Biomass Storage in Anoxic Marine Basins: Initial estimates of geochemical impacts and CO2 sequestration capacity

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Abstract

In combination with dramatic and immediate CO2 emissions reductions, net-negative atmospheric CO2 removal (CDR) is necessary to maintain average global temperature increases below 2.0 °C. Many proposed CDR pathways involve the placement of vast quantities of organic carbon (biomass) on the seafloor in some form, but little is known about their potential biogeochemical impacts, especially at scales relevant for global climate. Here, we evaluate the potential impacts and durability of organic carbon storage specifically within deep anoxic basins, where organic matter is remineralized through anaerobic processes that may enhance its storage efficiency. We present simple biogeochemical and mixing models to quantify the scale of potential impacts of large-scale organic matter addition to the abyssal seafloor in the Black Sea, Cariaco Basin, and the hypersaline Orca Basin. These calculations reveal that the Black Sea in particular may have the potential to accept biomass storage at climatically-relevant scales with moderate changes to the geochemical state of abyssal water and limited communication of that impact to surface water. Many key unknowns remain, including the partitioning of breakdown among sulfate-reducing and methanogenic metabolisms and the fate of methane in the environment, which can be monitored in part via changes in alkalinity, DIC, and pH. Given the urgency of responsible CDR development and the potential for anoxic basins to reduce ecological risks to animal communities, efforts to address knowledge gaps related to microbial kinetics, benthic processes, and physical mixing in these systems are critically needed.

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Biomass Storage in Anoxic Marine Basins: Initial estimates of geochemical impacts and CO_2 sequestration capacity

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Abstract

In combination with dramatic and immediate CO_2 emissions reductions, net-negative atmospheric CO_2 removal (CDR) is necessary to maintain average global temperature increases below 2.0 °C. Many proposed CDR pathways involve the placement of vast quantities of organic carbon (biomass) on the seafloor in some form, but little is known about their potential biogeochemical impacts, especially at scales relevant for global climate. Here, we evaluate the potential impacts and durability of organic carbon storage specifically within deep anoxic basins, where organic matter is remineralized through anaerobic processes that may enhance its storage efficiency. We present simple biogeochemical and mixing models to quantify the scale of potential impacts of large-scale organic matter addition to the abyssal seafloor in the Black Sea, Cariaco Basin, and the hypersaline Orca Basin. These calculations reveal that the Black Sea in particular may have the potential to accept biomass storage at climatically-relevant scales with moderate changes to the geochemical state of abyssal water and limited communication of that impact to surface water. Many key unknowns remain, including the partitioning of breakdown among sulfate-reducing and methanogenic metabolisms and the fate of methane in the environment, which can be monitored in part via changes in alkalinity, DIC, and pH. Given the urgency of responsible CDR development and the potential for anoxic basins to reduce ecological risks to animal communities, efforts to address knowledge gaps related to microbial kinetics, benthic processes, and physical mixing in these systems are critically needed.

Plain Language Summary

In addition to dramatically and immediately reducing CO_2 emissions, it has become necessary to actively remove CO_2 from the atmosphere in order to avoid the worst effects of climate change and meet the goals of the Paris Agreement. Several of the approaches that are currently being discussed to remove CO_2 from

the atmosphere involve trapping large amounts of CO_2 as organic carbon in plants or algae and then storing that carbon in the deep ocean. Here we ask how this type of carbon storage would likely impact the ecology and chemistry of deep ocean environments, depending on the amount of material placed and its location. Within the limitations of these first simple calculations, we find that specific anoxic basins like the Black Sea may have the potential to sequester climatically-relevant quantities of organic C for more than 1,000 years with moderate changes to deep water chemistry. It is our aim that these results motivate rigorous field and experimental studies to develop more nuanced models for the impacts of carbon storage in locations like the Black Sea.

Key Points

Organic carbon sequestration may be relatively efficient in parts of the ocean without O_2 or complex animal communities.

The Black Sea may have the potential to durably sequester climatically-relevant quantities of organic carbon.

Research is urgently needed to better understand potential biomass degradation rates and the mixing and transport of degradation products.

1. Introduction

Both dramatic, rapid CO_2 emissions reduction as well as enhanced atmospheric CO_2 removal are required to limit average global temperature increases to 2.0 °C or below. This 2.0 °C is considered critical for avoiding the most severe impacts of climate change (Armstrong McKay et al., 2022; IPCC AR6, 2021). There is therefore a global need to develop a suite of atmospheric CO_2 removal (CDR) techniques that operate at the gargantuan scale of excess anthropogenic CO_2 emissions while minimizing environmental and social risks. Ocean biomass sequestration is one of the primary CDR strategies discussed in recent strategy reports (National Academies of Science, Engineering, and Medicine, 2021) and can encompass a wide range of techniques including enhanced upwelling, seaweed farming, and crop waste sinking, among others. Each of these techniques presents a distinct suite of potential benefits and risks (Boyd et al., 2022), but there has been minimal research to date into the likely impacts of deep ocean biomass sequestration

on the water column and seafloor (c.f., Ocean Visions and Monterey Bay Aquarium Research Institute, 2022). Deep benthic seafloor ecosystems remain largely unexplored, and we learn more each year about their complexity and function (Orcutt et al., 2020). These seafloor environments are sensitive to the changes in geochemical and physical conditions that could result from biomass storage (Levin et al., 2023) in ways that are likely to vary substantially depending on local conditions.

In this contribution, we investigate the biogeochemical impacts of deep ocean biomass storage on or near the seafloor, focusing on environments that lack the O_2 required to support a canonical animal community or aerobic microbial respiration. We discuss differences between the biogeochemical processes that control the efficiency of organic carbon storage in oxygenated ("oxic") versus deoxygenated ("anoxic") environments, and we present calculations that constrain the potential biogeochemical impacts of biomass storage in three well-studied anoxic basins on Earth today. We exclude issues related to the cultivation or nutrient manipulation required for farming within the ocean, e.g., seaweed farming, such that our approach is generalizable to any marine or terrestrial carbon source.

2. Background

2.1 Organic carbon sequestration in oxic and anoxic environments

Throughout Earth history, the enhanced burial of organic carbon in seafloor sediments has been one of the principal mechanisms by which atmospheric CO_2 concentrations have declined from hothouse regimes. The Ocean Anoxic Events (OAEs) of the Mesozoic provide particularly dramatic examples of this phenomenon (Schlanger and Jenkyns, 1976; Jarvis et al., 2011; Owens et al., 2018). For example, during the Late Cretaceous period, atmospheric CO_2 concentrations were near ~1400 ppm (Du Vivier et al., 2015) and a particularly widespread ocean anoxia event (OAE-2, ~94 million years ago) facilitated the burial of massive, organic carbon-rich deposits across the proto-North Atlantic (Sinninghe Damsté and Köster, 1998; Raven et al., 2019). This 500,000-year-long burial event, representing an excess organic carbon burial of ~3 x 10^{18} mol C (132,000 Pg CO_2), drove a global carbon-isotope excursion in the residual marine DIC pool and is thought to have been so effective at reducing atmospheric CO_2 that it caused the Plenus cold event (Jarvis et al., 2011; Owens et al., 2016; Kuhnt et al., 2017). In marginal marine environments during OAE-2, local organic carbon accumulation rates of up to 2.15 g cm^{-2} kyr^{-1} were nearly 100x higher than modern averages for similar environments (Raven et al., 2019; Hülse et al., 2021).

Critical environments for carbon burial during OAE-2 and other similar events typically have high sedimentation rates, elevated local primary productivity, and limited O_2 penetration into sediment

porewaters (Hedges and Keil, 1995; Hartnett et al., 1998; Bianchi et al., 2018). In the absence of O_2, microorganisms can respire organic carbon using alternative electron acceptors such as nitrate and sulfate to break down many organic molecules, although certain (oxidized) molecules can become energetically inaccessible at low Eh (Boye et al., 2017). Anoxic conditions also limit the functionality of oxidative exoenzymes that rely on oxygen radicals or O_2 to generate small organic molecules (Sinsabaugh, 2010), which can be subsequently consumed by single-celled organisms. Microbial sulfate reduction produces sulfide, which can react with (sulfurize) certain functional groups in organic matter (Kohnen et al., 1990; van Dongen et al., 2006; Raven et al., 2021) and contribute significantly to rates of organic carbon preservation in sediments (Sinninghe Damsté and Köster, 1998; Raven et al., 2018; Hülse et al., 2019). Together, these processes supported CO_2 sequestration as organic-rich shales in anoxic basins during climatically sensitive intervals throughout Earth history and allowed these sedimentary rocks to serve as efficient repositories for the sequestration of atmospheric CO_2 over geologic timescales.

Another important factor limiting rates of biomass breakdown in anoxic basins is the absence of most eukaryotic organisms, including the vast majority of multicellular grazers. These organisms physically mix surface sediments and degrade organics, thereby enhancing biomass breakdown (Aller, 1994; Aller and Cochran, 2019). Although animals, e.g., nematodes, can survive periods of anoxia, anoxic conditions preclude growth for all but the most specialized eukaryotes (Fenchel, 2012). Instead, the principal organisms found in these basins are bacteria and archaea. Anaerobic fungi play a poorly constrained role in anoxic marine environments, but least 18 genera of anaerobic fungi have been reported so far (Hess et al., 2020), most of which are found in consortia with methanogenic archaea in animal gut and rumen studies. Of relevance for potential CDR applications, the effective absence of animals in anoxic environments means that human activities at the seafloor will not directly encounter complex animal ecosystems (Levin et al., 2023).

