Assessment framework to predict sensitivity of marine calcifiers to ocean alkalinity enhancement - identification of biological thresholds and importance of precautionary principle

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Abstract

Ocean alkalinity enhancement (OAE), one of the marine carbon dioxide removal strategies, is gaining recognition in its ability to mitigate climate change and ocean acidification (OA). OAE is based on adding alkalinity to open-ocean and coastal marine systems through a variety of different approaches, which raises carbonate chemistry parameters (such as pH, total alkalinity, aragonite saturation state), and enhances the uptake of carbon dioxide (CO_2) from the atmosphere. There are large uncertainties in both short- and long-term outcomes related to potential environmental impacts, which would ultimately have an influence on the social license and success of OAE as a climate strategy. This paper represents a synthesis effort, leveraging on the OA studies and published data, observed patterns and generalizable responses. Our assessment framework was developed to predict the sensitivity of marine calcifiers to OAE by using data originating from OA studies. The synthesis was done using raw experimental OA data based on 68 collected studies, covering 84 unique species and capturing the responses of eleven biological groups (calcifying algae, corals, dinoflagellates, mollusks, gastropods, pteropods, coccolithophores, annelids, crustacean, echinoderms, and foraminifera), using regression analyses to predict biological responses to NaOH or Na_2CO_3 additions and their respective thresholds. Predicted responses were categorized into six different categories (linear positive and negative, threshold positive and negative, parabolic and neutral) to delineate species- and group-specific responders. The results show that 34.0% of responses are predicted to be positive (N=33), 25.8% negative (N=25), and 40.2% (N=39) neutral upon alkalinity addition. For the majority of negatively impacted species, biological thresholds corresponding to 50~~100~~ to 500 µmol/kg NaOH addition were found. We thus explicitly emphasize the importance of including much lower additions of alkalinity in experimental trials to realistically evaluate *in situ* biological responses. The ultimate goal of the study was to provide an assessment of biological rates and thresholds predicted under NaOH/Na_2CO_3 additions that can serve as a tool for delineating OAE risks, guiding and prioritizing future OAE biological research and regional OAE monitoring efforts and communicate the risks with stakeholders. This is pertinent given the fact that at least some of the current regulatory frameworks likely do not assure safe biological space. With 60% of responses being non-neutral, a precautionary approach for OAE implementation is warranted, identifying the conditions where potential negative ecological outcomes could happen, which is key for scaling up and avoiding ecological risks.

1. Introduction

Anthropogenic carbon dioxide (CO_2) emissions have increased at an unprecedented rate and have contributed to global climate change and negative ecological and biogeochemical impacts in the oceans (Feely et al., 2004; Gattuso et al., 2018), to the extent of crossing six different planetary boundaries (Richardson et al., 2023). Oceans play a crucial role in attenuating the increase in atmospheric CO_2 through the absorption of the excess atmospheric CO_2 of roughly a quarter of anthropogenic carbon dioxide (CO_2) emissions, drawing down around 2–3 Pg C yr^{-1} in recent decades (Friedlingstein et al., 2022). However, without substantial CO_2 emissions abatement and CO_2 removal strategies, profound repercussions on climate, extreme weather events, and socioeconomic implications will follow. Ocean-based CO_2 removal and sequestration strategies (broadly referred to as marine CDR) are among the proposed CDR approaches that remove CO_2 and store it for geologically relevant times (National Academies of Sciences, Engineering, and Medicine, 2021). These mCDR approaches only complement CO_2 emission reductions and contribute to the portfolio of climate response strategies needed to meet the global goal of limiting warming to well below 2°C as established by the Paris Agreement. Various mCDR approaches have unique benefits and costs but differ in their value depending on their state of implementation, and whether they act globally and/or locally (Oschlies et al., 2023).

Ocean alkalinity enhancement (OAE) has the potential to mitigate climate change through increasing ocean uptake of CO_2, while simultaneously reversing ocean acidification (OA) and improving marine habitats. Despite mostly being in the concept stage, OAE is viewed with a high level of confidence as to its effectiveness: medium on environmental risk, but low on the underlying knowledge base (Eisaman et al., 2023; Gattuso et al., 2021; National Academies of Sciences, Engineering, and Medicine, 2021). One of the major concerns for OAE are large uncertainties in both short- and long-term OAE outcomes related to potential environmental impacts of OAE (Kheshgi, 1995; Bach et al., 2019), especially if OAE were to induce novel conditions in the marine systems that are outside the range of the natural variability, exposing organisms to conditions not experienced in their evolutionary history. The outcome of OAE as a successful climate strategy depends on a thorough and advanced understanding of the impacts of OAE implementation while avoiding or minimizing ~~avoiding~~ negative biological effects.

1.1 Leveraging ocean acidification research on marine calcifiers

Increased CO_2 uptake, which initially is absorbed by the ocean as dissolved CO_2, causes a decline in pH, shoaling of the saturation state horizon (Ω_{ar}) and reduced carbonate ion amount content in a process termed ocean acidification (Feely et al., 2004), causing negative consequences to marine biota, especially marine calcifiers, the structure and function of the vulnerable marine ecosystem, and alteration of the carbon cycle. On the other hand, chemical changes induced by OAE are inherently linked to reversing the OA process: increasing pH, shifting carbonate chemistry speciation towards lower aqueous carbon dioxide (pCO_2) and higher carbonate ion (CO_3^{2-}) content, as well as higher aragonite saturation state (Ω_{ar}). Such changes could either be within the ranges of the variability of the natural systems to which species are acclimatized, or outside them, creating novel conditions for which species might not have developed suitable acclimation strategies. As such, the biological outcomes are, due to their complexity, highly unpredictable.

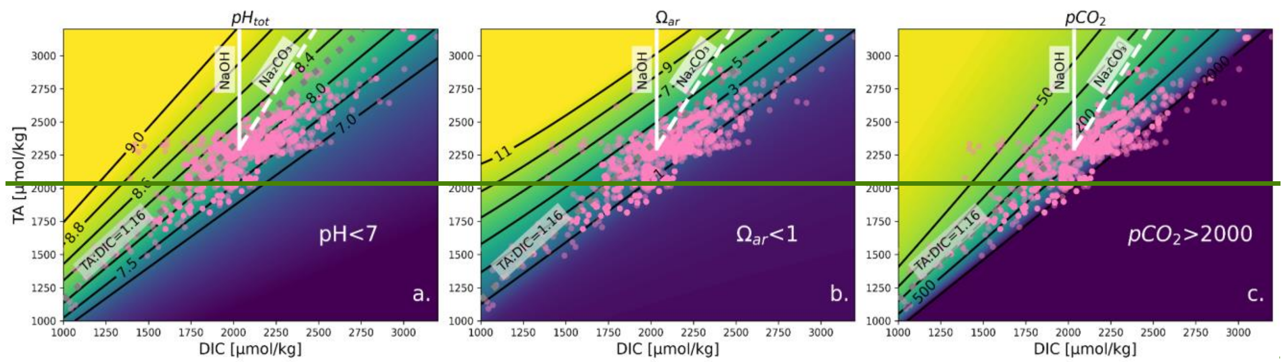
Scientific progress in over 20 years of OA research has brought substantial insights into the biological effects, with the most fundamental outcome being that calcifying organisms would be primarily affected (Riebesell and Gattuso, 2015), with the calcification process being one of the most susceptible pathways, underpinned by species differences in calcification mechanisms (Ries et al., 2009; 2011; Bach et al., 2013; 2015; Leung et al., 2022). However, OA focused heavily on investigating biological effects on the more acidic range of the carbonate chemistry conditions predicted under future scenarios and most of the studies focused on manipulating the level of pCO_2 rather than alkalinity. This resulted in poor understanding of the biological effects at the higher pH end of the carbon chemistry range (Renforth and Henderson, 2017). Some biological inferences can be made based on the understanding of the physiological mechanisms underlying the calcification mechanisms (Bach et al., 2019), but such insights are not adequate to provide sufficient understanding. Despite the lack of biological data at the upper ranges of pH and Ω_{ar}, this study builds on the premise that previous OA studies could be leveraged for assessment of biological responses under OAE. Comparative experimental work, meta-analyses, and the threshold work (Kroeker et al., 2013; Leung et al., 2022; Bednaršek et al., 2019; 2021b,c) have indicated that even very diverse responses can be grouped into categorical responses.

Calcification is a primary pathway of the organismal sensitivity to OA and ~~,~~ is directly implicated in growth and (abnormal) development across most of the marine calcifiers, and indirectly implying the the level of susceptibility to predation, Thus, it can be used as an ~~which can act as an~~ early warning response, ~~, and is directly implicated in growth and (abnormal) development across most of the marine calcifiers~~, while ~~it~~ also underlying~~ies~~ the ecological success of numerous marine calcifiers. ~~Calcification also underlies the ecological success of numerous marine calcifiers because it directly addresses the level of susceptibility to predation, which could lead to altered size of the overall population.~~ Studies also ~~clearly~~ show that the thresholds for calcification occurs at similar pH/Ω values as the thresholds related to the ~~for metabolic and~~ energy metabolism processes (Lutier et al., 2022; Bednaršek et al., 2019; 2021b,c). Finally, calcification is ~~It is also~~ directly implicated in the carbon export with significant biogeochemical implications that could also impact OAE efficiency. This study aims to systematically assess species calcification responses predicted under carbonate-based OAE compound additions. ~~and categorize them based on calcification rate responses.~~

1.2. Complex carbonate chemistry changes induced by various OAE compounds

Various OAE compounds added to the water change carbonate chemistry in a multifaceted way and require complex calculations of a multi-parameter problem. As the values of TA and DIC change, a variety of other parameters, such as pH, CO_3^{2-}, Ω_{ar}, and pCO_2, exhibit approximately linear relationships, with slopes that vary along these lines (see Fig. 1). This means that if TA and DIC vary in proportion to one another, then the values of these displayed parameters hardly change at a particular salinity, temperature, and pressure. With TA, DIC and the hydrographic conditions (salinity, temperature and pressure), one can fully constrain the carbonate system. Our method requires us to have *one* variable constraining the entire carbonate system. TA and DIC have the benefit that they can both be directly measured with high accuracy or calculated from other carbonate parameters. They are also both directly linked to OAE, as we are enhancing the TA which then allows DIC to increase over time due to the gradual uptake of atmospheric CO_2.

To demonstrate the changes of the carbonate system in the experimental system, Figure 1 shows the changes in carbonate parameters with the addition of two OAE compounds, i.e. NaOH (solid line) and Na_2CO_3 (dotted line) to seawater. When NaOH is added, only TA increases and when Na_2CO_3 is added, TA and DIC increase at a 2:1 ratio. This results in corresponding changes in pH (Fig. 1a), Ω_{ar} (Fig. 1b) and pCO_2 (Fig. 1c) and shows how much of a change is required to bring the system back to equilibrium with respect to the atmosphere.



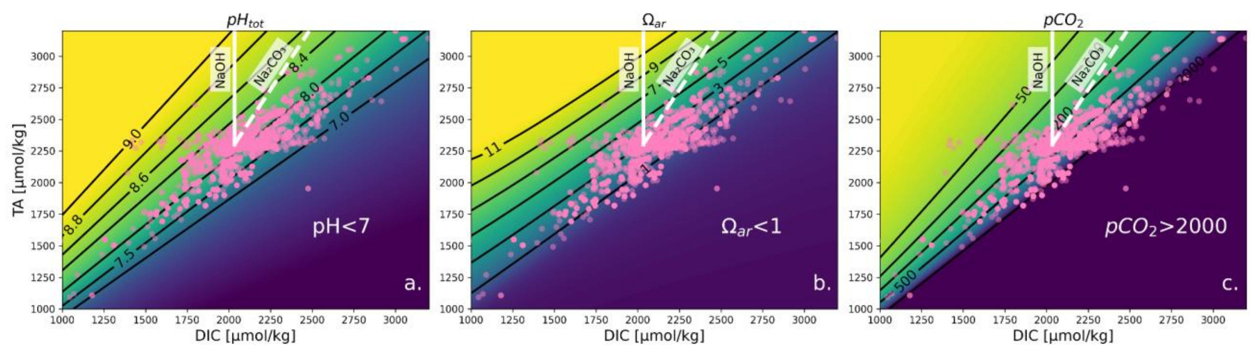


Figure 1: *The effect of changes in TA and DIC on the properties of seawater (S= 34.68, T=16°C, [SiO_2] = 50 µmol/kg, [PO_4^{3-}] = 0.5 µmol/kg, TA = 2303 µmol/kg, DIC = 2034 µmol/kg), adapted from Schulz et al. (2023). Pink dots represent experimental TA and DIC data used in our synthesis. Subfigures show pH_{tot}, aragonite saturation state and pCO_2. Calculations were carried out with the Python version of CO2SYS (Humphreys et al., 2022) using the stoichiometric dissociation*

constants for carbonic acid from Sulpis et al. (2020), for sulfuric acid by Dickson et al. (1990) and for total boron from Uppström (1974). ~~*The dotted grey line represents the pre-industrial TA:DIC of 1.16.*~~ *The solid white line indicates the effect of adding NaOH and the dashed white line indicates the effect of adding* Na_2CO_3*. This grouping of lines can be translated so that its initial position moves elsewhere to visualize different initial conditions. Note that at TA < 1000 µmol/kg and DIC < 500 µmol/kg this correspondence no longer holds true when considering* Ω_{ar}*, however, such conditions are rare in the ocean and not widely applicable. The same contour plot utilizing GLODAP data plotted instead of experimental data is shown in Supplement Figure 1.*

1.3 Testable conceptual framework based on the existing OA studies

Based on Ries et al. (2009), calcification responses can be categorized into six categories (Fig. 2): linear positive or negative response; threshold positive or negative response (exponential fit); parabolic response; and neutral (no significant) response. We hypothesize that these categories of responses based on ocean acidification data and delineated by Ries et al. (2009, 2011), could also be applicable to OAE dosing. For this meta-analysis, we have undertaken three steps: first, synthesize carbonate chemistry data at regional and global scales to obtain TA, DIC and Ω_{ar} correlations; second, conduct a literature review and collect available data from OA literature related to the calcification rate responses across the species of eleven groups of marine calcifiers; and third, run regression analyses and determine the category of calcification rate response to TA:DIC, further extending it with addition of NaOH and Na_2CO_3.

The most accurate way of predicting the responses to OAE addition is done based on the mechanistic understanding of calcification response to specific carbonate chemistry parameter(s). The hypothesis was that if mechanistic relationships with identified carbonate chemistry driver(s) are available for species, calcification rate under various feasible OAE scenarios can be predicted with greater accuracy and lower uncertainty. We further focused on investigating if the empirical results were consistent with mechanistic calcification predictions for a few selected species for which the mechanisms were known.

