

We gratefully thank Associate Editor for their time in reading our manuscript. Below we have a full detailed response to each comment posed by Associate Editor, Referee #1, Referee #2 and our revised manuscript. We hope that our manuscript is clear, concise and well representative of our study.

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Associate Editor Decision: Reconsider after major revisions (02 Jan 2018) by Katja Fennel

Comments to the Author:

Dear Authors,

10 Please upload your revised manuscript and responses to the reviewer comments according to the instructions you will be provided by e-mail. In addition to the responses you have already posted in the discussion forum, I would ask that you explicitly address the following comment by Reviewer #2:

15 "My criticism of the paper is that the multi-environmental model is presented very much at face value. The assumptions and construction seem very logical but the choice and constraint of the parameters is by and large opaque. In particular the relationship between the storage component of the multi-environmental model and the Galbraith and Martiny parameterization seems interesting and important but is not really discussed. How important is the storage term in controlling the overall response of the multi-environmental model? It is not at all clear from the 20 manuscript. I feel that some clarification and discussion along these lines is important for the reader."

Best regards, Katja Fennel

25 OUR RESPONSE

>>> In order to address this commentary from Reviewer #2, we have added a new figure (Fig.2) and expanded our multi-environmental model description. This had been down throughout the 2.1.4 Multi-Environmental Model section within the manuscript (below the Referee #2 here in this document).

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We gratefully thank Referee #1 for their time, constructive comments, and suggestions to our manuscript. Below we have a detailed response to each comment posed by Referee #1. We have amended the manuscript in hopes that it will be much improved and our study presented clearer.

35 Anonymous Referee #1

Received and published: 7 November 2017

Variability in marine phytoplankton stoichiometry can lead to differences in carbon export to the deep ocean. This manuscript expands on previous models (mainly Galbraith and Martiny, 2015 40 and Yvon-Durocher et al., 2015) to further our understanding of how various environmental factors lead to changes in phytoplankton stoichiometry. The authors show how incorporating factors, such as temperature, light, and phosphorus concentrations, are able to model variations across the global ocean that would otherwise be lost in more mainstream models using fixed C:P ratios. The manuscript overall nicely lays out the difference modeling approaches taken and how 45 they ultimately change the effect on carbon export in the global ocean. I want to point out that I am not a modeler and therefore cannot assess the math presented to its full extent, but I am a

biogeochemist and can provide a critique on the science presented in this manuscript. I believe this manuscript should be published with the revisions I have outlined below.

- 50 1) My first issue with the manuscript in general is the lack of nitrogen. The ocean overall is nitrogen limited and it is a bit worrisome that it is never mentioned. Why was nitrogen left out? There must be a reason, and including a sentence or two to explain why it has been left out would be sufficient without having to incorporate it into the models.

55 OUR RESPONSE

>>> This is a very important point and the reviewer comments make it clear that the justification of using P as a representative of nutrient availability needs to be clarified in our manuscript. The underlying reason for picking P rather than N is linked to ideas outlined by Tyrrell, 1999. On long time-scales, P is commonly considered the ultimate limiting nutrient whereas N is only limiting productivity and export on short time-scales. On long time-scales, nitrogen fixation/denitrification will presumably adjust the N inventory. Our modeling is focused on long term steady-state outcomes and we would like to avoid issues associated with modeling the N cycle (like getting N-fixation and denitrification rates correct). Thus, we chose to use P as a representative for nutrient availability. However, we do recognize that the reality may be more complex and hope to add an explicit nitrogen (and Fe) cycle in the future.

We have amended the manuscript to address this concern: “Phosphorus is used to represent the role of nutrient availability in controlling stoichiometry and C export. We chose this over N to avoid having to include a parameter rich N cycle. Furthermore, P rather than N is commonly regarded as the ultimate limiting nutrient (Tyrrell, 1999) and thus P availability represents the long-term steady-state biogeochemical equilibrium.”

- 75 2) My second issue is the inclusion of iron and iron deposition. It is mentioned several times throughout the manuscript and honestly seems to be thrown in haphazardly. Even calling the one region the iron-limited upwelling zone does not really make sense. I do not disagree that these regions are distinct from the subtropical gyres, but there needs to be another way to separate them. The simplest thing to do would be to remove all talk of iron and iron deposition as it does not add anything to the manuscript. If you choose though to leave it in, there needs to be more discussion and also a few references as there are currently none. I have listed below each mention of iron and have provided some input should you choose to include it.

OUR RESPONSE

85 >>>We agree with the reviewer on this point and realize that the references to Fe limitation are confusing. Thus, we have removed the labeling of iron-limited regions in the manuscript. Now, we only introduce the concept of iron limitation in the discussion as a factor contributing to setting surface macronutrient concentrations in tropical ecosystems.

- 90 3) My third issue is how phospholipids have been defined and treated within the model. The decision to functionally treat phospholipids with the storage pool needs to be justified or expanded upon as it is currently not clear. As the authors state, phospholipids are

95 localized within the cellular membrane (defined in the model as a functional pool) and  
not as energy storage molecules as suggested in the text. Lipids associated with energy  
storage, localized within intracellular lipid droplets, are generally non-phosphorus, highly  
reduced, and non-polar (see Levitan et al 2014 “Remodeling of intermediate metabolism  
in the diatom *Phaeodactylum tricornutum* under nitrogen stress”). This raises the  
question of how the authors have defined the storage pool, is it defined as utilized by  
organisms for energy storage or is it only in the sense that “this is a pool where some  
100 phosphorus is stored within the cell?”

OUR RESPONSE

>>> We agree that this can be confusing. Due to the similarity in behavior of P-lipids and P-  
storage (no other types of storage molecules like lipids or carbohydrates are considered here),  
105 they were treated as the same in the model to save parameters. To address this issue, we have  
attempted to clarify this issue in the manuscript.

The manuscript now reads as follows: “Phytoplankton can substitute  
sulfoquinovosdiacylglycerol (SQDG) for phospholipids in their cell membranes under low P  
110 conditions (Van Mooy et al., 2009). Similarly, P storage molecules are also regulated by P  
availability. Thus, we here assume that phospholipids and P-storage exhibit the same  
behavior and thus model-wise treated as one pool (Van Mooy et al., 2009).”

4) L34: First mention of iron-limited tropical upwelling region. Again, I would honestly  
115 remove “iron-limited” and just call the region the tropical upwelling region. These  
regions become macronutrient limited as well once you leave the immediate upwelling  
zone so its deceiving to just focus on iron. It is also known that the Southern Ocean is  
iron limited, so, again, it is deceiving to focus on iron in the upwelling regions when  
there are other regions that are iron limited.

120 OUR RESPONSE

>>>As stated in #2, we agree with this point and have changed the description of the tropical  
box as suggested.

125 5) L46: add “ppm” after ~46

OUR RESPONSE

>>>We changed this in the document.

130 6) L70: add “et al.” after Durocher

OUR RESPONSE

>>>We changed this in the document.

135 7) L76-85: Remove iron-stressed and iron-limited. The sentence “Iron deposition in the  
tropical upwelling. . .” is not correct. There is actually very little iron deposition to the  
tropics, the North African dust plume deposits iron to the tropical Atlantic but that is the  
one example (see Jickells et al 2005 “Global Iron Connections Between Desert Dust,

140 Ocean Biogeochemistry, and Climate”). Iron is upwelled along the coasts in these areas  
along with macronutrients, but it is incorrect to call that iron deposition.

OUR RESPONSE

145 >>>We have removed iron-stressed and iron-limited from this section. Iron limitation will  
now only be referenced in the discussion.

150 Within our paper we have added the following sentence to address this comment, “Here we  
will briefly discussion how iron limitation could play a significant role on phosphorus  
concentrations. The biogeochemical functioning of tropical regions are commonly influenced  
by iron availability in such a way that macronutrient levels cannot be fully drawn down by  
155 phytoplankton (Coale et al., 1996; Moore, 2004; Raven et al., 1999). The degree of nutrient  
drawdown has a strong impact on predicted (and observed) C:P. This environmental control  
on C:P could lead to highly non-linear controls on  $p\text{CO}_{2,\text{atm}}$  whereby increased export in the  
tropics leads to increasing  $p\text{CO}_{2,\text{atm}}$ . This relationship would differ in the subtropics, where  
iron is thought to stimulate nitrogen levels through nitrogen fixation, an iron exhaustive  
160 metabolic process (Wu et al., 2000). Iron’s potential control on nitrogen fixation could  
promote higher carbon fixation and further exported stoichiometric ratios in the subtropical  
regions leading to increasing  $p\text{CO}_{2,\text{atm}}$  (Wu et al., 2000). Thus, iron availability may play a  
complex role depending on whether there is an increased delivery in upwelling zones  
(leading to a potential declining global C export) or in the subtropical gyres (leading to a  
potential increase in global C export).”

8) L111-115: Questions 1 and 2 seem redundant, please remove question 1 or give more  
detail if it is in fact different from question 2.

165 OUR RESPONSE

>>>We recognize the confusion seen between the two research questions. The first is to  
determine the influence of cellular allocation strategies based on different environmental  
conditions (nutrients, temperature, and multi-environmental) on stoichiometric ratios. The  
170 second is to determine the influence of changing environmental conditions such as  
phosphorus concentrations and temperature on each stoichiometric model. In order to address  
this confusion, we have clarified the first question to include cellular allocation strategies.

175 Within our paper we have changed the research questions to read as follows: “We will  
explicitly address the following research questions: (1) How does environmental variability  
influence marine phytoplankton cellular allocation strategies and in turn the elemental  
stoichiometric ratio? (2) What are the effects of changing environmental conditions on  
stoichiometric ratios, carbon export, and  $p\text{CO}_{2,\text{atm}}$ ?, and (3) What is the influence of the  
environmental conditions among the three major surface biomes on carbon export and  
180  $p\text{CO}_{2,\text{atm}}$ ?”

9) L135: Where in the water column are you taking the phosphorus concentration?

OUR RESPONSE

185 >>> Phosphorus concentrations are prescribed within each box and then the model is run to steady state. The tropical and subtropical surface boxes extend down to a depth of 100 m, the high latitude surface box extends down to 1000 m, the thermocline box extends from a depth of 100 m down to a depth of 1000 m, and the deep box extends down to a depth of 4000 m. For the use of phosphorus within our multi-environmental stoichiometric model we use the concentration in the respective surface box.

190 10) L207: add “et al.” after Daines

OUR RESPONSE

195 >>> We changed this in the document.

11) L212: add “et al.” after Daines

OUR RESPONSE

200 >>> We changed this in the document.

205 12) L213: Expanding on the phospholipid justification, can you explain more why you choose a zero contribution for phospholipids? Although non-P substitutes can reduce the phosphorus incorporated into P-lipids, observations suggest non-zero quantities remain. For example, 1.3 +/- 0.6% P uptake in the P-limited Sargasso are incorporated into phospholipids (Van Mooy et al 2009 – mentioned in next correction) and phospholipids make up approximately 5% of particulate organic P in the P-limited eastern Mediterranean (Popendorf et al 2011 “Gradients in intact polar diacylglycerolipids across the Mediterranean Sea are related to phosphate availability”). Might it be more appropriate to have two distinct P-lipid/total cellular P values for high and low phosphorus regions?

OUR RESPONSE >>> We do in no way intend to imply that cells do not include P-lipids. Please see #3 for a detailed response to this point.

215 13) L215-216: For phospholipid substitution, a more appropriate reference would be Van Mooy et al 2009 “Phytoplankton in the ocean use non-phosphorus lipids in response to phosphorus scarcity” instead of Van Mooy et al 2006.

OUR RESPONSE

220 >>> We have added the Van Mooy et al. 2009 reference.

14) L228: add “et al.” after Daines

OUR RESPONSE

225 >>> We changed this in the document.

15) L282: . . .that underlies the subtropical gyres and equatorial upwelling regions (labeled M), and deep waters. . .

230 OUR RESPONSE  
>>>We changed this is in the document.

235 16) L314: “Iron limitation is implicitly simulated through its control on the tropical [P]. . .” –  
how does iron control phosphorus concentrations? This is not clear in the manuscript and  
I personally have not come across any such research stating such. Again, if you are going  
to keep iron in the manuscript please provide references of where you have gotten the  
information and expand on the explanation of how you can make this justification.

240 OUR RESPONSE  
>>>Iron was removed from the manuscript and only discussed briefly in the discussion  
section.

245 17) Table 2: Please switch the columns so that Range of fhd (sv) is first and references is  
second (will be consistent with Table 1).

OUR RESPONSE  
>>>We have switched the column to be consistent with Table 1.

250 18) L350: “This set of experimental runs was intended to capture the effects of changing  
levels of iron deposition. . .” – Again, talking about iron deposition in these tropical up-  
welling regions does not make sense and as you have not provided references I would  
just remove it all together. This experiment wanted to test the sensitivity of pCO<sub>2</sub> to  
nutrient availability, I believe that is a good enough reason and there is no need to  
mention iron limitation.

255 OUR RESPONSE  
>>>We agree with this reviewer that and have removed this reference to Fe limitation.

260 19) L377: Change variables to variable

OUR RESPONSE  
>>>We changed this in the document.

265 20) L379: Remove “iron stressed”

OUR RESPONSE  
>>>We changed this in the document.

270 21) Figures 6 and 10: I really like these figures and think you could include more in the  
discussion about the implications of how global temperatures will affect export. It is a  
nice way to tie your work with large scale impacts on biogeochemical cycles and reiterate  
the importance of the study.

OUR RESPONSE

275 >>>We completely agree this with observations. We hope to expand on the potential implications of global temperatures effect on export based on findings.

22) L477: add “the” before data

280 OUR RESPONSE

>>>We changed this in the document.

23) L589: remove iron-limited

285 OUR RESPONSE

>>>We changed this in the document.

24) L596: remove “iron deposition or”

290 OUR RESPONSE

>>>We changed this in the document.

25) L600: remove sentence “This observation suggests that pCO<sub>2</sub> may have a complex link : :”. You honestly have not shown anything to do with iron delivery and its link to pCO<sub>2</sub>, there is nothing included in the model that I saw and again have provided zero references about iron deposition

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OUR RESPONSE

>>>We agree with the reviewer, it has been removed from the document. Instead, we linked it to macronutrient availability.

300

26) L650: remove “thus”

OUR RESPONSE

305 >>>We changed this in the document.

27) L674: remove “which might be influenced by increased atmospheric iron deposition,”

OUR RESPONSE

310 >>>We changed this in the document.

28) L680: change separating to separate

OUR RESPONSE

315 >>>We changed this in the document.

29) References: There are a few references that are not mentioned in the manuscript. A couple are about iron cycling and I am curious if and where they were originally included and also possibly had more of an explanation associated with them of why you link iron to phosphorus? Cunningham and John 2017 Moore 2004 Raven and Falkowski 1999

320

Also, please move Van Bogelen and Neidhardt 1990 and Van Mooy et al 2008 references to after the Toseland et al 2013 reference

#### OUR RESPONSE

325 >>>We apologize for the missing use of these references. This has been fixed in the manuscript.

We gratefully thank Referee #2 for their time, constructive comments, and suggestions to our manuscript. Below we have a detailed response to each comment posed by Referee #2. We have  
330amended the manuscript in hopes that it will be much improved and our study presented clearer.

Anonymous Referee #2

Received and published: 1 December 2017

335Using a "classical" ocean carbon cycle box model and parameterizations of flexible elemental stoichiometry in surface ocean particulate, the authors examine the role of elemental composition in mediating the response of atmospheric CO<sub>2</sub> to ocean temperature change. There is a significantly different sensitivity when the particulate C:P ratio is represented by a "multi-environmental" (Ecological Stoichiometry and temperature dependent) framework compared to a  
340fixed, Redfieldian particulate composition. Most notably, compensation between temperature sensitivity of solubility and biological pumps reduces the sensitivity to subtropical temperature change as well as reversing and enhancing the response to tropical perturbations. Variable elemental composition and phosphorus storage modify the sensitivity of atmospheric pCO<sub>2</sub> to the efficiency of phosphate utilization in subtropics and tropics. The key message for is that  
345variable elemental ratios have non-negligible impacts on the ocean's control of atmospheric CO<sub>2</sub> and that the temperature sensitivity of solubility and stoichiometrically-mediated biological pumps have some interesting regional dependences.

I enjoyed reading this paper. I found it stimulating and thought provoking. There is a lot going  
350on. The authors combine classical carbon cycle box model with several parameterizations of elemental stoichiometry of the sinking particulate (and/or primary producers). The authors connect cellular scale physiology and global carbon cycle and have used and developed an appropriate framework with which to do so.

355My criticism of the paper is that the multi-environmental model is presented very much at face value. The assumptions and construction seem very logical but the choice and constraint of the parameters is by and large opaque. In particular the relationship between the storage component of the multi-environmental model and the Galbraith and Martiny parameterization seems interesting and important but is not really discussed. How important is the storage term in  
360controlling the overall response of the multi-environmental model? It is not at all clear from the manuscript. I feel that some clarification and discussion along these lines is important for the reader.

