**MS:** *Advancing on large-scale trends of apparent organic matter reactivity in marine sediments and patterns of benthic carbon transformation*

Freitas et al. present an integrated geochemical analysis of organic matter decomposition kinetics from a variety of marine environments, using (in part) a continuum decay model, created by Rutherford Aris and his coworkers and first employed by Boudreau and Ruddick (1991) – BR91, hereafter – in marine sediments.  The present paper aims to better constrain the range of the values of the parameters in the continuum model by taking into account associated porewater data; the hope is to obtain a better understanding of the environmental controls on the decay and preservation of organic matter (OM) as a consequence.  While the work presented here does constitute significant progress towards the authors' aim, the presentation is sufficiently muddled in places that it makes it difficult to evaluate the full extent of their progress, as I will explain below.

A - The model presentation sections 3.2.1.2 and 3.2.1.3 are difficult to understand and, as a consequence, could be incorrect.  I highlight the following points in the order they appear in the text:

    a) Equation (6), which is entirely equivalent to Eq (39B) of BR91, is valid only in non-bioturbated sediments; in that situation, the POC at any depth is only a function of parameters "a" and $v$, as the sedimentation rate is used to convert depth into age.  In bioturbated sediments (constant mixing and porosity), the appropriate form for POC (G) is given by Eq (49) of BR91,

$$G(x) = \int_0^\infty \frac{g(k, 0)}{\left(1 - \frac{\mu}{\sigma} e^{(\mu-\sigma)L}\right)} \left(e^{\mu x} - \frac{\mu}{\sigma} e^{(\mu-\sigma)L} e^{\sigma x}\right) dk \qquad (49)$$

which cannot be reduced to a form like Eq (6) of the present paper.  There is no caveat with regard to Eq (6) in this paper.  This makes me wonder if ascribing all OM reactivity to parameters "a" and $v$ is really correct if the sediment is bioturbated.  That may very well explain the lack of correlation later described in Figure 6 of the present paper.  That point has not been considered.

    b) To deal with bioturbated sediments, the authors bin the OM continuum by introducing $F_i$, which is the fraction of the total OM having reactivity between $k_j$ and $k_j + dk_j$.  Passing over the notational oddness of this "definition", I would have expected the authors to state this mathematically as something like

$$F_i = \frac{1}{POC(0)} \int_{k_j}^{k_j+dk_j} om(k,0)dk$$

(A)

Instead, the authors state (line 318-321) that $F_i$ is calculated by "integrating the initial probability density function (Eq. 4) … at time zero with

$$k_i = \frac{k_{j+1}}{2dk_j}$$

(10)

This confuses me to no end. Trivially, Eq (5) is the initial PDF, not Eq (4). More importantly, $k_i$ so defined in unitless, whereas it must have units of inverse time. To add to that confusion, the authors introduce a definition of $F_i$ via Eq (11),

$$F_i = F(k_j,0) - F(k_{j-1},0)$$

(11)

without ever telling us what $F(k_j,0)$ and $F(k_{j-1},0)$ represent or their mathematical definitions. Similarly, what are $f(k_1,0)$ and $f(k_{200},0)$ in Eqs (12) and (13)?

c) The symbols used in this manuscript are non-systematic, non-intuitive and idiosyncratic. The first example is the use of Greek letter $\tau$ for the Gamma function. The Gamma function is a well-known function in mathematics with symbol $\Gamma(x)$, just like sine is $\sin(x)$ and the exponential is $e^{-x}$. Changing $\Gamma$ is like changing e to another letter of the alphabet; simply not done. Another example is the use of multiple symbols for OM concentration, e.g., in some places POC(x), in some places G, as well as $C_i$ is Eq (1). F is used for fluxes on lines 486-490, but also the OM fraction, as note above; J is used for fluxes in Eq (27). We have lower case f with different meanings in Eqs (8)-(9) and (12)-(13). This might lead to a bit of confusion.

B - On another point, the authors spend some time establishing the need for their approach by pointing out some shortcomings of the method in BR91. Specifically, the BR91 approach is "compromised" by loss of sediment at the top during coring, by assuming steady state over long periods in slope and coastal sediments, and by the supposed non-uniqueness of a and $\nu$ values (Meister et al., 2013). Let's consider each of these three points.

a) Firstly, the method in BR91 does not require the concentration of OM at the sediment-water interface (SWI). It uses any data available and requires none at any specific depth. When sediment is lost, and the top of the core is erroneously set to depth zero. That depth error is translated into an error tin the

ages of the samples in the core.  The authors seem to think that only multicores can be used to avoid this.  While piston cores are problematic, properly collected gravity cores are far less prone to this problem, and that represents most of the data in BR91.

b) It is one thing to say that a non-steady state will affect calculated a and $v$ values and quite another to specifically show that the profiles used in BR91 are so afflicted by such effects that they cannot be trusted.  The authors have not demonstrated that this is a problem in BR91.  The cores used by the authors also have non-steady state effects (I can guarantee that), but they do not question their own use of a steady state model.

c) The authors state that Meister et al. (2013) show that different a and $v$ pairs can produce the same OM profiles.  My reading of that paper is that Meister et al. (2013) show nothing of the sort.  These latter authors show that the depth of the sulfate-methane transition zone (SMT) is not unique to a and $v$ pairs.  That in no way shows that the associated POC profiles are the same; in fact, Meister et al. (2013) display no POC profiles whatsoever.

