

## ***Interactive comment on “The combined impact of CO<sub>2</sub>-dependent parameterisations of Redfield and Rain ratios on ocean carbonate saturation” by K. F. Kvale et al.***

**K. F. Kvale et al.**

k.kvale@unsw.edu.au

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The authors would like to thank the reviewers for their helpful comments, which have improved the manuscript. Reviewer comments are shown below in boldface text. Author responses are shown in plain text. Revisions to the manuscript text are shown in italics.

### **Reviewer 3 Major Comments**

**“This paper discusses the results of a sensitivity study, where POC and PIC export are synchronously modified using pCO<sub>2</sub>-sensitive parameterisations. It confirms previous findings by Boudreau et al. 2010, that the ocean interior will**

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respond strongly to such changes in biological processes, whereas the surface ocean will not. While I think the general idea of the paper is interesting, I have some reservation about the paper's form and methodology, and about its publication in Biogeosciences. In its present form, the paper is merely discussing the results of a 'computer game' rather than giving insight about potential changes in ocean biogeochemistry, and there is not much new when compared to Boudreau et al. (2010). Hence, perhaps this paper is better suited to being published elsewhere in a lower impact journal. The model is not validated, parameterisations are used that are unsuitable for global use, and only two key processes are modified, whereas there are many others likely to be affected by increased ocean pCO<sub>2</sub>. Hence, I cannot recommend publication in Biogeosciences unless the paper undergoes major revisions.”

“Specific comments:

#### A- Model validation:

In the present version of the paper, we are not presented any evidence that would make us believe that the model results are realistic, even before the modifications on the export parameterisations are carried out. What is the model's annual mean primary production, how well does the export compare with current estimates and how well does it simulate calcification in the different ocean basins? Furthermore, can the authors convince us that their nutrient patterns make sense, and do they tell us how their results are linked to inaccuracies in the simulations of the before mentioned quantities? How well is the carbonate saturation simulated, when some components of the carbonate system are compared to e.g. GloDAP DIC and alkalinity? I don't think the reader can make any sense of the relative changes observed between control simulations and the different sensitivity tests, unless s/he is provided with a general sense on how good this model is performing.”

The authors thank the Reviewer for making several very good points which were also brought up by the other reviewers. The original manuscript lacked model validation, which is now included in a new section (new Section 2.4) and a new figure (new Fig. 1). Global integrated export is also now compared with other estimates in this new section.

**“B- Use of parameterisations:**

**I have strong reservations about the use of Riebesell et al. (2007) for a global study like this. The bizarre (and unjustified) equation (5) was probably derived from the result of one mesocosm study with unadapted organisms in a community dominated by diatoms, a high latitude community which lived in a Norwegian fjord, so not even in an open ocean environment. How can the authors just take this parameterisation without even cautioning the reader against its use, except for saying ‘that we are dealing with an incomplete sampling of biodiversity’. In fact, I think that using this stoichiometry for tropical regions, where much of the deviation from the control run is found, does not make sense, since diatom-dominated communities are uncommon at these latitudes, except for the coastal regions, hence the findings in Riebesell et al. (2007) are not applicable to these waters. A proper synthesis of all observational and laboratory evidence on the effects of ocean acidification on stoichiometry would have been necessary, taking also into account naturally acidic systems, such as in the Med sea.”**

The Introduction has been expanded following comments from the earlier Reviewers to give greater context to the parameterisations. While application of the Riebesell et al. (2007) parameterisation globally is viewed by the Reviewer as unjustified, it is currently being actively applied to the open ocean in low resolution, coupled biological-climate models (Oschlies et al., 2008; Tagliabue et al., 2011; and Floegel et al., 2011 are only a few examples). This suggests that demand for such a global POC export sensitivity to pCO<sub>2</sub> in the modelling community is high and of strong research interest, and that more appropriate empirical, globally applicable parameterisations are lacking. A

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synthesis of observational and laboratory evidence on the effects of ocean acidification on stoichiometry would be of tremendous scientific benefit to global carbon cycle modellers, but is beyond the scope of this paper.

