



Research paper

Organic matter source and thermal maturity within the Late Cretaceous Niobrara Formation, U.S. Western Interior



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ABSTRACT

The Late Cretaceous sedimentary record of the North American Western Interior Seaway is characterized by cyclic deposition of organic carbon-rich sediments. One notable interval during the late Coniacian-Santonian is recorded by the Niobrara Formation. The organic carbon-rich interval within the Niobrara Formation has been identified as Oceanic Anoxic Event (OAE) 3. Understanding the reason for this distribution of organic carbon within the Niobrara Formation requires a refined understanding of the source and maturity of the organic matter. In this study, we present lipid biomarker records from the USGS Portland #1 core (Cañon City, CO) to constrain the thermal maturity of the organic matter and the differing contributions of organic matter sources. Sterane and hopane thermal maturity indices indicate that the samples are somewhat immature with respect to oil formation and that there is strong agreement between different proxies for thermal maturity. Based on the distribution of *n*-alkanes, steranes, and hopanes, there is a significant increase in the contribution of algal organic matter during and after OAE 3, coeval with increased organic carbon accumulation. Although a consistent terrestrial contribution is observed, it is only a minor source of organic matter at the Portland core location and does not drive increased organic matter accumulation during OAE 3. Of particular note is the consistent influence of even-over-odd predominantly mid-chain length (C₂₁ to C₂₅) organic matter. This observation within the brackish to marine, not methanogenic WIS represents an expansion of the depositional settings in which even-over-odd predominance has been observed in mid-chain length *n*-alkanes. Pristane (Pr) and phytane (Ph) abundances are inconsistent with a redox control on Pr/Ph ratios and suggest an increase in the delivery and/or preservation of phototrophic organic matter as the source for pristane and phytane in the Portland core.

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1. Introduction

Late Cretaceous deposition in the North America Western Interior Seaway (WIS) is characterized by cyclic deposition of organic carbon-rich sediments (e.g. Pratt et al., 1993; Dean and Arthur, 1998; Meyers et al., 2005), particularly during Oceanic Anoxic Events (OAEs) 2 and 3 (Meyers et al., 2005; Locklair et al., 2011). The Niobrara Formation in the WIS records the latter event, which is of particular interest because, although it is not a global event (Wagreich, 2012), it represents a prolonged period (~3

Ma) of elevated sedimentary organic carbon accumulation within the WIS (Locklair et al., 2011; Tessin et al., 2015). The organic carbon-rich deposits from the Niobrara Formation continue to be of interest within the petroleum industry as a self-sourced resource play, especially with the advent of new technologies for oil shale extraction (Sonnenberg, 2011).

Sedimentary sequences that include the transition from low organic carbon accumulation to black shale deposition provide an opportunity to determine the causes of enhanced organic carbon accumulation. Sediments deposited within the Niobrara Formation include this transition from organic carbon-poor (0–2%) to organic carbon-rich (up to 10%). The Niobrara Formation is formally subdivided into two members: the Fort Hays Limestone and the Smoky Hill Chalk. The basal Fort Hays Limestone is relatively

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organic-carbon poor and consists of ledge-forming limestone beds separated by thin shales (Scott and Cobban, 1964). The overlying Smoky Hill Chalk was sub-divided by Scott and Cobban (1964) into seven informal units (the lower shale limestone (LSL), the lower shale (LS), the lower limestone (LL), the middle shale (MS), the middle chalk (MC), the upper shale (US), and the upper chalk (UC)). Previous research has identified OAE 3 in the LS and LL units of the Smoky Hill Chalk based on a positive $\delta^{13}\text{C}$ excursion and elevated organic carbon concentrations (e.g. Locklair et al., 2011; Tessin et al., 2015). The basal LSL unit of the Smoky Hill Chalk was deposited under conditions similar to the Fort Hays Limestone (Tessin et al., 2015), therefore, for our purposes, the Fort Hays Limestone and the LSL unit will be referred to as Interval 1. Interval 2 is defined by the positive $\delta^{13}\text{C}$ excursion and includes the LS and LL units of the Smoky Hill Chalk. Interval 3 includes the MS unit of the Smoky Hill Chalk. Intervals 1 and 2 are characterized by variable but high carbonate concentrations (average ~70%). The transition between the LL and MS units (Intervals 2 and 3) is marked by a decrease in carbonate concentrations (average ~40%; Locklair et al., 2011; Tessin et al., 2015).

Organic carbon accumulation was low (<2%) during Interval 1 and biological and geochemical proxy evidence suggests that the WIS was dominantly oxic during this time (Savrdá, 1998; Tessin et al., 2015, 2016; Lowery et al., 2017). Organic matter preserved within Interval 1 is characterized by low organic carbon to nitrogen ratios (C:N) and low hydrogen index values (Tessin et al., 2015). This nitrogen-rich and hydrogen poor organic matter has been interpreted as either predominantly terrestrial in origin or oxidized marine organic matter (Tessin et al., 2015). During Intervals 2 and 3, deposition occurred under oxygen limited conditions (Savrdá, 1998; Tessin et al., 2015, 2016; Lowery et al., 2017). At the onset of Interval 2 the elemental and isotopic composition of sedimentary organic matter changes (Tessin et al., 2015). Organic matter deposited within Intervals 2 and 3 is more nitrogen-poor and hydrogen-rich than Interval 1, indicating a change in the preservation and/or source of organic matter (Tessin et al., 2015).

