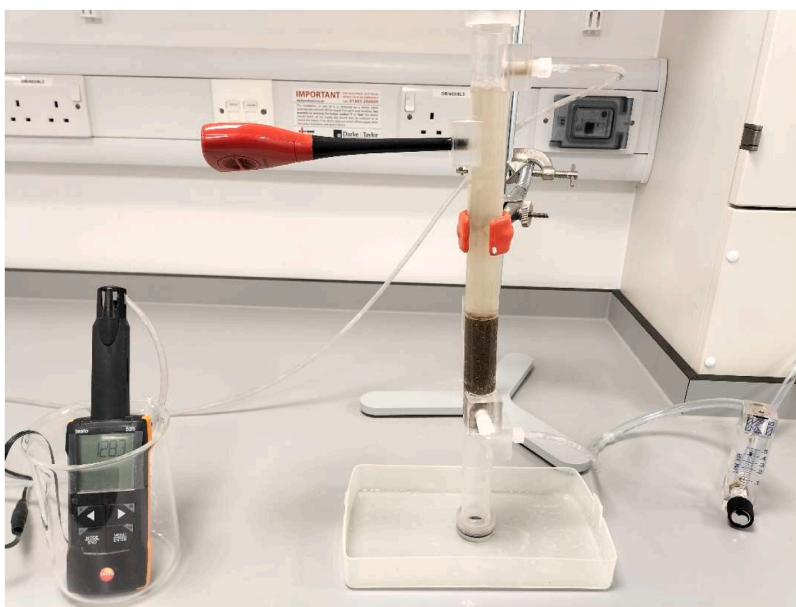


Fig. 3. CO₂ bubbling set-up.

Table 1
Dry bulk densities and carbon contents for the collected samples.

Samples	Activity ID	Latitude (°E)	Longitude (°N)	Water Depth (m)	Dry bulk density (kg/m ³)	TC (%)	PIC (%)	POC (%)
SSK018	1962,168	1° 01' 51.7800"	54° 11' 35.7360"	50	1619.5	0.983	0.884	0.099
SSK039	1962,636	0° 54' 14.8320"	54° 15' 26.7840"	54	1596.4	1.189	1.004	0.185
SSK040	2019,114	0° 52' 40.3320"	54° 10' 04.4760"	49	1535.2	0.348	0.283	0.066
SSK041	1962,639	0° 48' 13.7520"	54° 17' 05.1720"	61	1555.3	0.543	0.389	0.154
SSK042	2018,695	1° 01' 51.6000"	54° 14' 16.8360"	55	1217.2	4.850	0.650	4.200
SSK780	2019,134	0° 56' 30.012"	54° 10' 0.012"	54	1359.4	0.46	0.388	0.072
SSK781	2019,104	0° 55' 35.544"	54° 12' 58.032" N	51	1532.2	0.401	0.339	0.062
SSK783	2018,829	0° 53' 21.012"	54° 12' 25.2354" N	52	1463.5	0.68	0.644	0.036
SSK784	2002,689	0° 55' 30.2154"	54° 14' 48.516" N	57	1647	1.04	1.008	0.032
SSK790	1962,166	1° 9' 53.964"	54° 11' 41.352" N	53	1554.8	0.976	0.914	0.062
SSK792	1962,105	1° 8' 57.084"	54° 10' 17.436" N	51	1576.1	0.526	0.461	0.065

