Reply to referee 1

We would like to thank the reviewer for their constructive and positive feedback on our manuscript. Below we provide a response to all their comments and suggestions, and indicate how we have altered the manuscript in response; our responses are in blue, altered text is in shaded in grey.

There have been at least 2 related reviews of this topic in recent months here: https://scijournals.onlinelibrary.wiley.com/doi/full/10.1002/ghg.2311 , and a paper by Dong et al. Potential of CO2 Sequestration through Accelerated Weathering of Limestone on Ships that is in press at Science Advances. You can probably get a prerprint of the latter from Jess Adkins jess@caltech.edu

We thank the reviewer for bringing these recent papers to our attention.
Damu et al. (2024) is a research article which addresses the potential of construction grade limestone compared to lab grade limestone in a one-step AWL reactor using potable water. They discuss the CO_2 capture efficiency and effluent A_T based of different liquid to gas ratios for this specific reactor design. They highlight that $CaCO_3$ dissolution is the limiting step in the AWL process.
Dong et al. (2025) investigate the potential of AWL for ship-board applications both through benchtop-scale experiments and modelling. For there experiments they use a series of two-step AWL reactors changing water flow rate, solid holdup, and flow regime. They then modelled the instantaneous total efficiency and conversion efficiency for a ship-scale reactor while varying the solid holdup and limestone particle grainsize.

These two papers are experimental studies. Our paper provides a framework to compare the efficiencies of different reactor types based on inlet and outlet alkalinity and DIC values. We then provide an example of the use of this framework for different existing reactor designs. We further discuss the different reactor designs, the required feedstock for AWL, and the potential environmental impact. We have included the recommended papers in our discussion.

My comments:

1. Pg 1 line 19 Here and throughout - "large water usage" should read "large seawater usage" so as to make clear that the preferred application does not consume freshwater and that the real limitation is the cost and C footprint of pumping seawater, not the scarcity of seawater, unlike freshwater.

Recent studies, like Damu et al. (2024), use fresh water as feedstock for their AWL reactor However, in section 4: AWL feedstock, we highlight that seawater is the preferred feedstock for AWL.

2. Lines 64-73 Implies that rock weathering on land causes CO2 removal by the ocean. Rather, rock weathering on land consumes CO2 on land resulting in fully carbonated alkalinity that eventually reaches the ocean where it is stored. This alkalization of the ocean does not increase CO2 uptake by the ocean, but does increase the alkaline C stored there.

We have adjusted the text to make the CO_2 uptake by A_T increase more general.

Line 64 – 73: The natural weathering of silicate and carbonate rocks generates A_T (Berner and Berner, 2004), which is defined as the excess of base (proton acceptors) over acid (proton donors) (Dickson, 1981; Zeebe and Wolf-Gladrow, 2001). Increasing the A_T content of the surface waters shifts the carbonate equilibrium away from dissolved CO_2 towards bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. As a result, the pCO_2 of the surface water is reduced which drives a flux of CO_2 from the atmosphere towards the surface water. This increases the amount of CO_2 that can be sequestered and stored as dissolved inorganic carbon (DIC; defined as the sum of the aqueous [CO_2], [HCO_3^-], and [CO_3^{2-}] concentrations; Zeebe and Wolf-Gladrow, 2001) in the ocean. This natural process of ocean alkalinization, induced by the chemical weathering of rocks, has regulated atmospheric CO_2 and stabilized the climate over geological time scales (Berner et al., 1983).

3. Line 87 Delete “out”

“consisting out of …”is changed to “consisting of …”.

