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. Still, all of these systems would require extensive further evaluation prior to consideration of megatonne-scale CO_2 sequestration. Many key unknowns remain, including the partitioning of breakdown among sulfate-reducing and methanogenic metabolisms and the fate of methane in the environment. 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 meet the goals of the Paris Agreement and avoid the worst effects of climate change. Several of the approaches to remove CO_2 from the atmosphere that are currently

being discussed 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 carbon for more than 1,000 years with moderate changes to deep water chemistry. With these results, it is our aim to motivate rigorous field and experimental studies that 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, although its durability depends on local circulation.

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 – approximately 40 Pg or 40 Gt CO_2 per year – 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 biomass sourcing pathways from seaweed farming to land-based agriculture, each of which have their own distinct and complex issues that require separate attention. Our site-specific approach is intended to be generalizable to any marine or terrestrial carbon source and to motivate rigorous further rigorous research on these topics.

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) and had global consequences for biodiversity (Bambach, 2006). 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 at an average rate of ~0.26 Pg CO_2/yr), 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). Although OAE-2 occurred over much

longer timescales than are relevant for CDR, it provides valuable insights into the mechanisms of long-term organic carbon burial that might be leveraged to enhance rates of atmospheric CO_2 removal.

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 (MSR) produces sulfide, which can react with (or "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 continue to support hotspots of organic carbon burial today (Bianchi et al., 2018).

Another important factor limiting rates of biomass breakdown during OAE-2 and in anoxic basins more generally 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 some 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). Although anaerobic microbial ecosystems undoubtably have underappreciated diversity and provide ecosystem services for future discovery, eukaryotic organisms like animals and plants often have greater human cultural significance and regulatory protection, arguably making their consideration a higher priority.

Biomass breakdown rates differ for different organic materials, some of which 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). Rates of lignin degradation in anoxic marine systems are generally difficult 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). Therefore, biomass that is rich in lignins and other oxidized structural polymers is likely to be especially resistant to biological breakdown under anoxic conditions. In order to maximize the efficiency of carbon storage in CDR applications, it will be essential to consider the lability of biomass materials under site-specific conditions and to balance that efficiency against the full life-cycle and environmental impacts of a particular CDR pathway.

2.2 Impacts of enhanced organic carbon addition to the seafloor

Delivering large quantities of organic carbon to the seafloor for CDR 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). Anaerobic microorganisms that remineralize biomass in the absence of O_2 generate alkalinity, methane, reactive metals, and/or sulfide as well as CO_2 and DOM. After their release, these dissolved compounds will be transported away from seafloor installations by the general circulation around the sequestration site.

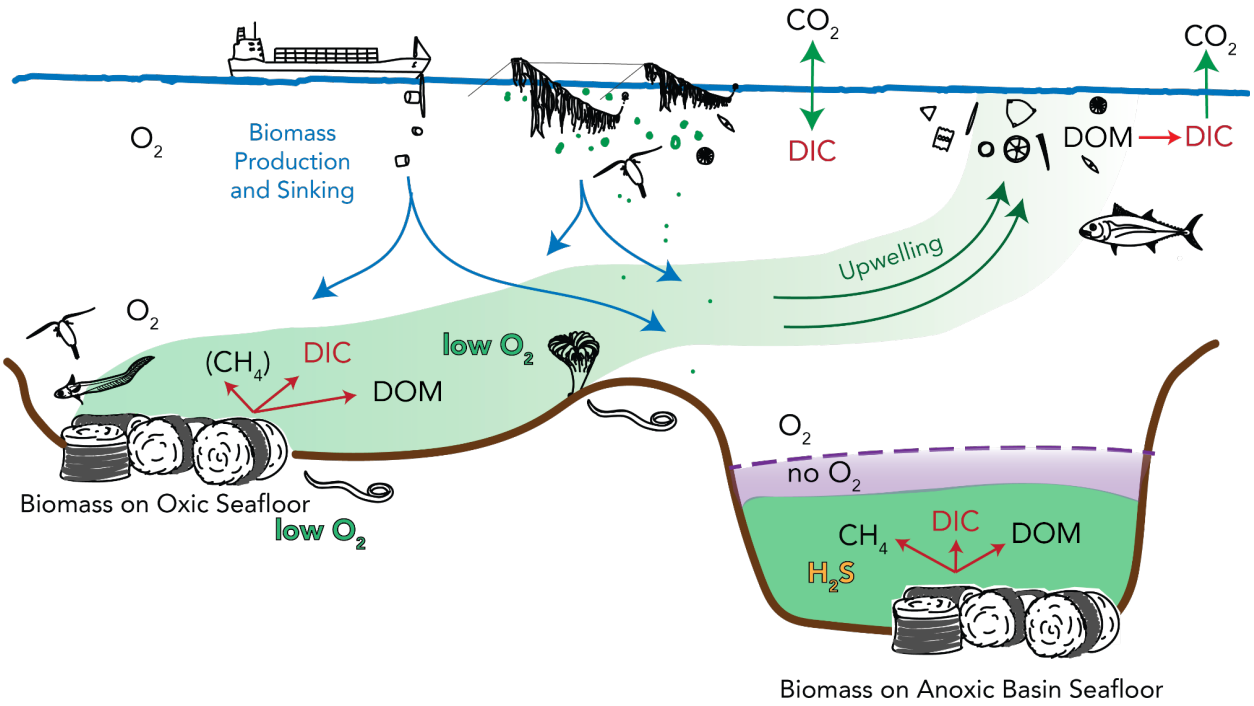

Fig. 1. Overview of potential outcomes for organic carbon sequestered in oxic and anoxic regions of the seafloor. Red arrows indicate potential pathways for sequestered biomass transformations in the environment: respiration to dissolved inorganic carbon (DIC), fermentation to DIC and methane (CH_4), 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).

