The effect of carbonate mineral additions on biogeochemical conditions in surface sediments and benthic-pelagic exchange fluxes~~Countering the effect of ocean acidification in coastal sediments through carbonate mineral additions~~

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Abstract. Coastal sediments are hotspots of biogeochemical processes that are impacting subsurface and overlying water conditions. ~~Along with its impact on calcifying plankton, ocean acidification also affects benthic biogeochemistry and organisms. Compared to the overlying water, f~~Fluid composition in sediments is altered through the ~~effect of the~~ mineralization of organic matter which under oxic conditions, ~~which can~~ further lower~~s~~ both pH and the carbonate saturation state. ~~This can potentially be counteracted by the addition of carbonate minerals to the sediment surface.~~ As a potential mitigation strategy for this sediment acidification, we explored ~~To explore the biogeochemical~~ the effects of mineral additions to coastal sediments~~.,~~ ~~W~~we experimentally quantified carbonate mineral dissolution kinetics of carbonate shells suitable for field application, and then integrated this data into a reactive transport model that represents early diagenetic cycling of C, O, N, S and Fe, and traces total alkalinity, pH and saturation state of $CaCO_3$. Model simulations were carried out to delineate the impact of mineral type and amount added, porewater mixing and organic matter mineralization rates on sediment alkalinity and its flux to the overlying water. Model results showed that the added minerals undergo initial rapid dissolution and generate saturated conditions~~.~~ demonstrating the potential of alkalinity enhancement in mitigating surface sediment acidification. Aragonite dissolution led to higher total alkalinity concentrations than calcite. Simulations of carbonate mineral additions to sediment environments with low rates of organic matter mineralization exhibited a ~~significant~~ substantial increase in mineral saturation state compared to sediments with high CO_2 production rates, highlighting the environment-specific extent of the ~~buffering~~ effect of mineral addition. Our work indicates that carbonate additions have the potential to effectively buffer surficial sediments over multiple years, yielding biogeochemical conditions that counteract the detrimental effect ~~of OA~~

~~conditionsof low pH sediment conditions~~of low pH sediment conditions on larval recruitment, and potentially increase benthic

30   alkalinity fluxes to support marine carbon dioxide removal (mCDR) in the overlying water.

1. Introduction

In coastal systems, ocean-freshwater mixing, terrestrial inputs, and active biogeochemical transformations (Cai et al., 2017; Soetaert et al., 2007) lead to natural fluctuations in pH that are large and decoupled from the decrease in pH observed in the

35   open ocean due to ocean acidification (Hofmann et al., 2011). Especially in shallow water environments, sediments play a significant role as benthic fluxes can constitute a substantial alkalinity source to the overlying water, increasing its buffering capacity ~~against ocean acidification~~ (Rassmann et al., 2016; Krumins et al., 2013; Cyronak et al., 2013b). Sediments receive organic matter (OM) from the overlying water which fuels the dissolution of carbonate minerals and early diagenetic processes. Aerobic respiration and other processes consuming dissolved O_2 can lead to steep pH decreases within the oxygenated sediment

40   and the interaction of OM mineralization and mineral dissolution determines the balance of the porewater carbonate system (Burdige et al., 2010; Jourabchi et al., 2005). Mineral dissolution and early diagenesis are connected through the changes in carbonate system which impacts mineral saturation states and hence the rate of dissolution (e.g., Morse et al., 2007). Apart from its impact on mineral dissolution, OM mineralization is also a significant contributor to alkalinity generation~~, in particular~~ under suboxic and anoxic conditions (~~Gimenez et al., 2018~~Hu & Cai, 2011a). These early diagenetic processes determine the

45   composition of the porewaters, which affect benthic calcifying organisms; furthermore, they can affect the biogeochemical conditions in the overlying water through benthic fluxes releasing nutrients and alkalinity.

~~Biological production of minerals by shell formation depends on the saturation state of the water, food availability, and other environmental parameters (Waldbusser et al., 2015). By altering saturation state, OA impacts ocean life, especially calcifying organisms in their larval and juvenile stages, eventually deteriorating coastal communities, fisheries, and shellfish industry~~

50   ~~(Fabry et al., 2008; Ekstrom et al., 2015; Barton et al., 2015). In shallow waters, strong benthic-pelagic coupling may impact organisms in multiple growth stages by changing carbonate conditions in both water and sediment columns (Waldbusser & Salisbury, 2014). However, in sediments, this impact is more critical due to p~~In surface sediments, porewater pH is generally ~~being~~ lower than in the overlying water, in particular when sediment O_2 uptake is elevated due to ~~biological transport by deposit feeders (Aller, 1982), or more broadly,~~ burrowing and irrigation activities by benthic macrofauna (e.g. Aller, 1982).

55   This exposes benthic organisms that live in the upper layers of the sediment ~~, for example because they have shorter siphons to access to the overlying water,~~ to more corrosive conditions (Green et al., 2013; Waldbusser & Salisbury, 2014~~; Zwarts & Wanink et al., 1989~~). Combined with abundant OM, e~~E~~nhanced supply of O_2 into the sediment ~~lowers pH, which can increase carbonate dissolution and~~also leads to elevated flux~~es~~ of alkalinity and DIC to the water column (Mucci et al., 2000; Burdige et al., 2007). ~~. This extends the impact of the benthos to the overlying water and affects the impact of ocean acidification in~~

60   ~~shallow water environments.~~

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In this study, we investigate the effects of the addition of carbonate minerals in the coastal sediments focusing on benthic alkalinity generation and release in a shallow water environment. Such ocean alkalinity enhancement (OAE) aims to buffer increased dissolved CO_2 in the ocean by dissolving carbonate or silicate minerals, producing alkalinity. OAE is mainly studied for its effect on ocean - atmosphere CO_2 exchange, the impact on organisms (Renforth & Henderson, 2017) and its potential to mitigate ocean acidification and lower atmospheric CO_2 concentrations (marine carbon dioxide removal; mCDR). Previous studies have shown that ~~OAE~~ increasing ocean alkalinity through enhanced weathering has the potential to reverse global ocean acidification in an intermediate CO_2 emission scenario (RCP 4.5) and reduce its impacts if emissions were to continue to rise throughout the 21st century (RCP 8.5) (Taylor et al., 2016). To date, OAE implementations ~~are mostly undertaken in~~ mainly target the open ocean ~~and~~ are aimed at identifying the potential of scaling up the mCDR efforts to a global scale (Fennel et al., 2023~~Montserrat et al., 2017~~). Recent studies also focused on the impact of OAE on marine ecosystems such as fish and plankton communities (Goldenberg et al., 2024; Paul et al., 2024; Ferderer et al., 2022). Only a few studies focused on coastal OAE and even fewer on sedimentary applications (Green et al., 2009, 2013; Hangx et al., 2009; Fuhr et al., 2024), where the effectiveness of OAE mainly depends on the dissolution rate of the mineral which is controlled by the mineral and the chemistry of the water and physical properties of the environment (Hartmann et al., 2013; Montserrat et al., 2017). One benefit of implementing OAE in coastal sediments is the generally higher rate of organic matter remineralization. This elevated CO_2 generation aids mineral dissolution, given most overlying marine waters are typically super-saturated with respect to carbonate minerals. Here, we simulate this effect of adding carbonate minerals to the sediment using a reactive transport model. We use measurements of carbonate mineral dissolution rates to assess the extent and duration of buffering in surficial sediments, and the impact on benthic alkalinity fluxes. Building on the previous work by Krumins et al. (2013) ~~and Rassman et al. (2016)~~ that explored the interaction of carbonate chemistry with early diagenesis in coastal sediments, our work identifies factors that determine the impact of sediment alkalinization on the spatial and temporal distribution of buffering by exploring the effect of mineral type, amount, organic matter remineralization rate and bioturbation.

2. Methods

2.1. Dissolution experiments

Dissolution rates for the minerals used in this model were derived from lab-based experiments detailed in Myers (2022). We provide pertinent details below. Two biomineral calcium carbonates, calcitic oyster shells *Crassostrea gigas* (below referred to as "bio-calcite") and aragonitic clam soft-shell clam shells, *Mya arenaria,* ("bio-aragonite") were collected from Oregon Oyster Farm in Newport, Oregon, USA and from Broad Cove in Yarmouth, Maine, USA, respectively. The biomineral samples were briefly cleaned, dried, crushed and sieved through a 2000 μm sieve and retained on 710 μm, for an approximately median grain size of 1 mm. We measured the mineral dissolution rate across four saturation states experimentally; $\Omega_{calcite} = 0.25$ (low), 0.45 (mid), 0.85 (hi) and 1.03 (saturated); carbonate chemistry conditions are detailed in Table S1. A flow-through, feedback-controlled with pH monitoring and CO_2 injection seawater system similar to Waldbusser et al. (2011) was used for manipulations at the Hatfield Marine Science Center (HMSC), Newport, OR, USA (additional details in Myers, 2022). pH

measurements from each manipulation tank were compared against a benchtop meter daily during the experiment. pH was

95 additionally compared against a reference sample in which pCO_2 and TCO_2, in situ temperature and salinity were measured to calculate pH on the NBS scale. pH (all tanks) and temperature (low and pre-treatment tanks) data were recorded every ten minutes. The ~~correlation coefficient~~coefficient of determination (R^2) between measured benchtop pH data and the pH data calculated from pCO_2/TCO_2 measurements for header tanks in all experiments was consistently greater than 0.9 across all experiments (Figure S2). Plug-flow style dissolution chambers were 2.5 cm ID, 12.7 cm long, schedule 40 PVC pipe, with 150

100 µm Nitex mesh on either end of the upright chambers. Approximately 50 ($\pm$ 0.1) grams of biomineral were used in each chamber, water was initially added slowly and agitated to remove air bubbles prior to initiating flow. Flowrates were controlled to 17 ($\pm$ 1.2) mL min^{-1} and experiments were run for three to four days to verify consistent alkalinity concentrations, as observed in trials conducted to optimize the experiment (Myers, 2022). Using the inlet and outlet measured alkalinity concentrations from an individual chamber (~~m~~mol alkalinity L^{-1}), the measured flow rate (~~mL min~~d^{-1}), and the known amount

