Controlling Factors on Organic Matter Accumulation of Marine Shale across the Ordovician–Silurian Transition in South China: Constraints from Trace-Element Geochemistry

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ABSTRACT: In recent years, significant progress in shale gas exploration has been achieved in the Upper Ordovician (Wufeng Formation)–Lower Silurian (Longmaxi Formation) shales in the Upper Yangtze area, South China. Although many studies have been carried out on the Upper Ordovician–Lower Silurian shales, the controlling factors causing organic matter accumulation of these shales remain controversial. This study uses trace-element geochemistry and sedimentological methods to evaluate terrigenous input, redox conditions and primary productivity to explore the mechanisms of organic matter accumulation. The variation of terrigenous fraction elements (Al, Th and Sc) concentrations reflect a mixed influence of sea-level change and weathering. The sea-level of the Upper Yangtze Sea went through two cycles of transgression to regression during the Ordovician–Silurian transition. The Linxiang Formation, Kuanyinchiao Bed and the upper part of Longmaxi Formation developed during the periods of regression, whereas the Wufeng Formation and the lower part of the Longmaxi Formation developed during the periods of transgression. The paleo-productivity indexes of TOC content, ratios of Ba/Al and P/Al, and redox conditions proxies of Mo concentration, ratios of U/Th and V/Cr generally display similar variation patterns with respect to the sea-level changes. High TOC contents and Ba/Al and P/Al ratios indicate the paleo-productivity was high on the sea surface, as shown by relatively good positive correlations between Th vs. TOC, and Sc vs. TOC. This indicates that the paleo-productivity was controlled by the nutrients input through weathering. The good positive correlations between redox conditions indexes (U/Th and V/Cr ratios) with TOC content reflects reductive preservation conditions (anoxic to euxinic), thus implying they were an important controlling factor for organic matter accumulation. Nevertheless, redox conditions were closely associated with sea level change and organic matter decomposition. Therefore, the sea-level change and weathering were the primary controlling factors for organic matter enrichment across the Ordovician to Silurian transition.

KEY WORDS: productivity, redox, sea-level change, shale gas, Sichuan Basin, Wufeng-Longmaxi shale.

0 INTRODUCTION

Marine organic-rich black shales in the geological record are generally considered as hydrocarbon source rocks (Katz, 2005; Ribouleau et al., 2003). Although these shales have very low permeability and porosity, they could form self-sourced shale gas and oil in place under certain conditions (Qiu and Zou, 2020a, b; Hao et al., 2013; Zou et al., 2010). With the increasing interests in shale gas and oil, it is necessary to understand the processes controlling accumulation and distribution of organic matter within these shales (Crombez et al., 2017; Zou et al., 2015; Tømmerås and Mann, 2008).

Organic matter enrichment is a complex process involving physical, chemical, and biological factors, such as primary productivity, bottom water condition, nutrient availability, terrigenous input, and post-depositional degradation processes.
(bacterial sulfate reduction) (Wei and Jiang, 2019; Lash and Blood, 2014; Wei et al., 2012; Burdige, 2007; Sageman et al., 2003; Murphy et al., 2000; Arthur and Sageman, 1994; Pedersen and Calvert, 1990; Demaison and Moore, 1980). However, the mechanisms of organic enrichment in black shale continue to be debated, focusing on two main controlling factors. The first considers high primary productivity resulting in high input of organic matter (Gallego-Torres et al., 2007; Sageman et al., 2003; Pedersen and Calvert, 1990), while the other considers anoxic water condition for the favorable preservation of organic matter (Mort et al., 2007; Arthur and Sageman, 1994; Demaison and Moore, 1980). To resolve these controversies, elemental geochemical proxies, such as trace element enrich factor, U/Th and V/Cr ratios, have been widely used to discriminate water-mass redox conditions from oxic, to suboxic and anoxic states (Zhu et al., 2018; Guo et al., 2007; Algeo and Maynard, 2004; Rimmer, 2004; Kimura and Watanabe, 2001). On the other hand, the ratios of Ba/Al and P/Al in sediment are widely used as proxies for primary productivity (Schoepfer et al., 2015; Yan et al., 2015; Paytan et al., 2007; Prakash et al., 2002; Dymond et al., 1992).

In recent years, significant progresses on shale gas exploration have been achieved in the Upper Ordovician–Lower Silurian organic-rich shales (Wufeng-Longmaxi shale) within and around the Sichuan Basin (Zhou et al., 2019; Ma and Xie, 2018; Zou et al., 2015; Guo and Zhang, 2014; Qiu et al., 2013). Three shale gas fields from the shale gas sweet-spot areas of the Wufeng-Longmaxi shale have been found in Weiyuan, Changing-Zhaotong, and Fuling with the proven reserves over 1.0×10¹² m³ (Qiu and Zou, 2020a). Shale gas production from the shale strata has been increasing rapidly, reaching 90×10⁸ m³ in 2017 and 154×10⁸ m³ in 2019 (Qiu and Zou, 2020a). Many studies have demonstrated that Wufeng-Longmaxi shale is well qualified as shale gas reservoirs and can be compared to marine shales in North American with respect to their total organic carbon (TOC), mineralogical composition, porosity, and pore size (Wang et al., 2014; Tian et al., 2013; Long et al., 2012). Although many studies on the Wufeng-Longmaxi shale in South China have been conducted, the controlling factors of the organic accumulation are still debated (Qiu et al., 2020, 2016; Zou et al., 2018a; Li YF et al., 2017; Zhao, 2016; Li Y et al., 2015; Yan et al., 2015). To understand the controlling factors influencing the organic matter accumulation in these shales, this study focuses on the relationships of organic matters (TOC) with redox conditions (Mo enrich factor, U/Th and V/Cr ratios) and productivities (Ba and P), these analyses are based on geochemical data from 173 fresh rock samples from three profiles in the Upper Yangtze area (Fig. 1).

