

The relationship between Late Devonian environmental evolution and organic matter enrichment

Yingying Ma

Beijing Haidian Kaiwen Academy, Beijing, 100000, China

Email: 20190703005@hd.kaiwenacademy.cn

Abstract: This study investigates the interplay between environmental evolution and organic matter (OM) accumulation during the Late Devonian, with a focus on the Frasnian-Famennian (F-F) transition in the Lengshuijiang section, South China. By analyzing geochemical proxies such as Total Organic Carbon (TOC), Phosphorus/Aluminum (P/Al) ratios, Chemical Index of Alteration (CIA), and Co/Ni ratios, we aim to elucidate the factors that controlled OM enrichment during this period. Our findings suggest that the processes driving OM accumulation, including primary productivity and preservation mechanisms, were closely linked to significant environmental changes. The data reveal that periods of high TOC coincided with anoxic or euxinic conditions, driven by global sea-level changes and oceanic stagnation, contributing to increased environmental stress and the F-F mass extinction. Additionally, fluctuations in CIA values indicate alternating warm and humid to cooler, more arid climatic phases, which likely exacerbated environmental stress and disrupted marine ecosystems. This research highlights the interconnectedness of climate, ocean chemistry, and biological evolution during periods of significant environmental upheaval, offering valuable insights into the processes that drove one of Earth's most profound biotic crises.

Keywords: Late Devonian, Frasnian-Famennian extinction, Organic matter accumulation, Geochemical proxies, Anoxia, Euxinia, Chemical Index of Alteration (CIA), Marine ecosystems, Paleoclimate, Environmental stress.

1. INTRODUCTION

The accumulation of organic matter (OM) in sedimentary archives is crucial for reconstructing ancient environmental conditions and assessing hydrocarbon resources.

Currently, the two most commonly accepted models for enhanced OM accumulation are the primary productivity model and preservations model. The primary productivity model suggests that high biological productivity in surface waters leads to the deposition of large quantities of organic material on the seafloor. This productivity is typically driven by the prosperity of primary producers, which are high sensitive to nutrient influxes. The nutrient supply, mainly associated with P, Ba, Zn and other biolimited elements, can result from volcanic activity, continental weathering, and other processes that enhance the bloom of phytoplankton and other microorganisms[1]. The subsequent death and settling of these organisms contribute to significant OM input on the seabed[2]. This model implies that nutrient-rich environments, such as those found in upwelling zones, are likely to exhibit substantial OM accumulation [3].

In contrast, the preservation model emphasizes the role of depositional conditions in inhibiting the decomposition of OM after it has been deposited. Anoxic (oxygen-depleted) and

euxinic (sulfide-rich) conditions are particularly favorable for OM preservation, as they prevent the aerobic degradation of organic material. During the Late Devonian, widespread anoxia, potentially driven by global sea-level changes and oceanic stagnation, created conditions that favored the preservation of OM [4]. Evidence for such anoxic conditions is found in the extensive black shale deposits from this period [2][5]. The Late Devonian period, known for its significant climatic and environmental transformations, presents a unique opportunity to examine the mechanisms driving OM enrichment. This study focuses on the interplay between primary productivity and preservation mechanisms within the context of Late Devonian environmental evolution.

The Late Devonian environment was marked by notable fluctuations, including a significant cooling event known as the Devonian glaciation and oceanic anoxia expansion [6][7]. These climatic changes affected sea levels, ocean circulation, and weathering processes, which in turn influenced the redox conditions of marine and lacustrine environments. Redox reactions, mostly driven by changes in oxygen availability, played a crucial role in determining biohabitability of organisms and the preservation potential of OM in sediments[8]. The transition from oxic to anoxic conditions facilitated the preservation of OM by reducing rates of decomposition and oxygen respiration[9].

