Evidence for the priming effect as an important control on the alteration of dispersed organic matter

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Abstract

Early diagenetic bacterial degradation affects preservation of organic matter (OM) by altering OM shortly after deposition, reducing the amount of OM preserved and lowering the hydrocarbon generation potential. To better understand diagenetic bacterial degradation of transported refractory organic matter (ROC) as well as the controlling factors behind early diagenetic OM degradation, forty samples from three wells with low thermal maturity are examined using optical organic petrology combined with programmed pyrolysis and whole rock geochemistry.

This study presents evidence that the priming effect (PE) within a marine depositional system significantly increased degradation of all types of OM, including ROC, brought on by increased organic productivity. Samples with evidence of bacterial degradation correlate with elevated concentrations of biogenic barium, an indicator of primary productivity. The input of labile OM resulted in an increase in the degradation rate of all OM types. It has been previously asserted that ROC undergoes minimal degradation through erosion, fluvial transport, and deposition in marine sediments, however the results of this study suggests that ROC was degraded shortly after burial. It is likely that the PE, regulated by productivity rate is an important control on the preservation of all OM types within marine source rocks.

Statement of the background

Several primary controls on OM burial and preservation are commonly recognized including OM composition and concentration, oxygen availability, as well as physical factors such as temperature, sediment texture, and bioturbation (Zonneveld et al., 2010 and references therein). Oxygen availability in the bottom water column is generally considered the most important primary control on OM preservation as oxygen availability largely determines the respiration and community structure of benthic organisms and bacteria (Tyson and Pearson, 1991; Zonneveld et al., 2010). These organisms are responsible for breaking down OM in the marine setting and the degradation of OM by anaerobic/anoxic fauna is considered far less efficient and effective than by aerobic micro-organisms (Tyson and Pearson, 1991; Zonneveld et al., 2010). This has led to the common interpretation that organic-rich mudrocks result from deposition in anoxic/euxinic conditions, which are more likely to result in a high degree of OM preservation (Tyson and Pearson, 1991).
In addition to factors such as sediment mixing due to bioturbation, and benthic and microbial community structure, a process known as the priming effect (PE) likely also plays an important role in OM preservation (van Nugteren et al., 2009; Guenet et al., 2010). The PE involves the relationship between the input of fresh, labile OM and degradation rates of more refractory OM in the sediment or soil (Aller, 1994; van Nugteren et al., 2009). In a majority of published studies (Kuzyakov et al., 2000 and references therein; van Nugteren et al., 2009; Guenet et al., 2010), an increase in labile OM induced a drastic increase in the remineralization rates of ROC, and even highly inert OM such as charcoal has been demonstrated to have a drastic increase in remineralization due to the PE (Hamer et al., 2004). Although this process has been extensively studied in soils, the effect of PE in regulating OM remineralization in marine environments is poorly documented (Hee et al., 2001; van Nugteren et al., 2009; Guenet et al., 2010). Experimental results by Guenet et al. (2010) demonstrated that the PE is controlled by general, widespread chemical mechanisms and must be considered in a variety of ecosystem types and that this stimulation effect is amplified under anoxic conditions (van Nugteren et al., 2009; Guenet et al., 2010).

It has previously been shown that ROC is a significant component of the TOC in Cretaceous strata and that TOC should be used with caution as a proxy for indigenous, labile OM (Synnott et al., 2017). It has also been shown that bacterial degradation is an important factor in the preservation of OM deposited in the Cretaceous (Synnott et al., 2016). Together these factors are an important control on the quality and rate of preservation of deposited OM within an organic rich mudrock, increasingly considered important as unconventional resources. This study seeks to build on this previous work and examine evidence of the PE taking place during deposition of Cenomanian-Turonian strata and the effect that the PE has on the OM within a marine basin during early diagenesis.

Aims and Objectives

It is hypothesized that the priming effect (PE) plays an important role in regulating the rate of bacterial degradation during early diagenesis as previously observed by Synnott et al. (2016; 2017). It is expected that a link will be observed between the degradation of OM and the rates of primary productivity as observed through trace elemental proxies, including barium. It is also anticipated that evidence of degradation will be observed in ROC macerals. This was hinted at in Synnott et al. (2017), however, this study increases sample numbers and further investigates the causes of this degradation. It is hypothesized that increased primary productivity results in increased rates of bacterial degradation of all OM types, including ROC, previously thought to be inert.

Materials and methods

The Second White Specks Formation was deposited during the transgressive phase of the Greenhorn Cycle in late Albian to early Turonian time. It is primarily composed of calcareous, organic-rich mudstone (Schröder-Adams et al., 1996). During the time of deposition, warm Tethyan waters from the south extended into the northern part of the Western Interior Seaway (WIS) allowing northward colonization by planktonic foraminifera and coccoliths (Bloch et al., 1999). The underlying Belle Fourche Formation is a westward-thickening wedge of non-calcareous to slightly calcareous mudstone and siltstone conformably overlying the Fish Scales Formation (Bloch et al., 1999; Yang and Miall, 2008). The Western Interior Seaway (WIS) during the deposition of the Belle Fourche Formation was dominated by colder, low salinity, boreal waters, and bottom water oxygen levels have been interpreted to be highly variable allowing some colonization by benthic organisms, limited OM productivity, and relatively limited OM preservation (Bloch et al., 1999).

