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δ^{13}C AND δ^{18}O ANALYSES OF CARBONATE CONCRETIONS AND NODULES AND THE EVIDENCE FOR A CRETACEOUS GREENHOUSE

JOSEPH BENINATI, Washington and Lee University
Research Advisor: Lisa Greer

INTRODUCTION

The sedimentary rocks of Slope Mountain, also known as the Marmot Syncline (Fig. 3, Shimer and McCarthy, this volume), have been interpreted to represent shallow marine, deltaic, and fluvial environments of the Torok Formation and Nanushuk Formation (Johnsson and Sokol, 1998). The Torok Formation and Nanushuk Formation are widespread across Alaska's North Slope, and are generally established to be Aptian-Cenomanian in age (Mull et al., 2003). Based upon a single sample containing a late Albian palynoflora (Reifenstuhl and Plumb, 1993), the age of the strata at Slope Mountain is thought to be Aptian-Albian (Johnnson and Sokol, 1998).

The middle-Cretaceous climate is most commonly interpreted as a greenhouse-world in which peak temperatures were as great as any other period in Earth's history (Frakes 1999; Wilson and Norris, 2001; Jenkyns et al., 2004). There is evidence of global CO_2 levels 4-5 times those of today, sea-surface temperatures approaching 20-21°C, and thermophilic flora and fauna spreading to high latitudes (Tajika, 1999; Herman and Spicer, 2010). These conditions were likely the result of greater heat circulation via Earth's oceans, changes in the land-sea geography, and increased regional volcanism (Huber et al., 1995; Herman and Spicer, 2010).

Stable isotope geochemistry has become a common method for uncovering Earth's climatic history. Accurate geochemical profiles from bulk Cretaceous carbonate samples can be difficult to assemble because post-depositional indicators often overprint original geochemical signals (Huber et al., Jenkyns et al., 2004; 1995). Carbonate concretions and nodules have been found throughout the Torok Formation and Nanushuk Formation (LePain et al., 2009), and present an opportunity to test the utility of stable isotopic geochemistry in climatic reconstruction for the Arctic. Concretions are diagenetic sedimentary structures that form when water is expelled out of sediment during compaction. As the sediment compacts, precipitate minerals fill the voids left by water and form a solid mass within the sediment. Recent studies have suggested siderite concretions can be a valuable proxy for depositional environments, atmospheric heat transport, and paleohydrology (McKay et al., 1995; Ufnar et al., 2008).

Understanding Earth's climatic record is increasingly important for modeling and predicting the effects of modern climate change. Our research compares geochemical and stable isotope analyses of Torok Formation and Nanushuk Formation concretions and nodules to other Middle-Cretaceous climate studies. Though limited studies have been conducted on Slope Mountain strata, no stable isotope data currently exists local to our field site. A number of analogous studies of Middle-Cretaceous marine carbonates and sideritized carbonates do exist, however (McKay et al. 1995; Ufnar et al., 2008; Suarez et al. 2015). These studies investigate concretions and nodules, Middle-Cretaceous siderite-bearing paleosols, and Middle-Cretaceous bivalves. We assess whether the bulk stable isotope data from marine carbonate concretion and nodule samples are accurate stable isotope proxies for climate. By comparing our data to prior regional studies, we hope to further the understanding of Middle-Cretaceous climate.

METHODS

Concretion and Nodule Sampling

Carbonates reported as "nodules," as defined by Mozley and Burns (1992), were considered concretions because a clear distinction could not be made. Thirty samples were collected *in situ* from eight stratigraphic sections on Slope Mountain (Fig. 3, Shimer and McCarthy, this volume), with a majority of samples from SM2 (Fig. 4, Shimer and McCarthy, this volume). We cut samples for thin section and geochemical analysis using the University of Alaska Fairbanks' Geoscience Department rock-saw. All further sample preparation and analysis took place at the Washington and Lee University Geology Department (W&L). Prior to geochemical analyses, 10% hydrochloric acid was applied to samples in order to eliminate those samples that did not possess a significant amount of carbonate minerals. We then powdered the concretion and nodule samples using a mortar and pestle or a SPEX SamplePrep 8510 Shatterbox for X-ray diffraction (XRD) and isotopic analysis. Bulk powder samples were used for all XRD and isotope analyses.

XRD Analysis

XRD analyses were conducted using a Diano 2100 E X-ray diffractometer. Sample powder was mounted on a 1" x 2" glass slide using 99% isopropyl alcohol. The XRD machine used Cu kα radiation set to 40 Kv. Each sample's rate scan lasted 20 minutes, with the exception of one sample that was run for 7 hours. Based off of identified and assumed mineralogy, 2-Theta Rates were assessed between 20° and 80°.