Here, we demonstrate the TA:DIC relationship with biological outcomes and show the application for the TA:DIC thresholds beyond which the responses become negative. Ultimately, we synthesize which calcifying species or groups are predicted to benefit or loss due to OAE, what constitutes a species-specific safe operating space related to the OAE and we delineate what experiments are most urgently needed to fill in critical knowledge gaps before massive OAE field implementation can be considered.

2. Methodology

2.1 Literature review of data on marine calcification impact by OA

To assess the impact of OAE on a range of marine calcifiers, we used existing studies on marine species calcification response that had aligned raw biological (calcification rate) data along with the carbonate chemistry. We searched within Scopus, Web of Science, and PubMed and used datasets that were archived in NCEI, OA-ICC and Pangaea. Through personal correspondence, we have additionally contacted lead authors of the studies whose data are not or are insufficiently archived, mostly to validate the predicted response. Searches for biological datasets relating to calcification rate and corresponding carbonate chemistry were conducted through November 2023, encompassing 68 existing studies. The aim was to cover a wide range of calcifying organisms across various functional groups and 84 species. For several functional groups data was easy to find (algae, coccolithophores, corals, foraminifera, mollusks and dinoflagellates), so no new studies were added after 10 to 15 studies were found. Seven studies were found for pteropods, five for gastropods, four for echinoderms, three for crustaceans and one for annelids. When reviewing the literature, we included data from the OA experimental studies related to the physical-chemical parameters (temperature, salinity, TA, DIC) and biological data related to calcification rate.

2.2 Use of TA:DIC instead of Ω_{ar}

Understanding the change in carbonate chemistry upon alkalinity addition is essential for the biological experimentalists who are conducting biological assessments to report on the effects of OAE. However, complex changes in the carbonate chemistry induced by alkalinity addition are not intuitive or straightforward; in fact, they are multi-parameter problems that require complex carbonate chemistry calculations. Using the TA:DIC ratio is a more practical way of looking at the impacts of the OAE treatment instead of using a single carbonate parameter because of the highly correlative relationship between TA:DIC and other carbonate system parameters (see Fig. 1).

With TA, DIC and the hydrographic conditions (salinity, temperature and pressure), one can fully constrain the carbonate system. Our method allows *one* variable constraining the entire carbonate system. TA and DIC have the benefit that they can both be directly measured or calculated from other carbonate parameters. They are also both directly linked to OAE, as we are enhancing the TA which then allows DIC to increase over time due to the gradual uptake of atmospheric CO_2 (Fig. 1 shows the changes in the carbonate chemistry system upon NaOH and Na_2CO_3 additions).

Our focus was on streamlining the process of expressing experimental results and subsequently reporting responses, with the goal of reducing the multi-parameter complexity into a single-parameter simplification. ~~As such, our focus was on simplifying the steps to express the results when conducting the experimental work, and subsequently, the reporting of the responses, with the aim to reduce the multi-parameter problem into a one-parameter simplification.~~ This step reduces multiple degrees of freedom into just two, i.e. TA and DIC, with the ratio allowing us to consider this as a 1-parameter problem. As such, TA:DIC is a simplistic and convenient way of describing the system, where we only need to understand the change in TA and DIC ratio, which is feasible for every OAE compound added to the experimental system. In addition, TA:DIC is also the best approximation for the CO_3^{2-} concentration. The insights from multiple biological experimental studies show that the CO_3^{2-} concentration is the representative driver of the calcification process for multiple calcifying groups, although not all, compared to aragonite saturation state (Ω_{ar}), which represents an empirical approximation. Furthermore, by using TA:DIC we do not have to choose a particular parameter to describe the changes in calcification. It could also work for the species in which other parameters drive the calcification, e.g. bicarbonate in autotrophic, Ω_{ar} in bivalves and H^+ flux in foraminifera. In that way, we standardize all the parameters that would otherwise influence the carbonate system and come up with a more uniform way to express the experimental conditions, which would then be useful for easier comparisons among the conducted experiments. For the ease of comparing TA:DIC with pH and Ω_{ar}, we refer the reader to Supplement Table 1 and Supplement Fig. 2.

2.3 Experimental biological and biogeochemical data

Based on the collected data, the range of pH and Ω_{ar}, experimental conditions used and their TA:DIC relationship was determined (Supplement Fig. 2 and Supplement Table 1). Most studies covered pH conditions from 7.5 to 8.5 and Ω_{ar} up to 5, with a few studies increasing pH up to 9 and exceeding Ω_{ar} of 10. This indicates the potential of leveraging such experimental studies as a baseline for predictive regression models of biological responses to a range of Ω_{ar} conditions, as expected under OAE studies.

Once biological data was compiled, units were standardized where possible. The main issue when compiling data was the lack of standardization of the calcification rates. A variety of calcification rate units were used across different studies. Where possible, the units were converted to mmol of $CaCO_3$ g weight^{-1} hr^{-1}. However, the data required to do so was not always readily available. Other units used for calcification rate were mmol of $CaCO_3$ m^{-2} h^{-1} and mmol of $CaCO_3$ m^{-3} hr^{-1}, and there was also data used as an indication of calcification rate with units mmol #$^{-1}$ h^{-1}, mmol h^{-1}, mmol cm^{-2}, % h^{-1}, where '#' indicates one individual. Growth rates and PIC production rates were used as indicators of calcification rate for single-cell organisms. For some species, direct calcification rates were not reported in the literature, instead only relevant parameters related to calcification (shell length, density, thickness) over time were available from the experimental studies. The decision was made to also collect these additional datasets because the statistical analyses of this study focus on the trend in the absolute numbers and would not change by being transformed into the rates. Data were analyzed on a species level, wherever rate units were the same. Hereafter, this is referred to as the species rate group. Where there were multiple studies available for the calcification rate of one species using the same rate units, the data were combined (e.g. *Emiliania huxleyi*).

2.4 Sorting species-specific responses into categories per calcification response

Responses were split into 6 categories: linear positive and linear negative, parabolic, threshold positive and negative, and neutral. The response was determined with a best-fit regression model, using the ordinary least squares method in Statsmodels for Python (see Seabold et al., 2010). See

Fig. 2 for an overview of these responses of calcification rate to increasing TA:DIC ratio.

The final response for each species was determined by the regression with the lowest p-value. This method is in contrast with the Ries et al. (2009) study where they chose the regression analysis that yielded the lowest square root of the mean squared error (RMSE) for a given species, and that was statistically significant ($p \leq 0.05$). When applying their method to our data, parabolic and exponential regressions were always favored over linear regressions. When examining these regressions, we found that choosing the best fit based on the lowest p-value yielded better fits, as this method prevents overfitting due to noise in the data. Where a linear regression had the best fit, we assigned a linear response, which could be either positive or negative based on the slope. The species with a significant exponential fit were categorized as threshold positive (+) or threshold negative (-), which was distinguished from the parabolic response with the fitted parabolic curve.

The best fit regression was assigned to each species and plotted, but only if the p-value was considered significant, i.e. lower than 0.05. These regressions were plotted along with a 90% prediction interval, which accounts for the variability of the experimental data. The species with a p-value > 0.05 were categorized as having no correlation (neutral response).

When there were multiple datasets obtained from different studies for the same species and rate units could not be combined, we took each response into consideration and reported the p-value and RMSE for each of the studies. Even when different studies reported varying calcification responses for the same species, we refrained from making a judgment by selecting a single overall response. This is because the variability among studies may be valid, especially given that species from different regional settings might be physiologically acclimatized and genetically adapted to different carbonate chemistry conditions.~~Even if there were different observed calcification responses for the same species in different studies, we avoided making a judgment on the studies by choosing an overall response since the heterogeneity among the studies can be true, especially when considering that species from different regional settings (as represented in the studies) might be differentially physiologically acclimatized and genetically adapted to the range of carbonate chemistry conditions.~~

The TA:DIC threshold was computed to indicate the point at which the current calcification rate (i.e. the calcification rate at the baseline) is reduced by a half for linear negative, threshold negative and parabolic responders. The thresholds and the amount of NaOH and Na_2CO_3 required (starting at 10 µmol/kg and then in steps of 50 µmol/kg) to reach this threshold were determined. For parabolic responders, the inflection points that tell us when the rate is predicted to change slope are also included in Supplement Table 2. Once the species' responses were determined, an attempt was made to group them based on functional groups. However, since species within the same functional group had varying responses, grouping them together meant these responses were no longer visible due to a wide spread of data. Therefore, most of the analysis remained on the species level (Table 1).

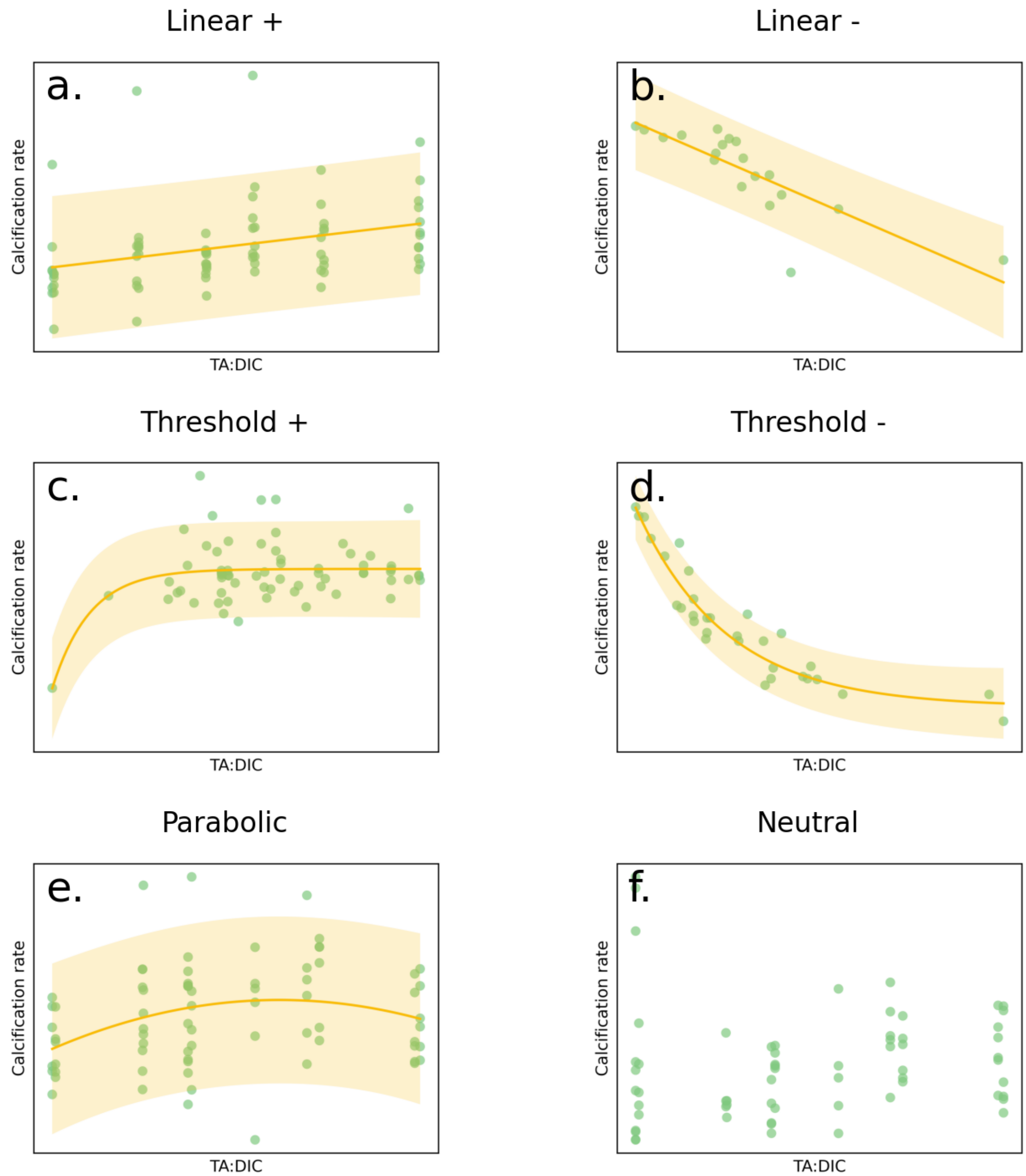


Figure 2: *Overview of the categories of responses between carbonate chemistry parameters (TA:DIC) and calcification rate: a) linear positive (calcification increase with increased TA:DIC); b) linear negative (calcification decrease with increased TA:DIC); c) exponential for the threshold positive response (calcification increase, plateauing at higher TA:DIC); d) exponential for the threshold negative response (calcification decline, plateauing at lower TA:DIC), e parabolic (calcification increase followed by a decrease at higher TA:DIC) and f) neutral (non-significant) response. Responses were only considered significant when $p < 0.05$, otherwise they were*

categorized as neutral. Yellow shading represents the 90% prediction interval. Note that TA:DIC on the x-axis corresponds to aragonite saturation state (see Fig. 1).

2.5 Conceptual framework to evaluate increases in TA:DIC

The regression models applied to each species could be used to predict calcification rates at higher TA:DIC ratio. We conceptually added alkalinity from the current calcification rate baseline. This baseline was computed for each species using CO2SYS with pCO_2 = 425 ppm and pH_{tot} = 8.1, for the average temperature and salinity for each species rate group, based on their respective OA dataset(s) (see Supplement Table 3). All CO2SYS calculations in this study were carried out with the Python version of CO2SYS (Humphreys et al., 2022) using the stoichiometric dissociation constants for carbonic acid from Sulpis et al. (2020), for sulfuric acid by Dickson et al. (1990) and for total boron from Uppström (1974). From this baseline, TA was added in the form of both NaOH and Na_2CO_3. These two compounds were chosen as they differentially change the carbonate chemistry settings, with NaOH changing TA:DIC in the 1:1 ratio, and Na_2CO_3 inducing a 2:1 TA:DIC change. For example, 10 µmol/kg of NaOH addition will increase TA by 10 µmol/kg and not affect DIC. For Na_2CO_3, 10 µmol/kg addition will increase TA by 10 µmol/kg and increase DIC by 5 µmol/kg. Figure 1 demonstrates the usefulness of this approach. For both NaOH and Na_2CO_3, 10 µmol/kg was conceptually added using the principles of mass balance approach for the carbonate system via CO2SYS. This was repeated for increments of 50 µmol/kg up until a total of 500 µmol/kg (when generating plots; when computing the thresholds, up to 1400 µmol/kg NaOH was added). The new TA:DIC ratios were estimated by adding the direct effect of ΔTA and ΔDIC due to chemical additions of NaOH (assume ΔDIC = 0) or Na_2CO_3 (assume ΔDIC = 0.5*ΔTA). A maximum of 500 µmol/kg was chosen to have more realistic additions of TA that resemble those appropriate within the OAE field trials (e.g. Wang et al., 2023). With the new TA:DIC ratios after TA addition, the species' regression models based on the fitted OA response data were used to compute respective calcification rates (note that added points with NaOH or Na_2CO_3 were not calculated as part of the regression). These data points were all plotted along with the experimental data, regression model and prediction intervals as shown in Fig. 3.