Specific biomass breakdown rates are especially sensitive to changes in oxygenation and available respiratory metabolisms. Generally speaking, aerobic and anaerobic microorganisms have the capacity to respire certain highly labile compounds at similar rates (Lee, 1992). However, anaerobic organisms have a limited capacity to metabolize more chemically resistant, recalcitrant molecules like lignins and other structural polymers (Benner et al., 1986; Cowie and Hedges, 1992; Hulthe et al., 1998; Marchand et al., 2005). Lignins are relatively oxidized compounds that represent a major proportion (often 15-35%) of biomass in the woody materials of terrestrial plants (Li et al., 2016). In sediments, lignins are generally resistant to rapid breakdown because specific steps in their degradation benefit from oxic exoenzymes and/or physical feeding by metazoans (Marchand et al., 2005). Demethylation of lignins, or the breakdown of methoxy ($–OCH_3$) side chains, can be achieved aerobically by some bacteria and fungi but

also anaerobically by sulfate-reducing, acetogenic, and fermenting bacteria as well as some methanogenic archaea (Young and Frazer, 1987; Mayumi et al., 2016). The degradation of the remaining carbon in lignin occurs in two major steps – the first, depolymerization, is the more chemically challenging step, and the second is lignin monomer metabolism (Agarwal et al., 2018). Most organisms capable of this depolymerization reaction (mainly fungi) use peroxidase enzymes that require oxic conditions. In the absence of oxygen, for example in ruminant guts, some anaerobic fungi can perform the first steps in lignin depolymerization and may partner with archaeal methanogens (Hess et al., 2020). In marine environments, most lignocellulose breakdown is conducted by bacteria (Benner et al., 1986). Rates of lignin degradation in anoxic marine systems are generally hard to detect (Benner et al., 1984; Keil et al., 2010) and woody (lignin-rich) archaeological remains are famously well-preserved in the Black Sea (Ballard et al., 2001). Although the consortia of organisms responsible for anaerobic lignin breakdown are only partly understood, it would be reasonable to hypothesize that a fungus or bacteria+methanogen consortium would be capable of conducting complete lignin degradation in anoxic marine basins at rates that are significant but likely orders of magnitude slower than rates for other major biomass components. Therefore, biomass that is rich in lignins and other oxidized structural polymers is likely to be especially resistant to biological breakdown under anoxic conditions.

2.2 Impacts of enhanced organic carbon addition to the seafloor

Seafloor organic carbon storage may impact benthic environments, the mid-water column, and 'downstream' regions such as upwelling zones (Siegel et al., 2021; Levin et al., 2023; **Fig. 1**). Most of these risks stem from the breakdown of sequestered biomass by heterotrophic organisms to generate dissolved species, including dissolved organic matter (DOM), CO_2 from respiration, or the products of anaerobic metabolisms like sulfide (H_2S) and methane (CH_4). Each of these species can impact downstream environments or modify the efficiency of carbon storage. CO_2 addition is a source of acidity and its carbon can be returned to the atmosphere if the host water mass returns to the surface (Siegel et al., 2021). Remineralized nutrients (e.g., ammonium, NH_4^+) may enhance productivity in downstream (surface) environments or drive changes in expressed anaerobic microbial metabolisms. The release of DOM, depending on its composition, can stimulate bacterial communities and change the local ecological structure (Boyd et al., 2022). DOM may also be a future source of CO_2 as it continues to degrade (Sexton et al., 2011; Paine et al., 2021). Lowered O_2 concentrations threaten the growth of most aerobic organisms and metazoans (Fenchel, 2012), although anaerobic microorganisms can still remineralize biomass by respiring other electron acceptors such as nitrate, manganese and iron oxides, and sulfate, which leads them to generate alkalinity, methane, reactive metals, and/or sulfide as well as CO_2 and DOM. After their

release, these dissolved compounds are transported away from seafloor installations by the general circulation around the sequestration site.

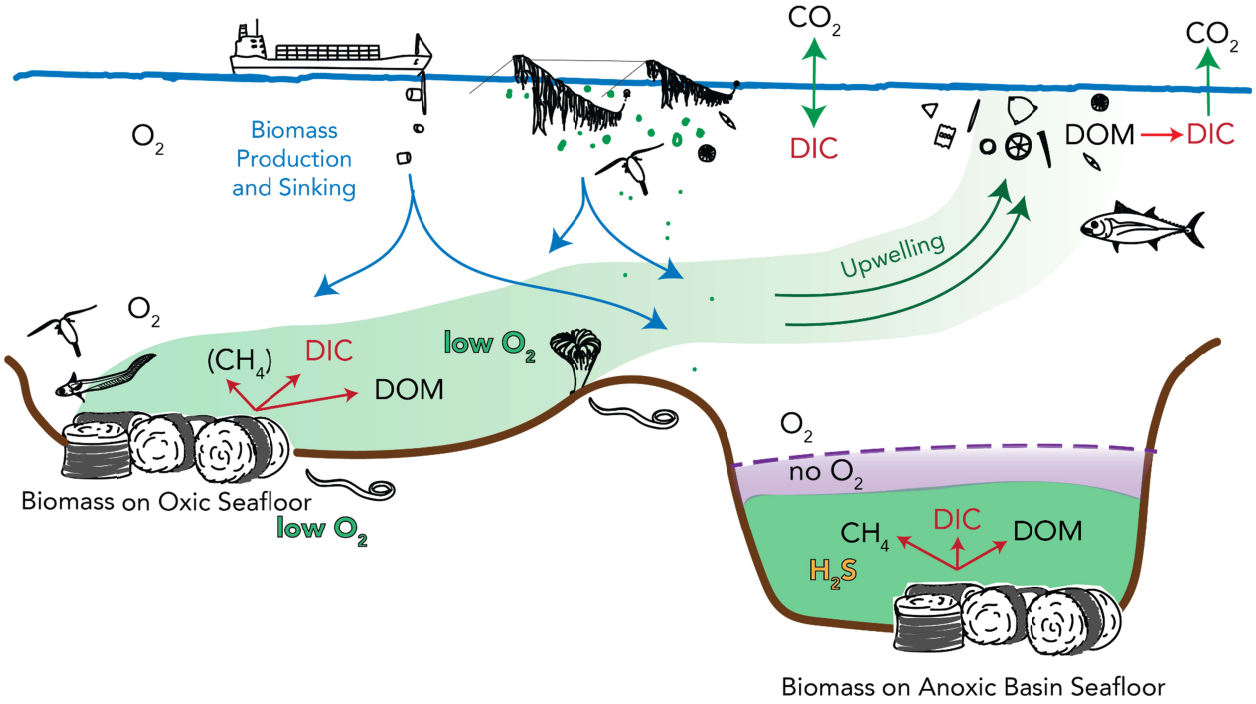

Fig. 1. Overview of potential outcomes for organic C sequestered in oxic and anoxic regions of the seafloor. Red arrows indicate potential pathways for sequestered biomass transformations in the environment: respiration to dissolved inorganic carbon (DIC), fermentation to DIC and methane (CH_4), or breakdown to dissolved organic matter (DOM). Organic matter respiration in oxic environments consumes O_2, while OM respiration in anoxic environments generally consumes sulfate (SO_4) and releases sulfide (H_2S). In the open ocean, dissolved species return to the ocean surface on the timescales of ocean mixing (hundreds to thousands of years).

The durability of ocean carbon storage therefore depends on the location (e.g. depth, environmental conditions, and downstream circulation) and form (overall recalcitrance) of organic carbon addition (**Fig. 1**). In the case of the free, unballasted (slow) sinking of either micro- or macroalgae, large amounts of dissolved carbon will be generated in the deep thermocline and mid-water column as material sinks in the form of both CO_2 and dissolved organic matter (DOM) (Krause-Jensen and Duarte, 2016). Depending on their location, these relatively shallow water masses often upwell back to the surface and release any produced CO_2 on timescales of decades to hundreds of years. In contrast, packaged and ballasted or otherwise densified organics may be effectively stationary on the seafloor, and the abyssal (>2,000 m depth) water masses they encounter generally return to the surface and ventilate their CO_2 more slowly,

over hundreds to thousands of years (Siegel et al., 2021). The location of sequestered biomass is thus an important determinant of the durability of sequestration on these longer timescales.

In sediments, degradation of overlying OM will cause biogeochemical effects that are similar to those seen in the water column, but these effects are more locally concentrated near the sequestration site. Organic matter accumulations will deplete electron acceptors in sediments, driving them toward more reducing conditions (Froelich et al., 1979) and causing bacterial and archaeal heterotrophic communities to adjust to favor anaerobic metabolisms. Seafloor communities may also be impacted by the introduction of epibiotic organisms, viruses, or chemical species carried in with biomass materials (Fraser et al., 2011). Locally elevated concentrations of organics may attract opportunistic scavengers to feed on the deposit. Nevertheless, the scale and severity of ecological effects will depend on the seafloor region selected for storage.

Below, we evaluate the potential impacts of biomass respiration on the biogeochemistry of deep anoxic basins, focusing on cycles of carbon (CO_2 and CH_4), sulfur (SO_4^{2-} and H_2S), nitrogen (NH_4^+ and NO_3^-), phosphate, alkalinity, and pH to inform a preliminary assessment of biogeochemical impacts and ecological risks. Using published estimates of basin circulation and mixing parameters, we also assess the durability of storage for dissolved biomass breakdown products in specific basins and estimate the timescales over which dissolved species may impact the upper water column. Finally, we discuss the potential capacity for major anoxic basins on Earth today – the Black Sea, Cariaco Basin, and Orca Basin – to sequester organic carbon at climatically meaningful scales.

