

The authors introduce a set of geochemical datasets measured on dissolved organic carbon (DOC) obtained from four redox-stratified lakes in Mexico. They compare these datasets with corresponding data obtained from particulate organic carbon (POC) and dissolved inorganic carbon (DIC). Through their analysis, the authors discovered that the concentrations and isotopic compositions of the DOC exhibit significant variability both between and within the lakes. This variability is attributed to differences in the origins of the DOC, which are associated with primary productivity linked to oxygenic and/or anoxygenic processes, redox conditions, and an old long-term DOC reservoir. The authors further extrapolate their findings to the 'DOC' hypotheses proposed for ancient oceans, including the PETM and Shuram events.

The subject is a topic of interest and of significance to the study of those redox-stratified environments, which, I believe, is well-suited for the *BG* readership. I am convinced that the data presented in this contribution will enhance our understanding of the biogeochemical cycle of carbon in such environments, and will provide a valuable reference for the study of DOC in ancient or future oceans. While I believe that this work deserves to be published, it is not yet ready for publication. From a technical standpoint, the writing in this manuscript contains numerous grammatical errors and is not yet at a journal-ready level. I have identified some of these errors, but there are likely more, and the manuscript must be thoroughly checked for technical soundness before it can be resubmitted. Furthermore, some of the discussion appears to be underdeveloped, and I had difficulty following the logic behind certain key conclusions. I have included some general comments below, as well as specific comments throughout the manuscript, which I recommend that the authors address (or at least consider) in order to improve the quality of their work.

We thank the reviewer for providing such detailed and constructive feedback for our manuscript, and for the positive appreciation of our work. We have addressed all of the general and specific comments made by the reviewer and we thank the reviewer for helping us to improve the quality of our report.

After corrections following the reviewer's comments, the text was reread by a colleague who is a native speaker of British English to correct the problematic grammar and phrasing.

General comments

Upon reviewing this contribution, I noticed that a significant amount of the discussion and conclusions drawn seem to rely heavily on data from an unpublished paper (Havas et al., submitted), which appears to also be authored by the same authors. This manuscript does not provide any information about those data, which makes it difficult for readers to verify and evaluate the validity of the findings. While I understand the authors' decision to split their data into separate articles, I believe they should consider adding more details to this manuscript to provide context and transparency for readers. Please see my specific comments below for suggestions on how to improve the presentation of this information.

As requested by both reviewers, we have added more information about the DIC/POC data from Havas et al. (submitted) where suggested, we have also specified in the introduction that the same samples were analyzed in this and the companion paper. We hope that these modifications will provide more context and transparency for readers.

Another point of concern is the authors' extrapolation of their results to the Neoproterozoic carbon perturbation event. They link the observed DOC concentrations in the studied lakes to the 'big DOC' hypothesis for the Neoproterozoic oceans and suggest that increased terrigenous DOC inputs could

have been necessary to generate high DOC: DIC conditions and initiate the Neoproterozoic carbon isotope excursions. That is because the proposed DOC concentration in that hypothesis is much higher than the observed values in these lakes. However, I do not believe that it is appropriate to make a simple analogy between today's anoxic lakes and Precambrian anoxic oceans. For one, the duration of today's lakes in redox-stratified conditions is not on the same timescale as the Precambrian oceans. These lakes are seasonally oxidized, which would consume the DOC that accumulated during earlier times, whereas the Precambrian oceans could have been permanently stratified over much longer timescales (millions of years). Additionally, the authors suggest that terrigenous sulfate input is the main oxidant of the DOC, which raises concerns. During a long river journey, there would be sufficient time for terrigenous DOC oxidation by sulfate and for equilibrium between newly-formed ^{13}C -depleted DIC and pre-existing 'normal' CO_2 . It is unclear whether the ^{13}C -depleted signatures could be transported into the oceans and preserved in the marine facies.

We thank the reviewer for these insightful and constructive remarks. While we agree there are limitations to the proposed analogy, we think that several aspects of that comparison can bring new insights about the geological intervals mentioned, and thus should be discussed. Discussing these points, as recommended by the reviewer and as described below, will better present the limits of our proposition while expanding its horizons.