We also determine the amount of NaOH needed to reach pH 9 for each study. This was computed for each species rate group using CO2SYS starting from pCO_2 = 425 ppm and pH_{tot} = 8.1, using ~~for a temperature of 20°C and~~ the average temperature and salinity, and by adding NaOH in increments of 50 µmol/kg until pH 9 was reached. ~~We have conducted this step for all the studies involving negative responders.~~

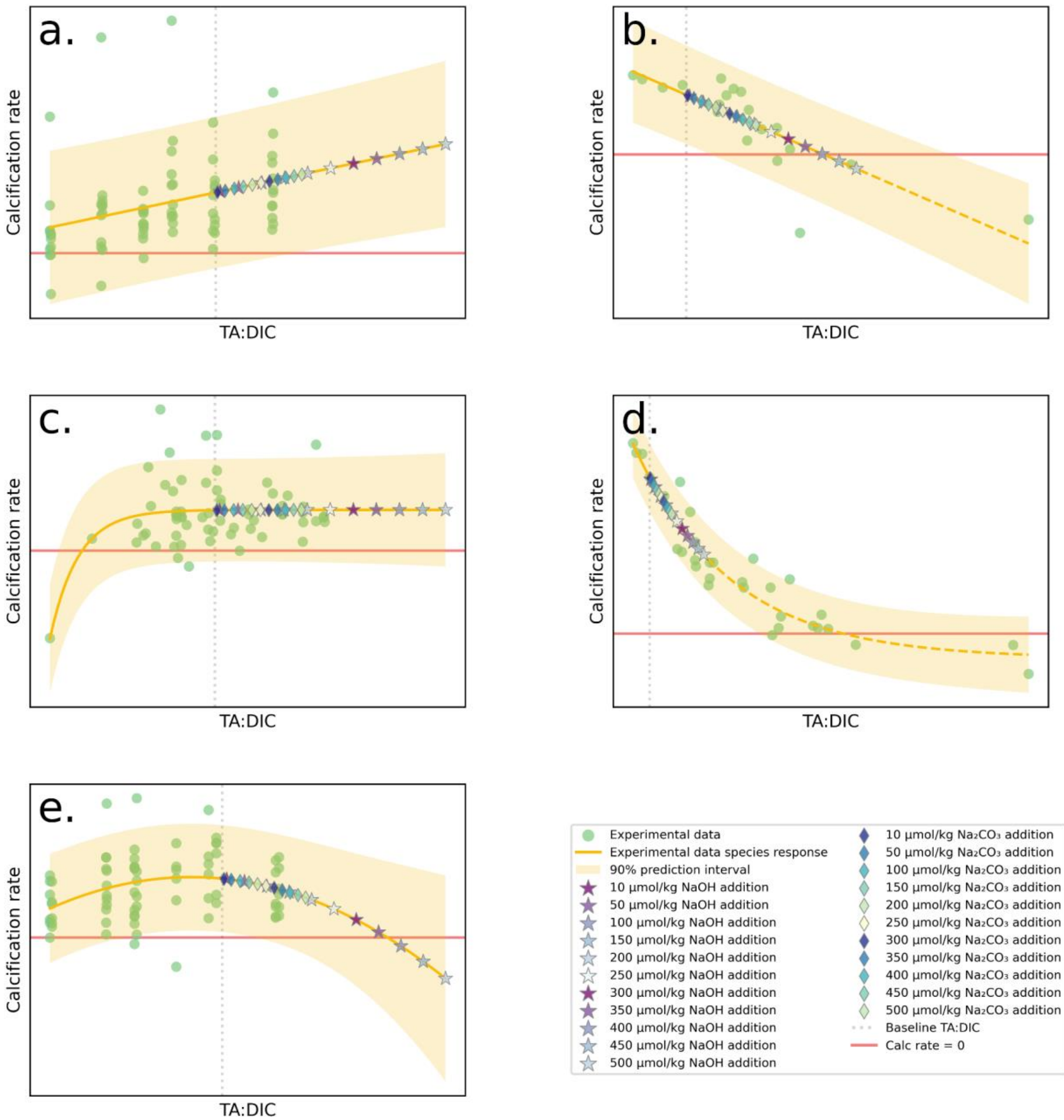
2.6 Evaluation of the biological responses based on alkalinity addition

The species with significant correlations were grouped visually based on their best-fit regression models and are classified into positive, negative, and neutral as the following:

1) *Positive responders*: species with predicted *linear positive* and *threshold positive* calcification rate response with increased TA addition.

2) *Negative responders*: species with predicted *linear negative*, *parabolic* and *threshold negative response* in calcification rate upon (a certain amount of) TA addition. For the parabolic responders, a concentration of NaOH was determined that indicates the threshold in TA:DIC beyond which the response becomes negative (see inflection points in Supplement Table 2).

3) *Neutral responders:* species with *no significant correlation* ($p < 0.05$) in calcification rate upon TA addition.



a.
b.
c.
d.
e.
Calcification rate
TA:DIC
Experimental data
Experimental data species response
90% prediction interval
10 µmol/kg NaOH addition
50 µmol/kg NaOH addition
100 µmol/kg NaOH addition
150 µmol/kg NaOH addition
200 µmol/kg NaOH addition
250 µmol/kg NaOH addition
300 µmol/kg NaOH addition
350 µmol/kg NaOH addition
400 µmol/kg NaOH addition
450 µmol/kg NaOH addition
500 µmol/kg NaOH addition
10 µmol/kg Na_2CO_3 addition
50 µmol/kg Na_2CO_3 addition
100 µmol/kg Na_2CO_3 addition
150 µmol/kg Na_2CO_3 addition
200 µmol/kg Na_2CO_3 addition
250 µmol/kg Na_2CO_3 addition
300 µmol/kg Na_2CO_3 addition
350 µmol/kg Na_2CO_3 addition
400 µmol/kg Na_2CO_3 addition
450 µmol/kg Na_2CO_3 addition
500 µmol/kg Na_2CO_3 addition
Baseline TA:DIC
Calc rate = 0

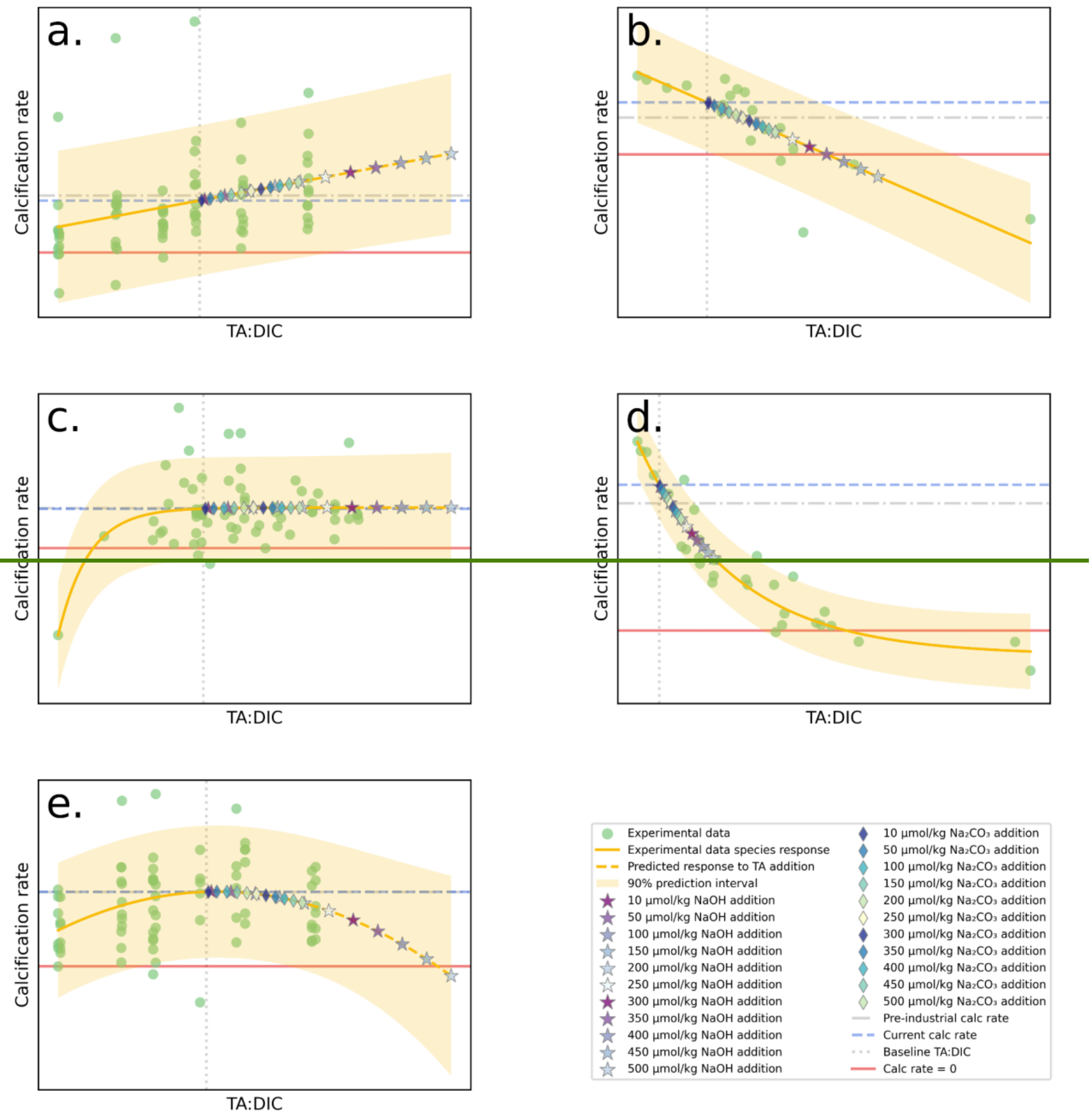


Figure 3*: Conceptual diagrams for five types of responses; a) linear positive; b) linear negative; c) threshold positive; d) threshold negative and e) parabolic response, plotted with experimental data from OA studies (green dots), predicted values at various additions of alkalinity (stars and diamonds), the regression line and prediction error margins fitted for a given species. The red horizontal line indicates zero net dissolution (calcification rate is equal to 0; dissolution rate = calcification rate). The grey vertical line indicates the baseline from which alkalinity is added. ~~The dotted lines indicate the pre-industrial (TA:DIC = 1.16) and current calcification rate (TA:DIC ≃ 1.12), in grey and blue, respectively.~~ NaOH and Na_2CO_3 addition is shown up to 500 µmol/kg.*

2.7 Determining threshold values indicative of negative biological response to OAE

The metrics to evaluate the sensitivity of calcification rate of the negative responders in this study were based on the amount of NaOH or Na_2CO_3 addition required to reduce the current calcification rate by a half. The greater the TA:DIC ratio value to trigger half calcification rate reduction, the less sensitive species was to NaOH addition. We refer to this TA:DIC ratio as the biological threshold, which we also report along with corresponding pH and Ω_{ar} and the associated uncertainty.. TA:DIC thresholds were converted to their respective pH and Ω_{ar}, which are affected by temperature and salinity. To calculate threshold pH and Ω_{ar} we ~~normalized for a temperature of 20°C and~~ used the average temperature and salinity per species rate group, as done for calculating the baseline.~~ This is because most experiments were done at constant salinities, but at varying temperatures.~~

2.8 Extraction of the carbonate chemistry data from the GLODAP dataset

We extracted total alkalinity, dissolved inorganic carbon, Ω_{ar}, and pH_{tot} from the Global Ocean Data Analysis Project GLODAPv2.2023 dataset (https://glodap.info). We used regression in MATLAB with a second-order polynomial equation to predict Ω_{ar} from the TA:DIC. The regression analysis was performed using data from various depth intervals (0–10m, 0–30m, 0–50m, 0–100m, 0–200m) regionally and globally. The regional analysis divided the global oceans into the following groupings: Arctic (north of 65°N), Southern (south of 40°S), North Pacific (north of 40°N), Central Pacific (40°S to 40°N), North Atlantic (North of 40°N), Central Atlantic (40°S to 40°N), and Indian Ocean (north of 40°S).

~~2.9. Calculating calcification in the pre-industrial times~~

~~With respect to the changes since the pre-industrial times, the aim was to examine the difference in calcification between current and pre-industrial, and to what extent NaOH addition is required to compensate for this difference. This was done by first inferring the industrial TA:DIC ratio of 1.16 (Feely et al., 2004) vs. a current TA:DIC of 1.12 (derived based on the current pCO_2 and global pH surface ocean value) and using the regression lines of TA:DIC vs. calcification rate to calculate the corresponding calcification rates (Fig. 3). In the next step, calcification rate was calculated due to the addition of NaOH and Na_2CO_3 from the species-specific baselines (see Method Section 2.5 for detailed explanation), specifically for the positive responders. This was done using the principles of mass balance approach for the carbonate system via CO2SYS, where the carbonate system is calculated for each increment of NaOH or Na_2CO_3 added. The difference between the pre-industrial calcification and current, increased by the NaOH was calculated and compared on the species level.~~

3. Results

3.1 Data collection for the calcification rate responses of different biological groups

We examined 68 datasets, which covered 84 different species that were divided into 11 different groups (Fig. 4). These functional groups were corals (20% of datasets), calcifying algae (18%), mollusks (14%), foraminifera (10%), dinoflagellates (10%), coccolithophores (4%), gastropods (8%), crustaceans (5%), echinoderms (4%), pteropods (5%), and annelids (1%). In the mollusks group, we have separated out the gastropod and pteropod because of a higher number of studies that explicitly cover these two groups. The group of gastropods refers to all gastropods that are not pteropods. If all three groups were combined (mollusks, gastropods, pteropods), this group would be the largest.

