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Ocean alkalinity enhancement reduces silica ballasting during export due to amplified dissolution

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Abstract.

Ocean alkalinity enhancement (OAE) is a carbon dioxide removal technology (CDR) proposed to store carbon dioxide (CO_2) in the ocean on human-relevant time scales. However, depending on OAE intensity, resulting shifts in seawater carbonate chemistry speciation could alter community-driven biomass build-up, particulate stoichiometry, and transformation during particle export. Using mesocosms in the eutrophic North Sea (Helgoland, Germany), we established six alkalinity levels under two dilution scenarios (localized vs. uniform OAE additions) for 39 days. Total alkalinity (TA) was increased stepwise to ΔTA_{max} = 1250 µmol kg^{-1} (250 µmol TA kg^{-1} increments) using NaOH with $CaCl_2$ to simulate cation release during calcium-based mineral dissolution, causing strong carbonate chemistry perturbations (e.g., pH > 9.25). Because response patterns were consistent across dilution scenarios, they were treated as replicates and assessed across the common pH_T gradient. Average phytoplankton bloom magnitude (chlorophyll *a* and particulate organic carbon in the water column, POC_{WC}) remained unchanged under unequilibrated OAE. In contrast, silica ballasting ratios declined with increasing pH_T: suspended biogenic silica to particulate organic carbon ratios (BSi_{WC}:POC_{WC}, where WC = water column) decreased by up to 50%, while exported BSi_{Sed}:POC_{Sed} (where Sed = sediment) decreased by 60%, indicating intensification during sinking. As OAE delayed spring bloom timing, these effects were only apparent within mesocosm-specific bloom and export events. The stronger decline in sinking compared to suspended BSi:POC is consistent with pH-enhanced BSi dissolution during export. Porosity of sinking particles increased with pH_T and co-varied with BSi_{Sed}:POC_{Sed}, suggesting particle-quality traits can modulate dissolution during transit. Remineralization metrics showed no treatment response, and particle sinking velocities did not scale with suspended or sinking silica ballasting ratios. Unequilibrated OAE may reduce silica ballasting, shoal carbon remineralization, and thus shorten sequestration timescales, potentially weakening net CO_2 removal, regardless of dilution scenario. Quantifying how pH-driven BSi dissolution interacts with bloom and export dynamics will be critical for evaluating OAE efficacy and ecological safety.

Keywords: ocean alkalinity enhancement, carbon, silica, ballasting, stoichiometry, diatoms, climate change, negative emission technologies (NETs), eutrophic, North Sea, mesocosm

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1 Introduction

Ocean alkalinity enhancement (OAE) is a carbon dioxide removal (CDR) strategy proposed to help restrict global warming to 2°C (Renforth and Henderson, 2017; Rogelj et al., 2018). It aims to mimic natural rock weathering on land by directly delivering alkaline material to seawater (Gattuso et al., 2018; Renforth and Henderson, 2017). OAE shifts seawater carbonate speciation towards carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), thereby lowering seawater carbon dioxide fugacity (fCO_2) and promoting further atmospheric uptake (Zeebe and Wolf-Gladrow, 2007). The process is considered capable of sequestering CO_2 on gigaton scales (3 - 30 Gt y^{-1}; Feng et al., 2017; Köhler et al., 2010; Renforth and Henderson, 2017) and may mitigate ocean acidification (Doney et al., 2009; Gattuso et al., 2015). Various OAE strategies have been proposed, with several already in practice, ranging from alkaline solution injection and mineral additions to electrochemical approaches (Eisaman et al., 2023). Yet their impacts on marine communities and the carbon sequestration they drive remain poorly understood, highlighting the need to evaluate OAE's overall CO_2 removal potential (Bach et al., 2019a; Gattuso et al., 2021; Suessle et al., 2025).

Marine organisms do not perceive alkalinity enhancement directly (Bach et al., 2019a), instead, the transient carbonate-chemistry shifts prior to atmospheric re-equilibration can influence plankton growth, community composition, and microbial processing (Antoni et al., 2025; De Castro et al., 2025; Ferderer et al., 2022; Marín-Samper et al., 2024b; Oberlander et al., 2025). Such responses can modify the efficiency of the biological pump (Boyd and Newton, 1999; Guidi et al., 2009), a process that sequesters atmospheric CO_2 (5 - 12 Gt y^{-1}; Boyd et al., 2019; Siegel et al., 2014) by gravitational settling of biogenic material from the surface to the deep ocean (Sarmiento, 2006). In many productive systems, diatom blooms dominate this export flux production, and diatom-derived biogenic silica (BSi) provides ballast that accelerates aggregate sinking and increases the depth of organic-matter remineralization (Armstrong et al., 2001; Honjo et al., 2008). Under OAE, reduced CO_2 availability could delay or dampen diatom blooms or shift competitive balances among taxa (Hansen, 2002; Pierella Karlusich et al., 2021; Raven, 1993; Riebesell et al., 1993). Associated changes in e.g., diatom size structure (Bach and Taucher, 2019; Sommer et al., 2015) could then modulate export pathways such as zooplankton grazing and fecal-pellet repackaging (Le Moigne et al., 2016; Stukel et al., 2011). In addition, BSi dissolution increases with pH and follows well-characterized reaction kinetics, such that OAE-driven pH perturbations are expected to reduce silica preservation during sinking and weaken ballasting, with converging support from laboratory and globally relevant field observations (Socratis et al., 2008; Taucher et al., 2022; Van Cappellen et al., 2002). However, most OAE studies primarily constrain production-side responses (e.g., diatom silicification or growth; De Castro et al., 2025; Ferderer et al., 2025; Iglesias-Rodríguez et al., 2023; Oberlander et al., 2025) but rarely resolve transformations of diatom-biomass along the sinking pathway. This is a key gap as ocean-acidification studies show that production-side responses of diatoms and silica formation can vary in sign and magnitude across contexts (Dutkiewicz et al., 2015; Gao and Campbell, 2014), whereas export-phase BSi dissolution

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provides clear directionality under pH perturbations. OAE-induced pH excursions could therefore weaken silica ballasting with depth, even when biomass build-up or community composition changes are only modest.

Where and how OAE is deployed will largely determine its ecological impacts and safe operating ranges (Dupont and Metian, 2023). To date, experiments in oligotrophic or subtropical settings only reported minor effects on community composition, microbial rates, and associated export, consistent with low nutrient availability and weak bloom/export signals (Guo et al., 2025; Marín-Samper et al., 2024a; Sánchez et al., 2024; Subhas et al., 2022; Suessle et al., 2025). In contrast, coastal regions are often considered more attractive for deployment due to logistical proximity to resources (Bach et al., 2019a; He and Tyka, 2023), but exhibit strong nutrient and temperature variability, recurrent blooms, and rapid community succession (Cloern, 1996; Kauppi et al., 2017). Although coastal regions only occupy a small fraction of the ocean surface, they are typically diatom-dominated (Abrantes et al., 2016; Malviya et al., 2016) and contribute disproportionately to global biological carbon sequestration (Borges et al., 2005; Mathis et al., 2024; Stukel et al., 2023). Moreover, coastal OAE is likely to occur via localized inputs (Eisaman et al., 2023), creating transient hotspots in alkalinity, pH, and fCO_2 with magnitude and persistence depending on local dilution and mixing (Anderson et al., 2025; Bach et al., 2019a), influencing the severity of ecological and export responses. Elevated alkalinity may also trigger unintended calcium carbonate precipitation, undermining OAE efficiency (Hartmann et al., 2023; Moras et al., 2022; Schulz et al., 2023) and potentially altering carbon export pathways (Suessle et al., 2025). In that sense, constraining OAE effects on biomass production and export efficiency in such productive coastal systems across a wide pH range is essential before large scale deployment.

