

Biogeosciences Discuss., community comment CC1

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Comment on bg-2021-330

A. Mucci (Referee)

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Referee comment on "Ocean Alkalinity Enhancement – Avoiding runaway CaCO<sub>3</sub> precipitation during quick and hydrated lime dissolution" by Charly Andre Moras et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-330-RC1>, 2021

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In this paper, the authors determine 1) how much alkaline material (CaO or Ca(OH)<sub>2</sub>) can be dissolved without inducing CaCO<sub>3</sub> precipitation in seawater, 2) what triggers CaCO<sub>3</sub> precipitation, and 3) how it can be avoided by limiting the OEA, through dilution with natural seawater or by lowering the temperature of the solution.

The objectives of the study are laudable because avoidance of CaCO<sub>3</sub> precipitation is one of the major challenges of OEA. As rudimentary as the experiments are, they do provide some insights but the choice of OEA substrates is less than ideal, given that they provide reactive surfaces (for heterogeneous precipitation) and carry a very large production carbon signature (calcination of limestone).

The descriptions of the methodologies are incomplete, the experiment during which the authors add Na<sub>2</sub>CO<sub>3</sub> is not described. It would appear that it may have been omitted or erased and, consequently, some of the statements in section 2.2.2 are blatantly wrong.

**Thank you for pointing this out. We agree that the Na<sub>2</sub>CO<sub>3</sub> method description is indeed lacking some detailed explanations. We will address this issue and will make sure that these experiments are clearly described, understandable and repeatable for the reader.**

The manuscript would greatly benefit from a more extensive review of the literature with respect to factors that control the spontaneous nucleation of calcite and aragonite from seawater. The authors are directed to a number of these in the specific comments that follow.

Finally, although the written English is acceptable, there are innumerable grammatical errors and the structure of several sentences is so awkward as to be incomprehensible.

Thanks for the additional references. The authors will add information and double-check grammar and structure.

Specific comments-

Lines 39-40: How much CaO or Ca(OH)<sub>2</sub> would be required to mitigate anthropogenic CO<sub>2</sub>? Would it be physically feasible to produce or displace so much CaO or Ca(OH)<sub>2</sub>? What would the carbon signature of producing and/or transporting this much CaO or Ca(OH)<sub>2</sub>? Under the IPCC IS-92S "business as usual" scenario, more than 4000 Gt of CO<sub>2</sub> will be emitted to the atmosphere by the end of this century. Hence, this OEA proposal would remove at most only 20% of the emitted carbon dioxide! The authors need to address the impact and feasibility of their proposed mitigation mechanism.

Currently, the global cement industry produces about 4.1 Gt of cement per year (<https://www.statista.com/topics/8700/cement-industry-worldwide/>). Depending on whether hydraulic (CaO · Al<sub>2</sub>O<sub>3</sub> · Fe<sub>2</sub>O<sub>3</sub>) or non-hydraulic (Ca(OH)<sub>2</sub>) is being produced, and assuming a Ca<sup>2+</sup> to C sequestration potential for CO<sub>2</sub> of 1.6, between 2.7 and 3.9 Gt of atmospheric CO<sub>2</sub> could be captured per year. This is on the order of CDR required to be built-up in the next 30 years, based on the shared socioeconomic pathways RCP2.6 scenario that would keep global warming below the 2 °C target (Huppmann et al., 2018). Furthermore, it is unlikely that there will only be one negative emission technology approach. In the marine realm alone, there are several currently under consideration, such as increasing open ocean productivity or marine biomass-fuelled bioenergy with carbon capture and storage (Gattuso et al., 2021).

Line 46: Calcination requires a lot of energy (heating to 1200°C) and the process produces a lot of carbon dioxide. Hence, is the proposed OEA really a feasible option?

Different strategies have been proposed to capture CO<sub>2</sub> during calcination, which would negate CO<sub>2</sub> emissions. Furthermore, with the rise of renewables, such energy-demanding process could be carbon-neutral. Finally, limestone-based minerals have certain advantages over others as they are highly abundant and have relatively quick dissolution rates. A last important point would be that they do not require fine grinding, as for instance hard olivine.