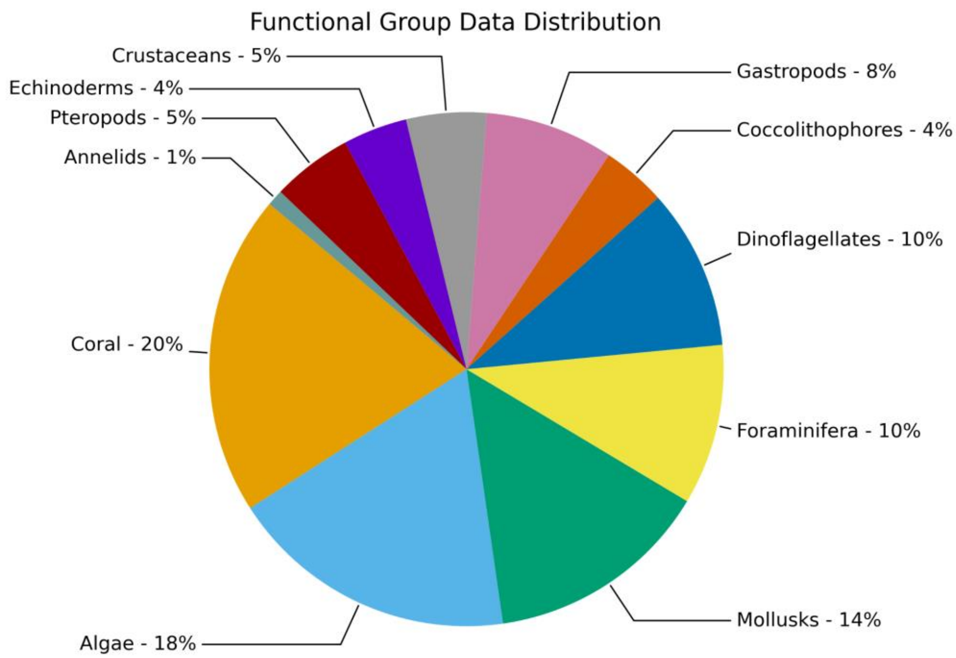


Figure 4: *Percent of studies for multiple groups (N=11) with available data for the calcification rate responses as part of data compilation of 70 studies covering 84 species).*

3.2 Species-specific responses to NaOH/Na_2CO_3 addition

Calcification rate responses of species from different groups were correlated to TA:DIC and summarized to obtain calcification rate response. The calcification rate responses encompassed linear (positive and negative), threshold (positive and negative), parabolic, and neutral responses, with the slope and the intercept of the response determining the type and the magnitude of the response. We present fitted responses of calcification rate per TA:DIC ratio for each examined species (Table 1; Supplement Fig. 4). When possible, we fit a regression to multiple datasets of the same species that used the same units. We also present the response with the additions of NaOH and Na_2CO_3 for each species per examined study and corresponding rate unit and their biological TA:DIC thresholds (Table 2; Supplement Table 4).

Table 1: *The summary of all the OA studies from which the chemical and biological data was collected, including the name of the species and group and the accompanying calcification rate unit. The response for each species rate group~~and rate unit~~ was determined by the regression with the lowest p-value, where the p-value was smaller than 0.05. These responses include p-value, goodness of fit (R^2) and Root Mean Square Error (RMSE) in this table. Non-significant responses are categorized as having a 'neutral' response. The type of response (linear positive or negative, threshold positive or negative, parabolic, and neutral) is indicated, as well as if this response is positive, negative or neutral.*

Studies	n	Group	Species	Rate unit	Response	Pos/Neg/ Neut	p-value	R2	RMSE
Vasquez-Elizondo et al. (2016)	4	Algae	*Amphiroa tribulus*	mmol/m²/hr	neutral	Neutral			
Sinutok et al. (2011)	16	Algae	*Halimeda cylindracea*	mmol/hr	neutral	Neutral			
Comeau et al. (2013)	71	Algae	*Halimeda macroloba*	mmol/g/hr	parabolic	Negative	0.0127	0.1200	0.0028
Meyer et al. (2015)	24	Algae	*Halimeda macroloba*	mmol/m²/hr	neutral	Neutral			
Sinutok et al. (2011)	16	Algae	*Halimeda macroloba*	mmol/hr	parabolic	Negative	0.0108	0.5000	0.0001
Comeau et al. (2013)	62	Algae	*Halimeda minima*	mmol/g/hr	neutral	Neutral			
Meyer et al. (2015)	24	Algae	*Halimeda opuntia*	mmol/m²/hr	linear +	Positive	0.0080	0.2800	0.0222
Comeau et al. (2013)	72	Algae	*Hydrolithon reinboldii*	mmol/g/hr	linear +	Positive	0.0053	0.1100	0.0026
Cornwall et al. (2018)	23	Algae	*Hydrolithon reinboldii*	mmol/m²/hr	neutral	Neutral			
Comeau et al. (2013)	72	Algae	*Lithophyllum flavescens*	mmol/g/hr	neutral	Neutral			
Johnson et al. (2021)	420	Algae	*Lithophyllum sp.*	mmol/g/hr	linear +	Positive	0.0000	0.1000	0.1136
Vasquez-Elizondo et al. (2016)	4	Algae	*Lithothamnion sp.*	mmol/m²/hr	neutral	Neutral			
Monserrat et al. (2022)	62	Algae	*Neogoniolithon brassica-florida*	mmol/m²/hr	neutral	Neutral			
Ries et al. (2009)	42	Algae	*Neogoniolithon sp.*	mmol/g/hr	parabolic	Negative	0.0000	0.4100	0.0003
Vasquez-Elizondo et al. (2016), Comeau et al. (2018)	26	Algae	*Neogoniolithon sp.*	mmol/m²/hr	neutral	Neutral			
Briggs-Carpenter et al. (2019)	425	Algae	*Porolithon onkodes*	mmol/m²/hr	linear +	Positive	0.0010	0.0300	0.8093
Comeau et al. (2018, 2019)	64	Algae	*Sporolithon durum*	mmol/m²/hr	parabolic	Negative	0.0012	0.2000	0.1704
Ries et al. (2009)	41	Annelid	*Hydroides crucigera*	mmol/g/hr	neutral	Neutral			
Fiorini et al. (2011), Langer et al. (2006, 2011)	14	Cocco.	*Calcidiscus leptoporus*	mmol/#/hr	neutral	Neutral			
*	233	Cocco.	*Emiliania huxleyi*	mmol/#/hr	parabolic	Negative	0.0000	0.1600	0.0000
Casareto et al. (2009)	14	Cocco.	*Pleurochrysis carterae*	mmol/m³/hr	neutral	Neutral			
White et al. (2018)	118	Cocco.	*Pleurochrysis carterae*	mmol/#	neutral	Neutral			
Meyer et al. (2016)	24	Coral	*Acropora millepora*	mmol/m²/hr	neutral	Neutral			
Camp et al. (2017), Comeau et al. (2013)	74	Coral	*Acropora pulchra*	mmol/m²/hr	parabolic	Negative	0.0000	0.2900	1.3257
Agostini et al. (2021)	18	Coral	*Acropora solitaryensis*	mmol/m²/hr	neutral	Neutral			
Comeau et al. (2018), Comeau et al. (2019)	81	Coral	*Acropora yongei*	mmol/m²/hr	linear +	Positive	0.0000	0.2900	1.9447
Bove et al. (2020)	27	Coral	*Duncanopsammia axifuga*	mmol/m²/hr	linear +	Positive	0.0016	0.3300	5.0785
Cornwall et al. (2018)	44	Coral	*Goniopora sp.*	mmol/m²/hr	neutral	Neutral			
Maier et al. (2009)	237	Coral	*Lophelia pertusa*	mmol/g/hr	linear +	Positive	0.0030	0.0400	0.0002
Bove et al. (2020)	65	Coral	*Montastraea cavernosa*	mmol/m²/hr	linear +	Positive	0.0154	0.0900	0.5047
Ries et al. (2009)	54	Coral	*Oculina arbuscula*	mmol/g/hr	parabolic	Negative	0.0000	0.8600	0.0001
Comeau et al. (2013)	72	Coral	*Pavona cactus*	mmol/m²/hr	parabolic	Negative	0.0002	0.2200	0.9093
Comeau et al. (2019)	49	Coral	*Plesiastrea versipora*	mmol/m²/hr	linear +	Positive	0.0069	0.1500	0.6003
Brown et al. (2022)	4	Coral	*Pocillopora damicornis*	mmol/g/hr	neutral	Neutral			
Comeau et al. (2013, 2018), Putnam-Gates et al. (2015)	117	Coral	*Pocillopora damicornis*	mmol/m²/hr	neutral	Neutral			
Evensen-Edmunds et al. (2016)	60	Coral	*Pocillopora verrucosa*	mmol/m²/hr	linear +	Positive	0.0132	0.1000	0.8297
Agostini et al. (2021)	18	Coral	*Porites heronensis*	mmol/m²/hr	neutral	Neutral			
Comeau et al. (2013)	72	Coral	*Porites rus*	mmol/m²/hr	linear +	Positive	0.0020	0.1300	2.0281
Okazaki et al. (2013)	75	Coral	*Siderastrea radians*	mmol/m²/hr	linear +	Positive	0.0004	0.1600	2.7886
Okazaki et al. (2013)	64	Coral	*Solenastrea hyades*	mmol/m²/hr	threshold +	Positive	0.0004	0.2300	2.0385
Krueger et al. (2017)	36	Coral	*Stylophora pistillata*	mmol/m²/hr	neutral	Neutral			
Pansch et al. (2014)	36	Crust.	*Amphibalanus improvisus*	mmol/g/hr	linear +	Positive	0.0000	0.4300	0.0004
Ries et al. (2009)	36	Crust.	*Callinectes sapidus*	mmol/g/hr	linear -	Negative	0.0000	0.4000	0.0082
Ries et al. (2009)	18	Crust.	*Homarus americanus*	mmol/g/hr	linear -	Negative	0.0014	0.4800	0.0079
Ries et al. (2009)	12	Crust.	*Penaeus plebejus*	mmol/g/hr	linear -	Negative	0.0124	0.4800	0.0006
Findlay et al. (2010)	6	Crust.	*Semibalanus balanoides*	mmol/g/hr	neutral	Neutral			
Tatters et al. (2013)	45	Dino.	*Alexandrium sp.*	1/hr	neutral	Neutral			
Hansen et al. (2007)	19	Dino.	*Ceratium lineatum*	#/hr	linear -	Negative	0.0000	0.6700	0.0043
Tatters et al. (2013)	45	Dino.	*Gonyaulax sp.*	1/hr	neutral	Neutral			
Hansen et al. (2007)	31	Dino.	*Heterocapsa triquetra*	#/hr	threshold -	Negative	0.0000	0.9100	0.0027
Wang et al. (2019)	4	Dino.	*Karenia mikimotoi*	1/hr	neutral	Neutral			
Tatters et al. (2013)	45	Dino.	*Lingulodinium polyedrum*	1/hr	neutral	Neutral			
Tatters et al. (2013)	45	Dino.	*Prorocentrum micans*	1/hr	neutral	Neutral			
Hansen et al. (2007)	21	Dino.	*Prorocentrum minimum*	#/hr	threshold -	Negative	0.0000	0.8800	0.0019

Studies	n	Group	Species	Rate unit	Response	Pos/Neg/ Neut	p-value	R2	RMSE
Brading et al. (2011)	175	Dino.	*Symbiodinium sp.*	#/hr	linear -	Negative	0.0010	0.0600	0.0066
Van de Waal et al. (2013)	12	Dino.	*Thoracosphaera heimii*	mmol/hr	parabolic	Negative	0.0002	0.8500	0.0000
Ries et al. (2009)	17	Echino.	*Arbacia punctulata*	mmol/g/hr	parabolic	Negative	0.0000	0.8900	0.0003
Courtney et al. (2013)	4	Echino.	*Echinometra viridis*	%/hr	linear +	Positive	0.0244	0.9500	2.3854
Courtney et al. (2015)	28	Echino.	*Echinometra viridis*	%	linear +	Positive	0.0009	0.3500	13.0388
Ries et al. (2009)	18	Echino.	*Eucidaris tribuloides*	mmol/g/hr	threshold +	Positive	0.0000	0.8400	0.0004
Keul et al. (2013)	205	Foram.	*Ammonia sp.*	mmol/#/hr	linear -	Negative	0.0277	0.0200	0.0000
Prazeres et al. (2015)	32	Foram.	*Amphistegina lessonii*	%/hr	parabolic	Negative	0.0008	0.3900	0.0010
Kisakurek et al. (2011)	16	Foram.	*Globigerinella siphonifera*	mmol/hr	neutral	Neutral			
Kisakurek et al. (2011)	14	Foram.	*Globigerinoides ruber*	mmol/#/hr	neutral	Neutral			
Reymond et al. (2013)	179	Foram.	*Marginopora rossi*	%/hr	linear +	Positive	0.0000	0.1900	0.0090
Uthicke-Fabricius et al. (2012)	47	Foram.	*Marginopora vertebralis*	mmol/g/hr	threshold +	Positive	0.0000	0.4000	0.0004
Sinutok et al. (2011)	16	Foram.	*Marginopora vertebralis*	mmol/hr	neutral	Neutral			
Prazeres et al. (2015)	32	Foram.	*Marginopora vertebralis*	%/hr	linear -	Negative	0.0006	0.3300	0.0005
Manno et al. (2012)	192	Foram.	*Neogloboquadrina pachyderma*	mmol/#/hr	linear +	Positive	0.0000	0.7100	0.0000
Oron et al. (2020)	96	Foram.	*Operculina ammonoides*	mmol/g/hr	linear -	Negative	0.0031	0.0900	0.0017
Manriquez et al. (2016)	74	Gastropod	*Concholepas concholepas*	mmol/g/hr	linear +	Positive	0.0000	0.2400	0.0009
Noisette et al. (2016), Ries et al. (2009)	173	Gastropod	*Crepidula fornicata*	mmol/g/hr	parabolic	Negative	0.0000	0.2100	0.0028
Garilli et al. (2015)	68	Gastropod	*Cyclope neritea*	mmol/g/hr	linear -	Negative	0.0020	0.1400	0.0037
Ries et al. (2009)	42	Gastropod	*Littorina littorea*	mmol/g/hr	linear +	Positive	0.0001	0.3400	0.0002
Bibby et al. (2007)	4	Gastropod	*Littorina littorea*	µm (shell thickness)	neutral	Neutral			
Garilli et al. (2015)	315	Gastropod	*Nassarius corniculus*	mmol/g/hr	parabolic	Negative	0.0000	0.2500	0.0064
Ries et al. (2009)	21	Gastropod	*Strombus alatus*	mmol/g/hr	linear +	Positive	0.0000	0.6400	0.0001
Ries et al. (2009)	33	Gastropod	*Urosalpinx cinerea*	mmol/g/hr	linear +	Positive	0.0000	0.5700	0.0001
Ries et al. (2009)	18	Mollusks	*Argopecten irradians*	mmol/g/hr	linear +	Positive	0.0097	0.3500	0.0002
Ramajo et al. (2016)	6	Mollusks	*Argopecten purpuratus*	mmol/g/hr	neutral	Neutral			
Zhang et al. (2011)	5	Mollusks	*Azumapecten farreri*	mmol/g/hr	linear +	Positive	0.0106	0.9200	0.0001
Ong et al. (2017)	24	Mollusks	*Cerastoderma edule*	mmol/g/hr	neutral	Neutral			
Sordo et al. (2021)	27	Mollusks	*Chamelea gallina*	mmol/g/hr	neutral	Neutral			
Gazeau et al. (2007)	20	Mollusks	*Crassostrea gigas*	mmol/g/hr	linear +	Positive	0.0001	0.6100	0.0000
Ries et al. (2009), Waldbusser et al. (2011)	28	Mollusks	*Crassostrea virginica*	mmol/g/hr	threshold +	Positive	0.0000	0.5600	0.0003
Ries et al. (2009)	25	Mollusks	*Mercenaria mercenaria*	mmol/g/hr	threshold +	Positive	0.0000	0.8300	0.0000
Ries et al. (2009)	14	Mollusks	*Mya arenaria*	mmol/g/hr	linear +	Positive	0.0001	0.7300	0.0003
Ninokawa et al. (2020)	13	Mollusks	*Mytilus californianus*	mmol/m²/hr	neutral	Neutral			
Ries et al. (2009), Gazeau et al. (2007)	86	Mollusks	*Mytilus edulis*	mmol/g/hr	linear +	Positive	0.0119	0.0700	0.0002
Gazeau et al. (2014)	11	Mollusks	*Mytilus galloprovincialis*	mmol/g/hr	neutral	Neutral			
Gazeau et al. (2014)	5	Mollusks	*Mytilus galloprovincialis*	mmol/m³/hr	neutral	Neutral			
Cameron et al. (2019)	30	Mollusks	*Pecten maximus*	mmol/g/hr	neutral	Neutral			
Comeau et al. (2010b)	5	Pteropod	*Cavolinia inflexa*	mm (shell length)	neutral	Neutral			
Comeau et al. (2009, 2010a)	12	Pteropod	*Limacina helicina*	mmol/g/hr	linear +	Positive	0.0000	0.8500	0.0001
Lischka et al. (2011, 2012)	119	Pteropod	*Limacina helicina*	mm (shell length)	threshold +	Positive	0.0003	0.1300	0.1303
Bednarsek (2021a), Mekkes et al. (2021)	117	Pteropod	*Limacina helicina*	µm (shell thickness)	parabolic	Negative	0.0000	0.1800	0.0038
Lischka et al. (2012)	28	Pteropod	*Limacina retroversa*	mm (shell length)	neutral	Neutral			