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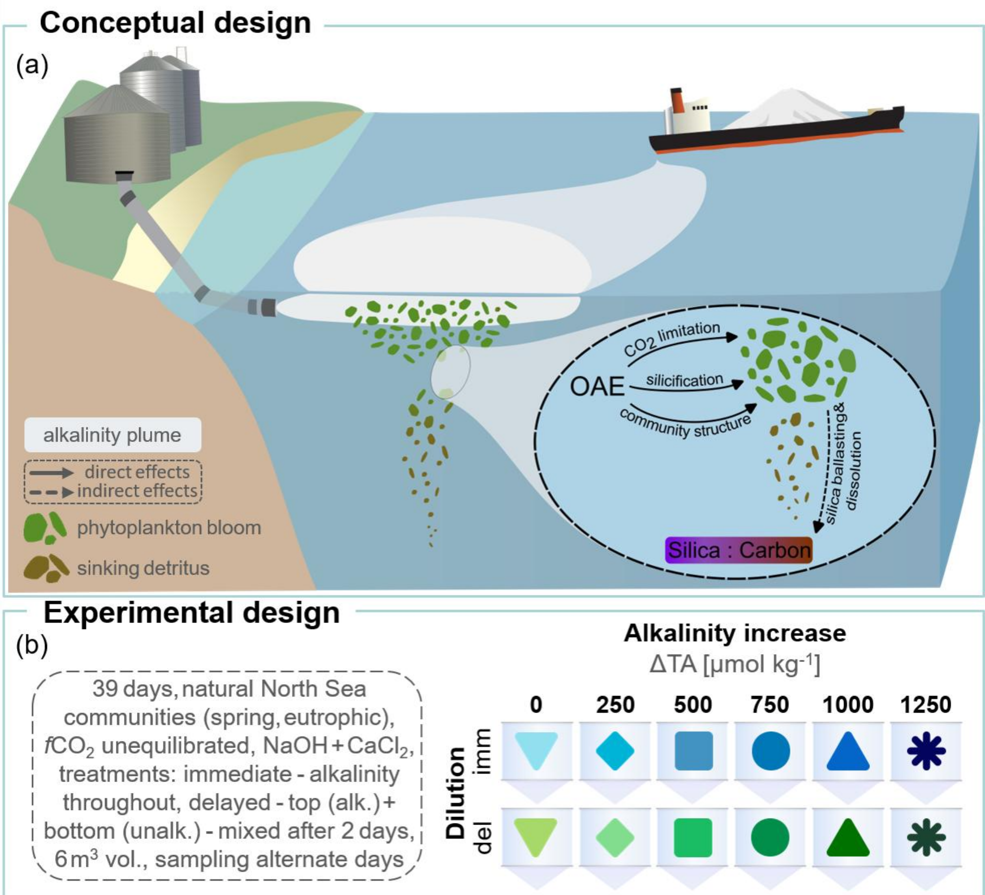

Figure 1. Conceptual and experimental framework of our mesocosm study on CO_2 unequilibrated OAE. *(a) Potential application scenarios and pathways by which OAE may change phytoplankton biomass, stoichiometry and subsequent export. (b) Setting and manipulation using 12 mesocosms subjected to two dilution modes. Delayed (del), representing localized application scenarios from point sources (e.g., coastal discharge); Immediate (imm), representing more uniform additions (e.g., ship-based). Levels in ΔTA given relative to background alkalinity of 2340 µmol kg*$^{-1}$*. Graphics adapted from Integration and Application Network, University of Maryland Center for Environmental Science https://ian.umces.edu/symbols/, last access: 21 October 2025).*

Here, we assessed the sensitivity of diatom-mediated export production and measured silica ballasting ratios (BSi:POC) of a plankton community from the North Sea (Helgoland, Germany) to CO_2-unequilibrated, carbonate-based OAE. Enclosing natural communities in mesocosms for 39 days, six alkalinity levels (ΔTA_{max} = 1250 µmol kg^{-1}) were applied using NaOH and $CaCl_2$ under two dilution regimes (Fig. 1). Originally designed to contrast point-source versus more distributed OAE additions (e.g., ship-based), we prioritized analysis along the shared pH_T gradient to isolate alkalinity-driven controls on bloom development and export (while retaining dilution-specific results for transparency). To our knowledge, this is the first OAE study in a eutrophic coastal system that spans a wide pH_T range and explicitly measures silica ballasting ratios in both water column and exported material by separating suspended from sinking particulate pools. This design provides mechanistic constraints on whether OAE alters biogenic silica preservation during export and thereby the efficiency of the biological pump, providing critical insight into future OAE deployment.

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2 Methods

2.1 Experimental setup and alkalization

On the 12th of March 2023, twelve in situ mesocosms were deployed in the south harbour of Helgoland (54°10'36.9"N, 7°53'36.0"E; North Sea, Germany) to investigate the effect of OAE on biogeochemical responses of a temperate eutrophic community from the North Sea. Each mesocosm consisted of a transparent cylindrical polyurethane bag (Ø = 2 m), which ended in a 1.6 m conical sediment trap, with an overall length of 3.5 m. It was suspended in a polyethylene floating frame, allowing for the observation of pelagic communities under natural temperature and light conditions. The mesocosms were filled with seawater originating from the Helgoland Roads observatory site (Wiltshire et al., 2010; water depth at site ~ 6 – 8 m). Using a peristaltic pump, water from 2 – 3 m depth (minimizing benthic influence) was screened (< 3 mm) and transferred into an intermediate reservoir. From there, all mesocosms were filled simultaneously with ~5.9 m^3. Pumping speed averaged ~14 m^3 h^{-1} to minimize biological stress, resulting in a ~12 h filling-process (for technical details see Bach et al., 2019b). Filling took place on 13th of March, marking day zero of the experiment. Before OAE manipulation, CTD profiles (CTD60M, Sea & Sun Technology GmbH, Germany) measured temperature, salinity, pH, chlorophyll *a*, dissolved oxygen, and photosynthetically active radiation to ensure homogeneity across mesocosms and alignment with conditions at the Helgoland Roads site (Wiltshire et al., 2010). The OAE manipulation was simulated using a CO_2-unequilibrated approach, meaning that dissolved inorganic carbon (DIC) was not raised alongside TA, deliberately resulting in strong (yet transient) perturbations of seawater carbonate chemistry (e.g. pH_T, $\Omega_{Ca/Ar}$) until re-equilibration with the atmosphere (Bach et al., 2019a; Renforth and Henderson, 2017). Accordingly, this strategy was chosen since it reflects a more realistic pathway for large-scale and economically feasible OAE implementation than CO_2 pre-equilibration of solutions prior to alkalinity release (He and Tyka, 2023). While the study-design encompassed varying dilution scenarios, to differentiate impacts of point-based versus more uniform alkalinity perturbations (Eisaman et al., 2023), here we will prioritize analysis of response signals over the common alkalinity gradient. Informing about environmental safety of varying application modes remains relevant, but is secondary to isolating alkalinity-driven bloom and export responses, governing OAEs overall CO_2 storage efficiency. For coherence with other publications coming from this experiment, the full treatment design is described below and the corresponding colour coding is retained in all figures.

The carbonate chemistry manipulation was realized four days after filling and aimed to simulate calcium-based OAE using NaOH and stoichiometrically proportionate $CaCl_2$ solutions to mimic cation release during mineral dissolution. Therefore, the mesocosms were split into sets of six: one set received alkalinity throughout the entire water column (immediate dilution), while the others were initially alkalized only in the top layer (delayed dilution) and mixed after two days. For this, 17 L of $CaCl_2$ solutions (in pre-filtered freshwater) were applied evenly across the perimeter of the mesocosm using a custom-built device (see Riebesell et al. (2013) for technical details), either over the entire depth (immediate) or only within the top 80 cm (delayed). To ensure full treatment delivery, an additional 17 L of freshwater was flushed into each mesocosm, applied either across the full depth or surface-only, further solidifying stratification in the delayed treatment through density

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differences (ΔPSU ≈ 0.5). To raise alkalinity, NaOH solutions (in pre-filtered freshwater) were then added using the same device, either throughout the full water column (immediate) or confined to the surface (delayed). In the delayed treatments, upper-layer alkalinity concentrations were intended to be doubled relative to the immediate treatments so that, the intended target alkalinity levels were reached only after mixing of the water column two days later. Alkalinity concentrations (post-mixing) were applied in increments of 250 µmol TA kg^{-1}, reaching ΔTA = 1250 µmol kg^{-1} relative to a background alkalinity of 2330 µmol kg^{-1}. To achieve mixing of the delayed dilution treatments and avoid procedural bias across treatments, all mesocosms were homogenized by bubbling pressurized air through the sediment trap, 48 h after manipulation. The order of $CaCl_2$ application was randomized, while NaOH application proceeded from lowest to highest treatment to avoid carry-over effects, alternating between equivalent levels of delayed and immediate dilution scenarios. Control mesocosms were treated similarly throughout the manipulation, but with freshwater only. Mooring positions along the pier were strategic in order to not have an alkalinity gradient along a natural one such as light availability. For details on changes in carbonate chemistry parameters see Fig. S1.

We note that CO_2 equilibration during our experiment was minimal (Fig. S1) yet realistic, considering that CO_2 re-equilibration with the atmosphere after alkalinity enhancement will typically take months to years under natural oceanographic conditions as well (He and Tyka, 2023; Jones et al., 2014) and was similar to other OAE mesocosm studies (Schneider et al., 2025). Accordingly, TA targets were intentionally high to maximize detectability of biological responses. NaOH was chosen for its rapid dissolution, enabling a controlled TA increase, and is viewed as a promising OAE feedstock due to its comparatively low environmental footprint (Eisaman et al., 2023; Iglesias-Rodríguez et al., 2023; Riebesell et al., 2023).