Stable Isotope Analysis

Additional sample powder obtained using the Shatterbox was analyzed for $\delta^{13}C$ and $\delta^{18}O$ data using a Thermo Scientific Delta V Advantage mass spectrometer and Finnigan GasBench II. Powdered samples were weighed to an average of 500 µg using a Sartorius Cubis Series MSE-3.6p balance. The mass of each powder sample was determined by its percent carbonate. Those samples that contained less carbonate were run with greater mass in order to generate a significant isotope signal. Triplets of each sample were run to improve accuracy. Many of the samples were composed of impure carbonates, and by preparing triplets of each sample, we further increased the probability of returning a significant isotope signal. After weighing, powders were flushed with 99% compressed He and pressurized to remove present-day atmospheric $\delta^{13}C$ or $\delta^{18}O$ signatures. Pure crystalized Acros Organics phosphoric acid (H_3PO_4) was heated into a liquid on a hot plate. The liquid H_3PO_4 was next reacted with each pressurized sample for no less than two hours. The prepared samples were then run in the mass spectrometer. $\delta^{13}C$ and $\delta^{18}O$ data were compared to the NIST NBS19 standard. $\delta^{13}C$ and $\delta^{18}O$ samples were corrected to the Vienna Pee Dee Belemnite (VPDB) standard. The VPDB values for $\delta^{18}O$ were then corrected Vienna Standard Mean Ocean Water (VSMOW) using the formula (Sharp, 2007):

$$\delta^{18}O_{VSMOW} = 1.03086 * (\delta^{18}O_{VPDB}) + 30.86 \text{ (Equation 1)}$$

We only used data for samples that returned no less than eight carbonate peaks with standard deviations less than 0.1. The greatest number of peaks our data returned was ten. Stable isotope data were analyzed using Isodat Acquisition software and then transferred to Microsoft Excel. $\delta^{13}C$ and $\delta^{18}O$ were plotted against each other and $\delta^{13}C$ and $\delta^{18}O$ were then individually plotted stratigraphically.

RESULTS

XRD Analysis

The purpose of our XRD analyses was to better determine concretion and nodule mineralogy. LePain et al. (2009) describes many of these concretions and nodules as containing siderite. The results of our XRD scans, however, do not suggest a significant siderite presence. Furthermore, five of our XRD scans did not return any identifiable peaks. In order to correct for this issue, we increased the XRD rate scan time and let one sample run overnight. This technique did not have a significant effect on our results. Figure 1 is exemplary of our XRD results. With the exception of quartz and carbonate, no additional mineralogy was able to be confidentially determined.

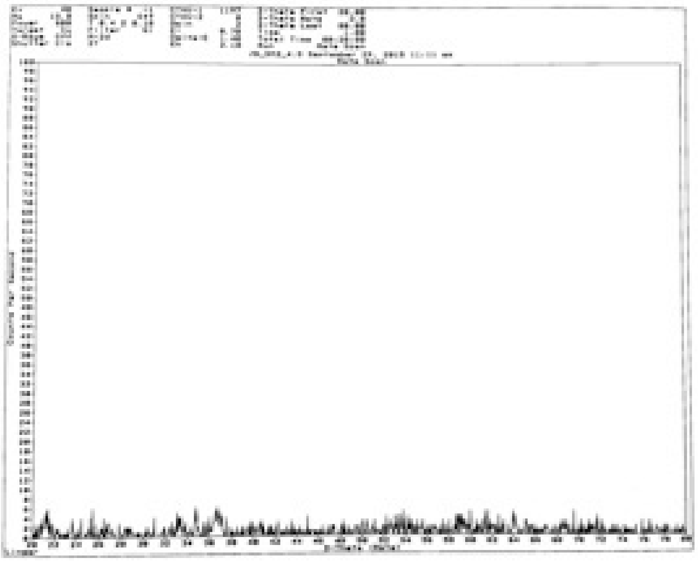

Figure 1. Exemplary XRD scan for SM2 concretion and nodule samples. The sample was run, as all except one were, for 20 minutes. The XRD machine used Cu kα radiation set to 40 Kv. No significant siderite presence is detected and, due to the lack of identifiable peaks, no mineralogy was confidentially determined.

