Seawater carbonate system considerations for ocean alkalinity enhancement research

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Abstract. Ocean alkalinity enhancement (OAE) is a proposed marine carbon dioxide removal (mCDR) approach that has the potential for large-scale uptake of significant amounts of atmospheric carbon dioxide (CO_2). Removing anthropogenic legacy CO_2 will be required to stabalise global surface temperatures below the 1.5-2 °C Paris Agreement target of 2015. In this chapter we describe the impacts of various OAE feedstocks on seawater carbonate chemistry, as well as pitfalls that need to be avoided during sampling, storage and measurement of the four main carbonate chemistry parameters, i.e. dissolved inorganic carbon (DIC), total alkalinity (TA), pH and CO_2 fugacity (fCO_2). Finally, we also discuss considerations in regard to calculating carbonate chemistry speciation from two measured parameters.

2.1 Seawater carbonate chemistry revisited

In the following sections the basic concepts of the seawater carbonate system are laid out, together with definitions of the key parameters.

2.1.1 Acid-base parameters and equilibrium chemistry

The acid-base equilibrium chemistry of seawater has been described in Dickson *et al.* (2007), and in Dickson (2010). These publications provide a lot of practical information related to studying the carbon dioxide system in seawater, describing tested approaches to measuring the four main parameters that are commonly used to describe seawater acid-base chemistry, as well as providing recommended values for the various equilibrium constants, *etc.* (as functions of salinity and temperature, and at 1 atm total pressure). For further insights, the interested reader is also referred to Zeebe & Wolf-Gladrow (2001).

The four parameters are DIC: the total dissolved inorganic carbon (expressed as an amount content of carbon atoms) in a sample of seawater (Eq. 1) ; TA: the total alkalinity (expressed as an amount content of hydrogen ions that are equivalent to the bases – defined relative to a specified equivalence point) in a sample of seawater (Eq. 2); pH_T: a measure of the amount

content of *total* hydrogen ion in a sample of seawater (Eq. 3); and fCO$_2$: the fugacity of carbon dioxide in air that is in solubility equilibrium with a sample of seawater.

(Eq. 1) $DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$

35   and

 (Eq. 2) $TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-)] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-]$
$$- [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] + \ldots - \ldots$$

with the last two terms denoting minor contributions of additional proton acceptors and donors.

(Eq. 3) $pH_T = [H^+]_F + [HSO_4^-]$

40   with $[H^+]_F$ describing the free hydrogen ion concentration. Finally, another important carbonate chemistry concept is that of the calcium carbonate saturation state (Eq. 4).

(Eq. 4) $\Omega = \dfrac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}}$

with K_{sp} describing the temperature and salinity dependent solubility product of a particular calcium carbonate morphotype such as calcite or aragonite.

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The equilibrium values for the amount contents of the various constituents of the acid-base equilibria in a sample of seawater are essentially dependent on the major ion composition of the seawater (usually approximated by the salinity), the temperature of the seawater, and the total pressure to which the seawater is subjected. Hence if the temperature or pressure of a seawater sample changes, these various equilibrium values will necessarily change. Thus, the pH$_T$ and fCO$_2$ of the seawater

50   will change as a consequence of changes in temperature and pressure, and it is important to note the temperature and pressure at which the measurements were made. For TA and DIC this is not a problem. The individual amount contents of unionized dissolved carbon dioxide, bicarbonate ion, and carbonate ion each change as temperature and/or pressure changes, but their total sum does not (the amount of carbon atoms that are in an inorganic form is conserved). Of course, this assumes that any redox reactions involving carbon do not occur on the relatively short timescales appropriate to the changes of

55   temperature or pressure. The same applies to the sum of the individual TA components.

Any two of these four parameters (DIC, TA, pH$_T$, fCO$_2$) can – in principle – be used together with the salinity, temperature, and pressure (so as to define suitable equilibrium constants) to calculate the state of the carbon dioxide acid-base system in a seawater sample. (The parenthetic note: "in principle", is an acknowledgement that – as a consequence of errors in the

60   measurements of these parameters and in the measurement of the associated equilibrium constants – the results from using alternate pairs of parameters will likely not be identical (Orr *et al.*, 2018). When one uses total alkalinity as a measured parameter, it implicitly incorporates all other acid-base equilibria occurring within the sample of seawater, *i.e.* in addition to the inorganic CO$_2$ system (Eq. 1). This is relatively straightforward if the total amount content of each acid-base system present has been measured directly, can be calculated from the sample salinity, or can safely be neglected. For each acid-

65 base system considered, one needs to know the total amount content for the acid-base system as a whole, as well as an acid-dissociation constant for each acid species (including those formed by dissociation of the nominal parent acid). Total alkalinity is thus a measurable parameter of the seawater acid-base system which, when expressed as an amount content, is a conservative variable, both on mixing and for changes in temperature and/or pressure. A useful consequence of the definition of the total alkalinity of a seawater sample is that the total alkalinity essentially does not change when CO_2 is in- or

70 outgassing by exchange with the atmosphere. However, there is a growing awareness that the presence of organic acids and bases in seawater can complicate the use of total alkalinity as a measurable parameter (see *e.g.*, Fong & Dickson, 2019). The contribution of such species to total alkalinity is usually neglected, especially for open ocean seawater samples.

It is not yet clear the extent to which this organic contribution to alkalinity exists in the oceans, and how it might vary with

75 place and time. If it is at a fairly low, stable, background level then, although its existence compromises the accuracy with which equilibrium calculations of the CO_2 properties can be made when using total alkalinity as a measured parameter, its existence can likely be ignored when assessing the implications of changes in alkalinity for changes in other CO_2 parameters. (This statement assumes that any error resulting from not measuring and/or explicitly interpreting the organic contribution to total alkalinity will constitute an approximately identical bias in both the values of total alkalinity that are used to infer a

80 change.)

2.1.2 Deffeyes diagrams

Deffeyes (1965) published a detailed description of how one could use 3-dimensional (contour) diagrams plotting individual seawater CO_2 system properties as a function of total alkalinity and total dissolved inorganic carbon for a seawater of a

85 specified salinity and at a particular temperature (and pressure). Insofar as this chapter is aimed at studies of ocean alkalinity enhancement, we feel such diagrams may be useful to help people to visualize the compositional changes that are involved in such processes.

For instance, imagine adding alkalinity to typical open ocean seawater. If an alkaline agent such as sodium hydroxide

90 (NaOH) is used this increases total alkalinity but does not change total dissolved inorganic carbon (the vertical red line, Fig. 1a). Alternately, alkalinity could be added as a soluble inorganic carbonate salt (*e.g.* ikaite, $CaCO_3.6H_2O$, or Na_2CO_3). This will increase both total alkalinity and total dissolved inorganic carbon in the ratio 2:1 (the dark grey line, Fig. 1b). As that modified water sample then equilibrates with the atmosphere, *e.g.*, takes up CO_2 from the air, DIC increases (indicated by the blue fCO_2 isoline, Fig. 1a). It is straightforward to assess the potential of 1 kg of a particular modified seawater to

95 remove CO_2 from the atmosphere. It is equivalent to the change in C_T between the modified and initial fCO_2 prior to the alkalinity addition. This concept takes into account that marine Carbon Dioxide Removal (mCDR) also includes scenarios in which an oceanic CO_2 source is reduced. Similar diagrams can be drawn to assess the impact of various TA additions on Ω or pH (Fig. 1b,c).

