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Interactive comment

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

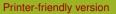
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This manuscript describes a mathematical technique for the analysis of serial oxidation results (i.e., thermograms), which effectively allows one to convert the temperature of oxidation on the x-axis of a thermogram to an activation energy (also on the x-axis) for the oxidation of organic matter occurring at that temperature. When combined with isotopic measurements of the CO2 being produced by the oxidation, the authors suggest that this can be used to infer information about the reactivity of organic matter in sediments.

I think that the results presented here for the one sample that was analyzed are in-





teresting and provide intriguing results. Some of the proposed uses of this approach (e.g., p. 17 line 4 p. 21 line 8) may indeed turn out to be correct, but these conclusions may also be a bit premature based on the information presented here.

Related to this I am concerned about the "validation" of the approach based on the analysis of a single suspended sediment sample, in part because little is presented in this analysis to independently verify the results. It seems to me that one way to verify this approach would involve taking well-defined organic compounds whose activation energy for oxidation is either known or can be estimated, subjecting them to ramped pyrolysis/oxidation and seeing if the activation energies that the analysis of these thermograms gives back agrees with these values. To be honest, I'm not sure how well-known or easy it is to obtain the activation energy for the oxidation of single organic compounds. However, a quick Google search of "activation energy oxidation of organic compounds" yielded what looked like a number of promising hits.

At the same time, I think there is actually some data in the literature that could be used in some simple, albeit qualitative, verification of the results discussed in section 5.3. For example, Westrich and Berner (1988) suggest, at least in the coastal sediments they studied, that organic matter which is less susceptible to decomposition may have a higher activation energy for decomposition (as one might infer from the results here in section 5.3). Similar observation are also presented in Middelburg et al. (1996). Although I'm not familiar with the papers cited on p. 12 lines 17-18, I also wonder whether information in these papers might be useful here as well.

In general, the presentation of the method is rather dense in places and there are several places where I found things confusing and/or where more information about the mathematical derivation is needed. Note that (x,y) refers to page x, line y.

1. Starting near the bottom of p. 6 (line 23) "thermograms" and "mass-normalized decay rates" seemed to be used somewhat interchangeably (also see the captions for Fig. 2-4). However, there was not a clear explanation (at least that I could find) about

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why this is the case. This may need to be clarified. Addressing this question should also help explain why the y-axes in Figs. 2, 3 and 4(b) all have different units.

2. (9, 20) - It was not clear which model is being referred to here by "our" model.

3. (10,19) – What are "short-range-order" minerals?

4. (10, 22) – Is there are reason why here and in Fig. 4 the x-axis has changed from temperature to time?

5. (13, 6) – Should it say "Eq. (30) can be solved for p by multiplying ...."?

6. (13, 8) - How exactly do you find the solution (i.e., the p vector) that satisfies Eq. (32)?

7. (14, 7-9) – How exactly does the method of Miura and Maki (1998) differ from that used here?

8. (14, 21-22) – If a higher  $\omega$  value results in a broader p(0,E) how can it also have "no effect on the shape of the distribution"? What am I missing?

9. (15, 3) – What are the dimensions of R, and do the bold 0's in the description of the first and last rows of this matrix mean that all of the other values in the row are 0? If this is so, other may also not be familiar with this notation, and I think this could be made a little clearer.

10. (15, 5) – What is meant here by "solving the constrained least squares"? I kept thinking this was similar in someway to how Eq. (32) was used to solve for the p vector, but Eq. (39) just didn't make sense to me in that way. Again, am I missing something here?

11. It's also not clear to me how Fig. 6 was generated, and the interpretation of this figure starting on line 7, p. 15.

12. (16,15) – What exactly is meant by "diversify the distribution of chemical bonds"?

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13. The general shape of the thermogram in Fig. 2 looks awfully similar to the p(0,E) distribution in Fig. 7. Does that means that activation energy scales linearly (more or less) with temperature of pyrolysis? In general that makes intuitive sense, and this is also discussed here briefly on p. 9, line 15. It will be interesting to see if this is a general trend observed across a broader range of samples.

References cited

Middelburg, J. J., G. Klaver, J. Nieuwenhuize, A. Wilemake, W. de Hass, T. Vlug, and J. F. W. A. van der Nat. 1996. Organic matter mineralization in intertidal sediments along an estuarine gradient. Mar. Ecol. Prog. Ser. 132, 157-168.

Westrich, J. T., and R. A. Berner. 1988. The effect of temperature on rates of sulfate reduction in marine sediments. Geomicrobiol. J. 6, 99-117.

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