Line 70: This is a challenge for most OAE strategies.

Noted

Lines 74-76: The critical threshold for the precipitation of aragonite is more relevant since this CaCO<sub>3</sub> polymorph nucleates and precipitates first (due to Mg<sup>2+</sup> inhibition - e.g., see Pan et al. (2021)). Among many others publications on the spontaneous nucleation and precipitation of calcite and aragonite from seawater and seawater-like solutions, including Chave and Suess (1970; L&O 15:633); Rushdi et al. (1992; Geolog. Rundschau. 81:571); Choudens-Sanchez and Gonzalez (2009; J. Sed. Res. 79:363); Ruiz-Agudo et al. (2011; GCA 75:284), Kontrec et al. (2021; Crystals 11:1075), and Pan et al. (2021).

The authors will review these research articles and add more background knowledge on CaCO<sub>3</sub> nucleation pathways into this section.

Lines 98-100: What was the salinity of the natural seawater? I could not find it reported in the text.

The seawater batches were collected at different times of the year. The salinities varied between 35.46 and 36.91. The authors will add all salinity data to the appendix.

The first paragraph of section 2.2.2 is likely incomplete as either an experiment is not properly described or, as written, many statements are blatantly wrong. I can only presume that the authors carried out an experiment during which they added the 1M Na<sub>2</sub>CO<sub>3</sub> solution to the natural seawater as results are presented in section 3.4.

This is correct. In these experiments, the authors used a 1M Na<sub>2</sub>CO<sub>3</sub> solution as alkaline agent. However, it is clear that this section is incomplete. More details on the experiments with 1M Na<sub>2</sub>CO<sub>3</sub> will be added.

Lines 124-125; 127-128: Irrespective of the amount of Na<sub>2</sub>CO<sub>3</sub> added, the saturation state of a Milli-Q solution with respect to CaCO<sub>3</sub> minerals will remain null as it is devoid of calcium ions. One cannot use CO<sub>2</sub>SYN to calculate the saturation state of a Na<sub>2</sub>CO<sub>3</sub> solution prepared in Milli-Q water with respect to CaCO<sub>3</sub> minerals.

The  $\Omega_{\text{CaCO}_3}$  values were not calculated for the 1M Na<sub>2</sub>CO<sub>3</sub> solution.  $\Omega_{\text{CaCO}_3}$  values were calculated for the seawater batch, to which the 1M Na<sub>2</sub>CO<sub>3</sub> solution was added. Then, with the changes in TA and DIC, the associated changes in  $\Omega_{\text{CaCO}_3}$  were calculated. The authors will rewrite this section to make it clearer.

Section 2.3: What is the precision and accuracy of the TA and DIC measurements?

The TA measurements were made in duplicates, and a standard deviation is reported, i.e., 0.8  $\mu\text{mol kg}^{-1}$ . The DIC measurements were made in triplicates, and similarly, a standard deviation is reported, i.e., 0.6  $\mu\text{mol kg}^{-1}$ . Using these measures of precisions and taking into account that they are referenced against a certified standard with very similar precision, the overall uncertainty for TA is 1.0  $\mu\text{mol kg}^{-1}$ , and 0.8  $\mu\text{mol kg}^{-1}$  for DIC (as calculated from an error propagation).

Line 158: Open-cell titrations?

This will be changed to “open-cell titration protocols”.

Lines 167-168: What fraction of the filters and how were filters introduced in the elemental analyzer? Why was an IRMS used? As a detector, as no isotopic data are reported?

The whole filter was introduced in the elemental analyser. To do so, the filters were folded and wrapped into small tin capsules, that were pressed into round-shaped balls. The elemental analyser is connected to an IRMS as the detector in our lab, hence the reason it was mentioned. We will clarify this in the text.

Line 180: What boron: salinity relationship did the author use in CO2SYS (Uppstrom (1974) or Lee et al. (2010))?

The authors used the boron to salinity relationship from Uppstrom 1974. This will be added.

Line 188: Although CO2SYS will return values of the stoichiometric solubility of calcite and aragonite ( $K^*$ ) at the temperature and practical salinity of interest, values of TA and DIC are not required since  $K^*$  values are independent of TA and DIC but are a function of  $t$  and SP (and P).

