

1. To improve the utility of carbonate I/Ca ratios as a paleotracer requires acknowledgement and quantitative understanding of the fact that dissolved iodine speciation in the ocean is not simply and solely a product of redox conditions. This study addresses this issue by incorporating a range of iodine transformations in the cGENIE model. The representations of iodine cycling are well thought out and appropriate, and cGENIE is a suitable model for paleoreconstructions. The model development and evaluation appear to be well conducted, and the manuscript is well presented. As well as paleo-oceanographers, the iodine model described is also likely to be of interest for those working on present day iodine cycling, such as biogeochemists and air quality modellers.

I have the following major and minor comments on the manuscript:

Major comments:

1. The model is limited in its ability to accurately model present day oxygen levels, and over-estimates levels in the north Pacific OMZ (L317, Fig 6; L513, L537-538). As iodine speciation in the model is a function of oxygen levels, this will affect model performance. Indeed, simulated present day iodine distributions are closer to observations when the model is forced to climatological oxygen values (L340). The accuracy of oxygen predictions for the geological past therefore requires scrutiny. Although the authors briefly allude to this issue (L538-543; L621), a more in depth and up front consideration is required. Is there any way the accuracy of paleo oxygen predictions made by cGENIE be assessed, and the uncertainty associated with this quantified? What future work is planned to reduce the uncertainty in predicted oxygen levels?

Thanks for the thoughtful question. The accuracy of assessing O₂ prediction in the paleo ocean is difficult because of the lack of direct measurements. The goal of this study is to provide a pathway for reconstructing paleo-O₂ using I/Ca proxy in order to grasp a full understanding of ocean oxygenation through cross comparison with other geochemical redox proxies.

We acknowledge that the O₂ distribution in the modern ETNP (Eastern Tropical North Pacific) between observation and the model has differences in detail. However, the broad O₂-depletion feature is simulated correctly. Due to the low spatial resolution of cGENIE, the whole ETNP only occupies three grids in the model framework. Meanwhile, the depth resolution close to 100-200 m in the surface ocean also limits the finer simulation of ODZ features.

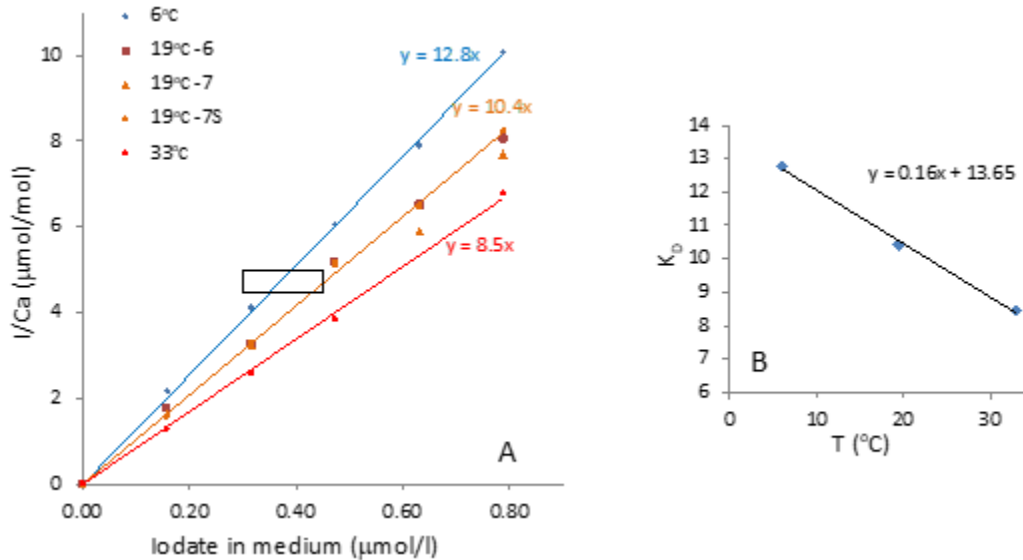
Therefore, cGENIE is better performed in predicting large scale redox distribution in the paleo-ocean (as it is originally designed to) instead of reproducing fine resolution ODZ in the modern.

In order to provide this same input to the readers, we will add the following summary to L543:

In addition, due to the low spatial resolution of cGENIE, the whole ETNP only occupies three grids in the model framework. Meanwhile, the depth resolution close to 100-200 m in the surface ocean also limits the finer simulation of ODZ features. We are indeed aware of these uncertainties associated with O₂ simulation in cGENIE. However, as a model targeted to assist paleoredox reconstructions, broadly reconstructing ODZ features in a coarse spatial resolution is acceptable.