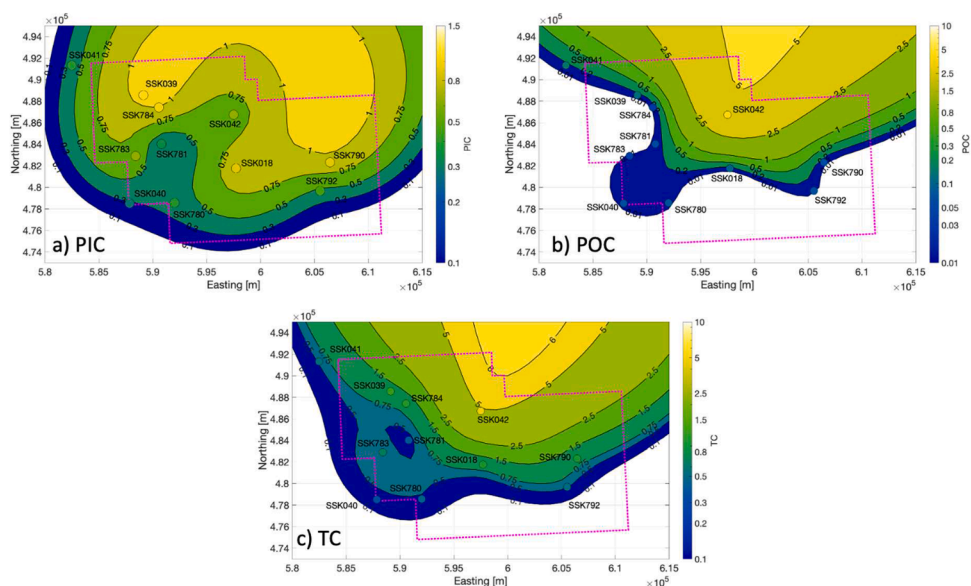


Fig. 4. Contour map of the samples with a) PIC (particulate inorganic carbon), b) POC (particulate organic carbon) and c) TC values (total carbon). The pink dotted line is the Endurance licence block boundary.

to the end of the bubbling periods of the experiment. The amount of CO₂ purged out of the column was monitored using a CO₂ analyser.

3. Results

3.1. Estimation of total sedimentary blue carbon stock at risk of loss

Table 1 represents the dry bulk densities and the carbon contents of the samples. The range of PIC values observed was 0.28 % to 1.008 %, while POC values ranged from 0.03 % to 4.2 %. Comparing these values with those recorded across the UK's Exclusive Economic Zone (EEZ) in a study by Smeaton et al., it was found that PIC varied from 0.01 % to 12.81 %, and POC ranged from 0.03 % to 4.85 % in the UK EEZ samples (Smeaton et al., 2021). Our samples fall within the range for the entire EEZ but there is significant variability for the PIC and POC across the shelf seas. Fig. 4 constitutes the contour map of the samples collected across the surface sediments above the Endurance site with TC, PIC and POC data.

The estimation of the total carbon stock across the endurance site (140 km²) integrated to a depth of 10 m beneath the sediment surface (Böttner et al., 2019), representative of the likely depth of disruption during a single leakage event inferred from pockmarks, was determined from the volume according to the following equation (Smeaton et al., 2021):

$$\text{Carbonstock(kg)} = \text{Volume(m}^3\text{)} \times \text{DryBulkDensity(kg/m}^3\text{)} \times \text{Carboncontent(\%)} \quad (1)$$

The calculations revealed that the TC stock across the Endurance site amounted to approximately 21.72 Mt, comprising on average 13.70 Mt of PIC and 8.02 Mt of POC. This value is only 5 % of the total amount of carbon which could be injected into the site but still shows that preservation of existing carbon is nonetheless an important consideration when manipulating CO₂ storage.

3.2. Estimation of carbon stock at risk of loss from a single leakage event

Despite the magnitude of this maximum amount of carbon which could be at risk of loss across the Endurance site, the potential for carbon loss from the sediments at a scale similar to that being stored in the reservoir, is very low. The primary risk for sedimentary carbon loss arises from a singular leakage event. The accidental leakage of CO₂ from a sub-seabed storage reservoir is regarded as an unlikely event (Metz et al., 2005) and could be mitigated through monitoring. Further the impact would be confined to a limited spatial area. As an analogue for this situation, we can examine the dimensions of pockmarks—sites where natural gas seepage has occurred over long geological periods and where disturbed sediments are visible on reflection seismic images of the subsurface—to gauge the sediment volume that might be deemed "vulnerable." For example, Schroot et al., studied the surface and sub-surface expressions of gas seepage to the sea bed in Southern North Sea and observed pockmarks with diameters ranging from 15 m to 100 m and depths of 5 m to 10 m (Schroot et al., 2005). Therefore, calculations were made to find the total carbon at risk from one leakage event (i.e., in a single pockmark of 50 m radius and 10 m depth) and revealed an estimate of 0.012 Mt of TC with 0.007 Mt of PIC and 0.004 Mt of POC which suggests a maximum amount of carbon at risk is only 0.002 % of the total capacity of storage in the Endurance site.