2.1.3 OAE impacts on seawater

As mentioned above, ocean alkalinity can be increased by various means. First, there are multiple minerals found in natural rocks which release total alkalinity content (TA) upon dissolution in seawater. Dissolution kinetics depend on how finely the minerals have been milled as well as on the mineral itself. For instance, olivine, a magnesium/iron silicate - $(Mg,Fe)_2SiO_4$, dissolves relatively slowly on the order of weeks to months and appears to have a relatively low solubility (Monserrat et al. 2017). On the other side of the spectrum, brucite, $Mg(OH)_2$, dissolution rates can only take hours (Moras et al. 2023). Another way to increase oceanic TA is to add it in 'liquid' or aqueous form, i.e. hydroxide ions – OH^-, which can be produced electrochemically from seawater (e.g. Rau et al. 2013, but also see Chapter 3).

Whichever the approach, once alkalinity is increased it raises pH, shifting carbonate chemistry speciation towards lower aqueous carbon dioxide ($[CO_2]$) and higher carbonate ion concentrations ($[CO_3^{2-}]$), as well as saturation states for various calcium carbonate ($CaCO_3$) morphotypes such as calcite (Ω_{calc}) and aragonite (Ω_{arag}). In this context, saturation states can be considered critical thresholds, and depending on application there are levels that should not be exceeded for extended periods of times. Avoiding critical saturation thresholds is important because $CaCO_3$ will precipitate inorganically through a number of mechanisms at higher Ω values. Such secondary precipitation should be avoided as it reduces the oceanic uptake capacity for atmospheric CO_2 and can even lead to runaway $CaCO_3$ precipitation where more TA is removed than had been added, reducing typical CO_2 uptake potential by a factor of eight (Moras et al. 2022).

In seawater there are three mechanisms for inorganic $CaCO_3$ precipitation, 1) homogeneously - in the absence of any soluble or particulate surfaces, 2) pseudo-homogeneously – in the presence of particulate or colloidal organics, and 3) heterogeneously – in the presence of solid mineral phases (Marion et al. 2009). The critical Ω threshold beyond which $CaCO_3$ formation would occur is highest for homogeneous and lowest for heterogeneous precipitation, with pseudo-homogeneous in between. In a natural setting, homogeneous precipitation is unlikely, as seawater is hardly void of organic or inorganic particles and/or colloids. For pseudo-homogeneous $CaCO_3$ precipitation, the critical Ω_{arag} threshold is about 12.3 (salinity 35, temperature 20°C). For heterogeneous precipitation, it depends on the so-called lattice compatibility between $CaCO_3$ and the mineral surfaces it precipitates onto. For instance, the mineral $CaCO_3$ has a perfect lattice compatibility, meaning that any existing pre-cursors will lead to precipitation at Ω above 1 (Zhong&Mucci 1989). The rate of precipitation is exponentially increasing with Ω, about 5-fold for a doubling in saturation state. In contrast, other mineral surfaces have lower lattice compatibilities, for instance $CaCO_3$ precipitation was observed for CaO and $Ca(OH)_2$ above an Ω of 7, while for $Mg(OH)_2$ rates appeared to be even further reduced (Moras et al. 2022, 2023). Furthermore, critical Ω thresholds are also influenced by grain size, salinity and dissolved organic matter concentrations (Moras et al. 2023), and most likely temperature as well.

Finally, it is noted that next to the un-equilibrated OAE approach (Bach et al. 2019), discussed here, there is also the possibility to equilibrate the seawater with respect to atmospheric CO_2 during TA addition which would reduce the
135   possibility of secondary $CaCO_3$ precipitation as Ω would be much lower for the same amount of TA added.

2.1.4 TA additions and critical Ω thresholds in the surface ocean

From a practical OAE standpoint, there will always be an Ω that one will try not to go beyond for extended periods of time to minimise potential secondary $CaCO_3$ precipitation. So, how much TA can be added then? This depends on initial in-situ
140   seawater Ω. Globally, both surface ocean Ω_{arag} and Ω_{calc} are highly correlated, at least on larger scales, with temperature and salinity. On smaller scales, there is also a biological component, i.e. photosynthesis increasing Ω and respiration decreasing it. Impacts of temperature and salinity changes on carbonate chemistry speciation are two-fold. While there is a direct effect of temperature on carbonate chemistry speciation (lowering $[CO_2]$ and Ω), the bigger impact on Ω stems from the higher CO_2 solubility in low temperature waters. The resulting higher $[CO_2]$ and lower TA/DIC, leads to a shift towards lower
145    $[CO_3^{2-}]$, and hence Ω. This is because $[CO_3^{2-}]$ is approximately equal to the difference between carbonate alkalinity (CA) and DIC in the ocean. These two temperature effects reinforce each other to largely explain the latitudinal gradient of surface ocean Ω (Jiang et al., 2015). Additionally, the apparent solubility product (K_{sp}') also contributes to its latitudinal gradient (Mucci, 1983).

150   When it comes to salinity, there is also a direct effect but the major driver is that in oceanic waters DIC and TA scale with salinity (mostly driven by water evaporation and precipitation), meaning that they will be significantly reduced at lower salinities. And for a similar oceanic pH at equilibrium with atmospheric CO_2, reducing salinity and DIC, for instance 5/fold, will reduce $[CO_3^{2-}]$ by a similar amount. And next to salinity-related reductions in $[Ca^{2+}]$ at lower salinities, this will reduce Ω. Globally, sea surface temperatures are highest in the tropics and subtropics and decrease towards higher latitudes (Figure 2A).
155   Similarly, there is a tendency towards higher salinity at low latitudes and lower salinities at high latitudes (Figure 2B). In concert, this leads to increasing Ω from polar to tropical waters. For instance, while there are polar regions in which Ω_{arag} is close to 1 on annual means, in large parts of the tropical surface ocean Ω_{arag} can be close to 4 (Figure 2C). Finally, as mentioned earlier, there are also biological drivers of sea surface Ω, for which a good indicator is CO_2 fugacity. Higher than current atmospheric pressures of ~425 µatm are indicative of respiratory CO_2 generation, reducing Ω, while pressures below
160   are typically driven by photosynthetic CO_2 fixation, increasing Ω. This modulating effect of biology on temperature- and salinity-driven global surface ocean Ω distributions can be seen by the upwelling of CO_2-enriched deep waters in the tropical Pacific where elevated fCO_2 results in lower Ω_{arag} (Figure 2C,D). Altogether, this determines how much TA can be added before a critical Ω threshold is reached. And using an Ω of 5 to avoid secondary $CaCO_3$ precipitation would allow about 5 times higher TA additions at high in comparison to low latitudes (Figure 2E).