2. Similarly, to make forward predictions of I/Ca ratios, modelled values of historic calcium concentrations are integral (L594). A brief description of how these are simulated, and discussion of the uncertainty in these values is required.
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Thank you for pointing this out. Our current conversion of modeled [IO₃] to I/Ca does not account for [Ca]_{sw}. This is because the impacts of [Ca]_{sw} on the [IO₃]-I/Ca relationship have not been quantified. Instead, the 2 calibrations of the relationship only evaluate the impacts of temperature and do not measure or vary [Ca] in the solutions used. Given the current state of knowledge, we used both the temperature and [IO₃⁻] from the model to determine I/Ca. Specifically, as described in the supplementary information in Zhou et al., (2014) referenced in line 595, different linear relationships between [IO₃] and I/Ca were observed at 6 °C, 19 °C and 33 °C in a series carbonate synthesis experiment (Figure S3). Then the distribution coefficient $K_D = (I/Ca) / [IO_3]$ for a given temperature was interpolated based on the linear relationship between temperature and K_D (Figure S3, attached below). For our Cretaceous model calibration, we derived the K_{DS} based on local temperatures (at each grid associated with sections) simulated by cGENIE and the linear relationship in Figure S3 in Zhou et al., (2014). We will clarify the details of this transformation in Section 4.3.



3. Figure 7 and L590: State what type of carbonate archive the I/Ca values were measured in. Were these archives likely to have been subject to any diagenetic alterations that could change the I/Ca ratio from that incorporated at the time of calcite synthesis?

Indeed, it is very important to address the post-depositional alteration/diagenesis when discussing I/Ca records. Post-depositional exposure to anoxic pore water could lower I/Ca in carbonates. While contamination from organically bound iodine could result in a false elevated I/Ca. According to Zhou et al., (2015), from which we adopted the I/Ca data, no noticeable iodine contamination was observed in any of the sections. Minor diagenesis was observed in Demerara Rise, Tarfaya, and Raia de Pedale, which were hypoxic sections and primary I/Ca was low. Therefore, the primary I/Ca signals from these sections were not terribly altered. We will add these clarifications into Section 4.3 for a more consistent logical flow.

L592: “Diagenesis of carbonate hosted I/Ca tends to lower the primary values (Hardisty et al., 2017). However, such an offset is hard to quantitatively predict based on our current knowledge. In addition, according to Zhou et al., (2015), from which we adopted the I/Ca data, most of the sections only suffered minor diagenesis. To simplify the Cretaceous I/Ca-IO₃ conversion, we regard the measured I/Ca as primary and acknowledge there is potential uncertainty.”

Minor comments:

1. At a number of points, the paper states that biologically mediated iodate reduction is assimilatory (L14, Figure 1, L197, L410). However, it is not yet established whether this process is assimilatory or dissimilatory (e.g. Hepach et al., 2020), it may even be a mixture of processes. This should be made clear in the manuscript. Biologically mediated iodate reduction in the model is represented as an assimilatory process, which is reasonable given the current state of knowledge, but it should be made clear that this is an assumption in the model construction.
-

Additional clarification will be added to line 197.

L197: “Phytoplankton-absorbed iodine is stored in the cell as IO_3^- , I^- , or other forms, followed by release during senescence (Hepach et al., 2020). While there is some uncertainty as to whether iodate reduction is assimilatory or dissimilatory (Hepach et al., 2020), it is necessary to clarify here that in order to simplify the simulation, the modeled IO_3^- tracer is assimilated by phytoplankton and incorporated into POM during photosynthesis (Elderfield and Truesdale, 1980) before being released back to the water column as I^- during remineralization (Wong et al., 2002; Hepach et al., 2020; Wong et al., 1985).”

2. In a few places throughout the manuscript (e.g. L77-79, L137-139, L422-424,) minor grammatical and/or wording improvements are needed to make the text more readily understandable.
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Words and grammar will be checked and fixed in these lines.

3. L87: This should be “deep” not “dissolved” chlorophyll maximum
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Will be changed according to reviewer’s suggestion.

4. L139 and elsewhere: Check and correct the spelling of technical terms e.g. ‘respiration’ and ‘saturation’
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These terms in L139 should be correct but will check those through the whole manuscript.

5. L149-151: Either add numbers 2-4 to the list of processes here, or remove the “(1)”.
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Will add numbers to each of the process for easier tracking.