This research paper aims to explore the relationship between Late Devonian environmental evolution and organic matter accumulation, with a focus on the primary productivity and preservation models based geological and geochemical investigations on the Upper Devonian shale-carbonate succession in South China. By examining geochemical proxies in sedimentary records across the Frasnian-Famenian transition, this study seeks to elucidate the factors that controlled OM enrichment during this period and their paleoenvironmental implications. The findings will contribute to a deeper understanding of the processes that drive OM accumulation and preservation in ancient sedimentary environments and environmental perturbations in South China that potentially led to biotic turnover, offering insights into the conditions that prevailed during one of the most dynamic periods in Earth's history.

2. METHOD

2.1 Sample Collection and Preparation

Samples were collected from the Lengshuijiang section, focusing on the Late Devonian interval. This section is dominated by shale-carbonate succession, and located in the Hunan Province, South China and has been systematically studied for biostratigraphy, sedimentology, and chemostratigraphy across the F-F extinction event[10][11]. The collected shale samples were carefully cleaned, dried, and pulverized for geochemical analysis.

2.2 Total Organic Carbon (TOC) Analysis

To determine the Total Organic Carbon (TOC) content, approximately 200 mg of each shale sample was subjected to a two-step acid treatment to remove any carbonate material. The samples were treated with 10% (volume) hydrochloric acid (HCl) at 60 °C for 12 hours twice, ensuring complete carbonate removal. After acid treatment, the samples were thoroughly washed with distilled water to remove any remaining HCl. The washed samples were then dried overnight at 50 °C and weighed. The TOC content was subsequently analyzed using a Euro-3000 analyzer at the Sample Solution Inc. Wuhan.

2.3 X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence spectrometry (XRF) was employed to determine the concentrations of selected major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Ti) and certain trace elements (including Ba, Ni, Cr, and V). For the determination of the Loss on Ignition (LOI), approximately 500 mg of pulverized sample was oxidized at 1000 °C for 1 hour. The oxidized sample was then cooled and thoroughly mixed with 5000 mg of lithium borate, a mixture comprising 67% $\text{Li}_2\text{B}_4\text{O}_7$ and 33% anhydrous LiBO_2 . Fusion glass disks were prepared by melting the

mixtures at 1200 °C. The final analysis was conducted using an AXIOS Minerals (PANalytical) spectrometer at the Sample Solution Inc. Wuhan .

2.4 Chemical Index of Alteration (CIA)

The Chemical Index of Alteration (CIA) was calculated to evaluate the intensity of chemical weathering for the F-F interval of Lengshuijiang section. CIA values were calculated using the following formula:

$$\text{CIA} = \left[\frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right] \times 100$$

Where CaO^* represents the CaO content in the silicate fraction. To correct for the presence of phosphate, the available P_2O_5 data was used to adjust the CaO values, calculated as $\text{CaO}^* = \text{mole CaO} - \text{mole P}_2\text{O}_5 \times 10/3$ [12]. If the corrected CaO^* value was higher than the Na_2O content, it was assumed to be equivalent to the Na_2O content [12]. This method of calculating the CIA provides insights into the intensity of chemical weathering and is based on established protocols[13][14][15][16].