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 organic matter may also attract opportunistic scavengers to feed on the deposit. The scale and severity of ecological effects will depend on the seafloor region selected for storage.

The effects of any CDR strategy on the deep ocean environment will need to be balanced against the effectiveness of that approach for removing CO_2 from the atmosphere and marginally reducing climatic havoc. The effectiveness of organic matter sequestration in the deep ocean depends on both storage

efficiency– the proportion of biomass that resists breakdown on a chosen timescale (section 2.1) – and the durability of atmospheric CO_2 removal – the timescale on which CO_2 is kept out of the atmosphere in any form (organic matter, DIC, DOM, or dissolved methane). The durability of marine biomass CDR is strongly dependent on the depth and downstream circulation of its storage location (**Fig. 1**). 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 organic materials that are effectively stationary on the abyssal (>2,000 m depth) seafloor will encounter water masses that generally return to the surface and ventilate their CO_2 more slowly, over hundreds to thousands of years (Siegel et al., 2021).

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*

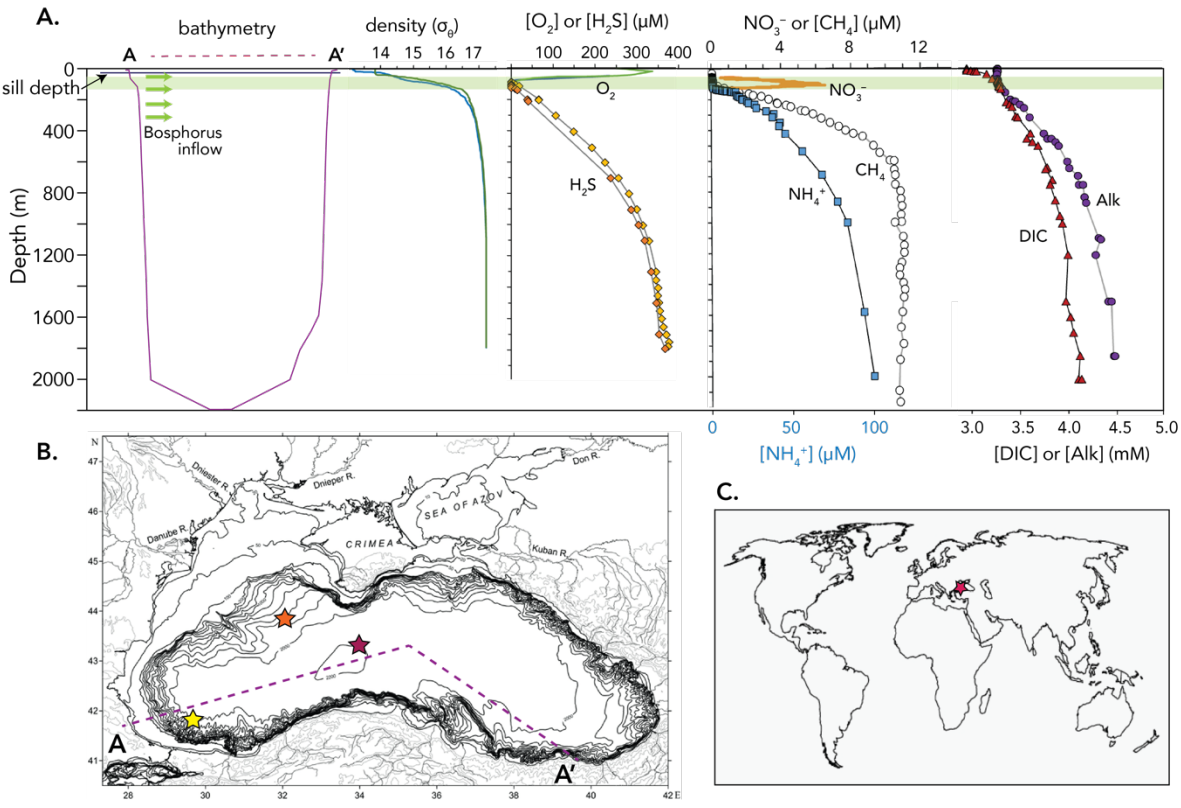

Fig. 2: Modern geochemical conditions in the Black Sea water column. (A.) Compiled literature data for the Black Sea. Circulation from Murray et al. (1991) and Ivanov and Samadurov (2001); density from Konovalov and Murray (2001) and Dubinin et al. (2022); [O_2] from Wakeham et al. (2003) and Dubinin et al. (2022); [H_2S] from Dubinin et al. (2022); [NO_3^-] and [NH_4^+] from Konovalov et al. (2006); [CH_4] from Reeburgh et al. (1991); [DIC] and Alk from Hiscock and Millero (2006). Results for nitrogen species, DIC, and Alk were converted from σ_θ units to approximate depth based on the density profiles and alignment in Dubinin et al., 2022). (B.) Map showing Black Sea bathymetry. Sampling locations are shown for methane (purple star), DIC and Alk (yellow star), and all other station samples (red star). Cross-section A–A' is 1120 km long. (C.) Global overview map showing the location of the Black Sea as a red star.

