Nitrogen isotope variations and environmental perturbations during Cenomanian-Turonian transition in the NE Tethyan realm, Koppeh-Dagh basin

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Abstract
The Cenomanian-Turonian Gharesu section in the east of Koppeh-Dagh basin have been investigated to determine the relationship between palaeoenvironmental perturbations and nitrogen cycling across OAE2. This succession is composed of 43 m shale and marl interbedded with glauconitic sandstone and lies between Aitamir-Abderaz formations boundary. The nitrogen isotope values fluctuate between 0‰ to +3‰ and TOC/TN ratios range from 3.5 to 20.5 in this section. The TOC/TN exhibits high ratios in the organic-rich sediments which were deposited in a low-oxygen environment because nitrogen-rich organic matter was preferably degraded in this condition. The δ15N values are also low in the organic-rich sediments which indicate a nitrogen fixation process as a consequence of greenhouse climate, enhanced productivity and expanded oxygen minimum zone during OAE2.

Keywords: *Koppeh-Dagh Basin, Environmental Perturbations, Nitrogen Isotope, OAE2, TOC/TN Ratio*

Introduction

Episodes of widespread black shale deposition are a characteristic feature of the mid-Cretaceous sedimentary record and have been termed Oceanic Anoxic Events (OAEs) (Schlanger & Jenkyns, 1976; Arthur *et al.,* 1987). Increased nutrient availability, intensified upwelling, weakened circulation, and possible density stratification caused the bottom water anoxia and the preservation of organic matter (Jenkyns, 2010). The last major mid-Cretaceous anoxic event, referred as Oceanic Anoxic Event 2 (OAE2) (e.g., Jenkyns, 2010) occurred across the Cenomanian-Turonian boundary (CTB) at 93.6 Ma (Ogg *et al.,* 2008). This anoxic event lasted for approximately 500 kyr (Sageman *et al.,* 2006; Voigt *et al.,* 2008), and marked the geochemical anomalies as a result of interplay between sea surface temperature, marine productivity and anoxia (e.g. Arthur *et al.,* 1987, Jarvis *et al.,* 2011).

In the Koppeh-Dagh basin in northern Iran, well-preserved Cenomanian-Turonian section is exposed and has rarely been subjected to reconstruct palaeoceanography of the NE Tethyan realm. Our previous study focused on foraminiferal assemblages and carbon-oxygen isotopic chemostratigraphy of the C-T section in Gharesu and revealed interpretation of the climate changes and the carbon cycling that improved the regional coverage of the paleoceanographic picture of OAE2 (Kalanat *et al.,* 2016; Kalanat *et al.,* in press).

In this study we present δ15N and TOC/TN data from Gharesu section, which provide valuable information to examine the palaeoenvironmental changes across the C-T boundary.

Geological setting and study area

The Koppeh-Dagh basin stretches over nearly 700 kilometers in the east of Caspian Sea. After the Cimmerian orogeny corresponding to the closure of the Paleotethys Ocean in Late Triassic/Early Jurassic, a Middle Jurassic post-collisional rifting event resulted in deposition of relatively deep marine sediments. Following this rifting, over 7 km thick sediments were accumulated until the Neogene above a regional post-Triassic unconformity (Robert *et al.,* 2014).

The Jurassic sequence of the Koppeh-Dagh basin is overlain by Cretaceous sediments deposited on the southern margin of Turan plate (figs. 1-A and 1-B), which are divided into 9 different formations (Shurijeh, Tirgan, Sarchashmeh, Sanganeh, Aitamir, Abderaz, Abtalkh, Neyzar and Kalat) (Afshar-Harb, 1979). The Cenomanian-Turonian sequence consists of two formations; the siliciclastics of Cenomanian Aitamir Formation and the hemipelagic sediments of the Abderdaz Formation (Turonian to Earliest Campanian in age).

The 43-m-thick study section covering the Cenomanin-Turonian boundary is located a few kilometers west of the Kalat city, near Gharesu village (Fig. 1-C). This succession consists of two units (Fig. 2): a) 27-m-thick dark shales and glauconitic sandstones of Aitamir Formation with very low carbonate contents (1.5-15%). Planktonic foraminifera are rare or absent in this part of section. This unit ends with a thick glauconitic sandstone. b) 16-m-thick light-color marl of Abderaz Formation with abundant planktonic foraminifera and carbonate contents up to 60%.

