Replies to Reviewer #1

We thank the reviewer for their critical assessment and positive comments on our manuscript. We also thank them for their keen eye in spotting various typos and slips. Below we explain how we addressed every suggestion during the revision of the manuscript. The reviewer's comments are in blue and our replies and consequent changes to the manuscript in black.

Suggestions on methodology and evaluation of results

(1) From the perspective of judging the result, I suggest adding the observed modern states, for example, the marine carbonate contents, and comparing the observed data with the absolute predicted data the model predicted. This steady state comparison would provide more convincing results for the improvement of the model. Could the observed data figures be added to Figure 4 and Fig. SI.6? Please consider.

We appreciate the motivation behind the reviewer's suggestion and added a comparison of the modern steady state solution from simulation PI-C-open and the observed modern carbonate system to the SI (Fig. SI.8) for context. We keep this comparison out of the main text because the purpose of our model development is not to improve the representation of the modern state but to improve the capability of the model to solve the carbonate system for oceans with Mg/Ca ratios unlike the modern. The MyAMI-derived K* that we use for this purpose have previously been validated against experimental data and theoretical models (Hain et al. 2015). In fact, our model development has slightly shifted the simulated modern carbonate system away from the previously observationally tuned modern state. In order to be able to propagate the MyAMI K* values into the calculating of carbonate preservation in deep-sea sediments, we switched from the look-up table of Ridgwell and Hargreaves (2007) to the explicit 1-D reaction transport calculation of Archer (1991). In doing so, we have somewhat lost the original sediment calibration against data of Ridgwell and Hargreaves (2007) but the differences are small (Fig. 4 in the manuscript) and our purpose here is to simply illustrate the implications of available (or none) Mg/Ca corrections in preparation of a new model release. We are currently working on a series of related GMD papers to fully describe the current state of the cGENIE universe, and one of these papers will include new parameter calibrations for a range of cGENIE applications, including geological carbon cycling and carbonate burial, and we will fully evaluate the fidelity of previous (muffin) vs. new (cookie) carbon cycle calibrations there.

Hain, M.P., Sigman, D.M., Higgins, J.A. and Haug, G.H., 2015. The effects of secular calcium and magnesium concentration changes on the thermodynamics of seawater acid/base chemistry: Implications for Eocene and Cretaceous ocean carbon chemistry and buffering. *Global Biogeochemical Cycles*, *29*(5), pp.517-533.

Hain, M.P., Sigman, D.M., Higgins, J.A. and Haug, G.H., 2018. Response to comment by Zeebe and Tyrrell on "The effects of secular calcium and magnesium concentration changes on the thermodynamics of seawater acid/base chemistry: Implications for the Eocene and Cretaceous ocean carbon chemistry and buffering". *Global Biogeochemical Cycles*.

Ridgwell, A., Hargreaves, J.C., Edwards, N.R., Annan, J.D., Lenton, T.M., Marsh, R., Yool, A. and Watson, A., 2007. Marine geochemical data assimilation in an efficient Earth System Model of global biogeochemical cycling. Biogeosciences, 4(1), pp.87-104.

Ridgwell, A. and Hargreaves, J.C., 2007. Regulation of atmospheric CO2 by deep-sea sediments in an Earth system model. *Global Biogeochemical Cycles*, *21*(2).

(2) Another suggestion is that it might be useful to add one or two depth-resolved profiles of other variables like Figure 8, to illustrate how the revised chemistry affects the deep ocean.

We followed the suggestion and add a SI figure (Fig. SI.5) with additional depth transects for carbonate and bicarbonate ion, pH and calcite saturation.

Main text

Line 54: Suggest the electric charge should be marked on the top right as line 56 does.

Thank you for pointing this out. We corrected this as suggested.

Line 193: Typo, two "K1", the second one should be "K2".

We thank the reviewer for spotting this oversight and corrected it.

Line 232: Suggest writing clearly the abbreviation of what "fCO2" is. It is not mentioned in the preceding text.

We added a definition of fCO2 as 'fugacity of CO2' alongside a short explanation.

Line 240: Typo, missing the right bracket.

We corrected this.

Line 246: E25 is wrong. It should be around "0.028", not "0.000416" (this is boron value).

