

## ***Interactive comment on “Anoxic iron and sulphur cycling in the cGENIE.muffin Earth system model (v0.9.16)” by Sebastiaan J. van de Velde et al.***

### **Anonymous Referee #1**

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van de Velde et al. titled “Anoxic iron and sulfur cycling in the cGENIE.muffin Earth system model (v0.9.16)” present an addition to the cGENIE model and incorporate more substantial iron and sulfur cycles into the framework.

The authors highlight the importance and need of this work nicely and their manuscript offers a breakdown of the model that is clear and well written.

I support the ultimate publication of this manuscript, however I recommend the authors further explain the reasoning behind these decisions and expand upon the following points:

Why only anoxic cycling? The oxic cycle of these two elements is fundamental to modern day biogeochemical systems and likely systems that have areas that are oxic

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but the deep ocean is predominantly anoxic. This then leads me to two questions. How has the model been calibrated to recreate realistically expected changes in the iron and sulfur system. Their assumption that they can recreate anoxic analogues has been discussed in length in Chapter 4 however. Secondly, how does the model transition between oxic and anoxic iron and sulfur cycles, I can't seem to see that distinction? For example, in the early Phanerozoic and Neoproterozoic with regions of the shelf being oxic. Also if these new anoxic fluxes are included in a present-day Genie run, can it still recreate present day?

Why have you not attempted to couple the cycles together, surely simple tests can be included to see if the premise of justification of the model is correct? (i.e. a simple investigation of how the P cycle is effected by this new iron cycle?). I think a simple check is required as it is the reason this model has been built, based on your introduction.

Page10: The authors write “regardless of the relative availability of different electron acceptors, in any one depth interval in the ocean, exactly the same proportion of organic matter will be degraded”. This means that regardless of the redox state of the ocean, the same amount of organic carbon will ultimately have to be produced and buried as to preserve the cascade of rigid degradation fluxes? Is this correct?

Page18 Lines13-17: I understand striving for simplicity however I believe the inclusion of a gypsum burial term is crucial to interpretations made from this model. As the formation and development of euxinia is traditionally dependant/associated with increases in sulfate input, it seems logical to suggest gypsum would become more quantitative post GOE (which is also seen within the rock record). Therefore, this assumption is only really adequate for pre-~2.5 Ga?

Page22 Lines 1-7: A ‘closed’ run of the model is a fair assumption but surely this is at odds with understanding the feedbacks of the Fe and S cycles on the overall systems dynamics? Likely restricting the interpretation and comparison to ancient analogues that you suggest is enough to test the model. For example, if feedbacks in the model

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that will be introduced in future work meaning that the model cannot recreate the analogues then this is a problem.

Section 4.1: You initialise the model at a ratio of 2:1 for Fe and S. Which is fair under modern conditions but when considering the Precambrian Earth which you are here. The high S input flux to maintain this ratio with the elevated hydrothermal flux is presumably unreasonable based on the dominance of ferruginous conditions in the Precambrian. Surely the fluxes of non-sulfidized iron minerals should allow/produce a non- 2:1 burial of Fe:S during this interval?

Page22 Line 30: Why are Fe carbonates negligible? If you are recreating a largely anoxic ferruginous Precambrian ocean, surely a decent amount of  $\text{FeCO}_3$  should precipitate? What is limiting its precipitation? I understand the work by Tosca and co. but I struggle to see how it is restricted in this model as it is essentially based on iron and carbonate concentration? This could surely be an interesting finding, or simply a consequence of your high sulfate input? This issue leads the use of the model to compare to, for example iron speciation data, to not be adequate as many sediments in the Precambrian have Fe carbonates being a large proportion of the reactive iron. Hopefully the sedimentary model can correct this, but should be noted.

Page23: These fluxes relative to each other may well be a consequence of your elevated sulfate input relative to Fe and attempt to achieve a 2:1 ratio. This strict 2:1 ratio as far as I am aware is due to your exclusion of a gypsum burial flux, however a greater justification of this 2:1 ratio or testing different ratios is required.

