The excursion of Nitrogen and Carbon isotope in the Lower Cambrian of Tarim Basin: Implication for the transformation of anaerobic and euxinic settling

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Abstract. The Nitrogen (N) along with Carbon (C), Rear earth elements (REEs) and trace elements (TEs) were detected in the lower Cambrian Yuertusi formation, Northwest Tarim Basin. Two sections of obvious isotopic and elemental cycles have been investigated, which reflects the sedimentary transformation from lower euxinic to upper anaerobic setting. The extreme negative excursion of kerogen $\delta^{13}C$ emerged in the bottom layer silica shales. The lowest value of kerogen $\delta^{13}C$ is up to -37‰, which is similar with the global “Base” excursion in the bottom of lower Cambrian. It could be inferred the deposition of Yuertusi formation might be occurred after the Neoproterozoic glacial. Consequently, the kerogen $\delta^{13}C$ of upper Yuertusi formation mostly exceeded -32‰, which could inferred the rapid rise of atmosphere and oceanic temperature. Based on the typical theory of isotope fraction, the $\delta^{13}C$ of bitumen should be lower than that of kerogen. The bitumen $\delta^{13}C$ in the upper Yuertusi formation varies from -34‰ to 31.5‰, which is lighter than the $\delta^{13}C$ of kerogen. Nevertheless, the $\delta^{13}C$ of bitumen in the bottom layer silica shales is heavier than the $\delta^{13}C$ of kerogen. This phenomenon has been noticed by previous researchers. The nadir negative excursion of bulk $\delta^{15}N$ occurred in the bottom of Yuertusi formation, which has been indicated the sedimentary environment of Euxinic photic zone. The assimilation of bioavailable nutrient N (either in form of $NH_4^+$ or $NO_3^-$) may have contributed to the persistently low $\delta^{15}N$ values. Ammonium may have served as the dominant nutrient N source for this period. The recycled $NH_4^+$ can be used directly or was sometimes oxidized to nitrate and then quantitatively used by phytoplankton to fuel primary productivity, which finally resulted into accumulation of high TOC and negative excursion of carbon isotope in the bottom of Yuertusi formation. It could be alternative interpretation for the depositional conditions of TOC-rich shales around Ediacaran-Cambrian boundary.

1. Introduction
Nitrogen (N) along with carbon (C), is a macronutrient essential for all living organisms. For every 100 carbon atoms that make up a cell, 2-20 nitrogen atoms need to be absorbed in different forms of life at different geologic times. The biogeochemical behavior of nitrogen is almost entirely dependent on the redox reaction mediated by microorganisms, and is less controlled by the long physical and

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chemical recycling of the lithosphere. Therefore, all life activities and evolution are inseparable from the participation of nitrogen. Although nitrogen in the atmosphere has a very high abundance, but because the nitrogen is inert gas, thus can be creatures use nitrogen source is usually to nitrate (NO$^\text{3}$), nitrite (NO$^\text{2}$), ammonium ion (NH$^\text{4}$) and soluble organic nitrogen (DON) in the form of the nitrogen form usually control the primary productivity in the Marine and terrestrial ecosystems. Studies on nitrogen content and isotopes in the past ten years have shown that, under specific sedimentary environments in different geological and historical periods, the cycle of nitrogen in the sedimentation, sedimentary diagenesis and maturation of organic matter particles has been influenced and major biogeochemical processes have been recorded. Nitrogen has a strong control over the carbon cycle (Canfield et al., 2006), which directly affect the enrichment of the type of organic matter in sediments. During the Ediacaran-Cambrian transition period, the dramatic evolution of organisms was bound to be accompanied by the conversion of occurrence forms in nitrogen reservoirs and the fraction of isotopes, which became an ideal geological background for the study of nitrogen isotopes. The study of global oil and gas geology shows that the Ediacaran-Lower Cambrian has the geological conditions to form black shale rich in organic matter, which is very rich in oil and gas resources, so it has become the focus of research institutions and industries around the world. Tarim craton belongs to a portion of the Rodinia supercontinent, located in the west Rodinia supercontinent nearby India Ancient land, South China Craton and Australia. The scientific debate on the sedimentary environment and development model of the lower Cambrian black shale in Tarim Basin continues to this day, and the geological understanding of the distribution scope and isochronous phase transition law of the black shale is still very fuzzy, which restricts the correct evaluation of the deep resource potential of Tarim Basin and the expansion of petroleum exploration in ancient formations. Through organic and inorganic nitrogen occurrence form, content and isotopic composition of research, combining with the recognitions of carbon isotope excursion, barite, molybdenum and vanadium enrichment and transform from euxinic to anoxic environment, it could be benefit to investigate the depositional conditions of TOC-rich shales around Ediacaran-Cambrian boundary. It would be helpful to effectively predict the Tarim basin in this key geological period the occurrence state of organic matter and the distribution range.

