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Nitrogen cycle dynamics in the Late Cretaceous Greenhouse

Christopher K. Junium [a,*], Stephen R. Meyers [b], Michael A. Arthur [c]

[a] Department of Earth Sciences, Syracuse University, Syracuse, NY, 13244, USA
[b] Department of Geoscience, University of Wisconsin, Madison, WI, 53706, USA
[c] Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

Great attention has been paid to the origin of anomalously low nitrogen isotope values during the Late Cretaceous. Nitrogen isotope values are often as low as −3‰ and are typically less than +2‰, even in relatively organic matter-lean sediments. Here we evaluate nitrogen isotope variability during a relatively quiescent phase of the Late Cretaceous Greenhouse, between Oceanic Anoxic Events 2 and 3, using the black shales of Demerara Rise (DR). Selection of this site allows us to isolate some of the factors that control nitrogen cycle dynamics and contribute to low nitrogen isotope values. New N-isotope measurements from ODP Site 1259 reveal $\delta^{15}N$ values that range from +0.2‰ to −3.5‰ and oscillate by 1.5‰ to 3‰ over 1.6 million years (Ma). Temporal calibration of our data using a new astronomical time scale reveals a strong ∼100 thousand year (ka) eccentricity cyclicity in $\delta^{15}N$. We attribute this cyclicity to oscillations in the position of the intertropical convergence zone (ITCZ) over DR that modulate upwelling intensity, chemocline depth and the degree of ^{15}N-depletion. We also recognize a statistically significant correlation ($p = 0.0022$) between the TEX_{86} indices and $\delta^{15}N$, with the lowest $\delta^{15}N$ corresponding to the highest TEX_{86} indices. This relationship suggests that the activity and ecology of ammonia oxidizing Thaumarchaeota and the $\delta^{15}N$ of dissolved inorganic nitrogen utilized by primary producers are linked. We therefore interpret the observed variability in the $\delta^{15}N$ data and TEX_{86} indices as primarily reflecting fluctuation of upwelling intensity and chemocline depth, and the significant inverse relationship between these data sets suggests that caution should be exercised when interpreting the TEX_{86} in terms of temperature in similar paleoenvironmental settings.

1. Introduction

The biogeochemical and climatic conditions that allow for the widespread deposition of black shales have remained a point of significant interest to the geologic community for many years (e.g. Schlanger and Jenkyns, 1976). One of the unusual characteristics of Oceanic Anoxic Event (OAE) black shales of the Mesozoic, and other Greenhouse time periods such as the Devonian, is that $\delta^{15}N$ can be anomalously low in the context of the modern nitrogen cycle (e.g. Kuypers et al., 2004; Junium and Arthur, 2007; Higgins et al., 2012; Ruvalcaba Baroni et al., 2015). The low $\delta^{15}N$ values are consistent with a biogeochemistry and microbial ecology that was vastly different than modern marine basins, including those that are anoxic (Haug et al., 1998; Fulton et al., 2012), a fact that is clearly seen in the biomarker record (Kuypers et al., 2004; Owens et al., 2016). Attention to this problem has naturally focused on OAEs since they are intervals of time that were characterized by global-scale environmental perturbations. Geochemical records of OAEs have revealed nitrogen cycle changes that were in-phase with the progression of paleoceanographic and geochemical changes through their duration (e.g. Dumitrescu and Brassell, 2006; Junium et al., 2015; Trabucho-Alexandre et al., 2010; Adams et al., 2010; Meyers et al., 2012; Owens et al., 2016). However, isolating the specific parameters that controlled the nitrogen cycle and contributed to ^{15}N-depletion remain difficult to extract from the complexities of OAEs.