To shore up their claim that simply fitting Eq (6) to their POC data is inadequate ("compromised"), the authors create a synthetic data profile and then demonstrate that various curves generated by Eq (6) with different a and $v$ values resemble the data, i.e., their Fig. S1.  Like the present paper, BR91 use a statistical fitting technique; if uniqueness was a problem, the BR91 approach would have failed to produce fits with high $R^2$ values, i.e., $R^2 > 0.8$ in every case, non-uniqueness does not seem to be a problem.

What the authors have failed to do is: 1) to show that fitting Eq (6) to their own data below the mixed zone of sediments gives statistically different a and $v$ values than their method that takes into account sulfate and methane profiles.  2) Show that the BR91 a and $v$ values as a group are demonstrably different than the values generated with their new method.  In fact, the opposite is true, as they state unequivocally in the conclusions (lines 900-901), their results for the $v$ parameter "corroborate previous findings (Arndt et al., 2013; Boudreau and Ruddick, 1991) that the RCM parameter $v$ is globally relatively constant ($v$ = 0.1–0.2)."  As for the a parameter, they state that based "on inverse model results, we narrowed the most plausible range of $a$ to $10^0$–$10^4$ years."  Reproduced below is Table 1 of the results in BR91.  Note that the 7th column reports the a values.  These values are in the range advocated by the present authors.

TABLE 1

*Continuum model fits (eq 39) to selected organic matter profiles in histotical layer of marine sediments*

| Core | Location | ω (cm kyr⁻¹) | Source | $\nu$ | Apparent Order | a (yr) | r* |
|------|----------|--------------|--------|-------|----------------|--------|-----|
| FOAM | Long Island Sound | 200 | Goldhaber and others (1977) and Westrich (1983) | 0.152 | 7.57 | 4.2 | 0.930 |
| SCR-44 | Santa Cruz Basin | 60 | Shaw (ms) | 0.202 | 5.95 | 70.4 | 0.929 |
| BX-6 | Peru Margin | 230 | Froelich and others (1988) | 0.278 | 4.60 | 22.5 | 0.929 |
| PC2 & TW2 | Peru Margin | 230 | Froelich and others (1988) | 0.052 | 20.2 | 0.16 | 0.937 |
| 10127 | Central Equatorial Pacific | 0.2 | Müller and Mangini (1980) | 0.139 | 8.19 | 14,000 | 0.926 |
| 10141&2 | same | 1.2 | Müller and Mangini (1980) | 0.193 | 6.18 | 10,184 | 0.935 |
| 7706-41K | Peru Margin | 150 | Reimers (1982) | 0.910 | 2.10 | 141.3 | 0.974 |
| 7706-36 | Peru Margin | 40 | Reimers and Suess (1983) | 0.804 | 2.25 | 231.7 | 0.978 |
| DSDP 58 | North Philippine Sea | 2.0 | Wapples and Sloan (1980) | 1.080 | 1.93 | 20,224 | 0.917 |

*Correlation coefficient

It is not necessary for the present paper to advance demonstrably questionable claims about BR91 in order to justify the development and use of their method. They need to show actual mproved robustness of their method. And in situations where the abundant chemical data available to the authors is absent, then Eq (6) may be all one can do.

C – The authors keep referring to the parameter a as the apparent reactivity of the organic matter. In non-mixed sediment the ratio $\nu$/a is the apparent reactivity. And in mixed sediment, no study has established the form of the apparent reactivity. Maybe the authors need to attenuate their discussion to those facts.

D – Lines 754-771. The discussion on the dominance of various oxidants seems isolated from previous work by many other authors. As an example, I reproduce Table 3 from Boudreau et al. (1998. JMR) that reports exactly the same thing for a number of other sites. Again, perhaps this other data should inform your discussion? You might want to search for other documents of this type in past publications.

Table 3.  Percent of carbon oxidized by various oxidants at the CJGOFS sites assuming steady state and some other coastal and marginal sites available in the literature‡.

| Site† | $O_2$ | $NO_3^-$ | Mn(IV) | Fe | $SO_4^=$ | $CH_4$§ | Total¶ |
|---|---|---|---|---|---|---|---|
| 3 | 15.0 | 3.65 | 15.9 | 1.63 | 52.7 | 0.97 | 100.0 |
| 4 | 73.7 | 14.2 | 2.39 | 0.65 | 8.84 | 0.15 | 100.1 |
| 5 | 53.4 | 20.3 | 0.0 | 0.0 | 25.9 | 0.46 | 100.1 |
| $S_4$ | 13.6 | 3.2 | 0.0 | 32.1 | 51.1 | — | 100 |
| $S_6$ | 17.4 | 3.8 | 0.0 | 50.9 | 27.9 | — | 100 |
| $S_9$ | 3.6 | 5.7 | 90.7 | 0.0 | <1.0 | — | 100 |
| FP1 | 6.0 | 13.5 | — | — | 80.5* | — | 100 |
| FP2 | 9.4 | 23.5 | — | — | 67.1* | — | 100 |
| FP3 | 9.7 | 11.7 | — | — | 78.6* | — | 100 |
| FP4 | 13.6 | 14.8 | — | — | 71.6* | — | 100 |
| LIS1 | 8.1 | 18.8 | — | — | 73.1* | — | 100 |
| LIS2 | 3.3 | 14.1 | — | — | 82.6* | — | 100 |
| QP2 | 68.6− | 6.8− | 1.3− | 0.03− | 6.0− | — | 100 |
|  | 74.1 | 12.1 | 2.3 | 0.06 | 10.8 | — | 100 |