Additional and re-phrased background is now provided in the Introduction regarding model parameterisations and their impact on the global carbon budget, and is as follows for POC export:

*“The efficiency of the biological pump has historically been thought to be controlled not by the availability of CO<sub>2</sub>, which is abundant, but by temperature, light, and the availability of nutrients nitrate (NO<sub>3</sub><sup>-</sup>) and phosphate (HPO<sub>4</sub>). Hence the fixed stoichiometry of the photosynthesis equation is typically applied to marine carbon cycle models, based on the empirically-derived Redfield ratio (Anderson, 1995). Thus enhanced CO<sub>2</sub> model experiments show increasing POC production is accompanied by proportional depletion of nutrient pools, which limits primary production (Schmittner et al., 2008). Mesocosm experiments by Riebesell et al., (2007) suggest the above fixed carbon-to-phosphate stoichiometry may vary by as much as a factor of 6 under high-pCO<sub>2</sub> conditions, significantly altering the efficiency of primary producers consuming DIC and reducing the effect of nutrient limitation. Near term (to 2100) high CO<sub>2</sub> model studies which incorporate a variable C:N (or P) ratio (e.g., Schneider et al., 2004; Oschlies et al., 2008; Boudreau et al., 2010) yield only a small additional negative impact on the global anthropogenic carbon budget as coincident changes in ocean physics compensate internally and air/ocean exchange is limited by the solubility pump.”*

And for PIC export:

*“Sufficiently reduced carbonate concentration lowers Omega, reducing the biotic carbonate precipitation rate (Zhong and Mucci, 1993). Seventy percent of total calcification is performed by pelagic coccolithophores, foraminifera, and pteropods, making their response to Omega particularly relevant for the global carbon budget (Zondervan et al., 2001). The reduction of biological carbonate production (particulate inorganic*

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carbon, PIC) as a response to increased  $p\text{CO}_2$  means less  $\text{CO}_2$  is released to the surface mixed layer as a by-product of calcification. This “ $\text{CO}_2$ -calcification feedback” (Ridgwell et al., 2007) is only a minor player in global carbon budgets over the short term (Gehlen et al., 2007; Ridgwell et al., 2009; Gangsto et al., 2010) with an expanding (but still minor) role on a millennial horizon (e.g., Heinze, 2004; Ridgwell et al., 2007; Gehlen et al., 2007; Boudreau et al., 2010). The most salient effects of the  $\text{CO}_2$ -calcification feedback are resulting changes to nutrient and carbonate profiles which could impact on ecosystem dynamics (e.g., Ridgwell et al., 2007; Boudreau et al., 2010). Carbon export away from the surface is also impacted by changes in calcification: sinking PIC acts as ballast for sinking POC (Klaas and Archer, 2002). Biogeochemical models often assume a fixed PIC:POC ratio (the Rain ratio) for this ballasting, but increasing  $p\text{CO}_2$  can reduce the aggregation of PIC by coccoliths and affect ballasting rates (Riebesell et al., 2000; Zondervan et al., 2001; Biermann and Engel, 2010). ”

#### “C- Model suitability

Since this model only includes a very limited amount of biology, I ask myself whether or not it is really suited to study the differential impact of modifications in so-called biological processes. Given that we do not know anything about the model tracers after a very poor model description (and validation), we are left to doubt whether or not there even is some degree of biological realism. Many global ocean ecosystem models now include complex nutrient dynamics, but this model does not seem to include any of this complexity. Furthermore, the second trophic levels (zooplankton) are also likely to be affected by changes in ocean pH, and they calcify, too and generate most POC. No information is given on zooplankton here, and neither is its role discussed in the conclusion section (e.g. Gangsto et al. 2009). Without any detailed information on the model tracers, this study turns into a mere computer game, as I mentioned above, and we may as well read the box model study by Boudreau et al. 2010. Furthermore, this