We agree that a major drawback in this analogy lies in the fact that the time during which DOC can accumulate in these modern stratified analogues and the Precambrian ocean differs significantly. Hence, we have added a clear cautionary statement in that sense (lines 573-575), and we have justified how this difference may or may not explain the discrepancy between the lakes' [DOC] and purported Precambrian [DOC]. We note that our discussion is a first attempt to test the plausibility of such large [DOC] in the Precambrian ocean, whereas most studies assume its *prima facie* reality, although no direct demonstration of its existence has so far been provided.

We agree that the monomictic nature of the lakes studied is another important difference with the Precambrian oceans. As we indicate in the text, the Black Sea, a permanently stratified basin, harbors even lower DOC concentrations, suggesting that the mechanisms producing the DOC might be the primary controls on DOC concentrations, despite differences in conservation potential (more or less DOC oxidation). Nevertheless, this is indeed a limitation to the suggested analogy with the Precambrian oceans, which were permanently stratified over much longer timescales. Hence we now address this point more clearly in the text (lines 569-573).

We do not precisely know the kinetics of DOC oxidation by sulfate reduction in rivers during the Neoproterozoic, but it would have been strongly dependent on the amount and lability/refractory nature of DOC that is being oxidized, as well as the distance between the continental source and the ocean. These parameters cannot be constrained but they would not necessarily lead to a full oxidation of the putative terrestrial OC pulse. Based on the previous discussion, we show that there is still no satisfactory explanation for the existence of a large Precambrian DOC reservoir (Line 579-581). Hence, terrestrial DOC appears as a potential source for this DOC, and is consistent with other pulses of continental supply (e.g. sulfates).

In the scenario we propose, it is indeed possible that at least part of the DOC is oxidized during the concomitant journey of DOC and sulfate in rivers. We now address this possibility in lines 604-606. Importantly, the requirement for generating the negative Neoproterozoic CIEs is to have a major influx of ^{13}C -depleted DIC. In the "big DOC" hypothesis, this is achieved *via* ocean DOC: DIC $\gg 1$, and partial oxidation of the DOC reservoir. In our proposition, allochthonous (e.g. terrigenous) supply is necessary to reach the required amounts of OC. Nonetheless, a partial (or even full) anaerobic oxidation of that OC before it reaches the ocean would allow the CIE to be recorded, as it still provides a source of ^{13}C -

depleted alkalinity, but would not change the conclusion of a decoupling between DI^{13}C -depleted and DI^{13}C -enriched pools.

Specific comments

Line 105: Please add a 'during'. Done.

Line 118: Double 'is', please delete one. Done.

Line 140: Before introducing the measurements of DOC concentration, you should provide information on how you get the DOC first.

The DOC concentrations and isotope compositions were measured on the bulk DOC. Therefore, there was no specific step of DOC extraction; it was directly analyzed from the acidified water. We now provide this information, and state what "bulk DOC" refers to in lines 150-152: "...to degas all the DIC and leave DOC as the only C species in solution. The bulk DOC was analyzed directly from the acidified waters (i.e. all organic C molecules smaller than $0.22\ \mu\text{m}$)".

Lines 147-148: Are you sure the gas was separated in a reduction column? I thought it should be in a GC column.

In the IsoToc device, in addition to water and halogen condensers, the main separation occurs in a reduction column filled with copper. It reduces the oxidized products other than CO_2 (mostly NO_x compounds to N_2) and removes the excess O_2 from the combustion. We have added the reference for the company manufacturing the IsoTOC (Line 156).

Line 161: Please define the 'DOC', namely tell the readers what is the 'DOC' you referred here, before this sentence.

The meaning of DOC is now clearly defined at the beginning of the introduction and in the method section (lines 49-51/150-152).

Also linked to figure 3; I would suggest to keep the order of lake consistent between descriptions in "Results" and the figure 3. From left to right, Alchichica, Atexcac...; or reorder them in results.

We have made the results section and figures consistent with the order of the lakes.

