



Direct evidence for organic carbon preservation as clay-organic nanocomposites in a Devonian black shale; from deposition to diagenesis



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ABSTRACT

The burial of marine sourced organic carbon (OC) in continental margin sediments is most commonly linked to oceanographic regulation of bottom-water oxygenation (anoxia) and/or biological productivity. Here we show an additional influence in the Devonian Woodford Shale, in which OC occurs as nanometer intercalations with specific phyllosilicate minerals (mixed-layer illite/smectite) that we term organo-mineral nanocomposites. High resolution transmission electron microscopic (HRTEM) images provide direct evidence of this nano-scale relationship. While discrete micron-scale organic particles, such as Tasmanites algal cysts, are present in some lamina, a strong relation between total organic carbon (TOC) and mineral surface area (MSA) over a range of 15% TOC indicate that the dominant association of organic carbon is with mineral surfaces and not as discrete pelagic grains, consistent with HRTEM images of nanocomposites. Where periods of oxygenation are indicated by bioturbation, this relationship is modified by a shift to lower OC loading on mineral surfaces and reduced MSA variability likely resulting from biological mixing and homogenization of the sediment, oxidative burn down of OC and/or stripping of OC from minerals in animal guts. The TOC–MSA relationship extends across a range of burial depths and thermal maturities into the oil window and persists through partial illitization. Where illitization occurs, the loss of mineral surface area associated with the collapse of smectite interlayer space results in a systematic increase in TOC:MSA and reorganization of organic carbon and clays into nano-scale aggregates. While the Woodford Shale is representative of black shale deposits commonly thought to record heightened marine productivity and/or anoxia, our results point to the importance of high surface area clay minerals for OC enrichment. Given that the vast majority of these clay minerals are formed in soils before being transported to continental margin settings, their mineralogy and attendant preservative potential is primarily a function of continental climate and provenance making these deposits a sensitive recorder of land as well as oceanographic change.

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1. Introduction

The burial of OC in marine sediments is one of the most fundamental biogeochemical processes on Earth and not only influences the temperature and oxygenation of the oceans and atmosphere but also comprises the primary source of hydrocarbons (Arthur and Sageman, 1994; Burdige, 2007; Hedges and Keil, 1995). Greater than 95% of organic carbon (OC) preserved at the surface of the Earth is buried in continental margin sediments, but the final por-

tion of OC finding its way into sediments constitutes only a small fraction (<0.5%) of marine primary production (Burdige, 2007; Hedges and Keil, 1995). However, anomalous concentrations of OC within specific intervals of the geologic record imply that the efficiency of carbon burial is variable, and likely attributable to changing environmental conditions.

The origin of anomalous organic enrichment in the geologic record and implications of these deposits remains controversial. While black shale intervals can be strikingly different from background sediment composition and show abrupt onset consistent with a single dominant control, studies of various examples point to a range of empirical associations suggestive of the interplay of various environmental influences (Arthur and Sageman, 1994). Controls most commonly suggested include low or depleted dissolved oxygen concentrations favourable to OC preservation

Abbreviations: EDS, energy dispersive spectroscopy; EGME, Ethylene Glycol Monoethyl Ether; IC, inorganic carbon; MSA, mineral surface area; OC, organic carbon; OM, organic matter; SEM, scanning electron microscope; TEM, transmission electron microscope/microscopy; TOC, total organic carbon; XRD, X-ray diffraction.

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(Demaison and Moore, 1979), productivity-dependent OC flux (Calvert et al., 1992; Pedersen and Calvert, 1990) and concentration of OC in sediments by a reduction in siliciclastic dilution (Tyson, 2001).

A first order association between total organic carbon (TOC) and mineral surface area (MSA) in modern continental margin sediments suggests another potentially important influence not commonly considered in ancient organically enriched shales (Mayer, 1994; Hedges and Keil, 1995). This relation is common to most modern sediments studied to date, irrespective of their depositional environment (Keil et al., 1994a; Mayer, 1994; Ransom et al., 1997; Bergamaschi et al., 1997; Keil and Cowie, 1999), although differences in environmental conditions such as nutrient availability and oxygenation are expressed as higher (high productivity, low-oxygen settings) or lower (long oxygen exposure times, high energy environments) OC loadings per unit surface area (Blair and Aller, 2012). An MSA:TOC correlation has also been demonstrated in ancient examples across a range of redox conditions and TOC values from 1% to 20% (Kennedy et al., 2002; Kennedy and Wagner, 2011). Mineral surface associated preservation of OC has the potential to be significant because detrital clay minerals comprise >60% of continental margin sediments and MSA is controlled by the abundance of some common clay minerals with very high surface area (Chamley, 1989; Hedges and Keil, 1995) such as smectite which has two orders of magnitude greater MSA than quartz silt or carbonate.

The physical or chemical mechanism(s) causing the TOC:MSA correlation is yet to be resolved but is key for understanding the extent and significance of this association. Some hypothesized preservative mechanisms include sorption (Keil et al., 1994a; Keil and Cowie, 1999; Mayer, 1994; Satterberg et al., 2003; Baldock and Skjemstad, 2000), physical sheltering or encapsulation by clay mineral aggregates (Ransom et al., 1997; 1998; Salmon et al., 2000; Bock and Mayer, 2000; Zimmerman et al., 2004) and intercalation within hydrating clay minerals as organo-mineral nanocomposites (Kennedy et al., 2002; Kennedy and Wagner, 2011; Theng et al., 1986; Jia et al., 2002; Chen et al., 2008; Sposito et al., 1999). Key questions that remain include how universal this mechanism of preservation is outside the studied examples, what type of mineral surfaces have preservative properties, how much mineral surface-associated OC preservation is influenced by environmental conditions such as varying productivity and oxygenation and/or diagenetic burial processes such as MSA loss through illitization and OC loss through hydrocarbon generation.