1 GEOLOGICAL SETTING

1.1 Paleogeographic Setting

During the Late Ordovician, the coupled South China Complex as a whole was located near the equator (Fig. 1a) (Torsvik and Cocks, 2013), and was still attached to the margin of Gondwanaland, even if it tended to be a separated plate during the Mid–Late Paleozoic (Metcalfe, 1994). This complex consisted of the Yangtze Block in the west (Fig. 1b), and the Cathaysia block in the southeast during the Early Paleozoic (Wang, 1985). From the Late Ordovician to Early Silurian, the Yangtze Block was occupied mostly by a shallow carbonate platform, and gradually evolved into a siliciclastic-dominated deep shelf (Zou et al., 2018a) (Figs. 1b, 1c), as a result of the amalgamation of the Yangtze and Cathaysia blocks (Su et al., 2009; Chen et al., 2004). From the late Katian Age to the Early Silurian, four main stratigraphic strata have developed in the following ascending order: The Linxiang Formation, the Wufeng Formation, the Kuanyinchiao Bed (KB) and the Longmaxi Formation. The Linxiang Formation was widely deposited on the Yangtze Platform, consisting mainly of gray limestone at the three studied sections. Lithostratigraphically, the Longmaxi Formation at many localities and is composed of two lithological parts, the lower black shale and the middle-upper grayish green shale, siltstone and sandstone (Rong et al., 2019). The black shales of the Wufeng and Longmaxi formations were extensively deposited on a deepening shelf notably in the Mid–Upper Yangtze Block (Ran et al., 2015; Chen et al., 2004). At the end of the Late Ordovician...
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(Hirnantian Age), rapid glaciation in Gondwana drove a rapid sea-level fall and widespread deposition of shelly limestones (i.e., KB) and/or coarser sandstones/siltstones containing the Hirnantian fauna in the Yangtze Block (Rong, 1984). Graptolites are the most common organisms in the Ordovician-Silurian boundary successions and are divided into several bio-zones, which are well correlated with other bio-zones around the world (Zou et al., 2018a; Chen et al., 2006, 2000).

1.2 Study Sections

Three sections located from proximal to distal areas on the Upper Yangtze were studied (Figs. 1 and 2), including the Shuanghe (SH), Qiliao (QL) and Tianba (TB) sections. The three main stratigraphic formations have been defined in the following ascending order: the Linxiang Formation (LXF), the Wufeng Formation, and the Longmaxi Formation (Figs. 2 and 3). LXF was widely deposited on the Yangtze Platform, consisting mainly of gray limestone at the three sections (Figs. 3a, 3c). At the top of the Wufeng Formation, several centimeters to less than one meter of black shelly mudstone commonly deposited as KB (Figs. 3c–3e). The Wufeng and Longmaxi formations are characterized by graptolites (Fig. 3f). The SH Section (28°23′52.9″N, 104°52′26.7″E) is located in Changning County, Sichuan Province. The Wufeng and Longmaxi formations are mainly composed of black calcareous shales with minor black argillaceous shales (Fig. 3a) with about 60 cm of KB (Fig. 2). This section is considered to have been deposited in an inner shelf depositional environment, but well below the wave base and far from shore (Fig. 1) (Zou et al., 2018a, 2015; Chen et al., 2004); The QL Section (29°52′44.4″N, 108°17′6.41″E) and TB Section (31°24′0.67″N, 108°52′36.59″E), are located in Shizhu County and Wuxi County, Chongqing City, respectively. The Wufeng and Longmaxi formations of these two sections are mainly composed of bedded chert with less black argillaceous shale (Figs. 2, 3b and 3d). QL Section is considered as having been deposited in a middle shelf depositional environment (Zou et al., 2018a), and the TB Section in an outer shelf-slope depositional environment (Fig. 2) (Zou et al., 2018a; Ran et al., 2015).

2 MATERIALS AND ANALYTICAL METHODS

2.1 Sampling

One hundred and seventy-three fresh samples were collected from three sections. Sampling interval is from the uppermost Linxiang Formation to the lower black shale parts of Longmaxi Formation across O-S boundary. During the process of sampling, any weathered surfaces and veins were removed. The cleaned parts of samples were crushed to ~80 and ~200 mesh size powder by using a Tema mill with a Tungsten Carbide barrel for further analyses.