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 receives freshwater inflows from several major rivers, mostly in its northwest, and has a positive water balance overall. The abyssal Black Sea is characterized by a relatively well-mixed benthic boundary layer below ~1750 m water depth (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 is 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.

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 the shelf and slope in the Black Sea therefore 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), but less than 1% of this methane

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). Water column methane concentrations are ~11 μM below 500 m and 10 nM at the surface (**Fig. 2**).

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.

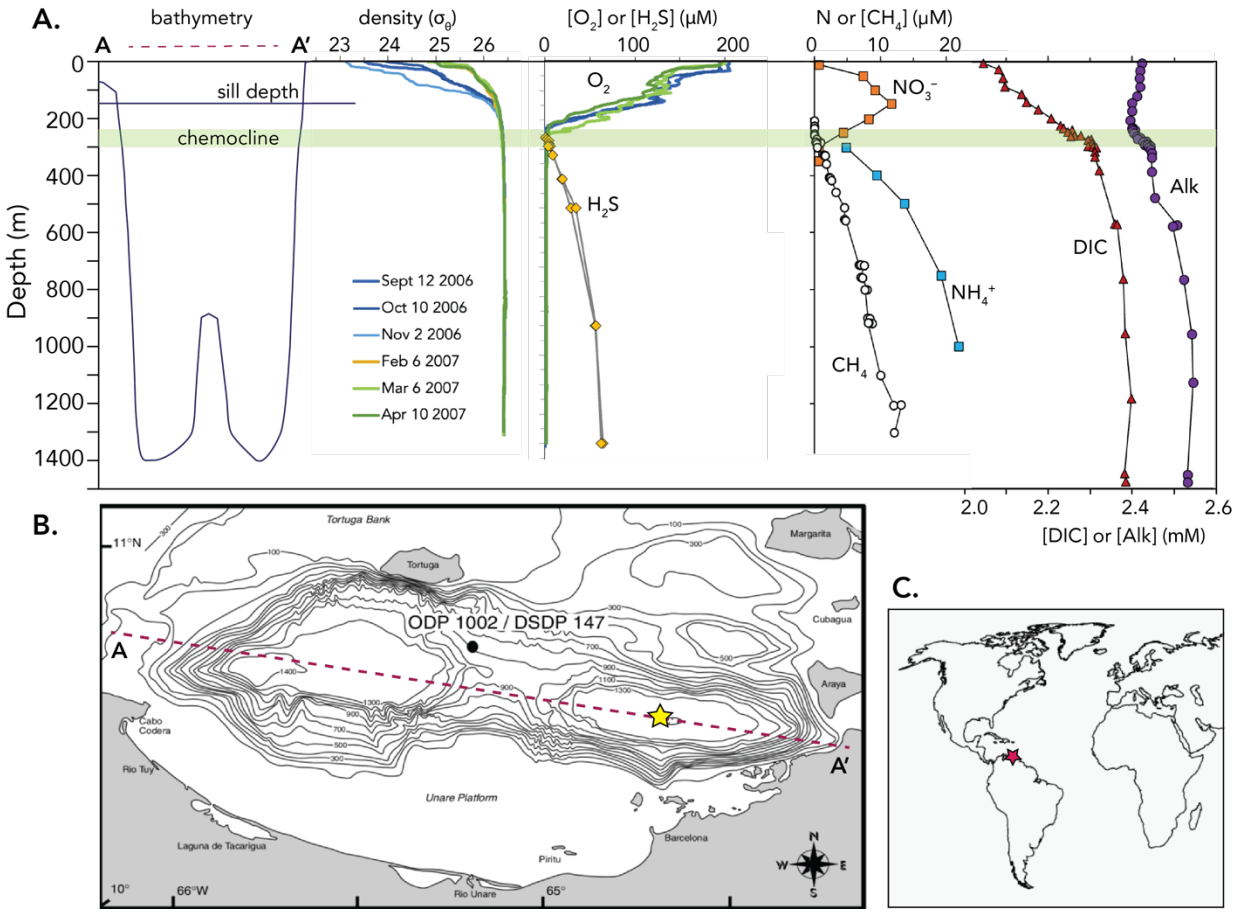

Fig. 3: Cariaco Basin geochemistry. (A.) Compiled literature data for Cariaco Basin. Density and [O_2] from the CARIACO time series database (http://imars.marine.usf.edu/CAR/); [H_2S] from Li et al. (2010);

269 [NO_3^-] and [NH_4^+] from Thunell et al. (2004); [CH_4] from Scranton et al (1988); [DIC] and [Alk] from
270 Hastings and Emerson (1988). (B.) Map showing Cariaco Basin bathymetry. The yellow star indicates the
271 location of the CARIACO long-term time series station and profile site for all data except DIC/Alk. The
272 cross-section A–A' is 200 km long. (C.) Global overview map showing the location of Cariaco Basin as a
273 red star.

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

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

294

295 2.3.3 *Orca Basin*

296 Orca Basin is a 200-meter-deep seafloor depression filled with anoxic, hypersaline water that underlies
297 ~2,200 meters of 'normal' oxygenated seawater in the Gulf of Mexico. The continental shelf bordering
298 Louisiana and Texas (USA) is pockmarked by many such basins, generally produced by the intersection of
299 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). Brines have been isolated from overlying seawater for at least 7,900 years (Addy and Behrens, 1990).