105 of sample added (g$_{mineral}$), the change in alkalinity in ~~m~~mol alkalinity g$_{mineral}^{-1}$ d^{-1} was recorded as (Eq. 1):

$$\Delta = \frac{([alkalinity]_{outlet} - [alkalinity]_{inlet})}{(mineral\ amount * flow\ rate)} \quad (1)$$

$$\Delta = \frac{([alkalinity]_{outlet} - [alkalinity]_{inlet})}{(mineral\ amount)} * flow\ rate$$

The early diagenetic model (see below) uses a rate law in which the volumetric dissolution rate R_d (in mol$_{mineral}$ m^{-3}$_{sediment}$ d^{-1}) depends on the concentration of the mineral (mol$_{mineral}$ m^{-3}$_{sediment}$), the saturation state Ω (= ion concentration product/solubility

110 K_{sp}) and the dissolution rate constant k_d (d^{-1}) (Jourabchi et al., 2008):

$$R_d = k_d[Mineral](1 - \Omega)^n \quad (2)$$

In the experiment, the dissolving mineral is the entire solid phase, so that g$_{mineral}$ = g$_{solid\ phase}$. Hence, the mineral concentration in mol$_{mineral}$/g$_{solid\ phase}$ is the molecular weight of the mineral ($MW_{mineral}$) and k_d can be calculated from the measured Δ as:

$$k_d = \frac{\Delta * MW_{mineral}}{\frac{dTA}{dR} * (1 - \Omega)^n} \quad (3)$$

115 where dTA/dR is the mineral to alkalinity stoichiometric ratio in the dissolution reaction (+2 mol$_{alkalinity}$/mol$_{mineral}$; Table 3) and n is the rate order.

2.2. Carbonate Chemistry Measurements

Alkalinity

Open-cell alkalinity titrations were conducted over the course of the experiment, utilizing a two-point titration after Edmond

120 (1970), as modified by Waldbusser et al. (2011). A micrometer burette was used with a micro pH probe with precisions of 0.002 mL and $\pm$ 0.02, respectively. The probe was calibrated with NBS calibration standards (pH = 4, 7, and 10) daily before being used to take measurements. As outlined in Waldbusser et al. (2011), Baker Analyzed Reagent grade 0.0995-0.1005 normal HCl acid was used as the titrant with reagent grade NaCl to a final molar concentration of 0.7 to minimize gap junction

potentials during titrations. Analytical precision and accuracy were compared against triplicate titrations and Dickson CRM batch 142, respectively, and found to have an average coefficient of variance of 0.07% and typically ±16 µmol or less, for precision and accuracy.

Dissolved Inorganic Carbon, pCO₂, and Carbonate Calculations

~~Validation samples for~~ pCO$_2$/TCO$_2$ samples were collected in clean amber glass ~350 ml bottles preserved with 30 microliters of saturated HgCl$_2$ and sealed with polyurethane-lined crimp-sealed metal caps. Analysis via the Burkalator was carried out to measure pCO$_2$ and TCO$_2$ via near-infrared detection following the procedure of Bandstra et al. (2006), modified for discrete samples as in Hales et al. (2005), Barton et al. (2012), and Hales et al. (2017). Liquid and gas standards were employed to ensure the accuracy of pCO$_2$/TCO$_2$ measurements. The system can resolve the accuracy and precision of TCO$_2$ concentrations within ± 0.02% and 2% for pCO$_2$ (Hales et al., 2017). Carbonate chemistry parameters were calculated using dissociation constants from Millero (2010). Salinity was measured on the sample bottles following pCO$_2$/TCO$_2$ measurements via a salinometer (8400B "Autosal" Laboratory Salinometer; Guildline Instruments, Sorrento, FL, US). Calculated carbonate chemistry variables presented in association with the mineral dissolution experiments were computed using CO2calc and the K_1 and K_2 carbonic acid dissociation constants from Lueker et al. (2000), K_{HSO_4} constants from Dickson et al. (1990), sulfate constants from Morris & Riley (1966), fluorine constants from Riley (1965), and boron constants from Uppström (1974).

2.3. Reactive transport modeling

A one-dimensional diagenetic model was developed to simulate the distribution of chemical species with depth in the sediment over time. The model domain extended 20 cm deep into the sediment discretized into 50 intervals with a linearly increasing grid size of 1 mm at the top and 1 cm at the bottom. The model included 13 state variables, representing chemicals involved in the main early diagenetic reactions, and mineral dissolution/precipitation (Table 1). At the upper boundary, the concentrations of solutes and fluxes of solids were imposed, while at the bottom boundary, no gradient conditions were imposed for all chemicals.

Table 1: State variables and their upper boundary conditions. ~~Concentrations as a function of salinity~~Seawater compositions are computed with *aquaenv* (Hofmann et al. 2010) for ~~a given pressure and temperature~~ the pressure, temperature and salinity given in Table 2.

Variable	Notation	Boundary condition
Oxygen	O$_2$	0.2 mM
Sulfate	SO$_4^{2-}$	Seawater composition, ~~f(salinity)~~
Total sulfide	TS	0 mM
Dissolved inorganic carbon	DIC	equilibrium with a given alkalinity and pH 7.96
Total alkalinity	TA	1.9 mEq/L (measured at Yaquina Bay)
Calcium	Ca^{2+}	Seawater composition, ~~f(salinity)~~
Magnesium	Mg^{2+}	Seawater composition, ~~f(salinity)~~

Iron	Fe^{2+}	0 mM
Ammonium	NH_4^+	0 mM
Nitrate	NO_3^-	0.02 mM
Carbonate mineral (s)	$CaCO_3$	$F = 0$ µmol cm^{-2} yr^{-1}
Iron oxides (s)	$Fe(OH)_3$	$F = 1$ µmol cm^{-2} yr^{-1}
Iron sulfide (s)	FeS	$F = 0$ µmol cm^{-2} yr^{-1}

150 The spatio-temporal evolution of the concentrations was described by an advection-diffusion equation with the addition of bioturbation and bioirrigation and the effect of reactions. Bioturbation was treated as a diffusive process (Boudreau, 1997) and bioirrigation was described as a non-local exchange between porewater at depth and the overlying water (Boudreau, 1984). The governing equations were:

$$\phi \frac{\partial C_i}{\partial t} = -\frac{\partial \phi u C_i}{\partial x} + \frac{\partial}{\partial x}\left(\phi(D_i + D_b)\frac{\partial C_i}{\partial x}\right) + \sum_r s_{ir} R_r + B_i \tag{4}$$

155
$$(1-\phi)\frac{\partial C_j}{\partial t} = -\frac{\partial (1-\phi)v C_j}{\partial x} + \frac{\partial}{\partial x}\left((1-\phi)D_b \frac{\partial C_j}{\partial x}\right) + \sum_r s_{jr} R_r \tag{5}$$

where t is time, x is depth in sediment, ϕ is porosity, C_i (C_j) is the concentration of the solute i (in mol/volume pore fluid; solid j in mol/volume solid phase), u is the burial velocity for solutes (v for solids), D_i is the diffusion coefficient of the solute i, D_b is the depth bioturbation coefficient, R_r is the rate of production/consumption through reaction r (in mass/total volume and time), s is the stoichiometric coefficient for solute i or solid j in reaction r; and B_i represents bioirrigation for solute i.

160 Porosity is constant with time but depth-dependent and exponentially decreases with depth reflecting steady state sediment compaction (Eqn. 6):

$$\phi_x = \phi_\infty + (\phi_0 - \phi_\infty)e^{-\frac{x}{\gamma}} \tag{6}$$

where ϕ_∞ and ϕ_0 are the porosities at infinite depth and at the top of the sediment, respectively, and γ is the e-folding distance for the porosity. Burial velocities were corrected for compaction (Berner, 1980):

165
$$u_x = v_\infty \frac{\phi_\infty}{\phi} \tag{7}$$

$$v_x = v_\infty \frac{(1-\phi_\infty)}{(1-\phi)} \tag{8}$$

Diffusion coefficients were calculated using the R package *marelac* after Boudreau (1997) at a given salinity, temperature and pressure (Soetaert et al., 2010) and corrected for tortuosity (Boudreau, 1996) so that:

$$D_i = \frac{D_{aq,i}}{1 - 2ln(\phi_x)} \tag{9}$$

170 where D_{aq} is the molecular diffusion coefficient of solute i in solution. The bioturbation coefficient decreases exponentially with depth below the mixed layer,

$$D_b = D_{b0}e^{-\max(0,\ x-x_m)} \tag{10}$$

where x_m is the depth of mixed layer and D_{b0} is the bioturbation coefficient at the SWI, calculated as a function of water depth (Middelburg, 1997).

175   Bioirrigation is defined as an exchange between the surface layer and deeper layers of the sediment which was constrained by an bioirrigation coefficient exponentially decreasing with depth~~bioirrigation coefficient~~:

$$B_x = \alpha_0 e^{(-\frac{x}{\varepsilon})}\phi_x\left(C_{i,0} - C_{i,x}\right) \tag{11}$$

where α_0 is the bioirrigation coefficient at the SWI, ε is the e-folding distance for bioirrigation and $C_{i,x}$ is the concentration of solute i at depth x.

