

Marine carbon dioxide removal, and ocean alkalinity enhancement in particular, have the potential to make a significant contribution to the world's efforts toward avoiding the worst effects of climate change.  $Mg(OH)_2$  is a promising alkalinity source, but understanding its dissolution kinetics and how to avoid runaway precipitation of  $CaCO_3$  that removes more alkalinity than was added is key to realizing this promise. I recommend "Effects of grain size and seawater salinity on magnesium hydroxide dissolution and secondary calcium carbonate precipitation kinetics: implications for ocean alkalinity enhancement" for publication, but only after the authors address my comments and questions listed below.

Abstract, lines 21-22: "while the slower dissolution of bigger grain size maintained a higher alkalinity/pH at the surface of particles, increasing  $CaCO_3$  precipitation rates and making it observable much quicker than for the intermediate grain size" Why would larger size have this effect? in the direction normal to the grain face, should be same in all cases, but is the argument lateral transport makes a parabolic alk/pH distribution with peak at center of grain face?

Thank you for the comment. We agree that the TA/pH would be consistent in the direction normal to the grain face. However, the larger grain sizes, taking longer to dissolve, provide high TA/pH environments for longer around the particles. This maintain of such high levels for longer than with small particles could allow for (pseudo-)homogeneous precipitation to occur.

Line 34: "To mitigate the effects of Ocean Acidification" No CDR process will meaningfully mitigate OA over a global scale, only local scales. I suggest changing to "To locally mitigate..."

This has been edited accordingly (line 34, **of the TRACK CHANGES document**).

Line 83: "laboratory air  $pCO_2$ " What was the lab  $CO_2$  value? if  $H_2O$  saturated, what was the temperature?

Thank you for the comment. The laboratory air was not recorded at the exact time, but the experiments run by Moras et al. (2023) occurred at a similar time and they recorded a laboratory  $pCO_2$  of  $479.1 \pm 4.3 \mu atm$ . The laboratory temperature was regulated by air conditioning, set to 21 °C.

Line 95: "For the grain size experiments, three grain size ranges were produced using two stainless steel sieves with 63  $\mu m$  and 180  $\mu m$  mesh sizes. The medium range, i.e., 63-180  $\mu m$ , was also used for the salinity experiments at ~36, ~28 and ~20." Did you measure the actual grain size distribution? I suggest making this measurement.

Thank you for pointing this out. This measurement has been attempted, but due to the high reactivity of the material with the matrix used for the analysis, no precise measurements were available. Therefore, a size fractionation using sieves was deemed more suitable.

Line 100 and throughout: How was omega determined?

$\Omega_A$  was determined using CO2SYS, and the measured TA, DIC, temperature and salinity at each data point, as mentioned in lines 153-156: **“ $\Omega_A$  and carbonate chemistry speciation were calculated from measured TA and DIC, providing temperature and salinity measurements, using CO2SYS (Sharp et al., 2021). To do so, the boric acid dissociation constant from Uppström (1974), the carbonic acid dissociation constant from Lueker et al. (2000), and the sulfuric acid dissociation constant of Dickson (1990) were selected.”**

Throughout: Why use free scale instead of total?

While total scale would have been more appropriate, the pH probe used throughout was measuring on the free scale. This was expected through the calibration using the mentioned buffers, and assessed and confirmed by providing measured TA, DIC, salinity and temperature data in CO2SYS and comparing the estimated  $\text{pH}_F$  from the software with actual measured pH. After reviewing all data points, the estimated  $\text{pH}_F$  from measured TA and DIC was identical to the measured pH with the above-mentioned probe.

Line 166: “After two hours, the maximum pH<sub>F</sub> recorded for the smaller grain size was  $8.76 \pm 0.04$ , which continuously decreased to  $8.68 \pm 0.00$  between 11 and 12 hours after  $\text{Mg}(\text{OH})_2$  addition. In contrast, the pH<sub>F</sub> for the medium and larger grain size increased to  $8.72 \pm 0.00$  and  $8.68 \pm 0.03$  after about eight hours and remained stable thereafter, respectively (Figure 1).” Why this behavior for small grains? no explanation is given.

Thank you for pointing this out. We indeed did not discuss this behaviour. We have added a paragraph in the discussion that covers this particular pattern (lines 338-346).

Line 184: “Finally, a small drop in DIC was observed after  $\text{Mg}(\text{OH})_2$  addition in all experiments, of about 80, 30 and 140  $\mu\text{mol kg}^{-1}$  in the small, medium and large grain size incubations, respectively.” Why? What is the physical mechanism?

