

Interactive comment on “An inverse method to relate organic carbon reactivity to isotope composition from serial oxidation” by Jordon D. Hemingway et al.

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Prof. Boudreau,

We thank you for your helpful concerns and feedback on our manuscript. Below you will find our response to your two reservations, along with some corresponding changes that we will make to the text once the discussion period ends. Because your two reservations were somewhat broad and open-ended, we have attempted to address them and explain our position and reasoning as best as possible. However, we invite further dialogue if anything is unclear or if you believe more explanation is required. We thank you again for your time and feedback.

C1

Hemingway et al. have offered an inverse model to extract the reactivity of organic matter (OM) and relate it to the isotopic composition via data obtained from a record of thermal decomposition of that organic matter. This is a technique that has been used with respect to petroleum formation and there exists published literature for that application. The present paper hopes to extend the method to the degradation of OM sampled in low-temperature aquatic systems.

The mathematics of the model appear to be solid (better than my own efforts in this area), including the use of a Lagrange multiplier to add constraints to the model solution. I do not think that the paper can be faulted on this account; nevertheless, I have two strong reservations.

Firstly, microbial enzymatic degradation of OM is not the same process as thermal decomposition. Microbes use enzymes to breakdown OM in order to increase the rate of this reaction. According to a very broad interpretation of transition-state theory, that result is obtained by altering the decay (reaction) mechanism so as to lower the activation energy of the reaction. The authors' thermal method is also based on activation energy, but on the activation energy for a thermal decomposition reaction. Thus, the microbial and the thermal activation energies are not guaranteed to be the same or even comparable. Assigning the thermally derived results to the microbial situation is not, at this time, experimentally justified.

RE: We thank the reviewer for allowing us to clarify this issue. While other studies have begun to compare OM thermal E values to those for microbial decay, both using laboratory incubations (e.g. Leifeld and von Lützow, 2014) as well as long-term bare fallow soil experiments (e.g. Barré et al., 2016), this has never been our intention in the present study. At no point do we imply that E distributions determined using the thermal analysis described here are identical, or even comparable, to those that would be obtained by serial oxidation by microbial respiration (e.g. Mahmoudi et al., 2017). In fact, to extend the reviewer's point, we expect that every oxidation pathway (microbial

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respiration, thermal analysis, uv light, chemical hydrolysis, etc.) will involve a unique transition state intermediate and will therefore likely result in a different E distribution. For example, lignin is highly thermally recalcitrant (Williams et al., 2014) yet degrades rapidly under uv light (Spencer et al., 2009).

Rather, here we present thermally derived E as a proxy for the range of the strength of chemical bonds experienced by carbon atoms within a sample. We emphasize that this is simply a method to separate a complex OM mixture along a particular lability "axis" (i.e. thermal lability) and measure the isotope composition at multiple points along that "axis." Thermally derived E , along with the corresponding isotope distributions, can then be directly compared across a sample set in order to infer differences in the molecular and isotope compositions between samples. For example, the observation that our test sample approaches an Fm value of 0 at $E > 200 \text{ kJ mol}^{-1}$ implies that this material is derived from OM-rich bedrock (see P21, L3-5), but says nothing about microbial recalcitrance (in fact, it is possible that rock-derived OM is highly bioavailable; see Petsch et al., 2001).

To emphasize this point, we will add and/or modify the following lines within the text:

1. (P1, L2-13). Throughout the abstract, we will add "thermal" before each use of the word "reactivity" in order to clarify that E values calculated here apply only to thermal analysis.

2.(P2, L33). We will add the following paragraphs:

"We note that the modeling approach developed here is broadly applicable to any serial oxidation technique, although the resulting E distributions will differ depending on oxidation pathway. For example, aromatic compounds such as lignin have been shown to be highly photoreactive (Spencer et al., 2009) despite their relatively high thermal recalcitrance (Williams et al., 2014) and will likely be described by lower E values when oxidized with uv light relative to PRO analysis. Here, we choose RPO because analysis is rapid (≈ 3 hours per sample), requires little material (≈ 150 to $250 \mu\text{g C}$),

C3

contains minimal preparation steps, and results in small kinetic isotope fractionation (Hemingway et al., 2017).