2.2 Analytical Procedures

Total organic carbon (TOC) contents were measured in the PetroChina Research Institute of Petroleum Exploration & Development. Sample powders (200 mg, ~80 mesh size) were firstly treated with 10% (volume) hydrochloric acid (HCl) at 60 °C to remove carbonate, and then washed with distilled water to remove HCl. Afterwards, the samples were dried overnight (50 °C) and then analyzed for TOC content using a LECO CS-230 analyzer.
Sample powders (~200 mesh size) for major elements analysis were first dried in an oven at 50 °C for about 1 h and then were mixed with flux (Li$_2$B$_4$O$_7$) in the proportion 1 : 5 to make fusion glass pellets. Finally, major element contents were measured using an automatic X-ray fluorescence spectrometer (XRF-1500) with those glass pellets. Sample powders (40 mg, ~200 mesh size) for trace element analysis were dissolved in distilled HF+HNO$_3$ in 15 mL savillex Teflon screw-cap beakers and high-pressure Teflon bombs at 120 °C for 6 days and dried. The dried samples were digested again with 2 mL HNO$_3$ until the solution became clear to ensure complete dissolution, then diluted to 50 mL for analysis. Finally, they were analyzed on a VG PQ2 Turbo inductively coupled plasma source mass spectrometer (ICP-MS). Major and trace elements were measured in the Institute of Geology and Geophysics, Chinese Academy of Sciences. The detailed procedures followed Li (1997). Generally, analytical precision for major element contents is better than 1%, and for trace element is better than 2%.

2.3 Data Normalization

Trace elements in black shale have different sources, including terrigenous, organic matter or authigenic minerals (Tribovillard et al., 2006; Algeo and Maynard, 2004; Morford et al., 2001; Calvert and Pedersen, 1993), researchers usually normalize trace-element concentrations to aluminum content to correct the dilution of these biogenic contents (e.g., calcium carbonate and opal) (Tribovillard et al., 2006). There are two correction methods for normalizing to Al: enrichment factors (XEF) and trace-elements/Al (X/Al). XEF commonly uses an average shale for the standard comparison (e.g., Post-Archean Australian shale, PAAS) (Taylor and McLennan, 1985).

The assessment of the authigenic fraction of Mo and U generally use enrichment factors, which can be calculated by the formula.

$$X_{EF} = \frac{(X/Al)_{sample}}{(X/Al)_{PAAS}}$$
where X and Al are the weight concentrations of element X and Al, respectively, and PAAS is the post-Archean average shale compositions (Taylor and McLennan, 1985). When X/Al > 3, it is regarded as a detectable authigenic enrichment, and when X/Al > 10 it is regarded as a substantial enrichment (Algeo and Tribovillard, 2009).

3 RESULTS

3.1 Organic Matter Abundance

Total organic carbon (TOC) contents in sediments are the residues of the organic matter produced in the sea surface (productivity) and decomposed through the processes of sinking and diagenesis. Therefore, the TOC content has a close relationship with productivity and can be used as a direct productivity proxy (Schoepfer et al., 2015; Pedersen and Calvert, 1990).

TOC contents of all samples are presented in Tables S1, S2 and S3. At the SH Section, all the samples from the three formations show significant differences in TOC content (Table S1 and Fig. S1). The TOC contents from samples in the Linxiang Formation are very low (avg. 0.1%). Although TOC contents of all samples from the Wufeng Formation largely vary from 1% to 5.7%, they significantly increase and cluster around 3.0% to 4.0% (avg. 3.6%). In the Kuangyinchiao Bed, all samples are characterized by lower values (1.5% to 3.4%, avg. 2.1%). However, all samples from the Longmaxi Formation are characterized by higher TOC contents (3.1% to 8.8%, avg. 5.0%).

At the QL Section, the TOC contents of all the samples are shown in Table S2 and Fig. S1. In the Linxiang Formation, a sample has very low TOC content (< 0.1%). Samples from the Wufeng Formation have highly variable TOC contents ranging from 2.6% to 13.0%, however they cluster around 3.0% to 5.0% (avg. 4.2%). TOC contents of three samples from the Kuangyinchiao Bed are characterized by higher values (6.6% to 7.5%, avg. 7.0%). In the Longmaxi Formation, all samples have higher TOC contents clustering around 6.0% to 8.0% (avg. 6.9%).

At the TB Section, TOC contents of all samples are presented in Table S3 and Fig. S1. TOC contents of three samples from the Linxiang Formation are very low (avg. <0.1%). Although all samples from the Wufeng Formation have significantly variable TOC contents ranging from 0.2% to 16.0%, they cluster around 2.0% to 4.0% (avg. 3.6%). All samples from the Kuangyinchiao Bed have relatively lower TOC contents (0.6% to 2.0%, avg. 1.4%). However, in the Longmaxi Formation, all the samples are characterized by high TOC contents ranging from 4.2% to 8.0% (avg. 5.8%).

3.2 Primary Productivity Proxies

Elemental ratios of Ba/Al and P/Al are usually considered as proxies for paleo-productivity (François et al., 1995; Murray and Leinen, 1993; Dymond et al., 1992). The Ba/Al and P/Al show high values in the upper part of Wufeng Formation (UPWF) and the lower part of Longmaxi Formation (LPLF, corresponding to graptolite zones: M. persculptus to A. ascensus for the SH Section, M. persculptus to A. ascensus for the QL Section, and M. persculptus to A. ascensus for TB Section), whereas the Linxiang Formation, lower part of Wufeng Formation (LPWF), KB and the upper part of Longmaxi Formation (UPLF, corresponding to graptolite zones: A. ascensus to P. acuminatus for SH Section, A. ascensus for QL Section, and A. ascensus to P. acuminatus for TB Section) display relatively low values (Tables S1, S2 and S3; Fig. S1). The values of Ba/Al and P/Al for the SH Section are 132 ppm% to 662 ppm%, with an average of 256 ppm%, and 197 × 10⁻⁴ to 1.690 × 10⁻⁴, with an average of 223 × 10⁻⁴, respectively. The ratios of Ba/Al and P/Al for the QL Section are 178 ppm% to 665 ppm%, with an average of 336 ppm%, and 25 × 10⁻⁴ to 515 × 10⁻⁴, with an average of 107 × 10⁻⁴, respectively. The ratios of Ba/Al and P/Al for TB Section are 223 ppm% to 1713 ppm%, with an average of 755 ppm%, and 15 × 10⁻⁴ to 842 × 10⁻⁴, with an average of 93 × 10⁻⁴, respectively. Compared with the PAAS (Ba/Al=65, P/Al=70 (×10⁻⁴)) (Taylor and McLennan, 1985), the paleo-productivity proxies of these recent samples have relatively higher values.