Further, I don't think the brown sediments are necessary, and the authors can also consider plotting DOC and $\delta^{13}\text{C}_{\text{DOC}}$ in one column, as well as for $\Delta^{13}\text{C}_{\text{DOC-DIC}}$ and $\Delta^{13}\text{C}_{\text{DOC-POC}}$. I would also suggest to merge figures 3 and 4 into one figure, with its panel arrangement just like as the figure 2. I believe doing the above will help the readers compare the data from different lakes clearer and more easily.

We prefer to keep figures 3 and 4 separate, because combining [DOC] and $\delta^{13}\text{C}_{\text{DOC}}$ data, which are different types of data, in a single graphic column would induce confusion and overload the graphic column of each lake. In figure 4, the graphs are plotted on very different scales, and combining them would obscure the visibility of the variations for each lake and between the lakes. We also feel that representing the sediment level at the base of each lake (in brown) provides a better visualization of the different water column depths in the four lakes.

Lines 165-167: How did you get the concentrations and isotopes of total carbon; the associated information was not found in the 'Method', please add some details.

Good to find a little information about how the $\delta^{13}\text{C}_{\text{Total}}$ was obtained in the table 1 caption; I suggest to present it in the main-text as well.

We agree with the reviewer that this part was missing in the previous version. We have thus added it in the method (lines 165-167).

Line 180: The authors did a comprehensive comparison of the data between DOC and POC or DIC in detail, but not even provide any information about the latter, like what are the values of concentrations or isotope compositions of POC or DIC and how to get them. Given much of discussion is based on the data from POC and DIC, I would suggest the authors to add some essential information about the POC and DIC.

The POC and DIC isotope data from Havas et al. (submitted) are only used in the current manuscript to provide a useful comparison with the $\delta^{13}\text{C}_{\text{DOC}}$. They are only discussed relatively to each other, *via* $\Delta^{13}\text{C}_{\text{DOC-DIC}}$ and $\Delta^{13}\text{C}_{\text{DOC-POC}}$ parameters.

We agree that basic information about $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$ data would provide more context for the reader. We have therefore added a short description of these parameters in lines 168-175 and additional numerical information from Havas et al. (submitted) where needed in the discussion (e.g. section 5.2.).

Lines 189-190: Syntax error for this sentence, please revise it.

We have rephrased that sentence as follows: "The $\Delta^{13}\text{C}_{\text{DOC-POC}}$ values decreased from ~ 1.3 ‰ in the upper waters to ~ -0.4 ‰ in the bottom waters but strongly increased to $+7.1$ ‰ at a depth of 12.5 m" (Lines 199-200).

Lines 245-246: No DIC or POC data profiles was presented in the figure 3; maybe the authors mean the figure 3 in the referred paper?? Please indicate it clearer.

The reviewer is correct and we have moved the reference to Fig. 3 to the end of the sentence about DOC. The passage has been rewritten (lines 263-266).

Lines 247-248: Here maybe the authors were trying to say 'DOC' rather than 'DIC'; also, more details about correlation between the average [DOC] and their salinity should be provided, such as adding the associated data or a figure to support the argument.

We have added statistical parameters (R^2 , p value) about these correlations to clarify and support the point made here: there is no significant correlation between DOC content and lake salinity, but there is one between DIC content and salinity (lines 266-269).

Lines 257-259: This sentence should arise earlier, at least before the data descriptions in the 'results'. Also refer to the comment for line 161.

We have moved this sentence about DOC to the beginning of the introduction.

Lines 267-272: I cannot follow the logic here. As I understand it, nutrient-limited condition would suppress not heterotrophic bacterial activity but also the oxygenic photosynthesis, how to result in the

fixed C in excess? Also, could you add more details about how much the excess C is, i.e., the actual C/N/P ratio.

On the one hand, C may be fixed in excess relatively to the amount of nutrients available for the biosynthesis of more complex molecules; it thus ends up being released out the cells (e.g. Hessen and Anderson, 2008; Morana et al., 2014). Therefore, more oligotrophic conditions favor higher DOC production. On the other hand, bacterial heterotrophic activity (which partly consumes DOC) is limited by the lack of nutrients (e.g. Dittmar, 2015). Therefore, more oligotrophic conditions also favor a higher quantity of DOC via higher preservation. In consequence, we state that these processes are consistent with the trend observed in our study, where higher DOC concentrations are found in lakes with more oligotrophic conditions. We have rewritten this section to make it clearer (Lines 282-290). Unfortunately, we do not have C/N/P data for the dissolved organic matter.