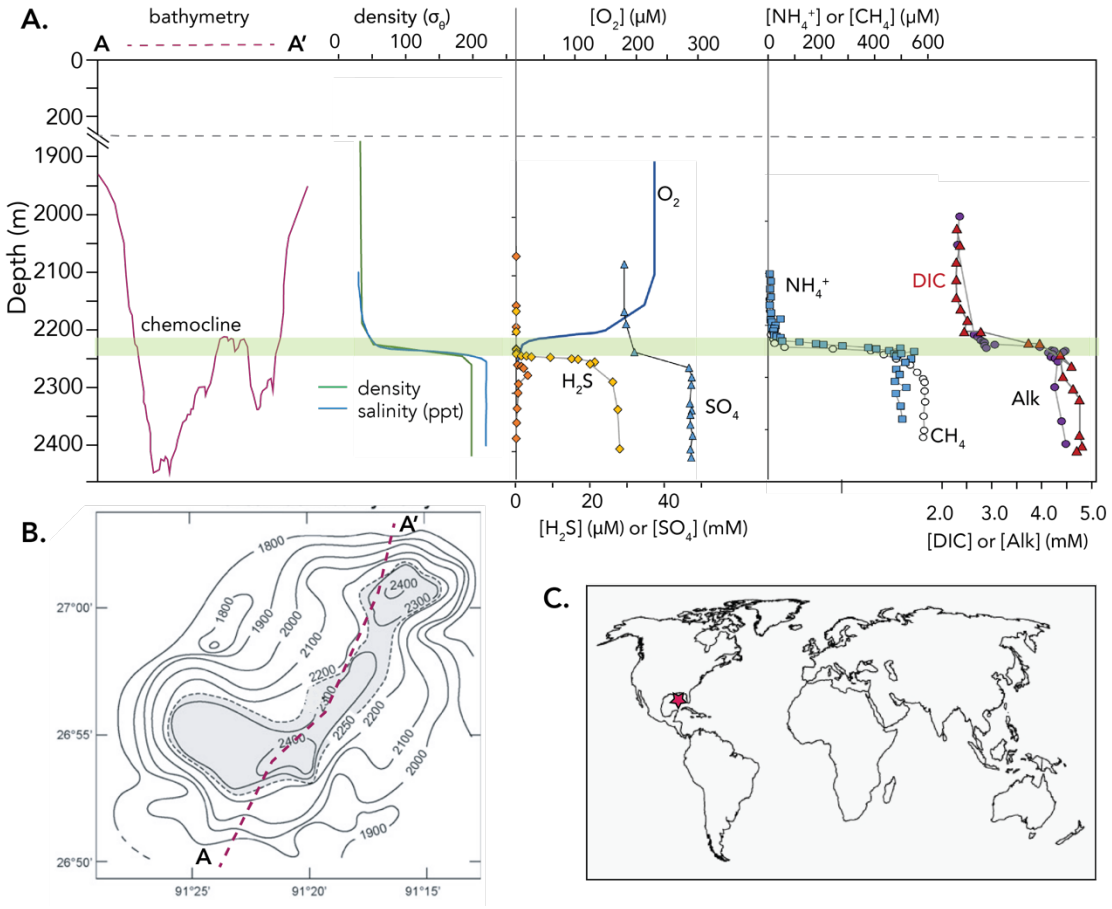

Fig. 4: Orca Basin geochemistry. (A.) Compiled literature data for Orca Basin. Bathymetry based on seismic reflection profiles from Shokes et al. (1977); density from Millero et al. (1979); salinity from Van Cappellen et al. (1998); $[O_2]$ from Trefry et al. (1984); $[H_2S]$ from Wiesenberg et al. (1984) and Van Cappellen et al. (1998); $[NH_4^+]$ and [Alk] from Van Cappellen et al. (1998), $[CH_4]$ from Wiesenberg et al. (1984), [DIC] from Sackett et al. (1979). (B.) Map modified from Tribovillard et al. (2009). The grey shaded area on the map corresponds to the lateral extent of the brine. The cross-section A–A' is approximately 28 km long. (C.) Global overview map showing the location of Orca Basin as a red star.

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 have been accumulating in the basin due to their very high densities (~1300 g/L) for thousands of 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 at ~2270 m depth during two cruises in the late 1970s (Wiesenburg et al., 1985), while Van Cappellen et al. (1998) reported 10 to 28 μM 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 calculate the geochemical impacts of biomass breakdown in the Black Sea, Cariaco Basin, and Orca Basin by mixing breakdown products into the abyssal volume of each site and calculating carbonate system parameters. Conceptually, this calculation evaluates a range of magnitudes for a single hypothetical sequestration event, assuming that most remineralization occurs immediately thereafter. This first simple approach has no time-dependence and does not include sinks for any released compounds (e.g., sulfide

oxidation). Instead, it constrains the scale of the peak acute perturbation implied by biomass breakdown at scale given basin geochemical conditions.

We apply 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 have smaller changes in NH_4^+ concentration than these estimates. 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	$C_{117}N_{16}P$	$32CO_2 + 85CH_4 + 16NH_4^+ + H_2PO_4^-$	+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. Conditions in Orca Basin brine exceed calibration limits for carbon system parameters, so we did not calculate pH or carbonate solubility change for this site. 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 total brine volume of 10.3 km^3 (Diercks et al., 2019). The vertical mixing rates within Orca Basin brine have not yet been measured directly.

