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The inertness of being organic

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Abstract

Organic matter protection, defined here as slowing of the oxidation of organic matter, is thought to result from a variety of mechanisms, which can be placed into two classes. Recalcitrant organic-organic linkages often account for protection on shorter time scales; biota intentionally create many of these linkages, leading to "selectively preserved" organic matter, and various humification reactions may produce others. On longer time scales, exclusion of biota or their digestive agents accounts for most protection, induced by factors such as clay mineral protection and anoxia. Longer term protection likely proceeds through a succession of different mechanisms, acting cooperatively. The papers of this session address kinetic and structural aspects of organic matter protection, in response to factors such as the hydrochemical cycle, organomineral aggregates, molecular aspects of nitrogen, and exposure to oxygen.
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Almost all organic matter produced in the oceans is highly labile material, but various mechanisms protect fractions of it against rapid heterotrophic attack. To protect here means to delay organic matter oxidation in the presence of oxidants that are thermodynamically capable of the reaction—i.e. render it inert. We observe apparent protection via the slowing of rates of decay with organic matter age, parameterized in various ways (Westrich and Berner, 1984; Middelburg, 1989), but mechanistic understandings of these rate slowdowns are sparse. This next section of papers reviews these mechanisms.

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Many hypotheses have been proposed to explain this delayed oxidation (see reviews in Francois, 1990; Tyson, 1995; Henrichs, 1992; Tegelaar et al., 1989; Derenne and Largeau, 2001). These hypotheses can be fit into the following two categories, which represent a variation on themes proposed by Sollins et al. (1996):

(1) *Organic recalcitrance.* Organic matter itself is difficult to break down due to recalcitrance of organicorganic linkages. Biomolecules vary in their ease of disassembly, at monomer, polymer, or supramolecular scales of organization. Hence, more recalcitrant assemblages at all of these scales are selectively preserved. "Humification"—the

abiotic formation of organicorganic associations from detrital biomoleculescan confer recalcitrance to the crosslinked products. Hypothesized humification reactions involving covalent bond formation include Maillard, lipid oxidation, glycation, vulcanization, and other reactions; alternatively, weaker forces such as the hydrophobic effect encapsulate labile biomolecules within more recalcitrant ones.

(2) *Biotic exclusion*. Organisms or their digestive agents are excluded or inhibited from access to the organic matter. Greater preservation of organic matter under anoxic conditions may be due to exclusion of organisms who can obtain high energy yields from substrate or who can facilitate biochemical digestion by physical breakage. Accumulation of metabolites may inhibit heterotrophic communities. Enclosure of organic matter in mineral fabrics may exclude either organisms or their digestive agents. The encapsulation hypothesis mentioned above might be considered to bridge into this category.

The relative importance of the various mechnisms probably changes with time scale.

1. Is protection on shorter time scales driven by biological needs?

Organisms synthesize biochemicals that are difficult to degrade, for reasons such as defense, structural strength, or storage. The consequent range of degradability leads to the importance of selective preservation hypotheses. Organisms use many mechanisms to selectively preserve certain biochemicals.

Incorporation into biomass that then survives (Lee, 1992) is an obvious, though often overlooked, form of protection. Dead tigers are more bioavailable than live ones. While most radiolabelled glucose added to soil is rapidly remineralized, the remainder is stabilized in microbial biomass and necromass (Ladd and Paul, 1973). Some selective preservation is due to organisms persisting in organic detritus.

Once in the detrital pool, biochemicals are likely to be preserved by their chemical attributes. Efficient heterotrophic harvesting of energy from organic matter oxidation can only be performed within cells, so that passage across cell membranes is required for organic decay. In short, organic matter protection can result from its indigestibility. Selective preservation is thus often associated with polymers that are difficult to hydrolyze or contained within biochemical matrices that are difficult to disassemble. For example, on short time scales, labile proteins held in cell membranes are digested more slowly than cytoplasmic proteins (Lee and Fisher, 1993). Multiphasic decay kinetics of chlorophyll implies similar heterogeneity of matrices holding the identical molecule (Sun et al., 1993). On longer time scales, labile proteinaceous material may be protected by algaenans (Nguyen and Harvey, 2003). Biotic tanning of proteins is known in terrestrial systems (Knicker, this volume), but analogous reactions occur in the oceanse.g., the sclerotization of proteins and chitin in crustacean shells.

