

Interactive comment on “The combined impact of CO₂-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 as boldface text. Author responses are shown as plain text. Revisions to the manuscript text are shown in italics.

Reviewer 1 Major Comments

“The manuscript ‘The combined impact of CO₂-dependent parameterisations of Redfield and Rain ratios on ocean carbonate saturation’ by authors Kvale et al. is a model sensitivity study testing a potential combined effect of changes in carbon to nutrient ratios of exported organic matter and pelagic calcification on the calcium carbonate saturation state of seawater. The main conclusion is that as a consequence of ocean acidification both effects will act as a positive feedback on a reduction of deep ocean calcite saturation, while the simple sum of both individual effects would yield a lower feedback. The topic ocean acidification is presently of high scientific interest, the study is clearly written and the results are interesting. However, the rationale for the respective parameterisations is not well explained.”

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The authors would like to thank the Reviewer for their compliments. All Reviewers pointed out the lack of background regarding the model parameterisations. 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 CO₂, which is abundant, but by temperature, light, and the availability of nutrients nitrate (NO₃⁻) and phosphate (HPO₄). 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 CO₂ 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-pCO₂ conditions, significantly altering the efficiency of primary producers consuming DIC and reducing the effect of nutrient limitation. Near term (to 2100) high CO₂ 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). Ninety 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 carbon, PIC) as a response to increased pCO₂ means less CO₂ is released to the surface mixed layer as a by-product of calcification. This “CO₂-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 CO₂-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 pCO₂ can reduce the aggregation of PIC by coccoliths and affect ballasting rates (Riebesell et al., 2000; Zondervan et al., 2001; Biermann and Engel, 2010).”

“Furthermore, the study lacks model validation, so that overly strong effects may be achieved by strongly biased background conditions.”

The authors are thankful for this comment; we have added a model evaluation section (new Section 2.4) which compares model equilibrium with gridded observations of DIC, alkalinity, calcite saturation and nitrate. We also added 1 figure (new Fig. 1).

“Major comments: The study quantifies the sensitivity of the organic and inorganic carbon pumps on ocean acidification via potential feedbacks on seawater saturation with respect to CaCO₃. The dependence of the calcification rate on

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seawater calcite saturation is taken from a study by Ridgwell et al, (2007). However, since calcite dissolution uses an exponential depth profile, the sensitivity of the calcium carbonate pump feedback is only partly covered.”

It is true that this model structure does not account for enhanced carbonate dissolution which might result from PIC passing through highly corrosive subsurface water. Creating such a dependency would shoal dissolution and accelerate carbonate recycling to the surface, further reducing deep ocean omega. However, ignoring a possible omega dependency for dissolution is standard OCMIP procedure, and the rationale behind it is well explained in the 2006 “Ocean Biogeochemical Dynamics” textbook by Sarmiento and Gruber, pages 371-374. Firstly, the dissolution rate for a particle of carbonate is much longer than the residence time of the particle in the water column, negating the dissolution effect of passing through undersaturated water. In addition, PIC dissolution appears to be controlled by additional poorly constrained factors beyond omega undersaturation, a study of which is beyond this model structure (it would require resolving both particles and biological interactions, which Mk3L cannot do). Though we ignore feedbacks from enhanced dissolution, there is value in isolating the impact resulting from changes to PIC production, which we show in our study as the combined interaction between reduced calcification and enhanced elemental ratios. Section 2.2, second paragraph, justifies this model configuration:

“Following OCMIP protocol (Dutay et al., 2002), model PIC dissolution below the surface layer utilises a rigid exponential depth dependency so changes to surface PIC production mostly affect the depth of complete PIC dissolution; i.e. increasing PIC production yields a more penetrating PIC inorganic chemical signal in the water column. The current arrangement maintains independence between inorganic and organic carbon pump feedbacks while allowing for interactions with carbonate chemistry from both. Note this independence is only true below the surface; the scaling factors applied at the surface for PIC and POC with respect to POP (Eqns. 4 and 8) allow for direct interaction between organic and inorganic export feedbacks via alteration of surface pCO₂

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and calcite saturation.”

The Summary and Conclusions section also discusses this issue in the second-to-last paragraph:

“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 to 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 combined carbonate anomaly would be enhanced following the deep ocean schematic in Figure 3.”

“Furthermore it is stated that below 3000 m PIC is completely dissolved (p. 6273, l. 19-20). Is this really true? How do the resulting alkalinity distributions look like?”

This comment refers to old pg. 6273, lines 18-21. The authors are thankful to the Reviewer for pointing out an error in the conclusions. Mk3L output did not include PIC through the water column, so we cannot conclude with certainty that all PIC was dissolved at 3000 m.