We thank the reviewer for spotting this error. We corrected it.

Line 264, 269: Typo, should be “Ω”, not “W”.

We corrected this.

Line 275-278: Suggest rechecking about the unit. If “T” multiply “R”, they should both in “K”.

Thank you for spotting this, we corrected the unit of “T” to “K”.

Line 277-279: Typo, should be “ΔVV”, not “DV”.

We corrected this.

Line 299, 342: Suggest writing clearly the abbreviation of what “F77, f90” is.

We corrected this.

Line 360: Typo, it should be “ppm” not “pm”.

We corrected this.

Line 503-505: Suggest reorganizing the sentences. “Ω increase is largely due to the [CO32-] and, to a lesser extent, the increased Ksp,cal”, is opposite to the E28 and basic understanding.

Yes, this sentence was wrong, thank you for alerting us. We changed it to: “In the deep Atlantic, the advected [CO_3^{2-}] increase compensates for the slightly increased Ksp,cal to cause a small Ω increase”.

Line 693: Typo, “experiment”.

We corrected this.

Line 758-759: The reference format is different from others.

We corrected this.

Figures in main text

Figure 2: Suggest the name of the explanation of the figure should be changed. Not “in situ K1”, but “Ks” because “K1”, “K2”, and “Ksp,cal” are all compared.

We corrected this.

Figure 3, 6: Suggest making clear the depth ranges of ocean “surface” and “benthic”. This might be already defined in the cGENIE model. A brief explanation for this could help the readers understand the difference of “surface” and “benthic” more clearly.

We added the following explanatory sentence to the caption of Figure 3: “The surface layer represents the uppermost 81 m of the water column and benthic values are from the deepest ocean grid box in every location.”

Figures in supplementary information

Fig. SI.2,3: Typo, missing “K” in each plot title.

We corrected this.

Replies to Reviewer #2

We thank the reviewer for their critical assessment, very constructive comments and suggestions, as well as their positive overall assessment of our manuscript. We followed or otherwise implemented most reviewer comments. Below we explain how we will address every suggestion during the revision of the manuscript. The reviewer's comments are in blue and our replies in black.

Suggestions General

1. pH and pCO_2 I see in the literature it is mixed for pCO_2 vs pCO_2 (I don't quite understand why it is sometimes given italics?). I don't think I have previously seen italics for pH (plus the two p's mean two different things). I generally argue for partial pressure of CO_2 to be rendered as PCO_2 to match with P as the symbol for pressure (though I acknowledge the double subscript is typographically annoying) and atmospheric CO_2 concentration (in ppm) as simply "atmospheric CO_2". I leave it up to you which form you use.

We went for the non-italicised small p for pH and used 'atmospheric CO_2' throughout the manuscript.

2. Equilibrium Constants I see that you have caveated that 'equilibrium constants' (and Ks) refers to stoichiometric/ apparent equilibrium constants on line 176 - but there are several mentions and equations before this (including in the abstract). The terminology within the field is frustrating. My understanding is that 'equilibrium constants' (the true ones, that are calculated using activity) really are constant and are generally given the symbol K. Incorporation of the activity coefficients into those termsgives us 'apparent equilibrium constants' (often given the symbol K*) which are poorly named because despite having 'constants' in the name they're not constant at all. The general confusion is promulgated by 'apparent equilibrium constants' being shortened to have the same name equilibrium constants. I think it would be clearer to refer to them as apparent equilibrium constants with the symbol K* throughout, and use K* or K*s in the text if you want to avoid having a lengthy phrase repeated many times.

We changed all Ks to K*s as suggested.

3. Figures are low resolution throughout Particularly noticeable for Figures 2, 3, 4, and 6 (zooming to look at an individual subplot).

We apologise for the low resolution. We attach the high-resolution pdf versions of all figures to the revised manuscript

Targeted suggestions

4. Lines 74-80: There's a list of three things 1) ionic strength, 2) interactions with carbon and boron, 3) complexation. Could you clarify if 2) and 3) are different things (as opposed to 3) being a specific type of 2))? That clarification needn't be in the manuscript if the distinction is clear to someone more familiar than me.