2. Geology background and samples

The Ediacaran-lower Cambrian of Tarim Basin was completely different from Yangtze Craton. The Qigebulake Formation of Keping outcrop in western Tarim Basin is composited of thick dolomite without the deposition of black shales, which is different from the isochronous Doushantuo formation of South China. Meanwhile, the lower Cambrian in the west outcrop is distinct with the lower Cambrian in the east depression of Tarim Basin. In the Kuluketage outcrop of east Tarim Basin, Ediacaran is consisted of thick volcanic rocks of Zhamoketi Formation, large sets of sand and shale of Yukengou Formation, dolomite and mudstone cyclic sedimentation water springs group and recorded Hangargiaoke formation at the same age of Gaskiers, the differences of lithology reflects the Tarim basin in the Ediacaran-the particularity and complexity of the distinctive quality of early Cambrian. So in order to achieve global Ediacaran-thus line near the geological understanding-ecological unification of climate and environment, need through the nitrogen forms, content and isotopic data, detailed study on the Tarim craton during this period of special geochemical and biological evolution process, through a single basin horizontal contrast, complement the big transformation time geological model of evolution of the biosphere.

The core samples were collected from the Keping outcrop, involved complete Yuertusi Formation. The analyses of carbon and oxygen isotope and trace element content in the Yuertusi Formation of Lower Cambrian have been conducted to investigate the sedimentary environment and the development model of black shales.

3. Results and Discussion
3.1. The isotopic and elemental stratigraphy of Yuertusi Formation

The carbon isotope curve of Yuertusi Formation varied from -14‰ to 9‰, involving two parts of negative excursion in the bottom layer silica and interbedded silica in the mud shales. Corresponding to the variation of carbon isotope, two excursion cycles also exist in the oxygen isotope curve. Therefore, it is indicated two sets of significant sedimentary transformation. The evidence of trace element could also indicate the redox conditions. The Uranium content exceeds 10 ppm up to 200 ppm in the lower section of negative excursion of carbon isotope. On the contrary, the Uranium content is lower than 10 ppm in the upper negative excursion of carbon isotope. The same tendency could also be observed in the stratigraphic curve of Mo content. The highest concentration of Molybdenum is up to 100 ppm, which distributes in the section of high Uranium content. The content of Mo is only 1.0–10.0 ppm in the negative excursion of carbon isotope. All of the carbon, oxygen isotope and trace element U, Mo indicate the distinct sedimentary environment in the Yuertusi formation of lower Cambrian. Furthermore, the redox proxy V/Cr could identify the sedimentary setting of bottom layer silica was euxinic and the upper interbedded silica in the mud shale deposited in the anoxic setting.

![Figure 1](image_url)  
Figure 1. The isotopic and elemental stratigraphy of Yuertusi Formation in the Lower Cambrian of Northwest Tarim Basin

3.2. The correlation of trace elements in the TOC-rich black shales

Rear earth elements (REEs) and trace elements (TEs) have been proverbially used to identify the redox setting. In order to investigate the deposition process of Yuertusi formation, the Uranium, Nickel, Molybdenum and Vanadium have been involved (Figure 2). Based on the redox charts of REE and TEs, two section of Yuertusi formation could be separated. One section is characterized by high U and Ni enrichment factors. Accordingly, the U/Th ratio exceeded 2 and the Ni/Co ratio could reach 10–60. On the contrast, another section is featured of low U and Ni enrichment factor (EF). Both of the U/Th and the Ni/Co ratios are lower than 10 in the second section with the decrease of U and Ni EF. All of the redox proxies of REEs and TEs indicated the obvious transformation of sedimentary environment from anoxic to euxinic.
3.3. The comparison of carbon isotope between the kerogen and bitumen