Humification mechanisms, whether they begin with monomers or polymers, can be regarded as ex vivo versions of the biologically induced reactions just discussed. Indeed, most hypothesized reactions can occur in vivo, especially as pathological excursions from normal cellular biochemical processes. They often represent breakdowns of in vivo control systems—e.g., in response to insufficient antioxidants. All such hypothesized reactions imply selective preservation of detrital biomolecules that were either inherently prone to crosslinking (possess reactive skeletons or functionality) and/or were in the wrong place at the wrong time (e.g., exposed to sunlight). Crosslinking reactions leave bulk composition largely unchanged, consistent with the emerging appreciation for constancy of bulk compositions during organic matter aging despite frequent loss from the analytical window (Hedges et al., 2001; Dignac et al., 2000).

Biologically intended humification merits attention. Extracellular or extrasomatic organic matter can be important to some biota for purposes such as food storage, biofilms, and perhaps electron shuttles. Crosslinking reactions make a sensible strategy to protect these materials against attack by other organisms. Organisms need only protect for use during their lifetime, and on longer time scales the materials might well be labile.

2. Protection on longer time scales

At longer time scales, it makes less sense for organisms to preserve organic matter. These longer survival times likely involve some form of protection that is inadvertent from a biological perspective.

Most long-term organic matter preservation in the ocean is in finely disseminated form in ocean margin sediments that have no oxygen present (Berner, 1982; Hedges and Keil, 1995). For protection beyond periods of decades (i.e. below the surficial mixed layer), the record indicates that exclusion of biota becomes a dominant theme.

Multiple factors may contribute to efficient burial in ocean margin sediments. Strong correlations between organic matter and clay contents, at sub-micrometer to landscape size scales, imply a strong role for clay mineral protection (Premuzic et al., 1982; Ransom et al., 1997; Bock and Mayer, 2000). Correlations with oxygen exposure (Hedges et al., 1999; Keil et al., this volume), and especially the natural experiments that change redox regime provided by turbidites (Cowie et al., 1998) and soils (Petsch et al., 2000), convincingly imply an interactive role for oxygen availability. Selective preservation alone cannot dominate protection in ocean margin sediments; or we would not see the majority of organic matter in ocean margin sediments degraded when suddenly exposed to oxygen. Oxidation fronts in turbidites also help rule out various correlates of oxygenated water columns as necessary agents for more complete oxidation (i.e. animals). Understanding the mechanism(s) of this anoxic inhibition of organic matter decay poses a major challenge and hypotheses such as metabolite inhibition (Aller and Aller, 1998) or absence of oxidative enzymes (Freeman et al., 2001) warrant much more attention.

3. Protection as a succession of mechanisms

Mechanisms of protection are not mutually exclusive; longer-term preservation likely involves selectively preserved and perhaps humified material in biota-excluding scenarios (Fig. 1). These mechanisms must often work interactively (Hedges et al., 1993), and only frustration will come from seeking simple answers to complicated scenarios. The question of whether selective preservation accounts for some fraction of overall protection is oversimplified; obviously, all preserved organic matter is selectively preserved. It is unclear whether some forms of humification occur on the way to longer-term preservation by the combination of mineral association and anoxic conditions that characterize ocean margin sediments. If so, humification presumably operates on those selectively preserved biomolecules that are most susceptible to the operant humification reactions. The inability of organic geochemists to identify the bulk of organic matter preserved beyond a period of months implies a significant role for humification.

Thus, different mechanisms likely play relatively important roles at different time scales (Fig. 1), not exclusive of one another but rather in a successive, cooperative manner (Hedges et al., 1993). Materials preserved at shorter time scales, perhaps protected by organicorganic linkages instigated by biological needs, will provide the primary feedstock for longer time scale mechanisms that are controlled by abiotic factors such as clay delivery and water depth. To reach various scales of immortality organic molecules would likely traverse through each of the preceding fields. No doubt, some slip through the narrow windows that escape one or more of these mechanisms; e.g., some organic matter is preserved in oxic sediments. John Hedges worked many of these time scales and made important progress in understanding and quantifying a plot like this.

