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The role of iron in the diagenesis of organic carbon and nitrogen in sediments: A long-term incubation experiment

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ABSTRACT

The burial and preservation of organic matter (OM) in marine sediments is tightly coupled to the diagenetic cycles of iron and manganese. Recently, it has been shown that approximately 20% of the sedimentary organic carbon (OC) may be bound to reducible iron oxides (Lalonde et al., 2012). These strong iron–OC complexes, formed within the oxic layer of the sediment, are transferred to the deeper anoxic sediment layers through sedimentation, physical reworking and bioturbation and are metastable over geological timescales. Using long-term (250-day) incubations under various redox and amendment conditions (Fe(II) and dissolved OM (DOM) additions), we examined the effect of iron on the early diagenetic transformations of OM in marine sediments. The fate of fresh, algal-derived DOM was monitored by tracking its stable carbon isotopic signature ($\delta^{13}C$). We demonstrate the incorporation of the ^{13}C-depleted tracer into the sediment through sorption (adsorption and co-precipitation). In the presence of iron oxides, we observed an increased transfer of the dissolved algal material to the solid phase, revealing the role of iron in shuttling DOM from sediment pore waters to sediment particles. Furthermore, we show that the presence of iron has a differential effect on OC and organic nitrogen (ON), with preferential preservation of OC and accelerated degradation of ON in the presence of reactive iron oxide surfaces. Hence, we propose that redox-sensitive metals may regulate the global redox balance through increased carbon preservation as well as exerting a control on the concentration of fixed nitrogen species in marine sediments.

1. Introduction

The burial and preservation of organic matter (OM) in marine sediments are important factors in modulating the concentration of atmospheric oxygen and carbon dioxide over geological time (Berner, 1989). Hence, elucidating factors that favor sedimentary OM preservation over its degradation is important. OM can be physically shielded from degradation by adsorption to mineral particles. In fact, over 99% of sedimentary organic carbon (OC) is bound to particle surfaces — the remainder is found as discrete organic debris (Hedges and Keil, 1995; Keil et al., 1994; Ransom et al., 1998a). The surface area of sedimentary mineral particles determines the abundance of OM binding sites and modulates OC–mineral binding, maintaining surface loadings at a near constant and universal value (0.5–1.0 mg OC m^{-2}) on continental shelves and margins (Keil et al., 1994; Mayer, 1994, 1995). Organic compounds can also be protected from microbial degradation through encapsulation within diatom tests (Arnarson and Keil, 2007; Ingalls et al., 2003), expandable-clay interlayers (Kennedy and Wagner, 2011), particle mesopores (Mucci et al., 2000), and macromolecular hydrophobic OM (Mariotti et al., 1981). Over the past 20–30 years, the identification of these processes has shaped our understanding of the fate of OM in sedimentary systems, but the exact nature of these preservative interactions as well as the conditions under which they form still remain unclear. Recently, metal oxides have been identified as key players in the physical protection of OM, accounting for the sequestration and preservation of ≈20% of the OC in marine sediments (Lalonde et al., 2012).

Sedimentary nitrogen is essentially affected by the same preservative associations as OC, but the two species display divergent degradation pathways. The production of N_2 through denitrification and anammox in marine sediments is an important component of the global nitrogen cycle, influencing the oceanic inventory of fixed nitrogen (Burdige, 2006). Bacteria mediate the bulk of both OC and ON mineralizations to CO_2 and N_2, but unlike OC remineralization, the traditionally accepted mechanisms of bacterial N_2 production are mainly confined to anoxic conditions (Burdige, 2006). A proposed alternative pathway of N_2 production in sediments (Devol, 2008) and soils (Yang et al., 2012) involves the direct oxidation of NH_4^+ by manganese and iron oxides, a

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thermodynamically feasible process under both oxic and suboxic conditions (Yang et al., 2012). Balanced equations for these processes are shown here:

$$FeOOH + 1/3NH_4^+ + 5/3H^+ \rightarrow 1/6N_2 + Fe^{2+} + 2H_2O$$

$$MnO_2 + 2/3NH_4^+ + 5/3H^+ \rightarrow 1/3N_2 + Mn^{2+} + 2H_2O.$$

Redox-sensitive metals, such as iron and manganese, strongly impact the turnover of both OC and ON in marine sediments, but OM also affects the diagenetic cycling of iron. The growth of authigenic amorphous iron oxide phases is, for example, strongly inhibited by OM bound to their surfaces (Schwertmann, 1966). The reduction of oxides in sediments may also be hampered by organic matter (O'Sullivan et al., 1995). Nanophases of iron oxides are the dominant reactive oxides in both marine and lacustrine sediments (Raiswell and Canfield, 2012; Van der Zee et al., 2003) and these redox-sensitive phases, when associated to OM, somehow resist reduction after thousands of years of burial in anoxic sediments (Hease et al., 1997).

Elucidating the role of iron and manganese oxides on the degradation/preservation of OC and ON in sediments is impeded by the intrinsic complexity (e.g., spatial and temporal heterogeneity) of these systems. Benthic macrofauna, for example, affect elemental transport and cycling within the uppermost sediment layers and create microenvironments and lateral variability through burrowing and surface feeding (Aller and Aller, 1998; Aller et al., 1996; Boudreau, 1986; Katsev et al., 2007; Michaud et al., 2005). Additional difficulty is imparted by the poorly characterized nature (chemical structure) and wide-ranging reactivity of sedimentary organic matter (LaRowe and Van Cappellen, 2011). Not only are the latter dictated by OM sources, but also by the depositional setting as well as the intensity and frequency of physical, biological and chemical reworking (Aller et al., 1996). Due to the large range of OM reactivities (half-lives ranging from 10 to 2000 years or longer (Hedges and Keil, 1995)), it is difficult to tease out the environmental and depositional factors that control OM preservation and degradation on the timescales of field observations or laboratory experiments.

