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$\delta^{13}C$ AND $\delta^{15}N$ ANALYSIS OF TOROK AND NANUSHUK FORMATION MUDSTONES AT SLOPE MOUNTAIN, ALASKA

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INTRODUCTION

We use $\delta^{13}C$ and $\delta^{15}N$ analysis of organic matter from the Torok and Nanushuk formations at Slope Mountain, Alaska to interpret atmospheric and oceanic chemistry and estimate precipitation variables during the Albian-Cenomanian, a known period of greenhouse conditions in the Cretaceous Arctic. $\delta^{13}C$ values from higher-plant organic matter are closely related to the carbon isotope composition of the ocean- atmosphere carbon reservoir (Gröcke 2002). $\delta^{13}C$ analysis and C/N ratios also make it possible to determine the different types of organic matter contributing to a system (Bocherens et al. , 1994; Gröcke, 2002). Thus stable isotope geochemistry of organic matter can also be used to differentiate fine-grained facies into marine, marginal marine, or terrestrial environments which would be impossible to determine by grain size and sedimentary structures alone.

GEOLOGIC SETTING

Slope Mountain, Alaska (N68.75º W149.03º), is located in the northern foothills of the Brooks Range, situated on the proximal margin of the North Slope foreland basin (Fig. 1, Shimer and McCarthy, this volume). The mountain consists primarily of strata from the Nanushuk and Torok formations which date to the Albian-Cenomanian ages of the Cretaceous (Johnsson and Sokol, 1998; LePain et al., 2009). The North Slope foreland basin, also known as the Colville Basin, developed on the Arctic Alaska micro plate (Bird and Molenaar, 1992). The south of the basin is bounded today by the Brooks Range, while the north is bounded by the Beaufort Sea where the Barrow Arch, a rift shoulder, separates the foreland basin from the extensional Canada basin to the north (Bird and Molenaar, 1992). In the west the basin continues to the Herald Arch, a subsurface structure beneath the Chukchi Sea, and the eastern edge of the basin narrows as the Brooks Range extends almost to the northern coastline near the Canada-Alaska border (Bird and Molenaar, 1992).

The age of the Colville Basin fill ranges from Middle Jurassic to Cenozoic and consists of deposits from the ancestral Brooks Range (Bird and Molenaar, 1992). The Nanushuk Formation is Albian–Cenomanian in age, while the Torok Formation is dated further back to the Aptian–Cenomanian (Mull et al,. 2003). The Nanushuk was deposited in topset, marine to shelf environments, while the Torok was deposited in deepwater, slope to basin environments (Decker, 2007). The Nanushuk Formation prograded over the silty mudstones of the Torok Formation as the units filled the foreland basin (Mull et al, 2003; Decker 2007). As exposed in outcrop at Slope Mountain, the complete succession the Nanushuk Formation and the upper portion of the Torok Formation present an opportunity to track environmental change through time using stable isotope analysis.

METHODS

Carbon and Nitrogen Stable Isotopes

Mudstone samples were collected throughout the measured stratigraphic sections. Most samples were taken in the lower portion of the study site, which likely represents the most proximal portion of the marine Torok formation. Only mudstones were being collected because sandstones do not contain much organic matter. Since much of the marginal marine to non-marine upper Nanushuk Formation mudstones are covered in talus, float samples were collected from carbon-rich locations in the Nanushuk Formation for comparative purposes.

Each sample was prepped at Oberlin College for **δ**^{13}C and **δ**^{15}N analysis based on the methods of Pansu and Gautheyroum (2006). Each sample was bathed in a 10% HCL solution for 24 hours to remove carbonate. They were then put through vacuum filtration and rinsed repeatedly to remove the solution. Samples were then placed in the oven overnight to dry.

Processed samples were run for isotopic analyses at the Washington State University - Stable Isotope Core Laboratory. Samples were weighed out in tin capsules and inserted into a Costech Elemental Analyzer (ECS 4010). A Thermofinnigan Delta PlusXP Mass Spectrometer Isotope was the used to perform mass spectrometry (IRMS) to determine C and N isotope values. These isotope values are reported using conventional delta notation (δ^{13}C, δ^{15}N) in parts per mil (‰) relative to Pee-Dee Belemnite (VPDB).