4. Table 1. I find some inconsistencies in the measured versus calculated data presented. For example, taking the listed At and DIC reported by Chou et al for ambient seawater (state 1), I get a pCO2 of 666 uatms, pH=7.84 and an Omega(ca) = 2.48 using CO2SYS, in contrast to those in table 1 of 420, 7.94 and 2.50 respectively. For state 2, the table lists At= 2.26 and DIC=2.96, that according to my calcs should yield pCO2 = 0.19 atm, pH= 6.42 and Omega(ca)= 0.11, whereas Table 1 listed 0.15, 6.52 and 0.11, respectively. For State 3 the Chou et al data are listed as 2.64 and 3.15 for At and DIC, respectively. These values yield a calculated pCO2 of 0.14 atm, pH= 6.63 and Omega(ca) = 0.20, in contrast to 0.15 atm, 6.72 and 0.20 listed in table 1, respectively. For States 4a and b, my calcs based on listed At and DIC are pretty close to those listed. The CaCO3 saturation states seem pretty accurately represented, which is the critical thing, however, with the data clooged together like they are, some non-representative data can arise, in particular pCO2=420 vs 666 uatms for State 1 seawater.

The pCO_2 represented in Table 1 is the ambient air or gas stream pCO_2. We agree that this is not well formulated in the text. We elaborated on this fact and added a column with the process water pCO_2 (fCO_2).

Line 115: "Table 1 shows the values for $pCO_{2,\,gas}$, $pCO_{2,water}$, A_T, DIC, pH, and Ω_{calc} …"

The other slight differences between the results calculated with AquaEnv and CO2SYS could result from the difference in the used dissociation constants (k1k2, khf or kf, and khso4 or ks). In AquaEnv the default value of the first and second dissociation constant of carbonic acid (k1k2) is from Leuker et al. (2000), the HF dissociation constant (khf or kf) is from Dickson (1990), and the HSO_4^- dissociation constant (khso4 or ks) is from Dickson (1990).

Table 1: Differences between the calculated values for state 1 - 3 between AquaEnv and CO2SYS for a temperature of 15 °C and a salinity of 35.

	AquaEnv			CO2SYS		
	fCO_2 (atm)	pH (-)	$\Omega_{calcite}$ (-)	fCO_2 (atm)	pH (-)	$\Omega_{calcite}$ (-)
State 1	0.000656	7.93	2.50	0.000666	7.84	2.48
State 2	0.0189	6.52	0.11	0.19	6.42	0.11
State 3	0.0139	6.72	0.20	0.14	6.63	0.20

5. Line 155 You mean "Because the input of AT from CaCO3 dissolution is twice that of the DIC supplied by CaCO3"? On the other hand, eq 1 show 1 mole of AT per mole of DIC produced, so what is meant here? There are 2 moles of potential alkalinity per mole of CaCO3.

With the sentence "… the input of A_T from $CaCO_3$ dissolution is twice that of DIC …", we mean that during $CaCO_3$ dissolution A_T and DIC increases in a 2:1 ratio. We have elaborated on this in the manuscript.

Line 155: "Because the input of A_T from $CaCO_3$ dissolution is twice that of DIC (2:1 ratio of A_T to DIC production), …"

For Eq. 1($CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$), in the manuscript, the logic we follow goes as follows.

On the left hand side (CO_2 + H_2O + $CaCO_3$), there is already 1 mole of DIC (in the form of aqueous CO_2) and 0 mole of A_T (as aqueous CO_2 is not part of the A_T equation (Zeebe and Wolf-Gladrow, 2001)*).*

On the right hand side (Ca^{2+} + $2HCO_3^-$), there are 2 mole of DIC and 2 mole of A_T ($2HCO_3^-$, as HCO_3^- is both part of the DIC and A_T pool).
This results in a net increase of 1 mole of DIC and 2 mole of A_T.
Thus, during the dissolution of $CaCO_3$, there is a 2:1 ratio of A_T to DIC that is produced.

6. Lines 165-6. "However, one can easily show that equilibration followed by mixing, provides the same CO2 transfer as mixing followed by equilibration." Not always true. If the mixing involves vertical mixing that could cause the CO2 supersaturated water to lose contact with the atmosphere, then full equilibration with air could take +1kyrs. This is touched on later in the paper when discussing efficiencies.

We have change the paragraph to account for the vertical mixing.

Line 163 – 166; "In our scheme, we assumed that the effluent process water first equilibrates with the ambient atmosphere, before it is mixed with the surrounding seawater. In reality, the process water will be mixed first with ambient seawater. If mixing involves vertical mixing of the process water supersaturated with CO_2, full equilibration will not be reached."