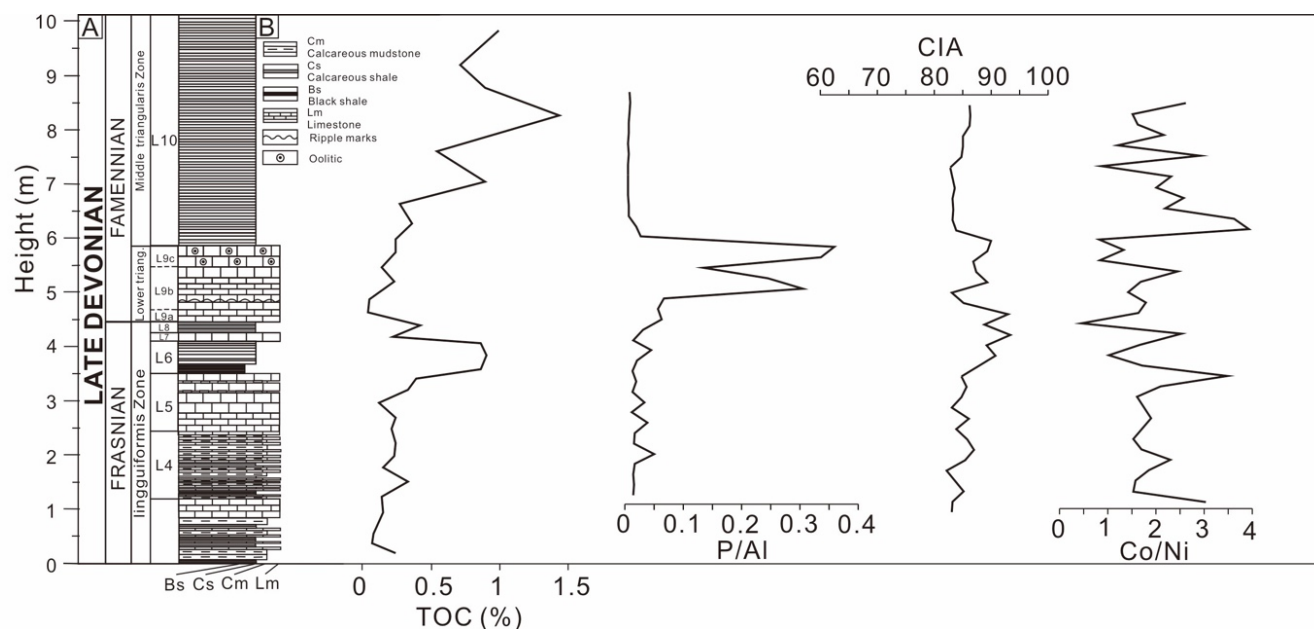


Figure1: Lithology, TOC, P/Al, CIA, and Co/Ni variations in the stratigraphy column of the Lengshuijiang section.

3. DISCUSSION

The stratigraphic variations in TOC, P/Al, CIA, and Co/Ni, as illustrated in Figure 1, provide valuable insights into the paleoenvironmental conditions during the Late Devonian period at the Lengshuijiang section. These geochemical proxies are crucial for understanding the factors influencing organic matter (OM) accumulation and preservation within this sedimentary sequence.

3.1 Total Organic Carbon (TOC) Variations

The TOC profile displayed in Figure 1 shows significant fluctuations throughout the stratigraphy, with elevated concentrations observed at approximately 3–4 meters and 7–8 meters in height, where TOC values reach up to 1.5%. These elevated TOC intervals likely correspond to periods of enhanced primary productivity or improved preservation conditions. According to the primary productivity model, increased biological activity in surface waters leads to a higher deposition rate of organic material on the seafloor[2][3][17][18]. The preservation model further emphasizes the role of anoxic or euxinic conditions in minimizing organic matter decomposition [19]. The co-occurrence of high TOC values with elevated Co/Ni ratios within these intervals supports the hypothesis that anoxic conditions were prevalent during these periods and conducive to organic matter preservation. In contrast, lower TOC values, ranging from 0.1% to 0.3%, are observed at approximately 0–2 meters and 5–6 meters in height. These intervals may indicate either reduced primary productivity or more oxic conditions, where the degradation of organic matter outpaced its accumulation[20][21]. The

correlation between decreasing Co/Ni ratios and lower TOC values suggests that more oxic conditions, which promote organic matter decomposition, were likely responsible for the observed reduction in TOC[19].