*Barcelos-Ramos et al. (2010), Fiorini et al. (2011), Iglesias-Rodriguez et al. (2008), Richier et al. (2011), Sciandra et al. (2003), Stoll et al. (2012), Gafar et al. (2018), Bach et al. (2011), Sett et al. (2014).

Within each of the 11 functional groups, several categories of calcification response occur within each functional group, with the most varied being the group of dinoflagellates and foraminifera, both showing 4 or 5 different categories of calcification responses (Fig. 5). Of the six types of responses of calcification rate vs. TA:DIC, 28% were linear positive (N=27), 9% linear negative (N=9), 6% threshold positive (N=6), 2% threshold negative (N=2), 14% parabolic (N=14) and 41% neutral (N=40).

Such responses could be further summed up into positive (linear and threshold positive), negative (linear and threshold negative, parabolic) and neutral responses (Fig. 6) when generalized across the calcification rate against the TA:DIC ratio. A summary of responses includes 34.0% positive

(N=33), 25.8% negative (N=25), while 40.2% show a neutral response (N=39).

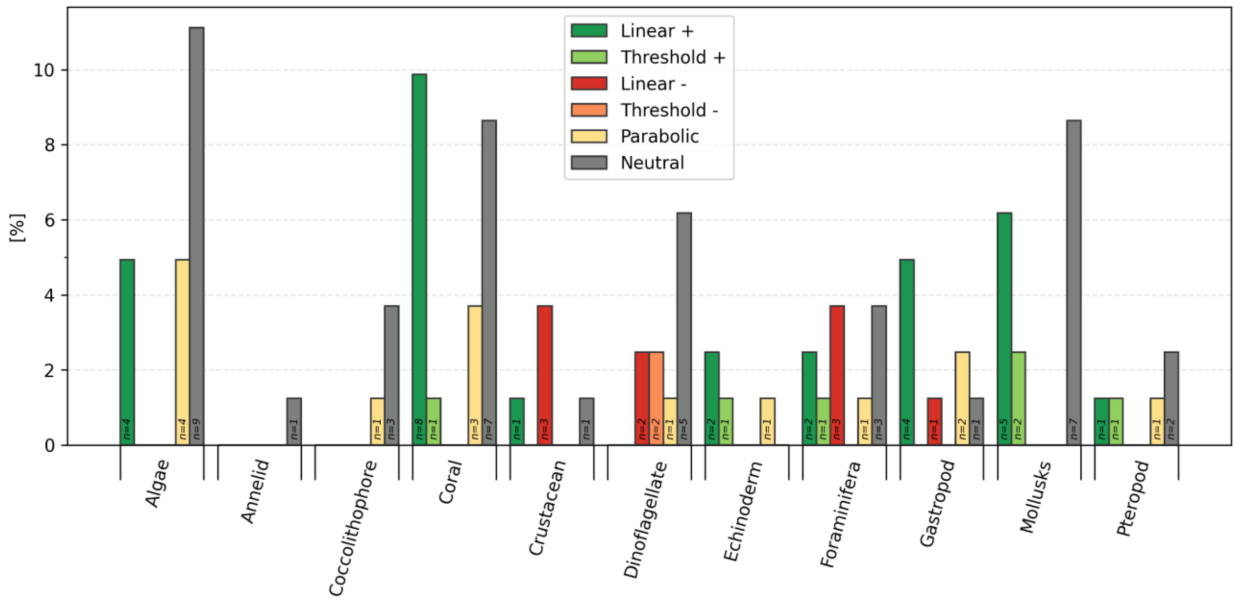


Figure 5: *Categories of calcification rate responses and percentage (%) response across eleven groups (calcifying algae, annelids, coccolithophores, corals, crustaceans, dinoflagellate, echinoderms, foraminifera, gastropods, mollusks, pteropods). The number on the bar indicates the number of studies of species included.*

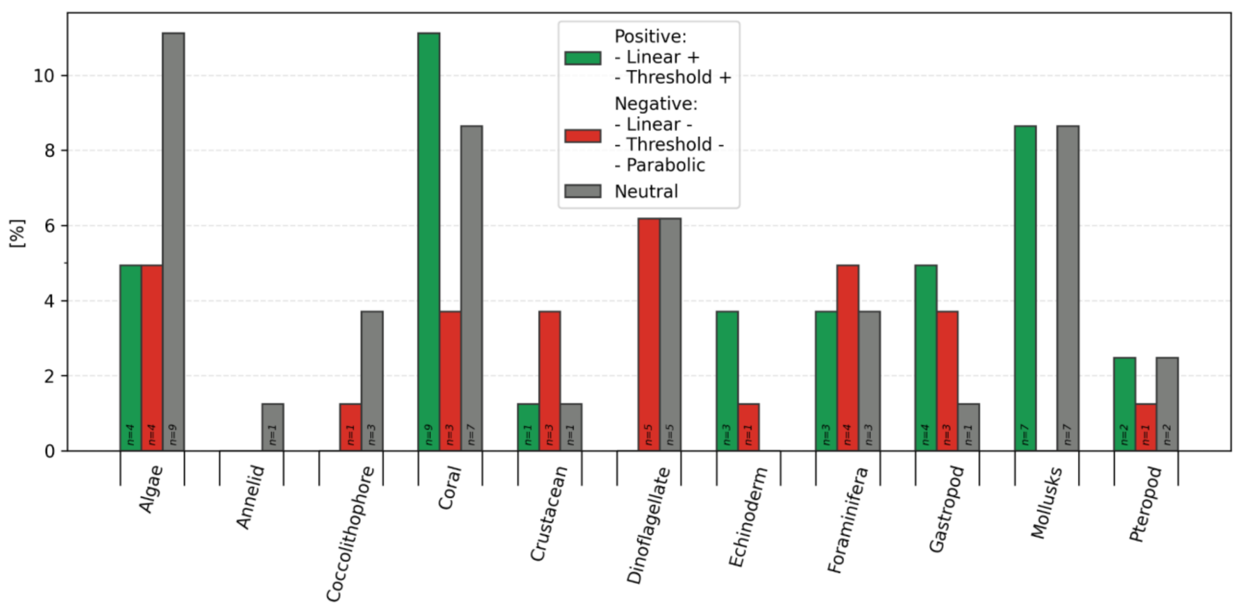


Figure 6: *Summary of percentage (%) responses in calcification rates as positive (linear and threshold positive), negative (linear and threshold negative, parabolic) and neutral across eleven groups (calcifying algae, annelids, coccolithophores, corals, crustaceans, dinoflagellate,*

echinoderms, foraminifera, gastropods, mollusks, pteropods). The number on the bar indicates the number of studies with species included.

3.3 Evaluation of the responses to NaOH/Na_2CO_3 additions

Upon added TA, the calcification rate in positive responders will increase, either in a linear or threshold positive response, where calcification plateaus, with the concentration being dependent on the species-specific rate of response (Fig. 2; Supplement Fig. 4). The negative responders (linear or threshold negative and parabolic) will be negatively impacted as follows: first, for the linear negative responders, addition of the Na_2CO_3 will linearly decrease calcification rate, but there is no associated threshold to it; second, for the threshold negative responders, calcification rate will decline in an exponential way until reaching a TA:DIC value where the response plateaus; and third, for the parabolic responders, the calcification rate will initially increase until reaching a certain TA:DIC threshold upon which calcification starts declining. The TA:DIC thresholds for negative responders are species-specific (Table 2; Supplement Table 4).

3.4 Threshold values indicative of negative biological response to OAE

The TA:DIC biological thresholds in Table 2 are determined by the amount of NaOH addition required to reduce calcification rate by a half (see Supplement Table 4 for Na_2CO_3 thresholds). These thresholds demonstrate the range of carbonate chemistry conditions over which the negative biological effects of OAE deployment might occur and are shown alongside the corresponding pH and Ω_{ar}. Uncertainties are higher for the experimental studies where the experimental temperature and salinity ranges were high (see Supplement Table 5), seeing as we use the average for each species rate group to compute the baseline and thresholds. ~~was much lower or higher than the 20°C we assume to calculate the thresholds. Experiments done at temperatures below 10°C include mainly pteropods and crustaceans, whereas experiments done at temperatures above 30°C were mainly for algae.~~

For the negative responders, TA:DIC thresholds range from 1.11~~3~~ to 1.74. The majority of species have reached their thresholds by an~~elow the~~ addition of 500 µmol/kg NaOH, though for 3~~6~~ species a NaOH addition of more than 500 µmol/kg is required to cross the thresholds in the TA:DIC range of 1.39~~8~~ to 1.74. The most sensitive species include Crepidula fornicata (gastropod), Limacina helicina (pteropod), *Neogoniolithon sp.* (algae), Homarus americanus~~*Ceratium lineatum*~~ (crustacean~~dinoflagellate~~) and~~,~~ *Oculina arbuscula* (coral) ~~and *Amphistegina lessonii* (foraminifera)~~, reaching their thresholds by ~~below 2~~100 µmol/kg addition of NaOH. Overall, gastropods and pteropods are the most sensitive groups, followed by algae and crustaceans, all requiring less than 200 µmol/kg addition of NaOH to reach their thresholds. ~~generally require between 5100 and 2300 µmol/kg to reach their thresholds.~~ Foraminifera, dinoflagellates ~~corals~~ and coccolithophores are the most resilient~~least sensitive~~ groups, with the linear negative responder *Ammonia sp.* of the foraminifera group requiringthe highest NaOH addition of 14~~5~~00 µmol/kg to reduce calcification rate in half.

For some negative responders (Arbacia punctulata, Nassarius corniculus and Penaeus plebejus), the baseline from which NaOH addition occurs was outside of the range of the experimental data and very close to a calcification rate of 0. These were omitted from Table 2 since our defined threshold does not give an accurate representation of their sensitivity to alkalinity addition.

Table 2: *Studies with negative responders (linear and threshold negative, parabolic) with demonstrated TA:DIC thresholds, indicating the amount of NaOH needed to halve the current calcification rate (i.e. at the baseline). The value for TA:DIC threshold is used to determine the pH and* Ω_{ar} *(at average temperature and average salinity per species). See Supplement Table 4 for* Na_2CO_3 *thresholds.*

Studies	Group	Species	Temp (°C)	Salinity	Rate unit	Threshold	TA addition	pH at threshold	ΔpH from baseline	Ω_{ar} at threshold	Exposure time
~~Ries et al. (2009)~~	~~Echinoderm~~	~~*Arbacia punctulata*~~	~~25.01~~	~~31.78~~	~~mmol/g/hr~~	~~1.15~~	~~10~~	~~8.11~~	~~0.01~~	~~4.40~~	~~60 days~~
~~Garilli et al. (2015)~~	~~Gastropod~~	~~*Nassarius corniculus*~~	~~22.16~~	~~38.00~~	~~mmol/g/hr~~	~~1.16~~	~~10~~	~~8.11~~	~~0.01~~	~~4.52~~	~~3 weeks~~
Noisette et al. (2016), Ries et al. (2009)	Gastropod	*Crepidula fornicata*	15.31	34.33	mmol/g/hr	1.13	50	8.17	0.07	3.77	6 months 60 days
Bednarsek (2021a), Mekkes et al. (2021)	Pteropod	*Limacina helicina*	10.50	32.34	µm (shell thickness)	1.11	50	8.19	0.09	3.07	-
Ries et al. (2009)	Algae	*Neogoniolithon sp.*	25.00	31.70	mmol/g/hr	1.17	50	8.16	0.06	4.87	60 days
~~Ries et al. (2009)~~	~~Crustacean~~	~~*Penaeus plebejus*~~	~~25.00~~	~~31.95~~	~~mmol/g/hr~~	~~1.17~~	~~50~~	~~8.16~~	~~0.06~~	~~4.89~~	~~60 days~~
Ries et al. (2009)	Crustacean	*Homarus americanus*	25.02	31.96	mmol/g/hr	1.19	100	8.22	0.12	5.49	60 days
Ries et al. (2009)	Coral	*Oculina arbuscula*	25.01	31.61	mmol/g/hr	1.19	100	8.22	0.12	5.46	60 days
Prazeres et al. (2015)	Foraminifera	*Amphistegina lessonii*	24.18	33.46	%/hr	1.21	150	8.27	0.17	6.10	30 days
Ries et al. (2009)	Crustacean	*Callinectes sapidus*	25.00	31.95	mmol/g/hr	1.23	200	8.32	0.22	6.71	60 days
Hansen et al. (2007)	Dinoflagellate	*Ceratium lineatum*	15.00	30.00	#/hr	1.18	200	8.38	0.28	5.15	14 d acclimation to irradiance; 7 days acclimation to experimental conditions; 14 days exposure to irradiance; 22 days stationary growth phase
Garilli et al. (2015)	Gastropod	*Cyclope neritea*	21.93	38.00	mmol/g/hr	1.23	200	8.31	0.21	6.61	-
Sinutok et al. (2011)	Algae	*Halimeda macroloba*	27.23	36.27	mmol/g/hr	1.26	200	8.30	0.20	7.38	2 weeks acclimation, 2 weeks incubation
Comeau et al. (2019)	Algae	*Sporolithon durum*	20.60	35.87	mmol/m**2/hr	1.22	200	8.32	0.22	6.31	27 weeks
Van de Waal et al. (2013)	Dinoflagellate	*Thoracosphaera heimii*	15.00	34.00	mmol/hr	1.23	300	8.46	0.36	6.56	21 days acclimation, 8 days experiment = total of >10 generations
Oron et al. (2020)	Foraminifera	*Operculina ammonoides*	25.00	37.00	mmol/g/hr	1.33	400	8.46	0.36	9.44	65 - 120 hours
Brading et al. (2011)	Dinoflagellate	*Symbiodinium sp.*	26.00	35.00	#/hr	1.33	400	8.47	0.37	9.54	2 weeks
Prazeres et al. (2015)	Foraminifera	*Marginopora vertebralis*	24.18	33.46	%/hr	1.33	450	8.53	0.43	9.78	30 days
Camp et al. (2017), Comeau et al. (2013)	Coral	*Acropora pulchra*	27.30	36.27	mmol/m^2/hr	1.38	500	8.52	0.42	11.05	n/a (natural conditions) 2 weeks acclimation; 2 weeks incubation
Hansen et al. (2007)	Dinoflagellate	*Heterocapsa triquetra*	15.00	30.00	#/hr	1.30	500	8.66	0.56	8.81	14 d acclimation to irradiance; 7 days acclimation to experimental conditions; 14 days exposure to irradiance; 22 days stationary growth phase
Comeau et al. (2013)	Coral	*Pavona cactus*	27.23	36.28	mmol/m^2/hr	1.38	500	8.52	0.42	11.03	2 weeks acclimation; 2 weeks incubation
Hansen et al. (2007)	Dinoflagellate	*Prorocentrum minimum*	15.00	30.00	#/hr	1.39	700	8.81	0.71	11.35	14 d acclimation to irradiance; 7 days acclimation to experimental conditions; 14 days exposure to irradiance; 22 days stationary growth phase
*	Coccolithophore	*Emiliania huxleyi*	17.30	35.12	mmol/#/hr	1.46	850	8.83	0.73	13.65	**
Keul et al. (2013)	Foraminifera	*Ammonia sp.*	26.00	32.75	mmol/#/hr	1.74	1400	9.11	1.01	22.27	59-96 days of culturing

