Geochemical characteristics and organic matter enrichment of the Late Ordovician-Early Silurian black shale in Nanchuan area, Sichuan Basin

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Abstract. The enrichment of organic matter in black shale is a controversial issue among the researchers and critical problem in the exploration of shale gas. In order to understand the relationship between sedimentary environment and organic matter accumulation in black shale of Wufeng Formation, Longmaxi Formation and limestone of Guanyinqiao Bed, multiple geochemical method, such as organic carbon, major and trace elements, are tested from the Nanchuan section. Research results show that the organic carbon is enriched in the middle to upper part of Wufeng Formation and the bottom of Longmaxi Formation. Ba and P contents exhibit a high primary productivity during Late Ordovician-Early Silurian in Sichuan basin. Redox proxies (V/Cr, Ni/Co) indicate that Wufeng Formation deposited in an anoxic environment and Longmaxi Formation deposited in euxinic condition, but Guanyinqiao Bed was predominated by oxic-dysoxic environment during the sedimentation. The poor relation between TOC and Ba, suggests primary productivity are not the major factors controlling the enrichment of organic matter, but an anoxic environment is the predominant condition causing the accumulation and preservation of organic matter suggested by a positive correlation between TOC and redox proxies.

1. Introduction
The mechanism of organic matter enrichment is a complex issue which have been harshly debated for decades. Much factors, including primary productivity, bottom water anoxia, clastic flux and even tectonic movement may conduct to accumulation of organic matter. However, most controversies focuses on two hypothesis toward “productivity” versus “preservation model”. The former model proposes that high primary productivity surface water is the critical factor for supplying abundant organic matter. The latter model argues that anoxia in the bottom water enhance organic matter preservation owing to diminish aerobic decomposition. However, it is obviously that no single control can explain organic accumulation in all sediments³⁴⁵.

The Upper Ordovician Wufeng formation and Lower Silurian Longmaxi formation organic-rich black shale in the Sichuan Basin have been studied as potential shale gas reservoir in terms of paleogeography, stratigraphy and lithology, however, the mechanisms of organic matter accumulation are not well understood yet. In this paper, we present trace elements and total organic carbon(TOC) on fresh core sample of Wufeng Formation-Longmaxi Formation in Nanchuan section, Southern Sichuan
Basin, and adopt redox-sensitive parameter and productivity indicaor to investigate the mechanism of organic enrichment of the black shale.

2. Geological setting
Sichuan Basin is a superimposed basin developing on the Yangtze platform in southwest China. During the Ordovician-Silurian transition, the Yangtze platform was surrounded by uplifts on three side and covered by a broad epeiric sea\(^6\). At this time, the organic-rich black shale are widely deposited in Yangtze sea and formed the Upper Ordovician Wufeng and Lower Silurian Longmaxi Formation (Fig.1).

The Nanchuan section located in southern Sichuan Basin. In ascending order, the Ordovician-Silurian boundary strata include Wufeng, Guanyinqiao and Longmaxi formation. The Wufeng and Longmaxi Formation are mainly compose of black shales, meanwhile, the Guanyinqiao Bed is composed of marl (Fig.2).

3. Samples and methods
A total of 33 core samples were collected from Nanchuan section, including 7 black shale samples from Wufeng Formation, 3 marl samples from Guanyinqiao Bed and 23 organic-rich shale samples from Longmaxi Fomation, respectively. All samples were pulverized to less than 200 mesh and tested for organic carbon content (TOC), major and trace elements. TOC content was tested using a CS-344 carbon-sulfur analyzer. X-ray fluorescence spectrometry (XRF) was used to identify major element (Si,Al,Ca,Fe,Ti). Trace elements (V,U,Ba,P,Cr,Ni) were analyzed using a inductively coupled plasma mass spectrometer(ICP-MS). All test were analyzed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

4. Results
4.1. TOC abundance
For Nachuan section, TOC value shows significant variation. Samples of Wufeng Formation has a TOC content ranges from 2.26% to 5.66% and average 4.39%. Guanyinqiao Bed displays a low TOC contents ranges from 0.61% to 0.84%(avg.0.71%). TOC of Longmaxi Formation ranges from 1.3% to 4.3%.
4.2. Major and trace element