3.2 Phosphorus/Aluminum (P/Al) Ratio

The Phosphorus is one of the most essential bio-limited elements to sustain life largely through phosphates, compounds containing the phosphate ion, PO_4^{3-} . The P/Al ratio serves as a proxy for paleoproductivity[22]. The observed variations in P/Al across the stratigraphy are indicative of fluctuating nutrient levels, which directly influence primary productivity. In Figure 1, high P/Al ratios are observed between approximately 5–6 meters in height above the F-F boundary, where the ratios reach up to 0.35. These drastically elevated P/Al ratios indicate periods of increased nutrient availability during the F-F transition, which likely drove higher biological productivity in surface waters. Such conditions could be attributed to enhanced continental weathering or upwelling, which supplies the necessary nutrients for phytoplankton growth [23]. The intervals with elevated P/Al ratios, corresponding with higher TOC values, suggest that increased nutrient availability and productivity were key factors driving organic matter accumulation during these periods. In contrast, low P/Al ratios are observed at approximately 0–4 meters and 7–9 meters in height, where the ratios drop to around 0.05. These lower ratios may reflect periods of reduced nutrient influx, leading to diminished primary productivity. Additionally, under anoxic conditions, phosphorus tends to diffuse from sediments back into the water column, potentially explaining the observed decrease in P/Al ratios in the organic-rich intervals [24][25].

3.3 Chemical Index of Alteration (CIA)

The CIA values provide insights into the intensity of chemical weathering and, by extension, the prevailing climatic conditions during sediment deposition. In Figure 1, high CIA values are observed between approximately 3–4 meters and 5–6 meters in height across the F-F transition, where the CIA values range from 85 to 90. These values suggest a warm and humid tropical climate, which would have intensified chemical weathering processes [13][14]. Such a climate would have promoted greater nutrient fluxes into the marine system, thereby enhancing primary productivity and contributing to organic matter accumulation. Low CIA values, ranging from 70 to 75, are observed at approximately 0–2 meters and 5–6 meters in height. These values correspond to colder and more arid conditions, where weathering processes would have been less intense, reducing nutrient supply and limiting primary productivity that climatic fluctuations played a significant role in controlling the delivery of nutrients to the marine environment, thereby influencing organic matter accumulation and preservation.

3.4 Co/Ni Ratio

The Co and Ni are commonly used redox-sensitive elements. The Co/Ni ratio, as shown in Figure 1, is utilized as a proxy for redox conditions, with higher values. In the stratigraphy, high Co/Ni ratios (ranging from 3.0 to 3.8) are observed between approximately 3–4 meters and 7–8 meters in height. These intervals suggest the presence of anoxic or euxinic conditions, which are favorable for the preservation of organic matter [19][27]. The correlation between these high Co/Ni ratios and elevated TOC values further supports the interpretation that reducing conditions were prevalent during these periods, leading to enhanced preservation of organic matter. Conversely, low Co/Ni ratios (ranging from 0.5 to 1.5) are observed at approximately 0–2 meters and 5–6 meters in height. These intervals likely reflect more oxic conditions, where the preservation of organic matter was less efficient due to increased aerobic degradation. The decrease in Co/Ni ratios correlates with lower TOC values, indicating that the redox conditions during these intervals were less conducive to the preservation of organic matter[28].

3.5 Synthesis and Paleoenvironmental Implications

The interplay between primary productivity (P/Al), preservation potential (Co/Ni), and weathering intensity (CIA) reveals a complex environmental evolution during the Late Devonian at the Lengshuijiang section. The high TOC intervals coincide with periods of high primary productivity and/or strong OM preservation under anoxic conditions. Conversely, lower TOC values reflect either reduced productivity or more oxic conditions that favored OM decomposition. The climatic

fluctuations, as inferred from the CIA values, suggest alternating warm/humid and cold/arid phases, which would have significantly impacted the nutrient supply and, consequently, the primary productivity. When compared with the Bakken Shale in North America, similar euxinic conditions are observed during key transgressive phases, where trace metals such as molybdenum (Mo) and vanadium (V) indicate the episodic expansion of euxinia. Both sections reveal that euxinia played a critical role in OM preservation, with high Mo and V concentrations signaling intense anoxia in the Bakken Shale, paralleling the Co/Ni-driven redox insights from the Lengshuijiang section. The geochemical data collectively suggest that both primary productivity and preservation mechanisms were critical in controlling OM accumulation during this period, with climate playing a pivotal role in modulating these processes [29]. The presence of photic zone euxinia (PZE) in the Bakken Shale further underscores the importance of surface water oxygen depletion, which may have occurred during similar intervals of enhanced primary productivity in both basins. This study contributes to a better understanding of the factors driving OM enrichment in ancient sedimentary environments, particularly during periods of significant climatic and environmental change such as the Late Devonian[30][31]. The findings emphasize the importance of integrating multiple geochemical proxies to reconstruct past environmental conditions and their influence on sedimentary OM accumulation.