I found the manuscript very interesting and thought provoking. I had a number of questions,  
365comments and need clarification on certain points which I will detail here. Some are more

important than others. While my recommendation is major revision, it is clarification that I would like to see, not changes to what has been done.

370 30) The Sarmiento and Toggweiler and contemporary carbon cycle models focused a lot on the sensitivity of atmospheric pCO<sub>2</sub> to "high latitude" changes. This isn't discussed here - perhaps there wasn't any as configured? Some comment would be useful and interesting in this regard.

#### OUR RESPONSE

375 >>> In this manuscript, we are focusing our efforts on the potential impacts of the low latitudes. Sarmiento and Toggweiler both found that high latitudes have a big impact on atmospheric pCO<sub>2</sub>. In no way do we disagree with this seminal work, we simply are trying to bring attention to the importance of low latitude processes as an additional mechanism(s) to consider when predicted biogeochemical feedbacks. We take their original findings into  
380 consideration when creating the model. In the box model, fhd, a bidirectional mixing term that ventilates the deep box directly through the high-latitude surface box, has a large impact on the magnitude of atmospheric pCO<sub>2</sub>. We prescribed the baseline value to be 45.6 Sv in our model but when we increase it to 108 Sv, the change in pCO<sub>2</sub> is ~105 ppm for C:P at Redfield proportions. Thus, high-latitude processes clearly have a major impact on ocean and  
385 global biogeochemistry.

To address this comment in the manuscript, we have added the following: "Although the focus of this study is to determine the impact of low latitude biogeochemistry on pCO<sub>2,atm</sub>, we point out that at Redfield stoichiometry, pCO<sub>2,atm</sub> increases by 100 ppm when fhd is  
390 increased to 108 Sv from its default value 45.6 Sv."

395 31) The stoichiometry of sinking particulate and of primary producers is certainly connected but not necessarily the same. The multi-environmental model is founded on primary producer physiology. Perhaps this potential difference should be flagged?

#### OUR RESPONSE

>>>We acknowledge that sinking particulate stoichiometry and primary producer stoichiometry can be different in certain regions but overall, it has been found to be reasonably linked (Teng et al. 2014). Thus, we find that this assumption is reasonable to a  
400 first order.

Within our paper we have added the following statement, "For certain values of the parameters, the model produced excessive nutrient trapping in the thermocline. In order to dampen the nutrient trapping, we tuned the remineralization depth. Assuming that 25% of  
405 the total export is respired in the thermocline with the remaining 75% exported into the deep ocean, produced a better match between the modeled and observed [P] in the thermocline box. Total export is made from both the stoichiometry of sinking particulate and of primary producers, based on Teng et al. (2014) this is a reasonable first order assumption."

410 32) I would have been interested to see a Droop-style model in the mix as its a relatively common tool - but there is more than enough going on here anyway.

OUR RESPONSE

415 >>>We believe that the Galbraith and Martiny (2015) model (nutrient-only model in our study) is qualitatively similar to the Droop model. Thus, we expect the outcome to be very similar (i.e., a direct dependence of C:P on P availability).

420 33) I very much like the spirit of the multi-environmental model. (Though I find the name a little odd). It accounts for the role of cell size in mediating nutrient affinity and cell composition (contribution of cell wall material). It was not made clear how sensitive the final parameterization or the outcomes of the box model are to the assumed cell size. Nor could I find any information about the cell size assumed (or modeled?) in the simulations.

OUR RESPONSE

425 >>>We do not assume that there is a single size characterizing all phytoplankton cells in our model. Instead, cell size is one of the key elements of cell strategy that we model. Smaller cells have greater specific nutrient uptake rates, but their cell wall and membrane occupies a greater fraction of their biomass than larger cells, and thus they have less space (specific to biomass) for investments in either photosynthesis or biosynthesis.

430 Figure 4 and 5 (now Figure 5 and 6) are meant to illustrate the predictions that our model makes in different environmental conditions. In the original manuscript, these figures showed model predictions for C:P ratios, biosynthesis investment, and photosynthesis investments. However, in each of these figures, the predicted cell radius is also varying. In order to make  
435 the predictions of our model clearer, we have augmented each of Figure 5 and 6 with an additional plot, showing how cell radius varies with environmental conditions.

440 Our model predicts a strong relationship between nutrient concentrations and cell size. In oligotrophic conditions the model predicts a radius under 1  $\mu\text{m}$ . When resources are abundant the model predicts much larger cells. Our model also predicts a weak, but non-zero dependence of both irradiance and temperature on cell size. Higher irradiances lead to smaller cells (due to a lower requirement for photosynthetic machinery), and there is a non-monotonic, concave relationship between temperature and cell size, which is due to a subtle interaction between biosynthesis efficiency (which varies greatly with T) and size dependent  
445 uptake rates.

34) The photosynthesis parameterization and allocation scheme is very reminiscent of Geider's models in spirit and mathematical form. What is the relationship?

450 OUR RESPONSE

>>>Our model is very closely related to the multi-compartment photosynthesis model presented in Talmy et al. 2013 (we incorrectly cited Talmy 2014 in the model description; this has been changed to correctly cite this paper). Geider is a co-author of this paper and indeed the modeling framework presented there is very much consistent with the  
455 photosynthetic models he has devised throughout his career. We utilized the functional responses which they derived in that paper to represent the allocation of photosynthetic machinery to either light harvesting or carbon fixation. Their model included other

compartments (photoprotection and biosynthesis) which were suited to the particular dynamic light environment that they were interested in studying. We use our own parametrization for biosynthesis. Talmy et al. 2013 found that the photoprotection allocation was not a large or greatly changing component of their allocations. We have therefore not included it would complicate our model with little change in our qualitative results.

On the other hand, the decomposition of photosynthesis into light harvesting and carbon fixation components is critical, and makes our model predictions agree much better with experiments studying the variations of C:P or N:P ratios with irradiance. Models that do not have this decomposition predict too large of a decrease in cellular allocations to photosynthesis at high-light levels. In a two compartment model, increases in allocations to carbon fixation cause the overall allocation to light harvesting to have a more mild decrease. The two-compartment treatment also seems more physiologically realistic than a 1-compartment, which only models photosynthetic pigments. Thus we used the functional forms and parameters that were derived (experimentally) in Talmy et al. 2013 for carbon-fixation and light-harvesting. We have added a small amount of text to better clarify the relationship.

35) The statement at line 235 that the "unique maximum of the growth rate occurs for the set of parameters that lead to co-limitation by nutrients, photosynthesis and biosynthesis" is very interesting and intriguing. Is that an emergent property? Is it obvious that it should be this way? I would have liked to hear more about this.

#### OUR RESPONSE

>>>It is commonly the case for mathematical models like ours that model the tradeoffs between different allocations of biomass to different physiological functions to have a unique solution with a maximum growth rate. The reason is that if one increases the investment a cell makes in some pool, this will decrease the investments in other pools. Thus, the only way for a cell to increase the photosynthetic rate is to decrease either biosynthesis or nutrient uptake rates, and vice versa. In such cases we generally find a unique solution at which the three rates,  $\mu_{\text{Photo}}$ ,  $\mu_E$ , and phosphorus are the same. This might be obvious for very simple models, or for people who primarily work using these models. Indeed, the easiest way to see what is going on is to imagine a simpler model with a similar style. For example, if we modeled a cell with fixed radius which is limited by either light or by biosynthesis, then the cell growth rate would be  $\min(\mu_{\text{Photo}}, \mu_E)$ . If we start with the biosynthesis allocation at 0, the growth rate of the cell will be  $\mu_E = 0$ , but  $\mu_{\text{Photo}}$  will be high because of all of the photosynthesis proteins. As E increases,  $\mu_E$  increases, and the cell grows faster. At this time,  $\mu_{\text{Photo}}$  is going down, but this doesn't affect  $\mu$ . At some value of E,  $\mu_E = \mu_{\text{Photo}}$  (since if  $E = 1$ ,  $\mu_{\text{Photo}} = 0$ ). This point will be the optimal strategy, since further increases in E will cause a switch to limitation by  $\mu_{\text{Photo}}$ , which decreases with increasing E.

We have actually been able to convert the intuitive picture described above into a mathematical proof. Since it does not require much additional space to include it, we have added it to the paper, along with a figure indicating graphically the idea behind the proof.

36) Phosphorus storage seems to be very important. Equation (13) controls a residual storage pool that constrains the parameterized stoichiometry to match the observed relationship between phosphate and particulate stoichiometry, as I understand it. Thus it strongly mirrors the Galbraith and Martiny model of equation (1). For me, some key questions concern this aspect of the model: How significant in the overall control of model stoichiometry is this component? If it dominates, then I could view the multi-environmental model in some way as a combination of the Galbraith and Martiny model with temperature sensitivity. Or does the more mechanistic and detailed physiology have a significant role? Either way, I think the mechanistic model is valuable and interesting but I would like to understand how much the results are driven by the storage of phosphorus. Its important for a number of reasons and I feel that this should be clearly discussed.

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#### OUR RESPONSE

>>>The impact of the residual pool on the overall size of the P pool is heavily dependent on environmental conditions, varying from a minimum of close to 0% to a maximum of just under 50%, for the combinations of parameter values used in all of our numerical experiments. Over most of the parameter range considered here, the contribution of the residual pool is much more modest, 10-20%. High values occur when phosphorus is available and the temperature is high. In these conditions, ribosomal contributions are decreased, but the residual contribution is high. In cold water, high P ecosystems, the residual contribution is approximately 25%, and in oligotrophic ecosystems it is close to 0.

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Thus, we view the mechanistic/physiological part of the model as being more significant, but it is important to acknowledge that we don't believe that this mechanistic model can on its own explain all of the observations of C:P in the ocean. In particular, it is not possible for the purely mechanistic model to predict the extremely low C:P ratios observed in some ocean regions. This is because the C:P ratio of the biosynthesis apparatus sets a lower limit. Even if we assume that proteins made an even smaller contribution to biosynthesis (which would cause biosynthesis to have a lower C:P), it would still be impossible to match the most extreme observations. If the C:P of the biosynthesis pool was variable or lower, then the contribution of residual pool would be somewhat smaller, but still necessary. (Better understanding the balance between ribosomes and non-photosynthetic proteins is likely a good direction for future research).

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In order to make the importance of storage, we have added an additional plot reveals the relative contribution of the storage pool to the total P pool as a function of environmental conditions, with a short discussion.

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37) A small thing, but I had to stop and think about equation (1) because  $[P]_o$  has different dimensions than  $[P]$ : the former is a ratio and the latter a concentration. I think it would be much clearer and more appropriate to denote  $[P]_o$  as in (13), with a symbol in accord with other variables that are ratios.

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#### OUR RESPONSE

>>>Thank you for noticing this, we have changed the notation so that  $[P]_0$  is now  $(P:C)_0$ , i.e. the P:C ratio predicted by linear regression at zero P concentration.

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38) The box model formulation makes sense; the inclusion of the thermocline reservoir is important for the sensitivity to changes in the subtropical surface. Some small details: how is the carbonate system solved? Is alkalinity fixed or is there an implicit carbonate pump?

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#### OUR RESPONSE

>>>Thank you for bringing this to our attention. The nonlinear carbonate system equations are solved using Matlab's `fsolve` function. We calculated the solubility constants using biome specific salinity and temperature. The solubility constant then is used to break up total carbon into  $p\text{CO}_2$ , bicarbonate and carbonate ions. Total carbon is quantified using the breakdown of carbon ions ( $p\text{CO}_2$ , bicarbonate and carbonate) and alkalinity concentration. Total carbon and its breakdowns (which we keep track of at each time step) are transported laterally to each box through our thermohaline circulation. We have added more detail to our box model design description, to make sure we are clear on how this model is created.

565

Within our paper we have added these lines to address this comment: "To quantify the breakdown of carbon into these components, we model the solubility pump, using temperature and salinity to determine the partitioning of inorganic carbon among total carbon within a box. The global mean alkalinity is prescribed according to the observed mean ocean values but is also subject to transport (Sarmiento and Toggweiler, 1984). Our box model simulates alkalinity and total inorganic carbon, which are conserved tracers from which the speciation of inorganic carbon in sea-water can be calculated. Biome specific salinity and temperature are used to prescribe the solubility constants of  $\text{CO}_2$  in seawater and the bromine concentration, which is taken to be proportional to salinity.  $\text{CO}_2$  cycles through the atmosphere via the air-sea gas exchange fluxes ( $f_{ah}$ ,  $f_{as}$ ,  $f_{at}$ ). We used a uniform piston velocity of  $5.5 \times 10^{-5} \text{ m s}^{-1}$  to drive air-sea gas exchange (DeVries and Primeau, 2009; Follows et al., 2002)."

570

575

39) The model doesn't resolve nitrogen, and I would expect that the allocation of nitrogen in proteins and pigments would be an important factor, perhaps more so than phosphorus. Does this actually matter? A comment on this would be helpful.

580

#### OUR RESPONSE

>>>This is an important point that was also raised by reviewer 1 (Referee 1: Response #1). In short, the reason for using P is its role as the ultimate limiting nutrient on long time-scales as well as to simplify the model and avoid an explicit N cycle.

585

40) Why does temperature affect biosynthesis but not photosynthesis (line 398) imposed from empirical observations? The model description tells us that  $Q_{10}=2$  for temperature dependences, but there is no discussion with regard to photosynthesis. Why this choice?

590

#### OUR RESPONSE

595 >>>We model photosynthesis as having a  $Q_{10}=1$ , which is consistent with physiological studies going back to Shuter 1979 that suggest that photosynthetic efficiency does not depend on temperature over physiologically relevant ranges. The discrepancy between photosynthetic and biosynthetic temperature dependence has traditionally been explained by referring to the differences in the chemistry and physics of the two processes. The electron transport chain relies on quantum mechanical processes, which are unaffected by variations in temperature in a physiologically relevant range. A good reference for this is Devault 1980, Quantum Mechanical Tunneling in Biological Systems. We have added some text to more explicitly explain our choice of temperature dependence parameters for different processes.

600  
605 41) The discussion of sensitivity to cell radius in lines 400-410 doesn't tell us what is the cell radius (or distribution of) in the model? Is it imposed or modeled (I presume the former but nothing is said in the paper). This should be clear.

OUR RESPONSE

610 >>>Cell radius is an emerging property based on the phosphorus concentration, light, and temperature on the cell.

42) Figures 3,4,5 are a bit small and fuzzy when printed.

OUR RESPONSE

615 >>>We have fixed these figures so they are clearer.

43) I'd really like to understand how important the storage term is in the overall control of figures 4 and 5. We see the variation in C:P and the relative allocation to biosynthesis and photosynthesis, but it's not clear how important the latter is to the former.

620 OUR RESPONSE

>>>We have included an additional figure (Figure 2, in current manuscript below) as part of our response to an earlier comment about the importance of phosphorus storage.

625 44) What is the cell size in the box model simulations? Is it imposed? Does it vary? How sensitive are results to  $r$ ?

OUR RESPONSE

630 >>>The cell size varies based on the phosphorus concentration, light, and temperature in each surface box when we are running the multi-environmental stoichiometry. When using the Redfield, nutrient-only and temperature-only stoichiometric models there are not explicit cell sizes but implicit varying ones.

635 45) The model is P based. However, as is alluded to in the manuscript, nitrogen and iron dynamics are important. Indeed P is found to be the proximal limiting in only a few areas of the global ocean, with N and Fe controlling things locally. So how does this affect the relevance of the model? Wouldn't N and Fe dynamics be more important at the individual scale? Would this (does this) mean that storage is most significant for P:C? Again, understanding the significance of storage for the outcomes here is very important.

640 OUR RESPONSE

>>>It is true that phosphorus rarely is a proximal limiting nutrient, whereas nitrogen and iron commonly limit productivity in the short term. However, on long time-scales P is commonly considered the ultimate limiting nutrient and our results are indeed based on long-term equilibrium states. However, it is also clear that the three nutrient cycles have complex interactions both within and outside the cell and we hope to add explicit N and Fe cycles in future iterations of the model.

46) Line 464: "nutirent"

650 OUR RESPONSE

>>>We have changed it in the document.

47) The contrasting temperature sensitivities of tropical and subtropical perturbations is very interesting. The dominance of the solubility term in subtropical responses is ascribed to the "large surface area" of the subtropical region (line 563). I don't think that's true: I think its because the subtropical surface feeds the subtropical thermocline which represents a significant contribution to global water volume. Hence, changes in subtropical solubility have significant leverage. Since tropical waters don't directly feed into any subsurface water mass, they do not have the same leverage. This is why the resolution of the thermocline box is important. The classic Harvardton Bear box models did not resolve the thermocline and so found very low sensitivity to subtropical perturbations relative to 3D circulation models. Resolving the thermocline in the box models brings them into consistency (this was the point of Follows et al, 2002). I thought this was why the authors had chosen the configuration which resolves a thermocline reservoir.