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Finally, the amount of atmospheric CO_2 that can be taken up, depends on the uptake factor η_{CO2}, denoting the ratio of the concomitant DIC increase per TA addition. This time, it is mainly determined by sea surface temperatures, with minor effects of salinity and biology. It ranges between 0.75 and 0.9, with higher values at lower temperatures closer to the poles (Figure 2F). The resulting DIC uptake potential for global surface waters, for a critical Ω threshold of 5 ranges between only

170 50 to up to 400 µmol kg^{-1}, being higher at high and lower at low latitudes (Figure 1G). It is noted though, that the CO_2 uptake factor plays only a minor role, and most differences in regional CO_2 uptake potential are driven by the amount of TA that can be added before a critical Ω threshold is reached.

175 **2.1.4 Cautionary note on apparent trends in regional differences for atmospheric CO_2 uptake**

When looking at the distribution of global DIC uptake potential calculated for a specific OAE application (Ω threshold), there appears to be a general trend for higher uptake at high and lower at low latitudes. However, that only applies to the open ocean, as coastal areas are not included in the underlying GLODAP climatology. And there, things are likely to look quite different, as these areas are heavily impacted by terrestrial influences such as freshwater input but also anthropogenic

180 disturbances such as nutrient runoff which affects biological processes, and hence the CO_2 uptake potential (see above), in particular as activity can be orders of magnitude higher than in the open ocean. Furthermore, seasonal changes to carbonate chemistry speciation, which can be quite large, are also not captured.

Furthermore, it is only an uptake potential and the realised increase in DIC critically depends on regional gas transfer

185 velocities, i.e. how quickly atmospheric CO_2 is equilibrating with the surface ocean, and for how long the surface water with increased TA is in contact with the atmosphere before eventually being subducted. And in this regard, three categories can be defined (He&Tyka 2023). The first are regions with relatively quick CO_2 equilibration and surface waters remaining in contact with the atmosphere on the relevant timescales. There, about a year after the TA increase ~80-100% of the CO_2 uptake potential can be realised. The second are regions in which CO_2 equilibration is again relatively quick, but significant

190 portions of the TA enriched surface waters lose contact with the atmosphere for some time before resurfacing eventually again, meaning that realising 80-100% of the CO_2 uptake potential can take decades. And lastly, there are regions with either quite slow equilibration and/or where significant portions of TA enriched surface waters lose contact with the atmosphere for relatively long times, e.g. regions of deep water formation. Here, the realised CO_2 uptake potential might only be 50% or less after a couple of decades.

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Finally, for calculating the DIC uptake potential, the TA increase before a certain Ω threshold is crossed is multiplied with the CO_2 uptake factor η_{CO2}. The latter also sees seasonal variability and might be quite different in coastal areas as opposed to neighbouring oceanic regions. However, not too much emphasis should be put on finding regions with high η_{CO2} as it is more critical how quickly the TA enriched surface waters are equilibrating with atmospheric CO_2 and for how long they

200 remain in contact (unless the waters have been pre-equilibrated during TA addition). Also, while water masses travel on the surface they might change temperatures, for instance when moving from low to high latitudes which would change η_{CO2}. Hence, instead of using η_{CO2} at the site of TA addition to estimate its DIC uptake potential, it is probably more conservative to use a global mean of 0.84.

205 Last but not least, it should be beneficial to not treat η_{CO2} or the DIC uptake potential as a measure of OAE efficiency. The latter should be assessed in two steps, i.e. first how much of a stable TA increase can be achieved, accounting for potential $CaCO_3$ precipitation, and second, how much of DIC is actually then taken up given a particular air-sea gas exchange and exposure time. Such approach takes into account the quite different time scales of TA and DIC increase.

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2.2 Sampling and storage of TA-enriched water

Sampling of discrete DIC, TA, pH and fCO_2 should generally follow protocols described in Standard Operating Procedure (SOP) 1 by Dickson et al. (2007). One caveat, however, is that these protocols were developed for common oceanic carbonate chemistry conditions. Here, we discuss additional measures for sampling and sample storage that may be
215 necessary for carbonate chemistry conditions specific to OAE (i.e. high TA, high pH, and high Ω). We acknowledge that many of the procedures described below are based on anecdotal evidence and need to be further scrutinized with increasing maturation of OAE research and ongoing improvements of this guide.

2.2.1 Specific problems to consider

220 In general, there are 4 processes that can alter carbonate chemistry conditions in a sample during its collection and storage. These are:

1) modifications via air-sample gas exchange (sampling)
2) modifications via biological activity such as respiration (storage)
3) modifications via the precipitation of $CaCO_3$ (storage)
225 4) modifications via diffusion of CO_2 into or out of sampling container walls (storage)

These four processes affect carbonate chemistry parameters differently and the effect size also depends to a large degree on the sample itself (Table 1). Sampling and storage procedures that describe how to deal with processes 1 and 2 can be found in SOP 1 by Dickson et al. (2007), such as how samples should be collected and stored, including thorough instructions of
230 what materials are recommended to be used and how they should be prepared.

$CaCO_3$ precipitation (process 3) has received less attention in SOP 1. This is because $CaCO_3$ precipitation is very slow under most natural seawater carbonate chemistry conditions and is therefore not considered to affect carbonate chemistry

conditions during sampling and storage of such waters. However, $CaCO_3$ precipitation accelerates gradually the further Ω deviates from 1. Extreme Ω values which are much higher than what is commonly observed in the oceans will be frequently encountered in OAE research. Indeed, Subhas et al. (2022) experienced this problem in their OAE experiments where TA and DIC concentrations in the OAE treatment samples declined during sample storage due to $CaCO_3$ precipitation. The precipitation of $CaCO_3$ reduces TA and DIC in a 2:1 molar ratio, also changing carbonate chemistry speciation (Figure 3). As discussed above, precipitation rates critically depend on Ω but are also influenced by the presence of organic/inorganic particles as precipitation nuclei (Zhang and Mucci, 1989; Marion et al. 2009, Moras et al., 2022; Fuhr et al., 2022), the Mg concentration (Moras et al. 2023), or the concentration of dissolved organic carbon - DOC (e.g. Chave&Suess 1970, Pan et al. 2021, Moras et al. 2023). Since, precipitation is usually difficult to predict in terms of how long a sample might be stable, it is advisable to treat the sample in such a way that the potential problem of precipitation is minimised/mitigated.

In the following we describe procedures to avoid changes in carbonate chemistry conditions upon sampling and storage of DIC, TA, pH, and fCO_2.