4. Session organization

This symposium focuses on the oceans, but most long-term organic matter protection occurs via burial with terrigenous minerals accompanied by poorly quantified amounts of terrigenous organic matter. This latter material originates during river passage, soil formation, or inheritance from upland rocks. The concentrations of organic matter in sediments are similar to those of soils (Hedges and Oades, 1997). Therefore, common themes likely account for organic matter protection among soils, sediments, and even source rocks. This session accordingly brought in comparative studies of rock, soils, and sediments with
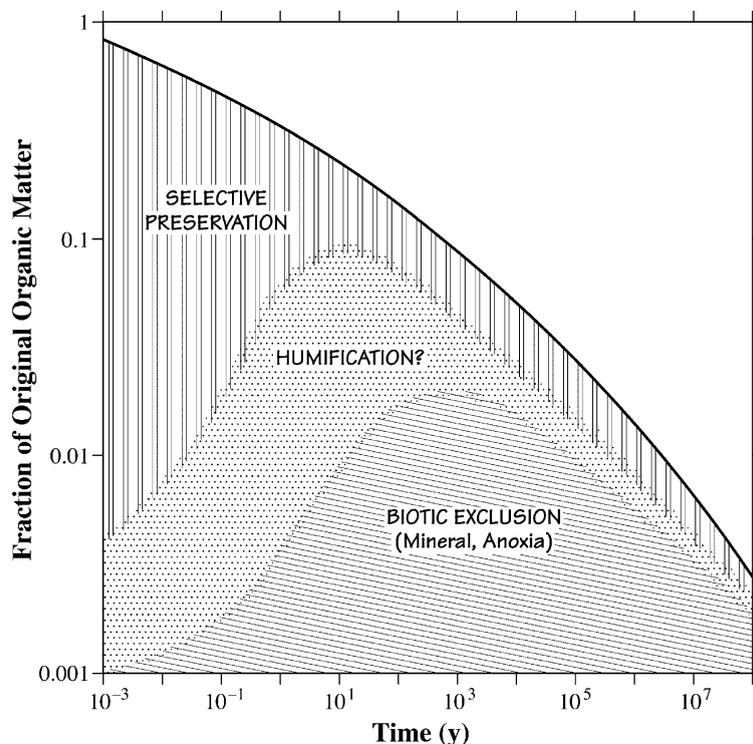
Fig. 1. Schematic diagram illustrating the succession and overlaying of various protection mechanisms of marine organic matter. The fraction of organic matter remaining (*y*-axis) as a function of time after primary production (*x*-axis) is calculated according to Eq. 11 of Middelburg (1989), assuming *a*=0.09*d*. According to this scheme, the majority of organic matter is preserved in its initial stages via some form of selective preservation, after which some portion undergoes some kind of humification reaction, and subsequently a smaller fraction undergoes further preservation in continental margin sediments. This diagram does not attempt to account for all preservation pathways or to quantitate their relative importance, but rather makes the point that the majority of organic matter preserved out to different time scales likely proceeds through successional overlays of these various protection mechanisms.

emphasis on mineral associations. These comparisons bring power to the narrower goal of understanding protection of organic matter in marine environments and are intended to encourage more marine scientists toward this comparative approach.

Blair et al. (2004) address the sources and fate of organic matter at continental scales, from exhumation of sedimentary rock organic matter in terrestrial watersheds, its alteration and augmentation in soils, transport and processing in river systems and subsequent alteration and burial in the oceans. They compare systems varying in the residence time of weathering products in upland and lowland parts of the watershed and in the shallow waters or surficial sediments of the depocenter, elucidating factors controlling the types of organic matter eventually buried. The conceptual model they present provides a

kinetic framework in which to interpret many differences in composition and concentrations found at different landocean interfaces.

Knicker (2004) reviews a variety of mechanisms thought to be responsible for the protection of nitrogenous compounds, a compound class important throughout John Hedges' career. Her molecular perspective on organic nitrogen addresses its biological formation and diagenetic evolution in soils and sediments. She draws the very significant conclusion that biotic alteration of organic matter leaves the nitrogenous compound pool dominated by peptides from soils through early diagenesis, while later survival shows a replacement of peptides by other compounds such as heterocyclic nitrogen.

K. Kaiser (presentation only) likewise compared protection mechanisms in these two environments

from a soil science perspective. He focused on mineral associations, considering them from morphological, chemical and genetic perspectives. His survey raised important questions about whether these associations derive from sorption vs. aggregation reactions, and emphasized the geometry of organo-mineral interactions.

Keil et al. (2004) build on their group's previous refinement of the hypothesis of oxygen exposure time (OET: Hartnett et al., 1998) control of organic matter degradation. As noted above, the old correlation between presence/absence of oxygen and organic matter concentrations was very attractive, but problematic because of covariation of so many other parameters when comparing oceanographic regions with varying oxygen concentrations (Hedges et al., 1999). The present paper shows that refining the OET calculation, by incorporating lateral transport times, strongly improves linear correlation between OET and organic loading.

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