OUR RESPONSE

>>> The reviewer is correct. The sensitivity of atmospheric CO<sub>2</sub> to solubility changes in a box in contact with the atmosphere depends on the volume of the subsurface ocean ventilated from that box and on the degree of air-sea disequilibrium as explained in Follows et al, 2002 and also in DeVries and Primeau 2009. (The disequilibrium effect can be significant for high latitude boxes that have a relatively small surface area and a vigorous exchange rate with deeper water masses). We thank the reviewer for allowing us to clarify the point we were trying to make, which is that because the nutrient supply to the subtropical gyres is dominated by the lateral transport of unused nutrients from the tropical box rather than by vertical exchange, the strength of the biological pump does not scale with the surface area of the subtropical gyre, whereas the volume of the thermocline box *very roughly* speaking scales as the area of the subtropical box, at least in the limit where the surface area of the tropical box is negligible compare to that of the subtropical box, simply because volume is equal to area times thickness.

To make the text clearer and more accurate we have revised it as follows: "The decrease in surface CO<sub>2</sub> solubility at elevated temperature is sufficient to overcome the increase in export due to higher C:P leading to a positive relationship between pCO<sub>2,atm</sub> and subtropical

685 temperatures. It is important to point out that the relative importance of the two competing  
effect depends critically on the physical circulation of the ocean. Predicted increases in  
stratification are often invoked as a mechanism that would decrease the vertical supply of  
nutrients, which one might think would further compensate for the effect of higher C:P.  
690 However, the strength of the biological pump in the subtropics is also influenced by lateral  
transport of nutrients (Letscher et al., 2015) so we argue that it is unclear if you should  
expect increasing, unchanged or decreasing C export in low latitude regions with ocean  
warming and stratification. Similarly, it is unclear how increases in stratification might affect  
the strength of the solubility pump. The sensitivity of  $p\text{CO}_{2,\text{atm}}$  to changes in subtropical  
temperatures depends critically on the volume of the ocean ventilated from the subtropics,  
695 i.e. on the volume of the thermocline box in our model. How this volume might change in  
response to a warming world is a complicated dynamical problem that is beyond the scope of  
the present work.”

## 700 **Marine Phytoplankton Stoichiometry Mediates Nonlinear Interactions Between Nutrient Supply, Temperature, and Atmospheric CO<sub>2</sub>**

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705

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| Keywords: Redfield Ratio, Traits, Carbon Cycling,

| ~~Working title: Feedbacks Between Marine Stoichiometry, Environment, and Atmospheric~~  
720 ~~CO<sub>2</sub>~~

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## Abstract

Marine phytoplankton stoichiometry links nutrient supply to marine carbon export. Deviations of phytoplankton stoichiometry from Redfield proportions (106C:1P) could therefore have a significant impact on carbon cycling, and understanding which environmental factors drive these deviations may reveal new mechanisms regulating the carbon cycle. To explore the links between environmental conditions, stoichiometry, and carbon cycling, we compared four different models of phytoplankton C:P: a fixed Redfield model, a model with C:P given as a function of surface phosphorus concentration ([P]), a model with C:P given as a function of temperature, and a new multi-environmental model that predicts C:P as a function of light, temperature, and [P]. These stoichiometric models were embedded into a five ocean circulation box model, which resolves the three major ocean biomes (high-latitude, subtropical gyres, and tropical upwelling regions). Contrary to the expectation of a monotonic relationship between surface nutrient drawdown and carbon export, we found that lateral nutrient transport from lower C:P tropical waters to high C:P subtropical waters could cause carbon export to decrease with increased tropical nutrient utilization. It has been hypothesized that a positive feedback between temperature and  $p\text{CO}_{2,\text{atm}}$  will play an important role in anthropogenic climate change, with changes in the biological pump playing at most a secondary role. Here we show that environmentally driven shifts in stoichiometry make the biological pump more influential, and may reverse the expected positive relationship between temperature and  $p\text{CO}_{2,\text{atm}}$ . In the temperature-only model, changes in tropical temperature have more impact on the  $\Delta p\text{CO}_{2,\text{atm}}$  (~41 ppm) compared to subtropical temperature (~4.5 ppm). Our multi-environmental model predicted a decline in  $p\text{CO}_{2,\text{atm}}$  of ~46 ppm when temperature spanned a change of 10°C. Thus, we find that variation in marine phytoplankton stoichiometry and its environmental controlling factor can lead to non-linear controls on  $p\text{CO}_{2,\text{atm}}$ , suggesting the need for further studies of ocean C:P and the impact on ocean carbon cycling.

## 1 Introduction

750 The discovery of large-scale deviations of phytoplankton stoichiometry from the Redfield  
| ratio in the past decade (~~M~~(Martiny et al., 2013a, 2013b; Weber and Deutsch, 2010) has  
| significant consequences for our understanding of the biological carbon pump and global  
| carbon cycling (~~F~~(Galbraith and Martiny, 2015; Moreno and Martiny, 2018). ~~Traditionally,~~  
755 ~~the biological pump is thought to be controlled by a combination of the vertical nutrient~~  
~~flux and nutrient utilization efficiency (also known as elemental stoichiometry).~~  
~~Traditionally, the biological pump is thought to be controlled by a combination of the~~  
~~vertical nutrient flux and nutrient utilization efficiency (also known as (which is closely~~  
~~related to elemental stoichiometry) (S~~(Sarmiento and Toggweiler, 1984). ~~Evidence that~~  
760 ~~elemental stoichiometry is variable thus adds a new dimension to the biological pump, and~~  
~~may lead to higher than currently expected carbon export in subtropical regions. Evidence~~  
~~that However, variable Evidence of latitudinal variations in the elemental stoichiometry is~~  
~~variable of exported organic material ( $C:P_{export}$ ) thus adds a new biological dimension to the~~  
~~biological this problem the carbon pump, and may lead to higher than currently expected~~  
~~carbon export ( $C:P_{export}$ ) in subtropical regions (Emerson, 2014; Tanioka and Matsumoto,~~  
765 ~~2017; Teng et al., 2014). Global carbon export has been estimated to range between 5 and~~  
~~12 Pg C/year (B~~(Boyd and Trull, 2007; Henson et al., 2011), but these projections have yet  
| to incorporate the ~~environmental~~ controls on  $C:P_{export}$ . Variation in  $C:P_{export}$  from Redfield  
| proportions can be linked to environmental conditions. There are two leading  
770 environmental parameters thought to control  $C:P_{export}$ ; nutrients, predominantly phosphate  
| concentrations, and temperature. Galbraith and Martiny used a simple three-box model to  
| show that variable stoichiometry driven by phosphate availability could enhance the  
| efficiency of the biological pump in the low-latitude ocean (~~G~~(Galbraith and Martiny, 2015).  
| In contrast, Yvon-Durocher and co-workers (2015) used a meta-analysis of global  
| temperature and stoichiometric ratios to propose that C:P increased 2.6-fold from 0° C to  
775 30° C. Thus, it is unclear if differences in nutrient supply, temperature, or some  
| combination of them, control the global variation in C:P of plankton and exported material.

There are two important ingredients missing from published studies that could alter  
| the interactions among phytoplankton stoichiometry, carbon export, and atmospheric  $pCO_2$   
| ( $pCO_{2,atm}$ ). The first is the presence of two ~~distinct unique distinct~~ low-latitude biomes,  
780 namely the equatorial upwelling regions and the macronutrient-depleted subtropical gyres.  
| In direct observations and inverse model analyses, these two biome types appear to have  
| unique elemental compositions, which leads to relatively increased rates of export from  
| oligotrophic gyres in comparison to equatorial upwelling regions (~~D~~(DeVries and Deutsch,  
2014; Martiny et al., 2013a; Teng et al., 2014). Thus, in order to properly represent global  
785 variations in surface plankton C:P and carbon export, it is essential to separately model  
| both ~~macronutrient-limited~~ subtropical gyres and ~~iron-limited~~ equatorial upwelling zones.

The second missing ingredient is that environmental factors beyond nutrient  
| availability may impact the elemental composition of surface plankton and  $C:P_{export}$ .  
| Temperature, irradiance, and nutrient concentrations are ~~all~~ important environmental  
790 factors, which influence the physiology and stoichiometry of phytoplankton. However,  
| surveys of phytoplankton C:P are insufficient to distinguish between the separate effects of  
| each factor on C:P due to strong environmental covariance. Cellular ~~trait-trait~~-based models  
| use detailed studies of phytoplankton physiology to determine how phytoplankton cells  
| should allocate their resources as a ~~function functional~~ of environmental conditions,

795 allowing us to model the interactive influence of temperature, nutrient concentrations, and  
irradiance on C:P ratios (G(Clark et al., 2011; Daines et al., 2014; Shuter, 1979; Talmy et al.,  
2014; Toseland et al., 2013). Numerous physiological mechanisms have been proposed to  
explain variation in phytoplankton stoichiometry, including growth rate (S(Sterner and  
Elser, 2002), photoacclimation (F(Falkowski and LaRoche, 1991; Geider et al., 1996;  
800 Leonardos and Geider, 2004, 2005), nutrient-limitation responses (G(Garcia et al., 2016;  
Goldman et al., 1979; Rhee, 1978), and temperature acclimation (R(Rhee and Gotham,  
1981; Toseland et al., 2013; Yvon-Durocher et al., 2015)). Through incorporation of such  
physiological responses, a trait-based model has revealed that differences in ribosomal  
content and cell size between warm-water, oligotrophic environments and cold-water,  
805 eutrophic environments are important mechanisms driving stoichiometric variation in the  
ocean (Daines et al., 2014). Thus, linking biome-scale variations in environmental  
conditions with a detailed trait-based model of phytoplankton resource allocation and  
elemental composition may enable us to more fully explore interactions among multiple  
ocean environmental conditions, the biological pump, and pCO<sub>2,atm</sub>.

810 ~~.Through incorporation of such physiological responses, a trait-based model has  
revealed that differences in ribosomal content and cell radius size between warm-water,  
oligotrophic environments and cold-water, eutrophic environments are important  
mechanisms driving stoichiometric variation in the ocean (Daines et al., 2014). Thus,  
linking biome-scale variations in environmental conditions with a detailed trait-based  
815 model of phytoplankton resource allocation and elemental composition may enable us to  
more fully explore interactions among ocean environmental conditions, the biological  
pump, and pCO<sub>2,atm</sub>.~~

Here we create a five ocean circulation box model~~five-box model~~, incorporating the  
three major ocean biomes, to study the feedback effects of variable stoichiometry on  
820 carbon export and pCO<sub>2,atm</sub>. We will explicitly address the following research questions: (1)  
How does environmental variability influence marine phytoplankton cellular allocation  
strategies and in turn the elemental stoichiometric ic ratio? (2) What are the effects of  
changing environmental conditions on stoichiometric ratios, carbon export, and pCO<sub>2,atm</sub>?,  
and (3) What is the influence of the environmental ~~gradients~~ conditions among the three  
825 major surface biomes on carbon export and pCO<sub>2,atm</sub>?

## 2 Methods

### 2.1 Stoichiometric Models

To quantify and understand the feedbacks between carbon export and pCO<sub>2,atm</sub>, we  
830 embedded four stoichiometric models into our five ocean circulation box model~~five-box  
ocean model~~. ~~Each~~ We included four distinct stoichiometric models to calculate C:P<sub>export</sub>  
~~Each model differs~~ of which differs according to ~~its~~ their complexity and how much  
environmental information they utilize. These are a static Redfield model that assumes that  
C:P<sub>export</sub> is ~~a constant~~ across ~~function of~~ across environmental conditions, a nutrient-only  
835 model that uses surface [P] to predict C:P<sub>export</sub> (from Galbraith and Martiny, 2015), a  
temperature-only model that uses *T* to predict C:P<sub>export</sub> (modified from Yvon-Durocher et al.,  
2015, and a multi-environmental model that uses light, *T*, and [P] to predict C:P<sub>export</sub>.

### 2.1.1 Static Redfield Model

840 Our control model uses a static Redfield stoichiometry. The Redfield ratio is based on an average value of organic carbon to phosphorus of 106:1.

### 2.1.2 Nutrient-Only Model

845 The nutrient-only stoichiometric model expresses phytoplankton C:P as a function of the ambient phosphate concentration:

$$C:P = \frac{1}{\kappa[P] + [P]_0} \quad (1)$$

where the parameters  $\kappa = 6.9 \times 10^{-3} \mu\text{M}^{-1}$  and  $[P]_0 = 6.0 \times 10^{-3} \mu\text{M}$  were obtained by regressing the reciprocal of C:P onto [P] (Galbraith and Martiny, 2015).

### 2.1.3 Temperature-Only Model

850 The temperature-only stoichiometric model expresses phytoplankton C:P as a function of temperature:

$$\ln(C:P) = \Pi(T - 15^\circ\text{C}) + b, \quad (2)$$

where the parameters  $\Pi = 0.037/^\circ\text{C}$  and  $b = 5.5938$  (Yvon-Durocher et al., 2015). The temperature-only model was created to determine the temperature responses of log-transformed C:P ratios centered at 15°C.

855

### 2.1.4 Multi-Environmental Model

We created a multi-environmental model which predicts how cell size, cellular radius, biomass allocations to biosynthesis and photosynthesis, and C:P ratios vary with temperature, light levels, temperature, and phosphorus concentrations. The multi-

860 environmental factor model was derived from a non-dynamic physiological trait-based model. We used a theoretical cellular-allocation trait model based on phytoplankton physiological properties that divides the 'cell' into several functional pools

865 which including which represent cellular investments in biosynthesis, photosynthesis, and structure, and a storage pool, which represents variations in the level of P-rich molecules such as polyphosphates. The functional pools are composed of biological macromolecules such as ribosomes, proteins, include pool the cell membrane, and storage molecules.

Storage carbohydrates, and lipids, and P-containing molecules such as polyphosphates and phospholipids. The model predicts the size of each pool as a function of light,  $T$ , and  $[P]$ . The

870 connect the fitness of a hypothetical phytoplankton cell in a given environment to its cellular radius and the relative allocation of cellular material to photosynthetic proteins, ribosomes, and biosynthetic proteins. We assume that real phytoplankton populations have physiological behaviors that cluster around the strategy that produces the fastest growth rate in each environment (Norberg et al., 2001), and use the stoichiometry of this

875 optimal strategy to model the elemental composition of cellular material (Figure 1).

Phytoplankton can accumulate large reserves of nutrients that are not immediately incorporated into the functional components of the cell (Diaz et al., 2016; Mino et al., 1998; Van Mooy and Devol, 2008; Mouginit et al., 2015). This storage capability varies among phytoplankton species, and depends on the particular nutrient under consideration:

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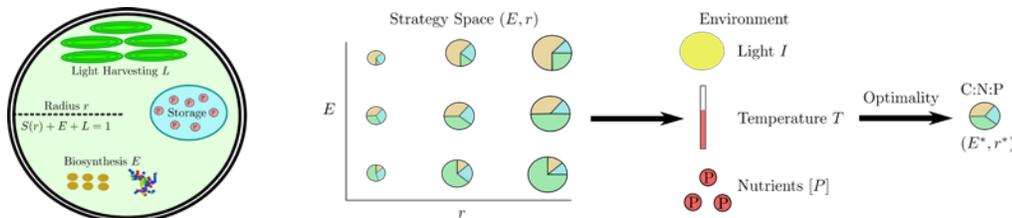
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880 the cost for storing physiologically relevant quantities of nutrients is low for nutrients with low quotas such as phosphorus, in comparison to nitrogen and carbon. Thus, the phosphorus storage is assumed highly plastic in comparison to carbon storage (Moore et al., 2013). Further, we assume that each cell dedicates a fixed fraction of its biomass to carbon reserves, and focus our modeling efforts on the variability of the stored phosphorus pool. To predict the size of the storage pool, we assume a linear relationship between stored phosphorus and ambient environmental phosphorus levels and used statistical modeling of an oceanic C:P dataset (Martiny et al., 2014) to calculate the constant of proportionality. The result is a relatively simple model that both qualitatively and quantitatively predicts the variation of C:P in plankton throughout the oceans.

890 Phytoplankton physiology is modeled through allocations of cell dry mass to three distinct pools: structure ( $S(r)$ ), biosynthesis ( $E$ ), and photosynthesis ( $L$ ). Allocations satisfy:

$$1 = S(r) + E + L, \quad (3)$$

where the variables  $S$ ,  $E$ , and  $L$  represent the *specific* allocations of cellular biomass.