2.3 Site Description: Modern anoxic basins

2.3.1 *Black Sea*

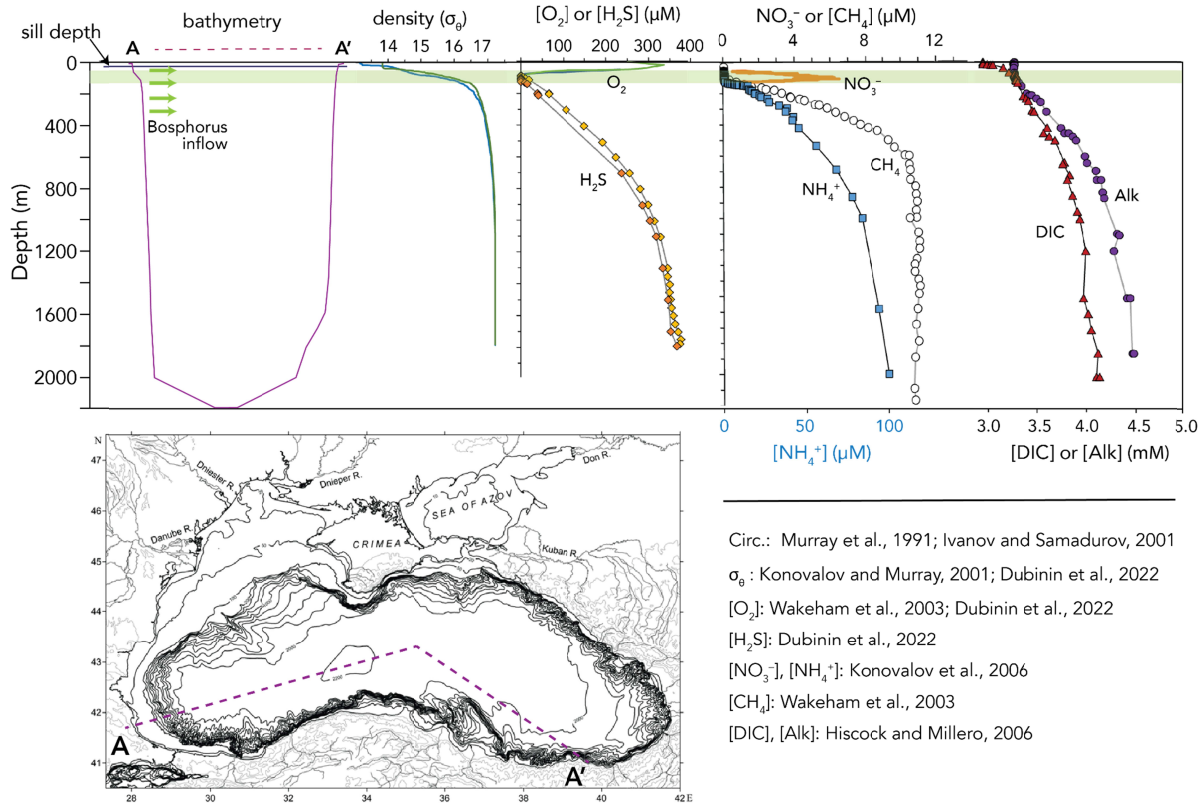

Fig. 2: Modern geochemical conditions in the Black Sea water column. Cross-section A–A' is 1120 km long. Results for nitrogen species, DIC, and Alk were converted from $\boldsymbol{\sigma_\theta}$ units to approximate depth based on the density profiles and alignment in (Dubinin et al., 2022).

The Black Sea is a vast sulfidic basin covering 322,367 km^2 in eastern Europe, with its ownership divided among Turkey, Romania, Bulgaria, Georgia, Russia, and Ukraine (**Fig. 2**). The Black Sea is unique in the modern world in terms of its biogeochemistry and scale. Its only connection to the global ocean comes from the Mediterranean via the Sea of Marmara and the Bosphorus straits, where the sill is just ~35 m deep. The Black Sea became salty approximately 7,100 yrs ago, when rising sea levels after the last deglaciation brought Mediterranean seawater over the sill of the Bosphorus straits and into the basin (Ryan et al., 1997), leading to the development of a strong density stratification. Today, inflowing seawater mixes with some amount of Black Sea water and sinks to fill the basin, mostly at intermediate depths (<700 m). The Black Sea also receives freshwater inflows from several major rivers, mostly in its northeast, and has a positive water balance overall. The combination of density stratification and high surface productivity leads to the depletion of O_2 below ~80 m water depth and the accumulation of sulfide below ~100-130 m water depth. Due to its long residence time in the deep basin (~2,000 yrs, (Lee et al., 2002), deep (>2,000 m) water in the Black Sea is relatively acidic (pH ~7.4) and has accumulated large

amounts of DIC (4,100 μM), ammonia (100 μM), phosphate (10 μM), alkalinity (4,400 μM), silica (350 μM) and DOC (0.5 mM) (Hiscock and Millero, 2006) (**Fig. 2**). Sulfide concentrations in the deep basin have varied over time, with reported values ranging from 350– 440 μM (Konovalov and Murray, 2001; Hiscock and Millero, 2006; Dubinin et al., 2022). Sulfide is a major contributor to the total alkalinity budget in the deep Black Sea (Hiscock and Millero, 2006).

Especially since the mid-20th-century, the biogeochemistry of the Black Sea has been substantially impacted by eutrophication, which provides an illustrative example of how the basin responds to changes in organic matter flux. Between the 1960s and 1980s, enormous fluxes of agricultural nutrients drove a more-than-doubling of primary productivity in the central Black Sea (Konovalov and Murray, 2001). This excess organic carbon was largely remineralized in the upper water column by oxic respiration and, after the depletion of available O_2, via MSR, which produces sulfide. Eutrophication over this period has caused sulfide production in the basin to roughly double, adding 0.13-0.22 Tmol excess H_2S/yr (Konovalov and Murray, 2001). This substantial perturbation to the upper water column led to an apparent shoaling of both the upper and lower interfaces of the sub-oxic zone (Konovalov 2001).

At moderate depths and especially near the shallow northwestern shelf, fluxes of organic matter to the sediments of roughly 0.47 Tmol of organic carbon/yr (Dubinin et al., 2022) are often sufficient to exhaust dissolved sulfate in pore water and drive methanogenesis (Reeburgh et al., 1991; Jørgensen et al., 2001). Sediments from moderate depths in the Black Sea produce substantial amounts of methane, releasing ~0.29 Tmol CH_4/yr to the basin, while abyssal sediments are thought to be sinks for methane overall (Reeburgh 1991). Methane is also injected into the basin from point sources like seeps and methane 'volcanoes,' which are concentrated at depths below 750 m. Total methane sources from seeps and other point sources are estimated to be ~0.39 Tmol CH_4/yr (Schmale et al., 2011). Nevertheless, less than 1% of the sedimentary methane released from both methanogenesis and point sources reaches the atmosphere due to a combination of slow mixing and active anaerobic oxidation of methane (AOM) in the anaerobic water column (~6 μM CH_4/yr) (Wakeham et al., 2003; Starostenko et al., 2010; Egorov et al., 2011; Schmale et al., 2011). Anaerobic methane oxidation in the water column appears to follow roughly first-order kinetics dependent on methane concentration;, and water column communities of anaerobic archaea can oxidize methane pulses efficiently (Wakeham et al., 2003; Schmale et al., 2011). Water column methane concentrations are ~11 μM below 500 m and 10 nM at the surface (**Fig. 2**).

The abyssal Black Sea is characterized by a relatively well-mixed benthic boundary layer below ~1750 m water depth (Murray et al., 1991), with a total volume of 75,137 km^3. The top of this benthic boundary layer is defined by the loss of a temperature gradient, and water exchanges slowly across this interface via primarily diffusive processes (Murray et al., 1991). Water movement and density homogenization within

the deep boundary layer are driven by thermal convection (Ivanov and Samodurov, 2001), while mixing within the mid-water column are driven primarily by mesoscale cyclonic and occasional anticyclonic eddies (Markova, 2023). Currents in the deep Black Sea thus differ from the well-known rim current system in surface water.

2.3.2 *Cariaco Basin*

The Cariaco Basin is a 200-km-by-50-km trench located on the Venezuelan continental shelf that is separated from the Caribbean Sea by a sill at ~150 m water depth. Since roughly the end of the last glacial period, restricted circulation in the 1400 m-deep basin and high surface productivity have caused the basin water to be sulfidic below ~350 m depth. Cariaco Basin was the focus of an international long-term time series program from 1995 to 2017 (Muller-Karger et al., 2019), which provides a high-resolution record of the relationship between upwelling and productivity in the basin.