Line 286: typo, 'of' Ok.

Lines 300-308: Sorry, I cannot follow the reasoning here. Actually, the release rate of DOC is directly related to PER rather than the fraction of DOC over total OM, right? The data, the fraction of DOC over total OM, just reflects a final result of multiple factors, including the release of DOC, an older long-term DOC reservoir (it should exist as the authors argued in the following discussion), or others. So, if the authors try to reach the conclusion of "the extremely high phytoplankton-release rates", I think they should start with an independent evidence for the percentage of extracellular release. Alternatively, it is also practicable to just exclude the possibility that other factors play a role. Otherwise, we could also say the high DOC over total OC ratios are just results of long-term DOC reservoirs in these lakes. Maybe I misunderstood it, but I would suggest the authors make this argument be clearer.

The reviewer is correct that the fraction of DOC over total OC (as we calculated it) integrates multiple factors, including DOC release rates and DOC accumulation over time. We have rephrased the paragraph to indicate that, since PER values as high as 99% have been reported in other systems, a majority of the DOC measured at depths of oxygenic photosynthesis could in theory result from a recent phytoplankton exudation. We also state clearly that PER was not measured in our study (Line 321-323).

Line 315: ¹³C-enriched DOC Modified.

Line 319: What does the CCB mean, please define it.

Typo corrected: CBB.

Line 322-325: I don't understand the logic here, how this sentence is linked to the above discussion? Can you elucidate it clearer? Also, I would suggest to include the data of εDOC-CO₂ into the figure 4.

We imply that the second option considered to explain the very positive $\Delta^{13}\text{C}_{\text{DOC-POC}}$ (namely, the production of less negative $\delta^{13}\text{C}_{\text{DOC}}$ via the utilization of a C fixation pathway different from the CBB) could work for the case of La Alberca but not for Atexcac. We have rephrased the sentence to make it clearer (lines 340-345).

The εDOC-CO₂ and $\Delta^{13}\text{C}_{\text{DOC-DIC}}$ parameters differ from each other only by a consistent 10±0.3‰. Thus, representing both in figure 4 would not visually bring new information, but it might possibly obscure the variability depicted by εDOC-CO₂ or $\Delta^{13}\text{C}_{\text{DOC-DIC}}$ within each lake, as it would broaden the scale on

the abscissa axis. Since we mainly refer to $\epsilon\text{DOC-CO}_2$ in the text, we now represent only that parameter in Fig. 4, but we report both parameters in Table 2.

Lines 377-378: 'an intracellular', not 'intracellular a'. Indeed, now corrected.

Figure 5 caption: Is the 'c' indeed different from the 'b'? It looks like to me that they are both a closed-system characterized by low CO_2 concentrations. In 'b', DOC and POC are produced concurrently, but in 'c', 'POC' first and then 'DOC'? Further, how to evolve into a closed-system, can you add some explanations? I think such a system may be difficult to form.

The difference between 'b' and 'c' is that, in the second system, in addition to low CO_2 concentrations, the lack of nutrients while high photosynthetic rates are maintained would lead to the fixation of large amounts of OC, which cannot be further anabolized and incorporated into the cell biomass (i.e. POC), and which are thus released as DOC. Hence, the fixed OC entering the cell biomass until nutrients are exhausted is formed first, while subsequently fixed OC is released as DOC.

In 'c' the DOC/POC ratio is very high so that, while both evolved from DIC under a closed system, the POC still imprints the fractionation of C fixation, while the DOC produced in a second step evolves toward the initial isotopic composition of the DIC.

As the activation of a DIC-CM is an energy-costly process, it has been thought to reduce the efflux of DIC (i.e. generating a closed system) from the cell back to the external medium (*cf.* lines 364), which would explain why it can lead to very small isotopic fractionations (e.g. Beardall et al., 1982; Iniguez et al., 2020; 'b' in Figure 5).