3.3 Redox Proxies

The bottom water redox conditions have significant influences on the accumulations of Mo, U and V in sediments. Under oxic conditions, Mo, U and V exhibit conservative behavior (Algeo and Maynard, 2008), whereas in the reducing conditions, these elements will be transferred from water column to the sediments by adsorption or by forming organometallic ligands (Tribovillard et al., 2006). Many studies have proved that the elemental ratios of Mo/Al, U/Th and V/Cr are useful proxies for the discrimination of paleo-redox conditions (Rimmer et al, 2004).

The ratios of U/Th and V/Cr of the samples are shown in Tables S1, S2, and S3, and in Fig. S2. At the SH Section, U/Th and V/Cr ratios of the samples from the Linxiang Formation are the lowest, ranging between 0.20 to 0.55 (avg. 0.41) and 1.08 to 1.49 (avg. 1.30), respectively. In the Wufeng Formation, U/Th and V/Cr ratios of the samples increase gradually (Fig. S2). Most of the data points cluster around 1.00 to 1.50 (avg. 1.24) and 2.00 to 4.00 (avg. 3.22), respectively. KB is characterized by lower U/Th ratios (0.49 to 0.87, avg. 0.63) and V/Cr ratios (1.78 to 2.34, avg. 2.04). However, U/Th and V/Cr ratios of the samples from the bottom part of the Longmaxi Formation increase abruptly as does the trend for TOC (Fig. S2). They are characterized by higher U/Th ratios (0.52 to 8.38, avg. 1.97) and V/Cr ratios (2.22 to 9.27, avg. 4.91), respectively.

At the QL Section, U/Th and V/Cr ratios of all samples are present in Table S2 and Fig. S2. In the Linxiang Formation, they are 0.13 and 1.47, respectively. Samples from the Wufeng Formation have highly variable U/Th and V/Cr ratios ranging from 0.14 to 2.05 (avg. 0.90) and from 1.32 to 9.66 (avg. 3.70), respectively. However, three samples in KB are characterized by higher ratios of U/Th (1.26 to 1.37, avg. 1.30) and V/Cr (4.57 to 5.77, avg. 5.09). In the Longmaxi Formation, the U/Th and V/Cr ratios reach the highest values, and they range from 1.25 to 2.25 (avg. 1.93) and from 6.00 to 8.00 (avg. 6.48), respectively.

At the TB Section, U/Th and V/Cr ratios of all samples are shown in Table S3 and Fig. S2. In the Linxiang Formation, they are 0.13 and 1.47, respectively. Samples from the Wufeng Formation have highly variable U/Th and V/Cr ratios ranging from 0.14 to 2.05 (avg. 0.90) and from 1.32 to 9.66 (avg. 3.70), respectively. However, three samples in KB are characterized by higher ratios of U/Th (1.26 to 1.37, avg. 1.30) and V/Cr (4.57 to 5.77, avg. 5.09). In the Longmaxi Formation, the U/Th and V/Cr ratios reach the highest values, and they range from 1.25 to 2.25 (avg. 1.93) and from 6.00 to 8.00 (avg. 6.48), respectively.
higher U/Th ratios (0.95–4.35, avg. 1.89) and V/Cr ratios (3.22–10.77, avg. 6.73).