This listing summarizes an escalation: the direct "ideal" ionic strength effect from extended Debye-Hückel theory is very weak, the effect of "non-ideal" ion-ion interactions with Mg and Ca on free-ion activity coeficients are also weak, and finally it is primarily the complexation of the majority of total carbonate ion by Mg and Ca that affects the fraction of total carbonate ion that is free. For Eocene seawater, this latter effect on pK2 and pKsp is an order of magnitude stronger than the sum of the former effects.
We clarified that 3) is an explanation of 2).

5. Line 85-86: The final line of this paragraph felt a little out of place (it gave me the impression the next paragraph was going to introduce PITZER models). I think it could go in line 82 just after you cite Hain et al 2015?

We followed the suggestion and moved this sentence to line 82.

6. Lines 224 - 226: You mention that the K*s for sulfate and fluoride are on the seawater scale - is that right? And if so, how is that done? K*s for sulfate and fluoride are typically left on the free scale because they're involved in the free -> total -> seawater scale calculation. To put the K* of sulfate from the free onto the total/seawater scale, you need to know how much HSO_4^- and SO_4^{2-} are in the solution, which is typically achieved by prescribing the total sulfur concentration, then using K* for sulfate to calculate the speciation. It could work if speciated products are prognostic variables from the model? Otherwise, I think you end up in a loop where you need the K* to calculate speciation to calculate the K* to calculate the speciation.

The carbonate solver in the model performs the first loop referred to by the reviewer: It first estimates the sulphur speciation based on K*s on the free scale and the speciation of fluoride on the total scale. These speciations are used to determine the conversion factors to the seawater scale, and the K*s of sulfate and fluoride are then updated with this conversion factor. This procedure is chosen to get estimates of K* of sulfate and fluoride on the same scale as the other K*s. We added a note to the manuscript to clarify this.

7. Section 2.4: Describes setting up the experiments, but starts with quite a few lines of highly technical details regarding seasonality and PIC:POC ratios before we get to what the experiments actually are, and what you've tested. As a reader, I feel this may be clearer if you flipped the section round to say something like (paraphrasing): "There are two main facets of the cGENIE carbonate system we wish to test:
1. Is the lookup table approach accurate enough?
2. How much does improving the K* calculation affect carbon cycle dynamics? In order to answer these questions, we designed a suite of simulations using different sets of K*s, which we split into three main categories: A) Mehrbach constants without any adjustment for changing seawater major ion chemistry B) Mehrbach constants with major ion chemistry correction of Yaakov and Goldhaber and Tyrrell and Zeebe (the current cGENIE model default) C) MyAMI derived constants Each category was run for both preindustrial and early Eocene seawater chemistry (see the full list in Table 1). To estimate the accuracy of the lookup table approach, we carefully chose a non-seasonal configuration (which minimizes the influence of non-linearities driven by seasonal sea ice extent), and also imposed a fixed pattern of $CaCO_3$:POC export by using the annual mean (which removes the carbonate compensation feedback). This ensures we isolated the impact of changingthe method of K* calculation. To understand how changing K* calculation routine affects the dynamic carbon cycle…" In other words putting the headline information at the top of the section, and the (necessary and useful) technical details of precisely which simulations and which configurations slightly later. You've already given this information in other sections, it's just a reiteration as a reminder and I think it will also make the sections dovetail nicely together (for instance it will then match exactly with the first sentence of your results section).

We followed the suggestion and restructured our experiment design description.

8. Table 1 - Is there a reason that the simulations are in this order? As in, the A, B and C. I would suggest sorting them in the order of: A) No correction, B) Current correction C) Lookup table correction (C2) Lookup table correction (temperature limited)) if it isn't a massive hassle.

We changed the order as suggested and renamed the experiments accordingly

9. Section starting line 386 - suggest adding some subtitles or equivalent to break up this paragraph.

We broke up the paragraph with line breaks and shortened it by reducing repetition.

10. Section 3.2 - the paragraph beginning on line 488 oscillates between observation and interpretation. I would suggest separating the results (what's happening with K*s, pH, etc. in the Arctic/Atlantic/Pacific) from the why (high

latitude strongly influenced by temperature limitations, Atlantic/Pacific primarily driven by…). Or separating this into subsections each dealing with a specific area.