Results of major and trace element are listed in Table (1). SiO$_2$ (detrital quartz and biogenic silica), Al$_2$O$_3$ (clay fraction), and CaO (carbonate content) are three major components of mudstone\(^\text{[8]}\). SiO$_2$ is the most abundant element with a value ranging from 16.31% to 78.66%, averaging 60.89%. Al$_2$O$_3$ is the second abundant element varying from 3.29% to 17.01% (avg. 10.7%). Next, CaO content is relatively high and variable, ranging from 1.09% to 25.42% (avg. 5.33%). The remaining major elements contents are all below 1%, including TiO$_2$, Fe$_2$O$_3$, Na$_2$O.

Some trace elements are chosen here to reveal the oceanic primary productivity and redox condition during late Ordovician-early Silurian. The concentrations of Ba and P are generally regarded as effective indicators to identify the surface water primary productivity. Samples of Wufeng and Longmaxi Formation black shale yield Ba contents ranging from 691.3 ppm to 1584.3 ppm, averaging 853.25 ppm. The contents of P show variable values between 358.5 ppm and 1034.7 ppm (avg. 520.2 ppm). Redox-sensitive elements (V, Cr, Ni) are generally concentrated in organic-rich shale. For Nanchuan section, V shows moderate values (25.4 to 672.3 ppm, avg. 209.2 ppm) in the black shale. Cr varies in the section with low values between 19.12 ppm and 144.5 ppm (avg. 65.7 ppm). The contents of Ni are similar with V and ranging from 29.2 ppm to 222.4 ppm, averaging 93.9 ppm.

![Figure 2. The stratigraphic distribution of the TOC, major and trace elements](image-url)
5. Discussion

5.1. Primary productivity

Phosphorus (P) is an essential nutrient element for oceanic organism and the concentration of P has been regarded as an effective proxy of primary productivity\(^9\). It is supposed transferred into sediment by incorporating with organic matters or by binding to Fe-oxyhydroxides. In addition, terrigenous flux are also the sources of P. In order to eliminate the effect of elastic influx. We chose the P/Al ratio to evaluate the surface water primary productivity. In the black shale of Wufeng and Longmaxi Formation, the P/Al ratio(avg.84.8) reveal relative stable and high-nutrient surface water during the late Ordovician (Fig.2). The primary productivity approached to peak value (498.1) in the Guanyinqiao Bed imply the high productivity.

Barium (Ba) of marine sediments is another frequent-used geochemical index to evaluate the paleoproductivity. Barite is the main carrier of barium in the water column\(^10\). However, Barium is mainly contained in two phases, including biogenic-related (organic matter, biogenic silica) and other not related to carbon export(terrigenous silicates, Fe-Mn oxides and hydroxides). Only the biogenic barium can directly reflect the primary productivity. Babio is determin from the total Ba concentration minus the Ba derived from terrigenous influx. Babio can be calculated as the following formula:

$$B_{bio} = B_{total} - A_{total} \times (Ba/Al)_{alu}$$
In this equation, it assumes that all the aluminium is derived from aluminosilicate origin. Ba and Al are the bulk concentrations of samples, Ba/Al_{alu} ration represent the aluminosilicate detritus of crustal rock input to the ocean. The ratio range from 0.005 to 0.01 in crustal rock and 0.0075 is generally used to calculate the Ba_{bio} content^{[11]}. However, barite, the main carrier of barium, could be dissolved in the anoxic and sulfate reducing condition. Thus, the Ba_{bio} values are relatively low in the black shale of Wufeng Formation and Longmaxi Formation. It do not interpret a low productivity. On the contrary, the extremely high Ba_{bio} concentration in the Guanyinqiao Bed reveal high primary productivity of surface water during the late Ordovician in Sichuan Basin (Fig. 2).