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**study does not only lack complexity in the simulation of the model ecosystem. Since this model does not even include a proper particle representation with aggregation processes etc. (the mesocosm experiment cited in this study also found significant changes in TEP production), I strongly question whether or not changes in export can really be discussed using this model. However, this is nothing the authors can do anything about. However, they can thoroughly revise their model description.”**

The above concerns expressed by Reviewer 3 regarding the lack of model description and evaluation are now addressed in the new Model Evaluation section. It is indeed true that the biological carbon cycle model used for this study is simple (it is also attached to a simple climate model), but that does not necessarily make it an inappropriate choice for understanding on a broad level the potential for two observed production pCO<sub>2</sub> dependencies to interact.

Biogeochemical models are notoriously underdetermined- Ward et al., (2010) provide an excellent comparison of parameter optimisation techniques in more complex models than what we use here, and show these more complicated models are sensitive to *a priori* assumptions and can have multiple “optimised” configurations. Increasing complexity in models does not necessarily improve their ability to match data, and may actually decrease predictive skill (Friedrichs et al., 2006). Remineralisation is still poorly understood (e.g., Buesseler et al., 2007), not only for autotrophic POC but also in the role of zooplankton (summarised in Le Quere et al. 2005). Additional model complexity for this study risks including responses in PIC and POC export not related to the simple parameterised changes in biogeochemistry (e.g., also including changes to ecosystem structure). While interesting and perhaps more mechanistically realistic, species interactions under the spectre of climate change are arguably as speculative as a global implementation of a mesocosm parameterisation.

The study goes beyond the earlier Boudreau et al. (2010) study with greater resolution of depth levels and examination of regional patterns.

## “D- Documentation of purpose of study, inclusion of relevant references

**This paper fails to give a background on the purpose of the study, and fails to include many important references on calcification, the study of physiological changes in ocean biota under sea water acidification and other climate-related impacts on marine ecosystems. It totally fails to discuss the impact of changes in ocean temperature on particle export and the remineralisation loop, which are very likely to modulate the projected changes in the model. The manuscript remains unacceptably vague when literature is cited or important findings are discussed, and does not include a discussion of other effects (impact of ocean acidification on the N cycle, for example, changes in stratification and nutrient availability). The authors mention that they only want to show that biogeochemical feedbacks are important, but again then the entire study turns into a computer game, and we can as well read Boudreau et al. (2010).”**

Reviewer comments regarding a lack of background are now addressed with an expanded Introduction section which also includes several more references. There is a large body of work surrounding calcification as well as other physiological responses to ocean acidification, and other general ecosystem impacts. The authors included the key references which are relevant to the specific topic of enhanced stoichiometric ratios and declining Rain ratios in climate models. The expanded background in the Introduction and model description sections now discusses other forces (temperature, stratification) which can influence C:P stoichiometry, the assumption of a uniform scaling for POC production and remineralisation, and the potential impact of particle aggregation on results. Details of the manuscript expansion may be found in the following section of minor comments made by Reviewer 3.

### Reviewer 3 Minor Comments

#### “Abstract:

**Rewrite entirely, as vague and we cannot judge what you find, since you do not**

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## mention here what kind of parameterisation you have used.”

The parameterisations used in the manuscript are named as:

*“biological dependencies of Rain and elemental ratios on pCO<sub>2</sub>”*

in the beginning of the abstract. Specific references to papers were avoided as per BGD policy outlines. The abstract now more explicitly states what we were looking for:

*“extreme-case carbonate saturation vulnerability to enhanced POC export and decreased PIC export at year 2500 using IPCC “Representative Concentration Pathway” 8.5.”*

and what we found:

*“Surface carbonate saturation is relatively insensitive ... global zonally-averaged ocean interior anomaly due to these feedbacks is up to 130% by 2500. A combined interaction between organic and carbonate pumps is found in export production ... ”*

**“This non-linear effect has...’ explain why?”**

The mechanism for increasing non-linear influence with depth is now explained as:

*“This combined effect has a negligible influence on surface carbonate saturation but does significantly influence ocean interior carbonate saturation fields (an anomaly of up to 45% in 2500) owing to different PIC and POC remineralisation length scales.”*

**“linear and non-linear effects’ Where do these come from?”**

The linear effect comes from the additive impact of enhanced POC export and decreased PIC export owing to the model parameterisations. The first Reviewer suggested a terminology change from ‘linear’ to ‘added’, and from ‘non-linear’ to ‘combined’, which makes their definitions less confusing. Also, the words ‘model parameterisation’ have now been replaced in the second sentence of the abstract to make this more clear:

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*“Here, biological dependencies of Rain and elemental ratios on  $p\text{CO}_2$  are implemented in a coupled Biogeochemistry-Ocean Model, the CSIRO-Mk3L, to establish extreme-case carbonate saturation vulnerability to enhanced POC export and decreased PIC export at year 2500 using IPCC “Representative Concentration Pathway” 8.5.”*

The combined effect is described in the abstract as:

*“A combined interaction between organic and carbonate pumps is found in export production, where higher rates of photosynthesis enhance calcification by raising surface alkalinity.”*

#### **“Introduction:**

**First paragraph: Be clear and always indicate the direction of observed change, e.g. avoid ‘vary’ ‘altering’ and ‘adjustments’ and give direction of the feedback.”**

‘Vary’ is changed to ‘increase’, ‘altering’ is changed to ‘increasing’, and ‘adjustments’ is reworded as:

*“There are important biogeochemical impacts from enhanced POC production efficiency related to remineralisation, e.g. expanding suboxic zones (Oschlies et al., 2008), a shoaled carbonate compensation horizon and decreasing deep water pH (Boudreau et al., 2010).”*

**“‘availability of carbonate’: Not true that equation (2) tells you about the ‘availability’. This is simply an equilibrium equation.”**

Text is now reworded to read:

*“The thermodynamic potential of calcification (Eqn. 2) is measured as calcium carbonate saturation ( $\Omega$ ), where the concentrations of calcium and carbonate are divided by the solubility constant  $K_{sp}$  (Eqn. 3).”*

**“P 6267, L12: ‘reduction...’ cite appropriate reference.”**

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Done.

**“P6267, L16: ‘which could impact...’ How?”**

Text now reads:

*“The most salient effects of the CO<sub>2</sub>-calcification feedback are resulting changes to nutrient and carbonate profiles which could impact on ecosystem dynamics by increasing surface alkalinity (e.g., Ridgwell et al., 2007; Boudreau et al., 2010).”*

**“P6267, L 19: ‘truncated nutrient’... explain.”**

‘truncated’ is now replaced with ‘shoaled’.

**“P 6267, L 21: ‘long term’ What is long term?”**

‘over the long term’ is removed for better clarity.

**“P6267, L 23: ‘ In the studies mentioned above’ Which studies? And why the low latitudes? Be precise.”**

Text now reads:

*“Of particular interest are the low latitudes which have been shown to be disproportionately vulnerable to the biogeochemical effects of enhanced POC production through enhanced gas exchange rates (Boudreau et al., 2010).”*

**“P 6269, L1: Riebesell et al. 2007, This study worked with a ‘shocked’, i.e. unadapted communities of coastal organisms. How can you justify it’s use for the global, open ocean and for century-scale change?”**

We justify the use of this gross parameterisation by limiting what we conclude with its application. This is a parameterisation which is being actively used in coupled biological climate models (e.g., Oschlies et al., 2008; Boudreau et al., 2010; Tagliabue et al., 2011; Floegel et al., 2011), as are parameterisations of acidification effects on the Rain ratio. This study points out a combined effect on carbonate saturation in models

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when these two types of scaling parameterisations are jointly applied. Real-world implications are strongly conditioned in the Summary and Conclusions section- please see the inserted text in the minor comments for p6274.