*Barcelos-Ramos et al. (2010), Fiorini et al. (2011), Iglesias-Rodriguez et al. (2008), Richier et al. (2011), Sciandra et al. (2003), Stoll et al. (2012), Gafar et al. (2018), Bach et al. (2011), Sett et al. (2014).

**26hrs, Acclimation for 7 generations, experiment/sampling for 2-3 generations, n/a, 8 days, 16 days, Acclimation for 12 generations, Pre-acclimation for 8-12 generations, 9 generations, Acclimated for at ~7 generations (5-15 days)

~~3.5 Comparison of current vs. pre-industrial calcification rates~~

~~To understand the extent to which OAE offsets the negative effects induced by OA, we have focused on positive (linear and thresholdexponential) responders from this study, which were negatively impacted by OA. Comparing their average pre-industrial calcification rate to the rates induced by OAE, we note that the change depends on the category of response (Supplement Fig. 3): in the species with the threshold positive rate, calcification is similar for the pre-industrial and current conditions. This is likely because this type of response retains maximum calcification rate across greater TA:DIC range, with species not being affected in their calcification by the changes occurring since pre-industrial times. On the other hand, linear positive calcifiers seem to be more severely impacted and current calcification rates are substantially lower compared to the pre-industrial calcification rates. It follows that for the positive linear responders, an increase using NaOH would compensate for the calcification rate loss since the pre-industrial times. For most of the investigated linear responders, there would have to be a NaOH addition of 50 to 100 µmol/kg (up to 0.2 ΔpH) to fully compensate for the difference between the pre-industrial and current conditions. However, two species *Amphibalanus improvisus* and *Azumapecten farreri* require up to 200 µmol/kg NaOH (up to 0.4 ΔpH), while some species, i.e. the coral *Siderastrea radians* might return to the levels of the pre-industrial calcification by a much smaller NaOH amount, less than 50 µmol/kg NaOH.~~

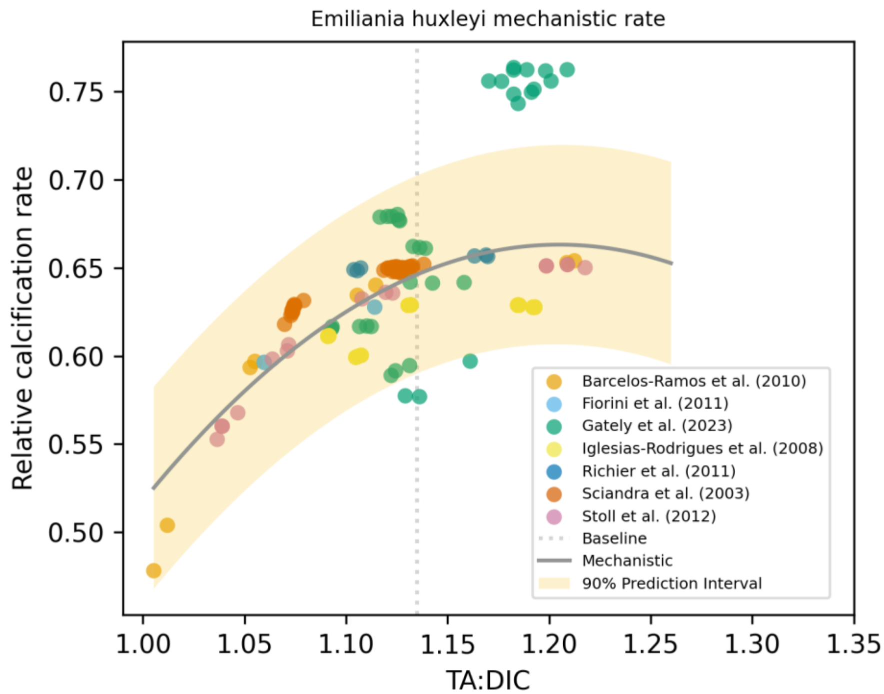
3.5 pH 9 threshold

We also compute how much NaOH needs to be added before reaching a pH threshold of 9, as per the US Environmental Protection Agency's rule for waste water not exceeding a pH of 9 when entering the coastal ocean (see NPDES manual, 2010). This amount averages at 1200 µmol/kg of NaOH for all species. For some species (Amphibalanus improvisus, Neogloboquadrina pachyderma, Limacina helicina, Limacina retroversa, Lophelia pertusa, and Semibalanus balanoides) this threshold was reached below 1000 µmol/kg, with Amphibalanus improvisus requiring the lowest amount of NaOH addition at 750 µmol/kg.

3.6 Comparing calcification mechanisms with the empirical studies

This study establishes the predictions of responses that ultimately need to be validated by field or experimental studies, this being the most pertinent for highly sensitive species. A good alternative to validating the predicted responses is to use species-specific mechanistic responses, which should be inherently more accurate than just empirical responses. Here, we compared the obtained results of this study with the predicted mechanistic relationship to determine to what extent mechanistic relationships can contribute to improved, i.e. more accurate and certain, OAE predictions.

For *Emiliania huxleyi*, we used the experimental TA and DIC data to calculate the [HCO_3^-], [H^+] and [CO_2] concentrations. Using the mechanistic rate equation from Bach et al. (2015) and their computed sensitivity parameters, we calculated and plotted the rate derived via mechanistic approach. We applied linear, polynomial (second-order) and exponential regressions and chose the best fit based on the lowest p-value, using the same method as for our experimental calcification rate data regressions. Like the mechanistic rate regression, our experimental calcification rate also shows a significant parabolic relationship for *Emiliania huxleyi* (see Fig. 9). However, when using the same approach for another coccolithophore species *Calcidiscus leptoporus* (Bach et al., 2015), our best fit did not align with the proposed mechanistic response; instead, a non-significant relationship was obtained using experimental data (Supplement Fig. 5). Such comparisons reveal species-specific relationships that are likely dependent on a lot of parameters, with one equation alone not being operable among different species from different regional settings.



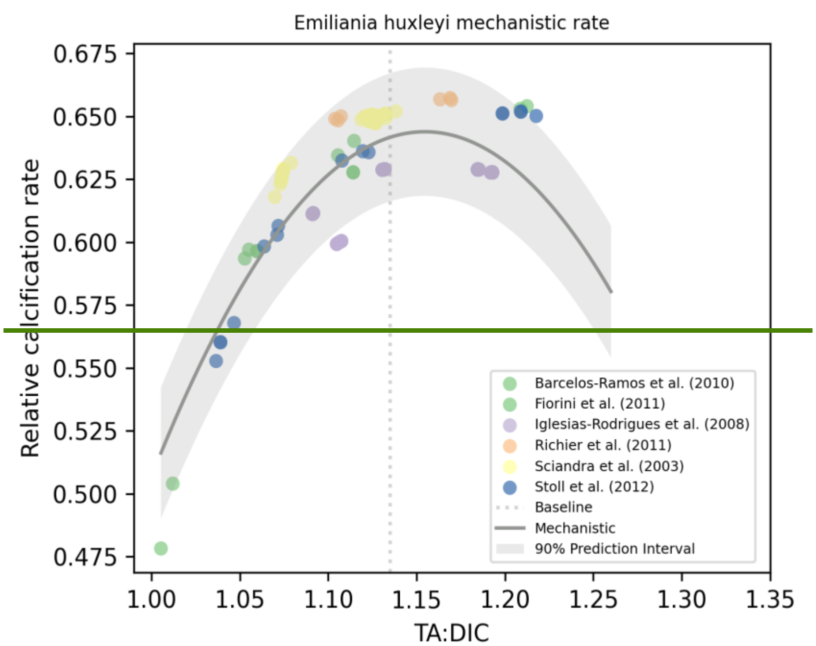


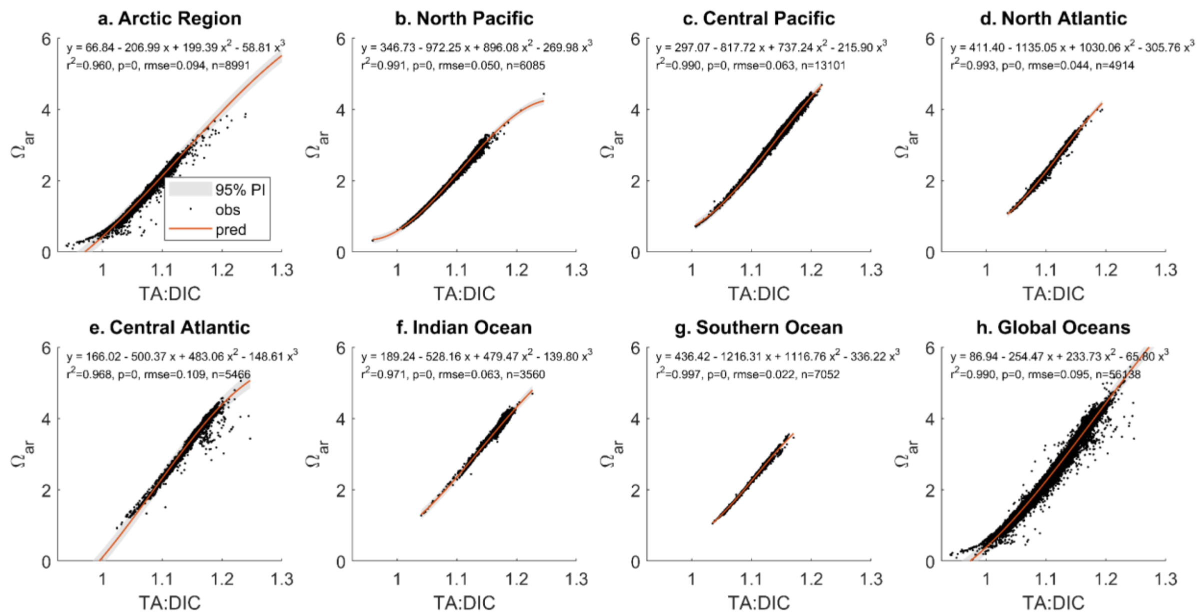
Figure 9: Mechanistic rate equation and parameters (a = 9.56e-1, b = 7.04e-4 mol/kg, c = 2.1e6 kg/mol, d = 8.27e6 kg/mol) taken from Bach et al. (2015) and fitted using experimental data for E. huxleyi (used data from the studies indicated in legend). Shading represents the 90% prediction interval.

For most species, we must still rely on empirical, single-parameter relationships, including saturation state, bicarbonate ion concentration and the substrate-to-inhibitor ratio (SIR) (i.e. the bicarbonate ion to hydrogen ion concentration ratio). When comparing empirical data from the experiments involving the mollusk, coral and coccolithophore groups against the SIR ratio, we found large discrepancies between this and SIR-proposed mechanisms (Supplement Fig. 6). For most of the coccolithophore group, the experimental rate regressions cannot be explained using SIR mechanisms. Only in the case of Calcidiscus leptoporus, the experimental and mechanistic responses remain the same. Reasons for these discrepancies could potentially be that SIR might insufficiently include the multitude of biological processes involved in the calcification (e.g. how carbon is provisioned or the ability to regulate calcifying fluid pH), as well as other environmental parameter variations. For mollusks, a quarter of the mechanistic rate regressions based on the SIR agreed with the experimental calcification rate regressions. The other 75% did not, especially for the studies with experimental conditions of $\Omega ar > 1$. For corals, the majority of coral species (N=14) were classified as having a linear positive mechanistic relationship when using SIR relationships. When comparing this to our experimental rate regressions, we only found agreements with the mechanistic regressions in 6 out of 18 species.

3.7 Global and regional carbonate chemistry data coverage based on GLODAP datasets

The compilation of chemical observational data (pH, Ωar, TA, DIC) was done for the GLODAP data across the regional ocean and global scales to determine the range of Ωar, TA and DIC (as represented by the TA:DIC ratio) and TA:DIC vs Ωar correlation down to the depths averaged over 200 m. This allows us to apply the thresholds even for the regions for which we do not have sufficient or reliable data or experimental coverage, making the inferences about the OAE impact even in those regions.