6. L155: It would be helpful to state here that these representations apply to water column reduction (i.e. process 1) and oxidation (i.e. process 2)
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Will add the clarifications according to reviewer’s suggestion.

7. L209 and SI Table 4: The machine learning model for sea surface iodide concentrations described Sherwen et al., 2019, was built using the data set in Chance et al., 2019, so it is not clear why this paper is referenced here and in SI Table 4? Were simulated iodide values from Sherwen et al., 2019, also used in the model evaluation?
-

The reviewer is correct that the citation here is incorrect. We will remove the wrong citation of Sherwen et al., (2019). Simulated iodide from Sherwen et al., 2019 was not used in the model.

8. Figure 3 and SI Figure 1: The coloured dots in these figures are very difficult to see, can they be increased in size, and/or the quality of the figures improved?
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The symbol size in Figures 3 and S1 will be adjusted larger for better visibility.

9. L179: The first sentence requires a reference, and/or more explanation, to make clear how this link between iodide and nitrification being considered here differs from the link with ammonium oxidation mentioned on L188. L432-441: Similarly, the reasoning for extending the proposed link between iodide oxidation and bacterial nitrification (L432-436) to a broader possible relationship with bacterial oxidising activity (L441) should be explained in a little more detail.
-

We agree with the reviewer that a distinction is necessary. To clarify, the link between iodide and nitrite oxidation is hypothetical and has not been explored previously to our knowledge. We will amend the above referenced sentence (see below) to clarify this point in the main text.

L179: “Given the overlapping redox potential between I and N (e.g., Rue et al., 1997; Cutter et al., 2018), we explore the potential for a link between areas of I⁻ and nitrification. To simulate this, we devise an alternative “Fennel” scheme, in which I⁻ oxidation rates vary as a function of ambient O₂, increasing with ambient O₂ concentrations towards some hypothetical maximum value following Michaelis–Menten kinetics (Fennel et al., 2005).”

10. L244: Why were only five different combinations of parameterisations tested, when nine combinations are possible? Please explain why the five tested combinations were selected.
-

We aim this manuscript to improve iodine cycle simulation based on previous work (Lu et al, 2018) which used lifetime-threshold combination and achieved some agreement with observations (their Figure S5). We tested additional parameterizations based on a combination of observations as well as hypothetical scenarios not yet grounded in field or experimental observation. Importantly, we purposefully chose to only test combinations of iodate reduction and iodide oxidation parameterizations where at least one of the parameterizations is grounded in observation. So far, only “threshold” (Lu et al., 2020) and “lifetime” (Truesdale, 1980) are based on field-based studies. Therefore, it would be reasonable to take the conservative approach through combining one field-based mechanism (“threshold”-reduction or “lifetime”-oxidation) with our novel but hypothetical alternative mechanisms. That said, it is straightforward for future users to combine any combination of parameterizations provided here.

1. L289: Elevated observed iodide concentrations in surface waters at low latitudes are thought to be a function of biologically mediated reduction and strong vertical stratification (allowing the iodide to accumulate). This should be noted in the text, and the ability of the model to account for the impact of vertical mixing on iodine distribution discussed.
-

The model does account for vertical mixing processes, which allows for surface water iodide accumulation in the way the reviewer recommends here. This can be seen in a plot of temperature vs latitude, which reveals higher stratification at low latitudes and weaker at high latitudes. This plot will be added into Supplementary Material.

11. Table 1. I think the 'reminO3lifetime- parameters do not need to be given for simulation 2 (as in Table 3).
-

Will be corrected based on reviewer's suggestion.

12. Throughout – insert space between numbers and units
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Will be corrected based on reviewer's suggestion.

13. L354: The assessment against I/Ca records has not yet been described at all, so perhaps should not be mentioned here. Consider including it within the main methods and results sections.
-

Will add citations (Zhou et al., 2015) to clarify the source of I/Ca data in L354.

14. L360: I think this should be -0.08 not -0.8?
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The typo will be corrected based on reviewer's suggestion.

15. L451: Is this necessarily the case, if iodate reduction in the model is already a function of oxygen concentration?
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Following sentence will be modified to clarify:

L448-451 (original) “This scenario might hence not perform well in replicating the ocean iodine cycling at intervals during the Phanerozoic when ODZs were highly expanded, or particularly during the Precambrian when the majority of the ocean was ferruginous or euxinic and highly depleted in O₂ (for example, summarized by Lyons et al., 2014).”