“The impact of increased CO₂ on organic carbon fixation is derived from the mesocosm study by Riebesell et al (2007). A scaling factor is calculated that scales the flux of organic carbon to pCO₂. The exact motivation of this parameterisation is not clear to me. First, I don’t know whether this refers to atmospheric or seawater pCO₂. Second, where does the ratio 2/700 in equation 5 come from? What does it represent? Third, the model is spun up with an atmospheric pCO₂ of 278, which means that the scaling factor at starting conditions

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would be slightly below one. This deviation is probably unimportant, but needs to be clarified.”

The pCO₂ used in this experiment is seawater pCO₂. This has been clarified in the text by replacing ‘ocean’ with ‘seawater’, old pg 6269 line 1. An extra sentence has been added after the scaling equation to explain the 2:700 ratio, which is used to interpolate the observed 1:350 ppm C:N stoichiometry to a doubling of CO₂. It now reads:

“In this equation, the 2:700 ratio interpolates the observed response of the 16:106 Redfield ratio at a pCO₂ of 350 μ atm to the observed response of the elemental ratio at a doubling of pCO₂ to 700 μ atm (Riebesell et al., 2007).”

We acknowledge that the scaling factor for POC export based on deviation from 280 ppm would indeed be slightly less than 1 in the equilibrium runs using pCO₂ of 278 ppm. We believe, however, that this small difference is unimportant when compared to the size of the forcing examined using the RCP8.5 scenario. New Fig. 2 can provide some perspective on the impact of a 2 ppm mismatch, where POC export (upper right plot) at year 1900 for the REDFIELD and RAINRED model configurations is less than 0.5 Pg C per year higher than the CONTROL configuration, where the pCO₂ is 295.8 ppm (a difference of 15.8 ppm, versus 2 ppm). A sentence addressing this has been added to the REDFIELD model configuration description:

“A 2 ppm discrepancy exists between the Fscale equilibrium and the RCP 8.5 pre-industrial atmospheric concentration, but the effect is negligible.”

“If the scaling factor for the organic carbon flux refers to in-situ pCO₂ (what I assume after reading the manuscript), this would yield spatially differing scaling factors already for the pre-industrial state. Are there any data supporting this spatial distribution? Due to the strong spatial variability of pCO₂ in the modern surface ocean this should be detectable, probably at least in the tropical Pacific where the scaling factor yields a value of 1.09.”

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The Redfield ratio is widely accepted to be a gross generalisation, with actual stoichiometric C:N:P ratios varying both in time and space. There are several references listed in the original Riebesell et al. (2007) paper which offer empirical and observational support for carbon over-consumption. See specifically Sambrotto et al., 1993 and Kortzinger et al., 2001. While there are numerous studies which have been published since the Riebesell paper that look at changes in Redfield stoichiometry using various in situ, mesocosm and tank experiment designs, the authors are not aware of any meta-analysis of global C:N:P with respect to pCO₂. This would be a very interesting study.

“The study does not provide any model validation. The high amount of export production (20 Gt C/yr) is probably an overestimation and would shift the sensitivity of the organic carbon pump towards the upper end. Furthermore, a model-data comparison of the carbonate system variables would be very interesting, since the distribution of omega looks fairly different from the GLODAP data. The depth of the calcite saturation level would also be a suitable indicator to assess model performance, and it would also be interesting for the results section which vertical movements of the saturation horizons can be expected in the present study. An assessment of model performance including a critical discussion of the effects of potential model misfits would be highly desirable.”

At first glance, pre-industrial integrated surface POC export production in Mk3L does indeed appear high (20 Pg C per year) when compared to other estimates of POC export (e.g., 9.8 Pg C per year from Jin et al., 2006). Nutrient and carbon fields in the interior ocean however look reasonable when compared with observations. The discrepancy between Mk3L values and others is due to the different depth levels which we use for reporting POC export. Jin et al. (2006) use a 75 m definition and Mk3L uses 25 m for the POC parameterisation. POC export at 80 m depth in Mk3L is roughly half of the 25 m value, which agrees with the Jin et al. (2006) estimate. For our study it should not matter whether we use the 25 m export value or the 80 m export value

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for our parameterisation, as the calculation is linear and not based on the initial POC value. In any case, a 25 m depth export value is more appropriate for a production parameterisation. A paragraph has now been added to the Model Evaluation section explaining this:

“Generally good agreement of model equilibrium carbon distributions with gridded observations suggests that POC and PIC export estimates from the model surface (a depth layer extending the upper 25 m) are appropriate, despite the apparently large initial export value for POC (about 20 Pg C per year for all model configurations) shown in Figure 2 at year 1900. Model POC export at 80 m (level 3 in Mk3L) is roughly half of the export at 25 m, which is in agreement with the Jin et al., (2006) estimate of 9.8 Pg C per year at 75 m depth. Model PIC export is more conservative than POC because of its longer remineralisation length scale. PIC flux at 25 m is 1.2 to 1.6 Pg C per year (compare with the Jin et al., 2006 estimate of 1.14 Pg C per year at 75 m depth).”