Materials and methods

In order to determine the nitrogen isotope ($\delta^{15}N$), total nitrogen (TN) and total organic carbon (TOC) values, the powdered samples were digested in 2N HCl for 24 hours to remove the carbonate portion of the samples. After three-times rinsing with pure water and freeze dehydration, appropriate amount of insoluble residue (IR) depending on TC (typically 1–10 mg), was set in a tin capsule. Nitrogen generated from the burnt tin capsule (burnt at 1000 ºC and reduced at 750 ºC) was analyzed using a Thermo Finningn Mat 253 installed with Flash 2000 Organic Elemental Analyzer at Kyushu University. The reproducibility of the measurements of the standard was ±0.2‰ (2σ). The isotope ratios are reported in standard delta (δ) notation in per mil (‰) (Table 1).

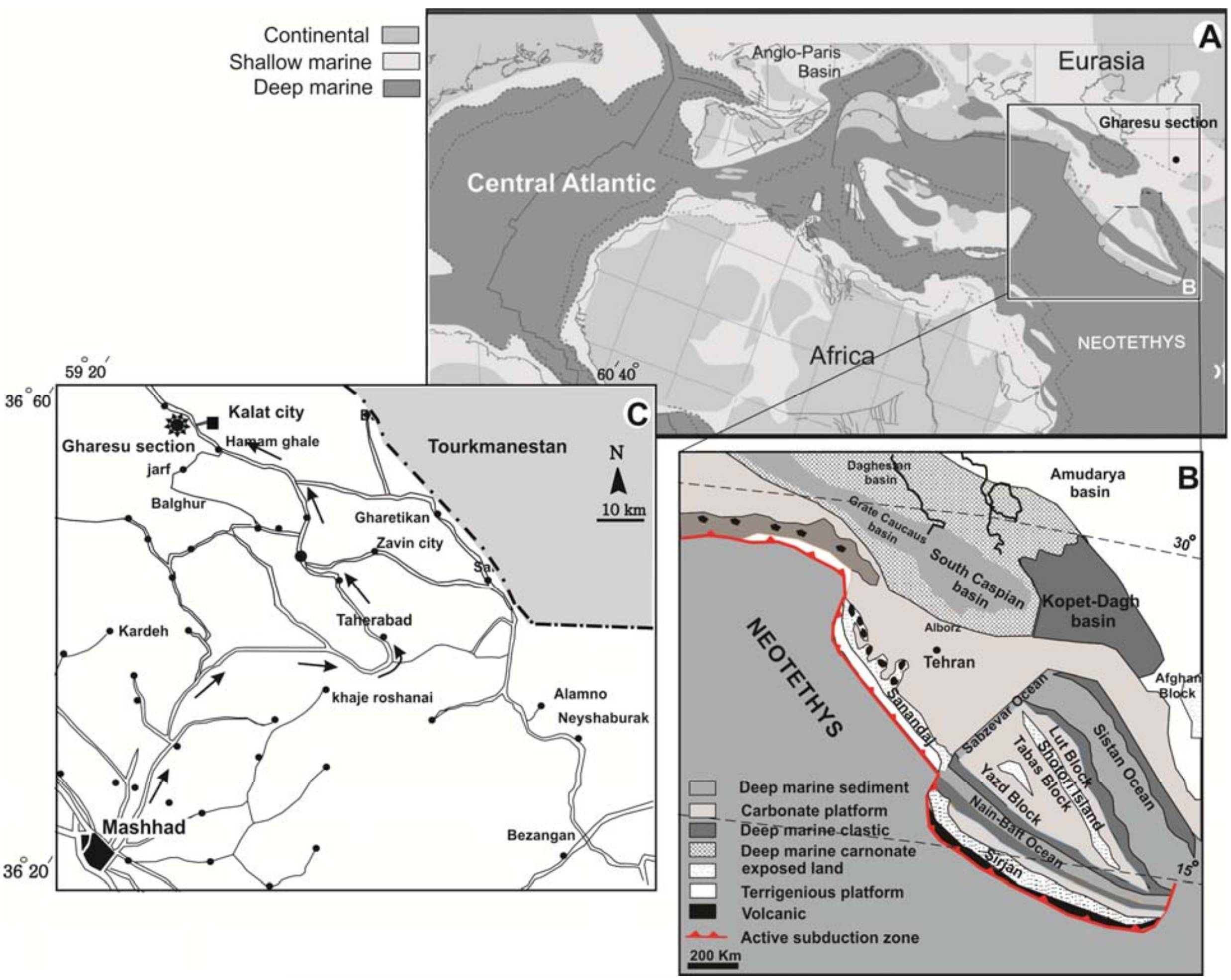

Figure 1. A- Palaeogeographical map of Cenomanian for central Atlantic and Tethys Ocean. B- Regional palaeogeography of Iran plate across Cenomanian (modified after Barrier & Vrielynck, 2008). C: Location map of study section in the east of Koppeh-Dagh basin. The main road of Mashhad to Kalat city is indicated by arrows.

Table 1. results of TOC/TN molar ratios and nitrogen isotope values across Gharesu section.

Sample No.	Height (m)	TN (%)	TOC (%)	TOC/TN	$\delta^{15}N$ (‰)	Sample No.	Height (m)	TN (%)	TOC (%)	TOC/TN	$\delta^{15}N$ (‰)
Gh 1	0.0	0.0387	0.28	7.27	1.0	Gh17	27	0.0138	0.07	5.76	0.9
Gh2	3.5	0.0398	0.81	20.55	-	Gh18	27.5	0.0552	0.34	6.30	1.6
Gh3	4.5	0.0476	0.82	17.36	0.4	Gh19	28	0.0519	0.27	5.32	0.8
Gh4	7.5	0.0654	0.44	6.87	1.0	Gh20	28.5	0.0527	0.25	4.88	1.8
Gh5	10.5	0.0569	0.50	8.85	-	Gh21	29	0.0482	0.20	4.23	1.3
Gh6	11.5	0.0638	0.49	7.79	1.3	Gh22	30	-	-	-	-
Gh7	12.5	0.0519	0.46	9.03	0.6	Gh23	31	0.0421	0.26	6.34	2.0