Below are my minor corrections that I believe the manuscript will benefit from.

Page1 Line 4: I agree that these cycles impacted other elemental cycles such as phosphorus mentioned here. As the model is not fully integrated into the cGENIE model, would it be fair to add to the title "... in the cGENIE.muffin Earth system model framework...?"

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Page1 Line 16: You say that you present patterns of concentrations of iron and its isotopes, why not sulfur concentrations and isotopes? However in the abstract it is said that this work has been done, so why hasn't it been shown?

Page3 Line2: Poulton et al., 2005, should be Poulton and Canfield, 2005? – same for page4 Line29.

Throughout the text Poulton et al., 2004a is referenced. Your reference list only has one reference that fits Poulton et al., 2004, so the “a” needs to be removed from the citations.

Page6 Line 1-2: following Vervoort et al. (in review). This means that the wind and albedo methods are not currently published so I recommend it is added here for completeness.

Equations throughout: Are these yearly fluxes? Please clarify in the text. e.g.  $\tau_{\text{bio}}=63.4$  days. When this value is used in equation 1, is it input as 63.4 or (63.4/365) to convert to years? This issue is continued throughout. What resolution is the model running at, please clarify somewhere in text.

Page7 Line 26: Is this value of 0.66 fixed for all model runs? I would have thought this value would have varied at different points in geological time? Would be good to test this simply by varying between set values or adding a discussion on where this value comes from and why it is 0.66.

Page8: First time I read through this: I might have not understood it, in which case, it should be clarified, but is the export of organic carbon not related to the concentration of oxygen? As with the Precambrian you can have the same euphotic zone thickness but substantially different oxygen concentrations. After further reading however: This is clarified later, on page 9. Why is it worded like the above originally on page 8? All reads a bit contradictory. The method of remineralisation should be cleared up.

Page8 Line 12: “key interactions the key interactions” text repeated.

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Page9 Equations: I don't see a difference between fDSR and fMG? Should there be? If so/if not, why?

Page11 Line 5: What is the concentration at which pyrite precipitation can occur? Also, in equation R9 of table 2, the pyrite precipitation doesn't seem to be dependent on iron concentrations and in the text, it says it is? Or at least, it is not discussed what the concentration of FeSp is until much later on, please define earlier to prevent hunting for the definition.

Page11 Line 10-15: Agreed that these four phases essentially make the iron redox proxy but greenalite is technically converted to magnetite or is at least heavily hypothesised to be. So, it should be clarified that it is not greenalite that is considered but magnetite.

Page12 Equation 11: Again, units seem inconsistent with the fluxes. Here,  $k_{scav}$  is equal to  $\text{mol}^{-1}\text{m}^2\text{h}^{-1}$ . Why are units now expressed in hours and not days or years? Go through full manuscript and ensure consistency or at least clarify what is put into the equation and what the flux units are.

Page12 Equation 12: What is  $L_{free}$ ? And as I am reading it, you seem to be doubling counting the  $L_{total}$  through this method as  $L_{ligand}$  is bound to ligand? OR is  $L_{free}$ , ligand that is not associated with Fe? Make this clear.

Page13 Line 8: "scavenged by POC"?

Page14 Line 25: A maximum rate of...?

Page16 Line 8: Independent of pH. This is a fair assumption for the current submission, however for further work it would be interesting to explore the impact of pH.

Page22 Lines 19-21: You say that these conditions are not meant to recreate any particular interval of Earth history but to justify initialising the model at 0.1PAL O<sub>2</sub> and 50% PO<sub>4</sub> input, you say this is done in order to simulate Precambrian conditions. I realise Archean vs. Proterozoic is significantly different, but you are clearly setting the

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model for mid-Proterozoic conditions so why hide it in this sentence? Need to be more clear throughout the text, when in the Precambrian you are referring to.

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Interactive comment on Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2020-312>, 2020.

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