The change in depth of the calcite saturation level is not different across model configurations owing to the OCMIP model configurations; the saturation horizon varies only a few tens of meters, variations too small to have confidence in for such a low-resolution model.

“I think the notation of linear and non-linear feedbacks (Fig. 3) is confusing, since even the individual feedbacks are probably non-linear. Why should their combination end up as linear? I would suggest to call them ‘combined’ and ‘added’ feedbacks. Furthermore, what is explaining the negative ‘added’ feedback (last row in Figure 3)? Do both feedbacks head into different directions and one is overcompensating the other, or is simply the combination of both yielding a stronger effect than the sum of the individual effects. It would be very illustrative to show also the results from the individual effects in Fig. 3.”

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

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configurations does not equal the net model response of carbonate saturation. The authors agree with the Reviewer that the term is confusing, and it has been replaced as suggested. 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

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in CO_2 leads to an increase in Omega), while an odd number of feedbacks in Routes 1 and 2 creates a net negative feedback (an increase in CO_2 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."

"Why are the feedbacks so strong in the eastern tropical Pacific and why only there? Does the model have exceptionally high export production in this area? Please show map of carbon export, which also needs to be defined in the manuscript. Is it the carbon flux at 100m depth?"

The feedbacks are strongest in the eastern tropical Pacific for reasons which are described in Section 3.2:

"Tropical regions show greater variability in Omega than what the global mean profile plots in Fig. 4 suggest. Figure 4 middle and right columns show the strongest impacts on carbonate saturation are confined to regions with strong POC enhancement, such as upwelling zones in eastern ocean basins. Linear and non-linear RAINRED anomalies in these regions are the largest nearing depths of complete PIC dissolution, hence are more apparent in the 3000 m depth plots (right column) than the 1000 m plots (middle column). The eastern Pacific in particular shows the strongest response, where the DeltaRAINRED anomaly is over 0.3 units at 3000 m depth (third row, right panel), a saturation change eight times that of DeltaCONTROL in this same region (not shown). The non-linear anomaly (bottom right panel) in this region is also significant, with a mitigating effect of about 20% the RAINRED anomaly value in this region (seen when comparing rightmost panels in the third and fourth row). As POC production is most enhanced in this region, the impact on PIC export production extends the deepest within this region by the fixed PIC dissolution gradient. In contrast to the eastern Pacific, the Indian Ocean has generally less POC and PIC production and hence has a weaker non-linear signal. While enhanced carbonate undersaturation and a small non-linear positive anomaly are seen by year 2500 in the Indian Ocean, the signal does

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not extend as deep as in the Pacific and the maximum non-linear anomaly values peak around 1000 m depth (bottom middle panel)."

Carbon export anomalies are now plotted in Figure 2, and export is defined in the Introduction as:

"defined here as the PIC flux from the model surface layer, which has a base of 25 m"

Reviewer 1 Minor Comments

"The use of the term Redfield ratios is confusing. According to Redfield et al. (1963) the Redfield ratios are constant elemental carbon to nutrient ratios for C:N:P of 106:16:1. Even if well motivated, any deviations from these ratios are simply element ratios and should therefore not be called Redfield ratio."

The Redfield term is now more narrowly applied in the text to only fixed stoichiometry, with 'elemental ratios' now replacing occurrences where it had been used to describe a variable ratio.

"p. 6266 l. 2: what is a 'biogeochemical climate'? Do you mean biogeochemical cycles?"

Original text is now replaced with the suggested terms.

"p. 6266, l. 3: replace 'on' by 'of'."

Text is replaced.

"p. 6266, l. 20-21: The impacts of ocean acidification on the organic and inorganic carbon pumps are presently not clear, but heavily debated. Therefore, it should be more carefully mentioned that there is a potential for changes, which will be tested in the present study."

'Potentially' has been inserted into the text in line 20.

"p. 6267, l. 10: replace 'a' by 'the'."

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Text is replaced.

"p. 6267, l. 18: please define 'export'."