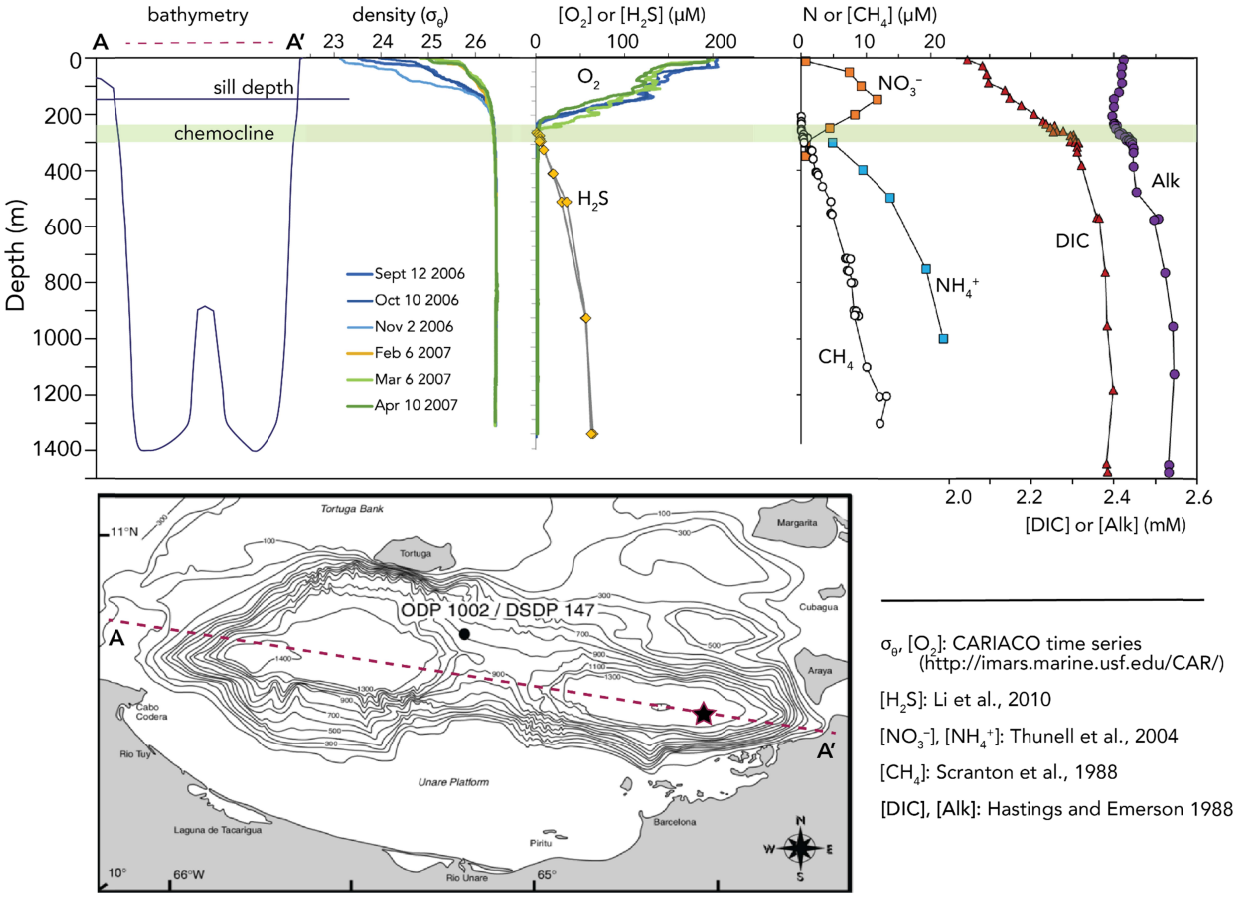

Fig. 3: Cariaco Basin geochemistry. The star on the map panel indicates the location of the CARIACO long-term time series station and profile site for all data except DIC/Alk. The cross-section A–A' is 200 km long.

Cariaco Basin is more weakly stratified than the Black Sea and experiences seasonal upwelling (Muller-Karger et al., 2004). The density gradient in the water column (**Fig. 3**) is driven entirely by a small temperature differential from ~18.1°C at the surface to ~16.8°C at depth, while deep water is less saline than surface water. Accordingly, eddy diffusion coefficients in eastern Cariaco Basin (Scranton et al., 1987) are ~30x higher than those measured in the Black Sea, which means that dissolved components mix toward the chemocline on much faster timescales. This temperature gradient is also not always stable, as Scranton et al. (1987) noted significant warming from 1955-1982 and the basin may have experienced a full overturn in the early 20th century (Zhang and Millero, 1993). Accordingly, concentrations of sulfide in the deep basin do not appear to be in steady-state and may be reset by tectonic activity and associated periodic intrusions of oxygenated seawater (Scranton et al., 2001).

Upwelling in the region drives elevated productivity and organic carbon export to the basin of about ~$1x10^{11}$ g C/yr (0.008 Tmol C/yr). In the sulfidic water column, most of this organic matter is respired via sulfate reduction. In the sediments, estimated methane fluxes of roughly 10 μmol cm^{-2} yr^{-1} (Scranton, 1988) suggests that at least 25% of the carbon delivered to sediments each year (75-80 μmol cm^{-2} yr^{-1}; Muller-Karger et al., 2004) is eventually consumed via methanogenesis, while 35% is consumed by sulfate reduction and ~40% is preserved (Raven et al., 2016). Although a total of nearly $7.1x10^8$ mol CH_4 yr^{-1} is produced in Cariaco sediments, roughly ~85% of this methane is oxidized in the anoxic water column (Reeburgh, 1976; Scranton, 1988). In the deep basin, the approximately linear increase in methane concentrations to ~10 μM is thought to primarily reflect methane sourced from the sediments (**Fig. 3**; Ward et al., 1987; Scranton, 1988).

2.3.3 *Orca Basin*

Orca Basin is a 200-meter-deep seafloor depression filled with anoxic, hypersaline water that underlies ~2,200 meters of 'normal' oxygenated seawater in the Gulf of Mexico. The continental shelf bordering Louisiana and Texas (USA) is pockmarked by many such basins, generally produced by the intersection of tectonics and salt dissolution. The total volume of brine in Orca Basin is ~10.24 km^3, and the basin area at the permanent halocline is 158 km^2 (Diercks et al., 2019). The physical capacity of the basin for a 10-meter-thick idealized biomass layer is equivalent to ~0.6 Pg CO_2 (14 Tmol C) as solids, ignoring any consideration of ballast or physical containment.

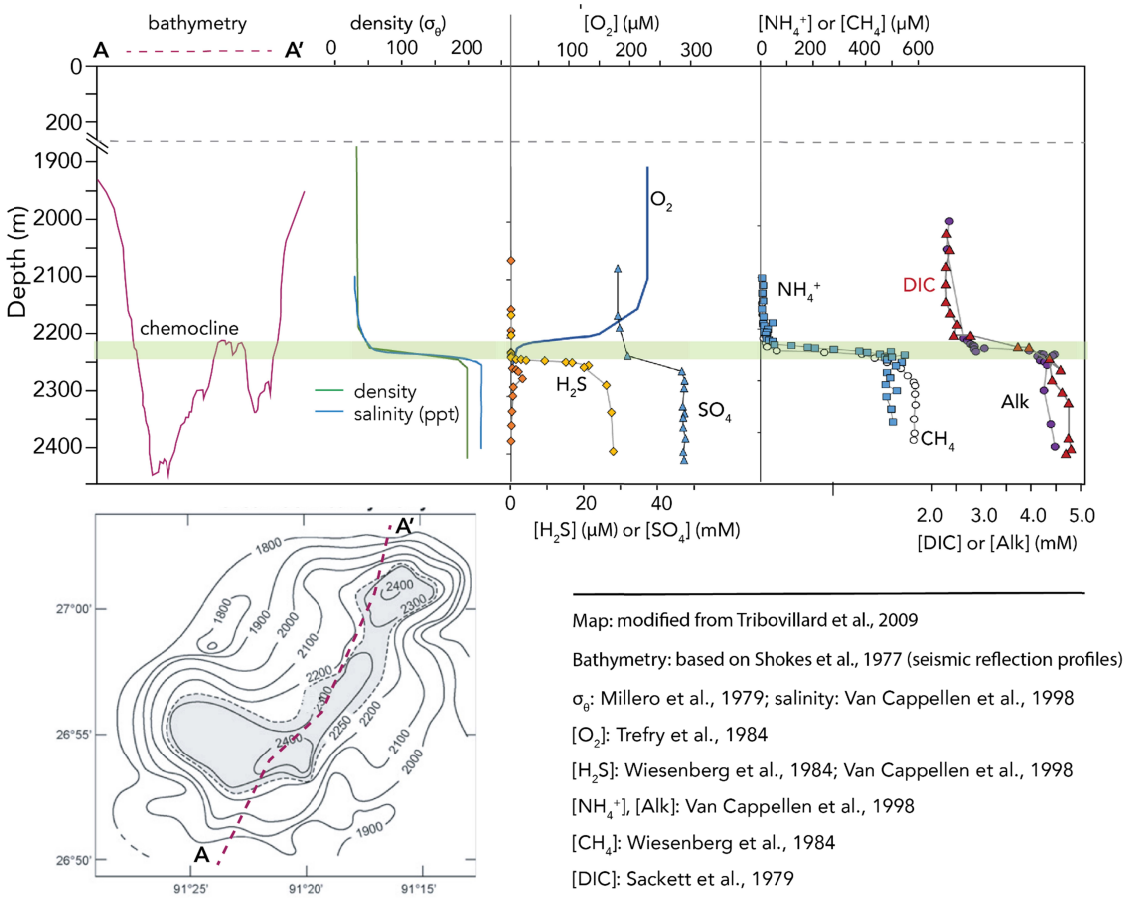

Fig. 4: Orca Basin geochemistry. The cross-section A–A' is approximately 28 km long.