2.2.2 Sampling considerations: filtration

It is advisable to filter carbonate chemistry samples upon their collection to remove particles. In oceanography, the cut-off between what is considered to be dissolved or particulate has been operationally defined by passing or being retained on a GF/F filter. Such a filter has a nominal pore size of 0.7 μm, but smaller pore sizes, for instance 0.2 μm which would remove bacteria at the same time and theoretically produce a sterile sample, have also worked in the past. Filtration has multiple benefits and might even be required:

1. Particles can serve as precipitation nuclei, which catalyse $CaCO_3$ precipitation during storage. Removing particles via filtration will therefore help to reduce the risks of secondary precipitation.
2. Removing particles will be necessary in case $CaCO_3$ precipitation has already occurred in-situ to not interfere with the measurements. This is because typical analytical procedures to measure DIC and TA rely on acidifying the seawater sample during analysis, meaning that any $CaCO_3$ present would re-dissolve and be measured as additional TA and DIC.
3. Filtration of the sample is also useful to remove substrate for biological breakdown and organisms that respire organic carbon. Respiration has limited influence on TA but strongly affects DIC, pH, and fCO_2 (Table 1). However, for samples intended to be stored longer than a few days, sterile filtration is not recommended but fixation with mercuric chloride ($HgCl_2$; Dickson et al. 2007).

Filtration can have negative side-effects that need to be considered and mitigated. Most obviously, filtration requires additional sampling gear which introduces contamination risks. Thus, all filtration gear must be prepared appropriately following SOP 1 in Dickson et al. (2007). The most critical issue is that filtration increases the risk of air/sample CO_2 gas exchange. This risk can be reduced when the sample is handled by gentle pressure-filtration (as opposed to vacuum filtration

which is prone to gas exchange, i.e. CO_2 degassing) in a closed system. For example, the sample could be pumped via a peristaltic pump using Tygon tubing (relatively impermeable for CO_2) through a membrane filter directly into the sampling bottle, filling it from bottom to top with significant overflow (Dickson et al. 2007, Schulz et al. 2017). Alternatively, the sample could be filled into a syringe (again, potential air/water gas exchange has to be minimised) and filtered through a syringe filter, again from bottom to top with overflow. CO_2 gas exchange would change DIC and hence is also a problem for pH and fCO_2 samples, which would also change. While TA samples are not affected by air/sample CO_2 gas exchange, they are sensitive to evaporation so exposure to the atmosphere must also be avoided.

2.2.3 General storage considerations

Samples for DIC, TA, pH, and fCO_2 should be prepared for storage and stored as described in SOP 1 in Dickson et al. (2007). If these samples have relatively high Ω values (as a rule of thumb $\Omega_{arag} > 12$ for filtered and $\Omega_{arag} > 5$ for unfiltered samples), they most likely require additional measures to avoid changes through $CaCO_3$ precipitation that could eventually occur during storage.

We reiterate that much of what is described below, while appearing to be logical, remains to be tested and validated in dedicated laboratory studies. Thus, care must be taken when adopting these preliminary recommendations.

2.2.3.1 Preparing DIC samples for storage

DIC changes with $CaCO_3$ precipitation in a 1:1 molar ratio (Figure 3). Eventual $CaCO_3$ precipitation can be avoided by adding a strong acid (e.g. hydrochloric acid - HCl) to the sample, although precautions have to be taken (see below). HCl reduces TA and hence Ω. Such addition also decreases pH, and increases fCO_2 in the sample but leaves DIC concentrations untouched. Increasing sample fCO_2 might, however, be a problem, if acid is added in excess to the added TA, as it will eventually raise fCO_2 above atmospheric levels and increase the risk of outgassing which would decrease DIC.

Hence, to reduce the risk for CO_2 outgassing it is advisable to dose the HCl additions to just compensate the TA addition, bringing Ω down to typical seawater levels, i.e. Ω_{arag} ~2). Also, prior to full mixing, there might be localised high fCO_2 microenvironments, hence exposure of the sample to air after acidification should be avoided, for instance by closing the lid. Again, equilibrated OAE samples most likely do not require such an acidification step (see 2.3.1).

To reduce sample dilution, it is recommended to use strong acids (e.g. HCl) at relatively high concentrations. The dilution of the DIC sample with HCl will need to be considered to calculate the DIC concentration of the undiluted sample.

2.2.3.2 Preparing TA samples for storage

TA changes due to $CaCO_3$ precipitation occur in a 2:1 molar ratio (Fig. 3A). $CaCO_3$ precipitation, due to initially high Ω, can be avoided by briefly bubbling the TA sample with pure CO_2 gas. CO_2 decreases Ω and pH, and increases DIC and fCO_2 but leaves TA unaffected (note that CO_2 is not part of the TA definition, Eq. 2). The approach was tested with 120 mL of
305   seawater sample where high purity CO_2 gas (4.5, i.e. 99.995%) was bubbled via Tygon tubing through a clean 1 mL pipette tip into the sample for 10 seconds (Lenc et al. 2023). The CO_2 flow rate was not determined but adjusted so that the bubbling did not lead to spill over in the 125 mL sample bottle. Measured pH declined from initially ~8.7 to well below 6 within 10 seconds so that Ω_{arag} went from ~9.5 to much below 1. Under these conditions, TA loss through $CaCO_3$ precipitation is impossible. It is noted that bringing the pH down to pH levels prior to the TA addition, i.e. around 8, would have reduced
310   Ω_{arag} sufficiently (< 5) to avoid $CaCO_3$ precipitation during sample storage if the sample had been filtered.

However, there are several aspects to consider when employing this sample fixation approach. First, impurities in the CO_2 gas could contaminate the TA sample. Particle impurities can be avoided by using filters. Gas impurities (e.g. NH_3) will be more difficult to remove so that it is important to use high-purity gases and test for potential TA impurities. Second,
315   bubbling with dry CO_2 gas directly leads to evaporation of water, increasing TA. It is unclear at this stage how relevant this problem is for a short bubble burst but it could be avoided by saturating the CO_2 gas stream with H_2O before bubbling the sample as for example described in (REF).

Finally, atmosphere-equilibrated OAE samples which have Ω levels below the critical thresholds described above, should
320   not require CO_2 bubbling. Although it is advised to actually calculate expected sample Ω from estimates of TA and DIC prior to storage.

2.2.3.3 pH and fCO_2 samples

Samples for pH and fCO_2 cannot be stabilised with any of the methods described above. Both, the addition of HCl or CO_2
325   would alter the carbonate chemistry speciation, including pH and fCO_2. There may be methods to reduce $CaCO_3$ precipitation via the addition of certain inhibitors such as DOC, but such methods would need to be developed. Thus, the recommendation for pH and fCO_2 of samples with high Ω is to measure them immediately after collection.