895 **Figure 1:** Diagram of physiological model. Phytoplankton strategies are represented in a two-dimensional strategy space ( $E$ ,  $r$ ). Each strategy is assigned a fitness in each environment using physiological principles, and the strategy with the highest fitness is selected to represent the local population. The stoichiometry of cellular components is used to calculate the stoichiometry of the functional pools in the cell.

900 The specific allocation of biomass to the cell membrane is inversely proportional to the cell radius ( $\frac{\alpha}{r}$ ) (Clark et al., 2011), which accounts for the changing relative volume of the cell-membrane with radius. The structure pool includes the cell membrane plus wall and other components ( $\gamma$ ), which are not related to photosynthesis or biosynthesis and is given by:

$$S(r) = \frac{\alpha}{r} + \gamma. \quad (4)$$

905 In an environment specified by  $T$ ,  $[P]$ , and light level ( $I$ ), the growth rate of a cell using a given strategy is the minimum of the following growth rates:

$$\mu = \min(\mu_E, \mu_L, \mu_P). \quad (5)$$

Here  $\mu_E$  is determined by the specific rate of protein synthesis,  $\mu_L$  is determined by the specific rate of carbon fixation, and  $\mu_P$  is determined by the specific rate of phosphorus uptake, or:

$$\mu_E = k_E(T)E, \mu_L = \frac{f_P(L,I) - \Phi_M(T)}{1 + \Phi_S}, \mu_P = \frac{1}{Q_P(r,E)} \frac{V_m(r)[P]}{K_P(r) + [P]} \quad (6)$$

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We assume that part of the energy captured by a cell via photosynthesis is used for maintenance ( $\Phi_M$ ), whereas the rest is used to drive the synthesis of new macromolecules ( $\Phi_S$ ), so that a cell growing at rate  $\mu_L$  is in energy balance. The efficiency of biosynthesis  $k_E$  and the carbon cost of maintenance  $\Phi_M$  are functions of  $T$ , whose dependence is modeled using  $Q_{10} = 2.0$  (Van Bogelen and Neidhardt, 1990; Broeze et al., 1978; Shuter, 1979). Uptake is regulated by a Monod function with kinetic parameters depending on the radius through the allometric scaling relationships derived from measurements of phytoplankton populations (Edwards et al., 2012) (Edwards et al., 2012):

$$V_m(r) = a_P r^{b_P}, K_P(r) = a_K r^{b_K} \quad (7)$$

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This use of allometric scaling relationships departs from the conventions adopted by Shuter (1979) (Shuter, 1979) or Daines et al. (1979) or Daines et al. (2014) (Daines et al., 2014), who assume that uptake rates are diffusion-limited. (2014), who assume that uptake rates are diffusion limited.

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The phosphorus quota for functional elements of the cell (thus not including any storage) is determined by the allocation to biosynthesis  $E$  and the percentage  $p_{DNA}$  of cellular dry mass allocated to DNA:

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$$Q_{p,biosynthesis}(E,r) Q_p(E,r) = \frac{4}{3} \pi r^3 \rho_{cell} p_{dry} \frac{(\alpha_E E P_{rib} + p_{DNA} P_{DNA})}{31} \quad (8)$$

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Here we assume that there is no contribution to the functional-apparatus P quota from phospholipids, which instead is merged with storage molecules. This differs from Daines et al. (2014) (2014), who assume that phospholipids occupy 10% of the cell by mass. Phytoplankton can substitute sulfoquinovosdiacylglycerol (SQDG) for phospholipids in their cell membranes under low P conditions (Van Mooy et al., 2009). Similarly, P storage molecules are also regulated by P availability. Thus, we here assume that phospholipids and P-storage exhibit the same behavior and thus model-wise treated as one pool. Phytoplankton can substitute sulfoquinovosdiacylglycerol (SQDG) for phospholipids in their cell membranes in low P conditions (Van Mooy et al., 2009). The function  $f_p$  is the cellular response, implying that it is appropriate to functionally treat them together with the storage pool.

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The function  $f_p$  is the response of the cell to light levels, and is chosen to capture the effects of both electron transport and carbon fixation on photosynthesis, and is closely related to a previous model derived by Geider and Talmy (Talmy et al., 2013) (Talmy et al., 2014). This prior model included four compartments: electron transport, carbon fixation, photoprotection, and biosynthesis. Talmy and co-workers (2013) found that the photoprotection allocation was not a large or greatly changing component of their allocations. We therefore do not include this within our model due to its high complexity

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950 with little qualitative results. Our biosynthesis was also separately parametrized. We also separately parametrized biosynthesis, it because it would require complicate our model with little change in our qualitative results. Including We have therefore not included

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955 The ~~On the other hand,~~ The decomposition of photosynthesis into light harvesting and carbon fixation components is critical, and makes our model predictions agree much better with experiments studying the variations of C:P or N:P ratios with irradiance. Models that do not have this decomposition predict too large of a decrease in cellular allocations to photosynthesis at high-light levels. In a two-compartment model, increases in allocations to carbon fixation cause the overall allocation to light harvesting to have a more mild decrease. The two-compartment treatment also seems more physiologically realistic than a 1-compartment treatment, which only models photosynthetic pigments. Thus, we used the functional forms and parameters that were derived (experimentally) previously in Talmy 2013, previously for carbon fixation and light harvesting (Talmy et al., 2013).

960 Our model interprets the light harvesting allocation,  $L$ , as being composed of proteins dedicated to carbon fixation ( $F_1$ ), such as RuBisCO, and proteins dedicated to light electron transport/light harvesting ( $F_2$ ), such as photosynthetic pigments. The rate of photosynthetic carbon fixation is a function of the allocations to each of these, which satisfy  $F_1 + F_2 = L$ . The relative allocations together determine the overall photosynthetic rate:

$$P_{\max} = \min(k_1 F_1, k_2 F_2), f_p = P_{\max} \left( 1 - \exp\left(\frac{-\alpha_{\text{ph}} \phi_M F_2 I}{P_{\max}}\right) \right). \quad (9)$$

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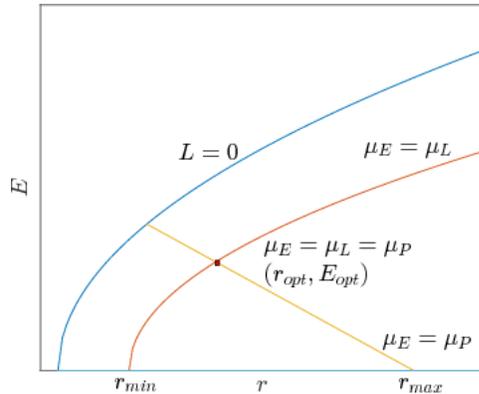
970 For a given  $I$  and  $L$ , there is a pair of values ( $F_{1,\text{opt}}, F_{2,\text{opt}}$ ) that maximize the photosynthetic rate  $f_p$ . We estimate the photosynthetic rate  $f_p(L, I)$  under the assumption that cells assume the optimal allocations to carbon fixation and electron transport. This model departs from the models developed by Shuter (1979) (1979) and Daines et al. (2014) (2014), which assume that energy acquisition is a linear function of light levels, with functional response linearly proportional to the cellular investment in light harvesting proteins.

975 We model photosynthesis as having a  $Q_{10}=1$ , which is consistent with physiological studies going back to Shuter (1979) 1979 that suggest that photosynthetic efficiency does not depend on temperature over physiologically relevant ranges. The discrepancy between photosynthetic and biosynthetic temperature dependence has traditionally been explained by referring to the differences in the chemistry and physics of the two processes. The electron transport chain relies on quantum mechanical processes, which are unaffected by variations in temperature in a physiologically relevant range (Devault, 1980). Required maintenance respiration rates are also modeled as having a  $Q_{10}=2.0$ . (Devault 1980). Required maintenance respiration rates are also modeled as having a  $Q_{10}=2.0$ .

980 We model the phytoplankton community residing in a given environment by assuming it consists solely of the phytoplankton type using the highest growth rate strategy in that environment. This strategy is found by solving for the values of  $r$  and  $E$  and  $E$  which that make

$$\mu = \mu_L = \mu_P = \mu_E \quad (10)$$

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**Figure 2: Diagram of strategy space.** The  $(r, E)$  plane is divided into a region in the first quadrant where  $L > 0$ , corresponding to the set of allowable strategies. The optimal strategy occurs at the point  $(r_{opt}, E_{opt})$ , denoted by the red rectangle, where  $\mu = \mu_L = \mu_P = \mu_E$ .

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We will now show that under two assumptions that will be true in nearly any realistic situation, a strategy maximizing  $\mu$  always exists, is unique, and satisfies  $\mu = \mu_L = \mu_P = \mu_E$  (Fig. The basic situation is depicted in figure 2).

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The function  $\mu_L$  is a function of the chosen strategy  $(r, E)$ , and it is an increasing function of  $r$  and a decreasing function of  $E$ . The first assumption is that light levels are sufficiently high that there exists some  $r_{min}$  such that  $\mu_L(r_{min}, 0) > 0$ , which means that light is sufficient for some phytoplankton to be able to overcome maintenance costs. The function  $\mu_P$  is a monotonically decreasing function of both  $r$  and  $E$ .

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Because there is a non-zero amount of  $P$  contained in the structure pool, and because uptake rates decline to zero with  $r$ , there will be some  $r_{max}$  at which  $\mu_P(r_{max}, 0) > 0$ . The second assumption is that  $r_{min} < r_{max}$ , which will be true for most realistic values of the light level. We note that for fixed  $r$ ,  $\mu_E$  is a monotonically decreasing function of  $E$ . Since none of  $\mu_E$ ,  $\mu_L$ , or  $\mu_P$  have critical points, the function  $\mu$  can only have a maximum at places where two or more of  $\mu_L$ ,  $\mu_P$ , and  $\mu_E$  are equal, or at the boundaries of the strategy space. On the boundaries of strategy space,  $E = 0$  or  $L = 0$  so that  $\mu \leq 0$ . We can exclude the

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boundary and focus on places where two or more of  $\mu_L$ ,  $\mu_P$ , and  $\mu_E$  are equal. We define two curves, one on which  $\mu_L = \mu_E$ , and the other on which  $\mu_P = \mu_E$ . The curve for which  $\mu_L = \mu_E$  begins at the point  $r = r_{min}$  and can be described by a monotonically increasing function  $E = g(r)$  on the interval  $[r_{min}, \infty]$ . This curve exists because  $\mu_E = 0$  when  $E = 0$ ,  $\mu_L > 0$  when  $E = 0$  and  $r_{min} < r$ , and  $\mu_L < 0$  when  $L = 1 - S(r) - E = 0$ , so that there is always a solution to  $\mu_L = \mu_E$  for fixed  $r > r_{min}$ . To see that the curve is an increasing function of  $r$ , consider the function  $V(E, r) = \mu_L - \mu_E$  and apply the chain rule to the equation  $V(g(r), r) = 0$  to find that along the curve  $E = g(r)$ :

$$\frac{dE}{dr} = g'(r) = \frac{-\frac{\partial V}{\partial r}}{\frac{\partial V}{\partial E}} \quad (11)$$

We consider the terms in equation 11 carefully. The function  $V$  is an increasing function of  $r$  because  $\mu_E$  is independent of  $r$  and because  $\mu_L$  is an increasing function of  $r$  (for a fixed investment in biosynthesis, a larger radius leads to a greater investment in photosynthesis and greater photosynthetic growth rate). Thus, the numerator of equation 11 is negative. The function  $V$  is a decreasing function of  $E$  because  $\mu_L$  is a decreasing function of  $E$  (greater investments in biosynthesis at fixed radius lead to smaller investments in photosynthesis) and  $\mu_E$  is an increasing function of  $E$ . Thus the denominator of equation 11 is negative, and the quotient on the right hand side is positive, so  $g'(r)$  is positive and describes an increasing curve.

By similar logic, we can define a curve  $h(r)$  that solves the equation  $\mu_P(h, r) = \mu_E(h, r)$ . This curve exists on the finite interval  $[r_l, r_{max}]$ , where  $r_l$  solves the equation  $\mu_P(1 - S(r_l), r_l) = \mu_E(1 - S(r_l), r_l)$ . Thus  $h(r)$  represents a decreasing curve from the point  $(1 - S(r_l), r_l)$  to  $(0, r_{max})$ . We can see that  $h(r)$  is always decreasing by using the chain rule on  $\mu_P(h, r) - \mu_E(h, r) = 0$ , just as in the previous argument.

The growth maximizing strategy must occur somewhere on the curves described by  $(g(r), r)$  and  $(h(r), r)$ . The functions  $\mu_1(r) = \mu(g(r), r)$  and  $\mu_2(r) = \mu(h(r), r)$  are continuously differentiable functions of  $r$  except where  $g(r) = h(r)$  (which must exist by the intermediate value theorem). Therefore the only place where  $\mu$  can have a maximum is at the place where  $g(r)$  and  $h(r)$  intersect, which is the strategy that leads to equality of all the growth rates. We refer to this strategy, as a function of environmental conditions, as

$(r_m(P, I, T), E_m(P, I, T), L_m(P, I, T))$ . Using this strategy we can predict the stoichiometry of the functional components of the phytoplankton population in a given environment.

We assume that real phytoplankton populations cluster near the optimal strategy in the local environment (Norberg et al., 2001):

$$(E_m, r_m) = \operatorname{argmax}_{(E, r)} \mu. \quad (12)$$

For all values of environmental parameters used in this study, the unique maximum of the growth rate occurs for the set of parameter values that lead to co-limitation by nutrients, photosynthesis, and biosynthesis, analogously to the predictions of Klausmeier et al. and co-workers (2004). The optimal strategy determines the model prediction of the

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C:P of functional components in a given environment by taking the quotient of the carbon and phosphorus quotas.

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**Table 1.** *Physiological Model Constants.*

PARAMETER	DESCRIPTION	VALUE	UNITS	SOURCE
$\alpha$	Proportionality coefficient for radius	0.12	-	(Toseland et al., 2013)
$\gamma$	Percent dry mass devoted to structure other than membrane	0.2	-	(Toseland et al., 2013)
$k_{E0}$	Synthesis rate of biosynthesis apparatus at $T_0=25$	0.168	hr <sup>-1</sup>	(Shuter, 1979)
$Q_{10,E}$	$Q_{10}$ of biosynthetic apparatus	2.0		(Shuter, 1979)
$\Phi_{M0}$	Specific carbon cost of maintenance at $T_0=25$	10 <sup>-3</sup>	hr <sup>-1</sup>	(Shuter, 1979)
$Q_{10,M}$	$Q_{10}$ of maintenance	2.0	-	(Shuter, 1979)
$Q_{10,P}$	$Q_{10}$ of photosynthesis	1.0		(Shuter, 1979)
$\Phi_S$	Carbon cost of synthesis	0.67	-	(Shuter, 1979)
aP	Allometric scaling constant for VMP	1.04×10 <sup>-16</sup>	(mol P)(hr) <sup>-1</sup>	(Edwards et al., 2012)
bP	Allometric scaling exponent for VMP	3.0	-	(Edwards et al., 2012)
aK	Allometric scaling constant for KP	6.4×10 <sup>-8</sup>	(mol P)(L) <sup>-1</sup>	(Edwards et al., 2012)
bK	Allometric scaling exponent for KP	1.23	-	(Edwards et al., 2012)
$\rho_{cell}$	Cell Density	10 <sup>6</sup>	g/m <sup>3</sup>	(Shuter, 1979)

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$p_{dry}$	Fraction of dry mass in cell	0.47	-	<del>FF</del> (Toseland et al., 2013)
$\alpha E$	Fraction of dry mass in biosynthetic apparatus devoted to ribosomes	0.55	-	<del>FF</del> (Toseland et al., 2013)
$P_{rib}$	Fraction of ribosomal mass in phosphorus	0.047	-	<del>SS</del> (Sterner and Elser, 2002)
$p_{DNA}$	Fraction of cell dry mass in DNA	0.01	-	<del>FF</del> (Toseland et al., 2013)
$PDNA$	Fraction of DNA mass in phosphorus	0.095	-	<del>SS</del> (Sterner and Elser, 2002)
$k_1$	Specific Efficiency of Carbon Fixation Apparatus	0.373	hr <sup>-1</sup>	<del>FF</del> (Talmy et al., 2013)
$k_2$	Specific Efficiency of Electron Transport Apparatus	0.857	hr <sup>-1</sup>	<del>FF</del> (Talmy et al., 2013)
$\alpha_{Ph}$	Light Absorption	1.97	m <sup>2</sup> /gC	<del>MM</del> (Morel and Bricaud, 1981)
$\phi_M$	Maximum Quantum Efficiency	10 <sup>-6</sup>	gC/ $\mu$ mol photons	<del>FF</del> (Falkowski and Raven, 1997)
$m_{lip}$	Fraction of cell membrane composed of lipids	0.3	-	<del>FF</del> (Toseland et al., 2013)
$m_{prot}$	Fraction of cell membrane composed of protein	0.7	-	<del>FF</del> (Toseland et al., 2013)
$p_{lip}$	Fraction of cell dry mass in storage lipids	0.1	-	<del>SS</del> (Sterner and Elser, 2002)
$p_{carb}$	Fraction of cell dry mass in storage carbohydrates	0.04	-	<del>SS</del> (Sterner and Elser, 2002)

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$C_{DNA}$	Fraction of DNA mass in Carbon	0.36	-	(S)(Stern and Elser, 2002)
$C_{rib}$	Fraction of ribosomal mass in Carbon	0.42	-	(S)(Stern and Elser, 2002)
$C_{prot}$	Fraction of protein mass in Carbon	0.53	-	(S)(Stern and Elser, 2002)
$C_{lip}$	Fraction of lipid mass in Carbon	0.76	-	(S)(Stern and Elser, 2002)
$C_{carb}$	Fraction of carbohydrate mass in Carbon	0.4	-	(S)(Stern and Elser, 2002)

The carbon quota is calculated as:

$$Q_C = \frac{\left(\frac{m_{lip}\alpha}{r} p_{lip} C_{lip} + p_{carb} C_{carb} + \alpha_E E C_{rib} + \left((1-\alpha_E)E + L + \frac{m_{prot}\alpha}{r}\right) C_{prot} + p_{DNA} C_{DNA}\right)}{\frac{4}{3}\pi r^3 \rho_{cell} P_{dry}} \quad (13+31)$$

Here we see the contributions of carbon contained in both functional and storage pools, the latter of which are assumed to occupy a fixed fraction of the cell independent of the environment (but linked to cell size).