The direct approach to identifying the relationship between mineral and OC is through imaging their association(s), but since they occur at 100 nanometer scales and require the technically challenging sample preparation of nanometer thick ultra-thin sections necessary to reveal crystal to crystal boundaries, most studies have focused on indirect means of characterization (Bock and Mayer, 2000; Keil et al., 1994b; Kennedy and Wagner, 2011; Mayer, 1999).

In contrast to the general idea that OC in marine sediments is comprised of discrete, mostly pelagic, particles (similar to those collected in sediment traps near the sea bed), studies of modern sediments show that >80% of these OC particles are mineralized within the first 30 cm downward from the sea floor (Mayer, 1994), and that >90% of the remaining OC cannot be physically separated from the mineral matrix (Keil et al., 1994a). It is the latter fraction that displays strong correlation with MSA. The mineral-associated fraction degrades at a rate five orders of magnitude slower than the same OC when desorbed from mineral surfaces (Keil et al., 1994a), so that the mineral-associated fraction becomes an increasing proportion of the TOC from the seabed downward (Keil et al., 1994a; Mayer, 1994), representing the most likely fraction to enter the geological record. A strong correlation ($R^2 = 85\%$)

between MSA and TOC documented in thermally immature Cretaceous sediments from the western interior seaway of North America (Kennedy et al., 2002) and the Deep Ivorian Basin of the eastern Atlantic (Kennedy and Wagner, 2011) suggests this may indeed be an important mechanism of OC accumulation in the geologic record. Both studies concluded that the relationship extended over MSA values sufficiently high to be diagnostic of smectitic clay minerals, suggesting smectite plays a key role in preservation.

Smectite shows a characteristic order of magnitude greater surface area than any other common sedimentary mineral because the silicate layers of smectite consist of an octahedral sheet sandwiched between two tetrahedral sheets, and these fundamental units stack together to form an interlayer between them (smectite $\sim 750 \text{ M}^2 \text{ g}^{-1}$, illite $< 150 \text{ M}^2 \text{ g}^{-1}$, and kaolinite or quartz silt $< 30 \text{ M}^2 \text{ g}^{-1}$). The interlayer is expandable so that interlayer sites are accessible to polar and non-polar organics, ions and water (Theng et al., 1986; Sposito et al., 1999; Jia et al., 2002; Williams et al., 2005; Brigatti et al., 2006; Chen et al., 2008). The preservative effect on OC by smectite has thus been hypothesized to be the result of incorporation of molecular scale organic compounds (derived from the physical or chemical breakdown of organic particles) in the clay interlayer space where it is protected from microbial degradation (Kennedy et al., 2002; Kennedy and Wagner, 2011). How this relationship might change with thermal maturation and diagenetic transformation of both the organic and mineral phases during burial has not previously been investigated in this context. It has long been known that deep burial of argillaceous sediments results in diagenetic transformation of expandable smectite into non-expandable illite (Hower et al., 1976). Illitization also commonly coincides with the ranges of depth and temperature of formation of oil from kerogen (Abid and Hesse, 2007), and is characterized by tetrahedral Al for Si substitution, dehydration, interlayer collapse, loss of internal surface area, as well as replacement of exchangeable cations in the interlayer by fixed K and/or NH_4^+ (Lindgreen et al., 2000; Dainyak et al., 2006). Although there is evidence that some carbonaceous material can remain within the illite interlayer (Ahn et al., 1999), illitization causes expulsion of most OM previously hosted in the smectite interlayer and may also be associated with polymerization of organic compounds (Williams et al., 2005). The loss of surface area and generation of hydrocarbons will alter the relationship between MSA and TOC if hydrocarbons are lost through migration, or increase the carbon to MSA ratio in the absence of migration.

This study investigates the relationship of MSA to TOC in the Late Devonian ($\sim 385 \text{ Ma}$) epeiric sea deposits recorded in the Woodford Shale (Comer, 1991). The Woodford Shale is both an important conventional and unconventional hydrocarbon source rock and broadly representative of a phase of worldwide OC deposition potentially related to significant changes in terrestrial weathering and soil formation associated with the expansion of vascular plants (Klemme and Ulmishek, 1991; Algeo et al., 1998). This study utilizes a two-part strategy to characterize the mode and mechanism of carbon burial and preservation. Initially we establish the typical relationship between TOC and MSA across the Formation using the bulk property parameters of MSA and TOC. We then focus on the mechanisms of that relation by direct imaging of organo-mineral associations at the relevant nanometer scales. While these relations can only be imaged over areas of tens of microns at a time, we argue that our observations are consistent with the MSA and TOC ratios of the bulk samples and can thus be up-scaled and taken as representative of the dominant mode of OC preservation in the Woodford Shale. Samples were collected from three cores at different depths in the basin selected to capture a burial-temperature gradient in order to understand the effects of burial diagenesis and clay illitization on the MSA–TOC relationship.

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