Forty samples were collected from thermally immature cores in south-central Alberta. Eighteen samples were taken from the Second White Specks Formation in well 102/07-12-042-21W4/00 (Well 1) located at 52° 36’ N, 112° 54’W. Twelve samples were collected from the Second White Specks Formation and upper part of the Belle Fourche Formation in well 100/07-29-042-12W4/00 (Well 2) located at 52° 38’ N, 111° 41’W. Of these samples, five are from the upper part of the Belle Fourche Formation and seven are from the Second White Specks Formation. Ten samples were taken from the Second White Specks Formation and upper part of the Belle Fourche Formation in well 102/03-33-049-10W4/00 (Well 3) located at 53° 16’ N, 111° 25’W. Of these samples, five are from the upper part of the Belle Fourche Formation.
and five are from the Second White Specks Formation. Samples were analyzed for organic petrology using the methodology of Synnott et al. (2017), in addition to standard cycles of programmed pyrolysis and inductively coupled plasma mass spectrometry (ICP-MS) in order to determine trace elemental composition.

Results and discussion

Correlation between the median reflectance values of amorphous organic matter (AOM) macerals and refractory organic carbon (ROC) macerals (R² = 0.58, n = 37, p < 0.05) implies a relationship between the processes that result in increasing reflectance in each OM population (Fig. 1). However, this relationship cannot be explained entirely by thermal processes because

Figure 1: (A) Correlation between median reflectance values of amorphous organic matter (AOM) macerals and refractory organic carbon (ROC) macerals. Without the influence of thermal processes, it would be expected that ROC reflectance would be independent of AOM reflectance, however, a close correlation is observed (R² = 0.58, n = 37, p < 0.05). (B) Comparison of median amorphous organic matter (AOM) maceral reflectance with the variability (standard deviation) of AOM reflectance by sample group. With increasing AOM reflectance, two groups become clear, non-bacterially altered samples, whose variability does not increase, and bacterially degraded samples whose variability increases drastically.
of the low thermal maturity of the Second White Specks Formation in these wells, and because the ROC has already inherited a high reflectance from its pre-exhumation-transport-burial history. Within the sample set, however, two distinct sample populations are observed based on AOM reflectance and its variability. With increasing median AOM reflectance, two distinct trends emerge based on the standard deviation of AOM reflectance (representing the variability of this value) (Fig. 1). In the first group, as the measured AOM reflectance increases, its variability does not, with the standard deviation increasing slightly from 0.05 to less than 0.10 (Fig. 1). Many of the samples within this group were taken from well 1 located approximately 87 km to the west of the next nearest sample site, and therefore, possibly of a slightly higher thermal maturity as mapped by Creaney and Allan (1990). The second sample population displays a linear increase in AOM reflectance standard deviation (variability) with increasing AOM reflectance beginning at a reflectance of approximately 0.25 %Ro (Fig. 1). It is likely that this increase in variability is due to diagenetic bacterial degradation as previously reported by Synnott et al. (2016) based on organic petrology and sulphur isotopic data.

TOC is generally considered to be the most direct proxy for primary productivity (Schoepfer et al., 2015), however, due to the influence of preservation processes such as bacterial degradation and variable anoxia (Synnott et al., 2016), this study further integrated Ba as a secondary productivity proxy, as measured using ICP-MS. Very little variation between the sample populations is visible in TOC (Average of 3.6 wt.% for bacterially degraded samples and 3.9 wt.% for non-bacterially degraded samples) with the highest TOC values belonging to samples that are not bacterially degraded (average of 5.05 wt.%). However, in both bacterially and non-degraded cases, TOC remains high and it is possible that TOC has been reduced by bacterial processes in the bacterially degraded sample populations. Therefore, it is likely that the Ba enrichment better reflects the relative productivity differences. Bacterially degraded samples have a substantially greater barium (Ba) content (average of 117.7 ppm) than non-degraded samples (average of 36.6 ppm) or samples that lie outside of these groupings (average of 52.5 ppm). The terrigenous fraction of barium must be determined in order to strengthen the use of Barium as a paleoproductivity indicator (Schoepfer et al., 2015; Liguori et al., 2016). This is done by determining the amount of barium in excess of the expected detrital Ba concentrations (assumed to be approximately equal with biogenic Ba) (Ba_{excess}) (Schoepfer et al., 2015; Liguori et al., 2016). Based on this method, the average Ba_{excess} of bacterially degraded samples is 92.5 ppm, whereas non-bacterially altered samples average 13.6ppm, with many of the non-bacterially altered samples having little to no biogenic Ba present.

The samples that belong to the bacterially degraded population have a higher enrichment of Ba indicating higher levels of primary productivity and input of labile OM. These higher levels of organic productivity are likely responsible for controlling the bacterial degradation of OM through the PE. With the input of labile OM, the rate of bacterial degradation will increase for all OM populations in the system (Aller, 1994; van Nugteren et al., 2009). The preferential breakdown of AOM is supported through the models of Thorp and Delong (2002) and Jansson et al. (2007), who assert that because labile OM contains more energy per unit mass, it will be preferentially broken down. It also supports the experimental results of Treignier et al. (2006), who found that the breakdown of ROC only occurred when there was a strong degradation of labile OM.

Conclusions

Organic petrology, ICP-MS, and programmed pyrolysis data was analyzed from cores from 3 wells in the upper part of the Cretaceous (Cenomanian - Turonian) Belle Fourche and the Second White Specks formations in order to examine the depositional and early diagenetic processes that affected OM in these sediments. This study builds on the previous conclusions of Synnott et al. (2016 and 2017) and the following conclusions may be drawn:

- The priming effect (PE) is an important factor in the preservation of OM in marine environments. The input of even a very small amount of fresh OM results in an increase in the remineralization and degradation rates of all OM, including ROC, in the sediments. It is likely that this process is at least partially responsible for regulating and initiating bacterial degradation and would be an important factor in the quality of preserved OM within the studied formations and the degradation of transported ROC.
• It cannot be assumed that ROC is transported and re-deposited in a sedimentary environment without any degradation. Evidence in this study demonstrates that this OM might be broken down by diagenetic bacterial degradation regulated by the PE.

References