L448-451 (modified) “This scenario might hence not perform well in replicating the ocean iodine cycling at intervals during the Phanerozoic when ODZs were highly expanded, especially when under low O₂ while above the IO₃ reduction threshold which inhibits I⁻ oxidation.”

16. L478: This sentence implies that temperature is the main driver of primary production, which is misleading – although temperature has some effect on primary production rates, it is not the dominant controlling factor in the surface ocean. The relationship between iodide abundance and temperature reported in Chance et al. 2014, is instead thought to occur due to the relationship between temperature and vertical mixing. This sentence should be rephrased to reflect this more accurately
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The sentence will be modified based on reviewer’s suggestion for better accuracy.

L477-478 (original): “The pathway of transforming IO₃⁻ into I⁻ in these oxidized waters is through primary productivity in the photic zone, which is temperature dependent (Chance et al., 2014).”

L477-478 (modified): “The pathway of transforming IO₃⁻ into I⁻ in these oxidized waters is through primary productivity in the photic zone, which resulted in I⁻ accumulation within the mixed layer (Chance et al., 2014). In the low latitudinal surface ocean, weaker vertical mixing resulting from warmer surface temperature allows I⁻ accumulation in the shallow mixed layer (Chance et al., 2014)

17. L512: Does “data” here mean model output? Please clarify in the text
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The word “data” will be changed to “model output” to clarify.

18. L563: As noted above, I feel that description of the comparison with I/Ca records in this section might be better as part of the main method and results sections, with just the discussion of the findings in section 4.3.
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We will introduce the OAE model earlier in the results section. An additional section 3.5 will be added to Results section (since section 2 is model description):

3.5 Ancient iodine: Oceanic Anoxic Event case study

“To assess the ability of cGENIE to reconstruct the iodine cycle in deep-time, we picked the parameters associated with highest M score in each of the ensembles (Table 2) and ran the model under the OAE2 scenario with variable PO_4 (Zhou et al., 2015). We calculated the pre-OAE stage modeled I/Ca based on the linear relationship between I:Ca and IO_3^- and temperature from carbonate synthesis experiments (Zhou et al., 2014). Importantly, this relationship is temperature dependent, so the temperature from the relevant model grid point was used for this calculation. The reconstructed I/Ca from each section (Figure 8) was then compared with the simulated I/Ca in the corresponding model grid, and the comparisons are presented by the M score (Figure 7). Note that most of the models reach highest M scores under $0.6\text{-}0.8\times$ modern PO_4 .”

19. Figure 8. The caption here appears to incorrectly list more combinations of parameterisations than the three shown.
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The additional parameter combinations were included by mistake and will be removed.

20. L623: “DOC remineralisation” as an additional parametrisation variation has not been mentioned in the text before this point, either add an explanation or remove.
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This will be removed from the text. The sentence will be modified as:

“Although we tested additional parameters in this study (Table S1), only those combinations listed in Table 1 (“lifetime - threshold”, “lifetime-reminO2lifetime”, “lifetime - Fennel”) perform well in replicating iodine gradients within the modern ocean (Figs. S2-4).”

21. Supplementary Information: A number of figures include “DOC remineralisation” as an additional parametrisation variation, but this is not explained anywhere in the text.
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Since “DOC” remineralization neither improves overall model skill score (Table S1) nor replicates any of the modern ocean iodine gradients (Figures S2-S4), we decide not to include this in the text. However, additional explanations of “DOC remineralization” will be added to the caption of Figure S1 where it appears for the first time.

An additional paragraph will be added into Section 4.1 after L363 to briefly demonstrate the role of “DOC remineralization”.

“Notably, our M score results also demonstrate a potentially minor role, if any, for iodine cycling with DOC. As described in 2.3.1, the “reminO2lifetime” and the “reminSO4lifetime” scales I⁻ oxidation and IO₃⁻ reduction with O₂ consumption and SO₄ reduction during the remineralization of POC (or POC and DOC), respectively. An alternative (with DOC remineralization) scenario was tested to combine the iodine redox reactions with DOC remineralization in cGENIE (Table S1). Compared to the default settings, adding the DOC remineralization-control to the I⁻ oxidation (“reminO2lifetime”) or IO₃⁻ reduction (“reminSO4lifetime”) does not increase the M score of the model. More than the overall M score, the simulation of latitudinal I⁻ trend in the defaulted no DOC-controlled iodine cycle models performs better in replicating the depth profiles, as well as the IO₃⁻ depletion feature in the ODZ (discussed in later sections), especially for “reminO2lifetime-threshold” ensembles.”

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