3.6 Implications for Environmental Change and the Frasnian-Famennian (F-F) Mass Extinction

The occurrence of shale sandwiched by carbonate indicates rapid sea level rise during the F-F transition. This could be related to the progressive onlapping of euxinic waters found here and in North America, during episodic marine transgression, which has major implications for the massive organic matter accumulation and, thereby, the Late Devonian mass extinction[32]. The environmental changes became unstable through our analysis of the Lengshuijiang section. These phenomena are not only important for understanding organic matter (OM) accumulation but also hold important implications for the biotic

crises of the Late Devonian, particularly the Frasnian-Famennian (F-F) mass extinction. This extinction event, one of the "Big Five" mass extinctions, is characterized by a severe loss of marine biodiversity, including significant declines in reef-building organisms and a variety of pelagic species[32]. The data presented in this study suggest that the environmental stressors leading to the F-F extinction were closely linked to the same processes that influenced OM accumulation. High TOC intervals, associated with anoxic or euxinic conditions as indicated by elevated Co/Ni ratios, coincide with periods of increased environmental stress[33]. Similar euxinic conditions are observed in the Bakken Shale, where euxinia is indicated by Mo and V enrichments, especially during the Hangenberg Event, marking another significant extinction event. In both cases, euxinia is coupled with high OM accumulation, reflecting oxygen-depleted environments that would have been detrimental to marine life. These anoxic conditions, likely driven by global sea-level changes and oceanic stagnation, would have created inhospitable environments for many marine organisms, contributing to widespread extinctions. Moreover, the fluctuations in CIA values throughout the stratigraphy reflect significant climatic shifts during the Late Devonian, alternating between warm, humid periods and cooler, more arid phases[34]. The Bakken Shale shows similar evidence of climatic shifts, as inferred from geochemical markers, which suggest alternating periods of high productivity and euxinia, contributing to environmental instability. These climatic oscillations could have exacerbated the environmental stress, leading to disrupted ecosystems and contributing to the mass extinction. The warm, humid conditions associated with high CIA values would have intensified chemical weathering, leading to nutrient influxes that may have initially boosted primary productivity. However, as these nutrients were consumed, the subsequent anoxia and euxinia likely led to rapid declines in marine oxygen levels, creating conditions unfavorable for many forms of life. In the Bakken Shale, these conditions are mirrored by trace metal enrichments and TOC peaks, further suggesting that nutrient-driven productivity initially surged but ultimately contributed to anoxic collapse. The F-F

mass extinction appears to be a culmination of these environmental factors. The stress from fluctuating redox conditions, combined with climatic instability, likely created a scenario where the resilience of marine ecosystems was compromised, leading to the widespread loss of biodiversity[35] [36]. The organic matter accumulation patterns we observe are thus both a record of these environmental changes and a contributor to the conditions that led to this significant extinction event. These findings highlight the interconnectedness of climate, ocean chemistry, and biological evolution, particularly during periods of significant environmental upheaval[37]. Both the Bakken Shale and the Lengshuijiang section provide critical case studies on how localized euxinia can have global biotic implications, especially during mass extinction events like the F-F crisis. These transformative events in Earth history are encapsulated in the shale spanning from South China and North America, and this study synthesizes this massive organic matter accumulation mechanism genetically related to sea level, climate, ocean chemistry and mass extinction[33]. The insights gained from this study provide a more nuanced understanding of the processes that drove one of the most profound biotic crises in Earth's history, offering lessons for understanding the potential impacts of modern environmental changes.