Gh8	13.5	0.0524	0.52	10.07	1.4	Gh24	31.5	0.0759	0.27	3.66	-
Gh9	15	0.0398	0.48	12.10	0.3	Gh25	32.5	0.0641	0.33	5.14	1.8
Gh10	17.5	0.0519	0.85	16.45	0.3	Gh26	33.5	0.0672	0.42	6.25	-
Gh11	18.5	0.0438	0.63	14.40	0.9	Gh27	35	0.0543	0.37	6.96	2.2
Gh12	20	0.0423	0.59	14.09	0.3	Gh28	38	0.0702	0.59	8.54	2.2
Gh13	21.5	0.0377	0.54	14.32	0.0	Gh29	39.5	0.0496	0.23	4.8	2.2
Gh14	22.5	0.0419	0.89	20.54	-3.5	Gh30	41.5	0.0705	0.30	4.26	3.0
Gh15	23.5	0.0263	0.45	17.22	-	Gh31	43	-	0.30	-	1.9
Gh16	26	0.0663	0.67	10.18	0.4						

Figure 2. A general view of Gharesu section. Light-color marls of Abderaz Formation cover the dark shale and glauconitic sandstones of Aitamir Formation.

Total nitrogen content (TN) and total organic carbon content (TOC) of the powdered samples were measured by a dynamic flash combustion method above 950 ℃ using Flash 2000 of Thermo-Fisher Scientific Co. Ltd. in Shinshu University of Japan. Accuracy of this measurement is about±0.02 ％for １.00% of measured value.

Results

Total organic carbon (TOC)

TOC contents range from 0.07 to 0.89 wt% with an average TOC of 0.46 wt%. TOC values are generally higher in the Aitamir Formation, especially in the two intervals (samples Gh 2, 3 and Gh10-16). Abderaz Formation is characterized by lower TOC values from 0.07 to 0.59 wt% (Table 1, Fig. 3).

Total nitrogen and TOC/TN ratios

Total nitrogen (TN) in the Gharesu section has low values range from 0.01 to 0.07% but the values are generally lower in the samples with higher TOC contents. Actually TN contents was measured to determine TOC/TN ratios. These ratios range between 3.5 and 20.5 in the Gharesu section and is high in two intervals of Aitamir Fomation at the top of *R. cushmani* zone (Gh2, Gh3) and *W. archaeocretacea* zone (Gh10-Gh16), which the values increase up to 10-20 (Table 1, Fig. 3).