3.2 Circulation Model

Dissolved products of biomass breakdown 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 $4.1x10^{-4}$ to $1.2x10^{-4}$ km^2/yr, equivalent to $4x10^{-6}$ to $1.3x10^{-5}$ 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 $1.3x10^{-2}$ to $2.7x10^{-3}$ 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.

In Orca Basin, the primary control on transport from the basin to the upper water column is the strong density interface at 2220–2250 m depth. Durability of Orca Basin storage is assessed in the context of this mixing barrier rather than through a stacked diffusion model.

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 "instantaneously" *in situ* 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**).

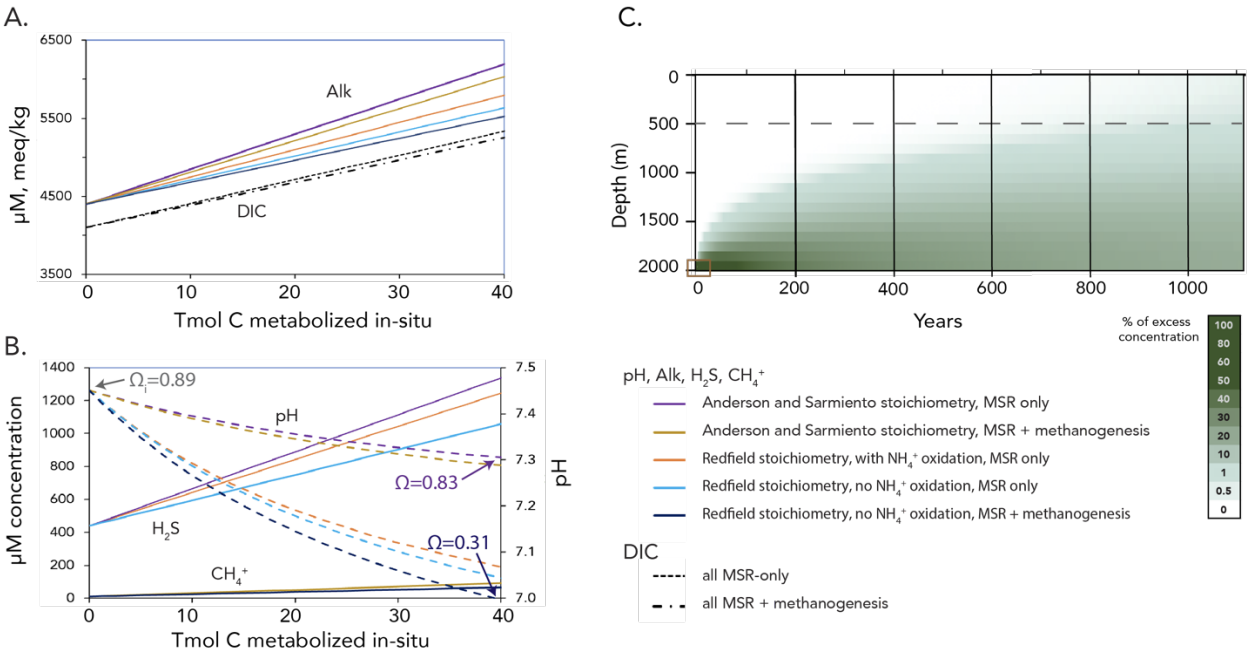

Fig. 5 Impacts of enhanced organic matter breakdown in abyssal western Black Sea water. A – Calculated changes in DIC (dashed lines), and alkalinity concentrations (solid lines) resulting from the instantaneous *in-situ* respiration of various total amounts of organic C by MSR (0 to 40 Tmol C), with or without methanogenesis, for a range of organic matter stoichiometries (Table 1). In scenarios 4 and 5, methanogenesis is presumed to metabolize 10% of respired organic C. **B –** Associated changes in abyssal Black Sea sulfide and methane concentrations (solid lines) and pH (dashed lines) for various scenarios. Annotations show the saturation state (Ω) of calcite ($CaCO_3$), which is undersaturated throughout. **C –** Modeled vertical mixing over time of a conservative tracer 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; these changes would be smaller for N-poor biomass. 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 (>2,000 m) sulfide concentrations to nearly 2,000 μM (from 400 μM) and drop pH to 6.87 (from 7.40).

	Mixing volume used	Example OC respired	Equivalent CO_2 stored	Area of 4-m-thick biomass (% of area)	Atm. comm. timescale
Black Sea	32,398 km^3	40 Tmol C	3.5 to 11.7 Gt CO_2e (50–85% efficiency)	2,160 – 7,219 km^2 (0.67–2.2% of area)	>1,000 yrs
Cariaco Basin	5,000 km^3	2 Tmol C	0.18–0.59 Gt CO_2e (50–85% efficiency)	111 – 364 km^2 (5.3–17% of west basin)	>10 yrs
Orca Basin	10.24 km^3	0.05 Tmol C	0.005–0.26 Gt CO_2e (50–98% efficiency)	3.1 – 158 km^2 (2 – 100% of brine area)	>10,000 yrs

Table 2. Scale of hypothetical scenarios discussed in the text. Equivalent CO_2 sequestration estimates apply a wide range of storage "efficiency," defined as the proportion of solid-phase biomass remaining unrespired after ~decades. "Atm. comm. timescale" refers to the expected approximate lag between the production of dissolved products and their potential communication to the surface ocean and atmosphere, discussed below. We emphasize that these straw-man scenarios are intended as points of discussion and are not prescriptive limits or goals for sequestration.