Calculations

δ^{13}C value of land plants were used to determine atmospheric **δ**^{13}C with the following equation from Arens et al. (2000):

$$\delta^{13}C_{atm} = (\delta 13C_{plants} + 18.67) / 1.10$$

Carbon nitrogen ratios can also be calculated from the data, by dividing the percent carbon by the percent nitrogen. This provides information about depositional environment and plant typology.

RESULTS

The **δ**^{13}C values **δ**^{15}N values and C/N ratios are included in Figures 1, 2, and 3. The **δ**^{13}C values ranged from - 22.50‰ and -26.09‰, with an average of -24.72‰, which is expected for terrestrial organic carbon from Cretaceous C_3 plants. C/N ratios ranged from 2.27‰ to 45.59‰.

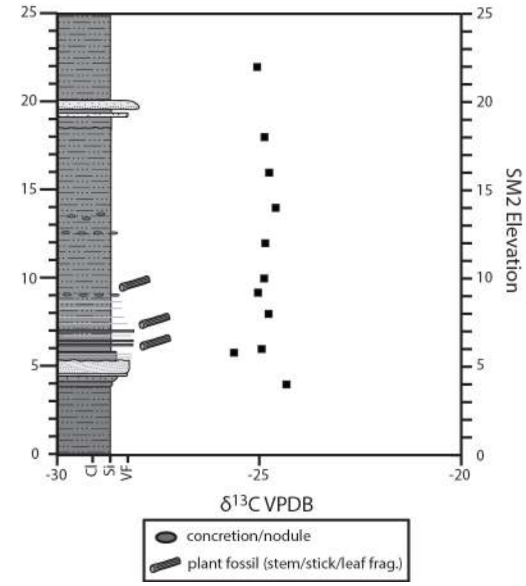

Figure 1. Changes in ***δ****^{13}C values shown in comparison to the stratigraphy for the first 25m.*

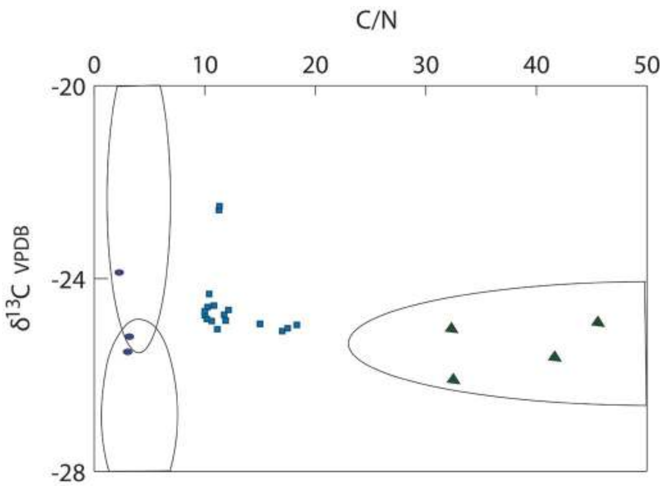

Figure 2. The relationship between ***δ****^{13}C values and C/N ratios indicates areas produced by marine algae, lacustrine algae, and C3 land plants (after Meyers, 1997). Most of the sample is a combination of algae and plant material.*

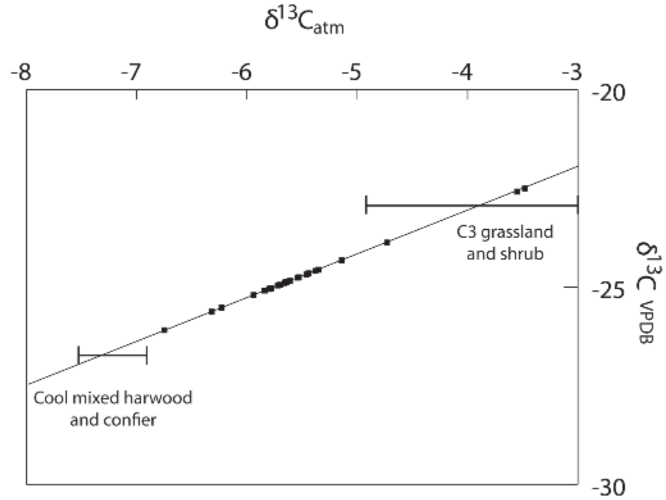

Figure 3. The comparison of $\delta^{13}C$ *values and* $\delta^{13}C_{atm}$ *values indicates changes in the environment (From Arens et al., 2000).*

SM2-5.8 (5.8m) had a more negative value of -25.62‰ than its surrounding values. This was coupled with a substantially higher C/N ratio of 41.64. This sample is a baseline for expected values for terrestrial C_3 plant values because this layer consisted of mostly fossilized plant remains.