7. Line 173 it's rather than its.

The typo has been corrected.

8. Line 199-200 " DeltaDIC buf seq represents the DIC that is retained (i.e. prevented from efflux to the atmosphere) due to the Ca(OH)2 buffering of the effluent (in the unbuffered scenario DeltaDIC buf seq = 0)." Not clear/true. CaCO3 + CO2 also generates some buffered, alkaline C from CO2 as Ca++ 2(HCO3)- and CO3aq—that will not degass to the atmosphere. So, use of CaCO3 is also offers some buffered sequestration. Use of unbuffered here is not appropriate. Less vs more buffered?

In the manuscript, we separate between an unbuffered and a buffered AWL (Caserini et al., 2021) *scenario. Throughout the text buffering refers to the addition of $Ca(OH)_2$ to the effluent process water after the $CaCO_3$ dissolution step. ΔDIC_{seq}^{unbuf} present the amount of DIC that is sequestered from the gas stream in the unbuffered scenario (without addition of $Ca(OH)_2$ to the effluent at the outlet of the reactor). ΔDIC_{seq}^{buf} present the extra DIC that sequestered in the buffered scenario through the addition of $Ca(OH)_2$ to the effluent after $CaCO_3$ has taken place. A ΔDIC_{seq}^{buf} of 0, does not mean that there is no DIC that is sequestered from the gas stream by $CaCO_3$ dissolution but that there is no addition of $Ca(OH)_2$, and thus no additional buffering has taken place.*

To make this point more clear, we have updated this section.

Line 197 – 201: "DIC_{inlet} is the DIC value measured in the process water at the inlet, ΔDIC_{carb} denotes the DIC that originates from $CaCO_3$ during dissolution, ΔDIC_{seq}^{unbuf} represents the DIC in the process water that originates from net CO_2 sequestration from the flue gas in the reactor through the increase in A_T from $CaCO_3$ dissolution. ΔDIC_{seq}^{buf} represents the DIC that is not

sequestered by $CaCO_3$ dissolution that is retained (i.e. prevented from efflux to the atmosphere) due to the $Ca(OH)_2$ addition to the effluent (in the unbuffered scenario $\Delta DIC_{seq}^{buf} = 0$).

9. Eq 8 There is (still) a math operation symbol missing prior to the last term.

Eq. 8: $DIC_{final} = f(A_{T,final}, pCO_{2,atm}) \approx DIC_{inlet} + \left(\frac{\partial DIC}{\partial A_T}\right)_{pCO_{2,atm}} \Delta A_{T,carb}$

Is changed to $DIC_{final} = f(A_{T,final}, pCO_{2,atm}) \approx DIC_{inlet} + (\partial DIC / \partial A_T)_{pCO_{2,atm}} \Delta A_{T,carb}$*, to make the multiplication sign (. , as indicated by the red circle) more clear for readers.*

10. Eq 9 is incorrect because it does not include a DelatDICbuffered component that is derived from CO2 via the reaction with CaCO3 and water. This eq assumes that there is zero buffered C storage derived from CO2 in reaction with CaCO3, which is false.

See response to comment 8 for explanation of the ΔDIC_{seq}^{buf}.

Equation 9 includes the increase in DIC through A_T addition from $CaCO_3$ dissolution and accounts for the re-equilibration with the atmosphere.

Eq. 9: $\Delta DIC_{seq}^{unbuf} = DIC_{final} - DIC_{inlet} - \Delta DIC_{carb}$

With $DIC_{final} = DIC_{inlet} + (\frac{\delta DIC}{\delta A_T})_{pCO_{2,atm}} * \Delta A_{T,carb}$

Thus $\Delta DIC_{seq}^{unbuf} = (\frac{\delta DIC}{\delta A_T})_{pCO_{2,atm}} * \Delta A_{T,carb} - \Delta DIC_{carb}$

The first term $((\frac{\delta DIC}{\delta A_T})_{pCO_{2,atm}} * \Delta A_{T,carb})$ *represents the extra DIC that can be stored in the process water due to the A_T increase from $CaCO_3$ dissolution after re-equilibration with the atmosphere.*

The second term (ΔDIC_{carb}) subtracts the DIC that is produced during the $CaCO_3$ dissolution and that is thus not sequestered from the flue gas.