180   **Table 2: Environmental parameters**

Parameter	Value
Salinity	35
Temperature	12 deg C
Overlying water pH$_{(total)}$	7.96
Pressure	1.013 bar
Seawater density	1.027 kg L^{-1}
Sediment density	2.65 g cm^{-3} (Boudreau, 1997)
Porosity decay with depth (γ)	5 cm (Rooze et al., 2016)
Porosity at the surface (ϕ_0)	0.8
Porosity at infinite depth (ϕ_∞)	0.6
Sedimentation at infinite depth (v_∞)	0.5 cm yr^{-1} (Middelburg, 1997)
Bioturbation mixing coefficient at the top (D_{b0})	30 cm^2 yr^{-1} (Middelburg, 1997, water depth <5m)
Bioturbation e-folding distance	1 cm (Soetaert et al., 1996)
Depth of mixed layer (x_m)	4 cm (Rooze et al., 2016)
Bioirrigation rate constant at the top (α_0)	200 yr^{-1} (Wang & Cappellen, 1996; Meile & Cappellen, 2003)
Bioirrigation decay with depth (ε)	3.5 cm (Thullner et al., 2009)

Reactions considered in the model include organic matter mineralization with aerobic and anaerobic pathways, reoxidation of reduced species and mineral formation/dissolution reactions (Table 3). Each reaction has an impact on the total alkalinity (TA), which were taken from previous studies ~~is defined as~~ (Wolf-Gladrow et al., 2007; Dickson, 1981).~~:~~

185 $$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-]$$
$$- [HF] - [H_3PO_4] - [HNO_2] \pm other\ bases/acids \ldots$$

Organic matter is mineralized using O_2, NO_3^-, iron (oxyhydr)oxides (FeOx) and SO_4^{2-} as terminal electron acceptors and modeled with Monod kinetics. The OM mineralization rate (R_C^0) was adjusted to yield a TA flux of ~1200 µmol cm^{-2} yr^{-1}. This value was chosen to match open core top incubations measured in Yaquina Bay (Myers, 2022), andwith the resulting R_C^0 value was being comparable to earlier measurements by D'Andrea & DeWitt (2009) (~200-460 µmol C cm^{-3} yr^{-1};), but and higher than values reported for deeper coastal shelf environments (Wang & Van Capellen, 1996; Krumins et al., 2013). Reactions considered further include nitrification, iron oxidation, sulfide oxidation with O_2 and FeOx, and iron sulfide oxidation, as well as the formation/dissolution of $CaCO_3$ minerals and FeS (Table 3). Following Rooze et al. (2020), at each time step, DIC is speciated to calculate CO_3^{2-} concentration and pH from DIC and alkalinity, assuming seawater concentrations of borate and negligible contributions of phosphate, silicic acid, nitrite and hydrogen fluoride and other acids or bases.

Table 3: Reactions included in the model. Benthic primary production is assumed to be negligible and organic matter has Redfield stoichiometry (a = 1, b = 16/106, c = 1/106). Alkalinity production or consumption in each reaction is determined following Wolf-Gladrow et al. (2007). The total mineralization rate is defined as $R_C = R_C^0 *exp(-x/\gamma_{om})$ after Wang & Cappellen (1996) where γ_{om} is e-folding distance for OM mineralization.

Reaction	dTA/dR	dDIC/dR	Reaction rate
Organic Matter Mineralization			
$(CH_2O)_a(NH_3)_b(H_3PO_4)_c$ + a O_2 => a CO_2 + b NH_4^+ + c HPO_4^{2-} + (-b+2c) H^+ + a H_2O	b - c	a	$R_{O_2}^m = RC\,[O_2]\,/\,(K_{O_2}^m + [O_2])$
$(CH_2O)_a(NH_3)_b(H_3PO_4)_c$ + 4a/5 NO_3^- + (4a/5 +b -2c) H^+ => a CO_2 + b NH_4^+ + c HPO_4^{2-} + 2a/5 N_2 + 7a/5 H_2O	4a/5 + b - c	a	$R_{NO_3}^m = (RC - R_{O_2}^m)\,[NO_3]\,/\,(K_{NO_3}^m + [NO_3])$
$(CH_2O)_a(NH_3)_b(H_3PO_4)_c$ + 4a $Fe(OH)_3$ + (8a+b-2c) H^+ => a CO_2 + b NH_4^+ + c HPO_4^{2-} + 4a Fe^{2+} + 11a H_2O	b - c + 2*4a	a	$R_{FeOx}^m = (RC - R_{O_2}^m - R_{NO_3}^m)\,[FeOx]\,/\,(K_{FeOx}^m + [FeOx])$
$(CH_2O)_a(NH_3)_b(H_3PO_4)_c$ + a/2 SO_4^{2-} + (a/2 +b -2c) H^+	b - c + a	a	$R_{SO_4}^m = (RC - RC_{O_2}^m - R_{NO_3}^m - R_{FeOx}^m)\,[SO_4]\,/\,(K_{SO_4}^m + [SO_4])$

Reaction			
=> a CO_2 + b NH_4^+ + c HPO_4^{2-} + a/2 HS^- + a H_2O			
Secondary reactions			
NH_4^+ + $2O_2$ => NO_3^- + $2H^+$ + H_2O	-2	0	$R_{NH_4}^o = k_{NH_4}^o [NH_4][O_2]$
Fe^{2+} + 5/2 H_2O + 1/4 O_2 => $Fe(OH)_3$ + $2H^+$	-2	0	$R_{Fe}^o = k_{Fe}^o [Fe^{2+}][O_2]$
HS^- + $2O_2$ => SO_4^{2-} + H^+	-2	0	$R_{TS}^o = k_{TS}^o [TS][O_2]$
HS^- + $8Fe(OH)_3$ + $15H^+$ => SO_4^{2-} + $8Fe^{2+}$ + $20H_2O$	+14	0	$R_{TS}^{of} = k_{TS}^{of} [TS][FeOx]$
FeS + $2O_2$ => Fe^{2+} + SO_4^{2-}	0	0	$R_{FeS}^o = k_{FeS}^o [FeS][O_2]$
Mineral precipitation/dissolution			
FeS + $2H^+$ <=> Fe^{2+} + $2HS^-$	+2 (dis)/-2 (prec)	0	$\Omega_{FeS} = [Fe][TS]/([H^+]K_{FeS}^{sp}\rho_{sw}^2)$ $R_{FeS} = \begin{cases} k_{FeS}^f(\Omega_{FeS}-1), & \text{if } \Omega_{FeS} \geq 1 \\ k_{FeS}^d[FeS](1-\Omega_{FeS}), & \text{if } \Omega_{fes} < 1 \end{cases}$
$CaCO_3$ <=> Ca^{2+} + CO_3^{2-}	+2 (dis)/-2 (prec)	+1 (dis)/-1 (prec)	$\Omega_M = [Ca^{2+}][CO_3]/(K_M^{sp}\rho_{sw}^2)$ $R_M = \begin{cases} k_M^f(\Omega_M-1), & \text{if } \Omega_M \geq 1 \\ k_M^d[Mineral](1-\Omega_M)^n, & \text{if } \Omega_M < 1 \end{cases}$

Table 4: Reaction constants. Carbonate dissolution rate constants determined experimentally in this study are described in the results.

Reaction parameters	Value	Source
R_C^0	400 µmol C cm^{-3} yr^{-1}	~~Experimental~~Calibrated to match experimental TA data
γ_{om}	5 cm	(Wang & Capellen, 1996)
$K_{O_2}^m$	0.02 mM	(Rooze et al., 2016)
$K_{NO_3}^m$	0.004 mM	(Rooze et al., 2016)
K_{FeOx}^m	130 mM	(Rooze et al., 2016)
$K_{SO_4}^m$	1.6 mM	(Rooze et al., 2016)

$k_{NH_4}^o$	5000 mM^{-1} yr^{-1}	(Rooze et al., 2016)
k_{Fe}^o	140 000 mM^{-1} yr^{-1}	(Rooze et al., 2016)
k_{TS}^o	160 mM^{-1} yr^{-1}	(Rooze et al., 2016)
k_{TS}^{of}	6 mM^{-1} yr^{-1}	(Rooze et al., 2016)
k_{FeS}^o	300 mM^{-1} yr^{-1}	(Rooze et al., 2016)
K_{FeS}^{sp}	$10^{-2.2}$ (mol/kg)^2	Wang & Van Capellen (1996)
k_{FeS}^f	$6*10^{-6}$ mol g^{-1} yr^{-1}	Wang & Van Capellen (1996)
k_{FeS}^d	10^{-3} yr^{-1}	Wang & Van Capellen (1996)
$K_{calcite}^{sp}$	$4.31*10^{-7}$ (mol/kg)^2	f(salinity) (Mucci et al., 1983)
$K_{aragonite}^{sp}$	$6.82*10^{-7}$ (mol/kg)^2	f(salinity) (Mucci et al., 1983)
k_M^f(calcite)	10^4 mM yr^{-1}	(Luff & Wallman, 2003)
k_M^f(aragonite)	10^5 mM yr^{-1}	(Luff & Wallman, 2003)
k_M^d (calcite)	5 yr^{-1}	(this study)
k_M^d (aragonite)	5.2 yr^{-1}	(this study)

205 *Application*

To establish initial conditions, each simulation was first run to steady state with a zero-deposition flux of calcium carbonate. After that, before adding 8 or 16 weight % (weight of mineral/ total weight of the sediment) CaCO$_3$ were added to the top 2 cm of sediment, representing the sudden, one-time addition of the buffering carbonate minerals. These, respectively. To assess the magnitude and temporal evolution of the impact of the alkalinization experiment on sediment biogeochemistry and benthic

210 fluxes, transient simulations using these new initial conditions were then carried out, covering periods of up to 50 years. To investigate the temporal evolution of buffering over longer time frames, additional 50-year simulations were carried out. To assess the potential impact of adding minerals to the sediment, effectively diluting the concentration of organic matter in the surficial sediment, we also carried out simulations in which the model was modified to include particulate organic matter (POM) and using an OM mineralization rate dependent on POC concentration (see Supplementary Information).

215 We tested the impact of several environmental factors on the buffering effect of carbonate mineral additions to surficial sediments in comparison to the baseline addition scenario (i.e., 8% calcite additionTable 5). Specifically, we variedlowered the overlying water pH from 7.96 to 7.8, representing the impact of ocean acidification. Finally, tThe depth of the bioturbated layer affects the distribution of minerals added, which may impact the effectiveness of the extent of buffering; it was varied from surficialthe relatively shallow mixing depth of 4cm in the baseline implementation (i.e., 4 cm) to the global average depth

220 of bioturbation of 10 cm (Boudreau, 1997). the rate of OM mineralization, as terminal metabolism has a major impact on sediment redox conditions, porewater composition and relative importance of different metabolic pathways; R$_C$$^\theta$ was varied

from the baseline value of 400 to 200 µmol/cm³/yr to represent environments with different O₂ penetration depths and differing mineralization rates. We also varied the deposition flux of iron (oxy)hydroxides from 1 to 10 µmol/cm²/yr to assess differences between sites that vary in the extent of coupling between Fe, S and C cycles. And as the rate of organic matter mineralization has a major impact on sediment redox conditions and porewater composition, R_C^0 was varied from the baseline value of 400 to 200 µmol/cm³/yr to represent environments with different O₂ penetration depths. Finally, simulations were carried out to assess the impact of the type of mineral in the system (calcite vs. aragonite). The spin-up simulations were specific to each model run, and as such represent the environmental conditions (e.g., high vs. low rate of mineralization, or a setting in which either aragonite or calcite are the only carbonate mineral considered).