Samples from 42.5m (SM1-14), 51.0m (SM2-51), and 52.5m (SM1-24) had lower C/N ratios of 3.07, 2.37, 3.17, respectively. SM1-14 and SM1-24 also had slightly more positive than average $\delta^{13}C$ values, while SM2-51 had a slightly more negative value. SM2-51 was also a crumbly, tan layer and not a mudstone.

SM1. 1-6 and Float – 1 both had low $\delta^{13}C$ values of -22.58‰ and -22.50‰ respectively.

Float 1 and Float 2 had high $\delta^{13}C$ values of -25.04‰ and -26.09‰ and high C/N ratios of 32.32 and 32.50 respectively. Float -2 also had a high C/N ratio of 45.59. These higher C/N ratios are indicative of C_3 terrestrial plants.

DISCUSSION

Paleoenvironmental context

Previous studies of the mid- to Late Cretaceous Arctic have indicated that the environment was very different from today. Evidence suggests that the mid-Cretaceous had a reduced equator to polar temperature gradient (Barron and Washington, 1982; Spicer and Corfield, 1992; Ufnar et al., 2004). It is also suggested that the mid-Cretaceous had decreased annual temperature variations, diminished seasonal temperature extremes, and limited below freezing temperatures in the arctic (Sloan and Barron, 1990; Ufnar et al., 2004).

Assuming a paleo-latitude between 71 °N and 89 °N, the Northern Alaska winter likely had almost 5 months of continuous darkness bounded by months of continuous twilight during the Late Cretaceous (Spicer and Herman, 2010). Based on wood anatomy, leaf margin analysis, and vegetation composition, the Cenomanian North Alaska had an air temperature of approximately 10 °C with a mean annual range of over 20 °C, but no lower than -11 °C (Spicer and Parrish, 1986; Parrish et al., 1987; Spicer and Parrish, 1990a; Spicer and Herman, 2010). At 60 °N, the Aptian – Albian had a mean annual temperature of around 16 °C (Huber et al., 1995, 2002), while the Late Albian had a temperature between 10 °C and 13 °C (Fassell and Bralower, 1999; Ufnar et al., 2004). Coal accumulation during this period indicates that precipitation was high (Spicer and Herman, 2010). Late Albian North Slope, Alaska precipitation estimation models indicate between 485–626 mm/yr, which is consistent with precipitation in modern peat-forming environments (Ufnar et al. 2004).

Carbon Stable Isotopes

Bulk samples were used for the carbon stable isotopes in this study. Wood would be ideal; however, it was not present throughout the study location. For stratigraphy purposes, bulk organic matter carbon isotope values of mudstones provides valuable information about variation throughout the stratigraphy. Dark mudstones are often carbonaceous and can provide some information about the paleoenvironment.

The $\delta^{13}C_{bulk}$ values in this study ranged from -22.50‰ to -26.09‰, which is expected for Late Cretaceous C_3 terrestrial plants, which usually range in $\delta^{13}C$ values from -20‰ to -28‰ (Salazar Jaramillo et al., 2016). The values in this study are slightly more negative than other studies from around the same time period. The variation in the values observed between study sites could be caused by both local and global factors. Differences in atmospheric CO_2 between the ages

Age	Location	δ¹³C ‰ (VPDB)	Source
Albian-Cenomanian	North Slope, Alaska	Bulk: -22.50% to -26.09%	This study
Aptian	Hokkaido, northern Japan	Wood: -25.4% to -21.8%	(Ando et al., 2002)
Cenomanian	Dakota Formation, Nebraska	Bulk: -24% and -23%	(Gröcke et al 2006)
Middle Maastrichtian	Lower Cantwell Formation, Alaska	Wood: -22.42% to -27.85%	(Salazar-Jaramillo et al., 2016)
		Bulk: -22.95% to -27.10%	
Aptian	Isle of Wright, England	Wood: (~ -29% to ~ -19%)	(Gröcke et al 1999).