The reviewer is correct, and our formulation was vague. We calculated  $K_{sp}$  based on temperature and salinity (Mucci, 1983), and then used it with addition-corrected calcium concentrations, together with CO<sub>2</sub>SYS-derived  $CO_3^{2-}$ , based on DIC and TA, to calculate  $\Omega_{CaCO_3}$ . We will clarify this in the revised version of the manuscript.

Line 191, Eqn. (3): Why use the Ca:chlorinity ratio rather than the Ca:SP ratio? Equation 3 would simplify to:  $[Ca^{2+}] = (0.01028/35) * SP + \Delta TA/2$ .

We agree, this is a much straight-forward approach, and will change it accordingly.

Lines 228-229: Unclear. "TA" does not precipitate, CaCO<sub>3</sub> does.

This will be reformulated as "when TA decreased".

Lines 247-251 and 259-267: Why are the results of this duplicated experiment repeated? The authors should comment about their reproducibility in section 3.3 and focus of the results of the dilution experiments in this section.

These results were not duplicated, but a new batch of TA+500  $\mu\text{mol kg}^{-1}$  was freshly prepared to be used in the dilutions experiments. For completeness, the undiluted treatment results were presented as well.

Lines 339-344: The threshold saturation value also determines the induction time, a variable that the authors did not investigate or refer to. Several studies have been conducted on the subject, including Morse and He (1993) and many others.

Following the research on CaCO<sub>3</sub> nucleation pathways, the authors will mention the induction time.

Lines 344-347: It should theoretically precipitate until saturation is reached, but precipitation kinetics decrease rapidly as saturation is approached and is strongly inhibited by the presence of DOM and orthophosphate. As the authors used natural seawater, both solutes must have played a role. What was the DOC and soluble reactive phosphate (SRP) of the natural seawater?

Unfortunately, DOC was not measured. From left-over water, however, we did determine phosphate concentrations in one of the seawater bathes, which was  $0.3 \mu\text{mol L}^{-1}$ . This information will be added to a table in the appendix.

Lines 350-351: Would this not have been revealed by the SEM examination of the precipitates?

Unfortunately, the SEM analysis did not show any obvious aragonite formation around CaO or Ca(OH)<sub>2</sub> particles, as they were taken at the end of the experiments, after 14 days for the first dilution experiment, and up to 48 days in other experiments. At these stages, relatively small CaO or Ca(OH)<sub>2</sub> particles are likely to be completely covered in CaCO<sub>3</sub> overgrowth. Furthermore, with EDX analysis, it is difficult to differentiate between CaO/Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> as the elemental composition is quite similar (note that there is always a carbon background from the polycarbonate filters). Hence, we could only speculate on the potential CaCO<sub>3</sub> precipitation on not yet dissolved particles. That was however different to the non-dissolving quartz particles, as their CaCO<sub>3</sub> overgrowth was clearly visible and distinguishable by element analysis with EDX.

Line 380: CO<sub>2</sub> capture upon calcination of limestone would have to be 100% efficient. This brings us back to the issue I raised earlier on in my comments about the net carbon signature and feasibility of the proposed OAE process.

Please see reply above.

Lines 383-384: A mere 14% of projected emissions by the end of this century!

It is actually more than double, what would be required to stabilize global temperature below 2 °C increase until the end of the century (see reply above).

Lines 391-392: How is this possible ( $\Omega_{Ar} < 1$ ), unless calcite is precipitated. Yet, the authors have established and shown (Figure 5) that, in most cases, only aragonite precipitated from their experiments. In other cases, the authors believe that vaterite was precipitated.

In our model simulations, precipitation stopped at an  $\Omega_{Ar} = 2$ . The re-equilibration with the atmosphere and resulting ingassing of CO<sub>2</sub> increases DIC and further lowers  $\Omega_{Ar}$ , i.e., in this case to be slightly below 1. This will be clarified.

Lines 430-433 and 445-447: The sentence structures are awkward and nearly incomprehensible.

These sentences will be reviewed and reformulated, implementing both reviewers' comments.