4 DISCUSSION

4.1 Paleo-Productivity

Total organic carbon (TOC) content, P and Ba are the three most widely used proxies for paleo-productivity analyses (Schoepfer et al., 2015; Shen et al., 2014). Organic carbon in the sediments comes from the sinking particles of organic material produced in the ocean surface, together with a component of terrigenous organic carbon in some coastal settings (Hartnett and DeVol, 2003). The organic matter (OM) would be decomposed by bacterial respiration before reaching the sediments (Ospahl and Benner, 1997; Deuser, 1971). Phosphorus (P) is an essential nutrient element for marine phytoplankton growth, and OM is the ultimate source of most P in marine sediments, thus, the total P is commonly used as the productivity indicator (Schenau et al., 2005). The burial of P is controlled by the pore water redox conditions and adsorption of Fe-oxhydroxides (Tribovillard et al., 2006). Many studies agree that barium (Ba) precipitated in sediments is usually accompanied by a high OM influx (Monnin, 1999; Gingele and Dalmke, 1994; Dymond et al., 1992). Therefore, the relationship between the abundance of Ba and OM supports the notion that Ba can be used as a proxy for paleo-productivity (François et al., 1995; Dymond et al., 1992). However, precipitated Ba in marine sediments dissolves and migrates under intense sulfate reduction environment (Torres et al., 1996; van Santvoort et al., 1996; van Os et al., 1991). Although the TOC content, P, and Ba concentrations are influenced during the processes of transportation, deposition, and diagenesis before fixation in the sediments, their concentrations or variation patterns can still be used to evaluate the paleo-productivity (Schoepfer et al., 2015; Zonneveld et al., 2010; Tyson, 2005; Pedersen and Calvert, 1990). In this study, the TOC contents of the SH Section are between 2.6 wt.% and 7.8 wt.%, with an avg. of 4.2 wt.%, those of QL Section are 2.6 wt.%–14 wt.%, avg. 6.0 wt.%, and those of TB Section are 1 wt.%–16 wt.%, avg. 4.7 wt.%, which are similar to the samples from the downslope sites of eastern Pacific off Callao, Peru (Neira et al., 2001), reflecting a mass of OM influx from the sea surface. UPWF and LPLF were suboxic-anoxic-euxinic conditions (Fig. S2), this may due to the influence of the frequent deposition of volcanic ash. When volcanic ash falls into the sea and under normal seawater conditions, the Cr will be in a soluble as CrO$_2^-$ (Tribovillard et al., 2006; Algeo and Maynard, 2004) and removed from the clastic fractions, whereas Th is a relative stable element and will be retained in the clastic fractions, thus, Th would mostly be transported to the sediments (González-Álvarez and Kerrich, 2011). This process could lead to the Th content increasing but the Cr content decreasing in the sediments. Meanwhile, redox sensitive elements U and V have the same covariant tendencies (a positive correlation) implying that their concentrations change may have limited effect on the different ratios of U/Th and V/Cr. Element Mo removed from seawater to sediments is closely associated with the intensity of reducing water mass, and more reducing water mass would promote Mo enriched in sediments (Tribovillard et al., 2012; Algeo and Lyons, 2006). A mass of volcanic ash from an eruption and then deposited from seawater surface into the bottom would disrupt the reducing settings, thus, diminishing Mo might migrate into the sediments.

4.2 Redox Conditions

Trace elements Mo, U, and V are sensitive elements for detecting variation in redox condition, and are usually enriched in reduction environments that migrated under oxidizing settings, thus, these elements are useful proxies for paleo-redox conditions and widely applied to analyse the redox conditions of ancient basins (Wang et al., 2019; Ocubalidet et al., 2018; Wei et al., 2016; Zhou et al., 2015; Tribovillard et al., 2012, 2006; Algeo et al., 2011; Algeo and Tribovillard, 2009; Algeo and Maynard, 2008; Algeo and Lyons, 2006; Rimmer, 2004; Morford and Emerson, 1999). Elements of Mo, U, and V have a similar variation trends in SH, QL, and TB sections (Fig. S2). The values of Mo, U/Th, and V/Cr are relatively high in LPWF, UPWF, and LPLF, but low in UPLF. The KB between Wufeng Formation and Longmaxi Formation has a disturbance with low values of Mo, U/Th and V/Cr.

4.2.1 U/Th and V/Cr ratios

According to Jones and Manning (1994), U/Th<0.75 indicates oxic water condition, U/Th=0.75–1.25 indicates suboxic water condition, and U/Th>1.25 indicates anoxic water condition, V/Cr<2 indicates oxic conditions, V/Cr=2.0–4.25 indicates suboxic and V/Cr>4.25 indicates anoxic water conditions. Thus, the U/Th and V/Cr profiles here reflect a variation from oxic-suboxic, to suboxic-anoxic, and to anoxic-euxinic environments in the Wufeng Formation, and a variation from euxinic-anoxic, anoxic-suboxic, to suboxic and to suboxic-oxic in the Longmaxi Formation upward. Furthermore, values of Mo, U/Th and V/Cr in LPLF are relatively higher than those in the UPWF. Therefore, we infer intermittent or weakly euxinic bottom water conditions during the deposition of the UPWF, and a more intense persistent euxinia during the deposition of the LPWF (e.g., Zou et al., 2018a, b; Li et al., 2017; Chen et al., 2016; Yan et al., 2015).

In the UPWF, the V/Cr ratios display the opposite variation patterns with Mo and U/Th (as shown in the TB Section, Fig. S2), this may due to the influence of the frequent deposition of volcanic ash. When volcanic ash falls into the sea and under normal seawater conditions, the Cr will be in a soluble as CrO$_2^-$ (Tribovillard et al., 2006; Algeo and Maynard, 2004) and removed from the clastic fractions, whereas Th is a relative stable element and will be retained in the clastic fractions, thus, Th would mostly be transported to the sediments (González-Álvarez and Kerrich, 2011). This process could lead to the Th content increasing but the Cr content decreasing in the sediments. Meanwhile, redox sensitive elements U and V have the same covariant tendencies (a positive correlation) implying that their concentrations change may have limited effect on the different ratios of U/Th and V/Cr. Element Mo removed from seawater to sediments is closely associated with the intensity of reducing water mass, and more reducing water mass would promote Mo enriched in sediments (Tribovillard et al., 2012; Algeo and Lyons, 2006). A mass of volcanic ash from an eruption and then deposited from seawater surface into the bottom would disrupt the reducing settings, thus, diminishing Mo might migrate into the sediments.