We believe that early  $\text{CaCO}_3$  nucleation could have been responsible for such decrease. This is discussed in a newly added paragraph, lines 342-346.

Fig. 2: What accounts for the large spread in time among the 3 replicates?

Thank you for pointing this out, we believe that the reviewer refers to the different start of precipitation between replicates such as the small grain size experiments, with precipitation starting on days 3, 4 and 7. This is an interesting point that is hard to answer with certainty. We believe that the nucleation process happening between the addition of  $\text{Mg}(\text{OH})_2$  and the measured drop in TA may vary due to factors such as surface area and high pH in the diffusive boundary layer. It is possible

that the suitable conditions to start this nucleation process were met earlier on in one replicate compared to the other.

Line 200: “Starting pHF were slightly different, recorded at  $7.99 \pm 0.05$ ,  $8.06 \pm 0.01$  and  $8.09 \pm 0.01$  in the salinity 20, 28 and 36 incubations, and increased to a maximum of  $9.19$ ,  $\pm 0.00$ ,  $8.91 \pm 0.00$  and  $8.72 \pm 0.00$ , respectively. In all incubations, similar logarithmic trends were observed for pHF (Figure 3).” Maybe I missed it above. Do you add the same amount of  $\text{Mg}(\text{OH})_2$  for all experiments (and if so what amount)? Or do you adjust the amount of  $\text{Mg}(\text{OH})_2$  to target a certain starting pH or omega (and if so, why do you have slightly different starting pH / omega values?)

Thank you for the comment. For each salinity, different amounts of  $\text{Mg}(\text{OH})_2$  were added, (more being added at lower salinity) to increase  $\Omega_A$  to similar values. These additions varied as at lower salinity, the concentration of calcium is lower ( $\sim 5.7$  mM instead of  $\sim 10$  mM at salinity 35). Therefore, to increase  $\Omega_A$  in lower salinity, a higher amount of alkalinity is required to increase  $\Omega_A$  to the same level, here being the desired target of  $\Omega_A \sim 9$ . The different starting pHF and  $\Omega_A$  conditions are also the result of the lower salinity. NSW was diluted with MilliQ to decrease the salinity down to 28 and 20. Therefore, the starting pHF and  $\Omega_A$  were lower. The text was edited as follow (lines 104-109): **“Varying amount of  $\text{Mg}(\text{OH})_2$  were used in the salinity experiments. The decrease in dissolved [Ca] following dilution with MilliQ led to higher amounts of  $\text{Mg}(\text{OH})_2$  to be added with decreasing salinity to reach a similar  $\Omega_A$  of about 9. Furthermore, preliminary tests conducted with the  $\text{Mg}(\text{OH})_2$  powder used for these experiments, despite having reagent grade properties (>98% pure), have shown that only about 75% of the theoretical maximum TA was generated. Therefore, the  $\text{Mg}(\text{OH})_2$  additions were adjusted accordingly, with additions varying from 23.3 mg kg<sup>-1</sup> in the salinity 36 experiments (and all grain size experiments) to 30.2 mg kg<sup>-1</sup> in the salinity 20 experiments.”**

Fig. 3: From the caption to figure 3, the goal is same starting omega. Do you list somewhere how much  $\text{Mg}(\text{OH})_2$  is added in each case?

The goal is the same  $\Omega_A$  indeed. The amounts of  $\text{Mg}(\text{OH})_2$  added will be incorporated into the text (lines 107-109).

Line 219: “Similarly, following  $\text{Mg}(\text{OH})_2$  additions,  $\Omega_A$  quickly increased to reach 8.6, 9.3 and 9.1 with increasing salinity.” If targeting same omega, why do you have different values? What exactly determined how much  $\text{Mg}(\text{OH})_2$  was added in each case? Somewhere the amount of  $\text{Mg}(\text{OH})_2$  added in each case should be listed.

Thank you for the comment. As mentioned above, the  $\text{Mg}(\text{OH})_2$  additions were adjusted to take into account the lower [Ca] at lower salinity and the “missing alkalinity”. Despite our best efforts, it is very likely that the 8.6  $\Omega_A$  recorded at salinity 20 is the result of early  $\text{CaCO}_3$  precipitation before the observed TA drop. Such precipitation would have lowered the final TA and DIC values, resulting in a lower maximum  $\Omega_A$ .