Nitrogen isotope ($\delta^{15}N$)

The nitrogen isotope record displays high variability from -3.5‰ to +3.0‰ throughout the Gharesu section. Except for the minimum values of Gh14, the range is reduced from 0.0‰ to +3.0‰. The δ^{15}N values are inversely related to TOC/TN ratios and in two horizons (Gh2, 3 and Gh 10-13) exhibit negative shifts (δ^{15}N below 1‰) (Table 1, Fig. 3).

Discussion

TOC/TN and $\delta^{15}N$ patterns

In the Gharesu section, the samples with higher TOC/TN ratios have δ^{15}N values near 0‰, whereas samples with lower TOC/TN ratios have δ^{15}N values more than 1‰ (Fig. 3). This pattern is similar to those reported in Cretaceous organic-rich sequences on the Demerara rise drilled by ODP leg 207 and indicate an antithetic relationship correlation between higher TOC/TN ratios and δ^{15}N depletion (e.g., Junium and Arthur, 2007; Meyers *et al.,* 2009).

During the mid-Cretaceous Demerara rise was located in the wind-driven upwelling zone of the southern north Atlantic (Poulsen *et al.,* 2001), which resulted in a long term productivity and deposition of a thick sequence black shale from Albian to Santonian (Meyers et al., 2006, 2009; Junium *et al.,* 2007). Study of Ocean drilling program sites 1257, 1258 and 1260 shows that small δ^{15}N values (between -4‰ and 0‰) is a feature common to all the black shale in this region. Correspond to small δ^{15}N values, TOC/TN ratios in the black shale sequence rise between 25 and 40 (Meyers *et al.,* 2009). Also, Junium and Arthur (2007) demonstrated that low δ^{15}N values ranging from 1.2‰ to -3.9‰ and TOC/TN ratios between 25 and 50 are characteristic of black shale deposited during C-T boundary of site 1260.

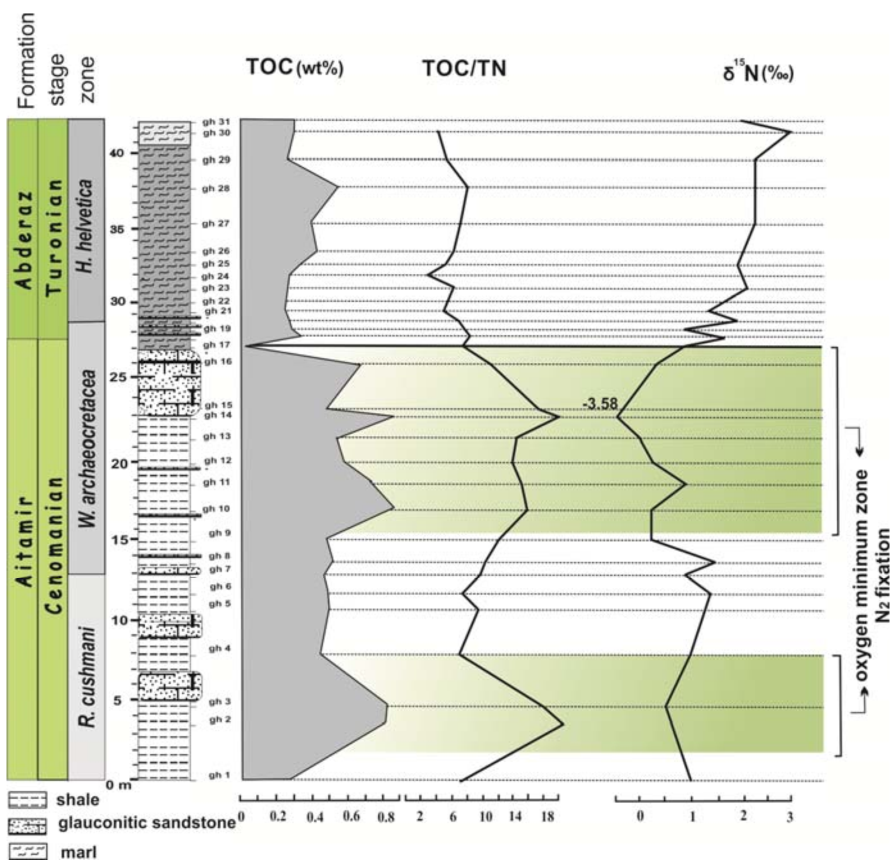

Figure 3. TOC/TN ratios and nitrogen isotope compositions of C-T in the Gharesu succession.