Measurements of cellular P partitioning indicate that the ribosomal RNA can sometimes contribute only 33% of the total P quota (Garcia et al., 2016). The additional phosphorus includes membrane phospholipids and storage compounds, luxury storage compounds, and polyphosphates, each of which can be up- or down-regulated in response to phosphorus availability in the environment. To model this phenomenon, we assume the existence of an additional stored P pool, whose size is a linear function of environmental P, or:

$$(P:C)_{storage} = \epsilon[P], \quad (14+42)$$

where  $\epsilon$  is determined by the best fit to the Martiny et al. (2014) (2014) data. Our model then predicts C:P as:

$$C:P = \frac{1}{(P:C)_{(E,m,r_m)} + \epsilon[P]} \quad (15+53)$$

The model parameter  $\epsilon$  is calculated by minimizing the residuals of the P:C ratio predicted by Eq.13 in comparison to the global data-set on particulate organic matter stoichiometry compiled by Martiny and others (2014). To maintain consistency with the linear

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1085 regression model of Galbraith and Martiny (2015). we restrict the dataset to observations from the upper 30 meters of the water column containing particulate organic phosphorus and carbon concentrations of greater than  $0.005 \text{ nM}$   $5 \mu\text{M}$ . Observations from the same station and the same day, but at different depths in the water column are averaged together. The P:C ratio of the functional apparatus is calculated using irradiance,  $T$ , and  $[P]$  data from the World Ocean Atlas (Garcia et al., 2014; Locarnini et al., 2013; oceancolor.gsfc.nasa.gov/data/10.5067/AQUA/MODIS/L3B/PAR/2014/), which are used to estimate environmental conditions at the location and date of particulate organic matter measurements. Light levels are computed by averaging irradiance over the top 50 meters of the water column, assuming an e-folding depth of 20 meters. Linear regression determines  $\epsilon = 2500 \text{ M}^{-1}$  which fits the data with an  $R^2 = 0.28$ . All parameters for the model are listed in Table 1.

## 2.2 Box Model Design

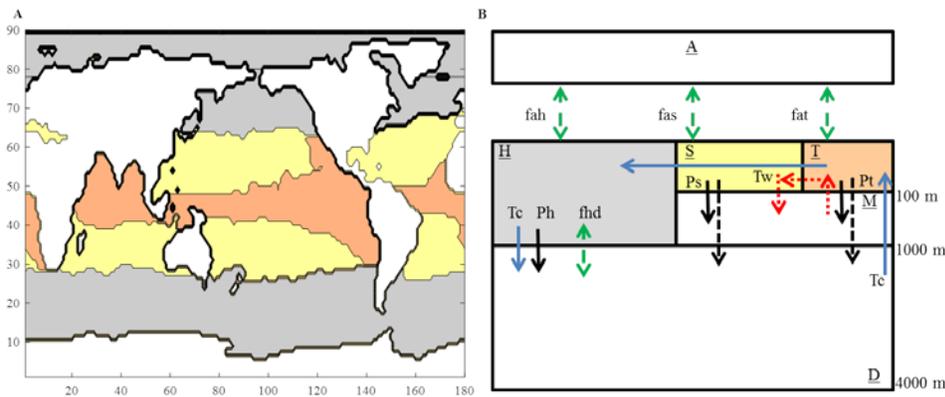
1100 To quantify the feedbacks between phytoplankton stoichiometry, carbon export, and  $\text{pCO}_{2,\text{atm}}$ , we formulated a five-box ocean circulation ~~box~~ model of the phosphorus and carbon cycles in the ocean coupled to an ~~and~~ atmospheric ~~boxe~~. The foundation of our model is based on the models introduced in Ito and Follows (2003) and DeVries and Primeau (2009). Phosphorus is used to represent the role of nutrient availability in controlling stoichiometry and C export. We chose this over N to avoid having to include a parameter rich N cycle. Furthermore, P rather than N is commonly regarded as the ultimate limiting nutrient (2015). ~~we restrict the dataset to observations from the upper 30 meters of the water column containing particulate organic phosphorus and carbon concentrations of greater than  $0.005 \mu\text{M}$ . Observations from the same station and the same day, but at different depths in the water column are averaged together. The P:C ratio of the functional apparatus is calculated using  $T$ ,  $[P]$ , and irradiance data from the World Ocean Atlas (Garcia et al., 2014; Locarnini et al., 2013; oceancolor.gsfc.nasa.gov/data/10.5067/AQUA/MODIS/L3B/PAR/2014/), which are used to estimate environmental conditions at the location and date of particulate organic matter measurements. Light levels are computed by averaging irradiance over the top 50 meters of the water column, assuming an e-folding depth of 20 meters. Linear regression determines  $\epsilon = 2500 \text{ M}^{-1}$  which fits the data with an  $R^2 = 0.28$ . All parameters for the model are listed in Table 1.~~

## 2.2 Box Model Design

1120  ~~$\text{pCO}_{2,\text{atm}}$~~ , we formulated a ~~five ocean circulation box model~~ five-box model of the phosphorus and carbon cycles in the ocean and atmosphere. The foundation of our model is based on the models introduced in Ito and Follows (2003) and DeVries and Primeau (2009). ~~Phosphorus is used to represent the role of nutrient availability in controlling stoichiometry and C export. We chose this over N to avoid having to include a parameter rich N cycle. Furthermore, P rather than N is commonly regarded as the ultimate limiting nutrient~~ (Tyrrell, 1999) and thus P availability represents the long-term steady-state biogeochemical equilibrium. The model includes three surface boxes, each corresponding to one of the major biomes: the tropical equatorial upwelling regions (labeled  $\mathbb{T}$ ), the subtropical gyres (labeled  $\mathbb{S}$ ), and the high-latitude regions (labeled  $\mathbb{H}$ ) (Figure 3). We

1130 define the oligotrophic subtropical gyre regions where the mean annual phosphate concentration is less than  $0.3 \mu\text{M}$  (Teng et al., 2014), with the remainder of the surface ocean assigned either to box T or box H based on latitude. We use these assignments to calculate the baseline physical properties of each region, including mean annual averaged irradiance and temperature. The subsurface ocean is divided into two regions: the

1135 thermocline waters that underlies the subtropical gyres and the equatorial upwelling regions (labeled M), and deep waters (labeled D) (DeVries and Primeau, 2009).



**Figure 3: Box Model Design.** A) Sea surface breakdown by region. All peach-colored regions represent the tropical surface ocean box, the cream-colored regions represent the subtropical surface ocean box, and grey regions represent the high-latitude surface ocean box. B) The model includes tropical (T), subtropical (S), and high-latitude (H) surface ocean boxes, a mixed thermocline (M) box, and a deep water (D) box. The thermohaline circulation  $T_c$  is set to 20 Sv, while the wind driven shallow overturning circulation is set to 5 Sv. The high-latitude mixing flux  $f_{hd}$  is set to 45.6 Sv. The thickness of Box H is 1000 m, and Box M is 900 m. Box T has a temperature of  $26^\circ\text{C}$ , box S has a temperature of  $24^\circ\text{C}$ , and box H has a temperature of  $7^\circ\text{C}$ . Box S covers 39% and Box T covers 25% of the ocean surface area.

To simulate the global transport of water between boxes, our model includes a thermohaline circulation (labeled  $T_c$ ) that upwells water from the deep ocean into the tropics, laterally transports water into the subtropics and high-latitudes, and downwells water from the high-latitude region to the deep ocean. Surface winds produce a shallow overturning circulation (labeled  $T_w$ ), that transports water from the thermocline to the tropics and then laterally into the subtropics. These circulations create teleconnections of nutrient supply in the surface ocean boxes. A bidirectional mixing term that ventilates the deep box directly through the high-latitude surface box (labeled  $f_{hd}$ ) represents deep water formation in the Northern Atlantic region and around Antarctica (Sarmiento and Toggweiler, 1984). The parameters  $T_c$ ,  $T_w$  and  $f_{hd}$  are considered adjustable parameters, which we calibrate using phosphate data from WOA13 (Garcia et al., 2014). In order to simulate the movement of particles, we included export fluxes ( $P_t$ ,  $P_s$ , and  $P_h$ ) of organic phosphorus out of each surface box.

Our box model simulates [P], alkalinity and various forms of C; total carbon in the surface boxes is partitioned into carbonate, bicarbonate, and  $\text{pCO}_2$ . The global mean [P] is prescribed according to the observed mean ocean value (Garcia et al., 2014). The export

of carbon is linked to phosphorus export using the  $C:P_{export}$  ratio. ~~To quantify the breakdown of carbon into these components, we model the solubility pump, using temperature and salinity to determine the partitioning of inorganic carbon among total carbon within a box. The global mean alkalinity is prescribed according to the observed mean ocean values but is also subject to transport (Sarmiento and Toggweiler, 1984). Our box model simulates various forms of C similar to alkalinity and total inorganic carbon, which are conserved tracers from which the speciation of inorganic carbon in sea-water can be calculated. Biome specific salinity and temperature are used to prescribe the solubility constants of  $CO_2$  in seawater and the bromine concentration, which is taken to be proportional to salinity. We use these calculations to determine the  $pCO_2$  value at standard pressure (1 atm) within each box. Box specific total carbon is calculated from the  $pCO_2$  value, bicarbonate, carbonate and alkalinity concentrations.  $CO_2$  cycles through the atmosphere via the air-sea gas exchange fluxes (fah, fas, fat). We used a uniform piston velocity of  $5.5 \times 10^{-5} m s^{-1}$  to drive air-sea gas exchange (DeVries and Primeau, 2009; Follows et al., 2002).~~ To quantify the breakdown of carbon into these components, we model the solubility pump, using temperature and salinity to determine the partitioning of inorganic carbon.  $CO_2$  cycles through the atmosphere via the air-sea gas exchange fluxes (fah, fas, fat). We used a uniform piston velocity of  $5.5 \times 10^{-5} m s^{-1}$  to drive air-sea gas exchange (DeVries and Primeau, 2009; Follows et al., 2002). Iron limitation is implicitly simulated through its control on the tropical [P], which is used as a control variable in our experimental runs.

We calibrated our model parameters (Tc, Tw, fhd) so that the macronutrients were at similar average values compared to World Ocean Atlas 2013 dataset for each location. We tested the sensitivity of modeled  $pCO_{2,atm}$  to the fluxes Tc, Tw, and fhd and found that with Tc = 20 Sv and Tw = 5 Sv (values that allowed the model to match [P] and alkalinity), the  $pCO_{2,atm}$  was sensitive to the value of fhd (Sarmiento and Toggweiler, 1984). Guided by values previously used in the literature we set fhd to 45.6 Sv (Table 2) but we also present results for the nutrient-only stoichiometry model at two extreme values of fhd, 18 and 108 Sv (Figure 4). The functional dependence of  $pCO_{2,atm}$  with changing subtropical and tropical [P] for each extreme value of fhd was quite similar, though the value of  $pCO_{2,atm}$  for the high fhd simulation was approximately twice that of the low fhd simulation (Figure 4). We found that our value of 45.6 Sv provides a modern  $pCO_{2,atm}$  value. Although the focus of this study is to determine the impact of low latitude biogeochemistry on  $pCO_{2,atm}$ , we point out that at Redfield stoichiometry,  $pCO_{2,atm}$  increases by 100 ppm when fhd is increased to 108 Sv from its default value 45.6 Sv.

For certain values of the parameters, the model produced excessive nutrient trapping in the thermocline. In order to dampen the nutrient trapping, we tuned the remineralization depth. Assuming that 25% of the total export is respired in the thermocline with the remaining 75% exported into the deep ocean, produced a better match between the modeled and observed [P] in the thermocline box. Total export is made from both the stoichiometry of sinking particulate and of primary producers, based on Teng et al. (2014) this is a reasonable first order assumption. For certain values of the parameters, the model produced excessive nutrient trapping in the thermocline. In order to dampen the nutrient trapping, we tuned the remineralization depth. Assuming that 25% of the total export is respired in the thermocline with the remaining 75% exported into the

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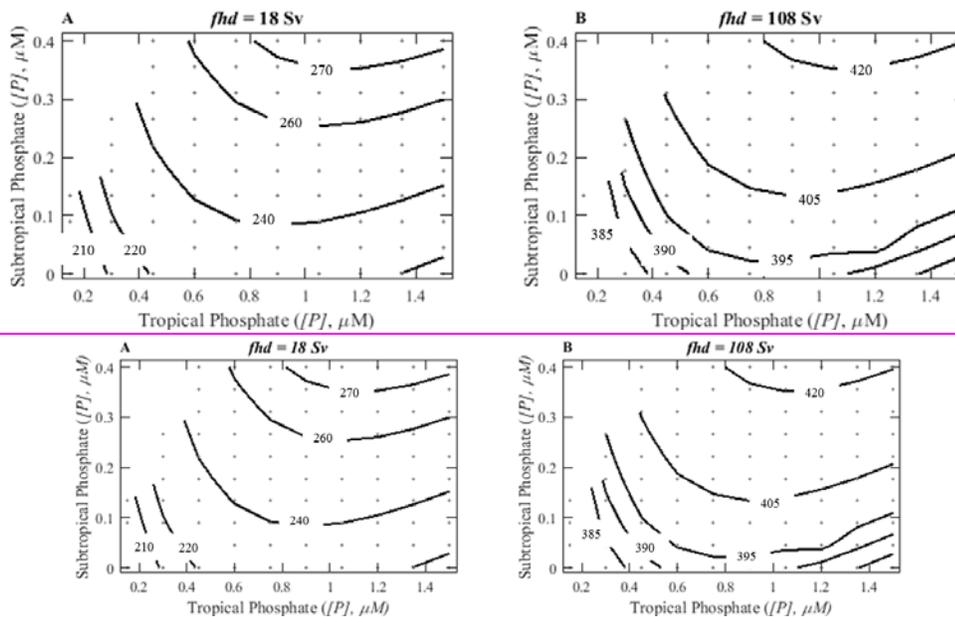
1210 deep ocean, produced a better match between the modeled and observed [P] in the thermocline box.

**Table 2: High-latitude deep water exchange range**

RANGE OF FHD [SV]	SOURCE REFERENCE SOURCE
38.1	(Sarmiento and Toggweiler, 1984)
3-300	(Toggweiler, 1999)
60	(DeVries and Primeau, 2009)
30-130	(Galbraith and Martiny, 2015)
18-108 (default value 45.6)	<a href="#">This Study</a>

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**Figure 4:  $pCO_{2,atm}$  (ppm) sensitivity to extreme  $fhd$  values under changing surface phosphate concentrations.** A.) Range of  $pCO_{2,atm}$  (ppm) using an  $fhd$  value of 18 Sv. B.) Range of  $pCO_{2,atm}$  (ppm) using an  $fhd$  value of 108 Sv.

### 2.2.1 Experimental Design

To address how changing environmental conditions affected stoichiometric ratios, carbon export, and  $pCO_{2,atm}$  we performed two tests; a change in nutrients and a change in sea

1225 surface temperature. These tests allowed us to observe how the relationships between environmental conditions, carbon export and  $p\text{CO}_{2,\text{atm}}$  depend on the mechanisms responsible for stoichiometric variation in the ocean. In order to account for the effects of particulate inorganic carbon (PIC) export, we multiply model predicted  $\text{C}:\text{P}_{\text{export}}$  by 1.2, consistent with previous studies (Broecker, 1982; Sarmiento and Toggweiler, 1984).