3.3. Results of the bubbling experiments

The elemental analysis results obtained for the samples collected from the top and bottom layer of the bubbling column throughout the experiments indicate a consistent reduction in the TC content from the beginning to the end of the experiment. The primary cause of this decline was the reduction in PIC content, while POC levels remained steady throughout the experiment. Fig. 5 shows the reduction in the TC, PIC and POC content for the sediments collected from the top layer and bottom layer of the five samples with Fig 4f showing the evolution of pH during the bubbling experiment. The reduction in TC content is around 75 % for the sample SSK 781 whereas for the samples SSK 784, SSK 790 and SSK 792, the decline was around 56 % to 63 %. The results of sample

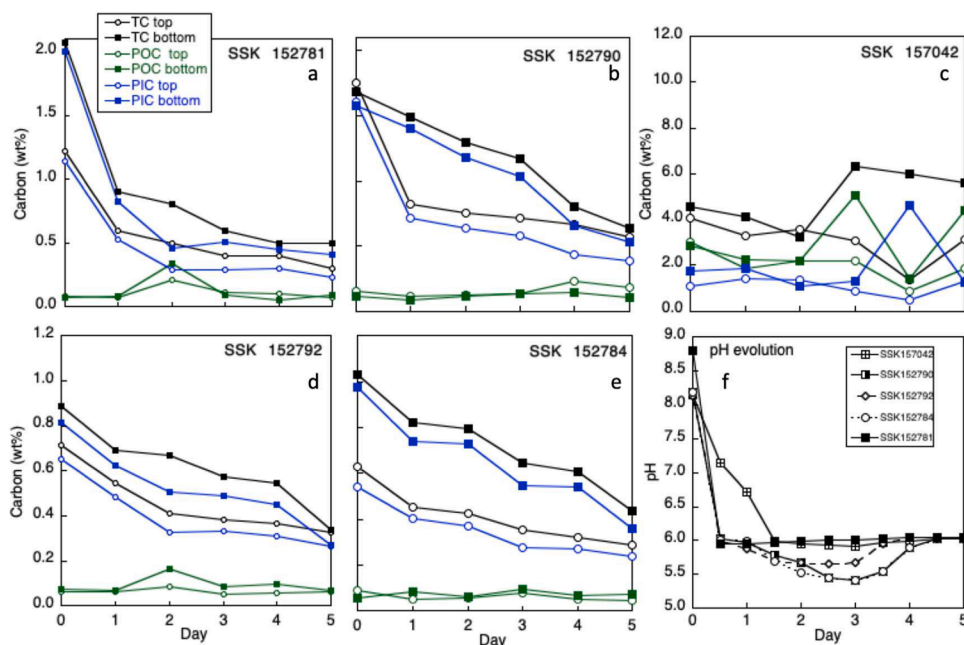


Fig. 5. Percentage of TC (black), PIC (blue) and POC (green) from start to end of the bubbling experiment for the samples from top (open symbols) and bottom layer (closed symbols) of the column (NB the sediments were bubbled from the bottom) in each of the cores (a-e). f shows the evolution of pH during the bubbling of the experiment with all seawater pH tending to ~ 6 after 5 days. For visual presentation of the data, panels a and b share the same vertical scale, as do panels d and e. Due to the higher initial TC content, panel c is plotted on a separate scale.

SSK 042 were anomalous compared to all other sediment samples showing some noise in the trend of TC, PIC and POC but have been shown to demonstrate that there is some uncertainty in either the TC analyses or considerable heterogeneity in the sediment content. While analysing the decline in PIC and POC percentages in the rest of the samples (Fig. 5), it was observed that the maximum decline in PIC was for the sample SSK 781 in accordance with the TC reduction which was around 80 % while the other samples showed a reduction of about 56 % to 66 %. POC remained nearly consistent throughout the experiment across all the samples as can be seen from the plot such that loss of PIC is the direct driver for loss of TC from the sediments during bubbling. In this case also the sample SSK 042 exhibited a nonhomogeneous behaviour in accordance with the TC results.