Seawater in Orca Basin is extraordinarily salty (47–318 psu; 258 g/kg; Shokes et al., 1977) due to dissolution of an exposed salt layer on its north and southeast rims. Brines accumulate in the basin due to their very high densities (~1300 g/L) and turn over very slowly, on timescales of ~7,900 years (Addy and Behrens, 1980). The pycnocline at the top of the brine sits at 2220-2250 m depth and acts as a strong impediment to mixing in either direction. Sinking marine particles and materials transported from the Mississippi are suspended at this interface, where they age and become substantially degraded (Trefry, 1984; Tribovillard et al., 2008; Diercks et al., 2019). Organic materials that do eventually sink into the dense brine produce OC-rich soupy muds that continue to be degraded slowly by sulfate-reducing and methanogenic microorganisms (LaRock et al., 1979; Hurtgen et al., 1999; Nigro et al., 2020).

Due to this long, gradual accumulation of OM breakdown products, Orca Basin brines are rich in DOM (89-278 μM or 2.5 x 10^9 mol C total; Diercks et al., 2019). Sulfate concentrations are high throughout the basin and exceed 40 mM in porewater throughout the upper 30 cm of sediments (Hurtgen et al., 1999). Although microbial sulfate reduction is active in the basin, iron concentrations are high and react

efficiently with sulfide to generate iron monosulfides. Reported concentrations of dissolved sulfides differ; maximum concentrations of 2-3 μM were reported within a narrow layer within the water column during two cruises in the late 1970s (Wiesenburg et al., 1985), while Van Cappellen et al. (1998) reported 10 to 28 uM sulfide in all samples with salinities above 200 ppm. Microbes use iron and manganese oxides in the upper pycnocline at 2200-2240 m depth (Van Cappellen et al., 1998), and iron sulfides precipitate at the interface between regions of active iron and sulfur cycling (Sheu and Presley, 1986).

Despite high concentrations of available sulfate and the observation that hypersaline conditions do not appear to limit MSR (Porter et al., 2007), methanogenesis is an active pathway of OM breakdown in the Orca Basin. Methanogens in this environment appear to use 'non-competitive' methylated substrates for methylotrophic methanogenesis, producing ^{13}C-depleted methane concurrent with MSR (Zhuang et al., 2016). Methane and other biogenic hydrocarbons accumulate to high concentrations (up to 3.4 mM CH_4) within the brine (Wiesenburg et al., 1985; Zhuang et al., 2016). Most of this methane is trapped by the lack of mixing across the pycnocline, but methane that does mix into overlying waters is likely to be oxidized by microbial communities in the overlying oxic waters of the Gulf of Mexico, which appear to be highly effective at methane oxidation and are primed from abundant petroleum seep sources (Kessler et al., 2011).

3. Methods

3.1 Organic matter stoichiometry

We estimate geochemical impacts on the mixed volume of each basin using a range of stoichiometries for organic matter breakdown that represent end-member compositions for carbohydrate-rich and lipid-rich biomass (Redfield, 1934; Anderson and Sarmiento, 1994), with and without ammonium reoxidation to nitrate (Hastings and Emerson, 1988). In terms of their impacts on pH, DIC, alkalinity, and sulfide, terrestrial biomass sources are approximated by the carbohydrate-rich end member; terrestrial materials with lower N:C ratios would make calculated NH_4^+ concentration changes overestimates. We first consider a case in which all biomass breakdown occurs via microbial sulfate reduction (MSR), which oxidizes biomass to CO_2 and nutrients while reducing sulfate to sulfide. Unlike oxic respiration, microbial sulfate reduction is a source of alkalinity, so its impact on pH is relatively small (Lyons et al., 1984). However, the precise ratio of total alkalinity (TA) to DIC produced during organic matter remineralization depends on the identity of the organic electron donor and its oxidization state (Gallagher et al., 2012); more reduced organic compounds like lipids (~CH_2) require more oxidizing power to generate CO_2 than more oxidized compounds like carbohydrates (~CH_2O). We convert widely used

literature estimates for ΔCO_2 : ΔO_2 into ratios of ΔCO_2:ΔSO_4 ratios by balancing electrons for each half reaction (Froelich et al., 1979; Middelburg et al., 2020). We also consider a case in which methanogenesis accounts for 10% of total organic C remineralization. In our simplified model, methanogenesis converts organic C to methane (CH_4) and CO_2 in a ratio that depends on the oxidation state of the organic C. This reaction does not produce alkalinity and therefore, in the absence of anaerobic methane reoxidation, has a relatively large effect on local pH. We present this full range of stoichiometries and metabolisms based on five scenarios (Table 1).

	Scenario	Organic Matter	Breakdown Products	ΔDIC : ΔAlk
1	Lipid-rich OM breakdown via MSR	$C_{117}N_{16}P$	$117CO_2 + 16NH_4^+ + H_2PO_4^- + 85H_2S$	+117:+170 (1:1.45)
2	Carb-rich OM breakdown via MSR with ammonium ox.	$C_{106}N_{16}O_{42}H_{175}P$	$106CO_2 + 16NO_3^- + H_2PO_4^- + 69\ H_2S$	+106:+122 (1:1.15)
3	Carb-rich OM breakdown via MSR without ammonium ox.	$C_{106}N_{16}O_{42}H_{175}P$	$106CO_2 + 16NH_4^+ + H_2PO_4^- + 53H_2S$	+106:+106 (1:1)
4	Lipid-rich OM breakdown via methanogenesis	$C_{117}N_{16}P$	$32CO_2 + 85\ CH_4 + 16NH_4^+ + H_2PO_4^-$	+32:+1
5	Carb-rich OM breakdown via methanogenesis	$C_{106}N_{16}O_{42}H_{175}P$	$53CO_2 + 53CH_4 + 16NH_4^+ + H_2PO_4^-$	+53:+1

Table 1. Reaction stoichiometries used for organic matter compositions and breakdown pathways. Balanced reactions linking organic matter to its products require H_2O and H^+ (not shown). OM = organic matter; MSR = microbial sulfate reduction.

All pH calculations were conducted using CO2SYS v.2.3, which accounts for sulfide, ammonia, and silicic acid alkalinity. Our analysis includes the linked cycles of carbon, nitrogen, phosphorus, sulfur, and alkalinity, but it excludes any interactions with iron or manganese cycling and the effects of organic acids.

Basin volumes were calculated in MATLAB R2018B using the trapz function at the 1 arcsecond resolution specified in the GEBCO 2022 bathymetry. In the abyssal Black Sea, although vertical mixing is relatively well constrained, very little data has been collected relevant to lateral mixing (Stanev et al., 2021). Therefore, as a first calculation, we focus only on the western portion of the Black Sea, and we mix the products of microbial reactions into a volume equivalent to 43% of the benthic boundary layer between 1750 m and the seafloor (Murray et al., 1991) to account for these uncertainties in lateral mixing. For Cariaco Basin, we calculated the volume of water in the eastern and western sub-basins separately as

well as the overlying seawater to 350 m, following observed concentration patterns in (Scranton et al., 2001). For Orca Basin, products are mixed into a volume of 10.3 km^3 (Diercks et al., 2019).

3.2 Circulation Model

Dissolved products of MSR will not be confined to the deepest layers of the water column. For the Black Sea and Cariaco Basin, we use published estimates for advective flow and eddy (turbulent) diffusivity to estimate vertical mixing and transport. In each case, we constructed a model composed of 0.1-km-thick, vertically stacked layers following Scranton et al., (1987) and Schmale et al., (2011). The general equation for this calculation is:

$$d[C]/dt = K_i * ([C]_{i-1} - [C]_i) * A_i / (V_i * \Delta z_i) + K_{i+1} * ([C]_{i+1} - [C]_i) * A_i / (V_i * \Delta z_i) + T_B * ([C]_B - [C]_i) / V_i$$

where [C] represents the concentration of any component, the subscript 'i' refers to a depth box, T represents advective flow in km^3/yr across the box boundary, z is box thickness (0.1 km), A and V are the area and volumes of each box boundary in km^2 and km^3 respectively, and K is eddy diffusivity in km^2/yr.

In the deep Black Sea, estimates for eddy (turbulent) diffusivity are lower than for most open-ocean sites, ranging from 4.1×10^{-4} to 1.2×10^{-4} km^2/yr, equivalent to 4×10^{-6} to 1.3×10^{-5} m^3/sec (Ivanov and Samodurov, 2001). The box model for the Black Sea uses 20 vertically-stacked, 0.1-km-thick layers (Schmale et al., 2011) to evaluate the timescales over which dissolved products of deep biomass respiration might impact the upper water column of the Black Sea. Below ~500 m depth in the Black Sea, transport is generally limited to turbulent diffusion (K_i). In the upper 500 m, each box receives advective flow from the Bosporus with return via upwelling (T_B) and outflow from the surface box (Schmale et al., 2011). The model is run with a one-year timestep for 1,200 years.

In Cariaco Basin, intermittent upwelling and a weak density gradient lead to higher estimates of eddy turbulent diffusivity than for the Black Sea, ranging from 1.3×10^{-2} to 2.7×10^{-3} km^2/yr (Scranton et al., 1987). The box model for Cariaco Basin uses 12 vertically-stacked, 0.1-km-thick layers and is run with 12 time steps per year for 200 years.