2.2 Sampling procedure and maintenance

Sampling was initiated on day one using a polypropylene tube integrating the upper 2 m of the water column with a volume of 4.5 L. Upon treatment additions, but prior to mixing (day five and six), samples in the delayed dilution mesocosms were collected separately from the top and bottom layers using 5 L Niskin bottles (Hydro-Bios, Kiel, Germany). Bulk water samples for the immediate dilution treatments continued to be taken with a polypropylene tube sampler. Post-mixing, all mesocosms were sampled every 2 days between 09:00 and 12:00 am using the same integrating polypropylene tube sampler. A CTD60M (Sea & Sun Technology GmbH, Germany) was cast in the beginning of every sampling for abiotic parameters such as temperature, salinity, pH, Chl *a*, oxygen (O_2) and photosynthetically active radiation. Then, per sampling occasion, 15 – 30 L of water were sampled (4 – 7 tubes), distributed into several containers dedicated to different analyses, and generally kept dark and at in-situ temperature until returned to the laboratory. Particulate material collected in the sediment traps (PM_{Sed}) was retrieved with a manual vacuum pump, maintaining pressures below 0.3 bar. The material was transferred into 5 L glass bottles (Schott Scandinavia A/S, Kgs, Denmark) and stored in the dark until processed in the laboratory (see Boxhammer et al., 2016 for technical details). Whenever subsamples were required, the sediment was gently re-suspended by rotating the bottles, ensuring a homogeneous mixture before withdrawal for further analyses. To limit shading and

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nutrient consumption from organism growth, the inner walls of the mesocosms were cleaned with brushes every six days. To further counteract shading, divers cleaned the outer walls with brushes on three occasions during the experiment.

2.3 Parameters

2.3.1 Sediment trap particulate matter fluxes and stoichiometry

Subsamples of PM_{Sed} were processed for determination of total particulate carbon and nitrogen (TPC/N_{Sed}), particulate organic carbon, nitrogen and phosphorus ($POC/N/P_{Sed}$), and biogenic silica (BSi_{Sed}). Particles were separated from seawater by enhancing coagulation and flocculation through the addition of 3 mol L^{-1} ferric chloride ($FeCl_3$) to the 5 L sediment bottles, followed by 3 mol L^{-1} NaOH to counteract pH reduction, thereby promoting efficient particle recovery (Boxhammer et al., 2016). After one hour of settling, the supernatant was carefully removed and the concentrated suspension was centrifuged for 10 min at 5200 g (6–16KS, Sigma Laborzentrifugen GmbH, Germany). A second centrifugation step (10 min at 5000 g, 3K12 centrifuge, Sigma) produced compact sediment pellets. These pellets were stored at −20°C and later shipped to Kiel for laboratory analysis. At GEOMAR, the frozen material was freeze-dried to eliminate residual moisture and subsequently homogenized into a fine powder using a cell mill (Edmund Bühler GmbH, Germany). The sediment powder was preserved in glass or plastic vials under cool and dark conditions. For analysis, the powder was transferred into silver (POC/N) or tin capsules (TPC/N): samples destined for POC/N_{Sed} determination were acidified with 1 mol L^{-1} HCl and dried overnight at 50°C, while those for TPC/N_{Sed} analysis remained untreated. Replicate measurements were conducted with a CN analyzer (Euro EA-CN, HEKAtech GmbH, Germany) following the protocol of Sharp (1974). Concentrations of particulate inorganic carbon (PIC_{Sed}) were calculated as the difference between TPC_{Sed} and POC_{Sed}. BSi_{Sed} and POP_{Sed} concentrations were measured spectrophotometrically according to Hansen and Koroleff (1999), after subsampling ~ 2 mg of the sediment. Prior to that, POP_{Sed} samples were pressure-cooked in 40 ml of deionized water including an oxidizing agent (Oxisolv, Merck) and BSi_{Sed} samples were leached in 0.1 mol L^{-1} NaOH at 85°C for 135 min to dissolve biogenic silicate, and the reaction was stopped with 0.05 mol L^{-1} H_2SO_4.

2.3.2 Water column particulate matter and photosynthetic pigments

For TPC/N_{WC}, POC/N_{WC}, and photosynthetic pigment analyses, subsamples were obtained by filtering water column material onto individual pre-combusted glass fiber filters (0.7 µm, Whatman). Filters designated for POC/N_{WC} were acidified using 2 mol L^{-1} HCl for ~ 2 minutes to remove inorganic carbon, while unacidified filters were collected for TPC/N_{WC}. Both sets were placed in pre-combusted glass petri dishes and dried overnight at 60°C. All filters were packed in tin capsules (8 × 8 × 15 mm; LabNeed GmbH, Germany), stored in a desiccator, and returned to Kiel. There, carbon and nitrogen contents were quantified using a CN analyzer (Euro EA-CN, HEKAtech) following the procedure described for the sediment trap samples. During the entire filtration for photosynthetic pigments (Chl *a* + Fucoxanthin), light exposure was minimized by covering the filtration racks with aluminum-foil. Subsequently, filters were stored in 2 ml cryovials at –80°C until further analysis. Pigment extraction was achieved using 100% acetone (HPLC-grade, Merck) and a cell mill (Precellys, France) with glass beads (0.5 mm). Samples were centrifuged at 10000 rpm (10 min, 4°C) and the supernatant filtered through a 0.2 µm PTFE syringe filter (13 mm, Lab Logistics Group). Concentrations of Chl *a* and Fucoxanthin within the supernatant were determined using High-Performance Liquid Chromatography (Thermo Scientific HPLC Ultimate 3000) according to Van Heukelem and Thomas (2001). Subsamples for BSi_{WC} were filtered onto cellulose acetate filters (0.7 µm, Whatmann) and immediately stored at -20°C. To dissolve the particulate silica, filters were leached in 0.1 mol L^{-1} NaOH at 85°C the following day. After 135 minutes, leaching was terminated by adding 0.05 mol L^{-1} sulfuric acid. Dissolved silicate concentrations were then quantified spectrophotometrically following the procedure of Hansen and Koroleff (1999).

2.3.3 Particle sinking velocities and porosities

Particle sinking velocities and porosities of sediment trap material were determined every two days by video-microscopy following methods described in Bach et al. (2012). Particles were imaged during gravitational sinking within a vertically mounted sinking chamber (cuvette 10 × 10 × 350 mm) positioned between a Raspberry Pi camera module (1920 × 1080 px; depth of field 1.5 mm) and a backlight. Sediment subsamples were diluted with 0.2 µm-filtered seawater (1:1 – 1:40, depending on particle density) and loaded into the chamber with a broad-tipped pipette. Measurements were conducted at in situ temperature (5 °C) in an airtight setup to minimize advection. Particles between 50 – 1000 µm were recorded for 20 min at 20 frames-per-second and 0.935 × magnification (3.274 µm px^{-1}). Several optical parameters allowed to identify multiple frames of a single particle during gravitational sinking. Prior to sinking velocity and porosity calculations, partially captured particles, or those out of focus were excluded based on python script (v3.9.18; Van Rossum, 2007 and openCV v4.6.0 Bradski, 2000) adjusted from Bach et al. (2012, for technical details see "Evaluation of sinking particles" in there). Subsequent sinking velocity and porosity calculations and data analysis was carried out using R-Studio (R Core Team, 2021) and ggplot2 (Wickham, 2016). Particle sinking velocities were calculated by applying a linear regression to their vertical position against time. Additionally, sinking velocities were corrected for temperature differences during measurements and for wall effects of the sinking chamber following (Ristow, 1997). Among the optical parameters acquired, equivalent spherical diameter (ESD) and image intensity (*Int*, grayscale range form 0 – 255) are established proxies to estimate particle porosity (Bach et al., 2019c), assuming more porous particles to transmit more light (higher grayscale values under backlit microscopy). To account for path-length effects, and larger particles typically being more porous than smaller ones (Laurenceau-Cornec et al., 2020), intensity was scaled with ESD to compute porosity:

$$Porosity = \left(\frac{Int}{255}\right)^2 * \mathrm{ESD} \quad (1)$$

Because marine particle size spectra are typically skewed towards smaller particles (Laurenceau-Cornec et al., 2020), we binned ESD into 50 – 100 µm, 100 – 250 µm, and 250 – 1000 µm (narrower bins for abundant small particles, broader for rarer large ones) and averaged sinking velocities and porosity within each bin. The 100 – 250 µm bin provided high particle

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count and the most informative signal for our analysis. It also matched the size of dominant aggregates observed from sediment trap material (Fig. S2), while also considered relevant for export processes (Clements et al., 2023; Puigcorbé et al., 2015). For clarity, we therefore focused on reporting exclusively this particle size class. We note that measurements were conducted ex situ; nevertheless, this approach has robustly tracked relative changes in particle dynamics in prior studies (Bach et al., 2019c; Baumann et al., 2021, 2023; Suessle et al., 2025).