The observed antithetic relationship between TOC/TN and $\delta^{15}N$ could suggest two hypothesis:

1- Terrestrially derived organic matter in the black shale. Terrestrial plant typically exhibit higher TOC/TN ratios and lower $\delta^{15}N$ than marine organic matter (Sampei & Matsumoto, 2001; Hoefs, 2004). However, high rock-Eval Hydrogen Index values indicate that the black shale sequences in the Demerara Rise contain predominantly marine organic matter (Meyers *et al.,* 2006; Junium *et al.,* 2007). The dark shale of low $\delta^{15}N$ interval of Aitamir formation also lacks distinct plant fossils.

2- Common diagenetic control on TOC/TN and $\delta^{15}N$ values. van Mooy *et al.* (2002) present a model that consider the degradation of ^{15}N-enriched protein fraction yield only small (1-2‰) negative shift in the $\delta^{15}N$ values which can not justify the large $\delta^{15}N$ depletion in the Demerara Rise black shale.

Therefore Junium and Arthur (2007) concluded that the antithetic relationship between TOC/TN and $\delta^{15}N$ values has been controlled by different factors and $\delta^{15}N$ depletion reflect primary changes in the nitrogen cycle.

TOC/TN ratios

The marine organic matter in the modern ocean usually has TOC/TN values between 5 and 8 (Emerson and Hedges, 1988; Meyers, 1994), somewhat elevated TOC/TN values are also found in modern sediments deposited under areas of high productivity of benthic algae (Meyers *et al.,* 2006). Because of a high ability to absorb light and a lower nutrient requirement (Baird and Middleton, 2004), high TOC/TN ratios are observed in benthic algae (18–43; Atkinson and Smith, 1983; Kennedy *et al.,* 2004). One example for high TOC/TN ratios in the modern oceans is Mediterranean sapropels having the TOC/TN range between 15 and 25 (e.g., Bouloubassi *et al.,* 1999). Furthermore, large TOC/TN ratios up to 40 were often reported from the Cretaceous black shale (Meyers et al., 2006 and 2009).

If the measured TOC/TN ratio preserves in the initial ratio, the high TOC/TN ratios of the high TOC intervals likely resulted from the enhanced productivity by benthic algae.

Processes after the primary production can alter (often increase) the initial TOC/TN ratio of organic matter. van Mooy *et al.* (2002) emphasized the importance of different modes between anoxic and oxic degradation of marine organic matters. They demonstrated that anoxic degradations via denitrification preferentially utilize nitrogen-rich amino acids and hence increase the TOC/TN ratio of residual organic matter.

In the Gharesu section, lower TOC/TN ratios occur in the low-TOC samples (Fig. 3). The highest value is coincident with TOC maxima in the uppermost Cenomanian. This propose that the sediments with high TOC/TN values in the Gharesu section deposited under an oxygen deficient condition, which was commonly well-developed in the high TOC sediments.

Nitrogen cycle and OAEs

The nitrogen cycle includes some processes such as nitrogen fixation, nitrification and denitrification (Zehr & Kudela, 2011) that converted nitrogen between the different chemical species (Fig. 4).

Nitrogen fixation is a process that fix atmospheric nitrogen into ammonia “NH_3” or ammonium “NH_4^{+}”:

$N_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ NH_3 + H_2$

Nitrification is the biological oxidation of ammonia or ammonium to nitrite “NO_2^-“ followed by the oxidation of the nitrite to nitrate “NO_3^-“:

$NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 2\ H_2O + 4\ H^+$

$NO_2^- + O_2 \rightarrow 2\ NO_3^-$

$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$

$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$

Denitrification is a microbially facilitated process of nitrate reduction that ultimately produces “N_2”:

$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2\ (g)$

The nitrogen cycle is of particular interest to ecologists because nitrogen availability can affect the rate of key ecosystem processes, including primary production (Zehr & Kudela, 2011).

In the modern oceans, N_2 fixation and nitrification are mainly associated with areas of low productivity but denitrification predominantly occurs in the oxygen-depleted waters and sediments underlying upwelling zones characterized by high productivity and high rates of organic carbon accumulation (Karl *et al.,* 2002).