4. Results and Discussion

4.1 The Black Sea: Biogeochemical impacts of organic matter sequestration

We estimated the potential short-term (decadal) impacts of biomass addition to the deepest part of the western Black Sea using the scenarios defined in Table 1. To calculate the effects of mixing organic

matter remineralization products into this environment, we use a volume of 32,398 km^3, which is equivalent to ~43% of the total volume of the abyssal benthic boundary layer (75,137 km^3). This reduced effective volume is an attempt to account for incomplete lateral mixing at depth and can be refined by future studies of advective flow dynamics within the layer (Markova, 2023). The amount of organic matter respired *in situ* over short (decadal) timescales was varied from 0 to 40 Tmol C, which is equivalent to 0–1.76 Pg (Gt) CO_2. Initial Black Sea deep water concentrations (NH_3 = 100 µM, H_2S = 440 µM, TA = 4400 µM, DIC = 4100 µM) were taken from Hiscock and Millero (2006) and Dubinin et al. (2022). Salinity (22 psu) and temperature (8°C) were taken from Murray et al. (1991) (**Fig. 2**).

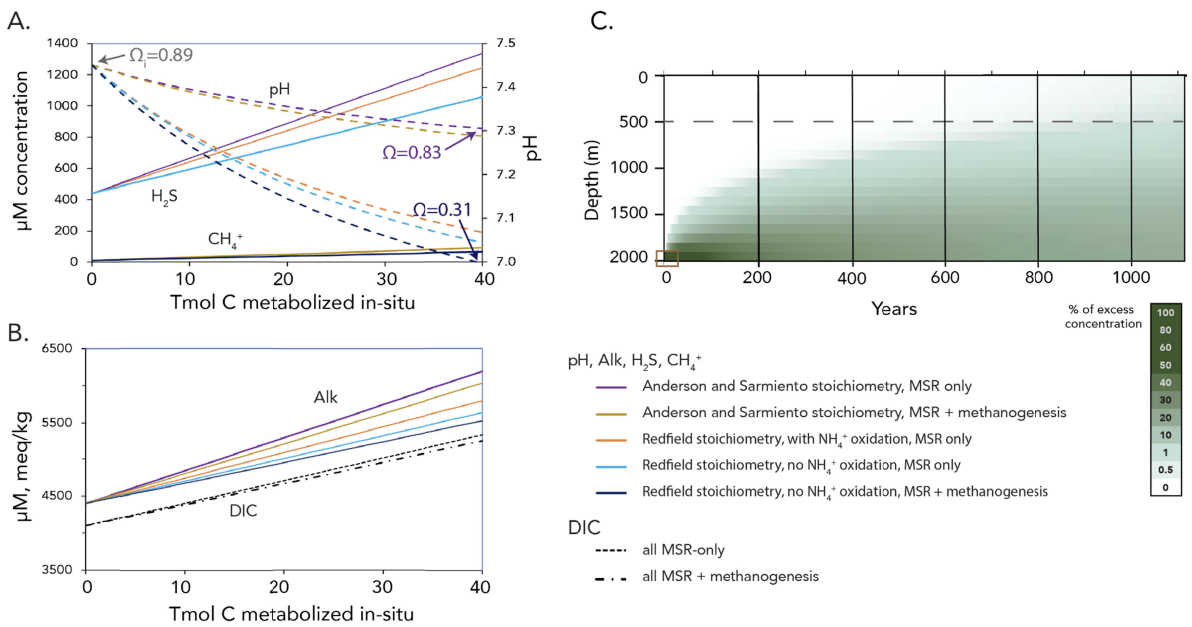

Fig. 5 Impacts of enhanced organic matter breakdown in abyssal western Black Sea water. A – Calculated changes in pH (dashed lines), and sulfide and methane concentrations (solid lines) resulting from *in-situ* respiration of organic C by MSR, with or without methanogenesis, for a range of organic matter stoichiometries (Table 1). In scenarios 4 and 5, methanogenesis is presumed to metabolize 10% as much organic C as MSR. Annotations show the saturation state (Ω) of calcite ($CaCO_3$), which is undersaturated throughout. **B –** Associated changes in abyssal Black Sea DIC and alkalinity concentrations. **C –** Modeled vertical mixing of a dissolved component (HS^-, HCO_3^-, NH_4^+ etc) added to the Black Sea at >2,000 m depth. Water depths above the dashed horizontal line experience advective flow.

If we consider only the effects of biomass respiration by MSR, ignoring methanogenic metabolisms and subsequent reactions (e.g., sulfide oxidation; scenarios 1–3 in Table 1), we estimate that the microbial

respiration of 40 Tmol C below 2,000 m water depth would increase sulfide concentrations from a current value of 440 uM to 1057–1337 μM, depending on mean organic C redox state (**Fig. 5**). Concurrently, in the absence of ammonium oxidation, ammonium concentrations would increase from 100 μM to 279–296 μM. Because MSR generates alkalinity as well as CO_2, the pH change associated with this breakdown would be ~0.15 – 0.41 pH units. This is in notable contrast to the oxic respiration of this same quantity of organic matter, which would cause pH to drop by more than 1 unit to a pH value of ~6.56 (calcite Ω ~0.12) due to the absence of MSR-derived alkalinity. The deep Black Sea is currently undersaturated with respect to calcite and aragonite, and therefore seafloor carbonates are minor and unlikely to substantially buffer, or be substantially impacted by, changes in pH at this depth. At even larger scales, the addition of 100 Tmol C (1.2 Pg C) respired via MSR *in situ* would raise deep-water sulfide concentrations to nearly 2,000 μM (from 400 μM) and drop pH to 6.87 (from 7.40).

Biomass breakdown may also occur via methanogenic metabolisms. More experimental data is needed to constrain the contribution of methanogenesis to biomass breakdown, which is likely to depend on both biomass type and on the engineered specifics of any proposed CDR operation (i.e., compression, containment, and placement of biomass). Canonically, methanogenesis is repressed in the presence of sulfate due to the slight energetic favorability of MSR (Froelich et al., 1979; Kristjansson et al., 1982). The overall effect of MSR-driven breakdown on basin dissolved sulfate concentrations is small, but sulfate may nonetheless be locally depleted, especially within interiors of sunken biomass or within underlying sediments. Even when sulfate is present, however, methanogenic organisms are frequently capable of operating alongside sulfate reducers using 'non-competitive' substrates like methanol or methylamine (Oremland and Polcin, 1982; Zhuang et al., 2016); lignin methoxy groups can also fall into this category (Hess et al., 2020). Additional data are needed to partition likely biomass breakdown for deep Black Sea conditions into MSR and methanogenesis under a range of engineering conditions and placement scenarios.

We calculate the effects of methanogenesis on abyssal Black Sea geochemistry through Scenarios 4 and 5, both of which make the assumption that 10% of total organic C breakdown moves through this pathway and exclude the potential later reoxidation of methane. For the same scale of total C respiration discussed above (40 Tmol C), the addition of 2–2.9 Tmol CH_4 would increase abyssal methane concentrations from current values of ~10 uM to 71–100 uM and add the equivalent of roughly 10–15 yrs of natural CH_4 production in the shelf and slope sediments of the Black Sea (Reeburgh et al., 1991). Organic matter breakdown in these scenarios leads to slightly larger changes in abyssal pH and saturation state than MSR alone (Fig. 5) because methanogenesis does not produce alkalinity, unlike MSR.

However, if the methane produced during methanogenesis is subsequently reoxidized anaerobically with sulfate, the summed reactions produce a net effect similar to breakdown via MSR alone (Middelburg et al., 2020).

One critical question impacting the feasibility of anoxic organic matter sequestration is the ability of local microbial communities to conduct anaerobic methane oxidation in the water column, removing methane from the system before it can escape to the atmosphere. Natural methane sources in the shelf and slope sediments of the Black Sea are large – approximately 0.29 Tmol CH_4/yr (Reeburgh et al., 1991; Schmale et al., 2011) – and they are frequently local and episodic due to seafloor tectonic and other processes. Methane sinks balance these inputs, largely through methanotrophy (methane oxidation) in the anoxic water column of 1 to several hundred nM CH_4/day and CH_4 fluxes into abyssal sediments (Reeburgh et al., 1991; Schmale et al., 2005). Studies in the similarly methane-rich Gulf of Mexico have observed 100-fold increases in methanotrophy rate constants in response to methane injection from the Deepwater Horizon oil spill (Kessler et al., 2011), and it has been argued that rates of Black Sea methanotrophy could respond similarly, given sufficient time for the methanotrophic community (with a doubling time of several months, Nauhaus et al., 2007) to grow (Schmale et al., 2011). Schmale et al. (2011) modeled the fate of the instantaneous injection of 11.2 Tmol CH_4 at 2,000 m water depth in the Black Sea (e.g., due to mid-depth hydrate destabilization or deep mud volcano eruptions) and concluded that this injection would cause a negligible 2–3% increase in the total modern Black Sea flux of methane to the atmosphere due to responsive rates of methanotrophy in the environment. Methanotrophy rates are also likely to show a positive relationship with increased methane concentrations as current methane concentrations in the Black Sea are near minimum thresholds for the activity of anaerobic methane oxidation (Valentine, 2011). Additional work is needed to validate these model results and better understand the capacity of these microbial methane oxidation processes to 'scrub' excess methane from the system.