4.2.2 Mo$_{\text{EFF}}$ and U$_{\text{EFF}}$ co-variations

Both molybdenum and uranium exhibit conservative behavior under oxic conditions, long residence time in seawater (∼450 kyr for U, ~780 kyr for Mo), and low concentrations in plankton (Algeo and Tribovillard, 2009). But Mo and U are activated under oxygen-depleted conditions, which can facilitate Mo and U in seawater to be transferred into the sediments, and this uptake parts of Mo and U from seawater are imputed to authigenic (Mo$_{\text{auth}}$ and U$_{\text{auth}}$) (Tribovillard et al., 2012; Algeo and Tribovillard, 2009; Algeo and Lyons, 2006; Algeo and Maynard, 2008). Elements of Mo, U, and V have a similar variation trends in SH, QL, and TB sections (Fig. S2). The values of Mo, U/Th, and V/Cr are relatively high in LPWF, UPWF, and LPLF, but low in UPLF. The KB between Wufeng Formation and Longmaxi Formation has a disturbance with low values of Mo, U/Th and V/Cr.
2004). Meanwhile, biogenic origin parts of Mo and U in the sediments may also dilute the trace-element abundance of a sample. Therefore, in order to eliminate the dilution of biogenic diluents (mostly calcium carbonate and opal), the enrichment factors (EF) of trace elements are usually applied (Tribovillard et al., 2006). The enrichment factors (EF) of trace elements were calculated as a formula: EF element \( X = \left( \frac{X_{\text{sample}}}{X_{\text{average shale}}} \right) / \left( \frac{Al_{\text{sample}}}{Al_{\text{average shale}}} \right) \), where the average shale is post-Archean Australian shale (Taylor and McLennan, 1985). If EF X is greater than 1, then element X is enriched relative to average shales and, if EF X is less than 1, it is depleted. The enrichments of Mo and U for the SH, QL, and TB sections display relatively high values (MoEF>10), only a subset samples show 3<MoEF<10 in the Lower Wufeng Formation, and (Mo/U)ath ratios of the samples mostly fall into the range of 0.3 to 3 times that of seawater (Fig. 4). This MoEF vs. UEF patterns of the samples are similar with the modern eastern tropical Pacific (Mexican margin and Peru margin) (Algeo and Tribovillard, 2009), reflecting low dissolved oxygen concentrations (<0.5 mL/L), i.e., anoxic to euxinic conditions in bottom water in the study sections during Late Ordovician to Early Silurian (Tribovillard et al., 2012).

4.2.3 Evaluation of water mass restriction

It is still debated whether the marine systems of the study area (Upper Yangtze Plate) during the Late Ordovician to Early Silurian, are restricted basins (Li et al., 2017; Liu et al., 2017) or unrestricted marine zones (Wang et al., 2019). In highly stable stratified or silled basins, the molubdate of bottom water supply is limited (Algeo and Lyons, 2006) or reductively released back into water column from sediments (Crusius et al., 1996; Jacobs et al., 1985), whereas uranium was affected by these conditions. Therefore, MoEF/UEF ratios are dramatically decreasing when the basin become more restricted (Zhu et al., 2018; Algeo and Tribovillard, 2009; Algeo and Lyons, 2006). The MoEF and UEF of the samples exhibit a well-defined covariant trend (Fig. 4), reflecting variation in Moath and Uath concentrations that closely mirrors patterns of redox variation, which is similar with the Eastern Tropical Pacific sites (unrestricted marine system) (Algeo and Tribovillard, 2009). Although there was central Sichuan uplift in the west, Cathaysia in the south, and some relatively small highlands (e.g., Xuefeng Mountains) in the east, the paleogeography of the Upper Yangtze Plate was mostly covered by seawater which connected with the Qinling Ocean in the north, and these uplifts did not restrict the sea water in the Upper Yangtze exchanging with the northern ocean (Wang et al., 2019; Zhang et al., 2013). Some authors (Li et al., 2017) applied Mo/TOC ratios to evaluate the marine systems of Late Ordovician to Early Silurian, and proposed that the Wufeng Formation of Late Ordovician under strongly restricted conditions, whereas the Longmaxi Formation of Early Silurian was predominantly restricted marine systems. However, the concentrations of Mo in the sediments were continuously increasing as the redox conditions were reduced (Figs. S2 and 4), this suggests that the water mass was not restricted and plenty of Mo was re-supplied by the water exchange, rather than Mo diminishing under restricted basins (Tribovillard et al., 2012; Algeo and Tribovillard, 2009). Furthermore, Algeo and Lyons (2006) pointed out the Mo/TOC ratios was invalid for low-oxygen facies in open marine systems. Therefore, we infer that the marine systems of the Upper Yangtze Plate during Late Ordovician to Early Silurian should be unrestricted.

4.3 Terrestrial Detrital Input

The positive carbonate isotope excursion observed in the Late Ordovician rocks around the world (Kump et al., 1999) and Sr isotope increasing during the Early Silurian (Gould et al., 2010) have been implied that the weathering of silicate rocks is elevated during this period. High level of CO2 concentration in the atmosphere (Kump et al., 1999) and a mass of fresh silicates exposed through the uplifts of orogeny (e.g., Taconic orogeny) or volcano eruption (Huff et al., 2010; Jagoutz et al., 2016; Swanson-Hysell and MacDonald, 2017) were considered the main reasons of the high weathering during the period of Late Ordovician to Early Silurian. The Cathaysia Plate continuously moving close and squeezing to Yangtze Plate from southeast to northwest during Late Ordovician (Ashgillian Stage) to Early Silurian (Rhuddanian Stage), where zones were uplifted, i.e., Qinzhou and Yichang uplifts, which resulted in the sedimentary hiatus of Wufeng to Longmaxi strata in Qinzhou and Yichang areas (Li et al., 1997; Chen et al., 2018). Therefore, the regional tectonic movements in the Yangtze Plate during Late Ordovician to Early Silurian probably also had some impact on the enhancement of weathering. The high weathering of silicates should have caused a plenty of detrital fragments eroded and flux into the sea.