Here, we focus on showing the results ranging over the 0–50m because this covers most of the biological habitat for examined species and it is where the OAE enhancement would induce the greatest changes. Over the 0–50 m depth, Ωar ranges from 0.2 to 5 and TA:DIC ranges from 0.1 to 1.25 and both parameters are correlated across all the regions, as demonstrated by the fitted second-order polynomial regressions, with $R2$ of 0.96 or higher, and all the correlations being significant (Fig. 7), with regional specific relationships not impacting the fit. All the correlation parameters are presented in Supplement Table 4. Similar fits were found at different depths. The conditions in the higher latitude regions are located at the lower range of Ωar vs TA:DIC, while the conditions in the low latitudes and temperate regions are at the upper range, with the highest values present in the central Atlantic and Pacific region. Such strong correlation as observed for Ωar vs TA:DIC does not exist with pH, regardless of the depth interval examined. While the correlations are still significant, they are broadly distributed and represented over a shorter TA:DIC range, with significantly lower goodness of fit (Supplement Fig. 4), with the correlations being highly regionally dependent due to pH and temperature co-linearity. Because of this, all further biological analyses are only done using the Ωar vs TA:DIC ratio.



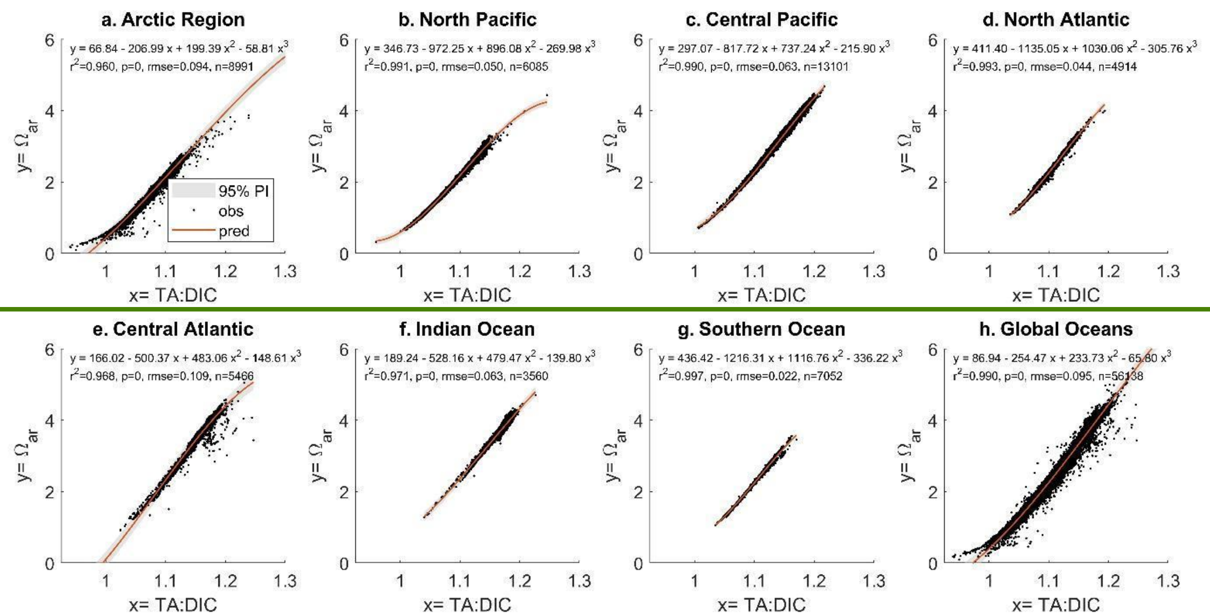


Figure 7: The range of observed Ωar and TA and DIC values (as represented by the TA:DIC ratio) values and the relationship with the best fitted curve between Ωar vs TA:DIC across regional (a-g) and global (h) scales based on the observational GLODAP dataset averaged over 0-50 m depth.

3.8 TA:DIC vs Ωar for experimental data and GLODAP

We compared the ranges of TA:DIC and Ωar of biological experimental data with field biogeochemical data (GLODAP) to examine if similar range of conditions and TA:DIC correlations are applicable over a broader, global dataset. For this, we plotted Ωar vs TA:DIC along with the GLODAP regression line for Ωar vs TA:DIC (Fig. 8). For each TA and DIC datapoint, the salinity and temperature specific to that data point were used to compute Ωar. We show the similarity in the conditions, which gives the validity of our experimentally derived thresholds to be extrapolated within the global GLODAP dataset.

Figure 8 also shows that various biological groups are clustered around specific TA:DIC ratios, for example, mollusks, coral and coccolithophores are represented on the lower, mid, and higher TA:DIC spectra, respectively, while dinoflagellates are randomly scattered off the TA:DIC line. This indicates that there is a general lack of data distribution in the upper ranges of TA:DIC ratio, especially for the groups that are lying at the lower and mid end of the TA:DIC ratio spectra. Plotting biological data from the OA datasets against the regional and global TA:DIC gradient derived from GLODAP (Fig. 7), we also observed that experimental data ranges were not always consistent with natural conditions, for example, having a lower Ωar at a higher TA:DIC ratio.

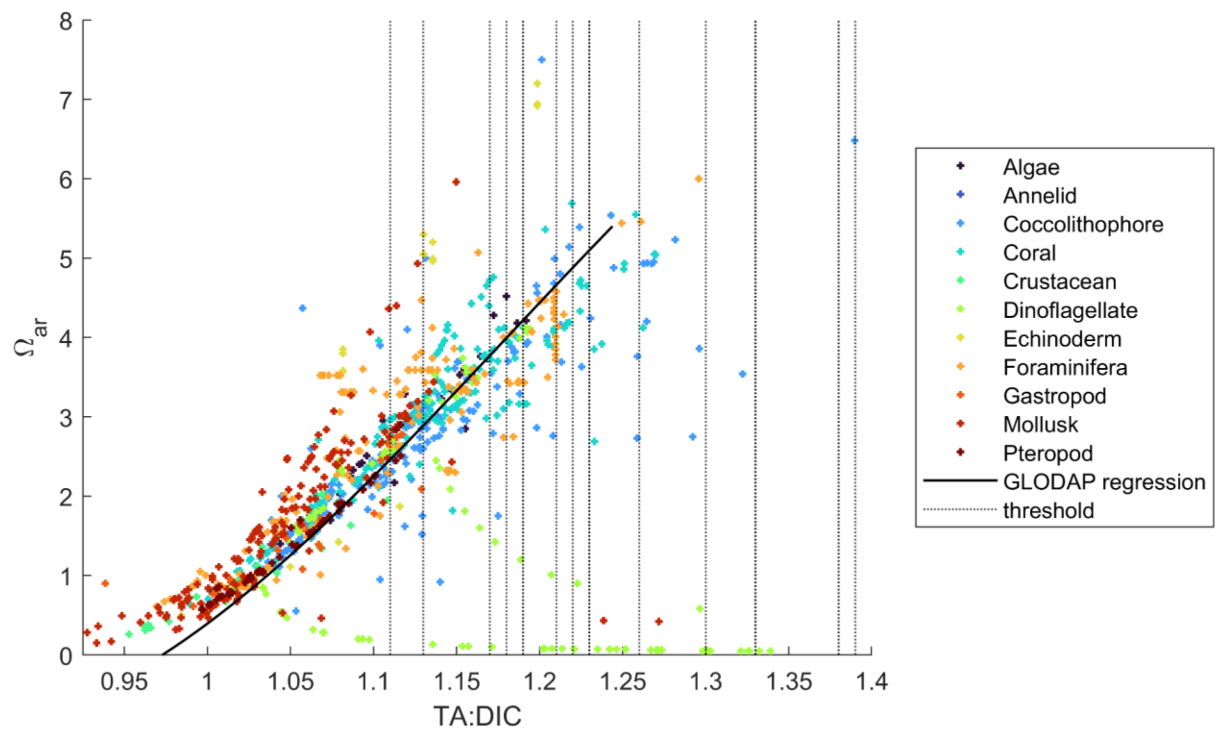


Figure 8: Experimental TA:DIC from experimental biological studies for eleven investigated functional groups (see legend) plotted against Ωar, with the latter being computed using experimental TA and DIC. The black line represents the regression line of TA:DIC and Ωar data from the GLODAP dataset (covering 0-50m depth). See Supplement Fig. 5 for GLODAP Ωar vs TA:DIC, from which the black regression line shown here is derived. The vertical dotted lines represent the thresholds shown in Table 2.

4. Discussion

OAE is a quickly developing strategy that is in the field-testing phase despite extremely limited understanding of the sequestration potential, biological implications and

environmental concerns. Hence, gaining insights of potential risks for the biological species and communities is essential and timely. In retrospect, it took decades for the OA research community to get a more accurate and comprehensive understanding leading to predictions of biological responses to OA (Riebesell and Gattuso, 2015). Without a very clear conceptual strategy for the OAE testing, the research community might also need years to decades before OAE-related implications are comprehensively understood. Consequently, there is an essential need to develop an assessment framework of predictive responses and testing strategies that will assist in OAE scaling and risk avoidance. This paper aims at developing such an assessment, where responses are categorized per species responses against TA:DIC. We propose to use the TA:DIC ratio in the biological studies reporting OAE results, as we believe it simplifies the system and makes it easier to use and translate the carbonate chemistry in the experimental setting. Such a TA:DIC ratio allows to ultimately standardize the biogeochemical and biological data and is useful for easier comparisons among the conducted experiments.

4.1. Identified strengths and limitations of the synthesis approach based on OA studies

Prior to conducting this study, several drawbacks were identified that could potentially limit such a synthesis work: first, insufficient amount of data at the upper range of carbonate chemistry conditions (high pH, high Ωar); second, experimental data under conditions with no relevance to natural settings (Fig. 8); and third, an insufficient number of validation studies under high TA conditions to validate the results of this synthesis. To overcome the first two limitations, the decision was made to combine multiple OA datasets for a single species with the aim to achieve a greater range in carbonate chemistry conditions, including higher pH, Ωar experimental values, which should reduce the uncertainty of the predictions. However, combining raw data on species calcification rate proved to be more challenging because even across the same species the reporting of the calcification rates was highly variable. The use of different measuring approaches of calcification rates while conducting OA studies generated data with divergent units that do not allow for the intercomparison of data and results. As different studies for a single species could not be combined, we chose to increase the number of studies and thus, the number of examined species. Based on the response categories from the OA studies (Ries et al., 2009), our hypothesis was that OAE will elucidate the same categories of responses, i.e. positive, negative and neutral. Within each of the groups examined, multiple categories of predicted calcification response were found. In this way, we demonstrated that it was possible to develop a useful framework for assessing and predicting species-specific OAE responses that can delineate different responders, identify species with greater OAE sensitivity and determine the thresholds where such negative responses could happen.

4.2 Synthesizing biological response under OAE identifies positive and negative responders

The greatest variability in calcification rate response upon NaOH addition was evident in corals, dinoflagellates, foraminifera, gastropods and pteropods, where four to five different categories of responses were found. Such variability confirms that the responses to OAE will

be species-specific and is related to various calcification mechanisms across the observed groups. Despite such specificity, the responses were summarized across three emerging groups of responses: positive, negative, and neutral (Fig. 6), which we discuss in the context of possible mechanisms of calcification or available OAE experimental studies used for validation.

Positive responders (34%) show an increased calcification rate upon alkalinity additions, observed within all functional groups besides annelids, coccolithophores and dinoflagellates. Corals mostly have positive and neutral responses, suggesting that coral species would not be negatively impacted during OAE field trials. This mostly positive response is validated by increased coral calcification, shown for two coral species of Acropora and Siderastre in experiments conducted by Palmer et al. (2022).

The metrics to evaluate the sensitivity of calcification rate for the negative responders (negative linear and threshold) to alkalinity addition was based on the amount of alkalinity addition required to halve the current calcification rate (Fig. 3; Tables 1, 2). The most negative responses were found in dinoflagellates (6% of all species), algae and foraminifera (both 5% of all species). However, these numbers are affected by the difference in data coverage per functional group. When comparing the ratio of negative to positive and neutral responses, crustaceans and dinoflagellates are expected to be most negatively affected. As such, these groups are one of the priorities for the future OAE experimental work to determine at which TA:DIC negative response happens. Dinoflagellates demonstrate negative response in 5 cases, 5 neutral responses and 0 positive (see Table 1; Supplement Fig. 4). The reason for negative response to OAE in this group is related to the fact that their growth gets limited at higher pH, with further carbon limitation playing a role at very high pH levels and low DIC concentration (Hansen et al., 2002; 2007). On the other hand, crustaceans only demonstrated positive response in one study (Pansch et al., 2014), while remaining results predict either negative or neutral response. While crustaceans are effective in retaining homeostasis at lower pH, they might be less so at higher pH, which was shown in the OA experiments by Ries et al. (2009) for three crustacean species (Callinectes sapidus, Homarus americanus, Penaeus plebejus), confirmed in the OAE study by Cripps et al. (2013) in Carcinus maenas. While studies are still lacking, physiological acid-base regulation at higher pH is associated with higher costs (Cripps et al., 2013). Crustaceans show a disrupted acid–base balance, evident through the increase in hemolymph pH, K^+, Na^+ ions and osmolality, coupled with a decrease in extracellular pCO_2 and HCO_3^-, indicative of respiratory alkalosis (Truchot, 1984;1986). This is often associated with hyperventilation, the aim of which is to flush out the hemolymph CO_2 to increase the affinity of oxygen uptake. However, while this might be a temporary physiological relief it also implies energetic costs, potentially also for calcification.

For the neutral responders or groups with no significant correlation between TA:DIC and calcification rates, it is somewhat uncertain to predict if such responses will be retained under OAE. While parabolic responders show a physiologically understandable parabolic type of dose-response, positioning the TA:DIC values where the threshold occurs is also

highly species-specific and potentially uncertain, meaning that it might depend on other environmental factors.

With respect to the coccolithophores, we note that this was the only group where data compilation on calcification rate across the groups was possible because the OA studies were conducted in a more uniform way, using similar approaches, and reporting the result in the same units. When data for E. huxleyi across the comparable studies was compiled (Barcelos-Ramos et al., 2010; Fiorini et al., 2011; Iglesias-Rodrigues et al., 2008; Sciandra et al., 2003; Stoll et al., 2012; Richier et al., 2011), a significant parabolic response was obtained (Table 1), although the goodness of fit was fairly low (R2=0.16). Despite lower R2, we decided to use the compiled dataset because of the increased statistical power. The parabolic response obtained aligns with Langer et al. (2006) and also with the parabolic type responses found in the synthesis studies by Paul and Bach (2020) and Bach et al. (2015). The threshold indicates the mechanisms of coccolithophore growth that are driven by CO2, which is shown to decline with alkalinity addition. The threshold based on all studies for E. huxleyi combined was positioned at a TA:DIC of 1.46~~57~~ (Ω_{ar} = 13.65~~48~~, see Table 2), which would be triggered at 85~~0~~0 µmol/kg of added NaOH. Comparatively with the phytoplanktonic diatoms, such growth limitation is predicted at a pCO_2 amount at 100 µatm (Riebesell et al., 1993). It is important to note that when these studies were analyzed individually, a mixture of different responses was observed. We emphasize the variability within the coccolithophore responses, which are species-specific and inherently related to the strain adaptation to their innate regional settings and dependent on a variety of other factors (Bach et al., 2015; Gafar and Schultz, 2018), including the longevity of the species, the experimental settings used in the study (e.g. nutrient-replete vs nutrient deficient conditions) and the presence or absence of (un)suitable light conditions. Interestingly, for all the coccolithophore species other than *E. huxleyi*, responses were neutral. For validation purposes, the results of our study could not be compared, either because the calcification rates were not studied or the calcification units were not comparable (e.g. Diner et al., 2015).