2.3.4 Community Respiration

Community respiration data of the mesocosms experiment from Helgoland form part of a broader study on microbial metabolic rates under OAE and were provided by Marín-Samper et al., with methodological and data processing details provided in previous publications (Marín-Samper et al., 2024a, b). In brief, respiration rates were determined from oxygen consumption following the Winkler method and recommendations by Bryan et al. (1976), Carritt and Carpenter (1966) and Grasshoff et al. (1999). At each sampling day, mesocosm water collected in 4.5 L polycarbonate bottles was used to rinse and fill eight 125 mL soda-lime bottles per mesocosm via silicone tubing fitted with a 280 µm mesh ensuring overflow and checked to be bubble-free. Per mesocosm, four bottles were immediately fixed (1 mL $MnSO_4$ and 1 mL alkaline NaI) to determine initial oxygen concentrations, while four were incubated in the dark for 24 h (opaque bags) in an incubator continuously supplied with harbor water to maintain in situ temperature. Environmental conditions were logged using HOBO sensors (UA-002-64, New Zealand) from 10^{th} – 30^{th} March (mean temperature: 8.43 ± 1.96°C day; 8.02 ± 1.64°C night; irradiance: ~0.20 µmol photons m^{-2} s^{-1}), but subsequent records were unavailable due to logger flooding. After incubation, remaining samples were fixed, allowed to settle for ≥ 2 h and acidified (1 mL of 5 mol L^{-1} H_2SO_4) prior to measurement. Oxygen concentrations were determined via titration with an automated colorimetric end-point detection (Dissolved Oxygen Analyzer, SIS, Germany), using 0.25 mol L^{-1} sodium thiosulfate ($Na_2S_2O_3$ x 5 H_2O). Community respiration (CR) rates were then calculated from the mean of the four replicates according to:

$$CR(\mu mol L^{-1} h^{-1}) = \frac{Conc_I - Conc_D}{h_D} \qquad (2)$$

where $Conc_I$ and $Conc_D$ represent the average oxygen concentrations of the initial and dark-incubated samples and h_D the incubation time in hours.

2.3.5 Bacterial Abundances

Bacterial abundances were determined every two days from 2 mL cryovials containing mesocosm water previously fixed with formaldehyde (final concentration 1%, 4 °C for 24 h, stored at – 80 °C). Enumeration was conducted by flow cytometry (FACSCalibur, BD Biosciences, USA) following the bacterioplankton protocol of Marie et al. (1999). Prior to measurements, samples were stained with SYBR Green I (1:10,000) and incubated for 15 min in the dark. Data acquisition was performed for one minute, and prokaryotic populations were gated manually for each run using floreader.io. Cell concentrations were calculated from the number of gated events relative to the calibrated flow rate (µL min^{-1}). Instrument settings, gating images, and detailed workflows were kindly provided by Antoni et al. (2025) and are publicly accessible via GitHub (https://github.com/Dom-Antoni/RETAKE_Analysis/tree/RETAKE-Microbiome).

2.3.6 Carbonate chemistry and nutrient concentrations

TA and DIC samples were collected with an overflow of approximately twice the target volume, ensuring minimal air contact. Samples were analyzed at room temperature within 12 hours of collection. To eliminate PIC_{WC}, both TA and DIC samples were filtered through 0.2 µm filters (Whatman). TA was measured in technical duplicates by two-stage open-cell potentiometric titration using hydrochloric acid (0.05 mol L^{-1}) on a Compact Titrosampler 862 (Metrohm, Munich, Germany) with a built in PT1000 temperature sensor. DIC was determined in triplicates via infrared absorption with an AIRICA system (MARIANDA, Kiel, Germany) coupled to a differential infrared gas analyzer (LI-7000, LI-COR Biosciences GmbH, Germany). Both DIC and TA values were corrected against certified reference materials (batch no. 197; Dickson, 2010). Additional carbonate system parameters were computed using the Excel-based CO2SYS macro (Pierrot et al., 2021), applying water column–averaged temperature and salinity measurements from CTD profiles, as well as dissolved phosphorous and silicate concentrations for corrections. Carbonic acid dissociation constants K_1 and K_2 were taken from Sulpis et al. (2020), sulphuric acid from Dickson et al. (2007), hydrogen fluoride from Perez and Fraga (1987) and total boron from Lee et al. (2010). DIC and TA derived *in-situ* pH_T was regressed against measured depth-integrated CTD pH to bring it on the total scale. Whenever outliers were detected DIC or TA carbonate chemistry speciation was calculated from the remaining parameter and CTD pH_T. Concentrations of dissolved inorganic nutrients (NO_3^- + NO_2^-, PO_4^{3-}, $Si(OH)_4$) were determined using UV-VIS spectrophotometry. Colorimetric analyses followed the procedures described Hansen and Koroleff (1999) and refractive index corrections were applied according to Coverly et al. (2012).

2.4 Bloom analysis

To align comparisons of mesocosms on a common biological clock (i.e., similar trophic state) we identified phytoplankton bloom start and duration separately for each mesocosm using Chl *a* dynamics. Although treatment-induced shifts in bloom timing are relevant to OAE environmental safety, a calendar-day fixed analysis would blur differences in OAE mediated biomass build-up and stoichiometry by inadvertently including or excluding bloom or non-bloom days for certain mesocosms. From sampled Chl *a* concentrations (note: for the delayed treatment, top and bottom layers were averaged on days 5 – 6) we reduced short-term noise by applying a centred 3-sampling-day moving average on raw values. Subsequently, we calculated the day-to-day slope of the smoothed series, which served as an additional criterion for identifying bloom onset and termination. We defined a mesocosm-specific baseline (B) as the median of smoothed Chl *a* values during days 1 – 6. Bloom detection started from day 7 (full treatment manipulation achieved). Bloom start was defined as the first day of a two-day period in which (i) smoothed Chl *a* exceeded a baseline-relative threshold on both days: Chl *a* $\geq (1+\alpha)*B$ (with α =

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0.35 and B = baseline), and (ii) the slope was positive on both days. Bloom end was determined only after the main Chl *a* peak and was defined as the first day of a two-day period in which (i) smoothed Chl *a* fell back to Chl *a* ≤ (1+β)*B on both days (with β = 0.70, and again B = baseline), and (ii) at least one day had a negative slope. Separate start and end thresholds were used to provide hysteresis (with α < β). Among various tested combination of α- and β-values the selected pair preserved sensible fit to the observed phenology of smoothed and raw Chl *a* patterns within all treatments. To further evaluate whether the chosen α- and β-values captured the various blooms equally well, we defined a reference bloom window around each mesocosms Chl *a* peak (bound by the local minima before and after the Chl *a* peak). We then calculated the area under the Chl *a* curve (termed AUC) for both the α- and β-based bloom window (green and red lines in Fig. S3) and its respective reference window (grey-shaded area in Fig. S3) for each mesocosm. The ratio of these areas ($AUC_{\alpha/\beta}$ / $AUC_{reference}$) was expressed as AUC_m% and used as a measure of how completely the threshold-based method captured each mesocosms bloom. A detailed visualization of the analysis per mesocosm can be found in Fig. S3, providing raw and smoothed Chl *a* values, baselines and thresholds, defined start and end days per mesocosm, as well as AUC_m% diagnostics. All analyses were conducted in R (R Core Team, 2021) using the `zoo` package (Zeileis and Grothendieck, 2005) for centred 3-day smoothing and windowed run tests (*rollapply*), and ggplot2 (Wickham, 2016) for visualization.