The bubbling experiments revealed an initial decrease in the pH of sea water above the sediments in the bubbling column. The initial sea water pH started between 8 and 9 in all the samples, as is typical of modern seawater pH, but this reduced to ~ 6 within 6 h of bubbling and then plateaued to stay near constant at a pH of close to 6 until the end of the experiment. An increase in alkalinity over the course of the experiment, was suggestive of dissolution of the PIC from the sediments. This dissolution was further confirmed by analysis of the alkalinity, salinity and the parameters of the CO₂ system in sea water at the beginning and end of the experiment for the sample SSK 781, where the measurements were taken (Table 2). The salinity of the samples were obtained using a VWR ATC Handheld Refractometer. The alkalinity, pH and temperature were obtained by running the samples in an auto-titrator (Metrohm 916 Ti-Touch), whereas the CO₂ system parameters were obtained using the software CO₂sys. It should be noted that there was the potential for some loss of CO₂ from the seawater samples taken at the end of the experiment, and before analysis via the auto-titrator which may explain the discrepancy in the end pH values between the experimental probe, and those yielded by the autotitrator.

As observed from the table, increase in the bicarbonate, carbonate ions and dissolved CO₂ concentrations for sea water in the end of the experiment indicate the increased dissolution of CaCO₃ by CO₂ bubbling.

4. Discussion

4.1. Exploring the experimental buffering capacity of released CO₂ via CaCO₃ dissolution

From the experimental results it is clear that upon exposure to the carbon dioxide there is a sustained decrease in PIC content, a rapid decrease in the pH of the seawater and, as evidenced from Table 2, a marked increase in the alkalinity of the seawater present in the column. From the change in the alkalinity of the seawater the dissolved calcium carbonate content can be determined to be ~ 15,000 μmol kg⁻¹. It is beneficial to consider how this value relates to the thermodynamically expected maximum dissolution under these conditions.

Under some simplifying assumption (see SI Section 1) the calcium carbonate solubility can be expressed as (Frear and Johnston, 1929):

$$[\text{Ca}^{2+}] = \left(\frac{K_{a1}K_{sp}K_H p_{\text{CO}_2}}{4K_{a2}} \right)^{1/3} \quad (3)$$

where [Ca²⁺] is the solution phase calcium concentration arising from the dissolution of the calcite due to carbon dioxide. K_H is Henry's constant for carbon dioxide and p_{CO_2} is the gaseous carbon dioxide partial

pressure where the remaining thermodynamic parameters are taken as reported for the carbonate system under seawater conditions and at a temperature of 18 °C (Humphreys et al., 2021). Further, given the bubbling pressure of the pure carbon dioxide gas used in the experiment will be essentially equal to atmospheric pressure, then on the basis of Eq. (3) the saturated calcium carbonate concentration is predicted to be 17,600 μmol kg⁻¹, with a corresponding solution phase alkalinity of 35,190 μmol kg⁻¹. At calcium carbonate saturation (with respect to calcite) and under 1 atm pressure of carbon dioxide the pH_{total} of the seawater is expected to be 5.9. These theoretically predicted values are comparable to those measured in the seawater samples after completion of the experiment, indicating that the system is close to or at the equilibrium state between CaCO₃ and CO₂. Note SI Section 2 provides a slightly fuller thermodynamic model of this system that enables a full account of the initial calcium and alkalinity of the seawater present in the experiment. Ultimately, for the present experiment the incomplete dissolution of the PIC from the sediment samples most likely reflects the near or complete saturation of the aqueous phase.

The rate of CO₂ addition is 40 ml/minute so the integrated carbon added to the experimental system is 40 × 30 × 60 = 72,000mls. Given that 1 mol of gas takes up 24 dm³, this represents 3 mol of CO₂ added to the experiment over 5 days. The final concentration of carbon 32,216 μmol/kg (when corrected for an initial DIC of 2400 μmoles) yields an addition of 29,816 μmol/kg which equates to 1.796 mmoles CO₂ in the 60 ml volume. Half of this final carbon is derived from the bubbling CO₂ and half from the CaCO₃ due to stoichiometry. The percentage of the bubbled CO₂ that was buffered into the seawater by dissolution is then half of the increase in carbon in solution at the end of the experiment divided by the total CO₂ added: 0.000898/3. Accordingly ~ 0.03 % of the flowing CO₂ was captured into dissolved form by dissolution of the CaCO₃ and the addition of alkalinity to solution during this dissolution. Although some of the leaking CO₂ in the experiment can be stored by increased alkalinity from CaCO₃ dissolution which acts to buffer the waters, this amounts to < 1 % of the bubbled CO₂ in this restricted volume experiment.

