Dear Editor,

In our response to 'reviewer 1', we will present our direct responses in 'bold' preceded by '>' in case of formatting problems:

The authors present a computationally-efficient parameterization of complex iron speciation chemistry, suitable for use in global ocean-biogeochemistry models. I think this is a paper worthy of publication, in principle, and my comments here are intended to help the authors improve the manuscript.

> We thank the review for his/her support of our paper, we will endeavour to address his/her comments in the following.

As I understand it, there are two reasons why speciation of iron could be important for global biogeochemistry. First, it affects the rate at which iron is scavenged onto sinking particles and thus removed from the water column. Second, it somehow affects the bioavailability of iron to microorganisms. Developing a mechanistic, quantitative understanding or iron speciation and its effects in the marine environment is certainly a worthy goal, and a significant challenge.

My primary suggestion for the paper is that the authors emphasize more strongly that this is a case in which model complexity is running up against the limit of sparse observational data. The model is introducing a new level of complexity into what are already fairly complex parameterizations (I would disagree with the authors' characterizations of other iron models as 'simple'), and there are scant data with which to judge whether or not these new aspects truly capture reality. For example, there are only a few limited observations of the apparently highly-variable Fe(II) concentrations, and despite significant effort, our understanding and quantification of ligand dynamics is still in its infancy. I would say that this work should be presented as fairly hypothetical, and is most useful to highlight the aspects of iron speciation that need to be better constrained by observations.

> We totally agree with the thrust of the reviewers comments and will amend the manuscript to make these points more explicitly. He/she is indeed correct that we hope that our study can show a way that modelling tools with adequate complexity can be used in the future alongside in situ techniques to further our understanding of iron cycling and speciation in the ocean. Our goal was to highlight a means by which such tests could be performed in global ocean models, thus permitted them to be compared/assessed under more realistic physical forcing that idealised experiments.

The study also presents an illustration of how dissolved iron speciation might respond to future environmental changes. The main conclusion here is that the presumably highly-bioavailable Fe(II) will become more abundant as the ocean acidifies, which the authors claim will provide more iron to phytoplankton. I am somewhat confused by this, in that I would have thought that this would also increase the scavenging rate by sinking particles as the Fe(II) is re-oxidized to non-ligand bound Fe(III), which might lead to less total dFe in the water column, and in fact reduce the availability of Fe, particularly if ligand-bound Fe is in fact fairly accessible to phytoplankton? Whether this is correct or not, I think it deserves comment.

> Firstly, it is worth us mentioning that the application of our model to the question of how climate change and/or acidification might impact Fe speciation was an illustration of how the modelling approach we describe can be applied to investigate pertinent questions. Turning to the results at 2100, the 'amount' of dFe present at Fe(II) indeed increases markedly by 2100. This is due to the impact of lower pH on Fe(II) oxidation rates, thus the conversion of Fe(II) to Fe(III) due to oxidation as a prelude to scavenging/complexation by organic ligands is reduced.

Aside from the effects of climate change and acidification on Fe speciation, the impact on bioavailability will be highly sensitive to the assumptions related to what precise Fe species are 'bioavailable' (as we state in the text). If phytoplankton access ligand bound Fe as well as free inorganic Fe (which mostly Fe(II)), then bioavailable Fe changes little. However there is a large increase for those species who are obliged to access free inorganic (i.e. uncomplexed Fe) due to Fe(II) making up a larger fraction of the total dFe pool by 2100. The reviewer is correct to note that it appears that ligand bound Fe is likely bioavailable to most phytoplankton, but for those phytoplankton species, there is a cost associated with the direct uptake of organically bound Fe rather than free inorganic Fe. What we are speculating is that future increases in the proportion of the dFe present as Fe(II) (due to pH decreases) have the potential to 'shift the balance' between inorganic vs organically complexed Fe such that it may be less advantageous to make the cellular investment in organic Fe uptake in the future ocean. We will amend the paper to make this point clearer.