2.5 Sediment Deposition analysis

Deposition events may not only occur at different points in time relative to the bloom start but could also exhibit different durations. Analysing sediment deposition on fixed calendar days, would therefore distort estimates of export magnitude and stoichiometry. Similarly to water column blooms, we identified sediment deposition events per mesocosm to align comparisons on a common biological clock and accommodate variation in the coupling of production and export. We used daily POC fluxes to quantify sediment deposition events and calculated cumulative export by summing daily fluxes to the end of the experiment and applied a centred 3-sampling-day moving average. From there, we calculated the day-to-day slopes (m) of the smoothed cumulative curve, which served as a deposition intensity proxy. Detection of sediment deposition events was restricted to a mesocosm-specific search window beginning at the day of water column bloom onset and ending at the day of bloom termination + w (an extension to the search window). To remove continuous background deposition prior to bloom-driven export events, we estimated a baseline slope (m_B) as the median slope from days ≥ 5 and < bloom onset, and defined relative deposition intensity as $m_{rel} = m - m_B$. For each mesocosm, we centred event detection around the day of maximum relative intensity (m_{max}), representing peak deposition. We then defined the start of deposition events as the first day within the search window where $m_{rel} \geq \alpha * m_{max}$ and the end of deposition events as the day where $m_{rel} \leq (1 - \alpha) * m_{max}$ (note, end detection was only allowed after m_{max} and water column bloom end). After testing several α and extended search windows (w) combinations, we chose α = 0.32 and w = 6 days. The combination yielded start and end days consistent with the observed phenology of cumulative POC flux and slope time series. To further evaluate the chosen α- and w-combination capturing the deposition events across mesocosms, we computed and compared two metrics: a) the cumulative flux captured by the detected event window relative to total cumulative flux over the experiment, and b) flux density, defined

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as the proportion of flux captured per day (i.e., captured cumulative flux divided by event duration in days). Here, we note that mesocosms exhibiting a secondary bloom (and associated deposition event) showed a lower proportion of total cumulative flux captured within the detected event window, reflecting export distributed across multiple pulses rather than a limitation of the detection approach; this did not affect our OAE analysis, as treatment comparisons were based on averages of the first bloom and associated deposition event. Detailed per-mesocosm visualization of the analysis can be found in Fig. S4, providing raw and smoothed cumulative POC flux values, slopes, detected start, end and peak deposition days, as well as proportion of total flux captured and flux density. All Analyses were conducted in R (R Core Team, 2021) using the `zoo` package (Zeileis and Grothendieck, 2005) for centred 3-day smoothing and windowed run tests (*rollapply*), and ggplot2 (Wickham, 2016) for visualization.

2.6 Statistical analysis

To assess OAE effects on biogeochemical water column and sediment parameters, daily responses (i.e., sampling days) were either averaged or summed up (for cumulative fluxes), yielding a single independent estimate per mesocosm for each analysis window (bloom phase, deposition event, or last experimental day as cumulative endpoint). Linear models were then fitted (across dilution scenarios) using measured *in-situ* mean pH_T as the primary explanatory variable. Where relevant, we also ran parameter regressions, including cross-phase fitting, linking bloom and sediment deposition averages. This allowed us to estimate effect sizes of within phase relationships and disentangle drivers of production–export coupling. Model assumptions were checked prior to analysis, i.e., linearity (residual–fitted plots and Reset test), homoscedasticity (scale-location plots and Breusch–Pagan test) and normality of residuals (qq-plots and Shapiro–Wilk test) with base R and the lmtest package (R Core Team, 2021; Zeileis and Hothorn, 2002). Whenever model assumptions were violated, either data transformations were applied, or outliers were flagged visually in figures and noted in statistical tables (Table S1). All plots, including diagnostics, were produced using ggplot2 (Wickham, 2016).

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3 Results

3.1 Carbonate chemistry and nutrient conditions under increasing OAE

Deployment of unequilibrated OAE across varying dilution scenarios was successful, achieving target alkalinity post-mixing (Fig. 1b, Fig. S1). Carbonate saturation states ($\Omega_{Ca/Ar}$) remained high after mixing and carbonate precipitation was triggered in the two highest alkalinity mesocosms from mid-experiment onwards, decreasing TA and pH_T (Fig. S1). This did not confound results, as analyses were based on measured pH_T (not target levels) and carbonate formation neither directly altered export magnitude, nor indirectly via increased particle sinking velocities (Fig. S5, Table S1). This is consistent to prior work (Suessle et al., 2025) and additionally, blooms of comparable magnitude occurred regardless (Fig. 2a, c). While CO_2 formation from carbonate precipitation and atmospheric ingassing occurred, the increase in fCO_2 over the experiment was relatively small in the two highest mesocosms (Fig. S1b, d). CO_2 levels closely tracked initial treatment spacing at $\Delta TA \geq 750$ µmol kg^{-1}, generally remaining below 50 µatm (down to $fCO_2 < 15$ µatm and $pH_T > 9.25$). Bloom-driven CO_2 drawdown was small and only evident under ambient or moderate alkalinity increases (Fig. S1). Initial nutrient conditions reflected typical North-Sea spring conditions (Wiltshire et al., 2010) and were sufficient to support ample biomass growth (Si ≈ 14.5 µmol L^{-1}, NO_3^- ≈ 17.7 µmol L^{-1}, PO_4^{3-} ≈ 0.05 µmol L^{-1}, Fig. S6). Increased alkalinity treatments initially showed slowed nutrient drawdown but did not alter overall consumption consistently (Fig. S6, Table S1) which closely followed bloom development throughout the experiment. Because export responses were consistent across dilution scenarios (immediate and delayed), they were treated as replicates and assessed across the common pH_T gradient (while retaining treatment colors for transparency). We focus here on water column driven export dynamics, while general carbonate-chemistry feedbacks and bloom-timing effects, relevant to OAEs environmental safety, are addressed elsewhere (Tammen et al., 2026).

3.2 Water column biomass and silica ballasting ratios

Across mesocosms, the calculated bloom onset and termination based on Chl *a* dynamics captured 95 ± 2.7% (mean ± SD) of the total biomass standing stocks (Fig. S3). Start and end days varied between day 7 and 15, and day 15 and 35, respectively (details in Fig. S3). Within blooms, averaged phytoplankton biomass metrics (Chl *a* and POC_{WC}) were not affected by the OAE induced pH_T-gradient and displayed similar concentration (Fig. 2b, c, Table S1). Averaged Chl *a* concentrations varied between 5.7 and 3.5 µg L^{-1} and POC_{WC} concentrations between 42.7 µmol L^{-1} and 27.8 µmol L^{-1} (Fig. 2b, c). Fucoxanthin tracked temporal Chl *a* dynamics (Fig. 2a, d), indicating diatom-driven blooms, and was likewise not affected by pH_T (Fig. S7, Table S1). In contrast, water column biogenic silica concentrations (BSi_{WC}) within blooms declined with increasing pH_T, by 40% from 5.5 to 3.3 µmol L^{-1} and water column silica ballasting ratios (BSi_{WC}:POC_{WC}) halved from 0.16 to 0.08 mol:mol (Fig 2e, f, Table S1). Over time, POC_{WC} concentrations generally remained elevated after build-up, albeit some variability, but BSi_{WC} concentrations showed a consistent rise followed by a pronounced decline across

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all mesocosms (Fig. S7). Consequently, water-column silica ballasting ratios (BSi_{WC}:POC_{WC}) decreased over the course of the experiment.

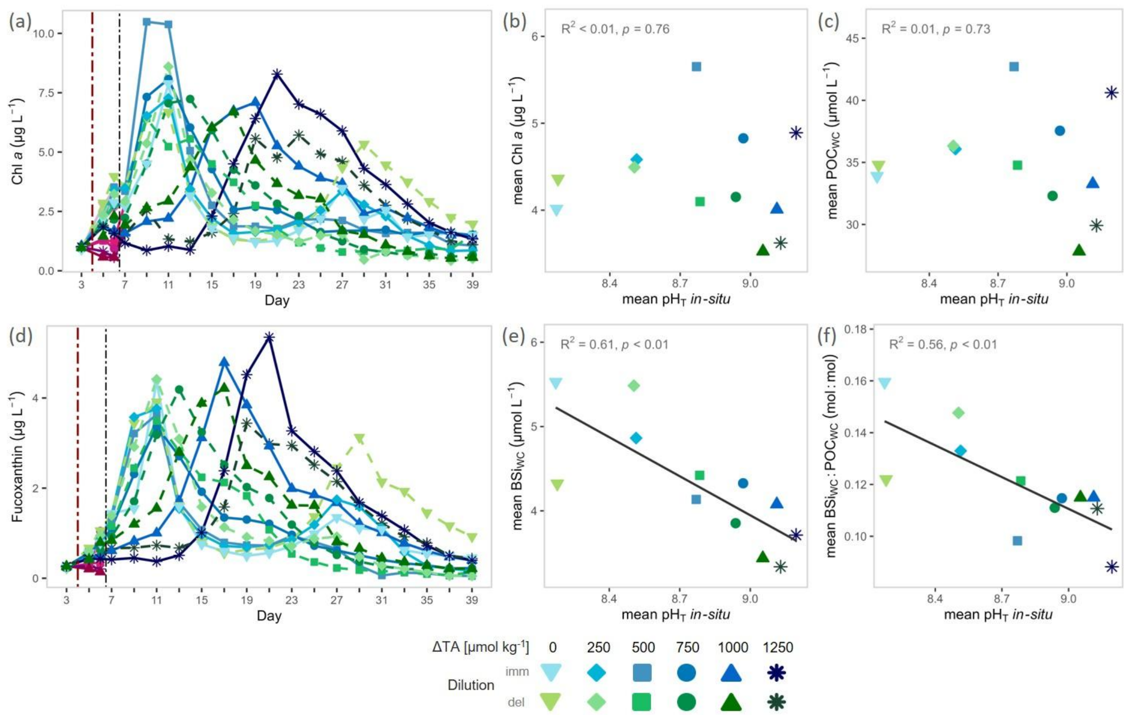

Figure 2. Phytoplankton biomass and silica ballasting ratios under OAE. *Temporal trajectories of (a) chlorophyll a (Chl a) and (d) Fucoxanthin concentrations. pH-gradient responses of bloom-window averages for (b) Chl a, (c) POC_{WC}, (e) BSi_{WC}, and for (f) water column silica ballasting ratio (BSi_{WC}:POC_{WC}). Note: The averaging windows for pH_T and each response variable differ among mesocosms, defined by the identified bloom window per mesocosm (see Sect. 2.4 and Fig. S3). Pink–purple symbols represent surface-layer measurements from delayed-dilution mesocosms on days 5–6; hue encodes the alkalinity addition (ΔTA, µmol kg^{-1}), with darker purple indicating higher ΔTA. The red dash-dotted vertical line marks the start of the alkalinity manipulation; the black dash-dotted line marks completion by mixing via the sediment trap. Grey annotations report statistical tests (see details in Table S1).*