Carbon cycle through the earth history was the direct geological record for the accumulation of organic matter, which was the consequence of sedimentary evolution. In the Yuertusi formation of Lower Cambrian around Northwest Tarim Basin, the isotope of organic carbon was detected into the two portions involving kerogen and soluble bitumen A (Figure 3). The δ\(^{13}\)C of kerogen indicated the most origin of organic carbon derived from biomasses. The extreme negative excursion of kerogen δ\(^{13}\)C emerged in the bottom layer silica shales. The lowest value of kerogen δ\(^{13}\)C is up to -37‰, which is similar with the global “Base” excursion in the bottom of lower Cambrian. It could be inferred the deposition of Yuertusi formation might be occurred after the Neoproterozoic glacial. Consequently, the kerogen δ\(^{13}\)C of upper Yuertusi formation mostly exceeded -32‰, which could inferred the rapid rise of atmosphere and oceanic temperature. Based on the typical theory of isotope fraction, the δ\(^{13}\)C of bitumen should be lower than that of kerogen. The bitumen δ\(^{13}\)C in the upper Yuertusi formation varies from -34‰ ~ 31.5‰, which is lighter than the δ\(^{13}\)C of kerogen. Nevertheless, the δ\(^{13}\)C of bitumen in the bottom layer silica shales is heavier than the δ\(^{13}\)C of kerogen. This phenomenon has been noticed by previous researchers. The original mechanism of carbon isotopic reversion has been interpreted as the biodegradation of methanogens. But if based on the characteristics of trace elements, the lower Yuertusi formation could more probably deposit in the euxinic setting.

Figure 2. The correlation of trace elements in the TOC-rich units of Yuertusi Formation
Figure 3. The comparison of carbon isotope between the kerogen and bitumen in the Yuertusi Formation of Northwest Tarim Basin

3.4 The composition and origin of Nitrogen isotope in the Ordovician and Cambrian source rocks

The δ15N of Sedimentary could be changed through both early and late diagenetic processes (Ader et al., 2016). Thus, the geological implication of δ15N values in rocks needs careful assessment of the diagenetic process. During early diagenesis, the biodegradation of some labile compounds releases bound nitrogen such as NH4+, which could be trapped by clay minerals in sediments or divorced out of the system. The isotope effect associated with this process is generally small (<1-2 ‰) when the deposition sites have high sediment accumulation rates, high organic carbon contents and reducing bottomwater conditions, although it can reach up to 4‰ in oxic diagenetic environments (Stüeken et al., 2016).

Generally, the average δ15N of modern marine sediments in the South Ocean is 6‰ (Kipp et al., 2018). The nadir negative excursion of bulk δ15N occurred in the bottom of Yuertusi formation, which has been indicated the sedimentary environment of Euxinic photic zone. The assimilation of bioavailable nutrient N (either in form of NH4+ or NO3-) may have contributed to the persistently low δ15N values. Ammonium may have served as the dominant nutrient N source for this period. The recycled NH4+ can be used directly or was sometimes oxidized to nitrate and then quantitatively used by phytoplankton to fuel primary productivity, which finally resulted into accumulation of high TOC and negative excursion of carbon isotope in the bottom of Yuertusi formation. The bulk δ15N of upper Yuertusi formation is around 2‰, which is indicated the biological alteration of denitrifying bacteria. The similar sedimentary environment has been observed in the lower Cambrian Xishanbulake formation (Є1x) and middle Ordovician formation of the east Tarim Basin. On contrast, the heaviest bulk δ15N of Upper Ordovician Lianglitage formation could reach 6‰, similar with the value of Modern Ocean, which is inferred the organic origin of algae (Figure 4).
4. Conclusions
The ecological system is the most sensitive portion of earth surface to environmental change. During the Ediacaran-Cambrian transition period, the dramatic evolution of organisms was bound to be accompanied by the conversion of occurrence forms in nitrogen reservoirs and the fraction of isotopes. The isotopic and elemental evidences indicated the recycled NH$_4^+$ can be used directly or was sometimes oxidized to nitrate and then quantitatively used by phytoplankton to fuel primary productivity, which finally resulted into accumulation of high TOC and negative excursion of carbon isotope in the bottom of Yuertusi formation. It could be alternative interpretation for the depositional conditions of TOC-rich shales around Ediacaran-Cambrian boundary.

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