1230 The first set of numerical experiments examined the sensitivity of  $p\text{CO}_{2,\text{atm}}$  to nutrient availability in the tropical and subtropical boxes for each of the three stoichiometric models. This set of experimental runs was intended to capture the effects of changing levels of iron deposition, which could lead to shifts in phosphorus drawdown by relieving iron limitation of diazotrophic phytoplankton in subtropical gyres and of bulk phytoplankton populations in equatorial upwelling regions. We varied tropical [P] from 0.15 to 1.5  $\mu\text{M}$  and subtropical [P] from  $1 \times 10^{-3}$  to 0.5  $\mu\text{M}$  by adjusting the implied biological export and determined the equilibrium  $p\text{CO}_{2,\text{atm}}$  values.

The second set of experimental tests was done to quantify how temperature modifies carbon export and  $p\text{CO}_{2,\text{atm}}$  for each stoichiometric model. Temperature influences 1240 carbon cycling in two ways within our model: through the solubility of inorganic carbon in seawater and through changes in phytoplankton stoichiometry within the temperature-only and multi-environmental models. Due to the well-known effects of temperature on  $\text{CO}_2$  solubility, it is generally predicted that there is to be a positive feedback between  $p\text{CO}_{2,\text{atm}}$  and temperature mediated by declining  $\text{CO}_2$  solubility at high temperatures. To 1245 study the relative strengths of the temperature solubility feedback and the temperature regulation of C:P feedback, we performed a numerical experiment in which we varied the sea surface temperature by five degrees in either direction of modern sea surface temperature. This represents a plausible range of variation under both ice-age and anthropogenic climate change scenarios. We varied tropical temperature from 21° to 31°C 1250 and subtropical temperature from 19° to 29°C, determining equilibrium  $p\text{CO}_{2,\text{atm}}$  values for combinations of temperature conditions.

### 3 Results

To quantify the linkages between phytoplankton physiology, elemental stoichiometry, and 1255 ocean carbon cycling, we divide our results into two parts. The first is a direct study of the stoichiometric models, comparing their predictions about the relationship between stoichiometry and environmental conditions, and in the case of the trait-based model, illustrating how cellular physiology is predicted to vary across these conditions. In the second part, we show how variable variables stoichiometry influences carbon export and 1260  $p\text{CO}_{2,\text{atm}}$ , under changing phosphorus concentrations and temperature. Within these results, we distinguish the influence or lack thereof of the three distinct biomes, biomes; in particular the iron-stressed equatorial upwelling regions and the macronutrient depleted subtropical gyres.

#### 1265 3.1 Multi-environmental and physiological controls on plankton stoichiometry

Our multi-environmental model captured several major mechanisms hypothesized to be environmental drivers of C:P ratios including a temperature dependence of many cellular processes, a link between growth rate and ribosome abundance, and storage drawdown during nutrient limitation. The predicted relationship between environmental conditions 1270 and C:P can be understood through the environmental regulation of three factors: (i) the

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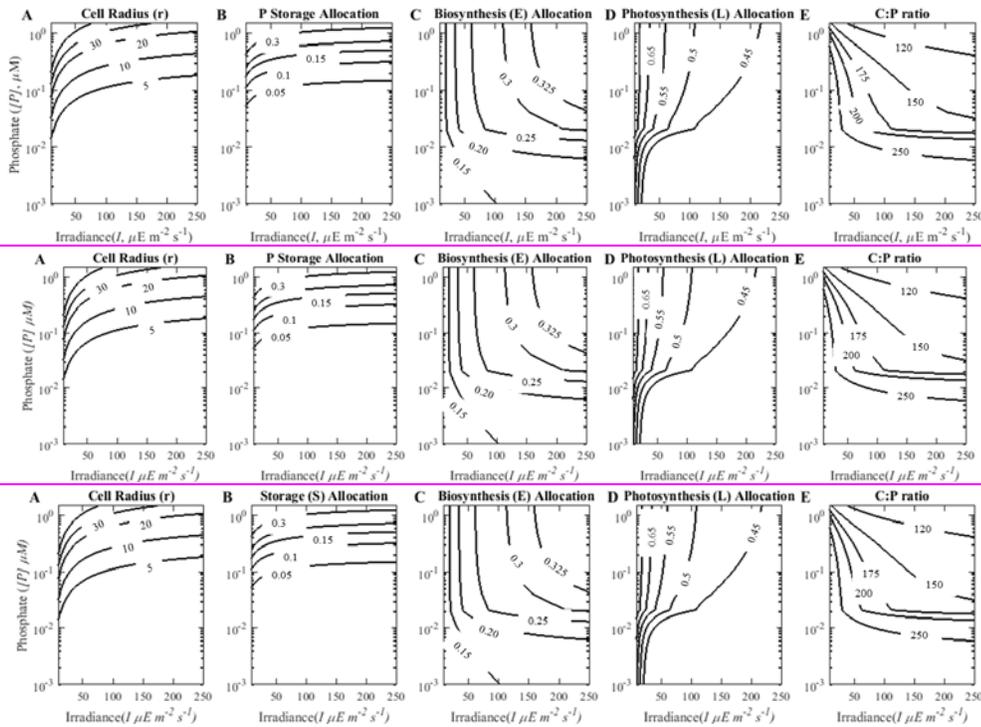
balance between photosynthetic proteins and ribosomes, (ii) the cell radius and associated allocation to structural material, and (iii) the degree of phosphorus storage. Our model predicted that for an optimal strategy, specific protein synthesis rates will match specific rates of carbon fixation. Thus, the ratio of photosynthetic machinery to biosynthetic machinery is ~~therefore~~ primarily controlled by irradiance and temperature. Increases in light levels lead to higher photosynthetic efficiency, higher ribosome content, smaller cells (due to a lower requirement for photosynthetic machinery), and lower C:P ratios (Figure 5). The response of C:P to light levels predicted by our model was muted in comparison to other subcellular compartment models because we separately modeled electron transport and carbon fixation (Talmy et al., 2013), and our predictions were consistent with the weak relationship between irradiance and C:P (Thrane et al., 2016) (Thrane et al., 2016) (Figure 5A).

Increases in temperature increase the efficiency of biosynthesis, but not photosynthesis ( $Q_{10} = 1$ ). Therefore elevated temperature lead to a reduced ribosome content relative to photosynthetic proteins and higher C:P ratios (Figure 6A). There leads to a non-monotonic, concave relationship between temperature and cell size, which is due to a subtle interaction between biosynthesis efficiency (which varies greatly with temperature), maintenance costs, and size dependent uptake rates.

Nutrient concentrations do not affect the ratio of biosynthetic to photosynthetic machinery but positively relate to both P storage and cell radius. Cell radius directly influences the specific rate of nutrient uptake, and indirectly biosynthesis and photosynthesis as the cell membrane and wall affects the space available for other investments. ~~The cell radius will vary with differences in phosphorus concentration, temperature and light levels. - small radius~~ This effect becomes pronounced at This effect is pronounced in oligotrophic conditions ([P] < 100nM), cell radius declines substantially below 1  $\mu$ m, decreasing the allocations to both photosynthesis and biosynthesis and driving up C:P ratios. Much larger values of the cell radius are observed at high nutrient concentrations.

P concentrations also influenced C:P through their direct control of P storage. We plotted the relative contribution of the storage compartment and the functional compartment to the P quota, as a function of environmental conditions. The impact of the residual pool on the overall size of the P pool is heavily dependent on environmental conditions, varying from a minimum of close to 0% to a maximum of just under 50%, for the combinations of parameter values used in all of our numerical experiments. In the vast majority of the parameter range considered here, the contribution of the residual pool is much more modest, 10-20%. High values occur when phosphorus is available and the temperature is high. In these conditions, ribosomal contributions are decreased, but the residual contribution is high. In cold water, high P ecosystems, the residual contribution is approximately 25%, and in oligotrophic ecosystems it is close to 0. Thus, C:P was predicted to be a decreasing function of [P] with two distinct regimes: a moderate sensitivity regime for [P] above 100nM, and a high sensitivity regime for [P] below 100nM.

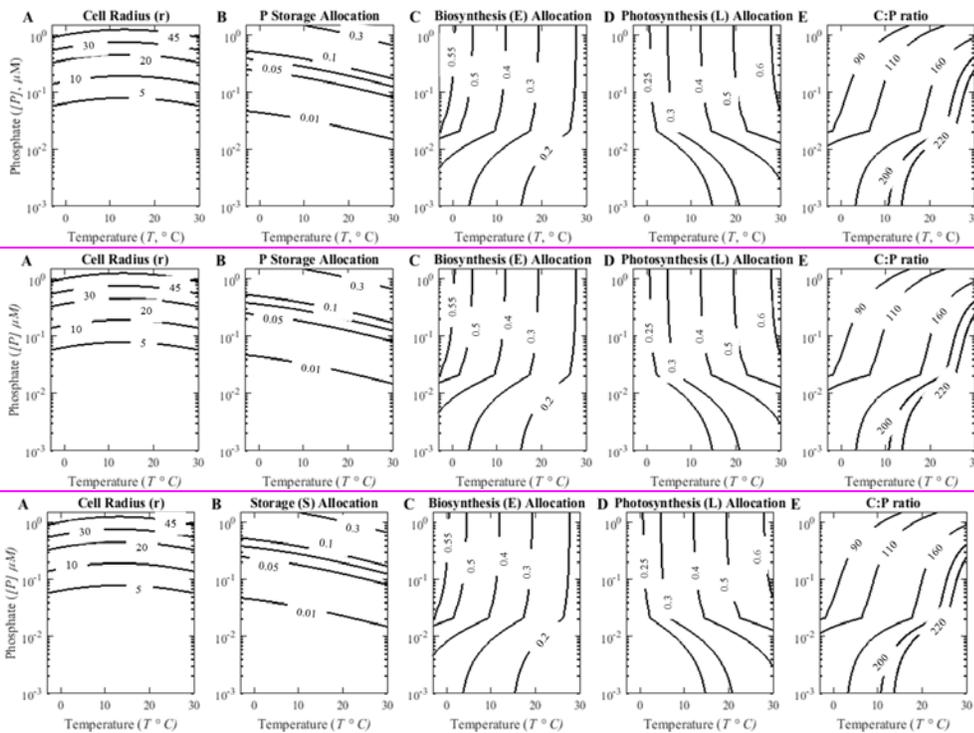
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**Figure 5: Influence of phosphate concentration and irradiance on cellular stoichiometry and cellular traits, at a constant  $T = 25\text{ }^{\circ}\text{C}$ .** A) Cell radius ( $r$ ). B) P storage allocation. C) Biosynthesis allocation. D) Photosynthesis (L) allocation. E) The C:P ratio. As irradiance increases, there is a tendency towards greater allocation to biosynthesis and lesser allocation to photosynthesis, which leads to lower C:P ratios. When phosphorus is very low, there is a large decrease in both biosynthesis and photosynthesis allocations due to the large relative allocation to the cell membrane. C:P ratios are inversely proportional to phosphorus concentration, driven by an increase in luxury storage and ribosomal content as P increases.

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**Figure 6: Influence of phosphate concentration and temperature on cellular stoichiometry and cellular traits, at a constant irradiance  $I = 50 \mu E m^{-2} s^{-1}$ .** A) Cell radius ( $r$ ). B) ~~P storage~~ Storage ( $S$ ) allocation. C) Biosynthesis allocation. D) Photosynthesis ( $L$ ) allocation. E) The C:P ratio. Consistent with the translation compensation hypothesis, increases in  $T$  led to a reduction in the allocation to biosynthesis and an increase in C:P.

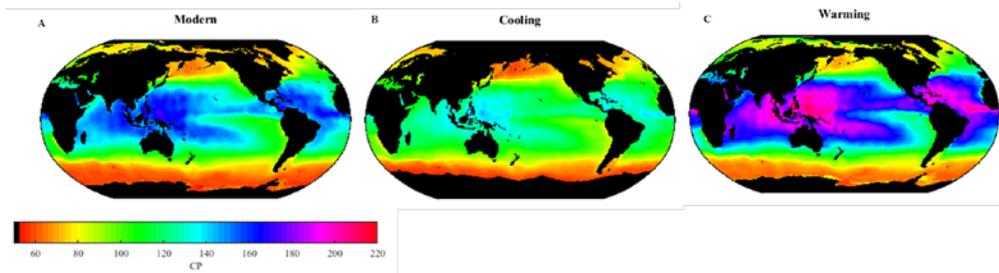
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We next used the outcome of the trait model as a multi-environmental model to predict C:P ratios in the modern ocean based on annual mean light,  $T$ , and  $[P]$ . Our predictions reproduced the global pattern (M(Martiny et al., 2014) with C:P ratios above the Redfield ratio in subtropical gyres and C:P ratios below the Redfield ratio in equatorial and coastal upwelling regions and subpolar gyres (Figure 7A). Additionally, our model also reproduced basin-scale stoichiometric gradients among similar biomes in each ocean, predicting the highest C:P ratios in the western Mediterranean Sea and the western North Atlantic Subtropical Gyre, and somewhat elevated C:P ratios in the South Atlantic Subtropical Gyre as well as the North and South Pacific Subtropical Gyres.

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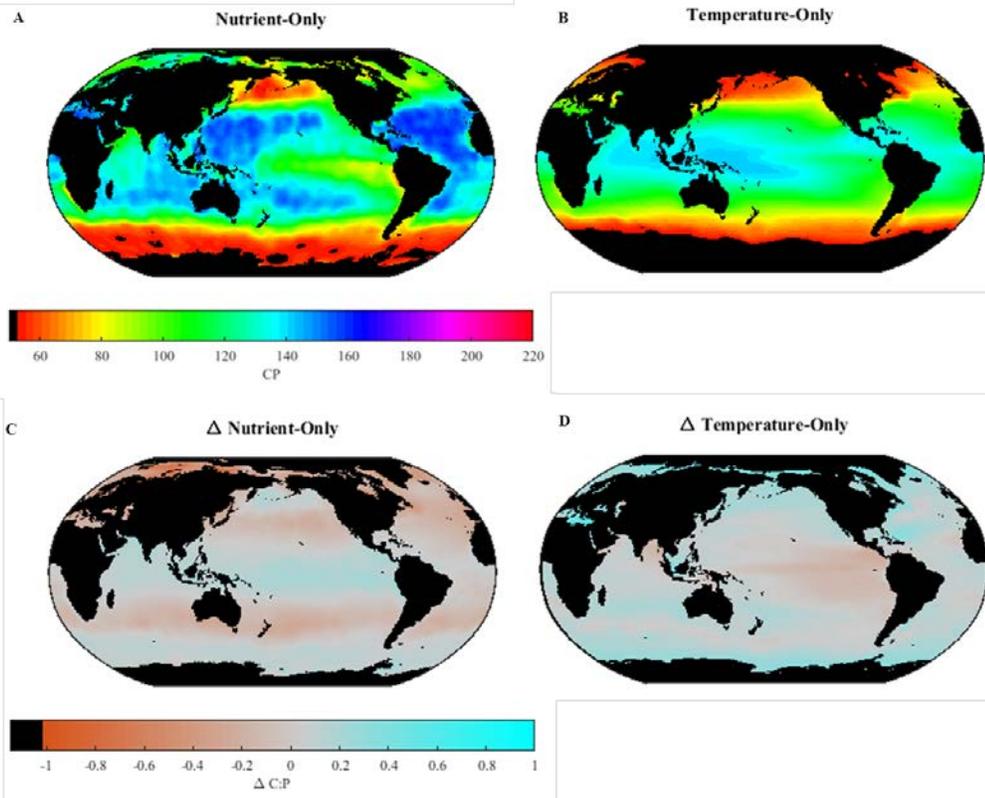
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**Figure 7: Predicted C:P ratios in the global ocean in differing climatic regimes.** A) C:P ratio under modern ocean conditions. Large differences in C:P are predicted between distinct types of ocean biome, with low C:P in equatorial upwelling regions and subpolar gyres, and high C:P in subtropical gyres. Regional differences between biomes of similar type are observed as well, with the low phosphorus Atlantic having a higher C:P than the Pacific. B.) C:P ratio under cooling temperature conditions (-5°C from the modern ocean). C) C:P ratio under warming temperature conditions (+5°C from the modern ocean). Each 5 degree change leads to a shift of 15% in the mean C:P ratio of organic matter.

To study the potential impact of sea surface temperature on phytoplankton resource allocation and stoichiometry, we used our multi-environmental model to predict C:P in ocean conditions both five degrees colder (Cooling environments) and warmer (Warming environments) than the modern ocean. According to our model, a five-degree increase (or decrease) in sea surface temperature would cause a 15% rise (or fall) in C:P ratios (Figure 7). This sensitivity suggested that the relative effect of  $T$  on biochemical processes could have large implications for biogeochemical cycles, making it important to determine the relative importance of physiological mechanisms regulating C:P ratios.