2.2.4. Use at your own risk

330   It is again emphasised that most of the recommendations above have not been fully tested and evaluated. In some cases, they are also based on common sense and first principles, hence please use at your own risk!

2.3. Carbonate chemistry measurements of TA-enriched water

Concerning measurements of carbonate chemistry parameters, there are different needs depending on scientific research
335   questions. Two levels of uncertainty have been proposed, one being able to detect relatively small carbonate chemistry

speciation changes of 'climate' signals, and the other being able to monitor shorter term or spatial variability which can be considerably larger, termed 'weather' signals (Newton et al. 2015).

Being able to resolve 'climate' signals requires measurement uncertainties equal or better than 2 μmol kg^{-1} for DIC and TA,

340   0.003 for pH and 0.5% for CO$_2$ fugacity. In comparison, for 'weather' signals better than 10 μmol kg^{-1} for DIC and TA, 0.02 for pH and 2.5% for fCO$_2$ are sufficient (Newton et al. 2015).

Concerning OAE, both thresholds could be aimed for depending on application. For example, if it is to monitor initial TA changes upon an alkalinity addition which can be on the order of several hundreds of µmol kg^{-1} of seawater, then aiming to

345   resolve such 'weather' signal with an uncertainty of better than 10 μmol kg^{-1} is probably sufficient. However, once this signal gets diluted and to monitor CO$_2$ ingassing and DIC increase over timescales of months an uncertainty for 'climate' signals must be aimed for. In fact, depending on dilution, this might even not be enough, highlighting the fact that monitoring, reporting and verification (MRV), i.e. in the end determining how many carbon credits can be assigned to a certain OAE effort, is likely to require modeling (Chapter X).

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In any case, a first step before measuring any carbonate chemistry sample would be to assess the accuracy (how far off are measurements with respect to certified reference materials) and precision (what is the standard deviation of replicate measurements) of one's instrumentation, allowing to estimate the overall uncertainty for each parameter in question. Another important point to consider is that OAE samples can be far off the concentrations of typical certified reference material,

355   meaning that checking for linearity can be important (see below for details).

Finally, for any measurements described below, the starting point should be the Guide to Best Practices of ocean CO$_2$ measurements (Dickson et al. 2007). Hence, with the exception for fCO$_2$, below we are mostly referring to discrete, not *in situ*, measurements, although the following considerations should also be taken into account for the latter.

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2.3.1 Measuring DIC

Acknowledging that OAE samples for DIC can be prone to air/sample gas exchange (see section 2.2.3.1), if the right precautions are taken during sampling and storage, they should be straightforward to measure. This is because DIC concentrations in a non-equilibrated OAE sample will be the same as for untreated seawater samples. However, in pre-

365   equilibrated samples DIC can be several hundreds of micromoles higher than typical seawater samples or certified reference material, meaning that the linearity of the measurement instrument and procedure has to be ascertained.

Linearity can be checked for by preparing and measuring Na$_2$CO$_3$ (ultrapure and dried at 280 °C for 2 h) solutions of increasing DIC (ideally prepared from a concentrated stock solution), covering the required concentration range, and

370 comparing the fractional offset of measured against theoretical concentrations for each measurement point (Figure 4). If the fraction does not change with concentration, the system response is linear and a 'one-point calibration' against a certified reference material will be sufficient. Using $NaHCO_3$ to create a DIC gradient is not ideal as it is not available in ultrapure form and without further modifications it would create high fCO_2 samples which would need additional precautions because of potential CO_2 degassing,

375 Finally, it is again emphasised that sample filtration prior to measurement is most likely a crucial step to first stabilise the sample in terms of reducing the potential for $CaCO_3$ precipitation and second, to remove any $CaCO_3$ that would have precipitated prior to sampling as it would interfere with the DIC measurement (see section 2.2.2 for details).

2.3.2 Measuring TA

380 When it comes to measuring TA, samples are likely to be enriched in comparison to the typical surface ocean. Hence, checking for linearity of the instrument setup like in the case for DIC is important. Again, this can be done by preparing suitable calibration standards, covering the required concentration range. However, unlike for relatively straight forward DIC measurements this requires interpreting pH titration data on the basis of chemical acid/base equilibria in a well-defined ion matrix, called seawater (precisely defining the zero level of protons). Hence, simply using Na_2CO_3 or $NaHCO_3$ in Milli-Q

385 water is not the ideal option. Instead, to cover the higher TA range, suitable amounts of $NaHCO_3$ could be added to seawater (Na_2CO_3 is not advisable as it is quite alkaline and might induce some sort of carbonate precipitation, impacting TA). If the TA range also requires concentrations lower than typical seawater, for instance for samples that had seen substantial amounts of $CaCO_3$ precipitation, then this can be easily achieved by diluting natural seawater with Milli-Q water (weight by weight). Again, checking for changes in the ratio of measured to theoretical TA along the measured TA gradient will tell if the

390 measurement system is linear. (compare Figure 4).

A last thing to consider is that high TA samples can need considerably more titrant if the molarity of the acid is not increased. Under certain circumstances this can lead to non-linearities, e.g. if the dosing unit needs calibration. Finally, as for DIC it is important that no $CaCO_3$ is present in the sample, hence an additional filtration step during sampling might be

395 required.

2.3.3 Measuring pH

If pH is measured by a glass electrode, following the recommendations in Dickson et al. (2007), there should be no additional precautions required for OAE samples, whether they be of high TA and pH or high TA and DIC, hence typical

400 seawater pH. Also, any $CaCO_3$ that has precipitated prior to sampling will not interfere with the measurements. However, if $CaCO_3$ has precipitated post-sampling, this will have decreased the pH and an erroneous reading will be made.

Concerning spectrophotometric pH measurements, one key element is the working range of the pH dye being used. It has been suggested that for sulfonephthalein indicator dyes it is between one pH unit below and above the indicator's pK_2, (see Hudson-Heck et al. (2021) and references therein). The latter is the pH for which the concentration of the double-unprotonated form of the dye is equal to that of the single-protonated one (Byrne et al. 1988). The two most commonly used pH dyes for seawater are meta-cresol purple (mCP) and thymol blue (TB), with pK_2 of ~8.0 and ~8.5, respectively, at a temperature of 25°C and a salinity of 35, although there are a number of studies that have extended on the salinity and temperature range (see Hudson-Heck et al. (2021) and references therein). That would suggest that seawater pH ranging from 7 to 9.5 could be measured at high accuracy and precision. However, in practice accuracy can be influenced by dye impurities, and their effect can even be dependent on pH. Hence, when unpurified dyes are used, it is highly recommended to check for the proper working range.

And indeed, we have found the working range to be significantly reduced for an unpurified mCP batch, for which we compared measured pH with calculated pH from measured DIC and TA (Figure 5). And while a pH deviation by 0.03 pH units at a pH of 8.5 might not seem much, it corresponds to about an offset of 30 μmol kg^{-1} in DIC or TA if this pH measurement would be used for carbonate chemistry calculations without correction, which is clearly way above both the 'weather' and 'climate' thresholds.