11. Lines 241-44 the total DIC increase in the equilibrated effluent water amounts to $\Delta DICtotal$ = 0.25mM in the unbuffered case, of which 76 % (0.19 mM) originates from CaCO3 dissolution and 24% (0.06 mM) is due to CO2 sequestration from the flue gas." Actually, 2.62 – 2.26 = 0.36 At produced = 0.18 mM C generated from the dissolution of CaCO3, but close enough? You imply that that 0.06mM is unbuffered dissolved CO2 when in fact most of it is Ca(HCO3)2aq + CaCO3aq, not CO2 or H2CO3!? A DeltaDIC/DelatAT = 0.25/0.36 = 0.69 seems very low. The assumption here that there is zero buffered CO2 storage is incorrect.

As can be seen from Table 1 in the manuscript, A_T in state 4a is 2.64 mM and not 2.62 mM as suggested by the calculation in the comment.
The change in A_T in the unbuffered scenario (A_T state 4a – A_T state 1 = 2.64 – 2.26 = 0.38 mM) is 0.38 mM produced during $CaCO_3$ dissolution.

Eq. 3: $\Delta DIC_{total} = \Delta DIC_{seq}^{unbuf} + \Delta DIC_{seq}^{buf} + \Delta DIC_{carb}$

$\Delta DIC_{total} = DIC_{state4a} - DIC_{state1} = 2.38\ mM - 2.13\ mM = 0.25\ mM$ *(see Table 1 in the manuscript).*

With $\Delta DIC_{seq}^{buf} = 0\ mM$ *for the unbuffered scenario*

With $\Delta DIC_{carb} = 0.19\ mM$ *as for every mole of $CaCO_3$ dissolution, 1 mole of DIC is produced and 2 mole of A_T (0.38/2 = 0.19).*

Thus $\Delta DIC_{seq}^{unbuf} = 0.06\ mM$ *(see response to comment 8 for explanation of* ΔDIC_{seq}^{unbuf}*)*

The $\frac{\delta DIC}{\delta A_T} = \frac{0.25}{0.38} \approx 0.65$ *is indeed low. This can be explained by the fact that the inlet water used in Chou et al. (2015) was not in equilibrium with the atmosphere (*fCO_2 *of 0.000656 atm) as pointed out by the reviewer. In state 4a, the process water is in equilibrium with the atmosphere (*fCO_2 *is 0.000420). If the inlet process water would be in equilibrium with the atmosphere, the DIC content would be 2.06 mM (calculated with AquaEnv). This would result in a* ΔDIC_{total} *of 0.32 mM and a* $\frac{\delta DIC}{\delta A_T} = \frac{0.32}{0.38} \approx 0.84$.

For Table 1 and the example calculations based on Chou et al. (2015), the aim was to give an example of the different states for a representative real life (bench-top) reactor setup. All the values calculated in Table 1 and used in the example calculations are based on the measured inlet and outlet A_T *and DIC from the two-step bench-top reactor from Chou et al. (2015).*

We have highlighted the fact that the inlet process water is not at equilibrium with the atmosphere both in Table 1 and after the calculations.

Line 114 -116: "Table 2 shows the values for $pCO_{2,gas}$, $pCO_{2,water}$, A_T, *DIC, pH, and* Ω_{calc} *in each of the four states for a representative case, which is based on data reported from a two-step bench-top reactor consisting of a separate gas-liquid and liquid-solid reactor (Chou et al., 2015, reactor design as further discussed below)."*

State	$pCO_{2,gas}$ (atm)	$pCO_{2,water}$ (atm)	A_T (mM)	DIC (mM)	ΔDIC_{seq} (mM)	ΔDIC_{carb} (mM)	pH (-)	Ω_{calc} (-)
(1)	0.000420	0.000656*	2.26#	2.13#	0	0	7.93*	2.50*
(2)	0.15 #	0.0189*	2.26	2.96*	0.83	0	6.52*	0.110*
(3)	0.15	0.0139*	2.64#	3.15#	0.83	0.19	6.72*	0.203*
(4a)	0.000420	0.000420	2.64	2.38*	0.06	0.19	8.16*	4.62*
(4b)	0.000420	0.000420	3.56*	3.15*	0.83	0.19	8.27*	7.74*

Line 251 – 252: It has to be noted that the inlet process water for this example from Chou et al. (2015) was not in equilibrium with the atmosphere ($pCO_{2,water}$ = 0.000656 atm instead of 0.000420 atm).