A definition of export in the Mk3L model is now included in the Introduction:

"defined here as the PIC flux from the model surface layer, which has a base of 25 m"

"p. 6267, l. 17-21: what do you expect from this reorganisation in terms of oceanic carbon sink and saturation state?"

Previous work has looked at the impact of individual variable ratio parameterisations on global carbon budgets and have found it to be minimal. The manuscript now mentions this- please see the new text in the first Reviewer comment.

"Eqn(5): what is the data base for this equation? What does 2/700 represent?"

The equation is now more thoroughly explained, please see the earlier response to the Reviewer's 5th comment.

"p. 6270, l. 26: what 'physical' feedback do you mean? Maybe the use of 'biogeochemical' would be more appropriate."

'No' is replaced with 'so' to better explain that there are no changes in the physics resulting from the CO₂ forcing that might impact on carbon chemistry through climate feedbacks.

"p. 6272, l. 8-11: remove the two sentences, this is all seen in Fig. 3"

Done.

"p. 6273, l. 15: which 'global mean profile plots' are you referring to?"

A figure reference is added to the sentence.

"p. 6274, l. 25: why is the PIC export insensitive to omega?"

'Export' should have been 'dissolution'. The sentence is now re-worded for better clar-

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ity.

“p. 6275, l. 8: replace ‘CO2’ with ‘CO-induced’”

Done.

“p. 6275, l. 13-15: Yes, but the biggest changes are seen at depth, while calcification appears at or close to the surface, where changes are much smaller.”

While it is true that the largest changes are seen at depth, the properties of water masses upwelled from depth influence ecosystem dynamics near the surface.

“Fig. 1: In the text it is stated that the blue line in the left panel is actually above the black line. However, since this is not visible in the Figure, the difference is probably not significant and not worth mentioning.”

If this statement is about p. 6271 lines 18-20, this small and almost indistinguishable difference in PIC export between the blue and black lines (RAIN and RAINRED, respectively) is the crucial explanation of the non-linear feedback which is one of the main points of the paper. The text in the ‘PIC and POC Surface Export’ section is now amended to reflect this:

“This incongruence is nearly indistinguishable in Fig. 2 but crucially reveals a “combined” exchange between Rain and elemental ratio feedbacks in the RAINRED simulation, where reduced PIC export (calcification) due to the decreasing carbonate saturation in the inorganic carbon pump is slightly tempered by the additional release of carbonate owing to an enhanced organic carbon pump.”

“Fig. 2: I don’t understand Fig.2. What are the bold arrows standing for? And why does the ultimate direction of a combination of feedbacks depend on the number of individual contributions? Shouldn’t the individual strengths also play a role?”

Figure 2 (now Fig. 3) is similar to a Bond graph (common in electrical engineering),

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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 blue line between the organic carbon and carbonate pumps. Route 3 follows the orange line through the carbonate pump. 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).

For example, in Route 1 an increase in surface CO_2 leads to an increase in photosynthesis (a positive feedback). An increase in photosynthesis increases POC export, and is also a positive feedback. Increasing POC export also increases remineralisation and H^+ release, so Route 1 up to this point is all a positive feedback. The increase in H^+ release in the deep ocean decreases CO_3 , which is a negative feedback. Increasing CO_3 in the deep ocean increases Omega, a positive feedback. There is one negative feedback in Route 1 (the flow from H^+ to CO_3) which means the net feedback of Route 1 of increasing CO_2 on Omega is negative; increased activity of the organic carbon pump leads to a net decrease of Omega. Likewise, because there is only one negative feedback in Route 3, the net feedback of increasing CO_2 on Omega via the carbonate pump is a reduction in deep ocean Omega. Route 2 goes through the organic carbon to the carbonate pump and has 2 negative feedbacks, which makes the net feedback (in that route) of increasing surface pCO_2 on deep ocean Omega positive. This plot 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.

In addition to a revised Summary and Conclusions section reproduced for the 8th major comment, the figure caption for Figure 3 has been reworded for better clarity:

“A qualitative schematic of feedback processes operating between organic and inorganic carbon pumps and carbonate saturation. The impact of the variable Rain and

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elemental ratio parameterisations on deep ocean carbonate saturation are shown as coloured pathways with fat arrows: Rain (orange), elemental (green), Rain and elemental (blue). Positive feedbacks (an increase in A leads to an increase in B) are presented in thin blue and negative feedbacks (an increase in A leads to a decrease in B) in thin red. An even number of negative feedbacks (red arrows) in a pathway sum to a positive feedback, while an odd number of negative feedbacks remain negative. The sign of the net feedbacks do not sum across pathways."

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