Table 5. Sensitivity analyses. Rows represent the scenario tested. Columns show the parameters changed.

Scenario/Parameter	R_c^0 (µmol/cm³/yr)	$Fe(OH)_3$ flux (µmol/cm²/yr)	Depth of mixed layer (cm)	Mineral type	pH in overlying water
Baseline	400	1	4	Calcite	7.96
Low OW pH	400	1	4	Calcite	7.8
High ML	400	1	10	Calcite	7.96
High Fe Flux	400	10	4	Calcite	7.96
Low R_c^0	200	1	4	Calcite	7.96
Aragonite	400	1	4	Aragonite	7.96

CO₂ drawdown

We estimated the potential impact of enhanced sediment TA fluxes on atmospheric CO_2 uptake in an enclosed bay using a simple box model. Water exchange is due to the tides, but riverine input is neglected, capturing summertime conditions at Yaquina Bay, OR (USA) when river discharge is low and metabolic rates are elevated. and riverine impact was assumed negligible, reflecting for example, the strong coupling of Yaquina Bay with the coastal ocean (Brown & Ozretich, 2007).

To estimate the order of magnitude of the impact of mineral additions on CO_2 uptake, we used a simple mass balance approach similar to Brenner et al. (2016), which focuses on the ratio of DIC over TA as the controlling factor of CO_2 uptake (Egleston et al., 2010). We calculated the mass balance for TA and DIC prior to and 2 years after the mineral addition and attribute the difference in atmospheric CO_2 exchange to the mineral addition. As described in detail in the Supplementary Information, we first estimated tidal water exchange from water level measurements. , and used unpublished temperature, salinity, and pH data (pers. comm. G. Waldbusser) from Yaquina Bay to constrain the The characteristics of the inflowing marine (alkalinity = 2.2 mmol L⁻¹, pH = 8.0) and outflowing bay water (alkalinity = 1.9 mmol L⁻¹, pH = 7.96) were chosen to be representative of a coastal setting such as Yaquina Bay and were informed by unpublished temperature, salinity, and pH data (pers. comm. G.

Waldbusser). ~~at a proximal sample site.~~ Combined with our modeled benthic exchange fluxes, this allowed us to estimate the alkalinity production in the water column (R_{TA}; Eq. 12). ~~which we interpret to be the consequence of net photosynthesis and aerobic respiration. Next, we used the alkalinity and pH to calculate the DIC and converted the net alkalinity production rate into net DIC production in the water column, assuming Redfield stoichiometry. This finally allowed us to estimate the CO_2 exchange flux necessary to close the DIC mass balance for benthic fluxes with and without mineral additions to quantify its effect on ocean CO_2 uptake.~~ At steady state, the alkalinity balance is given by:

$$F_i^{TA} - F_o^{TA} + F_b^{TA} + R^{TA} = 0 \tag{12}$$

where F_i^{TA} is the tidal influx of TA as a function of water exchange rate and oceanic TA ($F_i^{TA} = v[TA_{ocean}]$), F_o^{TA} is the tidal outflux of TA from the Bay to the ocean as a function of tidal velocity and TA of the study site ($F_o^{TA} = v[TA_{site}]$), F_b^{TA} is the benthic flux computed by the reactive transport model and R^{TA} is the areal net rate of water column TA production/consumption resulting from primary productivity and respiration.

Next, we used the alkalinity and pH to calculate the DIC and converted the net alkalinity production rate into net DIC production in the water column, assuming Redfield stoichiometry. This finally allowed us to estimate the CO_2 exchange flux (F_a^{DIC}) necessary to close the DIC mass balance for benthic fluxes with and without mineral additions to quantify its effect on ocean CO_2 uptake.

The mass balance for DIC is given by:

$$F_i^{DIC} - F_o^{DIC} + F_b^{DIC} + F_a^{DIC} + R^{DIC} = 0 \tag{13}$$

where F_i^{DIC} is the tide-driven influx of DIC ($F_i^{DIC} = v[DIC_{ocean}]$), F_o^{DIC} is the outflux of DIC ($F_o^{DIC} = v[DIC_{bay}]$), F_b^{DIC} is the benthic flux of DIC, F_a^{DIC} is the atmospheric CO_2 uptake (negative values indicate outgassing) and R^{DIC} is the net areal reaction rate producing/consuming DIC.

3. Results & Discussion

3.1. Mineral Dissolution Rates

Dissolution rates of minerals were highest under highly undersaturated conditions (Figure 1). For a given mineral saturation state, bio-aragonite dissolved slightly faster than bio-calcite. Dissolution rates are approximately proportional to the degree of saturation. Thus, the dissolution rate constant k_d for each mineral was estimated using Eqns. (1) and (2) with a dissolution order (n) of 1. Kinetic constant for aragonite dissolution was previously reported as 5 yr^{-1} (Luff & Wallmann, 2003) which was comparable to the 5.2 yr^{-1} derived from our measurements. For n =1, Jourabchi et al. (2005), reported a dissolution rate constant of 3.65 yr^{-1} while our estimation for bio-calcite was 5 yr^{-1}. The results are in line with previous data synthesis studies ~~This relationship is in line with previous reactive transport models~~ focused on mineral dissolution (Morse et al., 2007; Jourabchi et al., 2005; 2008~~; Krumins et al., 2013~~). ~~Thus, the dissolution rate constant k_d for each mineral was estimated using Eqns. (1) and (2) with a dissolution order (n) of 1.~~ Acknowledging the large variability in mineral dissolution dynamics (especially n) in previous studies (Adkins et al., 2021; Subhas et al., 2018) making it difficult to parameterize dissolution

280 process, we have taken *n* as 1 which provided a better fit to our shell dissolution rates. ~~Kinetic constant for aragonite dissolution was previously reported as 5 yr^{-1} (Luff & Wallmann, 2003) which was comparable to the 5.2 yr^{-1} derived from our measurements. For n =1, Jourabchi et al. (2005), reported a dissolution rate constant of 3.65 yr^{-1} while our estimation for bio-calcite was 5 yr^{-1}.~~
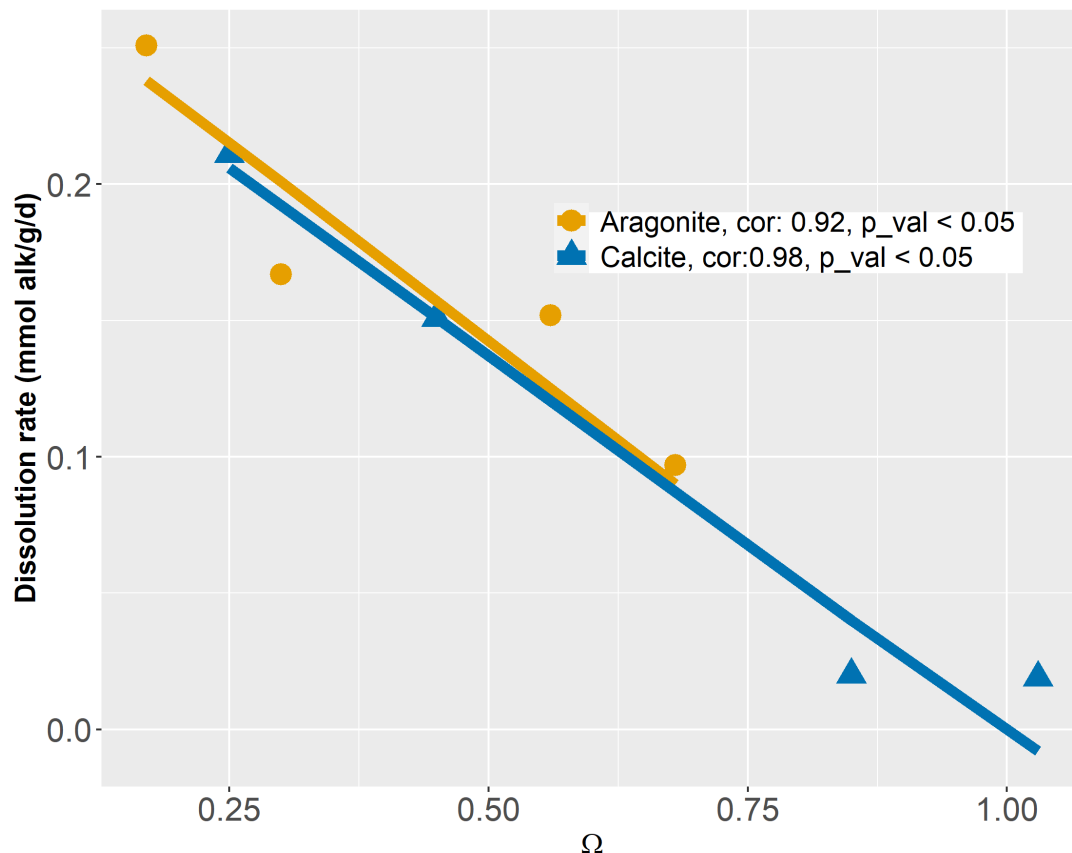
285 **Figure 1**: Saturation state for aragonite and calcite vs. their respective dissolution rates (mmol alk/g$_{solid}$/d). Lines show the fit with n=1. Cor: correlation between data and the fitted line. p_val: statistical significance of the fit.