4. CONCLUSION

This study provides a comprehensive analysis of the relationship between Late Devonian environmental evolution and organic matter (OM) accumulation in the Lengshuijiang section. By examining the variations in geochemical proxies, including Total Organic Carbon (TOC), Phosphorus/Aluminum (P/Al) ratios, Chemical Index of Alteration (CIA), and Co/Ni ratios, the research elucidates the complex interplay between primary productivity, redox conditions, and climatic influences during this period. The findings indicate that periods of enhanced OM accumulation are closely linked to both increased primary productivity, as suggested by elevated P/Al ratios, and improved preservation conditions under anoxic environments, as reflected in high Co/Ni ratios. The correlation

between high TOC values and these geochemical indicators underscores the dual importance of productivity and preservation mechanisms in driving OM enrichment. Furthermore, the CIA values provide crucial insights into the climatic backdrop of the Late Devonian, revealing that shifts between warm, humid conditions and cooler, arid phases played a significant role in modulating chemical weathering intensity and, consequently, nutrient fluxes into the marine system. These climatic fluctuations likely had a direct impact on primary productivity, influencing the overall patterns of OM accumulation observed in the stratigraphy. This study contributes to a deeper understanding of the environmental processes that governed OM accumulation during one of Earth's most dynamic periods. The integration of multiple geochemical proxies offers a robust framework for reconstructing paleoenvironmental conditions and provides valuable insights into the factors that control OM preservation in ancient sedimentary environments. Future research could build on these findings by exploring additional proxies and expanding the study to other regions to further refine our understanding of the Late Devonian environmental evolution.

References

- [1] Wang, R., Lang, X., Ding, W., Liu, Y., Huang, T., Tang, W., & Shen, B., The coupling of Phanerozoic continental weathering and marine phosphorus cycle. *Scientific Reports*, 10, 5794 (2020).
- [2] Demaison, G. J., & Moore, G. T., Anoxic environments and oil source bed genesis. In *Organic Geochemistry I*, Vol. 2, pp. 9-31(1981). Pergamon Press Ltd.
- [3] Cowie, G. L., & Hedges, J. I., The role of anoxia in organic matter preservation in coastal sediments: Relative stabilities of the major biochemicals under oxic and anoxic depositional conditions. *Advances in Organic Geochemistry 1991*, *Organic Geochemistry*, 19(1-3), 229-234. [https://doi.org/10.1016/0146-6380\(92\)90039-Z](https://doi.org/10.1016/0146-6380(92)90039-Z)(1992).
- [4] Liu, M., Chen, D., Jiang, L., Stockey, R.G., Aseal, D., Zhang, B., Liu, K., Yang, X., Yan, D., Planavsky, N.J., Oceanic anoxia and extinction in the latest Ordovician. *Earth and Planetary Science Letters* 588, 117553 (2022) .
- [5] Tessin, A., Hendy, I., Sheldon, N., & Sageman, B., Redox-controlled preservation of organic matter during "OAE 3" within the Western Interior Seaway. *Paleoceanography*, 30(6), 702-717 (2015). <https://doi.org/10.1002/2014PA002729>.