**“Equation (5): Define those numbers you use there. Where do they come from (2, 700)? Did they once have units- ‘pCO<sub>2</sub>’ should be given as ‘pCO<sub>2</sub>/[uatm]’, since I assume F should be unitless.”**

Done.

**“P 6269, L 4: ‘the same scaling’ How is this justified?”**

An identical scaling for enhanced C:N uptake and remineralisation is not without precedent, having been used by Oschlies et al. (2008). Still, we thank the Reviewer for the opportunity to mention a recent study which explores the sensitivity of carbon export in a more complex coupled biological-climate model to assumptions regarding remineralisation stoichiometry. The text has now been expanded to read:

*“Tagliabue et al. (2011) recently explored the sensitivity of carbon export to assumptions surrounding stoichiometric enhancement of remineralisation and found that the assumption used herein (equal enhancement of production and remineralisation) constitutes a high-end approximation of carbon export response, whereas a shedding of extra carbon as DOC in the surface reduces the POC export at 100 m depth. ”*

The focus of our study is extreme-case carbonate saturation sensitivity, hence using a high end approximation of POC export response is acceptable.

**“P 6269, L 19: Spell Gangsto correctly.”**

Done.

**“P6269, L21 ff: ‘does not account for particle aggregation...’ How does this impact your results? Come back to this in your Conclusions, detail the limitations of your model there.”**

The text has been modified to read:

*“This Rain ratio parameterisation does not account for particle aggregation (which would allow variable sinking rates), nor does it differentiate between particle classes, but it does demonstrate a latitudinal dependency which roughly aligns with observations, owing to the calcite saturation scaling factor gamma.”*

**“P6270: What about the potential impact of temperature changes on POC/PIC export? Discuss this somewhere!”**

Two sentences are now included in the Elemental Ratio Parameterisation section which highlights alternate possibilities:

*“The elemental ratio parameterisation explores response to ocean acidification only. Stoichiometric ratios might also be increased by increasing ambient temperature (Woods et al., 2003) or decreased mixed layer depth (Diehl et al., 2005).”*

Also, in the Summary and Conclusions section it is stated that:

*“Results are not projections of future ocean chemical climate because the model includes neither sediments nor radiative feedback.”*

**“Results:**

**General: Expand more on this ‘linear’ versus ‘non-linear’ effect you see, and why this difference is important to you? Does the ‘linear’ case mean that the POC effect dominates over the ‘PIC’ effect, and vice versa for the ‘non linear case’? If so, discuss why, what and where. Furthermore, give the relative size of the ‘linear’ and ‘non-linear’ effect (and clean up Summary and conclusion, so that the reader knows why this distinction is important to you).”**

The term ‘non-linear’ is applied to the feedbacks to describe the result that the sum of the changes in carbonate saturation owing to the 2 different export production model configurations does not equal the net model response of carbonate saturation. The

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term has now been changed to 'combined' to reduce confusion. Combined means that  $A + B$  does not equal  $A$  and  $B$  together, but instead is equal to  $A+B+C$ . The  $C$  is the combined component, and is what we see as an interaction between organic and inorganic carbon pumps. The definition is now clarified in a revised "PIC and POC Surface Export" section:

*"Said another way, the calculated direct response in abyssal carbonate saturation owing to changes in the Rain ratio, when summed with the calculated direct response owing to changes in elemental ratios, does not equal the actual model response in abyssal carbonate saturation. This combined chemical exchange is summarised in Fig. 3 and revolves about the enhanced consumption of free hydrogen in Eqn. 1 as part of enhanced POC formation. Figure 3 is similar to a Bond graph (common in electrical engineering), where individual components (photosynthesis, dissolution, etc.) are connected through effort ( $H^+$ ,  $CO_3$ , etc.) and flow (positive and negative feedbacks). In the figure, there are 3 routes that lead from increased surface  $CO_2$  to a change in deep ocean Omega. Route 1 follows the green line through the organic carbon pump. Route 2 follows the orange line through the carbonate pump. Route 3 follows the blue line between the organic carbon and carbonate pumps. The blue and red feedback lines which connect the components and effort show non-quantitative feedback resulting from an increase in component A, which causes component B to either decrease (negative feedback) or increase (positive feedback). Route 3, the combined impact via both carbon and carbonate pumps, occurs because inorganic carbon chemistry dictates a reduction in free hydrogen resulting in an addition of carbonate ions, according to  $HCO_3 \rightleftharpoons H + CO_3$ . This small increase in carbonate ion buffers the carbonate saturation which controls PIC export production in the model (shown as a blue pathway). In the RAINRED configuration, PIC formation is still reduced by the decreased saturation (orange pathway), but not as much as it is in the RAIN configuration where no additional carbonate input from altered photosynthesis occurs. Therefore, an even number of negative feedbacks in Route 3 creates a net positive feedback (an increase in  $CO_2$  leads to an increase in Omega), while an odd number of feedbacks in Routes*

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1 and 2 creates a net negative feedback (an increase in CO<sub>2</sub> leads to a decrease in Omega). Figure 3 says nothing about the cumulative effects of combining the net feedbacks in the 3 routes, nor does it say anything about the relative strengths of the net feedbacks.”

**“P6272: ‘striking pattern..’ no so striking to me, since the color scale is difficult to see. Fig. 3: Changes scales is plots. We can hardly see the effects.”**

**“P 6273: ‘Tropical regions...’ there I don’t think Riebesell et al. (2007) is applicable, since the communities are dominated by (non-calcifying) picophytoplankton, which were not dominant in the mesocosm study. Reflect on this in your manuscript.”**

Primary production in the tropical regions is subject to increasing POC export in our model from the Riebesell et al. (2007) parameterisation, which is based on a scaling of pCO<sub>2</sub>. Calcification feedback in this region comes from the Ridgwell et al. (2007) parameterisation of the Rain ratio based on Omega. Diagnosed CaCO<sub>3</sub> export estimates by Jin et al. (2006) do show non-negligible annual export of PIC in the tropical upwelling regions (e.g. the eastern Pacific). What we explore with this model study is the interaction between changes to calcification and changes to primary production, both of which are occurring in this zone. Caveats in the Summary and Conclusions section now include mention that the model does not contain multiple functional types or trophic levels- please see the text inserted two points below.

**“Summary and conclusions:**

**P 6274: What about temperature effects, see above.”**

Please see above comment.

**“P 6274: What about the effect of ocean acidification on calcifying organisms and their distribution, and on the nitrogen cycle? How will this influence your export effects?”**

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The conclusions are now more strongly caveated against drawing conclusions which would require more complex food web interactions and responses:

*“Likewise, the parameterisations reflect observed responses of an incomplete sampling of the biodiversity found in the global ocean, include neither multiple functional types nor multiple trophic levels, and the REDFIELD parameterisation in particular is tested beyond its calibration limit of 1050 ppm.”*

**“P 6274: ‘Insensitivity of PIC export to Omega...’ why is this? Do you believe it? If so, justify.”**

The text discusses this assumption:

*“The dependence of PIC dissolution on depth and not Omega might, on the other hand, be contributing to an underestimate of the combined effect by artificially lowering the depth of PIC dissolution below the zone of POC remineralisation. While the physical justification of widespread Omega-dependent PIC export is debatable (as summarised by Sarmiento and Gruber 2006 , pages 371-374), severely undersaturated water such as what is calculated in this hypothetical parameter test does approach a calcite dissolution e-folding timescale of a similar order to that of carbonate particle sinking. Should subsurface pooling of DIC owing to enhanced POC export and remineralisation accelerate PIC dissolution, the non-linear carbonate anomaly would be enhanced following the deep ocean schematic in Figure 3.”*

Comments from all Reviewers have helped us improve this manuscript. We are grateful to them for their thoughtful assistance.

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Interactive comment on Biogeosciences Discuss., 8, 6265, 2011.

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