

Sedimentary organic matter preservation: an assessment and speculative synthesis

Authors' closing comments

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Writing this synthesis paper has been in many ways like rearing a difficult child. We began with only the germ of an idea, raised up a sparingly coordinated body on largely borrowed resources, and finished with misgivings, second thoughts and mixed reviews.

We agree with most of the previous critical comments (identified here by the author's name; other references occur in the listing for the synthesis paper). Robert Berner is correct that our 3-component diagenetic model (Fig. 13) for sedimentary organic matter degradation is oversimplified, as are all compartmentalized models for natural organic degradation. We also acknowledge that for mineral surface area to remain relatively constant through a sedimentation–erosion cycle, that metamorphosed sedimentary rock must weather back to clastic minerals with textures similar to those from which the recrystallized rocks were initially formed - a scenario that seems reasonable to us. The inconsistency that we referred to with respect to the multi-G model is not with the central idea that various natural organic materials can be separated usefully into different reactivity classes, but with the often-made assumption that these kinetic categories depend primarily on the structures of the organic substrates, rather than on their physical setting. Berner's comment that animal guts might be important sites for sorptive partitioning of organic substrates brings to mind the observa-

tion of L. Mayer and colleagues (pers. commun.) that some marine worms feeding on whole sediments appear to secrete organic surfactants which may release sorbed organic nutrients for assimilation. Maybe we geochemists could learn a lesson from worms and custom-design competing surfactants, which then could be used to gently desorb sedimentary organic matter for isolation and study.

Thomas Pedersen would prefer a more productive and less surficial treatment of organic matter preservation than we offer. This difference in perspective depends in part on whether an ultimate or direct explanation is sought. Whether preservation of extremely labile small organic molecules is more remarkable in sorbed vs. "unaltered organic matter" (presumably in particulate form) is difficult to decide. We now know that most organic matter reaches the ocean floor in fast-sinking particles which are then rapidly and extensively mineralized. Given these daunting odds, it may be that a labile biochemical has a higher probability of preservation if it escapes from the fire of a rapidly degrading organic particle onto the protective surface of a nearby mineral grain.

Glacially-related fluctuations of %OC in texturally-uniform sediments similar to those described by Pedersen also have been observed by J. Murray et al. (unpubl. data) in deposits from the western Mexican margin. Surface area and organic carbon measurements on these sediments indicate that they oscillate

between monolayer-equivalent loadings during interglacial times and 2–4 times higher organic loadings during glacial times. These fluctuations are between the types of “normal” and “organic-rich” marine deposits which we described (e.g. Fig. 1), and are not inconsistent with the sorptive protection model as presented. The extent to which organic carbon distributions in other sedimentary environments may support or contradict the sorptive model is difficult to assess without additional information on sediment surface areas and organic compositions.

Larry Mayer's point is well taken that metal oxyhydroxides could be more important as degradative catalysts or ephemeral sorbents, than as electron acceptors. His suggestion also seems reasonable that the low organic contents of many deltaic sediments might result in part from insufficient local production to supply monolayer-equivalent loadings to the rapidly depositing particles. All river-shelf systems where paired comparisons are currently possible, however, exhibit losses of particulate riverine organic matter that equal or exceed replacement by marine-derived material (Keil et al., submitted; L. Mayer, pers. commun.). Large losses of particulate riverine organic matter therefore contribute at least as substantially as any limitation of marine-derived input toward the low organic carbon loadings of these deltaic deposits.

The suggestion by Mayer and Henrichs that polymerization of closely-packed sorbed molecules could lead to increased organic binding and recalcitrance should be given more experimental attention. One simple test would be to gently dissolve mineral grains in sequences of increasingly older sediment to determine whether the released organic molecules are progressively larger, less soluble, and more resistant to biodegradation. This experiment is particularly feasible for carbonate particles which could be gently dissolved with minimal alteration of the released organic material. Macromolecules formed by in-situ “polymerization” also might carry structural imprints of the mineral surfaces on which they formed, and hence information about the mechanisms by which the “monomers” were initially bound and subsequently cross-linked.

Susan Henrichs' comments on multi-site binding helped us appreciate how a reasonably soluble organic molecule might nevertheless be strongly

sorbed. An implication of this scenario is that individual functional groups might have a strong effect on the partitioning behavior of large molecules. This insight might explain more clearly the almost universal pattern of selective enrichment of nitrogen-containing organic molecules in soils and sediments that was discussed in the synthesis paper. Since electrostatic interactions are more far-reaching than van der Waals attraction and many other binding forces, alkyl ammonium cations should be particularly effective for initially tethering and tenaciously holding organic molecules to negative charge centers on mineral surfaces. Amine anchoring may be especially effective during the critical initial period when recently solubilized organic molecules are susceptible to biodegradation unless rapidly sorbed. Strong binding via an alkyl ammonium “arm” may even explain the extreme resistance of β -alanine and γ -aminobutyric acid to degradation in the oxidized horizon of the MAP turbidite (Cowie et al., in press).

Henrichs' mathematical model provides a powerful new tool for describing desorption/reaction processes in any environment where organic molecules are partitioned between water and protective surfaces. This model demonstrates that sorbed organic substance must be either intrinsically refractory and/or strongly bound to a protective surface in order to have a high probability of being preserved. We concur that the high reactivity and low partition coefficients we reported (Keil et al., 1994c) for organic matter desorbed from a Washington coast sediment core are inconsistent with her mathematical model. As noted in our paper, and in Mayer's comment, seawater alone desorbs a smaller fraction (< 15%) of total sedimentary organic matter than distilled water and KCl. The mineralization rate of the released organic material, however, is usually as high as previously reported. Factors beyond those described in our paper, or incorporated in the kinetic model, must be involved. The main observation that “old” desorbed sedimentary organic material is remarkably labile once removed from the sedimentary milieu remains unchanged, and unexplained.

The thought that DOM, like trace metals, might be scavenged from particle-rich coastal seawater into marine sediments (Henrichs' comments) makes good sense and is one example of the many implications of sorptive organic matter. Following this train of

thought, sedimentary organic materials should exhibit molecular characteristics which favor sorption. Conversely, “old” dissolved organic matter in the deep ocean may be one of the best available models for structural features which inhibit both biodegradation and sorption. As Henrichs points out, many distribution patterns of sedimentary organic matter might be explained simply by reversible sorption of large organic molecules onto protective mineral surfaces, without bringing oxic degradation into play. We do not agree, however, with the suggestion that the sedimentary OC patterns we have observed in the MAP turbidite and off the Washington coast could result from sorptive partitioning alone. In both environments, bulk organic carbon exhibits strikingly parallel distributions with pollen grains (Figs. 10 and 12B), which are nondiffusive and stable for millions of years under reducing conditions. A severe degradation process not observed under reducing conditions still seems necessary.

This paper and the accompanying critiques have provided us and the commentators a rare opportunity

to share diverse information, novel treatments and developing perceptions. We stress, however, that our synthesis departs well beyond the constraints of data or conventional peer review. Its publication should not be taken as an indication of either likelihood or merit. It seems probable that a major portion of sedimentary organic matter **may** be sorbed, and hence predisposed to a wide variety of reactions not possible for insoluble particles. The mechanisms and consequences of sorption, however, are poorly defined. Slow oxic degradation remains at best a possibility. The model of a shifting balance between protective sorption and “oxic” degradation in marine sediments is highly speculative. Only considerable experimentation will tell whether this fledgling concept can stand on its own two precepts.

We thank the four commentators for their thoughtful contributions and *Marine Chemistry* for giving us all this opportunity for flights of imagination.

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