4.3 TA:DIC thresholds related to biological sensitivity and their implementation

Lastly, and most importantly, a set of species-specific thresholds was developed in this study, with demonstrated application across the global Ω_{ar} vs TA:DIC conditions (Table 2; Fig. 8) The range of alkalinity additions to result in a threshold of 50% decline in calcification rate varied significantly between the species and the type of response, with the parabolic responders generally having the lowest thresholds compared to the linear or threshold negative responders. The TA:DIC thresholds upon TA application ranged between 5~~10~~0 to 14~~5~~00 µmol/kg of NaOH addition, pointing to the most and least species-specific OAE-related sensitivities, respectively. We emphasize that the threshold application should not only consider the magnitude of NaOH added, but also the duration or exposure time of the study. Biological risk from OAE implementation in the field can be comprehensively assessed by combining the exposure and magnitude in respective model or observational outputs. We note that we have only added experimental exposure to the studies for which we have extracted the thresholds but duration should always be considered when studying OAE impacts.

Biogeochemical model outputs show that OAE-related concentrations at the injection site are high for a short-time, but realistic field dosing upon rapid dilution due to mixing might be low. Wang et al. (2023) reported that the nearfield maxima in the respective investigation area of the Bering Sea is to increase TA by about 10 µmol/kg in the nearfield and by about 1 µmol/kg of NaOH in the farfield region. As such, we should be more concerned about the threshold of exceedance occuring at the low NaOH dosing, rather than at high NaOH additions, because these are more realistic and point to the most sensitive species.

Such field risk assessment is conceptually different from the thresholds generated in the OAE experiments conducted with the aim of gaining a wide-ranging empirical response, which implies very high treatment levels. Here, we explicitly emphasize the importance of including much lower additions of TA in the experimental treatment levels to better support biological understanding and OAE application in the field. In addition, prior to the lab experiments it would be important to identify what type of response is predicted in the experimental species. This is especially pertinent for the groups for which OA experimental data is limited and skewed towards the lowest TA:DIC ratio, which was the case for the mollusks and dinoflagellates (Fig. 8; Supplement Fig. 4).

In this study, we assume global surface ocean conditions to be standardized at a pCO_2 of 425 ppm and a pH of 8.1 as a control point for OAE compound additions. However, we acknowledge that in different habitats, pH 8.1 may not represent the baseline, meaning the amount of TA required to reach a threshold could vary. This is especially relevant in habitats with a lower baseline pH, where more TA would need to be added, meaning the threshold would not be reached as easily. Therefore, to obtain the most accurate and regionally applicable threshold for the species of interest, it is recommended that the baseline for OAE additions be determined based on local conditions.

~~In this study we assume global surface ocean conditions to be equal to a pCO_2 of 425 ppm and a pH of 8.1 in order to standardize this as a control point from where the OAE compound was added. However, we note that when applying OAE in different habitats, pH 8.1 might not be the baseline, implying that the amount of TA addition before reaching a threshold could be different than specified here. This is important especially in the habitats where pH baseline value is lower, and where the addition of TA would be greater, resulting in reaching the threshold value more easily. As such, to get the most accurate and regionally applicable threshold value for the species of interest, the recommendation is that the baseline for the OAE addition should be determined based on the local settings.~~

4.4 Bringing realism of OAE experiments to the field trials

OAE-related biological responses and risks are not going to depend solely on the concentration of OAE compound used but also on the baseline carbonate chemistry conditions at the site of deployment, such as baseline TA:DIC (pH/Ω_{ar}), duration of exposure and variability of carbonate chemistry parameters across horizontal and vertical depths. Physical parameters of importance are related to the dilution effect, mixing, retention capacity, as well as the rate of the equilibration effects of the air-sea CO_2 uptake (Ferderer et al., 2022; He and Tyka, 2023; Schulz et al., 2023; Wang et al., 2023). Variability on the seasonal and annual scales of the air-sea CO_2 uptake can have impacts not only on the chemical processes related to the variable OAE efficiency, but also for the biological implications related to the crossing of biologically sensitive thresholds. It is the combination of all these factors that creates baseline conditions to which biota would ultimately be exposed in their natural environment upon OAE deployment (Wang et al., 2023).

If similar conditions as induced by the OAE field trial are present as part of the natural variability within the species' habitat, it is more likely that the species might be adjusted to it. On the contrary, rapidly induced novel conditions might be the most detrimental. As such, it is worth considering if OAE deployments could be, when possible, carried out not as a single high dosage deployment, but rather as a more continuous, lower dosage application that would eliminate the swings and maxima in conditions, while also allowing more time for species acclimation or migration during the initial injection of the OAE deployment.

What is needed urgently for the community performing biological field trials is a best practice guide for evaluating the biological responses as part of the field environmental risk monitoring approach. Along with the guide for conducting the lab (Iglesias-Rodrigues et al., 2023) and field OAE studies (Cyronak et al., 2023), the recommendations in the risk assessment guide would address the topics of initial baseline conditions, identify suitable risk analyses, determine thresholds, and propose the development of regionally specific indicators for monitoring, while also identifying the guidance for the regulators. Ideally, such biological and environmental risk monitoring and assessment would be accompanied by the application of the physical mixing models with site-specific biogeochemical processes (Ho et al., 2023; Fennel et al., 2023) that can predict the maximum expected TA increase in the nearfield and farfield regions of the study site, representing a more realistic exposure and better informing further experimental work.

~~4.5 Comparison of calcification rate with the pre-industrial conditions~~

~~Species that exhibited positive calcification responses to OAE, as examined in this study, were the most impacted through reduced calcification due to anthropogenically driven OA since the pre-industrial changes. For these species, retentive addition of NaOH in the range of 10 to 200 µmol/kg NaOH would allow these species to fully bounce back to the pre-industrial calcification. Achieving such long-lasting increases of NaOH is currently not feasible in the field but shows additional mitigating benefits of OAE against OA. With continuous OAE implementation, the calcification of positive responders would be reversed back to their pre-industrial capacity, indicating that such co-benefiting effects could be considered within the context of OA mitigating effects and could be part of the ecosystem restoration and protection strategy. In addition, it is probably less likely that such reversal of the processes might lead to concern for the species as ecological winners and potential shift on the community level. However, current modeling efforts show that temporal and spatial extent of OAE as a mitigation capacity for OA is variable and might induce significant biogeochemical changes that further exacerbate ecological risks (González and Ilyina, 2018; González et al., 2016; Mongin et al., 2021). Nevertheless, with 40% positive responders, there is substantial opportunity for species-specific variations and an indication that some species could~~

~~indeed benefit beyond just improved calcification.~~

4.5~~6~~ Unknowns about ecological and biogeochemical implications call for the precautionary approach

The value of calcification as the proxy is indicative of organismal fitness which directly relates to OAE effects as harmful or beneficial for the species. From an ecological perspective, a total of 25.8% negative responders demonstrates a potential for negative implications. In addition, we note that this study did not include diatoms in the analyses, which are predicted to be negatively impacted by carbonate-based OAE (Ferderer et al., 2022), leading to possible community-based ecological shifts (Bach et al., 2019). The possibility of the ecological shifts should not be neglected given the variety of the positive responders, understudied effects of OAE in non-calcifiers and their relationship with the calcifiers through the grazing impact, and lastly, unknown and highly unpredictable indirect effects. In addition, the inferences on the neutral responders should also remain cautious.

From a biogeochemical perspective, it is reasonable to infer that OAE will introduce changes in calcification rate across species, potentially resulting in changing carbon export or carbonate counter pump. Species-specific responses in major carbonate producers, i.e. coccolithophores, foraminifera and pteropods show both, negative and positive response, which could have strong effects on biogeochemical fluxes (Riebesell et al., 2017; Bach et al., 2019). Increased calcification could result in thicker and denser shells, contributing to faster sinking and increased carbonate fluxes, while the negative calcification has an opposite effect. This could potentially induce changes on the subsurface total alkalinity at intermediate and deeper depths in the water column, and dissolution at or near the seafloor (Gehlen et al., 2011) or result in a potential feedback of increased CO_2 flux to the atmosphere (Gattuso et al., 2021). The full scope of ecological and biogeochemical shifts remains a high priority topic for future investigations and until these huge uncertainties are resolved, we should exercise a precautionary principle in considering the next steps of OAE field implementations.

4.6~~7~~ Potential confounding effects and the validation issues

This study only considered the changes in carbonate chemistry due to the addition of NaOH and Na_2CO_3. However, other OAE feedstocks contain compounds that could induce biological toxicity due to the presence of trace metals (Ni, Cu, Ca, Si; Bach et al., 2019), as well as potential negative environmental impacts due to secondary precipitation (Hartmann et al., 2022; Moras et al., 2022). This study also did not focus on the sensitivity across different life stages, even though stage-specific sensitivities to OAE are expected based on previous OA results. Furthermore, we did include data from experimental lab and field studies that involve multiple stressors in their experimental designs. As such, an additional impact of warming, dissolved oxygen, and light intensity on the OAE-induced responses was not determined, although they could elicit different biological pathways than OAE alone or have additional confounding effects.

The synthesis of the experimental studies always includes implicit biases that are based on the published experimental studies, the range and species used, regional coverage and heterogeneity.

Important consideration is the adaptation of the species used in the experimental studies because their calcification optimum might be pre-determined based on their local habitat conditions. Given that the baseline for the OAE-compound addition was chosen at the global current surface pH value, some of the thresholds might actually be lower than expected.

The predictive results of these studies need to be validated with subsequent studies, but a suitable approach to evaluate such predictions could be done by comparing mechanistic studies with the experimental data. One of the problems is the lack of a known mechanistic relationship of the calcifying species. However, a lot of mechanistic relationships are based on one parameter only. Ninokawa et al. (2024) and Li et al. (2023) emphasized that using only one parameter to describe the calcification process is insufficient and strongly recommended using at least two parameters for more accurate calcification predictions. Our findings agree with Ninokawa et al. (2024), for example, we observe that using SIR relationships to successfully describe calcification was limited to only a few species and that there are no generalizable patterns that could be applicable across multiple groups. This clearly delineates a major gap in the mechanistic understanding of calcification so far, the lack of which significantly limits our ability of ecological and biogeochemical predictions to OAE. As such, more research is urgently needed on broader mechanistic understanding of calcification across different species, and additionally, one parameter calcification processes should be replaced with more accurate and comprehensive methods using two or three parameters.

4.7~~8~~ Applications within the existing governmental regulations and the guiding principle

Our results, especially related to the use of biological thresholds or NaOH dosing, have applications outside the academic realm, most notably with policy-management governmental regulations. For example, we calculated the amount of alkalinity addition required to reach the pH threshold of 9, the maximum pH allowed by the US Environmental Protection Agency's for waste water entering the coastal ocean (see NPDES manual, 2010). To reach this threshold, ~~for the positive responders, around~~ 1200 µmol/kg of NaOH was required on average for all species, with the lowest threshold reached at 750 µmol/kg addition for Amphibalanus improvisus. This is ~~represents~~ a high concentration, and the thresholds for most of the negative responders with identified thresholds (Table 2) will be exceeded far below the regulatory standards of pH 9 (Table 2), especially if the exposure occurred over a duration period that matters for calcification and for the organism's physiological status. This case demonstrates discrepancy of the current chemical pH regulation and associated biological effects, where safe biological limits are not considered and biological harm is not prevented, thus likely induced. Despite the fact that achieving such high pH through continuous NaOH implementation is unlikely to occur in the field, such regulations are of particular concern and regulations to assure safety space for marine biota need to be urgently addressed and determined.

5. Conclusions and next steps

Sufficient certainty in predicting biological responses reduces the risks and supports safe operating space for OAE implementation and scaling up. Overall, given that almost 6~~7~~0% of examined species showed non-neutral response (either positive or negative), this calls for careful implementation of OAE until the safe operational temporal and spatial scales are identified and OA mitigation measures are established. The goal of this study is to serve as a baseline for prioritizing experimental and field OAE research and assess environmental risks. Such prioritization identifies those species for which experimental work needs to be conducted first. This would involve species with the greatest OAE-related sensitivity (negative responders), species with the greatest uncertainty in response, as well as the species with very strong predicted positive response that could potentially introduce a shift on the community level. In addition, it would also recognize the species for which the existing knowledge is sufficient and there is less immediate need for the OAE experiments. We hope that all presented tools provide guidance for the practicing and regulatory community considering OAE field application within the safe limits.

It is important to emphasize that this study is the first comprehensive synthesis of the effects of OAE. Ongoing updates and additional data would enhance its value, particularly when complemented by further experimental research. Similar datasets on OA exist for various biological parameters, including genetics, physiology, and survival data, as well as for non-calcifying organisms. This availability allows for the exploration of ecological implications and contributes to developing an ecosystem-based predictive risk assessment for OAE.

~~It is important to emphasize that this study represents the first synthesis of OAE effects. It would benefit from continuous updates and data additions, while cross-validated with further experimental work. Similar OA datasets are available for other biological parameters, including genetics, physiology, survival data, and also for non-calcifying organisms, allowing to study ecological implications and bridge towards building an ecosystem-based OAE predictive risk assessment.~~

Data availability

No additional data were generated as part of this study, they were all collected from the already published studies. The compiled data is currently available on request. The Python code used for computing baselines per species, conceptually adding alkalinity in the form of NaOH and Na2CO3, predicting calcification rate response, visualizing data and computing thresholds is available in the GitHub repository at https://github.com/hannavdmortel/OAE_calc_responses (last access: 24 July 2024) and is archived on Zenodo at https://doi.org/10.5281/zenodo.12806137 (van de Mortel, 2024). PyCO2SYS v1.8.0 (Humphreys et al., 2022) was used to solve for the carbonate system, with software available at https://doi.org/10.5281/zenodo.3744275 (Humphreys et al., 2023).

The code is stored at the following link: https://doi.org/10.5281/zenodo.12806137

Author contributions

NB designed and conceptualized the research and wrote the first draft of the paper. HvdM collected and curated data, conducted formal analyses and provided visualization. GP provided the analyses using GLODAP data, and also provided visualizations and formal analyses. MGR has provided formal statistical analyses and visuals. RAF and AD have provided insights, suggestions, and generated discussion about specific parts of the paper. All have contributed to the writing of this draft.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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