3.2. Early Diagenetic Modeling

290 To assess the impact of sediment alkalinization through the addition of carbonate minerals to the sediment, early diagenetic model simulations were carried out that describe the spatio-temporal distribution of porewater and solid phase constituents. Prior to the addition of minerals, the simulated porewater profiles show sequential depletion of electron acceptors with depth, with O_2, NO_3^- and reactive FeOx only present in the top 5 cm (solid lines in Figure 2). SO_4^{2-} is present throughout the depth range and only decreases by about 2.5 mM. As a result of mineralization reactions, the concentrations of reduced porewater

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295 constituents (TS, NH_4^+, Fe^{2+}) increase with depth (Figure 2). Reduced dissolved iron (Fe^{2+}) peaked around 1 cm then decreased with depth due to the precipitation of FeS, which in our baseline simulation limited the build-up of ~~TS~~ hydrogen sulfide (TS) and dissolved reduced iron (Fe^{2+})~~Fe^{2+}~~. These porewater profiles reflect the sequential use of electron acceptors in the mineralization of organic matter, through aerobic respiration and anaerobic pathways such as denitrification, dissimilatory iron and sulfate reduction. The dominant OM mineralization pathway was SO_4^{2-} reduction (78.9%) followed by aerobic

300 mineralization (17.2%), denitrification (3.9%) and iron reduction (0.06%).

DIC and TA show pronounced concentration increases with depth, reflecting OM mineralization (Figure 2 i,j). The pH profile exhibits a rapid decrease in the top centimeter to about 7, showing the impact of CO_2 production without the concurrent consumption of protons through aerobic mineralization (Table 3; Jahnke et al., 1994; Green et al., 2013). Below the oxic layer, active anaerobic OM mineralization pathways such as iron and sulfate reduction can generate considerable amounts of TA if

305 the reaction products are not oxidized (Thomas et al., 2009). This was observed in the buildup of reduced species such as TS (discussed below) which limited the drop in pH and increased saturation state (from 0.5 to > 0.8) in the deeper layers of the sediment (Fig~~ure.~~ure 2 k,l). pH values were in the lower part of the range reported in Krumins et al. (2013), reflecting the lack of carbonates buffering the pH prior to the mineral additions. Sulfate reduction produced the majority of the TA and DIC (Figure 3), consistent with the findings of Krumins et al. (2013), Brenner et al. (2016) and Gimenez (2018). Aerobic mineralization

310 produced considerable amounts of DIC in line with previous work (Thamdrup & Canfield, 2000) while generating ~~significantly~~ less TA than anaerobic processes and mineral dissolution (Figure 3), leading to a low porewater pH (Soetaert et al., 2007; Hofman et al., 2011). ~~Denitrification and Fe reduction were less impactful on both~~ DIC and TA production by denitrification and in particular dissimilatory iron reduction was substantially less~~.~~ With a high dTA/dR value (Table 3), TS oxidation with FeOx also contributed to alkalinity production. Consumption of TA was dominated by secondary redox reactions that oxidize

315 reduced species with O_2. Due to fast kinetics, Fe^{2+} oxidation with O_2, nitrification and precipitation of FeS were the major TA consuming reactions. ~~This contrasts with results of~~ Brenner et al. (2016) ~~who~~ identified sulfide oxidation and nitrification as the dominant alkalinity consuming processes in the shallow water sediments in Southern North Sea. This discrepancy may be due to the potentially substantial impact of ~~points to wide variability in~~ sulfide oxidation on alkalinity dynamics~~kinetics~~ in organically rich near shore sediments ~~reported by~~ (Krumins et al. ~~(~~2013~~)~~). The oxidation of reduced products of organic matter

320 mineralization such as ammonium, hydrogen sulfide and dissolved Fe^{2+} with O_2 all lower alkalinity, albeit using different amounts of molecular oxygen. However, the oxidation of hydrogen sulfide with iron oxide as electron donor produces a large amount of alkalinity, that either accumulates if the reduced iron produces is captured in the sediment or is removed if the Fe^{2+} subsequently reacts with O_2 in the oxic zone (see Table 3). ~~which has a considerable impact on the net alkalinity generation due to sulfate reduction.~~ Coupling of SO_4^{2-} reduction with FeS precipitation ~~was~~ has been shown to be an important mechanism

325 for TA burial on continental~~in~~ shelves ~~and with the lateral mixing it can provide a TA source in deeper Baltic Sea basins~~ ~~(~~(Gustafsson et al., 2019). However, in our simulations, FeS formation was limited by Fe availability, which led to the buildup of ~~therefore,~~ hydrogen sulfide ~~accumulated~~ in the porewater.

Effect of carbonate mineral additions

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After adding carbonate minerals, the concentration profiles of primary redox species largely remained unchanged (Figure 2). This is because the organic matter mineralization rate expressions (Table 3) do not contain dependencies on the carbonate system or pH, as is common in early diagenetic models (e.g., ~~Rassmann et al., 2018;~~ Jourabchi et al., 2008; Morse & Mackenzie, 1990). Mineral addition slightly decreased Fe^{2+} while increasing FeS concentrations. This is due to TA production due to carbonate dissolution, which elevates the pH and increases the saturation state of FeS (Table 3), promoting FeS formation which eventually can lead to the long term removal of reduced sulfur through pyrite burial (Hu & Cai, 2011a).

The added carbonate minerals started to dissolve in our model, producing 1 DIC and 2 TA per carbon (Burdige et al., 2010; Zeebe & Wolf-Gladrow, 2001), so that both the pH (Figure 2k) and porewater saturation state (Figures 2l and 4B) initially increased (Cai et al., 2011). After 2 years, CO_2 production ~~and~~ still lowered pH in the oxic layer and prevented full saturation~~.~~ However, Ω was always above 0.9 and reached 1 at and below a depth of approximately 2.5 cm and subsequent decrease was observed below 12 cm. ~~Buffering the surficial sediment is especially important as juvenile bivalves tend to reside in the shallower oxic layers (Green et al., 2009, 2013; Waldbusser et al., 2010)~~. Following the addition of carbonates, the extent of the undersaturated conditions was constrained to the top 2 cm only, while in the natural buffering scenario reported in Krumins et al. (2013) porewater remained undersaturated in the top 10 cm. This demonstrates the potential of OAE in mitigating surface sediment acidification and providing potential benefits for calcifiers living in the upper sediment layers. As mineral addition counteracts porewater acidification, it generates biogeochemical conditions conducive for the survival of juvenile bivalves.
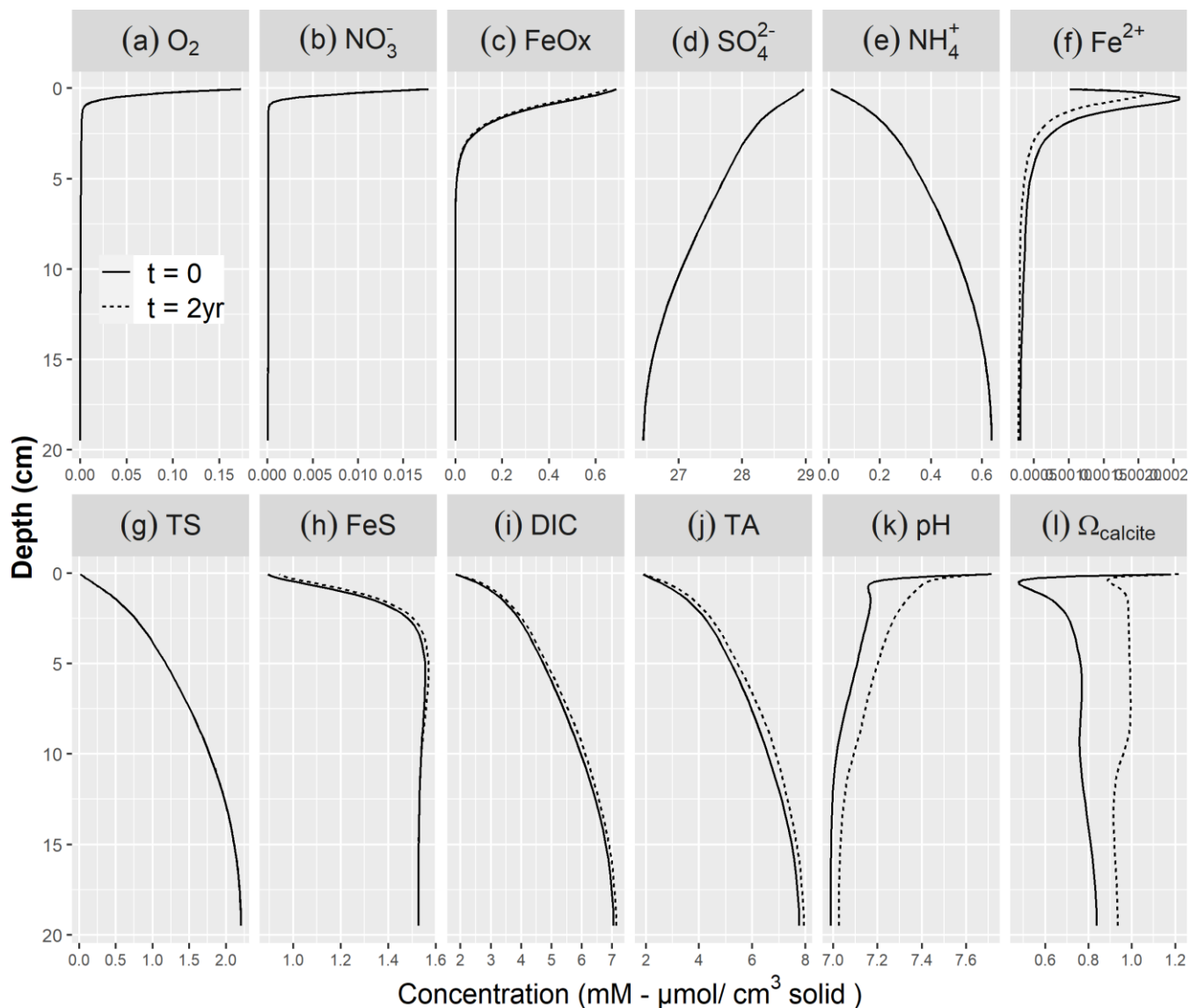
15

Figure 2. Simulated baseline porewater profiles of (a) O_2, (b) NO_3^-, (c) FeOx, (d) SO_4^{2-}, (e) NH_4^+, (f) Fe^{2+}, (g) TS, (h) FeS, (i) DIC, (j) TA, (k) pH and (l) $\Omega_{calcite}$ with 8% calcite addition. The solid lines denote the steady state profiles prior to the addition of calcite to the top 2 cm, while the dashed line indicate the simulated profiles 2 years after the mineral addition (some are coinciding with the solid lines and hence not visible). Dissolved constituents are in mmol/L porewater, while solids are given in μmol/cm^3 solid phase.