Here we present a new nitrogen isotope record from the black shales of DR through a relatively quiescent period in the mid-Turonian between OAEs 2 and 3. This interval of time is well-suited for our analysis because it is not associated with significant carbon cycle variability, any known global or regional reorganizations of ocean circulation, nor large changes in sea-surface temperatures (Bornemann et al., 2008; MacLeod et al., 2013). DR is also an excellent locality for isolating paleoclimatic and paleoceanographic signals because it does not have significant facies changes over the study interval (Erbacher et al., 2004). To evaluate these data we utilized a new astronomical time scale developed using quantita-

* Corresponding author.
E-mail address: ckjunium@syr.edu (C.K. Junium).

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tive cyclostratigraphic techniques (Meyers et al., 2001, 2012). This new time-calibrated nitrogen isotope record provides perspectives on the link between nitrogen cycling, redox state and planktonic Thaumarchaeota communities, as well as the climatic controls on nitrogen cycle dynamics in the Late Cretaceous.

1.1. Geologic setting

DR is located off the Northeast coast of South America, adjacent to Guyana and Suriname. DR itself is a partially subsided block of continental crust on which there are significant accumulations of Cretaceous through Paleogene sediments (Erbacher et al., 2004). Paleodepths in the Late Cretaceous are difficult to constrain beyond the fact that sedimentation was likely below storm wave base and not deeper than DR today. Modern depths range from nearly 3000 m at the northern edge to less than 1000 m where DR meets the modern South American continental shelf system. By the mid-Cenomanian the northern edge of the DR was deeper than 1000 m (Arthur and Natland, 1979; Wagner and Pletsch, 1999). Paleolatitudes during the Late Cretaceous interval are estimated to be between 5° and 15°N (Suganuma and Ogg, 2006).

Sediments from the mid-Cenomanian to the basal Campanian comprise an extraordinary accumulation of finely laminated hemipelagic black shales that span a range of lithologies from organic matter-rich limestones and chalks to organic matter-rich clays. Aside from intervals cemented by authigenic carbonates, the sequence is largely unlithified, and contains organic matter that is extremely well-preserved (e.g. Junium et al., 2011) with no apparent alteration from thermal maturation (Forster et al., 2004; Junium and Arthur, 2007). Sediments are almost exclusively laminated, and have an average organic carbon wt.% of ∼7%. Proxy data are consistent with protracted basinal anoxia, that was punctuated by short intervals of oxygenation indicated by rare bioturbation, benthic foraminifera (Friedrich et al., 2006) and occasional, thin-walled inoceramids (Erbacher et al., 2004).

2. Methods

2.1. Nitrogen isotope analyses

Core materials were acquired from the IODP core repository in Bremen, Germany. Samples were freeze-dried and powdered/homogenized in a tungsten-carbide ball mill. Powders were decarbonated using acetic acid buffered to pH 4 to minimize the potential of organic matter degradation during sample processing. Samples were allowed to react for 24 h and were rinsed 5X in distilled water. Rinsed samples were freeze-dried and powdered prior to analysis.

Isotopic analyses for nitrogen were performed using either a Costech elemental analyzer fitted with a 'zero blank' autosampler or an Elementar Isotope Cube; the elemental analyzer was coupled to a Finnigan MAT 252 or an Isoprime 100, continuous-flow, stable isotope mass spectrometer, respectively. Analyses were performed in the Stable Isotope Biogeochemistry Lab at The Pennsylvania State University or in the GAPP Lab at Syracuse University. Powdered, decarbonated samples were weighed and sealed in tin capsules for isotopic analysis and were oxidized at 1050 °C. Resulting NO_x gases were reduced in a copper reduction furnace at 650 °C. Data are reported using delta notation relative to atmospheric N_2 for nitrogen. Sample standardization was performed using the 2 pt. calibration method described by Coplen et al. (2006) using IAEA N1 and N2 for nitrogen in combination with a range of well-characterized in house nitrogen isotope standards (Devonian black shale, Peru mud, octaethylporphyrin and caffeine). Standard precision was often better than ±0.15‰ for N but is reported as ±0.2‰ to reflect reported precision from known isotopic values of IAEA reference materials.