Line 224: “Finally, DIC also decreased upon Mg(OH)<sub>2</sub> additions. An initial DIC drop was observed directly after Mg(OH)<sub>2</sub> additions of about 60 μmol kg<sup>-1</sup> at the lowest salinity and 30 μmol kg<sup>-1</sup> at the highest salinity. At a salinity of 28, a much smaller DIC drop was observed in one replicate. After a period of stable DIC conditions, DIC also dropped in a...” Why? What is the physical mechanism?

Thank you for highlighting this point, this “absence” of DIC drop is indeed questionable. While the drop in DIC in the salinity 36 and 20 experiments is clearly visible, the one in salinity 28 is more subtle. One could suspect that ingassing have decreased such DIC drop, but this cannot be verified in anyway. However, this observation has no implication of the remaining of the experiment, which is why this is not actively discussed.

Line 279: “Such ingassing is also occurring in the other experiments, but is likely hidden by the stronger pH<sub>F</sub> increase occurring during Mg(OH)<sub>2</sub> dissolution.” This doesn't make sense to me; I think you would see it just as well in the high pH case. Can you justify this statement quantitatively?

Thank you for the comment. We would like to clarify our point. When Mg(OH)<sub>2</sub> dissolves in seawater, the pH<sub>F</sub> increases due to the increase in TA. CO<sub>2</sub> will ingas as soon as the difference between water and atmospheric pCO<sub>2</sub> is negative (lower water pCO<sub>2</sub> lead to ingassing). If ingassing occurs, the increase in CO<sub>2</sub> will lead to a decrease in pH<sub>F</sub> (as per Bjerrum's plot). Therefore, these two processes are occurring simultaneously and in opposite direction. The smaller grain size reached a maximum pH<sub>F</sub> earlier than other grain sizes (~2h), suggesting full dissolution earlier, allowing for pH<sub>F</sub> to be recorded and the CO<sub>2</sub>-driven decrease to be observed. In the other experiments, the slower dissolution rate over 8h hides the CO<sub>2</sub> ingassing impact until nearly the end of the pH<sub>F</sub> recorded data. The decrease in pH<sub>F</sub> and would only become visible late on (after 12h).

Line 281: “For salinity, we did not observe major differences in initial dissolution rates within the range of salinities tested, with dissolution rates for salinities 36, 28 and 20 estimated at 391.6 ±2.6, 359.8 ±0.2 and 301.9 ±0.3 μmol of TA mg<sup>-1</sup> min<sup>-1</sup>...” These differences are quite significant: 25% variation!

This is a good point. The text has been edited in lines 293-296 to: **“For salinity, we did not observe major differences in there was a difference in initial dissolution rates within the range of salinities tested, with dissolution rates for salinities 36, 28 and 20 estimated at 391.6 ±2.6, 359.8 ±0.2 and 301.9 ±0.3 μmol of TA mg<sup>-1</sup> min<sup>-1</sup>, respectively. While these differences are not as significant as those in the grain size experiments, the dissolution rate decreased by about 23% between salinity 36 and 20.”**

Line 320: “Here, it could be higher pH levels and hence Ω<sub>A</sub> that are reached at a particle's surface as of having a larger diffusive boundary layer.” Why is this true in a direction normal to the grain surface?

Thank you for the comment. One main outcome of the research is the potential two processes occurring simultaneously for  $\text{CaCO}_3$  precipitation. The diffusive boundary layer plays a key role in providing high pH levels around the particles. These high levels allow for high  $\Omega_A$  to be generated around the particles. Marion et al. (2009) reported that at salinity 35, an  $\Omega_A$  of 12 was triggering pseudo-homogeneous precipitation. It is very likely that around the larger particles, these levels are much higher, allowing for homogeneous precipitation to occur within seconds, or even fractions of seconds. On the other hand, smaller particles present a smaller diffusive boundary layer, but the surface provided for the same amount of  $\text{Mg}(\text{OH})_2$  is much higher. There, the surface area allows for more  $\text{CaCO}_3$  to nucleate, as suggested by Zhong and Mucci, 1989.

Line 381: "... while the second maintains a higher pH around larger particles due to a larger diffusive boundary layer compared to smaller particles, which increases precipitation rates." I think this claim needs to be supported with data and/or modeling.

Unfortunately, we cannot provide any modelling data, but we edited the text as follow (lines 408-412): **"One major finding of this research was that two processes seem to occur during  $\text{CaCO}_3$  precipitation in relation to grain size, one where the higher surface area of smaller particles could increases precipitation rates, while the second may maintains a higher pH around larger particles due to a larger diffusive boundary layer compared to smaller particles, which increaseds precipitation rates."**