4.2. Thermodynamic implications for buffering of leaked carbon through reaction with CaCO₃ in the field

As evidenced above, under the experimentally probed conditions the vast majority of the carbon dioxide is flushed through the system, the gas bubbles through the water column with only a small fraction dissolving and interacting with the solution phase. This broadly reflects the expected situation in which there is a large and uncontrolled release of carbon dioxide from the storage. Under these conditions the dissolution becomes thermodynamically limited, such that the seawater reaches saturation with respect to calcium carbonate.

It is however beneficial to consider the potential implications of a slow leakage scenario. An acceptable leakage rate from such storage facilities is often taken as being as high as 0.01 % per annum but a well-regulated storage site might expect to have leakage rates as low as 0.0008 % per annum (Alcalde et al., 2018). Given that the carbonate present in the sediment equates to approximately 5 % of the capacity of the storage site, this raises the question: to what extent might this leaked carbon dioxide be re-sequestered by the sedimentary carbonate before it is released to the atmosphere? The above outlined thermodynamic considerations can provide some beneficial insights into this case, providing an estimate of what fraction of the leaked carbon dioxide may be *maximally* retained by reaction through dissolution of CaCO₃ within

Table 2

Sea water parameters at the beginning and end of the experiment for sample SSK781.

	Salinity	Alkalinity (μmol/kg)	pH	T (°C)	HCO ₃ ⁻ (μmol/kg)	CO ₃ ²⁻ (μmol/kg)	CO ₂ (μmol/kg)
SW (start)	36	2561.06	7.77	22.2	2240.4	131.6	28.1
SW (end)	56	32,648	7.44	21.9	30,274.1	1161.3	780.9

the sediment.

To give insight into this situation we make the following assumptions: First, under this slow release case, the carbon dioxide is not bubbling but becomes dissolved in the sedimentary pore water. Second, precipitation of calcium carbonate is taken to not occur to any significant extent in the pore waters (Emerson et al., 1982; Turchyn et al., 2021). Third, prior to the slow and sustained release the pore water composition is essentially the same as that of the bottom water i.e. it is oversaturated with respect to calcite. Fourth, due to the presence of calcite in the sediment, the saturation state of the pore water cannot drop below unity, i.e., we assume that although precipitation does not occur, calcite dissolution is fast and returns the system back to equilibrium (saturation).

On the basis of this simplified model we can predict the thermodynamically expected fate of the leaked carbon dioxide. For every molecule of carbon dioxide that dissolves into the pore water, two things may occur: either it may remain in the aqueous phase or it may undergo reaction with the calcite leading to the formation of bicarbonate. Carbon dioxide that does not undergo reaction and remains in the aqueous phase will eventually be returned to the atmosphere by degassing into the environment at the air-water interface. Conversely, carbon dioxide that is transformed into bicarbonate, by virtue of reaction with the calcite material, will remain in the aqueous phase due to the associated increase in the alkalinity of the seawater. Hence, in this later case the carbon dioxide will have been re-sequestered and essentially stored in solution.

From a thermodynamic perspective, the primary factor controlling the fate of the carbon as it passes through the sediment layer is the resulting local carbon dioxide partial pressure. This partial pressure will be controlled by the relative rates of the release (leakage) versus the rate of transfer across the sediment-water interface. Consider the two extreme cases. First, if the rate of transfer across the sediment-water interface is very slow then, as carbon dioxide leaks from the storage, the partial pressure of carbon dioxide will locally increase in the sediment layer, decreasing the pore water pH. Conversely, in the second situation, if the rate of transfer across the sediment-water interface is

fast compared to the rate of leakage then the partial pressure of carbon dioxide in the sediment layer will remain low and comparable to that found in the benthic water.

The presented simplified model allows us to consider what fraction of this dissolved carbon dioxide is expected, under the thermodynamic limit, to react to form bicarbonate under differing partial pressures of carbon dioxide present in the sedimentary pore water. Fig. 6 presents the maximum fraction of the leaked carbon dioxide that is expected to be re-sequestered through reaction with the sedimentary calcium carbonate. As a first approximation the mass or amount of carbon dioxide that can be re-sequestered can be determined by multiplying the reported fraction re-sequestered by the leakage flow rate.

Also depicted in Fig. 6 is the thermodynamically expected variation in the solubility of the calcium carbonate. Tending towards the high partial pressures of carbon dioxide and in accordance with Eq. (3), the solubility increases with roughly the cube-root of the partial pressure. Further numerical details are provided in the SI Section 3. Conversely, at low carbon dioxide partial pressures, the pore water will remain supersaturated with respect to calcite.