- [6] Sahoo, S.K., Gilleaudeau, G.J., Wilson, K., Hart, B., Barnes, B.D., Faison, T., Bowman, A.R., Larson, T.E., Kaufman, A.J., Basin-scale reconstruction of euxinia and Late Devonian mass extinctions. *Nature* 615, 640-645(2023).
- [7] Zhao, H., Shen, J., Algeo, T.J., Racki, G., Chen, J., Huang, C., Song, J., Qie, W., Gong, Y., Mercury isotope evidence for regional volcanism during the Frasnian-Famennian transition. *Earth and Planetary Science Letters* 581, 117412(2022).
- [8] Fang, C., Liu, M., Zhang, C., Tang, H., Li, J., Xing, G., Li, F., Xu, N., Wu, T., Liu, B., Middle Ordovician climatic and oceanic destabilization in a slope-setting of the Yangtze platform, South China, and its role as a regional brake on the Ordovician radiations. *Palaeogeography, Palaeoclimatology, Palaeoecology* 648, 112265(2024).
- [9] Percival, L. M. E., Bond, D. P. G., Rakociński, M., Marynowski, L., Hood, A. v. S., Adatte, T., Spangenberg, J. E., & Föllmi, K. B., Phosphorus-cycle disturbances during the Late Devonian anoxic events. *Global and Planetary Change*, 184, 10307((2020)). <https://doi.org/10.1016/j.gloplacha.2019.103070>.
- [10] Ma, X. P., & Bai, S. L., Biological, depositional, microspherule, and geochemical records of the Frasnian/Famennian boundary beds, South China. *Palaeogeogr Palaeoclimatol Palaeoecol*, 181, 325–346(2002).
- [11] Ma, X. P., Gong, Y., Chen, D., & Racki, G., The Late Devonian Frasnian–Famennian event in South China—patterns and causes of extinctions, sea level changes, and isotope variations. *Palaeogeogr Palaeoclimatol Palaeoecol*, 448, 224–244(2016).
- [12] McLennan, S.M., Weathering and global denudation. *The Journal of Geology* 101, 295-303(1993).
- [13] Nesbitt, H. W., & Young, G. M., Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature*, 299, 715-716 (1982).
- [14] Fedo, C. M., Nesbitt, H. W., & Young, G. M., Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. *Geology*, 23, 921-924(1995).
- [15] Young, G. M., & Nesbitt, H. W., Paleoclimatology and provenance of the glaciogenic Gowganda Formation (Paleoproterozoic), Ontario, Canada: A chemostratigraphic approach. *Geology*, 111, 264-274(1999).
- [16] Rieu, R., Allen, P.A., Plötze, M., Pettker, T., Climatic cycles during a Neoproterozoic “snowball” glacial epoch. *Geology* 35, 299–302(2007).
- [17] Zou, C., Zhu, R., Chen, Z.-Q., Ogg, J.G., Wu, S., Dong, D., Qin, Z., Wang, Y., Wang, L., Lin, S., Cui, J., Su, L., Yang, Z., Organic-matter-rich shales of China. *Earth-Science Reviews* 189, 51-78(2019).
- [18] Fang, C., Zhang, C., Meng, G., Xu, J., Xu, N., Li, H., Liu, M., Liu, B., Constraints on the Accumulation of Organic Matter in the Upper Permian Dalong Formation from the Lower Yangtze Region, South China. *Acta Geologica Sinica - English Edition* 98, 150-167(2023).
- [19] Tribouillard, N., Algeo, T. J., Lyons, T., & Riboulleau, A., Trace metals as paleoredox and paleoproductivity proxies: An update. *Chemical Geology*, 232, 12-32(2006).
- [20] Ge, X., Chen, D., Zhang, G., Huang, T., Liu, M., El-Shafeiy, M., Marine redox evolution and organic accumulation in an