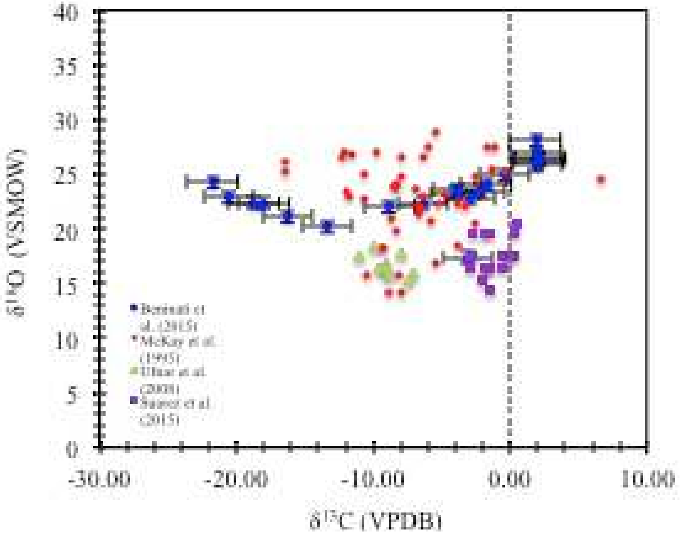

Figure 2. Plot showing $\delta^{18}O$ plotted against $\delta^{13}C$. Data from McKay et al. (1995), Suarez et al. (2015), et al and Ufnar. (2008) are included. Data from this study encompass and serve as boundaries for the supplemental data. A gentle positive and linear slope exists between $\delta^{18}O$ and $\delta^{13}C$ for this study's data. $\delta^{13}C$ values have greater variance than $\delta^{18}O$ values. The error bars on this study's data depict standard error.

Stable Isotope Analyses

$\delta^{18}O$ results range from 17.40-28.10‰ VSMOW with an average value of 23.66‰ VSMOW. $\delta^{13}C$ results range from -21.73-2.20‰ VPDB with an average value of -6.19‰ VPDB (Table 1). $\delta^{18}O$ and $\delta^{13}C$ were compared to three different studies: McKay et al. (1995), Ufnar et al. (2008), and Suarez et al. (2015). Figure 2 is a comprehensive plot of this study's $\delta^{18}O$ and $\delta^{13}C$ data plotted against these prior studies. With the exception of one sample from McKay et al. (1995), our results scattered across the range of all of these studies' data. Our data can be seen as bounding in a both a positive and negative to the proxy studies' data. In our study, $\delta^{13}C$ produced greater variance, with standard deviation of 8.38‰ VPDB. $\delta^{18}O$ results were more consistent, with standard deviation of 2.52‰ VSMOW. Our $\delta^{18}O$ and $\delta^{13}C$ results produce a gentle positive slope of 0.16. Data from McKay et al. (1995) and Suarez et al. (2015) also reflect similar positive linear slopes between $\delta^{18}O$ and $\delta^{13}C$.

Figure 3 shows our $\delta^{18}O$ and $\delta^{13}C$ data plotted against their respective stratigraphic positions on Slope Mountain. Again, $\delta^{13}C$ data show greater variance than $\delta^{18}O$ data. Stratigraphic position does not reflect any significant trends in $\delta^{18}O$ values, as the data remain vertically consistent. $\delta^{13}C$ values, on the other hand, are affected by geologic time and Cretaceous climate change. $\delta^{13}C$ tend to be more enriched moving up Slope Mountain, with two positive $\delta^{13}C$ excursions at 35.7 m and 45 m (Fig. 3).

DISCUSSION

Significant analogues for our $\delta^{18}O$ and $\delta^{13}C$ data are twofold: our samples all are taken from marine environments and our samples are all concretions or nodules. In comparison, Suarez et al. (2015) incorporated stable isotope data from bivalve shells, but not concretions. Ufnar et al. (2008) incorporated stable isotope data from siderite bearing paleosols, and while these samples may have similar mineralogy, they are from different depositional environments. Both of their data nonetheless suggest a greenhouse Middle-Cretaceous as evidenced through paleohydrology and atmospheric heat transport. Our results present an interesting intersection between both

Sample	Stratigraphic Position (m)	Average $\delta^{18}O$ ‰ (VSMOW)	$\delta^{18}O$ ‰ (VSMOW)	Average $\delta^{13}C$ ‰ (VPDB)	$\delta^{13}C$ ‰ (VPDB)
SM2-JB-3.9M-A	3.90		27.00		1.87
SM2-JB-3.9M-B	3.90		22.00		-8.78
SM2-JB-3.9M-C	3.90	24.60	24.90	-2.50	-0.45
SM2-JB-4M-A	4.00		21.10		-16.28
SM2-JB-4M-B	4.00		20.20		-13.32
SM2-JB-4M-C	4.00	21.20	22.30	-15.90	-17.95
SM2-6MCON-A	6.00		22.40		-18.69
SM2-JB-6MCON-B	6.00		22.90		-20.54
SM2-JB-6MCON-C	6.00	23.20	24.30	-20.30	-21.73
SM2-JB-7.8M-A	7.80		24.10		-1.74
SM2-JB-7.8M-B	7.80		22.80		-2.92
SM2-JB-7.8M-C	7.80	23.50	23.40	-2.30	-2.24
SM1-JB-7.2M-A	35.70		25.80		1.97
SM1-JB-7.2M-B	35.70		26.50		2.10
SM1-JB-7.2M-C	35.70	26.30	26.40	2.10	2.20
SM2-JB-39.5M-A	39.50		23.60		-3.82
SM2-JB-39.5M-B	39.50		22.30		-6.39
SM2-JB-39.5M-C	39.50	23.00	23.20	-4.70	-3.97
SM2-JB-45M-A	45.00		26.20		2.06
SM2-JB-45M-B	45.00		17.40		-3.13
SM2-JB-45M-C	45.00	23.90	28.10	0.30	1.86
	Mean:		23.66		-6.19
	Max:		28.10		2.20
	Min:		17.40		-21.73
	Standard Deviation:		2.52		8.38