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**Figure 8: Comparison of C:P between the multi-environmental model and the nutrient-only model and temperature-only model.** The upper panels show predicted C:P for the global ocean under the nutrient-only (A) and temperature-only (B) models, and the lower panels show the normalized difference, i. e.  $\frac{C:P_{\text{subcell}} - C:P_{\text{other}}}{C:P_{\text{subcell}}}$ , between the C:P in the subcellular model (C, D).

We compared the multi-environmental model to the predictions made by two other models: the nutrient-only model used by the Galbraith and Martiny model (2015), (2015), and our temperature-only model modified from Yvon-Durocher and co-workers (2015), (2015). These two models also successfully predicted the qualitative pattern of stoichiometric variation in the ocean, but were unable to replicate the full range of variation observed in the data (Figure 8). In particular, they misrepresented the North Atlantic Subtropical Gyre and the Southern Ocean, where the C:P ratio is at the extreme (Figure 8A, B). The nutrient-only model had a tendency to predict lower C:P ratios than the multi-environmental model in warm tropical and subtropical waters, and predict higher C:P ratios in cold waters (Figure 8A). This difference is driven by the temperature sensitivity of biosynthesis in the multi-environmental model, leading to increasing C:P in all warm water regions and decreasing C:P in cold water regions (Figure 8C). The multi-environmental model predicted a wider range of C:P in the ocean. The temperature-only model overall had

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higher C:P ratios globally compared with the multi-environmental model (Figure 8B) but suggested lower C:P in the gyres and higher C:P in high latitudes, especially in the Southern Ocean (Figure 8D).

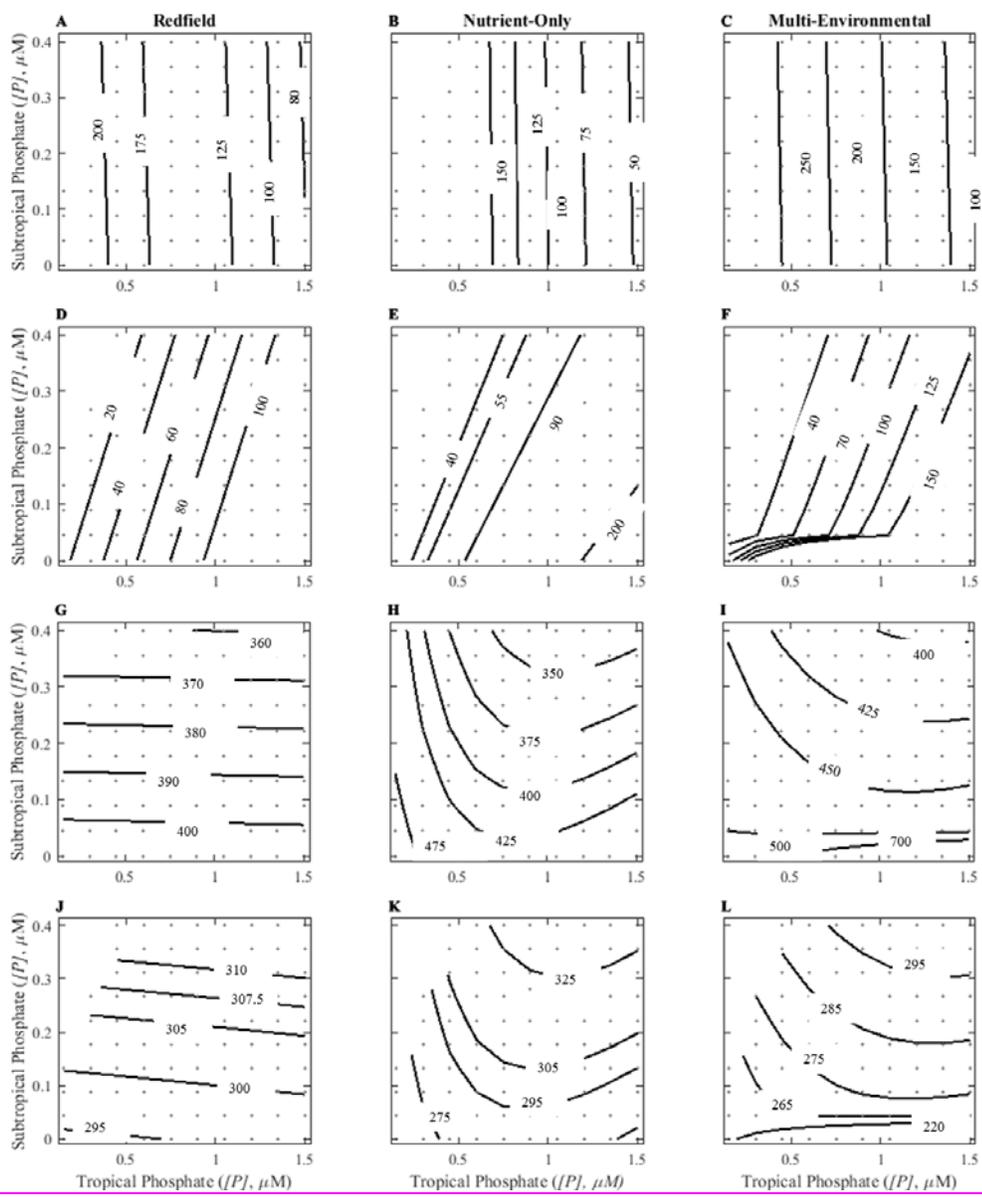
### 1385 **3.2 Impact of nutrient availability on carbon export and atmospheric pCO<sub>2</sub>**

1390 We next quantified the impact of nutrient availability in the tropics and subtropics on stoichiometry, carbon export and pCO<sub>2,atm</sub> (Figure 9A-L). Using a constant Redfield model (or the temperature-only model), we replicated the previously observed approximately linear relationship between surface [P] and pCO<sub>2,atm</sub> (equivalent to how pre-formed [P] will influence pCO<sub>2,atm</sub>) (Ito and Follows, 2003; Sigman and Boyle, 2000). We found that [P] drawdown in the subtropical box had a greater impact on carbon export, since export from the high-latitude box was not enhanced by the [P] supply from the subtropical box (Figure 9A, D, G). In the Redfield model, pCO<sub>2,atm</sub> appeared to be much more sensitive to subtropical [P] than tropical [P], which was partially due to enhanced carbon export in the subtropical box and partially due to the larger surface area of the subtropical box (implying a greater potential for CO<sub>2</sub> exchange) (Figure 9J).

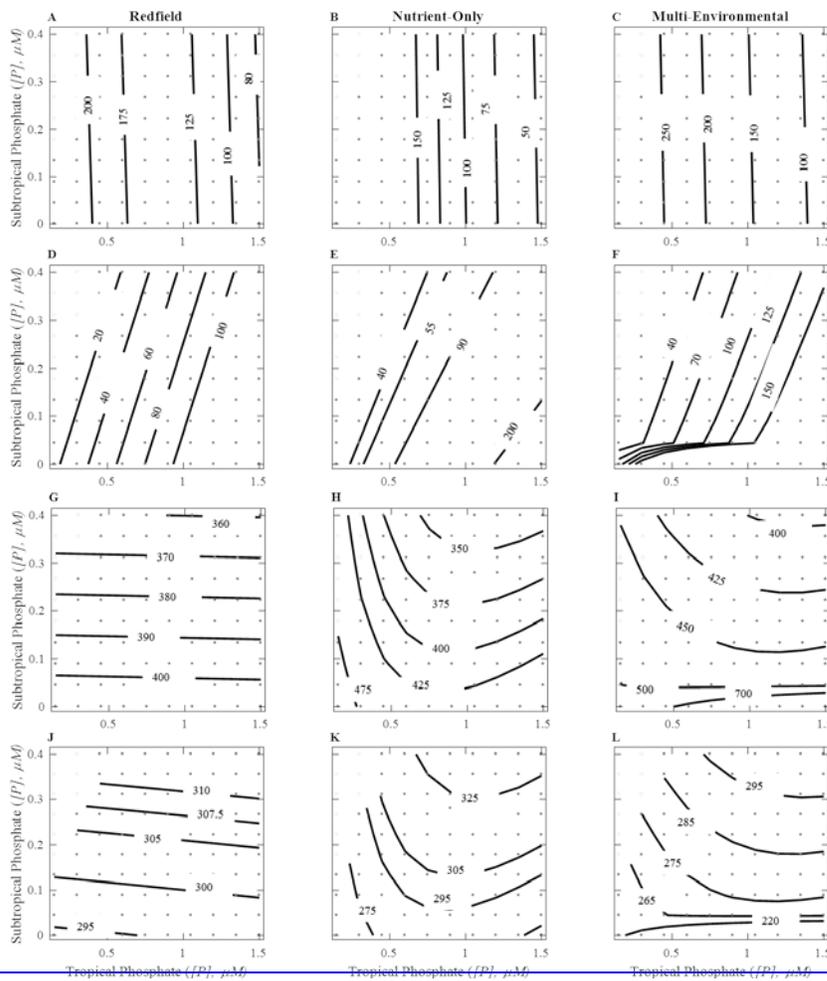
1400 In contrast to the predictions made using Redfield stoichiometry, when we used the nutrient-only model for phytoplankton stoichiometry, we observed a non-linear relationship between surface [P] and pCO<sub>2,atm</sub> (Figure 9B, E, H, K). At fixed tropical [P], there was a strong relationship between subtropical [P], export, and pCO<sub>2,atm</sub> in accordance with the findings of Galbraith and Martiny (2015) (Figure 9B, E, H). The total decline in pCO<sub>2,atm</sub> as subtropical [P] declined from 0.4 μM to 1 × 10<sup>-3</sup> μM could be more than 60 ppm, which was more than twice the decline that occurred in the fixed stoichiometry experiment (Figure 9K). We found a non-linear monotonic relationship between tropical [P] and pCO<sub>2,atm</sub>: when tropical [P] was high, declines in tropical [P] led to lower carbon export and increased pCO<sub>2,atm</sub>. However, this trend reversed when tropical [P] was lower (Figure 9K). The counter intuitive decline in pCO<sub>2,atm</sub> with higher export from tropics was driven by a teleconnection in nutrient delivery between the subtropical and tropical boxes. Increases in export in the tropical box due to increased [P] drawdown decreased the supply of [P] to the subtropics, which led to a decrease in the more efficient (higher C:P) subtropical export. Thus, the nutrient-only model predicted a greater decrease in subtropical export than the counter increase in tropical export.

1410 The multi-environmental model also predicted a non-linear relationship between surface P, carbon export, and pCO<sub>2,atm</sub>. However, the pattern was somewhat distinct from that of the nutrient-only model results (Figure 9C, F, I, L). First, subtropical [P] drawdown had a nonlinear relationship with pCO<sub>2,atm</sub>: when subtropical [P] was high, declines in subtropical [P] led to slight declines in pCO<sub>2,atm</sub>, and when subtropical [P] is low, small declines in tropical [P] lead to large declines in pCO<sub>2,atm</sub>. This intensification of the relationship between subtropical [P] and pCO<sub>2,atm</sub> was due to the nonlinear relationship between [P] and C:P predicted by the trait-based model (Figure 9I). The multi-environmental model predicted extremely high export, but only when [P] was lower than 0.05 μM (Figure 9C, F, I). Second, the effect of tropical [P] levels on pCO<sub>2,atm</sub> was strongly modulated by subtropical [P], reversing from a negative to a positive relationship as subtropical [P] declines (Figure 9I, L). The difference between the nutrient-only model and the multi-environmental model arose because the multi-environmental model incorporated a temperature impact on resource allocation and elemental ratios. Although

we were not varying temperature in these experiments, we did represent regional temperatures differences between the different boxes. The result is that a large stoichiometric contrast between the tropical and sub-tropical regions only arose when there was a large difference in nutrient levels between the two regions (Fig. 9L). However, both the nutrient-only model and the multi-environmental model predicted that carbon export and  $p\text{CO}_{2,\text{atm}}$  were sensitive to the interaction between regional nutrient availability and  $\text{C}:\text{P}_{\text{export}}$ .



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1435 **Figure 9: Carbon export ( $Tmol\ C\ yr^{-1}$ ) and  $pCO_{2,atm}$  (ppm) in changing surface phosphate concentrations.** Columns correspond to type of stoichiometry; Redfield (Left), nutrient-only (Middle), and multi-environmental model (Right). Rows correspond to either tropical carbon export (A through C), subtropical carbon export (D through F), total carbon export (G through I) or atmospheric  $pCO_2$  (J through L). The grey points represent  
1440 where  $pCO_{2,atm}$  was calculated, between spaces are interpolated.

### 3.3 Interactive effect of temperature on stoichiometry, carbon export and atmospheric $pCO_2$

1445 We next quantified the impact of sea surface temperature (SST) in the tropics and subtropics on  $C:P_{export}$ , carbon export, and  $pCO_{2,atm}$  (Figure 10A-D). The Redfield model predicts that increases in SST lead to a decline in the solubility of  $CO_2$  in seawater and consequently an increase in  $pCO_{2,atm}$  from 288 to 300 ppm ( $\Delta pCO_{2,atm} = 12$ ) (Figure 10A). This feedback was present with the same strength in the nutrient-only model (with

no  $T$  dependence on C:P), in which  $p\text{CO}_{2,\text{atm}}$  ranged from 268 to 280 ppm ( $\Delta p\text{CO}_{2,\text{atm}} = 12$ ) (Figure 10B).

In contrast to the Redfield and nutrient-only models, the temperature-only model predicted a negative linear relationship between  $p\text{CO}_{2,\text{atm}}$  and tropical sea surface  $T$  and a positive linear relationship between  $p\text{CO}_{2,\text{atm}}$  and subtropical sea surface  $T$  (Figure 10C). The decline in  $p\text{CO}_{2,\text{atm}}$  with tropical  $\text{SST}$  sea surface  $T$  was driven by an enhancement of export due to increased C:P at higher temperatures  $T$ s (Figure 11). At  $5^\circ\text{C}$  below modern ocean temperature  $T$ , the model predicted C:P in the tropics was 131 and subtropical was 121, resulting in a  $p\text{CO}_{2,\text{atm}}$  of 305 ppm. At  $5^\circ\text{C}$  above modern ocean temperature  $T$ , the model predicts a predicted C:P ratio in the tropics of 189 and C:P ratio of 175 in the subtropics. ~~subtropical was 175~~, resulting in a  $p\text{CO}_{2,\text{atm}}$  of 263 ppm. Tropical  $\text{SST}$   $T$  had more impact with  $\Delta p\text{CO}_{2,\text{atm}} = 41$  ppm compared to subtropical  $\text{SST}$   $T$ 's effect with a  $\Delta p\text{CO}_{2,\text{atm}}$  ranging range from 4 to 5 ppm (Figure 11).

Similar to the temperature-only model, the multi-environmental model predicted a negative linear relationship between  $p\text{CO}_{2,\text{atm}}$  and tropical  $\text{SST}$  sea surface  $T$  and a positive linear relationship between  $p\text{CO}_{2,\text{atm}}$  and subtropical  $\text{SST}$  sea surface  $T$  (Figure 10D). The decline in  $p\text{CO}_{2,\text{atm}}$  with tropical  $\text{SST}$  sea surface  $T$  was driven by an enhancement of export due to increased C:P at higher  $T$ s (Figure 11). In the subtropical region, the expected increase in export was mitigated by a decline in solubility. At  $5^\circ\text{C}$  below modern ocean temperature  $T$ , the trait-based model predicted that C:P in the tropics was 147 and that C:P in the subtropics was 155, resulting in an increase of  $p\text{CO}_{2,\text{atm}}$  to 279 ppm (Figure 11). Variation in tropical  $\text{SST}$   $T$ s over a  $10^\circ\text{C}$  span led to a significant decline in  $p\text{CO}_{2,\text{atm}}$ , with a  $\Delta p\text{CO}_{2,\text{atm}}$  of approximately 46, and tropical C:P ranging from 147 to 210 (Figure 11). Because the subtropical box has a large surface area, the decrease in surface  $\text{CO}_2$  solubility at high temperatures is sufficient to overcome the increase in export due to higher C:P leading to a positive relationship between  $p\text{CO}_{2,\text{atm}}$  and subtropical temperatures.