Our results ~~were~~ are in line with literature showing that the main alkalinity producing processes were calcite mineral dissolution, sulfate reduction, denitrification and sulfide oxidation with iron oxides (Krumins et al., 2013; Berelson et al., 2007). Although ~~some~~ organic matter mineralization ~~redox~~ reactions generate ~~generate~~ alkalinity, they ~~mostly~~ have lower

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355   dTA/dDIC ratios than mineral dissolution on a per carbon basis (Table 3), and the TA producing mineralization reactions are mostly coupled to TA consuming reoxidation reactions. Therefore, the net effect of (some) mineralization pathways on TA production can be limited (Krumins et al., 2013). For example, the amount of TA generated by benthic denitrification was almost balanced out by NH_4^+ oxidation (Figure 3) which results in the small effect of N cycling on alkalinity. This is in line with previous studies showing strong coupling between oxidation/reduction of N in the marine environment (Middelburg et

360   al., 1996) and its weak impact on buffering capacity of the overlying water (Hu & Cai, 2011b). However, because NH_4^+ is also produced by mineralization processes other than denitrification, the impact of N cycling on TA would change in environments where the importance of denitrification is different. Since reoxidation reactions are dependent on the availability of O_2, enhanced biological mixing can also increase TA consumption as previously demonstrated by Rao et al. (2014) for Fe^{2+} oxidation by O_2. Although total production of TA was around 1300 µmol cm^{-2} yr^{-1} (Figure 3, baseline with bio-calcite), total

365   TA fluxes from bio-calcite were slightly lower, which points to the importance of consumption of TA in the oxic layer as observed in Figure 3 as and previously reported in Krumins et al. (2013). Finally, before mineral addition, we observed a small production of calcite at the top of the sediment due to oversaturated conditions in overlying water. After the addition however, added mineral dissolved inat deeper layerspth which led to net dissolution and generation of alkalinity in the sediment column.
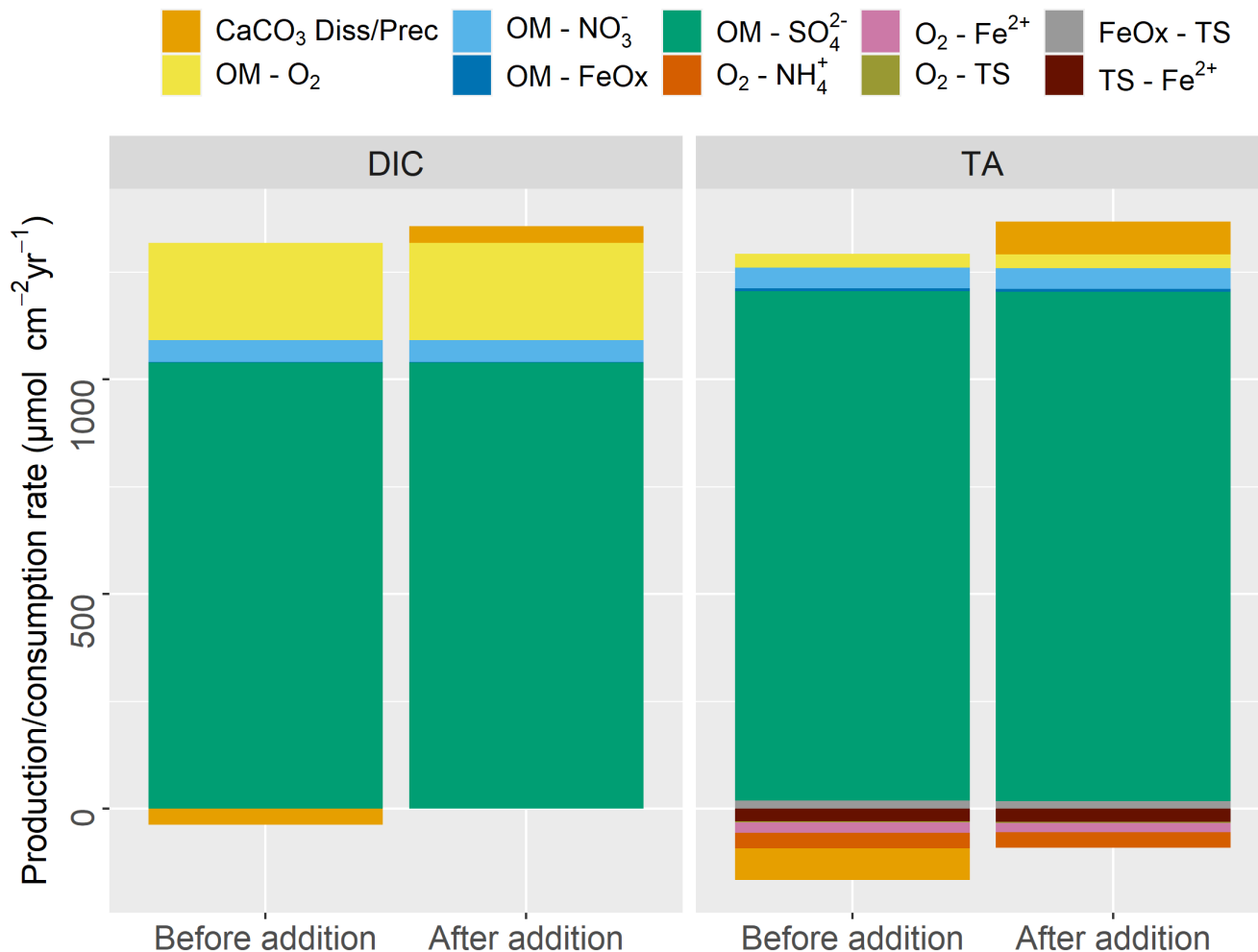
Figure 3. DIC and TA production (positive) and consumption (negative) by different early diagenetic processes integrated over the entire model domain for steady state (t = 0; before addition) and 2 years after the addition.

Temporal evolution of buffering with different minerals and amounts

Longer-term simulations (50 yrs) were performed to investigate the evolution of the buffering with time, considering different amounts and types of minerals added. We focused on the biogeochemical conditions in the top 10 cm of sediment, because the surficial sediment is most relevant for juvenile bivalves impacted by ~~ocean~~ acidification. Figure 4 shows the temporal evolution of TA and saturation state following the addition of minerals to the steady state conditions at t=0. Depth-averaged TA concentrations in top 10 cm peaked around the 2nd year after addition, with a significant drop starting around year 10 for the 8% mineral addition and around year 15 for the 16% addition and then return to steady state levels after more than 30 years

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380   (Figure 4A). Doubling the amount of mineral added generated slightly higher TA and extended the length of the peak buffering period. The simulation of aragonite addition produced higher alkalinity concentrations than that of calcite by approximately 0.3 mM at the peak time reflecting its higher solubility. However, TA levels in aragonite application dropped faster after approximately 10 and 15 yrs and approached the initial pre-mineral application levels after about 30 and 40 years, for 8% and 16% additions, respectively. In contrast, following the addition of However, in calcite. applications TA concentrations

385   remained elevated over longer time periods until the end of the simulations (year 50). Averaging over 4 cm yielded the same patterns (with slightly lower TA concentrations) as shown in Figure 4 (not shown).
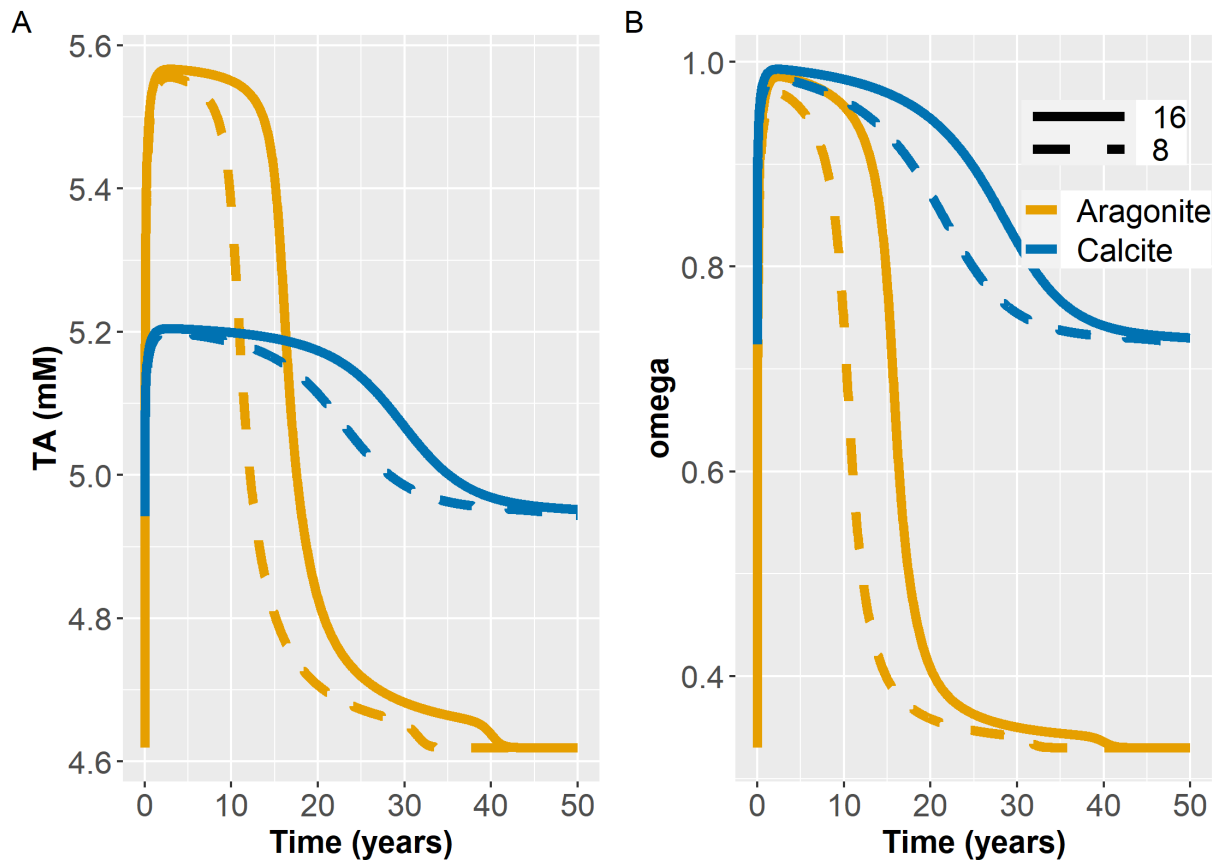

390   **Figure 4**. Temporal evolution of depth-averaged TA after addition of bio-aragonite and bio-calcite (A), and saturation states (B) in baseline simulation. Concentrations and saturation states are averaged over the top 10 cm of sediment. Colors show the type of mineral added. Solid and dashed lines show the addition of 16% and 8% respectively.