In a sharp contrast with the modern oceans, N_2 fixation was the dominant process in the vast areas of the Cretaceous oceans that were characterized by conditions of strong oxygen depletion during the oceanic anoxic events (Junium & Arthur, 2007; Meyers *et al.,* 2009)

During the anoxic events, NH_4^+ accumulates in the water because nitrification is an aerobic process and is limited by oxygen depletion. While NH_4^+concentrations increase, NO_x^- concentrations decrease during OAEs (Baroni *et al.,* 2014). This was a condition giving N_2-fixing microorganisms like cyanobacteria a competitive advantage over nitrifying and denitrifying bacteria (Kuypers *et al.,* 2004).

The $\delta^{15}N$ variation

The positive $\delta^{15}N$ values (about 5‰ to 8‰) are typical for modern shelf sediments (Altabet and François, 1994) but nitrogen isotope values are surprisingly low in some past intervals. Values near or below 0 ‰ commonly observed in ancient ‘‘black shales’’ deposited during periods such as mid-Cretaceous when organic matter-rich sediment was commonly deposited (Junium and Arthur, 2007).

As it has already mentioned, the nitrogen fixation takes place in the high productivity zones where the nitrate is depleted compared to other nutrients. Nitrogen fixers such as cyanobacteria and green sulfur bacteria can use dissolved N_2 with a $\delta^{15}N$ value of around 0 ‰ to produce organic matter with a $\delta^{15}N$ values ranging between -4‰ and +1‰ (Minagawa and Wada, 1986). Thus, enhanced nitrogen fixation results in decreasing of $\delta^{15}N$ value, when biologically useful nitrate (NO_3^-) is depleted in the sediment (Kikumoto *et al.,* 2014; Fig. 5).

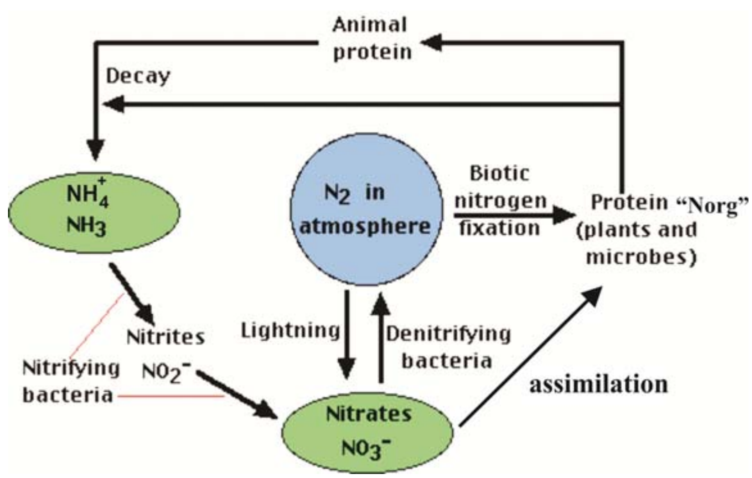

Figure 4. A simple diagram for the nitrogen cycle (modified after Zehr & Kudela, 2011).