Potential impacts of biogeochemical change in the abyssal Black Sea on human endeavors in the region are highly sensitive to the mixing, or lack thereof, between abyssal waters and the surface. The Black Sea is notably stratified, with minimal tidal action to add energy to the system (Stewart et al., 2007). We used estimates of eddy diffusivity (Ivanov and Samodurov, 2001) from water column profiles to calculate the rates at which dissolved products of organic C breakdown in the benthic boundary layer could be detected near the shallow redoxcline (~150 m depth). As shown in Fig. 5, dissolved components added to deep water from biomass respiration can remain contained within >500 m-deep, slowly ventilating water masses over hundreds of years. As a percentage of the initial excess concentration in the deepest box, the excess concentration in the 500-m-deep water column box is approximately 0.04% after 400 yrs, 0.25% after 600 yrs, 0.83% after 800 yrs, and 1.26% after 1,000 yrs. For a scenario with 40 Tg C addition and

600 μM initial excess sulfide in the deepest box, this would be equivalent to an increase in the concentration of sulfide at 500 m depth by 7.6 μM, or roughly 5% of current concentrations, after 1,000 years. From the perspective of the upper, upwelling water column, impacts of dissolved species are within the range of natural variability (e.g. (Konovalov and Murray, 2001; Dubinin et al., 2022) for >1,000 years, assuming a roughly steady-state circulation in the Black Sea.

Although much of the energy from respiration of biomass is conserved in the short term, it will eventually contribute heat to the system that could impact deep vertical stratification of the water column. If we assume a rough energy yield of ~25 kJ/mol for MSR, the respiration of 40 Tmol C would generate ~10^{15} kJ, which, if released over very short timescale of ten years, could be a significant fraction of the natural geothermal heat flux driving convection in the benthic boundary layer of 0.04 W/m^2 (Zolotarev et al., 1979), or $5.5*10^{15}$ kJ per decade. Changes in total energy flux and resulting water column stratification from metabolic processes could therefore become relevant for a hypothetical case of very large-scale, rapid implementation, but are otherwise unlikely to be significant.

All of the foregoing calculations focus solely on the products of *in situ* biomass respiration. Depending on the timescale being considered and the composition of sequestered biomass, respired C will represent some fraction of the total organic C added to the system. Initial experiments indicate that roughly 75% of lignin-rich terrestrial biomass may persist after 100 years of sedimentary storage under partially oxygenated conditions, and the efficiency of biomass storage is expected to be higher under anoxic conditions (Keil et al., 2010). For a range of possible storage efficiencies between 50% and 85%, the in-situ respiration of 40 Tmol C discussed above translates into a total sequestrations of 3.5 to 11.7 Pg (Gt) CO_2 equivalent. In such a hypothetical scenario, carbon would be stored in two distinct pools: 50-90% of sequestered carbon would be stored semi-permanently as solid biomass while 10–50% would be sequestered on a kyr timescale as either dissolved CO_2 or DOM. In terms of the physical size of such an installation, consolidated terrestrial biomass equivalent to 10 Pg CO_2 would, if deposited in a four-meter-thick layer in the deepest region of the western Black Sea, cover 6,170 km^2, or 3.5% of the >2,100-m seafloor (1.9% of total Black Sea area, an 80 x 80 km operation). The upper end of this range – a total amount, not an annual flux – is an enormous value, similar to the total production of crop waste across the entire planet in a year.

This highly simplified mass balance exercise suggests that the bulk geochemistry and stratification of the Black Sea may allow for moderate changes in the concentrations of H_2S, NH_4, alkalinity, and pH to result from the seafloor storage of a climatically relevant quantity of carbon. The scenario involving the in-situ respiration of ~40 Tmol C that we use for discussion purposes here is of the same order of magnitude in terms of increased organic C input as the 20th-century eutrophication of the Black Sea (Konovalov and

Murray, 2001). Importantly, however, biomass breakdown in abyssal waters has a diluted and delayed effect on chemocline and mixed layer properties relative to shallow biomass breakdown. Geochemical changes within the basin are also isolated from the global ocean by the singular connection at the Bosphorus. This physical restriction provides spatial bounds for monitoring and verification of any CO_2 removal activities and isolates its impacts to a relatively well-defined set of stakeholders in the region.

Despite the potential for gigatonne-scale CO_2 sequestration suggested by these broad calculations, we emphasize that this preliminary analysis has many limitations and also identifies potential risks that will require additional research. We assume that remineralization products mix rapidly within a volume equivalent to slightly less than half of the entire deep benthic boundary layer, neglecting acute or local impacts, which may be especially important for predicting sedimentary methane production. We do not explicitly consider reactions that re-oxidize sulfide or methane, and we do not yet have the experimental data to support precise predictions of biomass consumption via methanogenesis or methane reoxidation via methanotrophy. We also lack the necessary data to evaluate how seafloor heterotrophic communities – bacteria, archaea, and potentially fungi – will respond to a massive influx of biomass in this environment. And finally, more data is needed to constrain physical mixing and circulation within the deep Black Sea benthic boundary layer. It is our aim that these results motivate rigorous field and experimental studies to develop more nuanced models for the durability and ecological impacts of biomass storage in the Black Sea.

4.2 Cariaco Basin: Biogeochemical impacts of organic carbon sequestration

Using the same general approach and stoichiometric scenarios (Table 1) that we used for the Black Sea, we estimated the potential effects of biomass addition to the deep seafloor of Cariaco Basin. The amount of organic matter respired in situ was varied from 0 to 5 Tmol C, and initial geochemical conditions for the deep Basin are summarized in Figure 2.

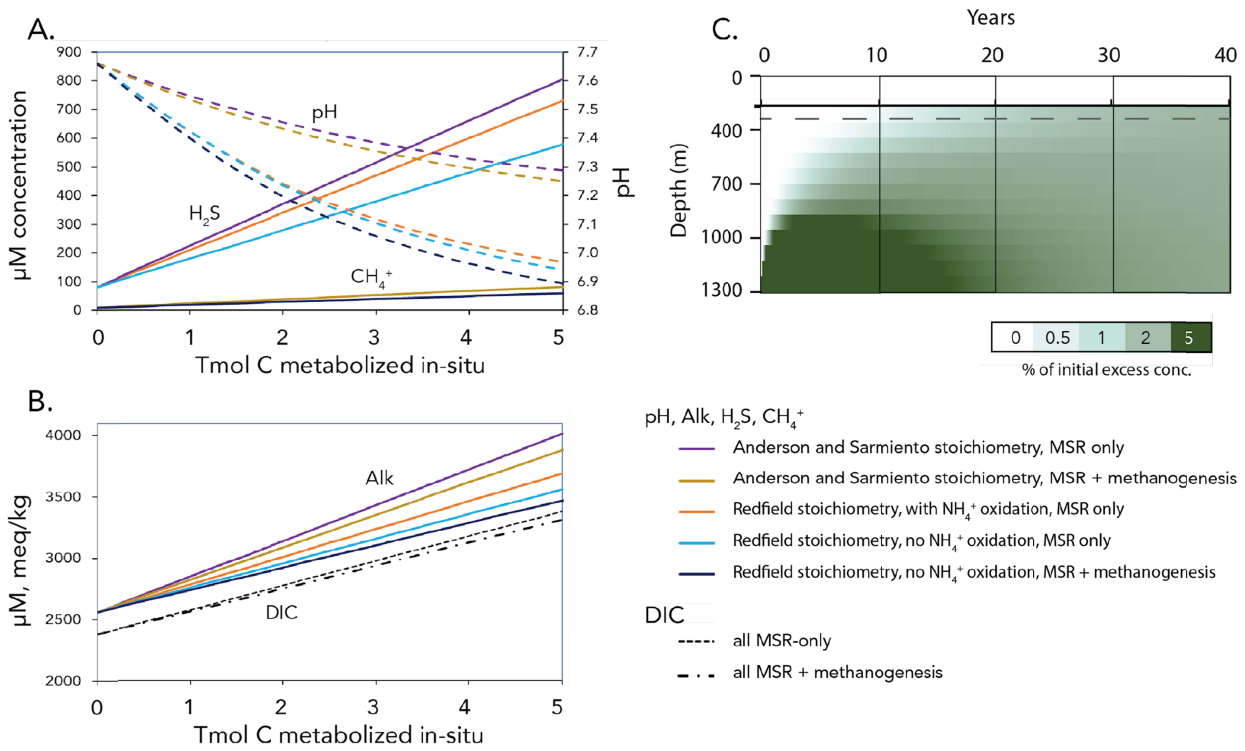

Figure 6. Effects of enhanced OM breakdown on Cariaco Basin water chemistry below 350 m water depth, based on scenarios in Table 1. In scenarios 4 and 5, methanogenesis is presumed to metabolize 10% as much organic C as MSR. **A –** Concentrations of sulfide or methane (solid lines) following various scenarios; sulfide concentrations in MSR-only scenarios 1 and 4 are the same for mixed-metabolism scenarios 2 and 5, respectively. **B –** Concentrations of DIC (dashed) and alkalinity (solids) following various scenarios. **C –** Mixing of dissolved species in the western Cariaco Basin over several decades. Calculations conservatively use eddy diffusion coefficients from Scranton (1987), although these lead to ~10x faster mixing than the values assumed by earlier work (Fanning and Pilson, 1972; Reeburgh, 1976).