In general, I would think that the authors should not present the speciation model here as a necessary, or even generally-desirable inclusion for ocean biogeochemistry models at this point, as it seems to me that the parameterization still needs better observations in order to verify its applicability. As such, I feel the most important part of the paper is section 5, which could be expanded to more explicitly emphasize the observations needed to improve our understanding of speciation and bioavailability. This is not meant to take away from the value of the work, which is certainly a useful contribution and one which I would hope will spur further quantitative investigation into iron speciation.

> We understand and acknowledge the reviewers suggestions. We are, of course, not saying every ocean biogeochemical model must include these aspects, but that our approach can provide a means for assessing hypotheses regarding Fe speciation and cycling in a three-dimensional and not only in simplified/idealised settings.

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Some specific comments.
- Abstract, Line 6: I would suggest adding text to the effect of: . . .simplified in such OGCBMs ’due to gaps in understanding and’ to avoid high computational cost. . .

> Acknowledged and addressed

- Abstract, Lines 9-11: The model makes predictions based on the assumptions which go in. I would suggest rewriting the sentence here as something like: We construct an Fe speciation model based on hypothesized relationships to environmental parameters (temperature, light, oxygen and pH) and some assumptions regarding Fe binding ligand strengths and distributions.

> Acknowledged and addressed

- I think the abstract should also include a list of the most significant hurdles to improving the parameterization, according to the authors - what data are most needed, given their insight into the sensitivities of iron speciation?

> Acknowledged and addressed

- Page 2777: Given the importance of bioavailability to the entire premise here, I would personally appreciate a bit more background on what is known, and how important this might really be (or not). What lines of evidence are available to show that iron speciation impacts its uptake by phytoplankton? How well has this been generalized across phytoplankton groups?

> Acknowledged and addressed, we will provide some details on what is known and hypothesised regarding which species of Fe are bioavailable and the mechanisms thought to be employed by the phytoplankton to gain access to these different Fe pools.

- I would find it helpful to have a table listing all the variables and their full names, and a flow-chart figure showing the various iron pools and the flow between them.

> Acknowledged and addressed

- I had a hard time understanding the description of model experiments (3.4). Perhaps it would be clearer if the experiments were simply listed in terms of their initial conditions, boundary conditions, and integration time. If the authors are mixing initial conditions of physical circulations and biogeochemistry from different spinups, this should be explained clearly. As it stands I have a hard time figuring out exactly what the simulations were.

> Acknowledged and addressed

- Page 2777. The main paragraph discusses how Fe bioavailabiilty depends on iron speciation. As a non-expert in this, I would really appreciate some more detail on the observational background for what forms of iron are accessible and which are not. Also, I would not say that dFe treatments are very simple (line 27) in other models - they often have a number of ad hoc equations and arbitrary functions to achieve the desired result.

> Acknowledged and addressed, as mentioned above, we will add detail on what is known about

which species of Fe are bioavailable and the mechanisms employed.

- Page 2779. Methodologically, the comparison to the calculation of inorganic carbon speciation is reasonable. However, there’s a big difference with iron speciation: DIC speciation is very well understood, whereas iron speciation remains full of mysteries.

> The reviewer is correct here, although we were using DIC speciation as an analogue to how equilibrium solutions can be used to account for complex chemical speciation. Nevertheless, the reviewer is correct that the processes behind DIC speciation are much better understood!

- Equation 3. k_ok should be k_ox.

> Acknowledged and addressed

- Page 2782, line 13. How ’identical’? Bitwise reproduction? Or just very similar? Also, I am confused about the terminology ’analytically’ vs ’iteratively’ on this and the next page, which appears to be inconsistent. By iteratively, you mean a numerical solution? If so, what does ’the analytical solution . . .was solved iteratively’ mean? (p 2782, line 20)

> In our solution of the analytical equations we did not use the explicit expression for the roots of a third order polynomial, but instead proceeded iteratively, as this is much less costly in terms of computations, a consideration that is important in 3-d modelling. The solution is therefore not exact, but only within a certain given tolerance. The reproduction is therefore not bitwise; however the resulting difference is insignificant for the biogeochemical questions that we want to address.