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 biomass type, the selected basin, and 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

471 and exclude the potential later reoxidation of methane. For the same scale of total C respiration discussed
472 above (40 Tmol C), the addition of 2–2.9 Tmol CH_4 would increase abyssal methane concentrations from
473 current values of ~10 uM to 71–100 uM and add the equivalent of roughly 10–15 yrs of natural CH_4
474 production in the shelf and slope sediments of the Black Sea (Reeburgh et al., 1991). Organic matter
475 breakdown in these scenarios leads to slightly larger changes in abyssal pH and saturation state than MSR
476 alone (Fig. 5) because methanogenesis does not produce alkalinity, unlike MSR. However, if the methane
477 produced during methanogenesis is subsequently reoxidized anaerobically with sulfate, the summed
478 reactions produce a net effect similar to breakdown via MSR alone (Middelburg et al., 2020).

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

499 Potential impacts of biogeochemical change in the abyssal Black Sea on human endeavors in the region are
500 highly sensitive to the mixing, or lack thereof, between abyssal waters and the surface. The Black Sea is
501 notably stratified, with minimal tidal action to add energy to the system (Stewart et al., 2007). We used
502 estimates of eddy diffusivity (Ivanov and Samodurov, 2001) from water column profiles to calculate the
503 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. Importantly, however, we do not yet fully understand the likelihood that stratification and ventilation rates in the Black Sea will substantially change in response to the changing hydrology and climate.

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 the purposes of this calculation, we apply a broad range of possible storage efficiencies between 50% and 85%, informed by these experiments and field observations. For this range of efficiencies, the in-situ respiration of 40 Tmol C discussed above translates into a total sequestration of 3.5 to 11.7 Pg (Gt) CO_2 equivalent. In such a hypothetical scenario, carbon would be stored in two distinct pools: 50-85% of sequestered carbon would be stored semi-permanently as solid biomass while 15–50% would be sequestered on a thousand-year timescale as either dissolved CO_2 or DOM. In terms of the physical size of such an installation, consolidated terrestrial biomass equivalent to 3.5 to 11.7 Pg CO_2 would, if deposited in a four-meter-thick layer in the deepest region of the western Black Sea, cover 2,160 – 7,219 km^2, or

537 0.67–2.2% of total Black Sea area. The upper end of this range – a total amount, not an annual flux – is an
538 enormous value, similar to the total production of crop waste across the entire planet in a year. Still, it
539 represents only a third of a year of anthropogenic CO_2 emissions, underscoring the scale of the problem
540 and the need for a broad portfolio of CDR techniques and rapid decarbonization to achieve global climate
541 goals.

542 This highly simplified mass balance exercise suggests that the bulk geochemistry and stratification of the
543 Black Sea may allow for moderate changes in the concentrations of H_2S, NH_4, alkalinity, and pH to result
544 from the seafloor storage of a climatically relevant quantity of carbon. The scenario involving the in-situ
545 respiration of ~40 Tmol C that we use for discussion purposes here (Table 2) is of the same order of
546 magnitude in terms of increased organic C input as the 20th-century eutrophication of the Black Sea
547 (Konovalov and Murray, 2001). Importantly, however, biomass breakdown in abyssal waters has a diluted
548 and delayed effect on chemocline and mixed layer properties relative to shallow biomass breakdown.
549 Geochemical changes within the basin are also isolated from the global ocean by the singular connection at
550 the Bosphorus. This physical restriction provides spatial bounds for monitoring and verification of any CO_2
551 removal activities and isolates its impacts to a relatively well-defined set of stakeholders in the region.

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

565

566 **4.2 Cariaco Basin: Biogeochemical impacts of organic carbon sequestration**

567 Using the same general approach and stoichiometric scenarios (Table 1) that we used for the Black Sea, we
568 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.