The vertical circulation and mixing timescale of Cariaco Basin are very different from the case of the Black Sea. Cariaco Basin is relatively well mixed below the chemocline at 350 m depth but is divided into eastern and western sub-basins that lack lateral mixing. Given seasonal upwelling and weak stratification in the basin, dissolved species from the deepest part of the basin reach the chemocline depth within about 20 years (**Fig. 6**). Accordingly, to assess the geochemical impacts of CDR-scale biomass addition, we calculated potential changes in deep water chemistry for this full volume of ~5,000 km^3. The remineralization of 2 Tmol of organic C in this volume increases modeled sulfide concentrations from an initial value of 80 uM to 262–375 uM, depending on the stoichiometry of the organic matter source and

the metabolic pathways used (scenarios 1–5). This amount of remineralization would also cause increases in NH_4^+ (from 20 uM to 75–82 uM) and CH_4 (from 10 uM to 28–36 uM). The appearance of excess sulfide and ammonium at the chemocline will enhance O_2 demand and may shoal the water column oxic-anoxic interface. More complex modeling efforts will be required to assess these dynamic interactions and the many linked redox reactions they impact near the chemocline.

The pH change associated with the in situ remineralization of 2 Tmol of relatively reduced (lipid-rich) organic carbon (scenarios 1 and 4) is ~0.2 units (from 7.66 to 7.45), while the pH change for more oxidized organic carbon (scenarios 2, 3, and 5) is 0.43 units (from 7.66 to 7.23). Unlike the Black Sea, the deep Cariaco Basin is supersaturated with respect to $CaCO_3$ (calcite Ω = 1.79). The larger pH change associated with scenarios 2, 3, and 5 would drive calcite to be undersaturated (**Ω** = 0.77), favoring dissolution (**Fig. 6**). Actual pH change would be strongly buffered by reactions with highly abundant carbonates in Cariaco Basin sediments (Aguilar et al., 2017).

The effectiveness of Cariaco Basin as a site for biomass storage and CDR is far more sensitive to the efficiency of biomass breakdown than the Black Sea because its weak density gradient and history of dynamic redox change raise the possibility of deep mixing and ventilation. Key targets for future research include this biomass breakdown efficiency and its trajectory over time, as well as understanding the responsiveness of water column methane oxidizing organisms to changes in methane flux. Using a range of estimates for terrestrial biomass storage efficiencies over several decades of 50–85% (Keil et al., 2010), the in-situ respiration of 2 Tmol C could represent a total initial carbon sequestration of 0.18–0.59 Pg CO_2 equivalents, with part stored as solid-phase bales stable over centennial timescales and the remainer present dissolved species with lower durability. In this scenario, this quantity of baled biomass would physically fill the lowest part of the western sub-basin (>1236 m depth, 1500 km^2 area, Scranton, 1988) to an average thickness of roughly 2.7 m. Establishing acceptable limits for environmental change requires collaboration by many stakeholders, most critically the local Venezuelan communities that are economically invested in both fisheries and any future CDR industry. As a first-order evaluation to guide this multi-stakeholder decision making, however, Cariaco Basin appears to have sufficient biogeochemical capacity to support meaningful quantities of biomass carbon storage and is deserving of further research attention, most importantly to address uncertainties related to upwelling and storage durability.

4.3 Orca Basin and other hypersaline basins

Orca Basin is much smaller than either the Black Sea or Cariaco Basin, with a total brine volume of just 10.2 km^3 (compared to 5,000 km^3 for Cariaco or 32,398 km^3 for the Black Sea). We can assess some

aspects of the response of Orca Basin to the placement and remineralization of organic matter, but the extreme ionic strength of Orca Basin exceeds the range of known equilibrium constants for the carbonate system and prevents meaningful pH calculations. We also lack sufficient understanding of the unusual Orca Basin microbial community (Nigro et al., 2020) to constrain the relative importance of methanogenesis and MSR within the brine. For illustration purposes, however, we can assume that some fraction of sequestered biomass breaks down through MSR and/or methanogenesis at a rate that is at least much faster than the rate of mixing across the water-brine interface.

Given the small volume of the brine, the *in situ* respiration of 0.05 Tmol C (2.2 Tg CO_2 equivalent) by MSR alone would increase DIC concentrations from 4.7 mM to 9.6 mM and simultaneously increase alkalinity from 4.4 mM to between 9.3 and 11.4 mM, depending on mean respired organic matter redox state. This amount of MSR would generate 2.4–3.5 mM H_2S and would increase NH_4^+ from 0.5 mM to ~1.2 mM. Alternatively, if breakdown proceeded exclusively via (methylotrophic) methanogenesis, breakdown of the same amount of organic carbon could increase DIC from 4.7 mM to 6.1–9.6 mM without adding alkalinity, lowering brine pH. The resulting methane would be sufficient to approximately double the already high natural concentrations of CH_4 in the brine (3.4 mM).

To place the results of this calculation in context, we need additional information about the rates of organic matter degradation within the Orca Basin brine and the ability of its slow-growing community to respond to a dramatic increase in carbon availability. The microbial community in Orca Basin consists primarily of halophilic sulfate reducers, methanogens, and ammonium oxidizers (Nigro et al., 2020), and rates of potential sulfate reduction are low and similar to other hypersaline brines (~10 to 76 nmol cm^{-3} d^{-1}; Hurtgen et al., 1999; Zhuang et al., 2016). Despite low rates of MSR and methanogenesis, Orca Basin is highly effective at minimizing breakdown of at least some types of organic matter. Well-preserved seaweeds and their epibionts and lipids have been described from Orca Basin sediments below 10 m depth, which is virtually unheard of in other settings (Kennett and Penrose, 1978; Harvey and Kennicutt, 1992) and indicates a remarkable absence or selectivity of heterotrophic degradation. Although electron acceptors (e.g., sulfate) are plentiful, organic materials are also abundant within the brine: DOM concentrations reach 0.24 mM DOC, and sinking particulate organic matter provides a consistent marine C source (Trefry, 1984; Shah et al., 2013; Diercks et al., 2019).

Many unknowns therefore remain about the capacity of microbial communities in anoxic, hypersaline basins to respond to rapid increases in organic carbon loading. Experiments are needed to assess the relative importance of sulfate reduction versus methylotrophic methanogenesis for biomass breakdown in hypersaline basins, and the sensitivity of breakdown rates to hypersaline conditions. Evidence for stimulated methanogenesis could represent a risk for enhanced methane release to the overlying water

column, and although oxic methanotrophy in the Gulf of Mexico can be relatively efficient (Kessler et al., 2011), the response of aerobic methane oxidizers in the water column requires further investigation.

Due to minimal mixing across the pycnocline, both solid- and dissolved-phase C in this system would be physically sequestered over kyr timescales. The effects of stimulated MSR are likely limited to the brine itself, although significant sulfide addition would make the brine sulfidic and impact metal cycling, primarily Fe and Mn. In order to assess the release of breakdown products and background hydrocarbons to the overlying water column in either endmember case, field data are needed related to how biomass sinking impacts mixing at the Orca Basin pycnocline. The scale of potential mixing in a real deployment would depend on the engineering choices that allow ballasted or densified biomass to sink through the pycnocline.

5. Summary and Conclusions: CDR potential of anoxic basins and key unknowns

Any future attempts at effective and responsible CDR are futile in the absence of immediate and dramatic CO_2 emissions reductions on a global scale and must be pursued in that context; emissions reductions are the most cost-effective and highest net reduction strategy currently available (IPCC AR6, 2023). If marine CDR is pursued as an approach to support decarbonization, its methods will need to both minimize ecological risks and maximize storage durability. Risk minimization will also require effective monitoring, reporting, and verification (MRV) to account for the actual efficiency of CO_2 storage in various parts of the ocean system.

By these criteria, anoxic basins in general and the Black Sea in particular may represent uniquely effective locations for the durable sequestration of atmospheric CO_2 as organic carbon. This process conceptually accelerates a central mechanism for climate recovery in the natural Earth system. Anoxic basins may reduce geochemical and ecological risks relative to well-oxygenated regions, where biomass degradation will have larger impacts on pH change and deep-sea ecosystems. Careful consideration of benthic impacts is crucial for any such activity (Levin et al., 2023).

The effective capacity of anoxic basins for CO_2 removal depends on the efficiency of organic carbon storage, which depends in turn on the stoichiometry and reactivity of the biomass materials selected. Although the Black Sea has by far the largest capacity for organic carbon sequestration, smaller but complementary contributions may be achievable from Cariaco Basin and anoxic hypersaline basins like Orca Basin. A primary challenge for CDR applications in Cariaco Basin will be the high and variable rates of upwelling in the basin, which will ventilate remineralized CO_2. For Orca Basin, a primary challenge is predicting biogeochemical behavior at very high ionic strength, necessitating site-specific

studies of the relative favorability of microbial breakdown processes. In all of these cases, the morphology and circulation of anoxic marine basins present opportunities for effective monitoring, reporting and verification of CO_2 sequestration and environmental effects. The combination of pH, DIC, and alkalinity data can constrain the relative rates of organic matter remineralization via microbial sulfate reduction and methanogenesis.

Additional research is needed to fill several key gaps in our ability to predict carbon cycling impacts of organic matter addition to anoxic basins and to inform decision making related to its potential future implementation as a CDR strategy. At a minimum, we will need to (1) test and parameterize remineralization rates for specific types and components of biomass under relevant conditions; (2) investigate the scale and recalcitrance of DOM generated from sequestered biomass; (3) evaluate the impacts of biomass placement on benthic carbon turnover and chemical profiles in sediments, and (4) develop basin-specific models for the physical transport and mixing effects of potential operations. These remaining scientific challenges are substantial, but anoxic marine basins have the potential to be substantive contributors to a global portfolio of CO_2 removal technologies and should be a priority for additional focused investigation.

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