Table 1. Tabular representation of all concretion and nodule $\delta^{18}O$ and $\delta^{13}C$ data. For each sample at a unique stratigraphic location, triplet bulk powder samples were run for $\delta^{18}O$ and $\delta^{13}C$ ratios. Average values for this triplet procedure are included. Below, fundamental statistics show comprehensive mean, maximum, minimum, and standard deviation values.

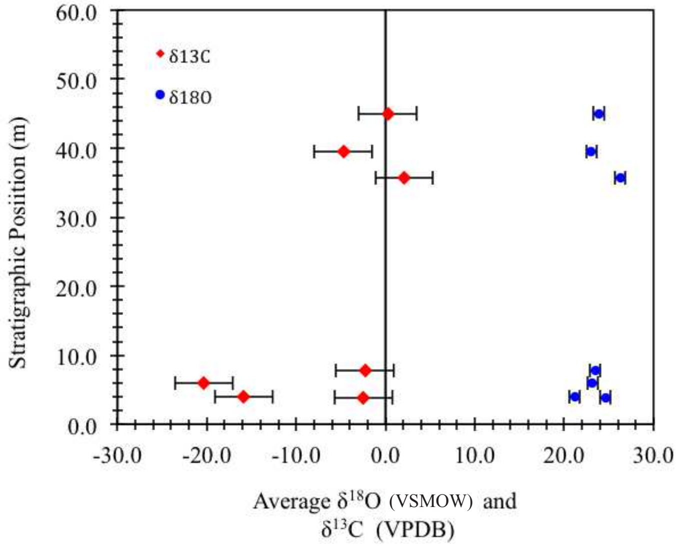

Figure 3. Average $\delta^{18}O$ and $\delta^{13}C$ each plotted against their stratigraphic position on Slope Mountain. These data are derived from the average values of each sample's triplet. Notice the consistent $\delta^{18}O$ VSMOW values contrasted against more variable $\delta^{13}C$ VPDB values that become more enriched moving up Slope Mountain. Error bars depict standard error.

previous studies. Mozley and Burns (1993) conducted a global study on concretionary marine carbonate samples and recorded values for δ^{13}C ranging from -40-10‰ VPDB and values for δ^{18}O ranging from 14-30‰ VSMOW. Our δ^{18}O results agree with these results, and while our δ^{13}C fall within this range, the variance is too large to consider significant. We attribute the large δ^{13}C variance to terrestrial contamination of plant and woody matter (see Ratigan, this volume). Johnsson and Sokol (1998) is the only stratigraphic field study that has focused extensively on Slope Mountain. Their interpretation of the area as a high-energy prograding deltaic system supports the possibility of terrestrial matter being introduced into marine environments. The introduction of terrestrial δ^{13}C into our system would result in both meteoric and ocean data being returned. A study done by Wilson and Norris (2001) on Middle-Cretaceous foraminifera produced δ^{18}O values ranging from 27-29‰ VSMOW. These values correspond to sea-surface temperatures ranging from 24-32°C and lie in accordance with our data. Their study, however, reports δ^{13}C values between 0-3‰ VPDB, which align with the minority of our data.

One of the major limitations of this study is the undetermined concretion and nodule mineralogy. The concretions were initially believed to contain large amounts of siderite, but our XRD analyses did not prove this to be correct. Given the agreement of our δ^{18}O and δ^{13}C data to that of Ufnar et al. (2008), it is possible that the concretions once contained significant percentages of siderite, but the minerals have since been altered and are now amorphous. We interpret the lack of present-day siderite to near-surface weathering processes. This interpretation has significant implications for our δ^{18}O and δ^{13}C results because our data may reflect isotopic signals of intensely altered minerals.

CONCLUSION

The results of our δ^{18}O and δ^{13}C stable isotope analyses are in agreement with prior studies that suggest a greenhouse Middle-Cretaceous climate. By comparing our data to that of prior studies, we were able to refine the understanding of Middle-Cretaceous climate and add isotope data local to Slope Mountain to the scientific community. Further analyses must be done to better understand the mineralogy and geochemistry surrounding the reported siderite concretions and nodules. With these analyses, we will greatly increase the reliability of this study's data and many others' data that focuses on using concretions for climate proxies.

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