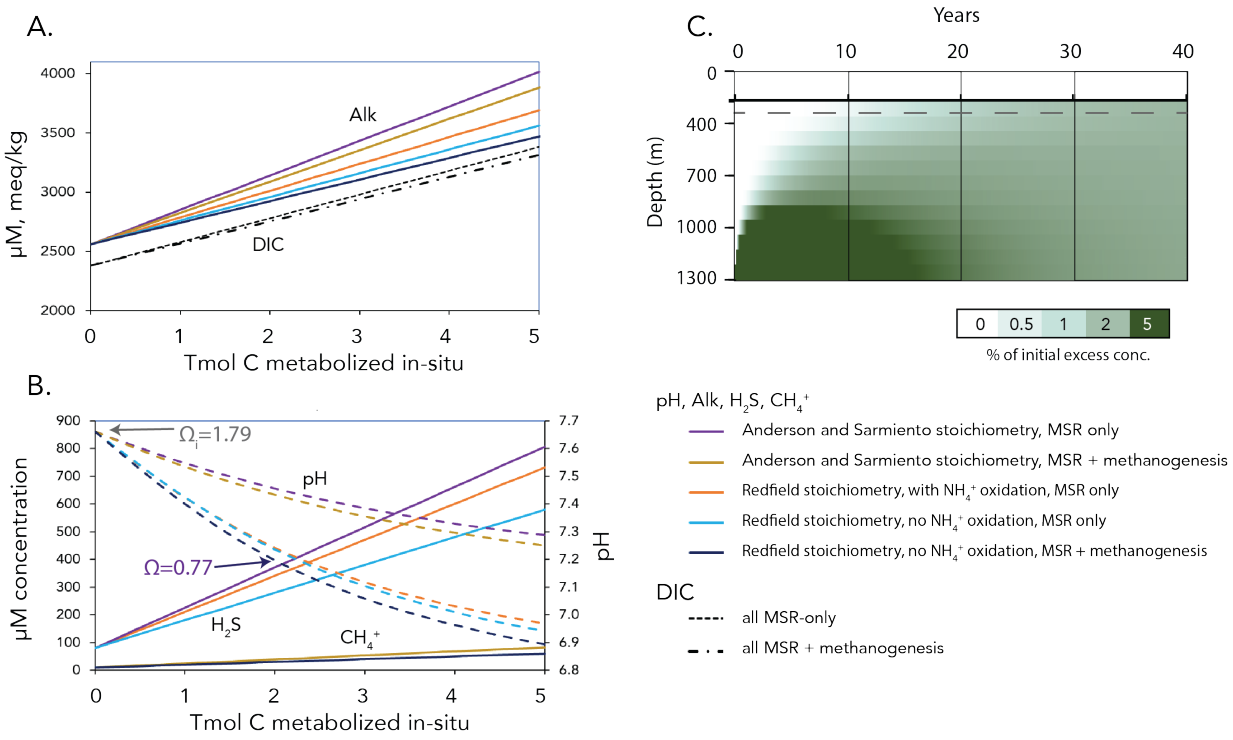

Figure 6. Effects of enhanced OM breakdown on Cariaco Basin water chemistry below 350 m water depth, based on scenarios in Table 1. In scenarios 4 and 5, methanogenesis is presumed to metabolize 10% of total respired organic C. **A –** Concentrations of DIC (dashed) and alkalinity (solids) following various scenarios for the instantaneous addition and respiration of various quantities of biomass. **B –** Concentrations of sulfide or methane (solid lines) and pH (dashed) following various scenarios; sulfide concentrations in MSR-only scenarios 1 and 4 are the same for mixed-metabolism scenarios 2 and 5, respectively. Annotations show the saturation state (Ω) of calcite ($CaCO_3$) for 0 and 2 Tg C. **C –** Mixing of a conservative tracer 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

587 (**Fig. 6**). Accordingly, to assess the geochemical impacts of CDR-scale biomass addition, we calculated
588 potential changes in deep water chemistry for this full volume of ~5,000 km^3. The remineralization of 2
589 Tmol of organic C in this volume (Table 2) increases modeled sulfide concentrations from an initial value
590 of 80 uM to 262–375 uM, depending on the stoichiometry of the organic matter source and the metabolic
591 pathways used (scenarios 1–5). This amount of remineralization would also cause increases in NH_4^+ (from
592 20 uM to 75–82 uM) and CH_4 (from 10 uM to 28–36 uM). The appearance of excess sulfide and ammonium
593 at the chemocline will enhance O_2 demand and may shoal the water column oxic-anoxic interface. More
594 complex modeling efforts will be required to assess these dynamic interactions and the many linked redox
595 reactions they impact near the chemocline.

596 The pH change associated with the in situ remineralization of 2 Tmol of relatively reduced (lipid-rich)
597 organic carbon (scenarios 1 and 4) is ~0.2 units (from 7.66 to 7.45), while the pH change for more oxidized
598 organic carbon (scenarios 2, 3, and 5) is 0.43 units (from 7.66 to 7.23). Unlike the Black Sea, the deep
599 Cariaco Basin is supersaturated with respect to $CaCO_3$ (calcite $\Omega = 1.79$). The larger pH change associated
600 with scenarios 2, 3, and 5 would drive calcite to be undersaturated ($\Omega = 0.77$), favoring dissolution (**Fig.**
601 **6**). Actual pH change would be strongly buffered by reactions with highly abundant carbonates in Cariaco
602 Basin sediments (Aguilar et al., 2017), which would add alkalinity to deep water.

603 The effectiveness of Cariaco Basin as a site for biomass storage and CDR is far more sensitive to the
604 efficiency of biomass breakdown than the Black Sea because its weak density gradient and history of
605 dynamic redox change raise the possibility of deep mixing and ventilation. Key targets for future research
606 include this biomass breakdown efficiency and its trajectory over time, as well as understanding the
607 responsiveness of water column methane oxidizing organisms to changes in methane flux. Using a range
608 of estimates for terrestrial biomass storage efficiencies over several decades of 50–85% (Keil et al., 2010),
609 the in-situ respiration of 2 Tmol C could represent a total initial carbon sequestration of 0.18–0.59 Pg CO_2
610 equivalents, with part stored as solid-phase bales stable over centennial timescales and the remainder
611 present dissolved species with lower durability. In this scenario, this quantity of baled biomass in a 4-meter-
612 thick layer would physically cover 5.3–17% of the western sub-basin seafloor (>1000 m depth, 2100 km^2
613 area, Scranton, 1988). Establishing acceptable limits for environmental change requires collaboration by
614 many stakeholders, most critically the local Venezuelan communities that are economically invested in
615 both fisheries and any future CDR industry. As a first-order evaluation to guide this multi-stakeholder
616 decision making, however, Cariaco Basin appears to have sufficient biogeochemical capacity to support
617 meaningful quantities of biomass carbon storage and is deserving of further research attention, most
618 importantly to address uncertainties related to upwelling and storage durability.