Another option for applying corrections is by direct means without the need for ancillary TA and DIC measurements (although they are recommended to check whether corrections are actually working within the desired pH range, which is actually quite important as we will see below). For that purpose, the absorbance ratios obtained with an unpurified dye need to be corrected. While the actual procedure is beyond the scope of this chapter, the reader is referred to detailed instructions in Douglas & Burne (2017) for mCP and Hudson-Heck et al. 2021 for TB. And again, for the uncorrected pH measurements we found a considerable offset of up to 0.06 pH units (Figure 6), corresponding to a ~60 μmol kg^{-1} inaccuracy in TA or DIC if this pH measurement would be used for carbonate chemistry calculations. Furthermore, the pH error is smallest around pK_2 and increases below and above. And while the impurity correction does fix the error close to pK_2 the observed trend remains. The fact that there is some sort of optimum curve behaviour around pK_2 points to an issue with the dye, rather than with measurements of DIC and TA. Hence, two separate linear corrections similar to the one with mCP (Figure 4) could be applied, or purified dyes being sourced.

Finally, as for potentiometric pH measurements the starting point for setting up spectrophotometric pH should be Dickson et al. (2007).

2.3.4 Measuring fCO$_2$

For fCO_2 measurements, air is being equilibrated with seawater, either via a CO_2 permeable membrane or in a so-called showerhead equilibrator. As for pH, any $CaCO_3$ in suspension will not affect equilibration and therefore also not fCO_2 measurements if precipitated pre-sampling. The only difference to typical seawater measurements is that fCO_2 can be relatively low for un-equilibrated OAE, e.g. below 100 μatm for a TA addition of ~500 μmol kg^{-1}. Hence, full equilibration
440   of seawater with the air to be measured might take a bit longer. Other than that, we do not see any particular issues.

2.4. Carbonate chemistry calculations

Carbonate chemistry calculations in an OAE context from two measured parameters can require additional considerations. One is that particular OAE applications not only change TA or eventually DIC but also the major ion composition of
445   seawater. For instance, for calcium-based OAE, with for instance calcium oxide or hydroxide - CaO and Ca(OH)$_2$, for each mol of TA half a mol of Ca^{2+} will be added. This is the same for magnesium-based OAE, for instance with Mg(OH)$_2$ or olivine. For example, increasing TA by 500 μmol kg^{-1} would increase both calcium and magnesium ions by 250 μmol kg^{-1}, i.e. both calcium and magnesium ions by 2.5 and 0.5% over seawater background levels at a salinity of 35.

450   For calcium-based OAE this means that calculations of calcium carbonate saturation states have to factor in the increase in the calcium to salinity ratio. In other words, using standard settings in various carbonate chemistry speciation programs, e.g. CO2SYS, seacarb, PyCO2SYS (for an overview see Orr et al. 2015), which derive calcium ion concentrations from salinity, will result in wrongly calculated saturation states. Hence, they would need to be calculated in a separate step from calculated carbonate ion and actual calcium concentrations (e.g. Moras et al. 2022), the programs being adapted, or special functions
455   used (for instance available for seacarb).

Furthermore, making changes to the matrix of the major ions in seawater also affects acid/base equilibria, i.e. stoichiometric dissociation constants such as for carbonic acid. Hence, one may also need to apply corrections to K$_1$ and K$_2$ for carbonic acid (Ben-Yakoov & Goldhaber 1972) which then can be used to calculate carbonate chemistry speciation, either by hand
460   (Zeebe & Wolf-Gladrow 2001) or by adapting available programs. Furthermore, the solubility product of calcium carbonate, K$_{sp}$, needs to be corrected which can be achieved by using the specific magnesium to calcium ratio in a seawater sample (Tyrell & Zeebe 2004). Finally, the effects of major (and minor) ion composition changes on carbonate chemistry speciation can also be assessed by Pitzer modeling (for an overview see Turner et al. 2016), and there have been several programs and functions made available by the SCOR Working Group 145, MARCHEMSPEC: Chemical Speciation Modelling in
465   Seawater to Meet 21st Century Needs (http://marchemspec.org/).

Competing interests

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

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Table 1: Direction and magnitude of change in a measured carbonate chemistry parameter due to various processes. Note that for process 4 the direction depends on whether CO_2 is diffusing from the walls into the sample or vice versa. Also, the direction of TA change in process 2 depends on which form of inorganic nutrients are being released during organic matter remineralisation

	Air-sample CO_2 exchange (process 1)	Respiration/Remineralisation (process 2)	$CaCO_3$ precipitation (process 3)	Absorption and diffusion of CO_2 from walls (process 4)
TA	N/a	+ / -	- - -	N/a
DIC	+++	++	- -	+ / -
pH	- - -	- - -	- - -	- / +
fCO_2	+++	+++	+++	+ / -