The Linxiang Formation (LXF) recorded the first global regression event, and the shelly limestone of KB was the product of the second global regression during the period of Late Ordovician–Early Silurian (Su et al., 2009, 1999). Therefore, there are at least two cycles of eustatic change during the time of Late Ordovician–Early Silurian. This would have significant influences on the detrital fractions flux into the sea.

4.3.1 Terrestrial detrital input during the deposition of Wufeng Formation and KB

Elements Al, Th and Sc primarily come from the terrigenous constituents (e.g., clay minerals) in the shales, thus, these elements are useful indicators for terrigenous input (Tribovillard et al., 2006). The concentrations of Al, Th and Sc of the samples...
from SH, QL and TB sections display variable patterns from bottom to top (Fig. S3). In the LPWF, the relative high concentrations of Al, Th and Sc were probably due to low sea level status and strong silicate weathering. In the MPWF in all three sections, a decreasing trend of Al, Th and Sc concentrations, reflecting on the one hand the sea level rise diminished detrital fractions flux into the study sites, but on the other the weathering weakened because of the temperature drop along with the decline of CO₂ concentrations. Sporadically high values in SH and TB sections might be caused by the deposition of turbidite or volcanic ashes. At the top part of Wufeng Formation of SH and QL sections, increasing trends of Al, Th and Sc concentrations would be related to boost terrestrial sediments influx because of the sea level drop. The Late Ordovician glaciation caused the sea-level to drop to a maximum of 100 m (Isosaki and Servais, 2018). Accompanied by the sea-level decline, the detrital fractions could reach from the SH Section to the QL Section, but the TB Section is located in a further location and seemingly not affected by the detrital influx. However, the concentrations of Al, Th and Sc in the UPWF from the TB Section shows a zigzag variation pattern, which probably reflect the influence of frequent volcanic eruptions. Previous studies have found up to 25 bentonite layers in the Wufeng and Longmaxi formations, and the majority of the bentonite layers distributed in the UPWF (Wu et al., 2018; Su et al., 2009). The variation patterns of the UPWF of the SH and QL sections are relative smoother than those of the TB Section, which would likely be related to the dilution of continental clastic sediments influx.

The uppermost strata of Late Ordovician are the Kuanyinchiao Bed (KB) which recorded the sea-level maximum drop because of the glaciation expansion, and developed shelly limestone in the SH, QL and TB sections. During the deposition of KB, the temperature became relative cold and most of the land was covered by ice, which caused weak weathering and less terrestrial fractions transported into the sea. The chemical index of alteration (CIA) drop to the lowest points during the period of KB deposition (Zou et al., 2018a), and the concentrations of Al, Th and Sc in all three sections display a fall back pattern, which support low terrestrial sediments influx as a result of global cooling.

4.3.2 Terrestrial detrital input during the deposition of Longmaxi Formation

The Late Ordovician glaciation lasted approximately 1 Ma and quickly ended up at the beginning of Early Silurian (Finnegan et al., 2011; Brenchley et al., 1994). As the ice retreated while temperatures warmed, more land was uncovered and could be weathered. Therefore, at the early stage of the Longmaxi Formation deposition (lower graptolite zone: M. persculptus), there were more detrital fractions weathered and transported into the sea. The concentrations of Al, Th and Sc from the bottom of Longmaxi Formation in the SH, QL and TB sections record these processes by the increase of detrital fraction flux (Fig. S3). There are peak values of Al, Th and Sc, reflecting an addition of terrestrial fraction influx. Meanwhile, two fall back values in the SH (located at 11.1 m) and QL (located at 8.9 m) sections may be caused by the dilution of carbonate rock fractions, and the increase of CaO (wt.%) values of these two samples support this deduction. Although the silicates weathering recovered from the Hirnantian global cooling, the concentrations of Al, Th and Sc from LPLF still demonstrate relative low values, this was probably due to the rapid sea-level rising at the same time offset the eroded detrital sediments transported to the study sites. Occasionally high values of Al, Th and Sc in this part may be caused by the deposition of turbidite or volcanic ash. Then the concentrations of Al, Th and Sc of the samples from UPLF of the three sections are increasing again, this may be due to the deposition locations become shallow and more terrestrial fractions can be transported there. The variations of Al, Th and Sc from the Wufeng Formation to the KB and the Longmaxi Formation reflect that the detrital influx was primary controlled by the silicates weathering and relative sea-level eustacy.