We therefore treat E as a proxy for OC chemical structure and emphasize that thermal reactivity is not equivalent to microbial reactivity in the environment (Leifeld and von Lützow, 2014). Rather, by comparing E profiles and corresponding isotope compositions across environmental samples or experimental conditions (e.g. before and after microbial degradation), our method provides a framework to probe how, if at all, OC source and turnover time (as measured by $\delta^{13}\text{C}$ and Fm) is related to its chemical composition (as predicted by thermal E distributions)."

Secondly, only two samples were tested with the method, and one, OM from a marine sediment, failed the test of the model assumptions. I am unaware of any other papers that have applied this technique to aquatic "low-temperature" sediments. That represents meager testing of the applicability of the model. The low-temperature geochemical community does not at this stage know if the method is useful, and the theory has significantly overstepped the acceptance of the methodology itself.

RE: Again, we thank the reviewer for raising this concern. However, we disagree with the reviewer's interpretation that the marine sediment OM sample "failed the test of the model assumptions." Rather, it is the analysis of OM *combined with* inorganic carbon (IC) that failed the model assumptions. This distinction is critical. The results from this sample (e.g. Fig. 4d) emphasize the need to decarbonate sediment samples prior to RPO analysis. Because decarbonation likely alters OM composition to some degree, there exists longstanding discussion on this topic in the organic geochemistry literature at large and the RPO literature specifically (Plante et al., 2013). By including this sample within the present study, we make a kinetic argument in favor of decarbonation – that is, we show that IC decay is mass-dependent in the presence of OM and therefore does not follow first-order kinetics. This result does not imply that OM decay from this sample fails the model assumptions.

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To the reviewer's larger point, we agree that additional samples would aid in solidifying the utility of the method in describing "low-temperature" OM. However, we believe that this is beyond the scope of this technical manuscript. As presented, central focus of this manuscript is the mathematical derivation of the inverse distributed activation energy model. To include additional samples, and to properly discuss and interpret their results within a geochemical context, would lengthen the manuscript considerably and, in our opinion, would detract from this central focus.

We note that this exact concern is the focus of a companion manuscript that is currently in preparation. In that publication, we subject dozens of samples to the model treatment presented here and interpret the environmental factors controlling differences in E distributions. Combining these two manuscripts would result in the mathematical treatment presented here being relegated to a supplemental discussion (as was the case for the original submission of our companion manuscript, to which those reviewers and editor suggested we separate the mathematical treatment). We believe that the mathematics and theory contain adequate nuance and require sufficient discussion to warrant this technical manuscript, rather than being relegated to a supplemental discussion. Thus, we believe that inclusion of multiple samples (and the corresponding geochemical discussion) is beyond the scope of this manuscript.

In order to emphasize that the results presented in this manuscript are preliminary (i.e. based on a single sample) and form a theoretical basis for future study, we will add and/or modify the following text:

P16, L11: "While further study is required to assess the general applicability of this technique, we propose $p(0, E)$ as a novel proxy to describe the distribution of carbon bond strength."

P17 L3-4: "We therefore propose combining $p(0, E)$ with serial oxidation isotope measurements to test the effects of..." By removing "is an ideal method to," this should remove any perceived speculation.

C5

P21 L8: "This result provides initial evidence for the utility of RPO E vs. isotope relationships..." Again, this rephrasing should remove any speculation, and more explicitly acknowledges that the results in the manuscript are indeed initial.

P21 L19: "We suggest that E vs. isotope relationships can provide new insight into understanding the compositional controls on OC source and residence time, although we note that further study is required in order to test the general applicability of this result."

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C6