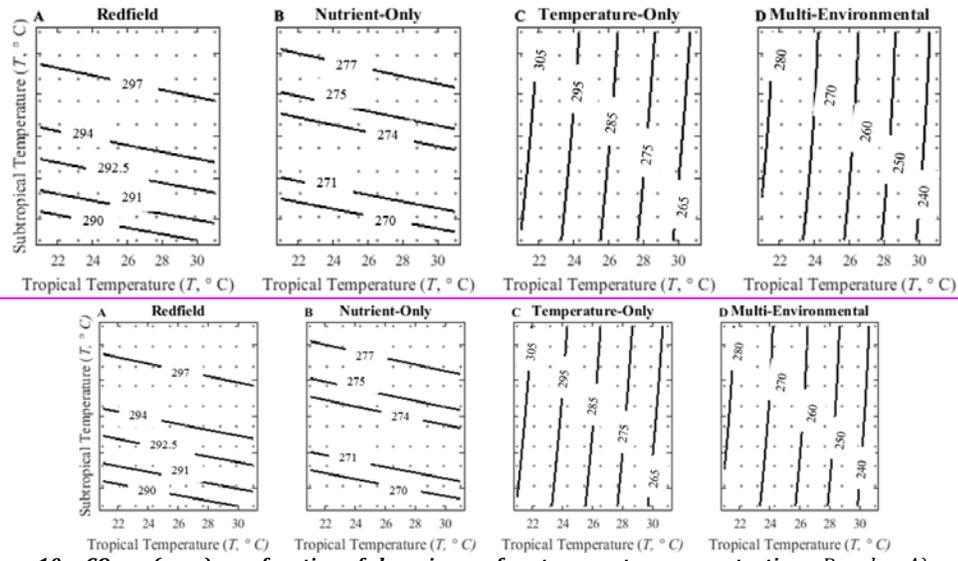


Figure 10:  $pCO_{2,atm}$  (ppm) as a function of changing surface temperature concentrations. Based on A) 1480 Redfield (fixed) stoichiometry model, B) nutrient-only stoichiometry model, C) temperature-only stoichiometry model, and D) multi-environmental stoichiometry model.

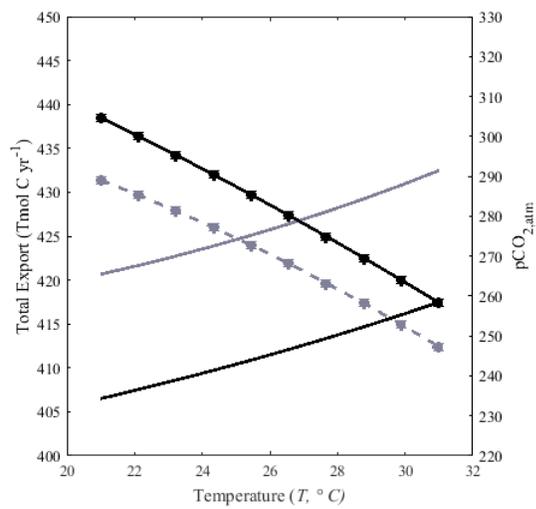
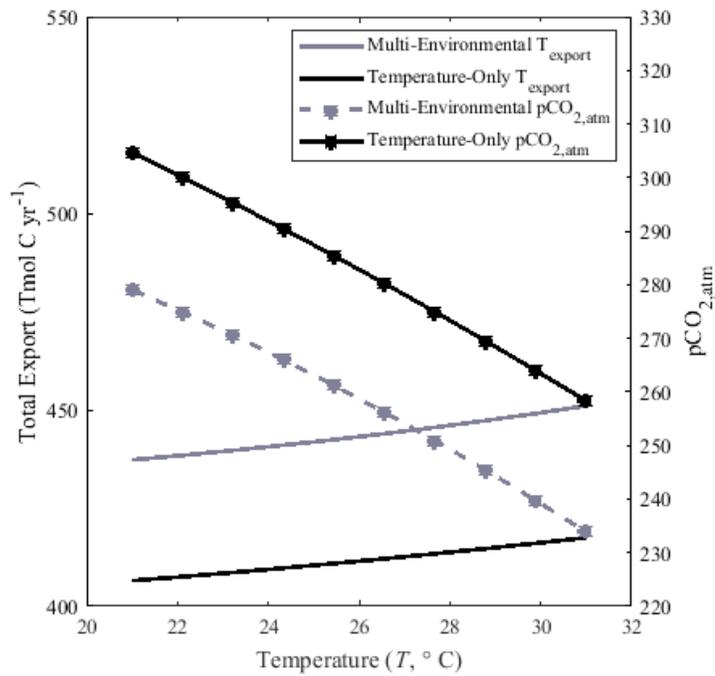


Figure 11: The effect of changing sea surface temperature (°C) on pCO<sub>2,atm</sub> and total carbon export (Tmol 1485C yr<sup>-1</sup>) in the temperature-only and multi-environmental model. Phosphate concentrations are 0.3 μM in the tropical and 0.05 μM in the subtropical box. Multi-environmental model total carbon export is the solid gray line,

and  $p\text{CO}_{2,\text{atm}}$  is the dashed gray line. Temperature-only model total carbon export is the solid black line, and  $p\text{CO}_{2,\text{atm}}$  is the dashed black line.

#### 1490 **4 Discussion**

Here, we found that variable stoichiometry of exported organic material moderates the interaction between low-latitude nutrient fluxes and ocean carbon cycling. A full connecting circulation allows for complete movement of nutrients between ocean regions resulting in strong linkages between nutrient supply ratios and cellular stoichiometric ratios (Deutsch and Weber, 2012). It has been shown that the inclusion of an oceanic circulation connecting high and low-latitude regions results in a feedback effect between high-latitude nutrient export and relative nutrient supply in low-latitudes (Sarmiento et al., 2004; Weber and Deutsch, 2010). Together, the inclusion of lateral transport between ocean regions and of deviations from Redfield stoichiometry within our model led us to predict the existence of strong teleconnections between the iron-limited tropics and the macronutrient limited subtropics. The degree of nutrient drawdown in the tropics had a strongly non-monotonic relationship with  $p\text{CO}_{2,\text{atm}}$  because this drawdown influenced both nutrient supply to the subtropics and tropical C:P. The idea of biogeochemical teleconnections has been proposed before, but we found that variations in stoichiometry greatly enhance the importance and strength of such linkages (Sarmiento and Toggweiler, 1984). Thus biome-scale variations in phytoplankton elemental stoichiometry may change the sensitivity of the carbon pump to iron deposition or other phenomena that regulate patterns of nutrient drawdown. We also see that the degree of nutrient drawdown had a strong impact on predicted (and observed) C:P leading to highly non-linear controls on  $p\text{CO}_{2,\text{atm}}$  whereby increased export in the tropics counter intuitively leads to increasing  $p\text{CO}_{2,\text{atm}}$ . ~~Large~~ This observation suggests that  $p\text{CO}_{2,\text{atm}}$  may have a complex link to iron delivery that is modulated by macro-nutrient availability and phytoplankton resource demand. Thus, ~~Large~~ scale gradients in stoichiometry can alter the regional efficiency of the biological pump: [P] supplied to high C:P regions leads to a larger export of carbon than [P] supplied to low C:P regions, giving an important role to the details of the ocean circulation and other processes that alter nutrient supply and phytoplankton physiological responses in different surface ocean regions. Therefore, biome-scale variations in phytoplankton elemental stoichiometry can lead to a fundamental change in the partitioning of carbon between the atmosphere and the ocean.

1520 We have created a box model to simulate the impact of the low latitude stoichiometric ratios, its environmental controlling factors and its relationships on  $p\text{CO}_{2,\text{atm}}$ . Low latitude phosphorus concentrations can be set in one of two fashions; through iron limitation and through nutrient availability. Here we will briefly discussion how iron limitation could play a significant role on phosphorus concentrations. The biogeochemical functioning of t  
1525 Fropical regions are commonly influenced by iron availability (Coale et al., 1996; Moore, 2004; Raven et al., 1999) in such a way that macronutrient levels cannot be fully drawn down by phytoplankton (Coale et al., 1996; Moore, 2004; Raven et al., 1999). The degree of nutrient drawdown has a strong impact on predicted (and observed) C:P. This environmental control on C:P could lead to highly non-linear controls on  $p\text{CO}_{2,\text{atm}}$  whereby increased export in the tropics leads to increasing  $p\text{CO}_{2,\text{atm}}$ . This relationship would differ in the subtropics, where iron is thought to stimulate nitrogen levels through nitrogen fixation, an iron exhaustive metabolic process in such a way that

1535 ~~macrophosphorus~~ nutrient levels cannot be fully drawn down by phytoplankton. The degree of nutrient drawdown has a strong impact on predicted (and observed) C:P. This environmental control on C:P could lead to highly non-linear controls on  $p\text{CO}_{2,\text{atm}}$  whereby increased export in the tropics leads to increasing  $p\text{CO}_{2,\text{atm}}$ . This relationship would differ in the subtropics, where iron is thought to stimulate nitrogen levels through nitrogen fixation, an iron exhaustive metabolic process (Wu et al., 2000). Iron's potential control on nitrogen fixation could promote higher carbon fixation and further exported stoichiometric ratios in the subtropical regions leading to increasing  $p\text{CO}_{2,\text{atm}}$  (Wu et al., 2000). Iron's potential control on nitrogen fixation could promote higher increases in both carbon fixation export and further exported stoichiometric ratios in the subtropical  $p\text{CO}_{2,\text{atm}}$  may differ, could it in essence iron's role in the low-latitude regions leading to increasing  $p\text{CO}_{2,\text{atm}}$  (Wu et al., 2000), though. Thus, iron availability may play a complex role depending on whether there is an increased delivery in upwelling zones (leading to a potential declining global C export) or in the subtropical gyres (leading to a potential increase in global C export). ~~It these ideas and the implementation of explicit iron concentrations within models could provide stronger results to that seen in this study. It is our belief that further research is needed to fully suppo~~

1550 Past studies using box models have found  $p\text{CO}_{2,\text{atm}}$  to be insensitive to low-latitude nutrients (Follows et al., 2002; Ito and Follows, 2003; Sarmiento and Toggweiler, 1984; Toggweiler, 1999). This phenomena was explored by DeVries and Primeau (2009) (2009), who showed that the strength of the thermohaline circulation is the strongest control on  $p\text{CO}_{2,\text{atm}}$ , and that changes in low-latitude export are relatively unimportant. Unlike our 1555 study, such earlier work relied on a uniform Redfield stoichiometry. However, we find that when stoichiometric variation is included, carbon export and  $p\text{CO}_{2,\text{atm}}$  become dependent on details of low-latitude processes.

It is important to recognize that a five-box model is an incomplete description of ocean circulation, and is meant only to identify the most important mechanisms, not to 1560 make precise quantitative predictions. In order for our model to adequately reflect important features of the carbon and phosphorus nutrient distributions, we had to carefully select the values of the thermohaline and wind-driven upper ocean circulations that lead to reasonable nutrient fluxes and standing stocks. The value of thermocline circulation,  $T_c$ , has been calibrated in different box models to range from 12 to 30 Sv 1565 (DeVries and Primeau, 2009; Galbraith and Martiny, 2015; Sarmiento and Toggweiler, 1984; Toggweiler, 1999). Representation of the wind driven overturning,  $T_w$ , in a simple box model has received less attention. Variations in the thermohaline circulation influence the abundance of nutrients in different boxes. Depending on the strength of this circulation, our model accumulated nutrients in the thermocline box and we tuned this parameter to 1570 most accurately mimic nutrient variation across ocean regions. Another caveat relates to our choice of the two-way flux values. Similar to the circulation values, a wide range of two-way flux values have been used in the literature. We therefore performed sensitivity experiments to find the best value for our full model set-up but the qualitative trends observed are insensitive to the choice of such fluxes.

1575 Nutrient availability and temperature have been alternatively proposed as drivers of variation in stoichiometric ratios in the global ocean, and the strong statistical correlation between temperature and nutrients throughout the ocean has prevented identification of the relative importance of each factor (Martiny et al., 2013 Nat Geo.

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Moreno and Martiny, 2018). We see that although temperature regulation of C:P<sub>export</sub> can influence pCO<sub>2,atm</sub>, this regulation is strongly dependent on the detailed control mechanism and also generally diverge from expectations based on the solubility pump. The decrease in surface CO<sub>2</sub> solubility at high elevated temperatures is sufficient to overcome the increase in export due to higher C:P leading to a positive relationship between pCO<sub>2,atm</sub> and subtropical temperatures. It is important to point out that the relative importance of the two competing effect depends critically on the physical circulation of the ocean. Predicted increases in stratification are often invoked as a mechanism that would decrease the vertical supply of nutrients, which one might think would further compensate for the effect of higher C:P. However, the strength of the biological pump in the subtropics is also influenced by lateral transport of nutrients (Letscher et al., 2015) so controlled the by lateral transport of nutrients rather than by vertical exchange is also influenced by lateral transport of nutrients (Letscher et al) so that the impact of increasing stratification might not be important so we argue that it is unclear if you should expect increasing, unchanged or decreasing C export in low latitude regions with ocean warming and stratification. Similarly, it is unclear how increases in stratification might affect the strength of the solubility pump. The sensitivity of pCO<sub>2,atm</sub> to changes in subtropical surface temperatures depends critically on the volume of the ocean ventilated from the subtropics, i.e. on the volume of the thermocline box in our model. How this volume might change in response to a warming world is a complicated dynamical problem that is beyond the scope of the present work.

Our results do not identify whether temperature or nutrient concentrations is the most important driver of phytoplankton C:P, but do suggest that the physiological effect of temperature could be important for ocean carbon cycling. Both the temperature-only and multi-environmental models predict that temperature increases enhance tropical export, causing substantial decreases in pCO<sub>2,atm</sub> with temperature. This relationship is the reverse of that predicted by the nutrient-only and Redfield models, and represents a sizable potential negative feedback on carbon cycling. The multi-environmental model also predicted that C:P responds in a nonlinear fashion to [P], with significantly increased sensitivity in highly oligotrophic conditions. Thus, a deeper understanding of the physiological mechanisms regulating phytoplankton C:P ratios are ~~thus~~ key to understanding the carbon cycle.

Our derivation of the multi-environmental model relies on several important assumptions. The growth rate in the multi-environmental model is determined by a set of environmental conditions and quantified by the specific rate of protein synthesis, carbon fixation and phosphorus uptake. The effect of growth rate on stoichiometry will likely be dependent on whether light, a specific nutrient, or temperature controls growth. The value of specific species of Q<sub>10</sub> leads to uncertainty in our multi-environmental model because of the range of possible values is highly dependent on the cell or organism being tested. In a study examining Q<sub>10</sub> of various processes within the cell, it was found that the Q<sub>10</sub> of photochemical processes ranged from 1.0 to 2.08, and for carboxylase activity of RuBisCO to be 2.66 (Raven and Geider, 1988). In addition to the high uncertainty between Q<sub>10</sub> values, there is high ambiguity associated with cellular inorganic P stores (e.g., polyphosphates and phospholipids) (Kornberg et al., 1999). P storage, such as polyphosphates, can serve as both energy and nutrient storage that may be regulated by unique environmental factors. Finally, we assume that our choice of the value of Q<sub>10</sub> for

1625 each metabolic process is a potential source of error within our model, because measured values are highly dependent on the cell or organism being tested, and it is difficult to extend these single-organism observations across species. Thus, we recognize multiple caveats within the trait-based model but expect that it improves our ability to link environmental and phytoplankton stoichiometry variation.

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## 5 Conclusions

We find that processes that affect nutrient supply in oligotrophic gyres, such as the strength of the thermohaline circulation, are particularly important in setting  $p\text{CO}_{2,\text{atm}}$  but via a complex link with  $\text{C:P}_{\text{export}}$ . By explicitly modeling the shallow overturning circulation, we showed that increased export in the tropics, which might be influenced by increased atmospheric iron dust deposition, may lead to increases, rather than decreases, in  $p\text{CO}_{2,\text{atm}}$ . Increased [P] drawdown in the tropics shifts export away from the subtropical gyres, and changes the mean export C:P in the low-latitude ocean. We would expect that nutrient drawdown leads to high export and declines in  $p\text{CO}_{2,\text{atm}}$ , but instead we find that variation in cellular allocation and adaptation can lead to counterintuitive controls on  $p\text{CO}_{2,\text{atm}}$ . Additionally, we find that it is even more difficult to ~~separate~~ ~~separating~~ nutrient supply and temperature controls on marine phytoplankton stoichiometry, carbon export, and  $p\text{CO}_{2,\text{atm}}$  and we need better physiological experiments and field data to fully understand the relative impact of the two factors. Nevertheless, it is likely that both play a key role in regulating phytoplankton stoichiometry,  $\text{C:P}_{\text{export}}$ , and ultimately ocean carbon cycling.

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**Author Contribution:** ARM - creation and analysis of the box model and primary writer of manuscript. GIH - creation and development of the trait-based model, and writing. FWP - assistance on the box model and editing of manuscript ~~of manuscript~~. SAL - assistance on the trait-based model and editing of manuscript. ACM - assistance on both models and

1650 writing of manuscript.

**Competing Interests:** The authors declare that they have no conflict of interest.

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