3.3 Sediment silica ballasting ratios decline across the pH_T gradient

Sediment deposition following bloom events in each mesocosm ranged between 37 and 81% of total export, varying with distinct deposition dynamics (e.g., secondary pulses following secondary blooms, Fig. S4). The onset of deposition lagged blooms by 3.5 ± 3.0 days (mean ± SD, details in Fig. S4), indicating tight but varying coupling of production and export of biomass, and showed no systematic delay under OAE. Within the defined deposition events, averaged POC and BSi flux magnitudes showed no detectable pH effect (Fig. 3b, d, Table S1), ranging from 6.2 to 2.2 µmol L^{-1} d^{-1} and from 1.2 to 0.6 µmol L^{-1} d^{-1}, respectively. In general, sediment-trap BSi fluxes were positively correlated with water column BSi production (Fig. S8, Table S1). Likewise, POC and BSi fluxes correlated positively (Fig. S8, Table S1) and followed temporal patterns similar to water column Chl *a* dynamics, but with the previously noted delay and more episodic, less uniform peaks (compare Fig. 2a, Fig. 3a, c). In contrast, sediment silica ballasting ratios (**BSi_{Sed}:POC_{Sed}**) declined sharply with increasing

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pH_T: deposition-averaged values fell by 60% from 0.27 to 0.10 mol:mol**,** while daily ratios decreased over time (Fig. 3e, f, Table S1). Other deposition-averaged fluxes (PON, POP, PIC) and experiment-integrated cumulative fluxes of all major elements were unaltered by OAE (Fig. S9, Fig. S10, Table S1). This confined the sediment signal to a) a compositional change rather than changes in bulk flux, and b) post-bloom deposition pulses, rather than continuous export.

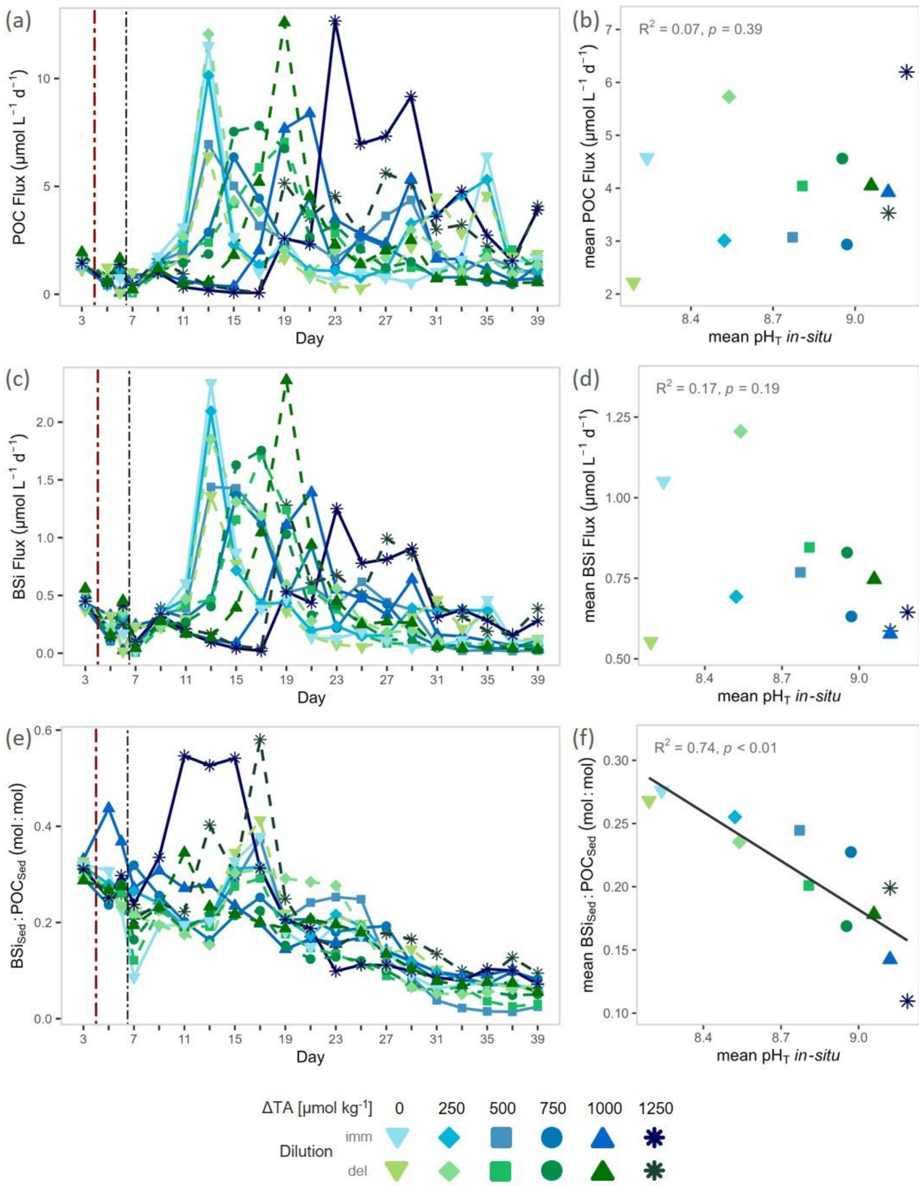

Figure 3. Organic matter export and silica ballasting ratios under OAE*. Temporal trajectories of (a) particulate organic carbon export (POC Flux), (c) biogenic silica export (BSi Flux), and (e) sediment silica ballasting ratio (BSi_{Sed}:POC_{Sed}). pH-gradient responses of deposition-window averages for (b) POC flux, (d) BSi flux, and (f) sediment silica ballasting ratio (BSi_{Sed}:POC_{Sed}). Note: The averaging windows for pH_T and each response variable differ among mesocosms, defined by the identified deposition window per mesocosm (see Sect. 2.5 and Fig. S4). The red dash-dotted vertical line marks the start of the alkalinity manipulation; the black dash-dotted line marks completion by mixing via the sediment trap. Grey annotations report statistical tests (see details in Table S1).*

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Notably, silica ballasting ratios (BSi:POC) increased from the water column to the sediment trap, rising approximately twofold at ambient alkalinity with diminishing enrichment as alkalinity increased (Fig. 4a, comparing Fig. 2f and Fig. 3f). Accordingly, sediment and water column silica ballasting ratios correlated, but exceeded a 1:1 scaling: each mol:mol decrease in $BSi_{WC}:POC_{WC}$ corresponded to a 1.73 mol:mol decrease in $BSi_{Sed}:POC_{Sed}$ (slope = 1.73, Table S1). Additionally, particle porosity in the 100 – 250 µm size class increased consistently with alkalinity-driven pH_T (Fig. S9, Table S1), and negatively correlated with sediment silica ballasting ratios (Fig. 4b, Table S1). These porosity changes, however did not translate into systematic changes in particle sinking velocities (Fig. S8; Table S1), which in general were unaffected by pH_T, aside from higher velocities under the highest alkalinity treatments (Fig. S9; Table S1). Consistent with this decoupling, sinking velocities also did not scale with either water column or sediment silica ballasting ratios (Fig. S8; Table S1). Finally, we found no evidence for enhanced POC remineralization as Chl *a*-normalized community respiration and bacterial abundances were unaffected by pH_T and did not scale with particle porosity (Fig. S11, Table S1).