At partial pressure below ca. 0.002 atm the pH of the pore water will decrease due to the increased carbon dioxide content; however, none of the calcite present in the sediment will be dissolved. This leaked carbon dioxide is thus expected to be transported through the sediment layer and will ultimately be degassed in to the atmosphere. Once the pH of the system drops further due to locally higher carbon dioxide partial pressures, the pore water will be driven to undersaturation and the calcite dissolution will become thermodynamically favourable. Note, the exact point of switch over here will depend on the initial saturation state of the pore water with respect to calcite. If the pore water is either at or just above saturation then the partial pressure of carbon dioxide required to overcome this solution phase buffering will be lower.

Once driven to occur, this dissolution process will lead to the concomitant formation of bicarbonate and cause an increase in the pore water alkalinity. In contrast to the previous case where the pore water saturation state remains above one, some of this leaked carbon dioxide is captured and due to the associated change in alkalinity (release of

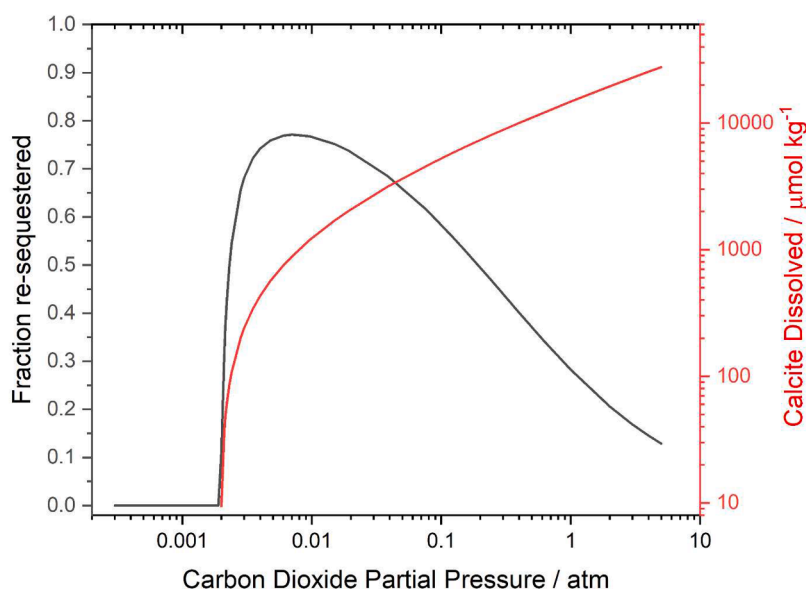


Fig. 6. Predicted variation in the sequestered carbon dioxide as a function of the local partial pressure (black line). Also shown is the increase in the dissolved calcium carbonate concentration in the seawater (red line). Note, first, at high partial pressures the calcite content increases approximately with the cube-root of the carbon dioxide partial pressure and second, the calcium carbonate only starts dissolving once the alkalinity initially present in the pore water has been titrated away. This calculation has been made on the basis of a simplified thermodynamic model, presented in the SI, evidencing the maximum carbon dioxide capturing due to reaction with calcium carbonate in the sediment. The model assumes the seawater is at a depth of 50 m at a temperature of 15 °C and that the initial alkalinity of the porewater is 2300 $\mu\text{mol kg}^{-1}$. Note at shallow depths, above ca. 1000 m, the re-sequestered fraction is relatively insensitive to the local water column pressure and hence seawater depth.

calcium ions), even once it has been transported to the open sea it will not be released as carbon dioxide into the atmosphere.

Interestingly, and as can be seen in Fig. 6, the fraction of the dissolved carbon dioxide that will be re-sequestered is predicted to go through a maximum at approximately 0.01 atm (for the given initial supersaturation state). The origin of this maximum can be understood from consideration of Eq. (3), the calcite solubility increases with the cube root of the carbon dioxide partial pressure; however, the concentration of the aqueous dissolved carbon dioxide increases linearly with the partial pressure of carbon dioxide as described by Henry's law. At high partial pressures a greater proportion of the dissolved carbon dioxide remains in the solution phase not reacting with the solid calcite.