This paper describes a long-term (250 days) incubation, carried out under different redox and amendment conditions, that assesses the fate of OM (partitioning, degradation, iron oxide association) over a longer timeframe than typical laboratory experiments. We systematically controlled the incubation conditions to more readily identify differences between oxic and anoxic OM degradation rates as well as the preservative interactions between OM and redox-sensitive minerals. A pulse of labile dissolved organic matter (DOM) derived from ^{13}C- and ^{15}N-depleted algae was added to a natural sediment slurry to study its degradation/preservation. Since there is little isotopic fractionation of the stable carbon isotopic signature ($\delta^{13}C$) during physical and biological processing of sedimentary OC and given that the $\delta^{13}C$ signatures of carbon sources are discrete and well constrained, $\delta^{13}C$ is a sensitive source indicator in this system (Bauer, 2002; Middelburg et al., 2000), allowing us to track the fate of the algal OM pulse within the solid and aqueous phases.

2. Materials and methods

2.1. Sampling

Sediment samples were collected at 325 m depth at station 23 (48°42.419′N, 68°38.387′W) in the Lower St. Lawrence Estuary onboard the *R/V Coriolis II* in May 2011. The first ≈20–25 cm of the grab core sample (fine silt/clay, porosity ≈ 0.85) was homogenized, removing visible living macrofauna, seashells and detritus. The wet sediment was transferred to glass jars and stored on-board and in the laboratory at 4 °C for less than 4 months in order to preserve the native microbial communities and chemistry of the sediment. The bulk of the sediment remained anoxic during storage as only the surface of the sediment within the jar was in contact with the atmosphere.

2.2. Fresh algal dissolved organic matter

Algal dissolved organic matter (DOM) was liberated from *Nannochloropsis* algae cells (Reed Mariculture) through cell lysis following repeated freezing in liquid nitrogen and thawing. Lysed cells were diluted with deep Pacific seawater (DOM concentration < 1 mg L^{-1}), centrifuged for 20 min at 19,000 *g* and filtered through a 0.7-μm glass fiber filter to generate a highly concentrated DOM solution. The algal-derived DOM is ^{13}C- and ^{15}N-depleted ($\delta^{13}C = -41.34 \pm 0.12‰$, $\delta^{15}N = -5.12 \pm 0.26‰$) relative to the natural sedimentary material ($\delta^{13}C = -24.29 \pm 0.10‰$, $\delta^{15}N = +5.67 \pm 0.22‰$), making it easy to follow its progressive integration into the sediment and degradation during the incubation. For example, a 6% addition of carbon and a 9% addition of nitrogen through the incorporation of algal DOC and DON, respectively results in a 1‰ depletion in sediment $\delta^{13}C$ and $\delta^{15}N$.

2.3. Slurry incubation setup

The incubation setup is illustrated in Fig. 1. The 24 glass amber 250 mL vials (12 duplicate experimental conditions) were filled with wet homogenized sediment (14.6 g dry weight) in 175 mL of seawater giving a total volume of approximately 200 mL. Each vial was sealed with a custom designed PTFE cap lined with a Viton O-ring. Three ports were machined into the caps to accommodate standard PEEK fittings for gas purging and transfer as well as reagent additions. Three parallel sequences of 8 vials (4 amendment conditions done in duplicate) connected in series by PTFE tubing were incubated at 4 °C under different redox conditions using a flow-through gas method (≈30 mL min^{-1}). The first two series were maintained either oxic or anoxic using air or nitrogen gas, respectively. The redox conditions in the third series of incubations alternated monthly between oxic and anoxic conditions for the duration of the experiment.

After one week of redox equilibration, each set of 8 vials was amended with fresh algal DOM (final concentration 36.1 mmol L^{-1}) and/or dissolved ferrous iron ($FeCl_2 \cdot 4H_2O$, final concentration 4.25 mmol L^{-1}), making 4 duplicate experimental scenarios: A. addition of iron(II) and OM (Fe–OM scenario), B. addition of iron(II) only (Fe scenario), C. addition of OM only (OM scenario) and D. control vials containing only the original sediment and seawater (Control scenario) (Fig. 1). Algal DOM and dissolved iron were injected as anoxic solutions through the septum port of each vial. Under oxic conditions, Fe(II) is expected to undergo rapid oxidation and precipitation as an iron oxide.

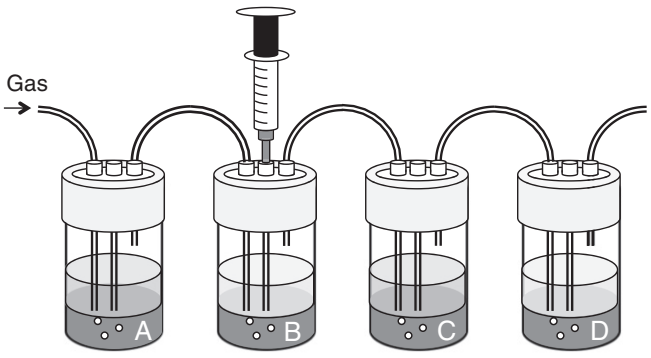

Fig. 1. Illustration of the incubation setup. Incubations were carried out under 3 different redox conditions (anoxic, oxic, and mixed redox) by purging the overlying water with nitrogen gas, air, or alternating between the two gases. The sediment–seawater incubations were spiked with A) Fe(II) and DOM (Fe–OM scenario), B) Fe(II) only (Fe scenario), C) DOM only (OM scenario) and D) no addition (Control scenario). Note that each vial was duplicated (in series) in this experiment (8 vials per redox condition, 24 vials in total).