Being less stable than calcite, aragonite had a slightly faster dissolution rate constant and a larger solubility product (Burdige et al., 2010). Therefore, it generated higher TA concentrations and benthic fluxes early on. Because of its higher solubility, it initially took aragonite slightly longer to reach saturation than calcite (i.e., orange curve reaches maximum slightly after the blue one). As the rate of dissolution is set to be proportional not only to the degree of undersaturation but also the carbonate mineral concentration (Eq. 2), doubling the mineral addition had a more pronounced effect for aragonite which was approaching saturation more slowly than calcite (Figure 4B). Burial of carbonate minerals below 10 cm led to a faster decrease in TA in aragonite due to its higher dissolution. Initial conditions in 50 years simulations with calcite had higher saturation state than aragonite implementation therefore, after the impact of addition got buried, calcite leveledlevelled at higher saturation state and TA than aragonite.

*Buffering response for different environments*Sensitivity analyses

The impact of mineral additions on the generation of alkalinity depends not only on the type of mineral added, but also on which early diagenetic processes dominate (Figure 3). The relative magnitude of these processes depends on a number of factors, including the rate of organic matter mineralization, the extent of bioturbation, the deposition fluxes of potential electron acceptors such as iron oxyhydroxides, and the composition of the overlying water. Varying these factors in our model, we explore their impact on both the environmental conditions in the surficial sediment as well as the impact on benthic alkalinity fluxes.

In our simulations, under all scenarios, mineral saturation states reached similar values at the end of the 2 years with a low R_C^0 scenario generating the highest values (blue dots in Figure 5A). However, saturation was reached fastest in the deeper mixed layer bioturbation scenario which then decreased by years 1 and 2. Baseline, high FeOx flux and low R_C^0 scenarios showed a similar time course, while the addition of aragonite instead of calcite exhibited the slowest increase in saturation state (Figure 5A). Depth-averaged TA concentrations were highest following the addition of aragonite (Figure 5B). Deepening the bioturbation layer did not have much of an impact, the high FeOx flux scenario produced slightly lower TA than the baseline and the lowest amounts of alkalinity were produced by the low R_C^0 scenario. pH was buffered the most and increased the most and fastest in the aragonite implementation, followed by low R_C^0 conditions (Figure 5C). Although the deep mixed layer scenario increased pH faster than the baseline and high FeOx flux scenarios, these three scenarios converged to a similar pH as buffering the impact of mineral dissolution developed. The highest benthic TA fluxes were generated during the dissolution of aragonite while the lowest values were produced in the low R_C^0 scenario (Figure 5D). Baseline and deeper bioturbation layer scenarios produced very similar results while high FeOx flux scenario produced slightly lower TA fluxes. Lowering overlying water pH led to decreases in saturation state and pH while increasing concentration and flux of alkalinity.
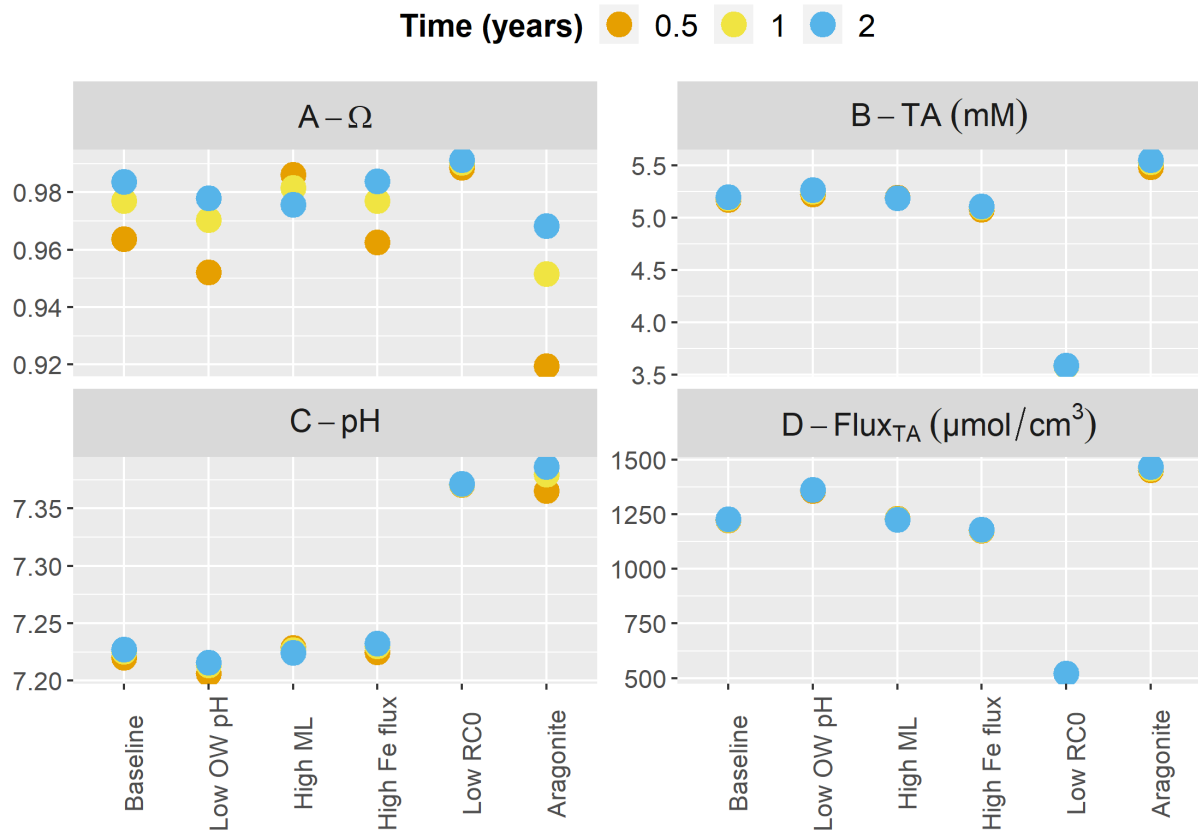
Figure 5. Buffering response ~~2 years~~ after carbonate mineral additions for a range of environmental conditions. Concentrations are averaged over the top 10cm. Scenarios listed on the x axis (from left to right) represent: baseline simulation ~~with calcite~~; baseline with lower overlying water pH representing ocean acidification scenario (7.8); baseline with deeper mixed layer (10 cm); baseline with higher Fe flux (10 µmol cm^{-2} yr^1); baseline with lower R_C^0 (200 µmol cm^{-3}); baseline with aragonite instead of calcite.

~~Due to the higher solubility and hence larger degree of undersaturation, initial aragonite dissolution was faster than calcite. Hence, aragonite produced the largest TA in 2 years, generated highest benthic TA fluxes, and increased the pH the most. The addition of aragonite produced more buffering than the scenario with lower OM mineralization which shows the potential of artificial buffering overcoming the acidification impact due to OM mineralization.~~

~~Increased FeOx input to the sediment led to enhanced FeOx reduction which produced TA. However, increased reoxidation of Fe^{2+} led to decreased availability of O$_2$ and consumption of TA. This balanced out the additional TA produced through FeOx reduction and led to an additional net consumption of ~46 µmol cm^{-2} yr^{-1} of TA. Overall, increased iron oxide supply led to~~

slight decreases in TA concentrations and fluxes showing an effect similar to decrease in OM mineralization rate in a smaller magnitude as also seen with small increases in pH (Figure 5).