We broke up this section with line breaks too and revised it to reduce the jumping between geographic areas

11. Section 3.3 starts with an excellent and very clear description of the impact of changing major ion chemistry, which I think would be better earlier in the manuscript.

We moved this section to the introduction.

12. In Figures 3 and 6 - is it an option for ΔK* maps to be shown using a percentage of the value in the upper plot? It looks to me like they're just about the right order of magnitude that that might work well and would simplify interpretation for non experts.

We followed the suggestion and replaced the difference plots in these figures with plots of percentage changes

13. Line 512+522: "Total DIC in the ocean is 24 PgC higher". Would it be possible to give this as a percentage (or give the total, or give in units of concentration for average seawater DIC change)? I think that would make it easier to interpret in a glance.

We followed the suggestion and added percentages.

14. Paragraph beginning line 611: There are a lot of interesting results here, but they're quite densely packed and from a lot of different simulations. Would a small table work for easy cross comparison of the simulations? Or something to that effect so it is straightforward to parse and compare ΔDIC in EE-C-Open vs EE-B-Open etc.

A full comparison of all these results is already shown in Fig. 7, but we have added the values to the plot to convey the same information as would be in the table. We also added more references to subpanels of the figure to the text to make the connection clearer

Typographical amendments (I've used green for suggested additions and red strikethrough for suggested deletions).

15. Figure 1: Add Mg/Ca to the figure legend. Make the y axes tick labels on the right grey to match the Mg/Ca label. In the figure caption, put the charges on the ions into superscript.

Done.

16. Line 60: "compared to 52 mmol kg −1 today, (Timofeeff et al. [2006], Brennan et al. [2013], Hain et al. [2015]))." (added brackets around passive citation).

Fixed.

17. Line 60-63: "The first order consequence of higher Cretaceous [Ca2+] (as we will illustrate later) is that to produce a relatively similar ocean surface

carbonate saturation state (or global weathering rate) to the present day, the ocean carbonate ion (CO32-) concentration would have had to have been lower as carbonate saturation involves the product of both [Ca2+] and [CO32-]" (to keep the sentence in the conditional tense) Or alternatively if you could put them both into the non conditional: "The first order consequence of higher Cretaceous [Ca2+] (as we will illustrate later) is that the ocean carbonate ion (CO32-) concentration would have been lower than the present day, assuming a similar ocean surface carbonate saturation state (or global weathering rate)".

We simplified the sentence as suggested.

18. Line 66: "(e.g., Henehan et al. [2019])" (has a space in the bracket just before 2019).

Fixed.

19. Line 143: "cbsyst (Branson et al. [2023]), and KGENgen (Whiteford et al. [2025])" (extra n in Branson and decapitalised GEN).

Fixed.

20. Line 206: "contribution from $SO4^{2-}$" (I think that's correct it should be sulfate right?)

We intended to write about sulfide (S2-) here, which can contribute to alkalinity at low pH or reducing conditions (Dickson et al. 1981).

21. Line 240: "in the case of methanotrophy (Reinhard et al. [2020])." (closed the bracket at the end of the paragraph).

Fixed.

22. Line 242: "Dissolved Ca2+ and total SO_4^{2-} (HSO_4^- + SO_4^{2-}) are typically" (removed the O_4^{2-} to make it total sulfur is sulfate plus bisulfate).

Fixed.

23. Line 260: "concentrations is < 1 µatm (Ridgwell 260 [2001])." (closed the bracket after citation).

Fixed.

24. Lines 264 and 269: WΩ.

Fixed.

25. Lines 277 and 279: DΔ.

Fixed.

26. Line 360: "(270 pmµatm/atm pCO_2)" (I think the original pm is probably a typo meant to be ppm? If it's partial pressure it should technically be in µatm/atm, though the difference between that and ppm is irrelevant for this work).

Fixed.

Line 367: "Tyrrell and Zeebe (2004)" (extra r in Tyrrell).

Fixed.

5. Line 536: "alkalinity from the model) theimpacts on carbonate" -> "alkalinity from the model) the impacts on carbonate" (added a space in the impacts).

Fixed.

6. Figures SI.2 and SI.3 are missing K in the label.

Fixed.

References

Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep Sea Research Part A. Oceanographic Research Papers*, *28*(6), pp.609-623.