4.4 Organic Matter Accumulation Factors

The mechanisms of organic accumulation in black shale continue to be debated (Yan et al., 2015; Wei et al., 2012; Mort et al., 2007; Murphy et al., 2000; Demaison and Moore, 1980). The controversies focus on whether the enrichment of organic matter is mainly controlled by primary productivity (the organic carbon flux) (Gallego-Torres et al., 2007; Sageman et al., 2003; Caplan and Bustin, 1999; Pedersen and Calvert, 1990) or by conditions that favor the preservation of organic matter under anoxic water column (Mort et al., 2007; Arthur and Sageman, 1994; Demaison and Moore, 1980). The covariance diagrams of TOC vs. detrital elements (Th and Sc), paleo-productivity indexes (Ba/Al and P/Al), and redox indexes (Mo/Al and U/Th) were used to analyze this dispute of organic matter accumulation factors (Fig. 5). There are relatively positive correlations between detrital elements concentrations (Th and Sc) and TOC contents, reflecting the significant influences terrigenous inputs (including volcanic ash) have on the organic matter accumulation (Figs. 5a, 5b). The volcanic ash fell into the seawater on the one hand accelerated the organic deposition rate via absorbing dissolved organic matter particles suspended in water column. Volcano ash brought plenty of nutrient elements promoting the productivity of the sea surface. The ratios of Ba/Al and P/Al have negative or no obvious correlations with TOC content, respectively, probably reflecting of the loss of Ba and P in anoxic or euxinic conditions (Figs. 5c, 5d). In addition, the Ba/Al ratios from TB Section are highest than those of SH and QL sections, indicating the strongest upwelling on the platform margin where the TB Section was located. The high paleo-productivity view is consistent with previous conclusions (Wang et al., 2019; Li et al., 2017). The high positive correlations between ratios of Mo/Al and U/Th vs. TOC contents for the SH and QL sections (Figs. 5e and 5f), indicate that the reducing conditions are controlling factors for organic matter accumulation. Nevertheless, the weak correlations between redox proxies and TOC contents in the TB Section were probably due to the disturbance of upwelling on the platform margin (Figs. 8e and 8f). The redox conditions were probably caused by the process of organic matter decomposition exhausting the water column oxygen (Wang et al., 2019) or sea-level rise that reduced the dissolution of oxygen in the bottom water mass.

4.5 Organic Matter Accumulation Models

Before the deposition of Wufeng Formation, the sea level was in a global regression period and developed the limestone of
Linxiang Formation (Su et al., 1999), thus, LPWF was still influenced by the relative shallow water depth, which is supported by the high terrestrial input and oxic-suboxic redox conditions (Fig. 6a). Along with the sea-level rise during the Middle to Upper part of the Wufeng Formation, the bottom water became more reduced, meanwhile, the weathering brought plenty of nutrients to boost the sea surface productivity, this led to a great deal of preserved organic matter (Figs. 6b, 6c). During the deposition of KB, the sea-level drop to the lowest point because of global glaciation (Delabroye and Vecoli, 2010), which caused weak weathering. Therefore, less nutrients were transported into the sea to promote the paleo-productivity. Meanwhile, most of the study area became shallow water which caused a disadvantage for the preservation of organic matter (Fig. 6d). During the deposition of KB, the sea-level drop to the lowest point because of global glaciation (Delabroye and Vecoli, 2010), which caused weak weathering. Therefore, less nutrients were transported into the sea to promote the paleo-productivity. Meanwhile, most of the study area became shallow water which caused a disadvantage for the preservation of organic matter (Fig. 6d). After the Late Ordovician glaciation, there were relatively thin strata (less than 0.5 m) with high values of Al, Th and Sc, recording the increased weathering at the bottom of the Longmaxi Formation and at the same time the sea-level to rise quickly (Fig. S3). Along with the increased weathering and rising sea-level, the paleo-productivity promoted and dissolved oxygen in the bottom water declined, therefore an abundance of organic matter accumulated during this period (corresponding to graptolite zones: \( M. \ persculptus \) to \( A. \ ascensus \)) (Fig. 6e). Then the sea-level became relatively low again and the organic matter accumulation also diminished in UPLF (corresponding to graptolite zones: \( A. \ ascensus \) to \( P. \ acuminstus \)) (Fig. 6f). Therefore, the silicates weathering variation and sea-level changes of the Yangtze Ocean were the main controlling factors for paleo-productivity, redox conditions of bottom water and organic matter accumulation.

5 CONCLUSIONS

(1) The ratios of U/Th, V/Cr, and Mo concentrations of the samples reflect that the bottom water was low dissolved oxygen concentrations in the study profiles during the period of Late Ordovician to Early Silurian. The redox indexes further indicate intermittent or weakly euxinic bottom water conditions during the deposition of UPWF, and a more intense persistent euxinia during the deposition of LPLF. The continuously increased Mo concentrations with the redox conditions become reduced, which reflects the basin was not restricted and could not retain the Mo element resupplied by the water exchange.

Figure 5. Crossplots of TOC vs. terrigenous detrital input, redox conditions and paleo-productivity indexes.
Figure 6. Schematic depositional model showing the co-variation of sea level, terrigenous detrital input, redox conditions, and paleo-productivity during different stages of Late Ordovician to Early Silurian (modified from Zou et al., 2018a).

(2) The high values of TOC, Ba and P of the samples from SH, QL and TB profiles show a high paleo-productivity during the Late Ordovician to Early Silurian. High nutrient elements (Ba, P, etc.) and terrestrial elements (Al, Th, Sc, etc.) are closely related to silicates weathering and sea-level changes.

(3) The silicates weathering effected the nutrients influx into the sea. The sea-level eustacy also had a significant influence on the terrigenous input, upwelling nutrients flux and oxygen concentration of bottom water. So, the silicates weathering and sea-level eustacy are the primary factors for organic matter accumulation during the period of the Late Ordovician to Early Silurian.

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