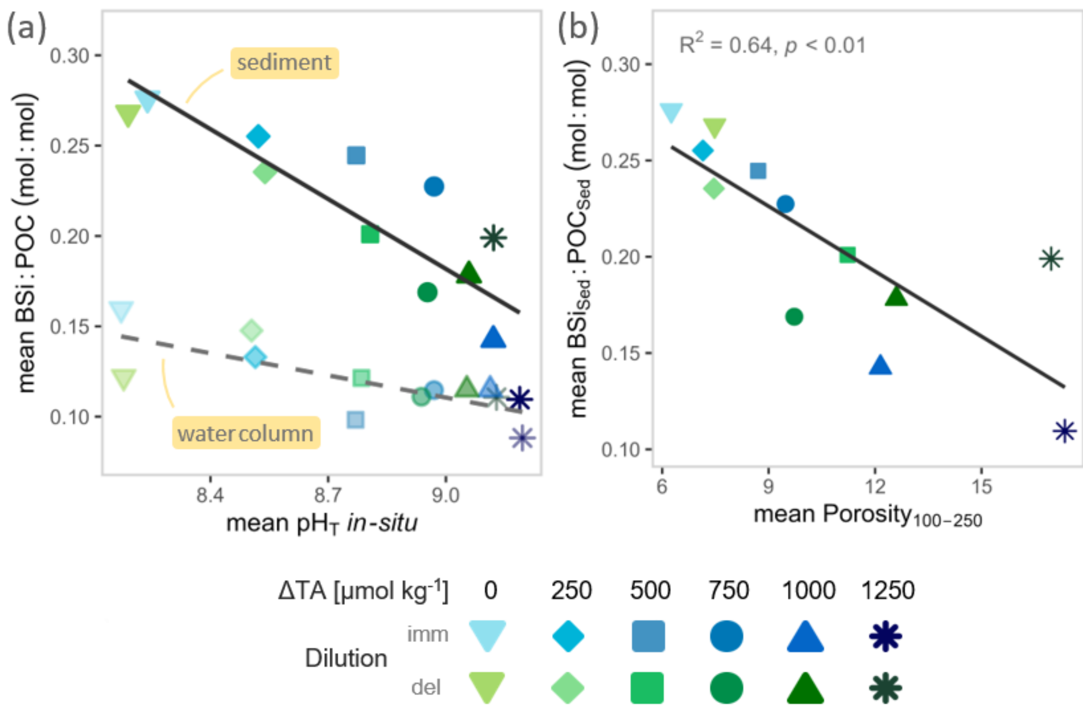

Figure 4. Enrichment of silica ballasting ratios and links to particle structure. *(a) Visualizing export-phase intensification of silica ballasting ratios across the pH_T gradient via variable slopes; dark solid regression line + opaque symbols = sediment, light dashed regression line + transparent symbols = water column. (b) Parameter regression within deposition phase for sediment silica ballasting ratio vs. mean particle porosity (in 100-250 µm size class). Note: To link processes across phases, sediment parameters ($BSi_{Sed}:POC_{Sed}$, $Porosity_{100-250}$) were averaged over each mesocosm's deposition window, whereas water column silica ballasting ratios ($BSi_{WC}:POC_{WC}$) was averaged over each mesocosm's bloom window; for (b) pairs were matched by mesocosm for regression. Both, bloom and deposition windows (and thus averaging days) differ among mesocosms (see Sect. 2.4, 2.5; compare Figs. S3 and S4). Grey annotations report statistical tests (see details in Table S1).*

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4 Discussion

This study shows that diatom-derived silica ballasting ratios in sediment material (BSi_{Sed}:POC_{Sed}) decreased by 60% across the applied alkalinity-induced pH_T gradient. Given the pivotal role of diatoms in global carbon sequestration (Brzezinski et al., 2015; Le Moigne et al., 2012; Ragueneau et al., 2006; Tréguer et al., 2018), our results indicate that OAE-driven pH_T excursions can modify biological-pump functioning in ways that are relevant for net CO_2 removal estimates. Below, we outline plausible processes driving changes in the build-up and export of silica while recognizing that multiple processes can co-occur in multi-factorial mesocosm experiments.

4.1 pH-enhanced silica dissolution decouples ballasting from biomass build up

Within bloom phases, average BSi concentrations and water column silica ballasting ratios (BSi_{WC}:POC_{WC}) declined across the alkalinity-induced pH_T gradient, despite unchanged bloom magnitudes (Chl *a*, POC_{WC}) across treatments. Notably, the decoupling of silica from bulk biomass was even more pronounced in sinking compared to suspended material. Together, these observations suggest enhanced BSi dissolution at higher pH_T. Because seawater is generally under-saturated with respect to silica (Lewin, 1961), dissolution rates can be substantial, reaching up to 43% of gross production rates during blooms (Beucher et al., 2004). Moreover, dissolution rates are known to increase at higher pH (Brady and Walther, 1989; Socratis et al., 2008; Van Cappellen et al., 2002), due to facilitated hydrolysis of siloxane bonds at the frustule surface (Barker et al., 1994). In line, BSi_{Sed}:POC_{Sed} exhibited a steeper decline across the applied pH_T gradient (Fig. 4a, see slopes in Table S1), suggesting that silica loss intensified during particle transit. Living diatoms protect their frustules with organic coatings (Lewin, 1961; Van Cappellen et al., 2002), but upon senescence (i.e., bloom termination and export), bacterial degradation of these coatings strongly accelerates pH-enhanced BSi dissolution (Bidle and Azam, 1999). Given the higher dissolution rates in older material, our results are consistent with chemically controlled BSi loss, as silica frustules lose their coatings and become increasingly susceptible to pH-driven hydrolysis during transit. This mechanism could explain the observed decline in water column silica ballasting ratios (BSi_{WC}:POC_{WC}) by up to 50% per unit increase in pH, a number consistent with chemical studies reporting a 60–70% per-unit-pH sensitivity of dissolution rates (Dove and Elston, 1992; Greenwood et al., 2005). Additionally, the global-scale pH sensitivity of BSi dissolution was estimated by a hallmark study reporting a 17% increase in export Si:N under end-of-century ocean acidification (at RCP 8.5; Taucher et al., 2022). This is consistent with 56% decrease in dissolution per unit pH decline and, despite the opposite sign of the perturbation, falls within our estimate of up to 60% increase in dissolution (measured from BSi_{Sed}:POC_{Sed}) per unit increase in pH, further supporting a view of chemically controlled dissolution.

For context, POC and BSi fluxes remained positively correlated across treatments (Fig. S8), consistent with the canonical role of biogenic silica in ballasting organic carbon export. Despite this, recent OAE work has documented changes in DSi drawdown and BSi dynamics (Ferderer et al., 2022; Gately et al., 2023; Paul et al., 2025), but direct evidence for impacts on BSi dissolution under OAE still remain limited, particularly along the sinking pathway. A key distinction of our experiment

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was the strong carbonate-chemistry perturbation (pH_T > 9.25) extending beyond the range typically tested to date (pH_T = 8.2 – 9.0; Ferderer et al., 2024, 2025; Gately et al., 2023; Guo et al., 2024, 2025; Li et al., 2024; Suessle et al., 2025), across a highly resolved gradient (duplicated, six alkalinity levels). Smaller perturbations would inherently reduce pH-sensitive dissolution and, with fewer treatment levels and/or replication, make subtle responses harder to distinguish from background variability. Detectability is further constrained by smaller or inconsistent blooms, reported in many studies (1 – 5 µg Chl *a* L^{-1}; Ferderer et al., 2024; Guo et al., 2024; Kousoulas et al., 2025; Suessle et al., 2025), whereas our experiment consistently reached above 7.5 µg Chl *a* L^{-1}. Higher biomass likely increased signal-to-noise ratios by leveraging dissolution changes and in combination with the long experimental duration allowing for a full bloom progression in all treatments (onset to export). Critically, our clearest fingerprint emerged when separating suspended from sinking material, with the pH signal intensifying during transit (Fig. 4a), shown by > 1 slope when scaling BSi_{WC}:POC_{WC} with BSi_{Sed}:POC_{Sed} (Table S1). Studies focusing only on suspended pools or production metrics (Ferderer et al., 2025; Gately et al., 2023; Subhas et al., 2022), would miss the export-phase intensification, leaving the signal too weak to detect in the suspended fraction. Notably, reduced water column BSi at otherwise similar biomass build-up, has been reported for a diatom-dominated OAE experiment (pH ≈ 8.6; Ferderer et al., 2022), though the authors could not resolve the responsible mechanism. Moreover, their signal did not propagate into sediment trap material, potentially because of the lower export magnitudes compared to our study, likely limiting the detectability due to noise. Finally, although the OAE studies discussed here span diverse ecosystems, ocean-acidification work has shown that the pH sensitivity of silica dissolution is global (Taucher et al., 2022). It further supports the directionality implied here and suggests that null results under OAE may instead reflect limited pH-range forcing and/or resolution, both statistical and methodological, rather than the absence of a dissolution response.

