

Biogeosciences Discuss., referee comment RC1
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Comment on bg-2021-330

A. Mucci (Referee)

Referee comment on "Ocean alkalinity enhancement – avoiding runaway CaCO_3 precipitation during quick and hydrated lime dissolution" by Charly A. Moras et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-330-RC1>, 2021

In this paper, the authors determine 1) how much alkaline material (CaO or Ca(OH)_2) can be dissolved without inducing CaCO_3 precipitation in seawater, 2) what triggers CaCO_3 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_3 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_2CO_3 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.

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.

Specific comments-

Lines 39-40: How much CaO or Ca(OH)₂ would be required to mitigate anthropogenic CO₂? Would it be physically feasible to produce or displace so much CaO or Ca(OH)₂? What would the carbon signature of producing and/or transporting this much CaO or Ca(OH)₂? Under the IPCC IS-92S "business as usual" scenario, more than 4000 Gt of CO₂ 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.

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?

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

Lines 74-76: The critical threshold for the precipitation of aragonite is more relevant since this CaCO₃ polymorph nucleates and precipitates first (due to Mg²⁺ 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).

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

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 Na₂CO₃ solution to the natural seawater as results are presented in section 3.4.

Lines 124-125; 127-128: Irrespective of the amount of Na₂CO₃ added, the saturation state of a Milli-Q solution with respect to CaCO₃ minerals will remain null as it is devoid of calcium ions. One cannot use CO2SYS to calculate the saturation state of a Na₂CO₃ solution prepared in Milli-Q water with respect to CaCO₃ minerals.

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

Line 158: Open-cell titrations?

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?

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

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 S_p (and P).

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

Lines 228-229: Unclear. "TA" does not precipitate, $CaCO_3$ does.

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.

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.

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?

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

Line 380: CO_2 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.

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

Lines 391-392: How is this possible ($\Omega_{\text{ar}} < 1$), 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.

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