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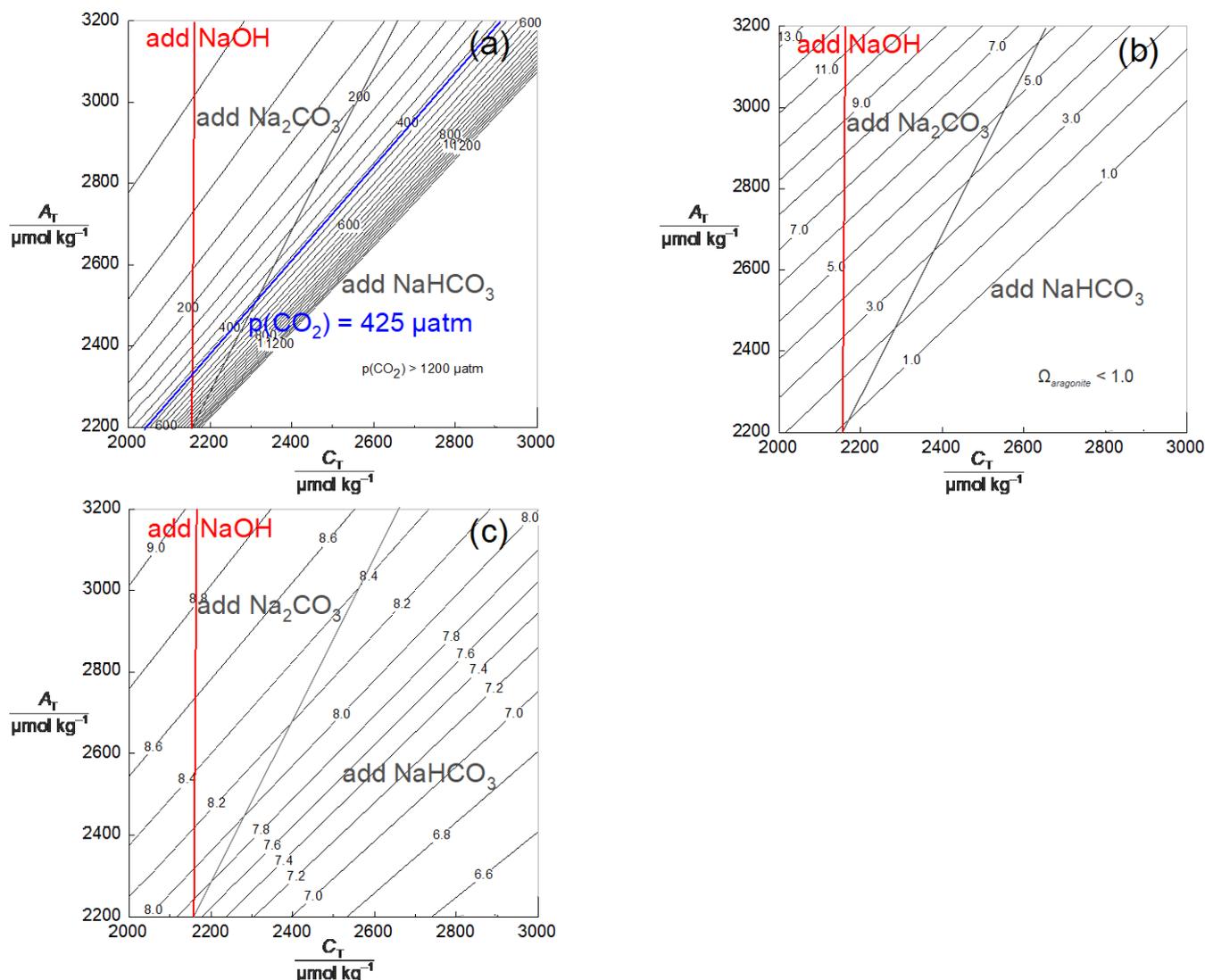
Figure 1: Implications of changes in C_T and A_T on the properties of undersaturated seawater appropriate to the California Current region. (S = 33.5, t = 10 °C, A_T = 2200 µmol kg^{-1}, C_T = 2150 µmol kg^{-1}). (a) p(CO$_2$); (b) aragonite saturation state (Ω_{arag}); (c) pH$_T$. Calculated using CO2SYS_v2.1.xls (Pierrot et al., 2006 – see text for details). The red line indicates the effect of adding NaOH, the grey lines of adding Na$_2$CO$_3$ (upper grey line) or NaHCO$_3$ (lower grey line); the shaded area covers the range of compositions achievable from adding a mixture of Na$_2$CO$_3$ and NaHCO$_3$. If a different initial seawater is chosen, this whole grouping (red and grey lines together with the grey shaded area) can be translated (moved without any distortion or rotation) so that its initial position is elsewhere on these Figures.

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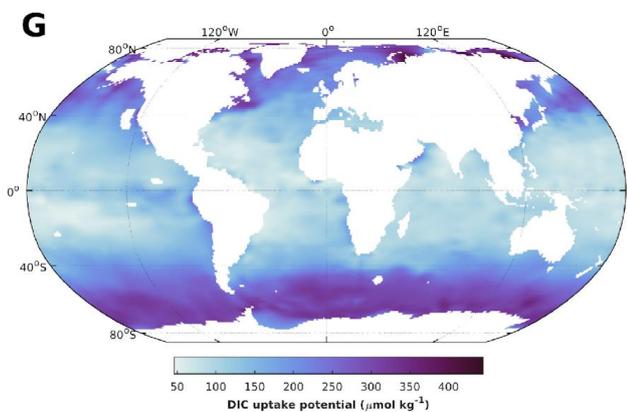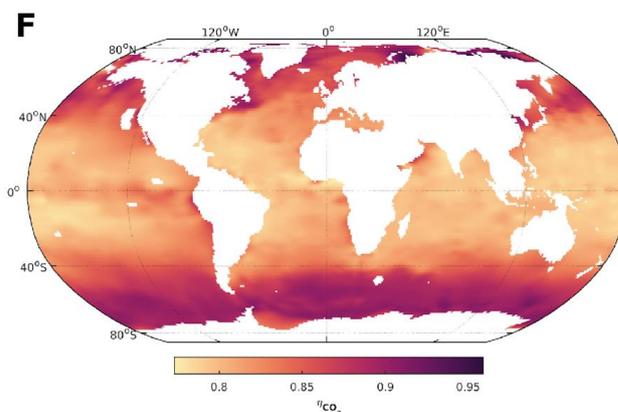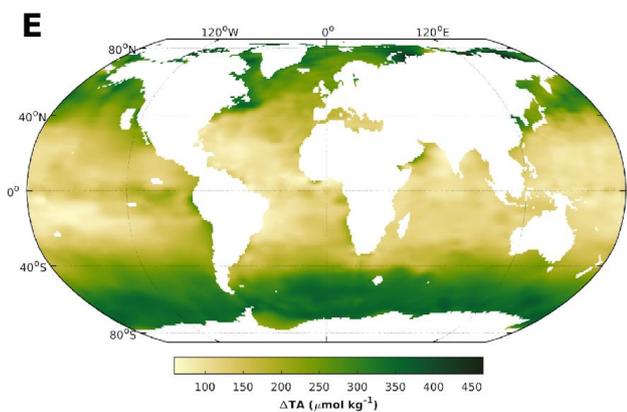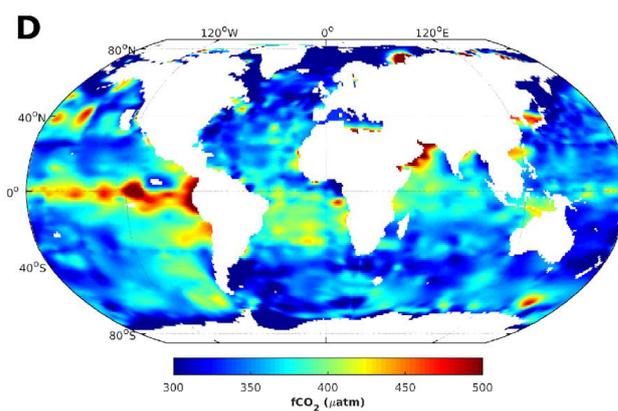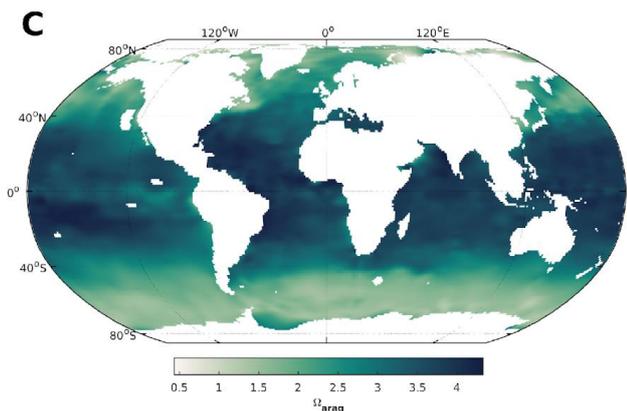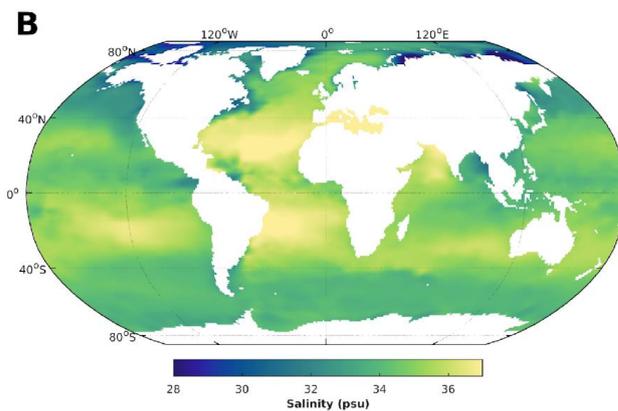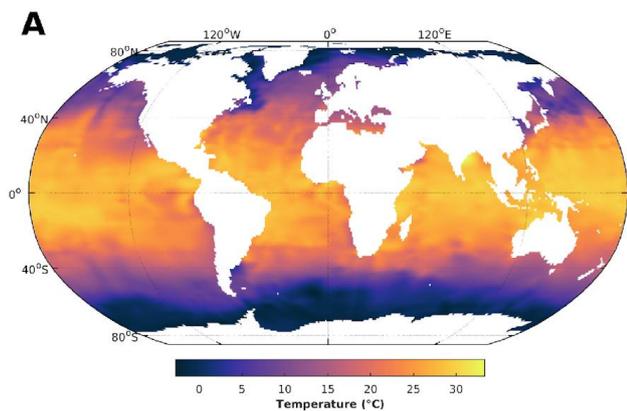
Figure 2: 1x1 degree GLODAP climatology (Lauvset et al. 2016) for surface ocean (upper 30 m) temperature (A), salinity (B), aragonite saturation state (C) and fCO2 (D), the latter two calculated from GLODAP dissolved inorganic carbon and total alkalinity using the stoichiometric dissociation constants for carbonic acid from Sulpis et al. (2020), for sulphuric acid by Dickson et al. 1990, and total boron from Uppström (1974), the concentration by which total alkalinity can be increased in order to reach an aragonite saturation state of 5, ΔTA (E), the CO_2 uptake factor ηCO_2 (F), and the resulting increase in DIC by uptake of atmospheric CO_2 upon air-sea equilibration (G). For details see text.