While these mechanisms deserve to be further explored in dedicated studies, they are simply proposed here as conceptual models to explain the data. We now emphasize this in the text in lines 366-367 and also in a short summary paragraph (lines 383).

Lines 398: It is weird to only dissection one lake, which is not even the one who has the most DOC accumulation.

The outline aims to illustrate the source/production of DOC (5.1.1) and then its fate (partial degradation and accumulation; 5.1.2). The first three lakes are used to illustrate the production of DOC, while the fate (partial degradation and accumulation) is illustrated by the case of Alchichica.

As discussed in 5.1.1, the prominent DOC peaks can only be directly related to autochthonous production in the first three lakes, but we also mention why these peaks cannot be explained by a degradation process (see answer to previous comment). Thus, the autotrophic production of DOC and its isotopic signatures are discussed through the lens of these three lakes. At the beginning of 5.1.2, we expressly discuss why the case of Alchichica may or may not be different. Since it appears that DOC isotopic signatures are more consistent with the bacterial degradation hypothesis (i.e. refractory DOC originating from DOC and POC heterotrophic partial degradation), we use this lake as an example of DOC fate.

We have modified the title of section 5.1.2. to indicate that Alchichica is used to exemplify the possible fate of DOC in the Mexican lakes.

Line 416: It should be 'C isotope'. Corrected.

Line 421: Should be 'consistent'. Corrected.

Line 438: Delete the 'it'. Deleted.

Line 453: Please provide the actual values of POC or $\delta^{13}\text{C}$ here. It means the figure 3 in the referred paper?

We have now deleted the reference to figure 3 to avoid confusion. Based on a previous comment we have also added the relevant data about $\delta^{13}\text{C}$ from Havas et al. (submitted). While we provide the exact changes in DIC and DOC concentrations, there is no change in [POC] and $\delta^{13}\text{C}_{\text{POC}}$, as indicated in the text, and therefore no values to provide.

Line 455: 'DOC isotope compositions'. Corrected.

Lines 451-465: Too much discussion derives from "Havas et al., submitted", which makes it impossible to verify and further evaluate.

We have added the relevant values for the DIC/POC data to show how they contribute to our analysis of the DOC data. We have also rephrased the paragraph to make it clearer.

Lines 466-467: Syntax error, please revise it. We have rewritten the sentence.

Line 501: It is weird to include two 'important'. We have rewritten the sentence (Lines 533).

Line 544: I suggest to transfer the unit 'PgC' to mM to help the readers compare it with the above.

We would like to thank the reviewer for this comment because after rereading the paper by Burdige and Komada (2015), we realize that we made a mistake about the unit of that number and the fact that it only considers coastal and continental margin benthic fluxes (water depths <2000m). This latter actually amounts to 180 TgC.yr^{-1} . In addition, Burdige and Komada (2015) report a value of 100 TgC.yr^{-1} for water depths > 2000m. Thus, the total DOC benthic flux would be 280 TgC.yr^{-1} or 0.3 PgC.yr^{-1} .

While Burdige and Komada (2015) describe the significance of this benthic flux relative to other DOC fluxes to the ocean (e.g. from rivers) and its importance for the specific oceanic recalcitrant DOC reservoir, the benthic DOC flux seems small compared to the entire oceanic DOC reservoir of 660 PgC. This is in part because, in the modern O_2 -rich ocean, most of the OC from primary production is remineralized into DIC (e.g. Jahnke, 1996: doi.org/10.1029/95GB03525; Burdige and Komada, 2015). Therefore, the argument about the benthic flux is not as strong here.

In contrast, anoxic bottom waters would likely allow a greater DOC flux from the sediments back to the water column (Dadi et al., 2017; Peter et al., 2016: [10.1002/2016JG003425](https://doi.org/10.1002/2016JG003425)). However, this was not quantified at a global scale. Nonetheless, Fakhree et al. (2021) discuss how the advent of eukaryotes may not have represented such a radical change, as ballasting with metal oxide particles and OC flocculation as particles already in the Neoproterozoic would go against the view of isolated single-cell prokaryotes that would float in the ocean for longer time periods.

In order to simplify and shorten this section, we have decided to remove this argument and delete this part of the discussion.