2.2. Data analysis, astrochronologic testing, and time scale construction

An astronomical time scale for site 1259A was constructed from the wt.% $CaCO_3$ data of Friedrich et al. (2008), using multitaper method (MTM) (Thompson, 1982) evolutive power spectral analysis (EPSA) (Park and Herbert, 1987; Meyers and Hinnov, 2010), MTM evolutive harmonic analysis (EHA) (Meyers et al., 2001), average spectral misfit analysis (Meyers and Sageman, 2007; Meyers et al., 2012), and frequency domain minimal tuning (Park and Herbert, 1987; Meyers et al., 2001). Statistical evaluation of the correlation between $\delta^{15}N$ and other geochemical variables (TEX_{86}, wt.% $CaCO_3$, wt.% TOC and wt.% insoluble residue) utilizes the phase-randomized surrogate approach introduced by Baddouh et al. (2016) (see also Ebisuzaki, 1997). This method is designed to evaluate data sets that are collected on different sampling grids (e.g., as is the case with $\delta^{15}N$ vs. TEX_{86}), and permits a reliable assessment of the statistical significance of the results. Data analysis, astrochronologic testing, and time scale construction use the Astrochron package for R (Meyers, 2014; R Core Team, 2015).

3. Results

Application of the average spectral misfit method (Meyers and Sageman, 2007) confirms the presence of a dominant ∼400 ka cycle in wt.% $CaCO_3$ and wt.% total organic carbon, consistent with the interpretation of Friedrich et al. (2008) (Fig. 1). A floating astronomical time scale was constructed using frequency domain minimal tuning; the spatial frequency drift of the long eccentricity cycle (405 ka) is tracked for all results that achieve an 80% F-test confidence level (see Supplement). A sedimentation rate history is subsequently derived by assigning this variable spatial cycle a constant temporal period of 405 ka. Finally, a floating astronomical time scale is created by numerically integrating the sedimentation rate curve, which is then anchored to an age of 91.2 Ma at the base of biozone CC12/Sn (Bornemann et al., 2008). Nitrogen isotope data and complimentary data from Bornemann et al. (2008) and Friedrich et al. (2008) (TOC wt.%, TEX_{86}, $\delta^{18}O$) were adjusted to the ATS.

We sampled core material recovered during Ocean Drilling Program Leg 207, Site 1259A, through the mid-Turonian interval. Nitrogen isotope values range from +0.2 to −3.5‰ and oscillate over shorter stratigraphic intervals by 1.5 to 3‰ (Fig. 2). Spectral analysis of the $\delta^{15}N$ data, once adjusted to the ATS, reveals a strong ∼100 ka cycle and little variance at ∼400 ka (Figs. 1 and 2). $\delta^{15}N$ values correspond significantly to TEX_{86} indices presented in Borenemann et al. (2008) ($r = -0.70$, $p = 0.0022$; Fig. 3), but we do not observe significant statistical correlation with wt.% TOC, wt.% $CaCO_3$, or insoluble residue (wt.% total organic carbon, $r = -0.28$, $p = 0.1108$; wt.% $CaCO_3$, $r = 0.16$, $p = 0.3812$; insoluble residue, $r = -0.11$, $p = 0.5486$; Fig. S5).

4. Discussion

4.1. Nitrogen isotopes and black shales

Black shales from the Cretaceous have $\delta^{15}N$ values that range from −4 to +1‰ (Rau et al., 1987; Kuypers et al., 2004; Junium and Arthur, 2007; Ruvalcaba Baroni et al., 2015), with some notable outliers (Jenkyns et al., 2007). By contrast, recent OM-rich sediments from modern environments remain positive, and range from +2 to +15‰ (Altabet et al., 1995; Galbraith and Kienast, 2013). In ancient black shales $\delta^{15}N$ values near or below 0‰ have led to the interpretation of ^{15}N-depletion associated with N_2-fixing cyanobacterial their biomass is typically near −1‰ (Bauersachs et al., 2009). Additionally, biomarker evidence demonstrates that