12. Lines 247-8 If Ca(OH)2 is so great, why even bother with CaCO3?

The calculation in this section are specific for the case of the bench-top two-step reactor of Chou et al. (2015). In line 149 to 152 in the manuscript, it is mentioned that the $CaCO_3$ dissolution could still be significantly improved. The two recent papers mentioned by the reviewer both highlight that the $CaCO_3$ dissolution is the limiting step in AWL.

It is thus not that $Ca(OH)_2$ is so much better than $CaCO_3$, but $CaCO_3$ is the limiting step and needs to be further improved (e.g. by increasing the reaction time (Kirchner et al., 2020; Caserini et al., 2021), reducing particle size (Caserini et al., 2021; Kirchner et al., 2020), or increasing the hydrostatic pressure (Caserini et al., 2021)). The steps taken to improve $CaCO_3$ dissolution is mentioned later in the manuscript under section 3: Different reactor designs for AWL.

Like proposed by Caserini et al. (2021), $Ca(OH)_2$ can be used to buffer the excess unreacted CO_2 but the use of $Ca(OH)_2$ comes with a additional CO_2 and energy penalty from the production process, which is mentioned in section 4: AWL feedstock.

Line 149 -152: "Note that the effluent at state 3 in the example two-step reactor is not in equilibrium with respect to $CaCO_3$ dissolution ($\Omega_{calc} < 1$, Table 1). This indicates that the effectiveness of $CaCO_3$ dissolution in the reactor design of Chou et al. (2015) could still be improved (e.g. by implementing a longer residence time)."

13. Line 281-2 You mean 150,000 m^3. OK so this example is very water inefficient, but not representative of what an optimized system can do as later shown?

We have changed 150.000 m^3 to 150 000 m^3.
We have removed "thus illustrating the large water footprint of AWL" as this indeed is only the case for this specific example and is not representative for more optimized reactor designs.

14. Line 318-21 What evidence is there that these numbers are representative of optimized AWL systems?

These values are indeed not representative for more optimized reactor designs with more efficient $CaCO_3$ dissolution. We have added an extra sentence to elaborate on the fact that the difference in unbuffered (only $CaCO_3$ dissolution) and buffered ($CaCO_3$ dissolution and $Ca(OH)_2$ addition) CO_2 sequestration efficiency will become smaller.

Line 325 – 326: "However, when improving reactor designs to increase the $CaCO_3$ dissolution efficiency the gap between the unbuffered and buffered CO_2 sequestration efficiency will become smaller."

15. Line 440-2 Why not add the Ca(OH)2 at the beginning of the DR pipe rather than awkwardly at the end?

The idee of the dissolution reactor (DR) from Caserini et al. (2021), which is a tubular reactor that extends below the water surface to the deeper parts of the coastal zone to improve the $CaCO_3$ dissolution reaction by increasing the hydrostatic pressure. If $Ca(OH)_2$ would be added at the start of the DR, A_T would mainly be produced by $Ca(OH)_2$ as the dissolution of $Ca(OH)_2$ is faster than the dissolution of $CaCO_3$. This would increase the $\Omega_{calcite}$ and reduce

the amount of $CaCO_3$ that would eventually dissolve. Therefore, in the DR as much $CaCO_3$ is dissolved as possible. Only the necessary amount of $Ca(OH)_2$ is added after the DR in the buffering reactor (BR), which is much shorter than the DR, to compensate for the leftover unreacted CO_2.

16. Line 469 – Need to emphasize that AWL is not going to impact freshwater supply, but it will require lots of seawater where pumping cost will be the main issue and the need for coastally located CO2 sources.

See comment 1.