In the extreme case of 5 atm partial pressure of carbon dioxide in the sedimentary pore water, on average approximately 90 % of the carbon dioxide will remain dissolved as carbon dioxide (concentration 187,300 $\mu\text{mol kg}^{-1}$) and the remaining 10 % will react with calcite. Under these conditions (5 atm P_{CO_2} at a depth of 50 m, 15 °C and with an initial alkalinity of 2300 $\mu\text{mol kg}^{-1}$) the resulting increase in the calcium concentration is predicted to be (27,700 $\mu\text{mol kg}^{-1}$). It should be emphasised that this thermodynamically based estimation presents the maximum re-sequestration fraction at this extreme carbon dioxide partial pressure; kinetic limitation of the system may only serve to decrease the re-sequestration. Furthermore, it should be noted that the actual partial pressure in the sediment layer will depend on the rate of transfer into (leakage) and out of the sediment layer.

A key conclusion of this analysis is that, even though the leakage rate may be minimal as compared to the quantity of carbonate in the sediment layer, it is likely that a very significant portion of this escaped carbon dioxide will not be captured by the carbonate sediment and the released gas will instead – eventually – be vented into the atmosphere. As shown in Fig. 6 it is predicted that both high and low partial pressures of carbon dioxide in the sediment layer lead to significant quantities of the leaked gas escaping from the sediment without re-sequestration. However, it should be noted that the low pressure limit is dependent on the initial saturation state of the porewater. The exact partial pressure of carbon dioxide required to drive the pore water out of supersaturation will depend on the initial saturation state present in the sediment, which will be influenced by local respiration rates.

5. Conclusion

Geological carbon storage has the potential to play a significant role in reducing CO₂ emissions and combating climate change. Minimizing the risk of leakage is crucial for ensuring the integrity of carbon storage sites and maintaining the effectiveness of carbon capture and storage (CCS) in contributing to overall carbon budgets and climate change mitigation efforts. The security of blue carbon reservoirs in seafloor sediments above storage sites during assessments of leakage risks is also a vital component to considerations of geological carbon storage. In this study, the amount of carbon at risk of disruption during a leakage event in a CCS reservoir in the North Sea is quantified. Total carbon at risk of disruption across the Endurance site was 21.72 Mt but this reduces to 0.012 Mt if the loss is considered only during a single leakage event. Given that CaCO₃ is most at risk then 0.007 Mt is our final estimate of likely loss which is just 0.002 % of the total capacity of the storage site.

Laboratory bubbling experiments to explore the stability of blue carbon stored in sediments above offshore storage, showed that POC contents are stable in sediments during CO₂ leakage, but PIC is dissolved by the CO₂. The pH reached at the end of the experiments, ~ 6, could be modelled to be the result of the experimental set up reaching thermodynamic equilibrium between CO₂ and CaCO₃ in the sediments. In this limited volume experiment, a small fraction of the total CO₂ that is passed through the system is neutralised by the release of alkalinity in PIC-rich sites storing it as dissolved inorganic carbon in the ocean. The CO₂ flux exceeds the buffering capacity of CaCO₃ in this limited volume experiment, but our thermodynamic calculations suggest that a

significant fraction of leaked CO₂ may be buffered by CaCO₃ in the shallow marine sedimentary environment. We present a framework for calculating the proportion of leaked CO₂ that may be re-sequestered into solution by interaction with dissolved calcium carbonate. Conversely, POC-rich sites have a lower risk of blue carbon loss from a leakage event, but lack any neutralisation or restorage potential. Moreover, minimizing leakage is crucial for ensuring blue carbon security within CO₂ storage sites.

CRedit authorship contribution statement

Malini Kallingal: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Tom Kettlety:** Writing – review & editing, Visualization. **Christopher Batchelor-McAuley:** Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis. **Rosalind E.M. Rickaby:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Rosalind E. M. Rickaby reports financial support was provided by Natural Environment Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Research was funded by Natural Environment Research Council (NERC) [NE/W004976/1] as a part of Agile initiative program at the Oxford Martin School. The authors are grateful to the staff of the British Geological Society core store in gaining access to the samples. The authors would also like to thank Dr. Christopher Day, Research Fellow in stable isotopes, Department of Earth Sciences, University of Oxford for his assistance with the instrument Elemental Analyser.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ijggc.2025.104408](https://doi.org/10.1016/j.ijggc.2025.104408).

Data availability

Excel files all available as Supplementary Files with the manuscript

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