Despite significant research on the Niobrara Formation, the fundamental question of how the source of organic matter changes throughout the formation remains unanswered. In this study, we present lipid biomarker records from the USGS Portland core to evaluate the thermal maturity and variations in organic matter source within the Niobrara Formation to characterize the organic matter accumulated before, during, and after the previously identified “OAE 3” interval. The degree of thermal maturity is evaluated first, because increasing maturity can significantly alter biomarker distributions and complicate paleoenvironmental reconstructions. Organic thermal maturity is assessed, using sterane and hopane stereochemistry indices (Mackenzie et al., 1980; Seifert and Moldowan, 1986), and compared with previous RockEval and vitrinite reflectance-derived estimates of thermal maturity (Locklair, 2007). The evolving sources of organic matter within the WIS are subsequently evaluated using the distribution of n-alkanes, steranes C_{27} – C_{30} and sterane/hopane ratios in order to distinguish between organic matter sources including marine phytoplankton and zooplankton, higher plants, algae, and bacteria (e.g. Moldowan et al., 1985; Peters et al., 2005). Finally, the pristane and phytane ratios are compared with previous biological and geochemical estimates of paleo-redox conditions to evaluate the viability of this proxy for reconstructing redox conditions in the geologic past.

2. Methods and materials

The USGS #1 Portland core was drilled and continuously cored near Cañon City, CO (Dean and Arthur, 1998). The Portland core is located within the deep, central axis of the WIS; this region

contains a complete record of the onset of black shale deposition (Fig. 1). It is also located outside of the most thermally-mature regions of the basin, where more thermal alteration of organic matter might be expected. Significant work has been conducted on the Portland core, which allows for comparison to other biological and geochemical studies (Savrdá, 1998; Locklair et al., 2011; Tessin et al., 2015, 2016; Lowery et al., 2017). The 75-m thick Late Cretaceous Niobrara Formation section of the Portland core was sampled at 0.5 m resolution at the USGS Core Research Center in Denver, CO (Fig. 1). Chemostratigraphy for the core is based on carbon isotope and total organic carbon (TOC) records presented in Tessin et al. (2015), which were used to identify Intervals 1, 2, and 3.

Samples analyzed for organic geochemical analyses were ground to <75 μm and homogenized in an alumina shatterbox. Between 5 and 20 g of sample was then extracted on a Dionex Automated Solvent Extractor (ASE) 300 with a 9:1 dichloromethane:methanol (DCM:MeOH) mixture at 100 °C and 1500 psi. Each extract was evaporated to dryness under a gentle stream of N_2 . The apolar fraction was separated using silica open column chromatography by elution with 3 mL hexane. The eluent was then dried under a gentle stream of N_2 and stored at 4 °C before final analysis.

Apolar compounds were identified via gas chromatography-mass spectrometry (ThermoScientific Q8000 Triple Quadrupole MS paired to a Trace 1310 Gas Chromatograph) and compared with retention times of reference compounds. Mass spectrometer data was analyzed using OpenChrom. The abundances of steranes and hopanes were determined based on masses of m/z 217 and 191, respectively. Odd/even preferences of long-chain length n-alkanes were determined using carbon preference index (CPI) and odd-even predominance centered at $n\text{-C}_{31}$ (OEP₃₁), which were calculated as follows (Bray and Evans, 1961) (Scanlan and Smith, 1970):

$$\text{CPI} = \frac{2(n - \text{C}_{23} + n - \text{C}_{25} + n - \text{C}_{27} + n - \text{C}_{29})}{n - \text{C}_{22} + 2(n - \text{C}_{24} + n - \text{C}_{26} + n - \text{C}_{28}) + n - \text{C}_{30}} \quad (1)$$

$$\text{OEP}_{31} = \frac{n - \text{C}_{29} + 6(n - \text{C}_{31}) + n - \text{C}_{33}}{4(n - \text{C}_{30} + n - \text{C}_{32})} \quad (2)$$

Mid-chain length odd-even predominance was calculated based on by adapting OEP₃₁ and calculating the OEP of n-alkanes 21–25. The terrigenous/aquatic ratio (TAR) was used to evaluate the relative abundance of long-chain (C_{27} – C_{31}) to short-chain (C_{15} – C_{19}) n-alkanes as follows (Bourbonniere and Meyers, 1996):

$$\text{TAR} = \frac{n - \text{C}_{27} + n - \text{C}_{29} + n - \text{C}_{31}}{n - \text{C}_{15} + n - \text{C}_{17} + n - \text{C}_{19}} \quad (3)$$

3. Results and discussion

3.1. Sterane and hopane thermal maturity indices

Thermal maturity is generally defined as the extent of alteration of organic matter by heat-driven reactions — an important process in the conversion of sedimentary organic matter to petroleum. A series of biomarker indices used to evaluate the degree of thermal maturity (Fig. 3) have been developed based on the predictable transformation of the stereochemical configuration of terpanes and steranes - associated with increasing thermal maturity (see Peters et al. (2005) for discussion of biomarker stereochemistry). For example, as thermal maturity increases, the isomerization of C-20 in the C_{27} and C_{29} 5 α ,14 α ,17 α (H)-steranes has been shown to

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