A lower pH in the overlying water that represents ocean acidification led to a lower pH in the porewater and less saturated conditions in surface sediments (Figure 5). This promoted mineral dissolution and therefore led to increased TA production and flux to the overlying water. This demonstrates the sensitivity of buffering towards the overlying water conditions. Deeper bioturbation led to faster downward mixing and subsequent dissolution of the added mineral which then led to rapid increase in TA, pH and saturation state (also seen in dpH/dTA, Figure S4). Higher mixing led to faster transport of minerals inducing enhanced dissolution in year 0.5 (i.e., Figure 5, higher buffering 0.5 than 2 years after mineral addition). However, faster transport extended the depth of buffering and diluted dissolution products, which caused a slight decrease in pH and saturation state after 2 years at the top 10 cm (Figure 5). Increased FeOx input to the sediment led to enhanced FeOx reduction which produced TA. However, increased reoxidation of Fe^{2+} led to decreased availability of O_2 and consumption of TA. This balanced out the additional TA produced through FeOx reduction and led to an additional net consumption of ~46 µmol cm^{-2} yr^{-1} of TA. Overall, increased iron oxide supply led to slight decreases in TA concentrations and fluxes, and small increases in pH showing an effect similar to decreasing the OM mineralization rate (Figure 5). A lower pH in the overlying water led to a lower pH in the porewater and less saturated conditions in surface sediments (Figure 5). This promoted mineral dissolution and therefore led to increased TA production and flux to the overlying water. This demonstrates the sensitivity of buffering towards the overlying water conditions. TA production and flux was significantly lower in low OM reaction rate scenario (Figure 5D) which showed the critical impact of OM mineralization on TA dynamics. The lower rate of OM mineralization decreases TA production, both through the reduction of overall mineralization rates, and the reduction of the relative contribution of anaerobic mineralization pathways like dissimilatory sulfate reduction. The low rate of aerobic mineralization also led to reduced H$^+$ production, which in turn slows carbonate dissolution (Morse & MacKenzie, 1990). However, even with lower dissolution, this situation led to higher pH than the baseline suggesting that the artificial buffering might not be needed to maintain saturated conditions in environments where OM reactivity is low. On the other hand, especially iIn deeper layers where the surficial mineral addition is not as effective, TA and mineral saturation states will be lower due to lower anaerobic TA production. Notably, the effect of changing the OM mineralization rate is not linear, and halving the rate reduced the benthic alkalinity flux by a factor of about 2.5. In our simulations, the lower OM mineralization rate led to depth-integrated reduction by 29% for aerobic mineralization, 19% for denitrification, 55% for sulfate reduction and 380% for mineral dissolution. Aside from the (minor) impact on the partitioning of OM mineralization between metabolic pathways, this mainly reflects that changes in mineralization rates lead to differences in the porewater conditions, which in turn alter the rate of mineral dissolution/precipitation. Due to the higher solubility and hence larger degree of undersaturation, initial aragonite dissolution was faster than calcite. Hence, aragonite produced the largest TA in 2 years, generated highest benthic TA fluxes, and increased the pH the most. The addition of aragonite produced more buffering than the scenario with lower OM mineralization which shows the potential of artificial buffering overcoming the acidification impact due to OM mineralization.

3.3 Limitations and challenges

Our model demonstrates the potential for coastal sediment alkalinization to improve the biogeochemical conditions for juvenile calcifying organisms living in surficial sediments. However, alkalinity fluxes are ~~highly~~ sensitive to overlying water conditions, temporal changes in overlying water should be considered. These changes include the impact of short-term diel patterns and small scale spatial heterogeneity ~~in photosynthesis and respiration impacting~~ on benthic fluxes (Gadeken et al., 2023~~Cyronak et al., 2013b; Yamamato et al., 2015~~), seasonal changes such as temperature (Rao et al., 2014) and long-term changes such as anthropogenic impacts (Pacella et al., 2018; e.g. eutrophication, Cai et al., 2011). In addition, in particular in near-shore shallow water environments, one may have to take into consideration the input of groundwater (Cyronak et al., 2013a), advective flow through sand ripples (Huettel et al., 1998) and other factors driving advective flow in marine sediments (Santos et al., 2012), which can impact sediment biogeochemistry and alkalinity fluxes. Furthermore, the prediction of the time course of buffering by mineral dissolution may need to consider dissolution rate expressions that account for changes in mineral surface areas, rather than bulk concentrations (Morse et al., 2007), and the potential for ~~loosing~~ washing away or enhancing dissolution (Meysman & Montserrat, 2017) of minerals deposited to the sediment in high-energy environments.

Our results indicate a lasting buffering effect of mineral additions. This finding depends on the kinetics of the mineral dissolution rate, in particular the reaction order. Given the range of observations (Adkins et al., 2021; Subhas et al., 2018), the temporal evolution of the dissolution rates in the field needs to be explored further. In addition, our model assumes that the minerals are mixed into the upper 2 cm of sediment, matching recent field manipulation experiments in Yaquina Bay. However, an important consideration is how the minerals are applied to the surface sediment. For example, a simple 'top-dressing' approach would involve less disturbance to the sediment and less labor than surface raking, but may be washed away more easily, and react less readily with the metabolic acids produced in the underlying sediment. Thus, optimal mineral application and subsequent effects clearly requires field trials across a range of hydrodynamic settings

3.4 Potential impact of benthic fluxes on marine CO$_2$ uptake

Benthic alkalinity fluxes are critical for water column C dynamics especially in shallow water environments where water column and atmospheric interactions are more sensitive to processes occurring in the sediment (Brenner et al., 2016). The significant decrease in shells due to overharvesting has likely altered alkalinity cycling in estuarine waters, such as Chesapeake Bay (Waldbusser et al., 2013). One outcome of this benthic-pelagic connection is the impact of benthic fluxes on oceanic CO$_2$ uptake which was estimated to have significant influence in the North Sea (Thomas et al., 2009), and the potential for shallow water sediment alkalinization to alter overlying water.

We estimated the potential impact of enhanced sediment TA fluxes on atmospheric CO$_2$ uptake in Yaquina Bay, OR (USA) using the diagenetic model output (baseline scenario) in a simple box model at the peak buffering period (~2 years after

addition). The bay was found to be net heterotrophic, with tidal exchange and net respiration in the water column impacting
505 air-sea CO_2 flux ~~in the bay~~the most. The impact of sediment buffering on the air-sea CO_2 was estimated as the difference in atmospheric CO_2 fluxes between before and after the mineral addition. Mineral addition resulted in a TA flux enhancement of ~126 µmol cm^{-2} yr^{-1} and a decrease in CO_2 flux ~~n increase of CO_2 uptake~~ by approximately 58 µmol cm^{-2} yr^{-1}, which was comparable to previous studies (Brenner et al., 2016). Scaling to a 10 m water depth (or per liter of water), this stoichiometrically estimated marine carbon dioxide removal (mCDR) due to the application and subsequent dissolution of
510 carbonate minerals by the sediments results in a similar amount of mCDR as the current estimates of the anthropogenic C (C_{anth}) concentration in the US Pacific coast waters, 30-60 µmol L^{-1} (Feely et al. 2016, Pacella et al. 2024). It is important to note three key points in this estimate: (1) the uptake of C_{anth} by marine waters from anthropogenic activities results in an increase of DIC without any concurrent change in alkalinity, thus acidification. (2) alkalinity enhancement shifts the carbonate speciation and allows increased uptake of atmospheric CO_2 by marine waters. Thus, ocean alkalinity enhancement increases
515 the total amount of C_{anth} in seawater. However, while C_{anth} and DIC both increase with OAE, (3) the mineral dissolution due to sediment respiration ~~buffering~~ results in an increase in the TA~~Alk~~:DIC ratio, thus providing the mCDR benefit of atmospheric removal as well as mitigating existing acidification impacts. The annual mCDR effect modelled here, while notable compared to the total anthropogenic impact, is however miniscule compared to the total air-sea exchange flux, which is driven by ~~in~~ tidal exchange of DIC and alkalinity between the bay and the coastal ocean and biogeochemical processes in
520 the water column. The signal to noise of this potentially significant effect also highlights the existing measurement challenges in accurately discerning OAE effects within coastal systems.

4. Conclusions

Our study successfully combines lab experiments and modeling to investigate the impact of coastal alkalinity enhancement, points to critical aspects to be considered and presents the potential of carbonate additions as a mitigation strategy for the
525 effects of climate change in coastal settings. We demonstrated that addition of minerals increased pH and saturation state of the sediment over the timespan of a few months and had the potential to persist over 30-40 years after which subsequent additions might be needed to sustain buffering. During the peak buffering period, porewater in the top 10 cm of the sediment was almost fully saturated with respect to the mineral added, which implies favorable conditions for benthic calcifying organisms. We showed that two main pathways of producing TA in the sediment were sulfate reduction and mineral dissolution
530 with sulfate reduction having a larger impact. We also demonstrated that the type of mineral was an important factor ~~in quantifying~~affecting benthic fluxes and that the application of an increased amount of minerals was effective in extending the duration rather than the strength of the buffering.

Our analysis suggests that buffering through mineral additions to coastal sediments can establish biogeochemical conditions that are conducive for the growth and development of calcifying benthic organisms. However, the effect of mineral additions
535 can vary substantially between environments. Sensitivity analyses demonstrated that the OM mineralization had a significant impact on mineral dissolution, pH and mineral saturation. The type of mineral added also showed significant effect with

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aragonite producing more TA and higher pH. Increased mixing depth led to a faster increase in saturation state while increased iron flux caused reduction in TA concentration and benthic fluxes. Overall, the addition of minerals with ~~faster~~ higher

540 dissolution rates would be most effective especially in environments with high OM degradation and undersaturated water conditions. Similarly, the type of mineral and the environmental conditions affect m~~arine~~ CDR potential through benthic fluxes. Importantly, the implementation of OAE can lead to unforeseen effects, including ecological feedback such as changes in species composition (Bach et al., 2019; Köhler et al., 2013), and the effectiveness of carbonate additions may depend strongly on site characteristics. Thus, studies should combine field, lab and modeling components (Meysman & Montserrat, 2017) to improve predictive capabilities and decrease uncertainty.

545 ~~Ocean acidification research gained popularity in the past decade, but with its complicated effects on ocean life and biogeochemistry through a range of biogeochemical processes, it still is challenging to predict its overall impacts in the ocean (Riebesell and Gattuso, 2015; Middelburg et al., 2020). In coastal systems, $CaCO_3$ can act as a natural buffer. Combined with other anthropogenic impacts (i.e., eutrophication, Cai et al., 2011; Egleston et al., 2010) the impact of ocean acidification would be enhanced and therefore require interventions to sustain ecosystem health (Waldbusser et al., 2015). However, large~~

550 ~~scale geoengineering methods such as OAE can have large uncertainties with regard to side effects and implementation (Caldeira et al., 2013). These side effects can include unforeseen ecological feedback such as changes in species composition (Bach et al., 2019; Köhler et al., 2013) and the potential rapid changes after OAE implementations (González et al., 2018). Therefore, studies should combine field, lab and modeling components (Meysman & Montserrat, 2017) to improve predictive capabilities and decrease uncertainty.~~

555 **Code Availability**

The reaction transport model can be found at: https://bitbucket.org/MeileLab/kadir_oa/src/master/

Data Availability

Data for this manuscript is available in Myers (2022).

Author contribution

560 Lab experiments were designed by GW and TM, carried out by TM with the guidance of GW. KB developed the numerical model with guidance of CM and carried out the simulations. KB prepared the initial draft of the manuscript with significant input from CM, TM and GW.

Competing interests

The authors declare that they have no conflict of interest.

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