Review of Inclusion of MyAMI-derived Mg/Ca corrections to the marine carbonate system in the cGENIE.cookie Earth system model (v.0.9.90)

Summary

Adloff et al have brought the MyAMI model (which is a PITZER model used to simulate ionic interactions in fluids) into cGENIE (a widely used carbon cycle model of intermediate complexity). This has improved cGENIE's representation of carbonate chemistry, predominantly at times in the geological past where seawater [Ca^{2+}] or [Mg^{2+}] were different to the modern day ocean. Adloff et al. explain the current implementation of carbonate chemistry in cGENIE, and point out which parts are replaced by the new scheme. MyAMI is comparatively computationally intensive, so Adloff et al. emulate MyAMI using a quadrilinear interpolation scheme. They first validate that this quadrilinear interpolation results in minimal difference against the full MyAMI code, then test the implementation against a preindustrial ocean, and finally demonstrate the magnitude of differences for an ancient ocean (in this case Eocene) with different major ion chemistry.

Interpretation

I believe the scientific content of this article to be excellent, and have no significant concerns or queries about the core principles under discussion. The authors should be commended for their inclusion of a large amount of technical detail, though at times this obscures the key points. My suggestions are below, and I have attempted to give my reasoning alongside each one so you can evaluate my perspective in considering whether they are worth incorporating. I have structured this as follows:

1. general suggestions that would affect things in multiple parts of the manuscript
2. specific line suggestions
3. typographical corrections

Everything that follows is a suggestion only, and are mostly aimed at improving clarity rather than any fundamental changes.

Suggestions

General

1. <u>pH and pCO_2</u>
   I see in the literature it is mixed for pCO_2 vs *p*CO_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 P_{CO_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.

2. <u>Equilibrium Constants</u>
   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 terms

gives 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.

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

Targeted suggestions

1. 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.

2. 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?

3. 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.

4. 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 changing the 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).

5. 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.

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

7. 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.

8. 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.

9. 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.

10. 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.

11. 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.

Typographical amendments

(I’ve used **green** for suggested additions and ~~**red strikethrough**~~ for suggested deletions).

1. 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.

2. 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).

3. Line 60-63: “The first order consequence of higher Cretaceous $[Ca^{2+}]$ (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 (CO_3^{2-}) concentration would have **had to have** been lower as carbonate saturation involves the product of both $[Ca^{2+}]$ and $[CO_3^{2-}]$” (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 $[Ca^{2+}]$ (as we will illustrate later) is that the ocean carbonate ion (CO_3^{2-}) concentration would have been lower than the present day, assuming a similar ocean surface carbonate saturation state (or global weathering rate)”.

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

5. Line 143: “cbsyst (Bra**n**son et al. [2023]), and K~~GEN~~**gen** (Whiteford et al. [2025])”
   (extra n in Branson and decapitalised GEN).

6. Line 206: “contribution from S**O_4**$^{2-}$”
   (I think that’s correct it should be sulfate right?)

7. Line 240: “in the case of methanotrophy (Reinhard et al. [2020]**)**.”
   (closed the bracket at the end of the paragraph).

8. Line 242: “Dissolved Ca^{2+} and total S~~O_4^{2-}~~ (HSO_4^- + SO_4^{2-}) are typically”
   (removed the O_4^{2-} to make it total sulfur is sulfate plus bisulfate).

9. Line 260: “concentrations is < 1 µatm (Ridgwell 260 [2001]**)**.”
   (closed the bracket after citation).

10. Lines 264 and 269: ~~W~~**Ω**.

11. Lines 277 and 279: ~~D~~**Δ**.

12. Line 360: “(270 ~~pm~~**µatm/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).

13. Line 367: “Ty**r**rell and Zeebe (2004)”
    (extra r in Tyrrell).

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

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