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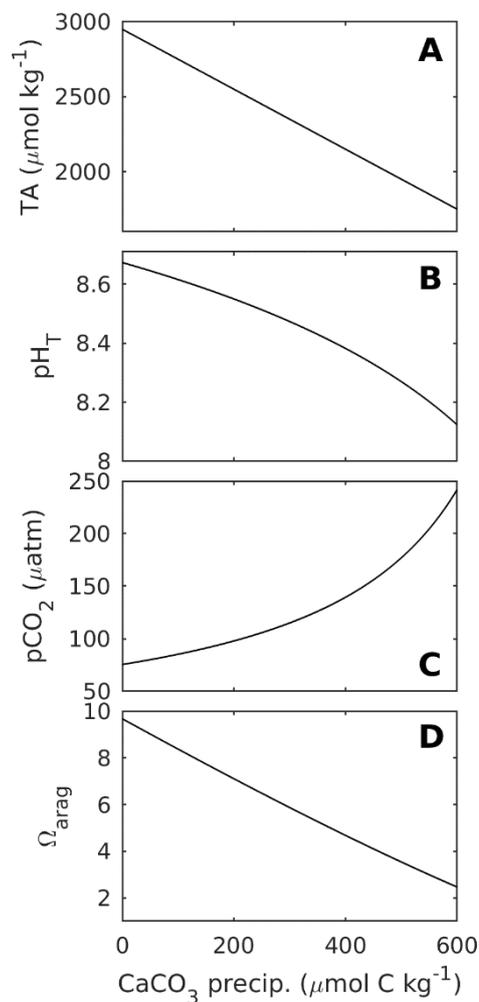


Figure 3: Changes in TA (A), pH$_T$ (B), pCO$_2$ (C) and Ω_{arag} (D) in response to CaCO$_3$ precipitation, i.e. DIC removal. Carbonate chemistry calculations were for a salinity of 35 at 20 ℃ as described in Figure caption 1. Starting TA and DIC were 2950 and 2100 μmol kg^{-1}. Please note that for 1 mol of CaCO$_3$ precipitated, 1 mol of DIC is consumed.

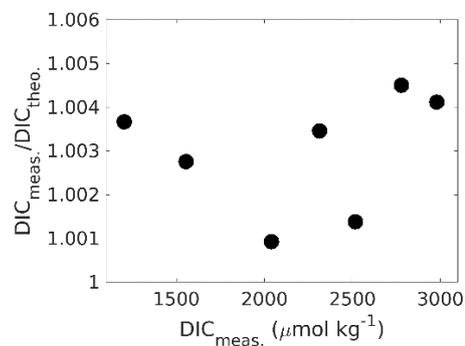



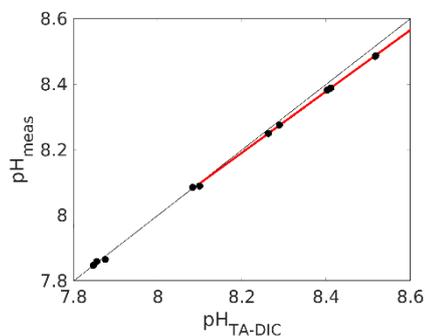
Figure 4: Measured DIC concentrations versus the ratio of measured to theoretical DIC, showing that DIC is measured
640   between ~0.1 to 0.4% higher than theoretically predicted from self-prepared Na_2CO_3 solutions, without obvious trend across
the DIC range.

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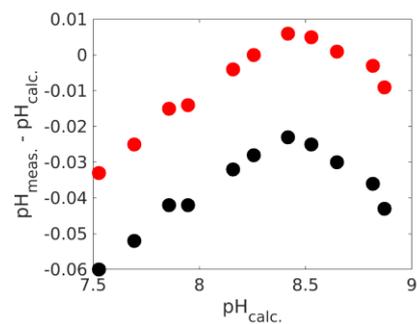
Figure 5: Calculated (see Figure caption 1 for details) vs. measured pH (total scale) using an unpurified batch of mCP. The
red line denotes a linear fit through the data above a pH of 8.1

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Figure 6: Calculated (from measured DIC and TA) pH versus the difference between measured and calculated pH (total scale). The black dots are values prior to the impurity correction and the red ones after (see text for details).