5.2. Redox conditions
Redox-sensitive element are widely used in geochemistry to estimate the oxygen degree of bottom water during sedimentation. Especially the ratio of V/(V+Ni), V/Cr, Ni/Co, U/Th, are considered as reliable indicators for paleoredox conditions. These trace elements ratio generally display a positive correlation with TOC abundance. Vandium and Ni are sequestered in water column under anoxic conditions. While U and Th exhibit similar geochemical behavior. Uranium will stay insoluble U^{4+} under highly reducing conditions and get enrichment in sediments. Whereas U^{6+} keep soluble under oxidizing condition and loss in sediments^{[12]}. In addition, thorium remains insoluble as Th^{4+} and is unaffected by the redox conditions of the water column. Therefore, high V/(V+Ni), V/Cr, Ni/Co, U/Th values are considered to indicate dysoxic-anoxic condition, In general, the ratio of V/(V+Ni)>0.5, V/Cr>4.25, Ni/Co>7 and U/Th>1.25 indicate an anoxic environment^{[13]}. The higher ratio represents a deeper anoxic or euxinic bottom water. Otherwise, an oxic-suboxic environment display a low ratio of the redox-sensitive elements. In Nachuan section, the black shale samples from Wufeng Formation and Longmaxi Formation has a high ratio of V/(V+Ni) (avg.0.68), V/Cr(avg.4.23), Ni/Co(avg.7.13), U/Th(avg.0.88), indicate a long time continual anoxic environment during the sedimentation. But the low redox-sensitive element ratios in the Guanyinqiao Bed, reveal that there were a short time oxic-suboxic condition occurred during the late Ordovician-early Silurian (Fig.2).

**Figure 3.** Crossplots of the redox condition and productivity proxies versus TOC
5.3. Factors controlling the accumulation of organic matter

The accumulation of organic matter is a complex geochemical process, it is largely dependent on a high organic carbon supply and favorable environment to preserve in the sediment. Although much factors controlling the enrichment of organic matter, including clastic influx, eustatic fluctuation and tectonic movement, productivity and preservation condition are considered as the most critical factors. Within the Nanchuan section in this article, paleoproductivity indices P/Al and Ba\text{bio} suggest that the Wufeng and Longmaxi black shale were deposited in the high nutrient surface water mass. That would supply abundant organic matter deposited into the sediment\textsuperscript{14-16}. According to the crossplot of the P/Al and Ba\text{bio} versus TOC(Fig.3), there is a relatively positive correlation between the TOC and the ratio of P/Al(R\textsuperscript{2}=0.13),Ba\text{bio}(R\textsuperscript{2}=0.11). However, the high ratio of P/Al and Ba\text{bio} in Guanyinqiao Bed display a low TOC content in the diagram, suggest that productivity is not the only factor controlling the organic matter enrichment. The ratio of redox indices reveal that Guanyinqiao Bed was deposited under oxic-suboxic bottom water. That will cause the organic matters being oxidized and lost in the sediment. Whereas, in the diagram of redox parameters cross TOC content, the ratio of V/(V+Ni), V/Cr, Ni/Co, U/Th show a strong positive correlation with TOC content throughout the whole section. Especially, the correlations of V/(V+Ni) vs. TOC(R\textsuperscript{2}=0.39), V/Cr vs. TOC(R\textsuperscript{2}=0.47) indicate that organic matters accumulation mainly result from the anoxic bottom water but not the primary productivity (Fig.3). Therefore, both high productivity and anoxic condition contributed to the accumulation of organic matter in Wufeng and Longmaxi black shale, but the latter is much more significant in this research section\textsuperscript{17-18}.

6. Conclusions

Base on the analysis of TOC abundant, major and trace element of the late Ordovician-early Silurian black shale from the Nanchuan section, south Sichuan Basin, we draw the conclusions as following:

(1) Productivity indices(P/Al,Ba\text{bio}) suggest that the Wufeng and Longmaxi black shale were deposited in high primary productivity surface water columns.

(2) Redox proxies(V/(V+Ni), V/Cr, Ni/Co, U/Th) indicate that the black shale were deposited under anoxic bottom water mass, which insure the organic matter could be well-preserved in the sediment.

(3) Both productivity and redox condition affecting the accumulation of organic matter, but the water column oxygenation level is the critical factor that restrict the organic enrichment of Wufeng and Longmaxi black shale.

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