619

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, adding uncertainty to model results (Table 2). 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.

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, 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 preserving 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). We can therefore constrain the maximum rates of biomass breakdown in Orca Basin from field observations and sediment core data, while the minimum rates of breakdown for some biomass types may approach zero. We explore relevant sequestration scales using an extremely conservative value of 50% for the minimum biomass retention efficiency and a maximum efficiency of 98%, which is based on observations of extremely slow biomass breakdown and intact Sargassum materials in the sediments.

Given the small volume of the brine, the *in situ* respiration of 0.05 Tmol C (2.2 Tg CO_2 equivalent) by only MSR (no methanogenesis) 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, much of which would likely be removed by subsequent reactions with iron to form iron sulfide minerals (Van Cappellen et al., 1998). Redfieldian biomass would increase NH_4^+ from 0.5 mM to ~1.2 mM, although changes would be smaller for high C:N materials. Alternatively, if 10% of breakdown proceeded 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 increase the already high natural concentrations of CH_4 in the brine (to 1.1 mM from 0.75 mM). Regardless of breakdown pathway, 0.05 Tmol C may translate into meaningful quantities of CO_2 storage, but this calculation is highly sensitive to actual breakdown rates for the biomass type chosen. A 4-meter-thick layer of biomass across the entire deep Orca Basin brine region (158 km^2, Diercks et al., 2019) could contain as much as 0.26 Pg CO_2e and would release ~0.05 Tmol C if it were 98% efficient. As for the other case studies, this calculation assumes highly idealized engineering scenarios and considers only immediate geochemical breakdown products without time-resolved processes. Extensive further analytical and modeling work are needed to evaluate the downstream impacts of geochemical change within the Basin and to understand their interactions with microbial ecology, DOM, and mixing across the pycnocline.

A critical knowledge gap for evaluating Orca Basin CO_2 removal potential is the how its slow-growing microbial community would respond to a dramatic increase in carbon availability. Experiments are also needed to assess the relative importance of sulfate reduction versus methylotrophic methanogenesis for biomass breakdown in hypersaline basins, the rates of these processes, 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 thousand-year 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 that of 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 and durability 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, conceptually accelerating a central mechanism for climate recovery in the natural Earth system. Although anoxia can also be present in environments like fjords, river deltas, lakes, and upwelling zones, these systems are generally more challenging for CO_2 sequestration because they lack the scale, stability, sulfate availability, and/or isolation of permanently anoxic marine basins. Anoxic basins may reduce geochemical and ecological risks relative to well-oxygenated regions, where biomass degradation will have larger impacts on pH, deoxygenation, and deep-sea ecosystems (Levin et al., 2023). These regions also avoid risks of carbon mobilization due to bottom trawling or seabed mining, and they minimize the economic, social, and political complexities of work in coastal environments. Nonetheless, deep-sea microbial ecosystems have substantial value for microbial diversity, exobiology research, and the preservation of sedimentary records, along with opportunities for future discovery. All of these factors will need to be balanced against potential marginal reductions in harmful climate outcomes when making future decisions about trial or full-scale deployments of biomass-based marine CDR. Future decision making must also consider the full life-cycle of biomass sources, which are excluded from analysis here.

The effective capacity of anoxic basins for CO_2 removal depends on both the efficiency of organic carbon storage, which depends in turn on the stoichiometry and reactivity of the biomass materials selected, and its durability, which is also a function of site circulation. 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 in brines with unusual chemistry, necessitating site-specific studies of the relative favorability of microbial breakdown processes. In all of these cases, the often restricted circulation of anoxic marine basins presents 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.

If future work concludes that the biomass storage efficiency in the Black Sea and Orca Basin is high on relevant timescales (e.g., 85% over decades or more) and that benefits of action outweigh risks, then biomass storage at these sites might be able to contribute to global CDR goals of 1–10 Pg CO_2e/yr (2.5 –

718 25% of current annual emissions). For the hypothetical scenarios in Table 2, the Black Sea and Orca Basin
719 might together sequester on the order of 10 Pg CO_2e total, or about a year of humanity's CDR needs over
720 the next century (IPCC AR6, 2021). An enormous effort will be required to develop a suite of parallel CDR
721 approaches that can achieve ongoing CO_2 storage at the required scale.

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

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733

734 **Open Research**

735 No data or software were produced as part of this study.

736

737 **Acknowledgments**

738 We thank Adam Subhas (WHOI) and Max Lloyd (Penn State) for valuable discussions about carbonate
739 chemistry and lignin breakdown pathways. We also thank Cameron Allen (UCSB) for his assistance with
740 the early stages of the project. Funding for this work was provided by a grant to UCSB from the
741 Grantham Foundation for the Protection of the Environment.

742

743 **Conflict of Interest Statement**

744 In addition to her primary role as UCSB faculty, Raven serves as the Chief Science Officer for, and holds
745 equity in, Carboniferous, Inc., a seed-funded startup company exploring potential applications of deep
746 marine biomass sequestration. The research presented here was conducted and funded entirely via research
747 grants to UCSB. An unconflicted PI is formally involved for all CDR-related funds and mentorship plans
748 in the Raven group. No other co-authors have real or perceived COIs to disclose.

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