Although the decline in water column and sediment BSi:POC ratios suggests enhanced pH-driven silica dissolution, we note that a corresponding increase or hampered drawdown of dissolved silicate (DSi) was not detectable from water column concentrations. The signal was likely obscured by rapid re-assimilation during bloom phases, with treatment-specific differences in bloom dynamics (exponential vs. gradual development) further masking its detectability. Additionally, DSi enrichment within pore-water of sinking aggregates, likely a substantial fraction of dissolution-derived silica, did not contribute to water column measurements and was also not quantified from sediment trap samples, hindering silicon mass-balance approaches. Together, these constraints limited our ability to resolve dissolution signals from water column DSi alone, although we acknowledge that enhanced silica regeneration certainly occurred and is mechanistically implied by the observed BSi losses.

4.2 Constraints on alternative drivers of silica ballasting losses

Although our results strongly suggest pH-driven chemical control of silica dissolution, we evaluated whether other production-side (silicification, community composition) or export-side (remineralization, sinking time) processes could alternatively explain the BSi:POC response under OAE. Physiologically, higher pH could in principle impede silicification by maintaining higher Si solubility and steepening the pH gradient diatoms must overcome within their silicification

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compartments (Martin-Jézéquel et al., 2000; Vrieling et al., 1999). However, direct experimental evidence under OAE is still scarce (Ferderer et al., 2024, 2025; Gately et al., 2023; Oberlander et al., 2025), and responses under acidification are inconsistent, with silicification reported to both increase and decrease (Hervé et al., 2012; Petrou et al., 2019). While we did not directly quantify per-cell silicification, it is generally thought to increase at lower growth rates (Martin-Jézéquel et al., 2000; Timmermans et al., 2004). In our experiment however, Chl *a* dynamics suggest that diatom growth decreased at higher alkalinity (early exponential vs. delayed gradual bloom development) consistent with our alkalinity perturbations reducing CO_2 to long-known growth-limiting levels (~ 1 µmol kg^{-1}, fCO_2 < 15 µatm; Raven, 1993; Riebesell et al., 1993). In summary, these production-side considerations argue against a simple, uniform decline in species-level silicification to explain the observed decline in water column silica ballasting.

Further, community shifts could reduce water column silica ballasting ratios if OAE favored e.g., fewer diatoms relative to non-silicifying taxa, or more lightly silicified diatom species. Yet, evidence that OAE consistently drives community changes of sufficient magnitude to generate the strong BSi_{WC}:POC_{WC} signals observed remains limited (Groppelli et al., 2026; Guo et al., 2024; Li et al., 2024; Subhas et al., 2022; Xin et al., 2024). While we did not resolve taxonomic composition or diatom size spectra, ocean-acidification studies have shown, that elevated fCO_2 can favor larger diatoms, a pattern attributed to alleviated diffusive CO_2 limitation and downregulation of energetically costly CCMs with increasing cell size (Bach and Taucher, 2019; Rost et al., 2008; Sommer et al., 2015; Wu et al., 2014). By extension, CO_2 limitation under unequilibrated OAE could bias competitiveness towards smaller taxa, consistent with Kousoulas et al. (2025), identifying specific larger diatom species as losers under unequilibrated OAE (low fCO_2). In a system typically dominated by large diatoms (Wiltshire et al., 2010) and subjected to CO_2 limitation exceeding its natural variability (Kirchner et al., 2020), such a competitive shift could be clearly expressed as a restructuring toward smaller diatoms. Yet smaller diatoms are generally thought to be more heavily silicified (per cell; Ragueneau et al., 2006; Sarthou et al., 2005), which at similar bloom magnitudes (see Chl *a*, POC_{WC}) would predict higher BSi per carbon biomass; this directionality directly opposes our observations, reinforcing pH-driven BSi dissolution as the dominant explanation. However, we acknowledge, that community shifts remain a plausible contributor to observed water column BSi_{WC}:POC_{WC} signals, but they would not explain why the strongest decline in silica ballasting ratios occurs in exported material.

Lastly, changes in microbial carbon remineralization or particle sinking time could in principle alter sediment trap silica ballasting ratios (BSi_{Sed}:POC_{Sed}). Because organic carbon remineralization proceeds faster than silica dissolution, exported particles typically become enriched in BSi relative to POC with depth (Armstrong et al., 2001; Karakuş et al., 2025; Ragueneau et al., 2006). Consistently, we observed a two-fold enrichment of BSi:POC from the water column to the sediment trap at ambient alkalinity, but this enrichment was significantly reduced at higher alkalinity. Such a pattern would require systematic pH-driven changes in remineralization rates and/or residence time during sinking (i.e., sinking velocities). However, biomass-normalized remineralization proxies (CR:Chl *a*, Bac:Chl *a*) showed no systematic variation with pH, nor with particle porosity, known to enhance bacterial remineralization during transit (Grossart and Ploug, 2001; Ploug et al., 2002). Likewise, particle sinking velocities showed no consistent relationship with pH (aside from the pronounced increase

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associated with carbonate precipitation) and were not systematically related to porosity, also known to influence settling speed (Azetsu-Scott and Passow, 2004; Bach et al., 2019c). Thus, export-side changes in organic carbon remineralization metrics or sinking time were not apparent in our dataset. Taken together, the evaluated production- and export-side alternatives are not consistent with the observed direction and magnitude of the silica ballasting ratios (BSi:POC) response, further supporting pH-driven BSi dissolution to be the most likely explanation.

In addition to pH, we would like to extend our considerations to particle-quality traits. Aggregate microenvironments may modulate BSi dissolution during export. Higher aggregate porosity can enhance porewater exchange, which has been linked to elevated BSi dissolution in sinking particles (Moriceau et al., 2014; Passow et al., 2003). BSi dissolution kinetics are hampered by DSi accumulation in aggregate porewater, suppressing dissolution relative to freely suspended diatom frustules (Moriceau et al., 2007), with the net effect of porosity depending on the balance between porewater exchange and Si-solute build-up. In our mesocosms, porosity of sediment-trap particles increased along the alkalinity-induced pH gradient during bloom-following deposition events. Although we cannot quantify how strongly porosity contributed to BSi dissolution, the tight covariation between porosity and BSi_{Sed}:POC_{Sed} (Fig. 4b) suggests that particle-quality traits may provide an additional control on export-phase BSi loss, and could modulate the pH signal.

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5 Implications and Outlook

Our results indicate that OAE may decrease silica ballasting ratios via pH-enhanced BSi dissolution. In our experiment, higher pH reduced BSi:POC ratios most clearly in exported material, implying that a smaller fraction of carbon is transported to depth before remineralization. Such shoaling of remineralization would shorten carbon-sequestration timescales and shift nutrient regeneration upward in the water column. Enhanced dissolution would also regenerate DSi in the upper ocean, with context-dependent consequences for carbon export: in silicate-limited systems, regenerated DSi may sustain diatom production and partly buffer ballasting losses, whereas in Si-replenished systems weaker silica ballasting would more directly reduce carbon sequestration potential. The magnitude and potentially even the sign of these feedbacks may further depend on co-factors that modulate silicification and export efficiency, such as iron availability. Ecologically, dissolution-driven increases in upper-ocean DSi availability could also reshape phytoplankton community structure, with cascading effects on aggregation, grazing, and energy transfer to higher trophic levels, including fish. Together, these interacting feedbacks imply that OAE impacts on export and food-web transfer efficiency may be non-linear and ecosystem specific. Future OAE work should therefore constrain pH-driven silica dissolution across contrasting ecosystems and seasons, explicitly resolving suspended versus sinking pools and accounting for bloom versus background states, to identify where OAE can be applied without unintentionally weakening the biological carbon pump.

Data availability

The datasets presented in this study can be found in PANGAEA:

https://doi.org/10.1594/PANGAEA.992023 (Suessle et al., 2026), https://doi.org/10.1594/PANGAEA.986507 (Schulz et al., 2025), https://doi.pangaea.de/10.1594/PANGAEA.987501 (Tammen et al., 2026)

Supplement link

The supplement related to this article is available online at:

Competing interests

The contact author has declared that none of the authors has any competing interests. This manuscript is not associated with a conference.

Disclaimer

will be added by journal

Authors contribution (in no particular order)

Study design and conceptualization: PS, KS, LK, UR

Sampling and laboratory analysis: PS, JS, JKT, LK, LMS, KS

Data analysis and interpretation: PS, NS, JBR, KS

Writing (original draft): PS, KS, JBR

Writing (reviewing and editing): PS, with comments from all co-authors

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Review statement

The review statement will be added by Copernicus Publications listing the handling editor as well as all contributing referees according to their status anonymous or identified.

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