- Equation 17. It looks like this equation might have a typo - the coefficient for Tk seems too large?

> We thank the reviewer for their keen eyes! The typo has been amended.

- Bioavailable Fe (p 2786, line 23). I think it should be explained why Fe(III)Ls is bioavailable, but the more weakly bound Fe(III)WLw is not. Presumably you are assuming that Ls are siderophiles of microbial origin, designed to facilitate uptake?

> Acknowledged and addressed

- I would recommend changing the notation of ’proportion’ of Fe(II), and similar, from pFe(II) to perhaps the ’fraction’ fFe(II). Calling it pFe(II) could make a reader expect that this is the negative log of the Fe(II) concentration, analogous to pH.

> Acknowledged and addressed

- Importance of seasonality, p 2787. The modelled seasonal changes are interesting, but are they real? Can they be backed up with some observations?

> Not as of yet (to our knowledge), except perhaps in the fact that observed Fe(II) shows marked variability in response to environmental changes. We would suggest that parallel to this observed variability in space, there could also be substantial variability in Fe speciation on seasonal and sub-seasonal time-scales.

- Page 2788. Lines 15-16. This does not sound like particularly good agreement to me, given that even the ranges differ by a factor of more than two. I would suggest that comparisons such as these (and other locations in the text citing unquantified ’good agreement’) be removed. I would suggest figures, tables, or correlation coefficients between observed and modeled values be provided instead.

> At this stage, and given the high variability in Fe(II) on short time and space scales, we decided against direct 'point by point' comparison between our coarser resolution model output with observations (especially as errors in other aspects of the model, e.g., resolution, scales of environmental forcing etc may not agree with point measures). Hopefully with more and more Fe(II) measurements being made under the auspices of the GEOTRACES programme such a comparison could be possible in the future. On the other hand, we agree with the reviewer's comment regarding how we report the model results. We aimed to show that our model showed (aside from Hansard's data in the Pacific) a good general agreement in terms of trends.

- Figure 4a shows only minor departures from 1, except in coastal regions. Does this mean this is actually a very small effect, except in the green coastal regions?

> Not exactly, it means that in off shore waters most of all of the dFe pool is deemed bioavailable due to the fact that low dFe concentrations mean all ligands are saturated and thus when we assume FeLS as part of the bFe pool bFe/dFe is very close to 1. In coastal waters dFe concentrations are much higher in total, so much of the Fe is lost from bioavailable forms. Nevertheless, although fbFe is low in costal waters, high overall dFe results in high absolute levels of bFe.

- Figure 5. Do the authors really think it’s likely that the ligand-bound iron is not accessible? I think it’s fine to show this, but if so perhaps the authors could explain more thoroughly why.

> Clearly, its seems that both ligand bound and free inorganic Fe is nominally 'available' to most phytoplankton (but not all). The idea behind this figure and the associated experiment was to examine how assumptions about which Fe species made up the bFe pool (perhaps for different phytoplankton species) impact upon on the amount of bFe available and thus potential Fe limitation. It is interesting to us as it shows that in some areas, free inorganic Fe can provide a lot of bFe, which would imply that access to organically complexed Fe need not be ubiquitous. We have added for detail on the rationale for these experiments.

- Figure 7. Are these measured profiles in the same place as the model profile? Why is there so much variability in measured Fe(II) over such a short distance? Is this typical? Some comment about this would be helpful.

> The profiles are indeed very close, as we state in the figure legend, profile 8-4 is at 47° 35.852' N 165° 58.760' E and 8-14 is at 47° 51.220' N 166° 15.244' E. Evidently high frequency variability in Fe(II) as a response to parallel changes to the environmental conditions is a key feature. This is why we decided not to make a point by point comparison between the model and the observations since issues with model resolution and perhaps incorrect environmental forcings (e.g., temperature, irradiance) that are not errors in our Fe model per se may complicate such a comparison. Therefore we examined the general trends and magnitudes in our modelled Fe(II) field.

- The references by Boye seem to be missing.

> Acknowledged and addressed