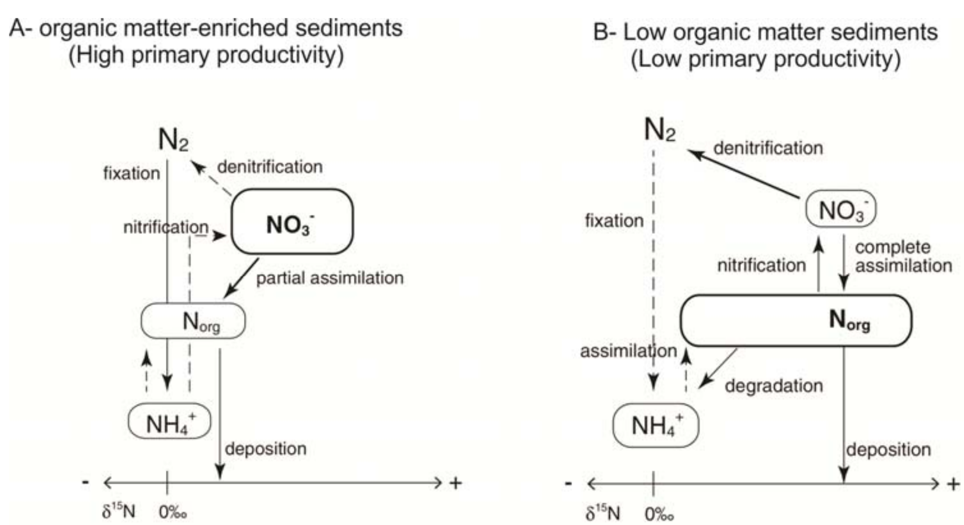

Figure 5. proposed model for nitrogen cycling in the high and low organic matter sediments. Solid arrows are dominant processes, whereas dotted arrows were minor (modified after Kikumoto *et al.,* 2014).

In contrast, in low productivity condition anammox (anaerobic ammonium oxidation) bacteria and denitrifiers utilize a portion of the dissolved nitrate in water columns and release N_2 that is preferentially depleted in ^{15}N. The remaining nitrate is consequently enriched in ^{15}N, which is eventually inherited to the assimilated organic matter with a typical $\delta^{15}N$ range of 5–8‰ (Fig. 5) (Liu and Kaplan, 1989; Ganeshram *et al.,* 2000).

Baroni *et al.,* (2015) compiled several available $\delta^{15}N$ data in the poroto-North Atlantic from OAE2 and compare them with new data for three open ocean and two coastal sites. They documented large regional differences in the magnitude of $\delta^{15}N$ negative shift based on effect of oxygen deficiency. They also found that the more oxygenated water in the costal sites (water depth ≤ 100) show minor negative shifts (-0.1 to -0.5‰), while larger shifts (-1 to -3‰) were observed in the central ocean with the water depth of more than 1000m.

In the Gharesu section, the $\delta^{15}N$ exhibit values near 0% in the samples with higher TOC and TOC/TN contents which suggest a low oxygen condition that favored nitrogen fixation throughout the period of deposition (Fig. 3). The $\delta^{15}N$ negative excursion for Gharesu section is about -0.7‰, (in compare with average 0.3 ‰ in the OAE2 interval) which represents an intermediate oxygen deficiency in this section.

Palaeoenvironmental interpretation

Palaeoenvironmental reconstruction of ancient ocean indicates that the warming peak at mid-Cretaceous and the greenhouse condition were largely caused by increased pCO_2 (Leckie *et al.,* 2002). The overall warming in the sea surface temperature would have increased evaporation and enhanced hydrological cycle, rock weathering and delivered nutrients to the oceanic basins. These conditions would have stimulated algal productivity and intensified suspension and accumulation of organic matter. The combination of deep water warming and oxygen consumption expanded the oxygen minimum zone (Meyer *et al.,* 2009). Kuypers *et al.* (2001, 2002) proposed that under this condition the dominant mode of photosynthesis shifts from eukaryote algae to nitrogen-fixing planktonic bacteria. Evidence for the abundance of both cyanobacteria and green sulfur bacteria in the mid-Cretaceous black shales support this hypothesis (Kuypers *et al.,* 2004). More N_2 fixation in the high productivity and oxygen depleted environments is a likely explanation for lower $\delta^{15}N$ values of the higher TOC/TN samples.

The high TOC/TN and low $\delta^{15}N$ values in the organic matter-rich sediments of Gharesu section (Fig. 3) together with the results obtained by oxygen stable isotope and $\Delta^{13}C$ data (Kalanat *et al.,* in press) indicate that these intervals were deposited under warm climate with high productivity and an extended oxygen minimum zone. After OAE2, deposition of Abderaz Formation was continued in the normal condition of the sea water associated with light-color marls and higher carbonates contents than Aitamir Formation, leading to variation in TOC/TN and $\delta^{15}N$ values.

Conclusion

Nitrogen isotope values and TOC/TN ratios in the Gharesu section show an antithetic trend across Cenomanian-Turonian boundary. A common feature to the two high organic intervals is the low $\delta^{15}N$ that falls around 0‰ and implies enhanced nitrogen fixation. The low $\delta^{15}N$ values correspond to the high TOC/TN ratios. This suggests selective microbial degradation of nitrogen-rich organic matter components in the suboxic water column. We propose that greenhouse condition, accelerated hydrological cycle, increased run off and nutrient input provide the condition for high primary productivity and nitrogen cycling changes across OAE2.

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