Table 1. This table shows different **δ**^{13}*C values for different locations and ages that are comparable to Slope Mountain.*

could affect the **δ**^{13}C values. Latitude, temperature, and plant type could also have an effect on values. For example, the expected value of a C_3 plant is different than that of algae.

Comparing results from Slope Mountain to other Mid to Late Cretaceous studies provides insight into the variation of the values. Aptian (Mid-Cretaceous) marine sediments from central Hokkaido, northern Japan had a **δ**$^{13}C_{wood}$ range from -25.4‰ to -21.8‰. The curve of **δ**$^{13}C_{wood}$ was found to parallel the **δ**$^{13}C_{carbonate}$ curve from a Pacific guyot (Ando et al., 2002). These values are slightly more positive than those from Slope Mountain, and this could be caused by differences in latitude, temperature, or plant type.

During the Cenomanian, **δ**$^{13}C_{bulk}$ values from the Dakota Formation in Rose Creek Pit, Nebraska. ranged between -24‰ and -23‰ (Grocke et al. , 2006). Younger Middle Maastrichtian (Late Cretaceous) samples from the Lower Cantwell Formation, Alaska had **δ**$^{13}C_{bulk}$ range from -22.95‰ to -27.10‰ and **δ**$^{13}C_{wood}$ range from -22.42% to -27.85‰ (Salazar-Jaramillo et al. 2016).

These values are very similar to this study and come from a nearby location.

An Aptian study of the Isle of Wight in England found **δ**$^{13}C_{wood}$ to vary based on isotopic composition of global CO_2, not local environmental impacts (Gröcke et al., 1999). This suggests that changes seen between the Slope Mountain Samples and others are due to differences in climate throughout time.

Modern studies indicate that **δ**$^{13}C_{atm}$ values can depend on depositional setting and diagenesis. Nearshore environments tend to have more negative values than offshore (Dickens et al., 2004). Recent sediment from the Alaskan-Siberian arctic had more positive **δ**^{13}C values in sediments from estuarine environments, while C/N ratio were lower towards estuarine environments. River deltas had a value of ~ -25‰, sounds ranged from ~ -23‰ to -22‰, and open shelf was ~ -21‰ (Naidu et al., 1993).

Isotopic changes in plants can occur during early diagenesis of lignified plant tissue, which causes fossil wood to have slightly more depleted **δ**^{13}C values compared to modern plants (Benner et al. 1987). Diagenesis is change caused by physical, biological or chemical factors in sediments after lithification. In Miocene to Holocene sediments, diagenesis has been shown to not cause a significant shift in **δ**^{13}C (Dean et al., 1986) and indicates that it is unlikely to affect values of sediments from the Cretaceous.

The comparison of the **δ**^{13}C values with the C/N ratios from this study (Fig. 2) indicates that most of the bulk organic matter samples are a combination of algae and C_3 plant material. Lower C/N ratios are indicative of a planktonic source. SM1-4, SM1-6, and SM2-52 had lower values, indicative of algae. The increase in algal organic matter does not appear to correlate with lithology. In contrast, SM2-5. 8, Float -2, Float 1, and Float 2 were indicative of C_3 plants and were recovered from mudstones with abundant plant fragments.

The comparison of the **δ**^{13}C values with the **δ**$^{13}C_{atm}$ values (Fig. 3) indicates an environment most similar to somewhere between a cool mixed hardwood and conifer forest and a modern C_3 grassland and shrub environment. C_3 grassland environments did not exist until the Cenozoic, but these values are indicative of a warmer Cretaceous environment. Many of the plant fragments observed in the field were sphenophytes (equisetum, or horsetails), which are spore-bearing plants with a modern **δ**^{13}C values range from -25.0‰ to -28.8‰ (Milligan et al. , 2010).

The **δ**^{13}C values, ^{13}**δ**C_{atm} values, and the C/N ratios produced from this study imply that Arctic Alaska was warm and wet during the Albian. This data supports previous research and adds more detailed information to greenhouse Arctic conditions. These results demonstrate the utility of stable isotope analysis of bulk organic matter in mudstones and show that an increase in sampling would provide important insight into the variations of local depositional patterns and global environmental conditions throughout the Albian-Cenomanian.

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