intraself basin, NE Sichuan Basin during the Late Permian. *Marine and Petroleum Geology* 140, 105633(2022).

[21] Liu, W., Liu, M., Yang, T., Liu, X., Them, T.R., Wang, K., Bian, C., Meng, Q.a., Li, Y., Zeng, X., Zhao, W., Organic matter accumulations in the Santonian-Campanian (Upper Cretaceous) lacustrine Nenjiang shale (K2n) in the Songliao Basin, NE China: Terrestrial responses to OAE3? *International Journal of Coal Geology* 260, 104069(2022).

[22] Walton, C.R., Hao, J., Huang, F., Jenner, F.E., Williams, H., Zerkle, A.L., Lipp, A., Hazen, R.M., Peters, S.E., Shorttle, O., Evolution of the crustal phosphorus reservoir. *Science Advances* 9, eade6923(2023).

[23] Ingall, E., & Jahnke, R., Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis. *Marine Geology*, 139, 219-229(1997).

[24] Schoepfer, S. D., Shen, J., Wei, H., Tyson, R. V., Ingall, E., & Algeo, T. J., Total organic carbon, organic phosphorus, and biogenic barium fluxes as proxies for paleomarine productivity. *Earth-Science Reviews*, 149, 23-52 (2015).

[25] Becker, R.T., Marshall, J.E.A., Da Silva, A.C., Agterberg, F.P., Gradstein, F.M., Ogg, J.G., The Devonian Period, *Geologic Time Scale 2020*, pp. 733-810(2020).

[26] Liu, M., Chen, D., Zhou, X., Yuan, W., Jiang, M., Liu, L., Climatic and oceanic changes during the Middle-Late Ordovician transition in the Tarim Basin, NW China and implications for the Great Ordovician Biodiversification Event. *Palaeogeography, Palaeoclimatology, Palaeoecology* 514, 522-535(2019).

[27] Calvert, S. E., & Pedersen, T. F., Chapter Fourteen: Elemental Proxies for Palaeoclimatic and Palaeoceanographic Variability in Marine Sediments: Interpretation and Application. In *Proxies in Late Cenozoic Paleooceanography* (pp. 567-644)(2007).

[28] Liu, W., Liu, M., Yang, T., Liu, X., Them, T.R., Wang, K., Bian, C., Meng, Q.a., Li, Y., Zeng, X., Zhao, W., Organic matter accumulations in the Santonian-Campanian (Upper Cretaceous) lacustrine Nenjiang shale (K2n) in the Songliao Basin, NE China: Terrestrial responses to OAE3? *International Journal of Coal Geology* 260, 104069(2022).

[29] Li, S.-z., Xu, Q.-c., Liu, M., Liu, G.-h., Li, Y.-f., Wang, W.-y., Yang, X.-g., Liu, W.-b., An, Y.-f., Sun, P., Liu, T., Ding, J.-h., Li, Q.-c., Fang, C.-g., Formation, evolution, reconstruction of black shales and their influence on shale oil and gas resource. *China Geology* 7, 551-585(2024).

[30] Percival, L.M.E., Marynowski, L., Baudin, F., Goderis, S., De Vleeschouwer, D., Rakociński, M., Narkiewicz, K., Corradini, C., Da Silva, A.C., Claeys, P., Combined Nitrogen-Isotope and Cyclostratigraphy Evidence for Temporal and Spatial Variability in Frasnian-Famennian Environmental Change. *Geochemistry, Geophysics, Geosystems* 23, e2021GC010308(2022).

[31] Kemp, D.B., Suan, G., Fantasia, A., Jin, S., Chen, W., Global organic carbon burial during the Toarcian oceanic anoxic event: Patterns and controls. *Earth-Science Reviews* 231, 104086(2022).

[32] Copper, P. Evaluating the Frasnian-Famennian mass extinction: Comparing brachiopod faunas. *Acta Palaeontologica Polonica*, 43(2)(1998).

[33] Śliwiński, M. G., Whalen, M. T., & Jed, D. A. Y., Trace element variations in the middle Frasnian punctata zone (Late Devonian) in the Western Canada sedimentary basin—changes in oceanic bioproductivity and paleoredox spurred by a pulse of terrestrial afforestation?. *Geologica Belgica*(2010).

[34] Bahlburg, H., & Dobrzinski, N. ,Chapter 6: A review of the Chemical Index of Alteration (CIA) and its application to the study of Neoproterozoic glacial deposits and climate transitions. *Geological Society, London, Memoirs*, 36(1), 81-92(2011).

[35] Cui, Y., Shen, B., Sun, Y., Ma, H., Chang, J., Li, F., Lang, X., Peng, Y., A pulse of seafloor oxygenation at the Late Devonian Frasnian-Famennian boundary in South China. *Earth-Science Reviews* 218, 103651(2021).

[36] Uveges, B.T., Junium, C.K., Boyer, D.L., Cohen, P.A., Day, J.E., Biogeochemical controls on black shale deposition during the Frasnian-Famennian biotic crisis in the Illinois and Appalachian Basins, USA, inferred from stable isotopes of nitrogen and carbon. *Palaeogeography, Palaeoclimatology, Palaeoecology* 531, 108787(2019).

[37] Becker, R. T., Königshof, P., & Brett, C. E., Devonian climate, sea level, and evolutionary events: An introduction. *Geological Society, London, Special Publications*, 423(1), 1-10(2016).